2015 Joint Southeastern/Southwest Regional Meeting 1

Hydroxychalcones as inhibitors of *Streptococcus mutans* biofilms

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Streptococcus mutans has been implicated as the major etiological agent in the initiation and the development of dental caries due to its robust capacity to form tenacious biofilms. Ideal therapeutics for this disease will aim to selectively inhibit the biofilm process while preserving the natural flora of the mouth. Several studies have demonstrated the efficacies of flavones on *S. mutans* biofilms and have reasonably established the mechanism of action through their effect on *S. mutans* glucosyltransferases (GTFs). These enzymes metabolizes sucrose into water insoluble and soluble glucans, which are an integral measure of the dental caries pathogenesis because they play a role in mediating irreversible attachment of *S. mutans* to the tooth and also provide an extracellular matrix, shielding the bacteria from the host immune response, mechanical stresses, and antimicrobial agents. Encouraged by the reported findings on flavanols, we have utilized the crystal structure of GTF-SI, one of the major contributors of glucan synthesis to screen hydroxychalcones, precursors of flavonoids and isoflavonoids. We have identified low micromolar inhibitors of *S. mutans'* biofilm and GTFs. Subsequently, we have synthesized a library of compounds to optimize the activity of the lead scaffold.

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F_{420} cofactor dependent glucose-6-phosphate dehydrogenase from *Mycobacterium tuberculosis*: Kinetic and biophysical characterization of wild-type enzyme and a His40 mutant

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Tuberculosis (TB) is a deadly infectious disease that currently affects about one third of the world's population. Our study focuses on F_{420} cofactor dependent glucose-6-phosphate dehydrogenase (FGD), an enzyme found within *Mycobacterium tuberculosis (Mtb)*, the causative agent of TB. FGD catalyzes the first step of the pentose phosphate pathway, where it uses the oxidized F_{420} cofactor to convert glucose-6-phosphate (G6P) to 6-phosphogluconolactone, yielding the reduced cofactor $F_{420}H_2$. The Baker group has proposed a mechanism for the FGD reaction, suggesting that Histidine 40 (H40) acts as the active site base which initiates the FGD reaction (Figure 1). We aim to investigate this proposed mechanism, using site-directed mutagenesis, circular dichroism spectroscopy, binding assays, steady state and pre-steady state kinetic methods. Here, we will discuss the results of the characterization of *wild-type* FGD (*wt*FGD) and an FGD H40A mutant. The dissociation constant (K_d) for the F_{420} cofactor was found to be 8.7 ± 0.7 nM for *wt*FGD and 119 ± 26 nM for FGD H40A, therefore suggesting that the

H40 residue plays a role in anchoring the cofactor into the active site. The *wt*FGD steady state kinetics yielded a k_{cat} of 1.40 ± 0.03 s^{-1} while the pre-steady state kinetics revealed only a fast phase with k_{obs} of 4.20 ± 0.03 s^{-1}, thus implying that the hydride transfer step is not rate-limiting. FGD H40A was found to be catalytically inactive, even though it could bind both F_{420} and G6P. Based upon this data, we conducted crystallography screens with the inactive H40A mutant, in an effort to yield an FGD crystal structure with both the cofactor and the native substrate, G6P bound within the active site of the enzyme.

Reference

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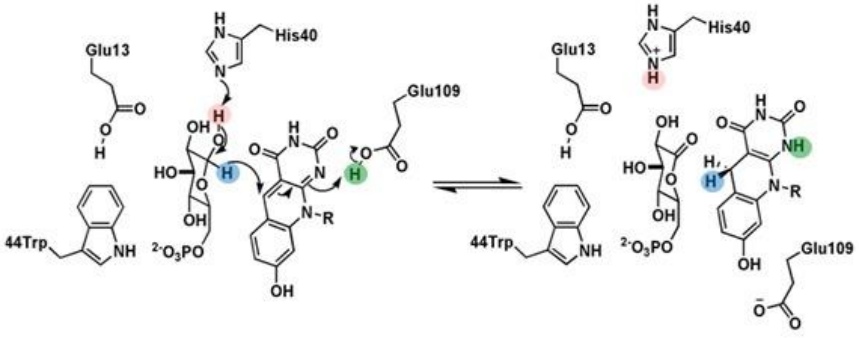

Figure 1. Proposed mechanism for FGD reaction [1]

2015 Joint Southeastern/Southwest Regional Meeting 3

A small molecule screen identifies a natural product that disrupts the fungal cell wall integrity pathway by targeting Hsp90

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Echinocandin antifungal drugs such as caspofungin (CAS), although potent and well-tolerated, have a narrow spectrum of activity and drug resistance is a serious problem. New therapies are needed to overcome these limitations. In this project, our goal is to discover natural products that improve CAS activity by disrupting the fungal cell wall integrity pathway (CWIP), which is involved in the adaptation to cell wall stress exerted by this drug. Because the CWIP is regulated by the transcription factor Rlm1 in the model yeast *Saccharomyces cerevisiae*, signaling through this pathway can be monitored with a *lacZ* reporter driven by Rlm1-responsive promoter elements. Using this promoter-reporter system in a new high-throughput assay, we have screened 4,576 natural products from our in-house collection and identified compounds that improve CAS potency in fungal pathogens. A sesquiterpene quinone compound named puupehenone (PUUP) was identified that enhanced CAS activity in CAS-resistant clinical isolates of *Candida albicans* and also in the inherently CAS-insensitive pathogen *Cryptococcus neoformans*. To investigate its CAS-potentiating mechanism, we

conducted transcript profiling in *S. cerevisiae*. Our studies revealed that CWIP-related genes that were strongly induced by CAS alone were not induced by CAS + PUUP; thus, PUUP synergizes with CAS by preventing cell wall repair through the CWIP. Further studies revealed that PUUP targets Hsp90. The transcript profile of PUUP was similar to that of the Hsp90 inhibitor celastrol. Genes encoding chaperones and co-chaperones involved in heat shock response were strongly induced by PUUP. To confirm PUUP's effect on Hsp90, a well-established promoter-reporter assay system was used that monitors the rat glucocorticoid receptor (GR), an Hsp90 client protein. We observed that PUUP inhibited GR induction in a concentration-dependent manner. We also showed that PUUP inhibits the activation of the yeast protein Mpk1, another Hsp90 client protein. Because Mpk1 is a critical kinase in the CWIP pathway, this result demonstrates that PUUP inhibits the CWIP by disrupting Mpk1 activity. In summary, using a new high-throughput assay, we have identified a mechanistically validated compound that improves CAS potency in fungal pathogens. Further evaluation in mammalian models of fungal infection will be required for its development into an effective therapy in combination with echinocandins.

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Development of high-throughput screening of WecA for identification of novel antibacterial agents

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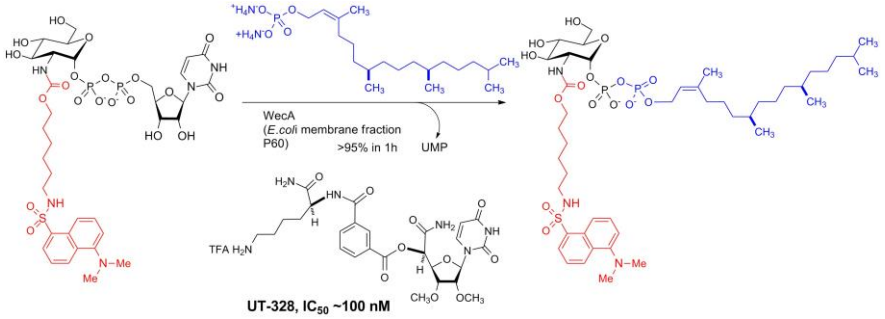
WecA is an essential enzyme in growth of *Mycobacterium tuberculosis* (Mtb) and some other bacteria. It catalyzes the transfer of GlcNAc-1-phosphate moiety of UDP-GlcNAc to polyprenyl phosphate, yielding polyprenyl-GlcNAc-pyrophosphate (prenyl-GlcNAc-PP). Prenyl-GlcNAc-PP is the first lipid-linked intermediate involved in the synthesis of the bacterial cell wall core structure. In order to perform high-throughput screening (HTS) against WecA, we have developed a convenient assay using a UDP-GlcNAc fluorescent conjugate and *cis*-phytyl phosphate as WecA substrate mimics that can be converted to the corresponding prenyl-GlcNAc-PP analog in high yield. By using the new assay method, a library of compounds has been screened, and a few compounds were identified as strong WecA inhibitors. We present the minimum structure requirement of the prenyl-P in WecA assays, and new WecA inhibitors identified in this program.



WecA-catalyzed biosynthesis of *cis*-phytyldiphosphoryl-α-D-*N*-acetylglucosamine analog and a new WecA inhibitor **UT-328**. These assays are not dependent on radioisotopes.

2015 Joint Southeastern/Southwest Regional Meeting 5

Investigating enzymatic resistance to fosfomycin by FosB in Gram-positive bacteria

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Fosfomycin, a broad spectrum antibiotic, is used clinically to treat lower urinary tract infections and gastrointestinal infections and has been suggested for treatment of multi-drug resistant bacterial infections. However, fosfomycin resistance enzymes limit the efficacy of the antibiotic in the clinical setting. A better understanding of the enzymatic mechanism of fosfomycin resistance could be used to increase the efficacy and use of fosfomycin.

One resistance enzyme, FosB, is a M^{2+}-dependent thiol-transferase found in Gram-positive bacteria and modifies fosfomycin by catalyzing nucleophilic addition of a thiol to fosfomycin resulting in an inactive compound. *In vitro* time course kinetic analyses for FosB from four different bacterial strains using L-cysteine and bacillithiol (BSH) reveal a preference for BSH over L-cysteine. A probe of the metal dependent activation of FosB by Ni^{2+}, Mg^{2+}, Zn^{2+}, and Mn^{2+} indicates the highest activation of FosB is observed with Mn^{2+} as the metal cofactor, whereas Zn^{2+} inhibits the FosB enzymes. Thus, FosB is a Mn^{2+}-dependent BSH transferase.

Several high-resolution crystal structures of FosB have been determined. They reveal a BSH binding pocket and suggest a highly conserved loop region must change conformation to bind fosfomycin. Hydrogen-Deuterium Exchange Mass Spectrometry (HDX-MS) experiments were utilized to investigate the structural dynamics of FosB. HDX-MS data analysis for this enzyme incubated with various substrates and cofactors has yet to provide evidence of BSH binding or loop movement. To further probe the dynamics, NMR analysis is currently underway. Comparison of preliminary ^{15}N HSQC spectra with and without fosfomycin indicates some peaks shift, but assignment of the backbone has not yet been completed.

2015 Joint Southeastern/Southwest Regional Meeting 6

Metabolomic analysis of volatile organic compounds emitted from decomposing human cadavers

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Estimation of time-of-death using parameters that can be measured when a body has been located is an important and active area of research in forensics. One type of measurement that has been a major component of models of time-of-death is the set of volatile organic compounds (VOCs) emitted from the body during the decomposition process. Numerous studies have reported the identification of time-dependent VOCs from both human cadavers and animal models, but data from human cadavers comes from a very limited set of environments. We have sampled VOCs from human cadavers as they decompose in southeast Texas at the Southeast Texas Applied Forensic Science (STAFS) facility at Sam Houston State University (SHSU). Cadavers were placed in pairs four different times of year for over two years, and VOCs emitted from their oral cavity and belly region were sampled daily using polydimethylsiloxane-divinylbenzene solid-phase microextraction fibers. The fibers were then analyzed by gas chromatography-mass spectrometry (GC-MS) at the Texas Research Institute of Environmental Studies (TRIES) at SHSU. The large amount of resulting data was then analyzed first by hand using ChemStation and the NIST-08 database, then using various metabolomics analysis tools including XMCS with R, XCMS Online, and AMDIS with MET-IDEA. Some metabolites were tracked as unknowns and have not yet been unambiguously identified. Others were identified with the help of the NIST-08 database and select standards. Identified compounds include some VOCs that originate with insects that take up residence in the cadavers (long-chain alkanes from maggots, for example). Observed variation between cadavers and between seasons will be discussed.

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Analysis of site directed mutants of diacylglycerol kinase-β by LC-MS/MS and bi-substrate kinetics

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Diacylglycerol kinase-β (DGKB) mediates the phosphorylation of diacylglycerol (DG) to form the bioactive lipid phosphatidic acid (PA). DGKB is critical to intracellular phospholipid metabolism and signaling, and plays an essential role in membrane lipid homeostasis in many Gram-positive pathogens including staphylococcus aureus. A previous study suggested DGKB exists as a dimer with 8 salt-bridges at the amino-terminal interface even though it crystallized as a monomer. The current work focuses on characterizing the monomer/ dimer distribution of DGKB through analysis of specific ionic residues in the putative dimer interface on dimerization and enzymatic activity. LC-MS and LC-MS/MS methods were developed and applied to these goals.

2015 Joint Southeastern/Southwest Regional Meeting 8

nNav1.5 blockers for breast cancer metastasis therapy

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In strongly metastatic breast cancer MDA-MB-231 cells, nNav1.5 is upregulated about 1,800-fold. By contrast, Nav currents are not recorded in weakly metastatic MCF-7 cells or non-cancerous MCF-10A mammary epithelial cells. One of the factors contributing to breast cancer metastasis is the ability of highly aggressive cancer cells to degrade extracellular matrices (ECM) mediated by various extracellular proteases such as cysteine cathepsins. nNav1.5 activity enhances ECM invasion by increasing the activity of acidic cysteine cathepsins B and S through the acidification of the pericellular microenvironment. The Na^+/H^+ exchanger (NHE1) is over-activated in breast cancer cells and is the central regulator of intracellular and perimembrane pH and that its activity is enhanced by the function of nNav1.5 channels. In a recent study, it is found that nNav1.5 activity in MDA-MB-231 cells increased the activity of the NHE1, promoting acidification of the cancer cell microenvironment, and subsequent activation of acidic cathepsins. Accordingly, nNav1.5 function is really important and any small molecule blocker of this channel will reduce the breast cancer cell invasiveness. We have developed a 3D-QSAR model and have used this model to design small molecules with nNav1.5 blocking activities near 1mM (IC_{50}). We have shown that nNav1.5 blockers inhibit the invasion of MDA-MB-231 cells at concentrations as low as 1mM. These compounds do not affect cell viability at concentrations ≤10 μM, demonstrating that the inhibition of Na+ currents and cell invasion do not result from cytotoxicity. Structurally similar compounds that do not block the nNav1.5 currents had no effect on invasion showing the direct relation between nNav1.5 blockade and the cell invasion inhibition. Results of design, synthesis and biological evaluation of such nNav1.5 blockers will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 9

Analysis of the bi-substrate kinetics of sphingosine kinase-1 inhibitors

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Sphingosine kinase 1 (SK1) mediates the phosphorylation of sphingosine (SPH) to form sphingosine 1-phosphate (S1P). S1P is a bioactive phospholipid involved in cellular apoptosis, proliferation and survival. The SK1/S1P system plays a role in several human diseases, including cancer and cardiovascular diseases. SK1 inhibitors are proposed to reduce metastasis, induce apoptosis and to sensitize tumor cells to radiation and chemotherapeutics. Inhibitors of SK1 that are specific, potent and efficacious will be useful tools to help clarify the enzymology, cell biology of SK1 in human disease. This work presents a rational approach to the search for novel SK1 inhibitors using computational approaches and the characterization of newly discovered inhibitors using bi-substrate kinetics using an in-housed developed LCMS/MS-based activity assay.

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Kinetic studies of n–heterocyclic carbene–ruthenium complex in catalytic radical reduction

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The stoichiometric amount of classical antioxidants is required to degrade reactive oxygen species (ROS), resulting in reduced antioxidant activity *in vivo* with time. This has inspired the search for metal-based antioxidants that can degrade ROS catalytically. We showed that the organometallic complex comprising a ruthenium center (**Ru1**) reduced radical monoanion $ABTS^{\bullet-}$ (2,2'-azino-bis(3-ethylbenzo-thiazoline-6-sulfonate)) catalytically in aqueous solution by a transfer hydrogenation-like process. Generally, in transfer hydrogenation an organometallic complex catalyzes the transfer of H_2 from isopropyl alcohol to desired unsaturated substrates, thereby using alcohol as a source of H_2. Similarly, **Ru1** reduced radicals catalytically using alcohols as the required H_2 source. Thus, reaction rates were dependent upon the types of alcohols (tertiary vs. non-tertiary). Furthermore, **Ru1** catalytically slowed down the oxidative formation of $ABTS^{\bullet-}$ radicals, depleted all the radicals formed and was still catalytically active after multiple cycles. The aforementioned **Ru1** is the first report of an organoruthenium complex that can catalytically inhibit the oxidative formation of radicals as well as catalyze the radical reduction in aqueous solution by a transfer hydrogenation-like process and thus, maybe useful for combating diseases associated with oxidative stress.

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Expanded structure-activity relationship analysis of small molecule autotaxin inhibitors

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Autotaxin (ATX) is a ubiquitous tumor-promoting ectoenzyme that hydrolyzes lysophosphatidylcholine (LPC) to form the bioactive lipid mediator lysophosphatidic acid (LPA). LPA activates specific G-protein coupled receptors to elicit downstream effects leading to cellular motility, survival, and invasion. Through this pathway, upregulation of ATX is linked to conditions such as cancer and cardiovascular disease. ATX crystal structures indicate the catalytic domain contains multiple binding regions including a polar active site, hydrophobic tunnel, and a hydrophobic pocket. This finding is consistent with the promiscuous nature of ATX hydrolysis of multiple and diverse substrates. We have previously identified activity gaps during synthetic optimization of a lead identified initially using computational methods. This work describes synthesis of analogs to address noted activity gaps to further understand ATX inhibition.

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Design and synthesis of platinum-containing quinazoline-based tyrosine kinase inhibitors as anticancer treatments

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ErbB family tyrosine kinases are highly pursued targets in cancer chemotherapy. Mutationally activated or overexpressed ErbB kinases like EGFR and Her-2 often lead to cancer cell survival and aggressive proliferation. Small-molecule inhibitors such as

Gefitinib and Lapatinib that target the kinases' ATP binding sites have shown potent antiproliferative properties in cell lines bearing corresponding upregulated ErbB kinases. In particular, irreversible inhibitors that alkylate solvent-exposed enzymatic cysteine residues with arylamide electrophiles have been demonstrated to overcome drug resistance caused by secondary mutations. Here, we introduce a series of novel kinase inhibitors, which were generated by conjugating ATP-mimicking quinazoline scaffolds with platinum-based electrophiles. The quinazoline scaffolds are designed to bind to the target kinase active site with high affinity and selectivity while the platinum-containing moieties form a coordinative bond with the cysteine residue to achieve irreversible inhibition. Several of the target molecules showed promising binding properties in competition binding assays and high selectivity for the targeted kinase domain in a panel of 145 wild-type and clinically relevant kinases (KinomeScan, DiscoverX, Fremont, CA). In order to find a potential hit, we assembled and screened a library of such tyrosine kinase inhibitors by combining different metal containing moieties and ATP analog structures. The kinetics of metal-cysteine binding greatly depends on the surrounding ligands and the positioning of the metal complex in the active site. The library members were tested for antiproliferative activities in NCI-H1975 lung cancer cells (EGFR, L858R and T790M mutations) and SK-BR-3 breast cancer cells (Her-2 positive) to identify hits and establish structure activity relationships. Some platinated inhibitors exhibited greatly enhanced activity compared to the unplatinated counterparts.

2015 Joint Southeastern/Southwest Regional Meeting 13

Combining metabolite-based pharmacophores with Bayesian machine learning models for *Mycobacterium tuberculosis* drug discovery

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Integrated computational approaches for *Mycobacterium tuberculosis* (*Mtb*) are useful to identify new molecules that could lead to future tuberculosis (TB) drugs. Our approach uses information derived from the TBCyc pathway and genome database, the Collaborative Drug Discovery TB database combined with 3D pharmacophores and dual event Bayesian models of whole-cell activity and lack of cytotoxicity. We have prioritized a large number of molecules that may act as mimics of substrates and metabolites in the TB metabolome. We computationally searched over 200,000 commercial molecules using 66 pharmacophores based on substrates and metabolites from *Mtb* and further filtering with Bayesian models. We ultimately tested 110 compounds *in vitro* that resulted in two compounds of interest, BAS 04912643 and BAS 00623753 (MIC of 2.5 and 5 mg/mL, respectively). These molecules were used as a starting point for hit-to-lead optimization. The most promising class proved to be the quinoxaline di-*N*-oxides, evidenced by transcriptional profiling to induce mRNA level

perturbations most closely resembling known protonophores. One of these, SRI58 exhibited an MIC = 1.25 µg/mL versus *Mtb* and a CC_{50} in Vero cells of >40 µg/mL, while featuring fair Caco-2 A-B permeability (2.3 x 10^{-6} cm/s), kinetic solubility (125 µM at pH 7.4 in PBS) and mouse metabolic stability (63.6% remaining after 1 h incubation with mouse liver microsomes). Despite demonstration of how a combined bioinformatics/cheminformatics approach afforded a small molecule with promising *in vitro* profiles, we found that SRI58 did not exhibit quantifiable blood levels in mice.

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Electronic structure of light-harvesting antennas in purple bacteria

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Light-harvesting antennas are protein-pigment complexes that play a crucial role in natural photosynthesis. The antenna complexes absorb light and transfer energy to photosynthetic reaction centers where charge separation occurs. The goal of this work is to study the electronic structure of the pigment networks of light-harvesting complex I (LH1), LH1 with the reaction center (RC-LH1), and light-harvesting complex II (LH2) found in purple bacteria. As the pigment networks of LH1, RC-LH1, and LH2 contain thousands of atoms, conventional DFT and *ab initio* calculations of these systems are not computationally feasible. Therefore, we utilize density functional theory (DFT) in conjunction with the energy-based fragmentation with molecular orbitals (EBF-MO) method as well as a semi-empirical approach employing the extended Hückel (EH) model Hamiltonian to determine the electronic properties of these pigment assemblies. Our calculations provide a deeper understanding of the electronic structure of natural light-harvesting complexes, especially their pigment networks, which could assist in rational design of artificial photosynthetic devices.

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Computational studies of spin trapping of biologically relevant radicals by new heteroaryl nitrones

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New heteroaryl nitrone spin traps have an excellent ability to add free radicals to produce stable products. The effects of new heteroaryl (thiadiazoyl and furoxanyl) substituents on a parent nitrone spin trap have been computationally studied using *ab initio* methods at the Hartree-Fock (HF) and second-order Møller-Plesset (MP2) levels with the 6-31G(d), cc-pVDZ and cc-pVTZ basis sets. The calculations show that new heteroaryl nitrones are very reactive, with thiadiazoyl substituted-nitrones being the most reactive spin traps and 1,2,4 – thiadiazol -5-yl nitrone is the most polar spin trap. Additionally, the thermodynamics of the spin trapping of new heteroaryl nitrones at C-site and O-site with the biologically relevant radicals (•H, •CH_3 and •OH) has been studied using HF/6-31G(d). The calculations show that thermodynamically, the spin trapping of furoxan-3-yl nitrone with •H, •CH_3 and •OH radicals gives the most stable spin adducts at the C site while furoxan-4-yl nitrone with these radicals gives the most stable spin adducts at the O site. However, the spin trapping at the C site of new heteroaryl nitrones is highly exothermic as compared to the O site of the nitrone, with no

activation energy barrier for any of the radicals studied. Finally, the thermodynamics of the spin trapping of DMPO, PBN and FxBN with •OH radical has also been studied using Density Functional Theory (DFT) with M06/6-31*. The spin trapping of FxBN with •OH is thermodynamically favored over the spin trapping of DMPO and PBN with •OH. The double spin adduct of FxBN with •OH radical is thermodynamically favored over the monoadduct of FxBN with •OH radical. This work provides the understanding of the chemical and physical basis that influences the spin trapping efficiency of the new heteroaryl nitrones with biologically relevant radicals and the corresponding stability of their spin adducts.

2015 Joint Southeastern/Southwest Regional Meeting 16

Designing neutralizing antibodies for Marburg and Ebola viruses

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The filoviruses, Ebola and Marburg, cause deadly hemorrhagic fever in humans. Absence of any proven effective treatment for filovirus-infected patients has costed thousands of lives in the last Ebola virus outbreak. Mapping the molecular interactions of the virus glycoprotein (GP) with the antibody is important for therapeutic strategies. Starting with a low-resolution structure of Marburg GP complexed with an antibody MR78, we first refine the structure using phenix.rosetta protocols. We determine the critical antigen-antibody interactions required for neutralizing the virus. Further, we generate a position specific scoring matrix that can be used to rapidly screen and compare the antibody repertoire of infected and naïve humans to find antibodies that are close in sequence and structure to neutralizing antibodies. These antibodies can further be optimized to enhance the binding affinity and neutralization properties against filoviruses.

2015 Joint Southeastern/Southwest Regional Meeting 17

Theoretical aspects of the molecular imprinting of penicillin

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This work introduces a computational study on the molecular imprinting of penicillin in methyl methacrylate/ methacrylic acid copolymer. Presented copolymer can be used as the enteric coating for antibiotic to create a barrier protecting the medication from low pH of the stomach. This computational study presents: penicillin and polymer active sites, cave models with interaction energy analysis (between antibiotic and monomers), solvent influence on the binding energy, and pH effect on the polymer coating.
The density functional theory, DFT, method has been used for all structural, vibration frequency, and solvent calculations.

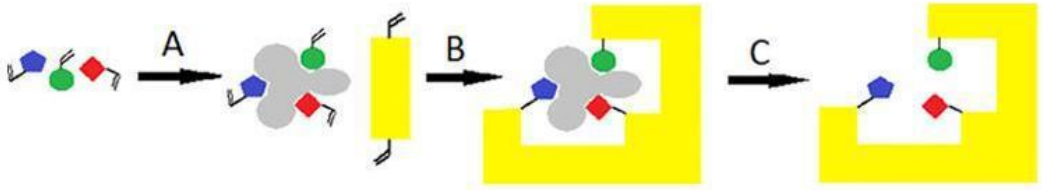

Figure 1. MIP process: (A) self-assembly; (B) polymerization; (C) solvent extraction

2015 Joint Southeastern/Southwest Regional Meeting 18

Opportunities for computational prediction of contaminant toxicity, fate, and transport properties to support disaster response

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The proper response to a chemical spill is predicated on the availability of information regarding the spilled agent. Important engineering and environmental decisions must be made to protect human health and safety. Environmental fate and transport behavior can be predicted from fundamental physicochemical properties, but if these properties are unknown or unavailable at the time of the incident, responders need scientific support. Using the Jan. 2015 Elk River Chemical Spill as a backdrop and motivation, I will highlight the need in the disaster response community for more rigorous, on-demand, accessible, and fast methods to predict physiciochemical properties for use in fate, transport, and toxicity modeling, and detail some of our efforts in this regard. I will issue a call to action and assert that computational chemistry practitioners, not the emergency response community, have a responsibilty to the public good to bring the development and implementation of such models into reality.

2015 Joint Southeastern/Southwest Regional Meeting 19

Phosphoramidate hydrolysis catalyzed by hHINT1: A cluster-model DFT computational study

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Human histidine triad nucleotide binding protein 1 (**hHint1**) is a member of a ubiquitous and ancient branch of the histidine triad protein superfamily. Human Hint1 is a homodimeric protein that catalyzes the hydrolysis of model substrates, phosphoramidate and acyl adenylate, with high efficiency. While a variety of interactions with Hint1 family have been discovered, little is known about the enzymatic activity and the underlying atomic-level details of the catalytic mechanism. Computations employing density functional theory (DFT) computations were used to explore the possible catalytic mechanism for the hydrolysis of substituted adenosine monophosphate (AMP) by hHint1. The previously proposed catalytic mechanism includes three important steps: (1) the nucleophilic reaction of His112; (2) the N-P bond breaking of phosphoramidate; and (3) the nucleophilic reaction of water molecule. The attack of the N atom from His112 on the phosphoryl group could produce five-coordinate phosphorane intermediate and the attack of H_2O influences the related intermediate to revert to

monophosphate substrate AMP. The results of the proposed mechanism are also used to suggest transition state analogue.

2015 Joint Southeastern/Southwest Regional Meeting 20

Characterization of C-X...π interactions using state-of-the-art computational techniques

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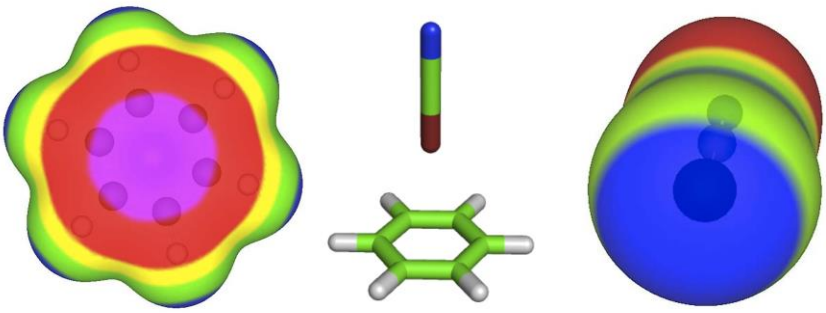
Halogen bonds have been recognized in the past decade as important noncovalent interactions that play roles in biomolecular structures and material design. Most typically, halogen bonds are viewed as occuring between a bound halogen and a bound electronegative atom, such as oxygen or nitrogen. These types of halogen bonds have been the subject of many theoretical and experimental studies and their properties are known relatively well. It has recently been determined that π systems, such as those in aromatic rings, can also serve as halogen bond acceptors. The properties of these C-X...π (X = Cl, Br, I) interactions have not been extensively characterized and are the subject of many recent investigations. Given the relative complexity of the electrostatic potentials of aromatic systems, the optimum geometries of C-X...π complexes are not as easily determined as those of more typical C-X...O or C-X...N systems. Because aromatic systems have large surface areas and high polarizabilities, and because halogens are large and have high polarizabilities, dispersion forces, as well as electrostatic forces, play a large role in stabilizing C-X...π complexes. Here we describe work aimed at characterizing interactions occurring between several halogen bond donors (HX, HCCX, and NCX) and benzene using modern computational chemistry methods. Accurate binding energies for various geometrical configurations of these complexes are generated at the CCSD(T)/aug-cc-pVQZ level of theory while symmetry adapted perturbation theory (SAPT) calculations are used to estimate the relative contributions of electrostatics, dispersion, and induction in stabilizing the complexes. Additionally, the performance of several density functional theory methods, with and without empirical dispersion corrections, is assessed in terms of their ability to accurately describe these C-X...π systems.



2015 Joint Southeastern/Southwest Regional Meeting 21

Prediction of pKa via a QM/QM approach

***Prajay Patel**, PrajayPatel@my.unt.edu, Jiaqi Wang, Angela K. Wilson. Chemistry Dept, University of North Texas, Denton, Texas, United States*

Three implicit solvation models, C-PCM, COSMO, and SMD, were utilized to calculate the pK_a values of a set of Ni-group hydrides in acetonitrile using a direct thermodynamic scheme. The influence of solvation model, density functional and basis set choice within a hybrid two layer QM/QM approach (ONIOM), atomic radii applied to build a cavity in the solvent, the size of the high-layer region in ONIOM calculations, and inclusion of Grimme's empirical dispersion correction in DFT calculations on the predictions of pK_a values were examined. The DFT functionals considered in this study include the local spin-density approximation (LSDA), generalized gradient approximation (GGA), meta-GGA, hybrid-GGA, hybrid-meta-GGA, and double-hybrid-GGA functionals. The results were calibrated by experimental pK_a values. The impact of the percentage of HF exchange used for hybrid functionals was considered. These investigations provide useful insight about models needed for the prediction of thermodynamic properties of transition metal hydrides.

2015 Joint Southeastern/Southwest Regional Meeting 22

Structures, relative energies, and ligand dissociation energies of $Ir_x(CO)_y(NHC)_z$ clusters

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Small iridium clusters catalyze a broad range of reactions. Besides traditional ligands like phosphines, N-heterocyclic carbenes (NHCs) show great potential for as li9gands for catalytic processes. The low energy isomers of the iridium clusters with carbonyls and NHCs, $Ir_x(CO)_y(NHC)_z$ complexes (x=1, 2, 4) were investigated using density functional theory and coupled cluster CCSD(T) theory. The CAM-B3LYP functional predicted the most consistent reaction energies as compared to CCSD(T) for mono- and di-iridium clusters. The CAM-B3LYP functional was used to predict the ligand dissociation reactions for larger $Ir_4(CO)_y(NHC)_z$ clusters. Both electronic effects and steric effects contribute to an increase in CO dissociation energies and a decrease in NHC dissociation energies as more CO's are substituted by NHC's. For tetra-iridium clusters, the ligands on the apical and bridging sites have lower dissociation energies than those on the equatorial and axial sites in the basal plane and some dissociations reactions result in a μ_3-CO.

2015 Joint Southeastern/Southwest Regional Meeting 23

The pivotal role of di-copper catalysis in 1,3-dipolar cycloadditions: A reaction valley study

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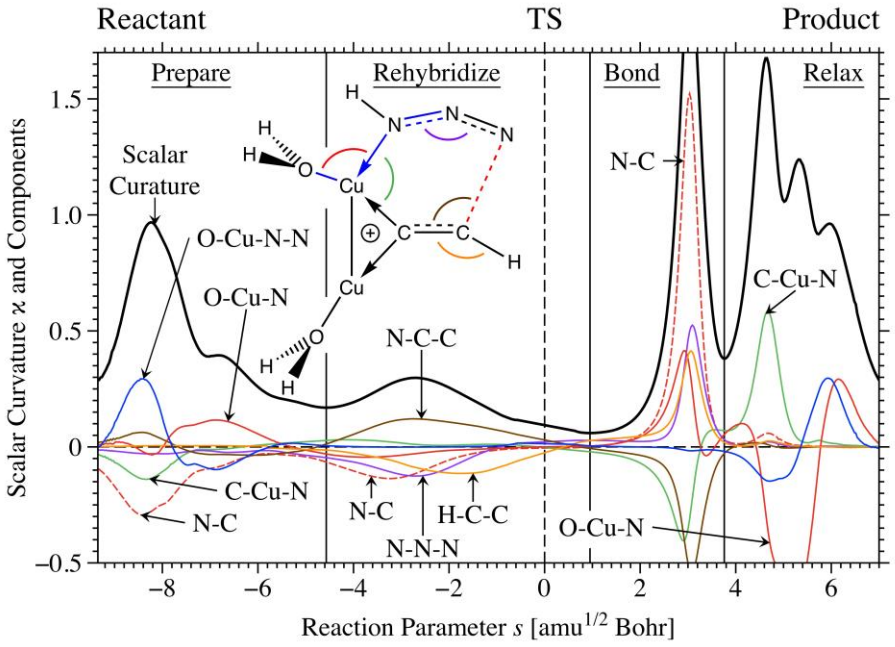
Catalysis is one of the major chemical challenges of our time. Transition metal catalysis specifically has the potential to facilitate the synthesis of desirable chemicals. This work is a mechanistic investigation of homogeneous catalysis utilizing an off-mainstream methodology: Rather than investigating just the energetics of a catalyzed reaction, the potential energy surface is explored in the vicinity of the reaction path following it from its start to its end. In this way, the reaction valley is studied for the purpose of unraveling the coupling between vibrational and translational motions of the reaction complex, which is decisive for the mechanistic outcome.
A dual level approach was used, based on Coupled Cluster theory for the energetics and a lower level method for the description of the reaction valley. Decomposition of the reaction path curvature into internal coordinate components allows identification of chemical events, such as rehybridization and bond formation, as they occur along the reaction path (See Figure). Eight Cu-catalyzed 1,3-dipolar cycloadditions to acetylene are analyzed. A di-Cu catalyst converts a one-step mechanism to a two step-mechanism, where each step has a significantly lower barrier than the non-catalyzed reaction. Electronic reasons for the effectiveness of the Cu catalyst in the cycloaddition reactions will be discussed.



For the Cu-catalyzed 1,3-dipolar azide-alkyne cycloaddition (ΔE^a = 13.9, $\Delta_R E$= 10.7 kcal/mol, CCSD(T)), the scalar curvature (bold black line) of the reaction path is given as a function of the mass-weighted arc length *s* of the path. The transition state is at *s*= 0. The colored lines show the changes in the curvature components associated with the internal coordinates of the complex.

2015 Joint Southeastern/Southwest Regional Meeting 24

Computational investigations of structural, electronic, and wavefunction effects on molecular hyperpolarizability

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Having previously found no satisfactory level of theory or basis set at which molecular hyperpolarizability is accurately calculated (with respect to experimentally determined values), this research surveys various other factors that may contribute to large calculated hyperpolarizability (and better agreement with experiments). In addition to molecular electronic features like dipole moment and electrostatic potential, wavefunction contributions from excited states, as determined by CISD and MCSCF wavefunctions have been considered. Small organic reference molecules have been considered as well as substituted saccharins and their transition metal complexes.

2015 Joint Southeastern/Southwest Regional Meeting 25

Nature of metal ion mediated second shell hydrogen bonds

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We investigate the role of induction effects in a zinc ion mediated second-shell hydrogen bond that plays a critical role in the mechanism of allosteric regulation in the paradigm sensor protein *Staphylococcus aureus* CzrA. Using a model of the metal-binding site of CzrA, we show via Natural Bond Order (NBO) and Symmetry-Adapted Perturbation Theory (SAPT) calculations that charge the charge transfer (CT) effect withdraws greater charge from atoms participating in hydrogen bonding in the presence of Zn(II) than in the apo state. Preliminary results suggest that polarization may play a significant role in helping strengthen the metal ion mediated hydrogen bond in CzrA.

2015 Joint Southeastern/Southwest Regional Meeting 26

Ionic liquid binary mixtures with organic solvent as an electrolyte for wide temperature and high performance supercapacitor applications

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The capability of supercapacitors to work over a wide temperature window (-40 °C to +80 °C) has drawn attention in many applications like space, military and some industries. The main limiting factor for a wide temperature window is the stability of electrolyte. Organic and aqueous electrolytes have lower boiling points and cannot be used in high temperature applications. Ionic liquid electrolytes have been explored in supercapacitors because of their high thermal stability (>200 °C). Pyrrolidinium-based ionic liquids are a widely used class of ionic liquids because they have lower melting temperature. A significant increase in the temperature window has been obtained by using ionic liquid binary mixtures as electrolytes. The binary mixture of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr14-TFSI) and 1-propyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr13-TFSI) is particularly attractive. Unfortunately, since both electrolytes are highly viscous, this results in a low ionic conductivity of the mixture which leads to lower electrochemical performance. Conductivity measurements and DSC analysis show that by adding an organic solvent to this binary mixture, the conductivity can be increased without decreasing the temperature window. Also the electrochemical performance of coin cell supercapacitors

were tested using Pyr14-TFSI and Pyr13-TFSI ionic liquid binary mixture in organic solvent as the electrolyte and carbon nano fiber as the electrode material. Coin cell supercapacitor with Pyr14-TFSI and Pyr13-TFSI did not work at -50 °C, in contrast the ionic liquid binary mixtures in organic solvent electrolyte showed 93% retained in specific capacitance at -50 °C at 10mV/s.

2015 Joint Southeastern/Southwest Regional Meeting 27

Study of the effect of anion on the x-ray crystal structures and thermal properties of 1,3-dibenylimidazolium based ionic liquids

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Three crystals of 1,3-dibenylimidazolium ionic liquid systems with varying the anions, bromide (I), triflate (II) and bistriflimide (III) were synthesized. X-ray diffraction measurements on single crystals of each of the ionic liquids demonstrated a unique structural organization of cations and anions. The nature of the π-π interaction between the phenyl-phenyl and phenyl-imidazolium rings and hydrogen bonding between the anion and the acidic hydrogen of imidazolium ring, are affected by the anion. Crystal I with the bromide ion has an additional interaction due to the presence of water molecules in the crystal lattice. Water molecules have strong interactions with bromide ions and also form hydrogen bonds with the acidic proton on the imidazolium ring. The size of the anion plays an essential role in the self-assembly of the ions in the crystal structure. The enthalpies of melting and melting temperatures of these systems will be correlated to differences in the crystal structures.

2015 Joint Southeastern/Southwest Regional Meeting 28

A novel technique for energy resolved measurements of gas phase ion molecule rearrangement and decomposition reaction kinetics

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Kinetic and dynamic studies of metal cations on organic substrates have long been important in elucidating the fundamental nature of reactions in organometallic chemistry. However, energy resolved measurements of these kinetic barriers can be difficult as they are often submerged with respect to separated reactant energies and require systems with well defined internal energy. Presented is a molecular beam apparatus designed to study single-photon initiated decomposition and rearrangement reactions (SPIDDR). The jet cooled ion-molecule encounter complex receives activation energy via single photon absorption allowing reaction product formation. Production of daughter fragment species is monitored to determine the microcanonical rate constant, k(E). Deuterium-labeled organics are studied to gain mechanistic insights via the kinetic isotope effect.

2015 Joint Southeastern/Southwest Regional Meeting 29

Energy resolved transition metal assisted decomposition of simple organic molecules

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The ability for transition metals to lower barriers in a reaction, and to facilitate selective product yield is widely utilized, but not fully understood. Our knowledge of how transition metals are able to facilitate the breaking and forming of chemical bonds has progressed substantially in recent decades due in large part to numerous ion beam type experiments. These gas phase experiments are able to probe the fundamental nature of reactions catalyzed by transition metals because of the unparalleled ability to study the reaction in a controlled environment free of complicating factors such as solvent effects.

Our group's research adds to this body of knowledge by utilizing a technique developed in our laboratory which allows us to monitor the decomposition of simple organics electrostatically bound to a single metal cation at resolved internal energies. Analysis of the temporal development of the products of these reactions allows us to parse out details of the reaction mechanism. Recent results from these experiments will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 30

Single photon initiated dissociative rearrangement reactions (SPIDRR) of transition metal ion/molecule systems

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Gaseous reactions between transition metal ions with organic molecules have been studied for decades as these represent idealized systems that demonstrate catalytic action. These studies have primarily been the province of guided ion beam and ion cyclotron techniques. Indeed, a wealth of thermochemical data has been recorded for ion/molecule reactions. However, these traditional techniques are far less apt at describing the reaction kinetics and dynamics of such systems. This is particularly true when the kinetic barriers that separate reactants from products are at energies below the separated reactants (typically deamed submerged barriers). These reactions occur at the collision frequency and despite their obvious significance to catalysis, have yet to suffer significant experimental exploration.

This presentation describes our current progress at quantifying aspects of exothermic, idealized ion/molecule reactions where submerged barriers control the reaction kinetics and dynamics. This is accomplished by freezing the reactants as a binary cluster in a supersonic expanding beam. The cluster absorbs a photon of laser energy to overcome submerged kinetic barriers and progress to products. The charged dissociative products are monitored in real time in a modified time of flight mass spectrometer, providing a direct measurement of reaction kinetics at well-specified cluster energies. Recent

results for transition metal mediated aldehyde decomposition reactions will be presented.

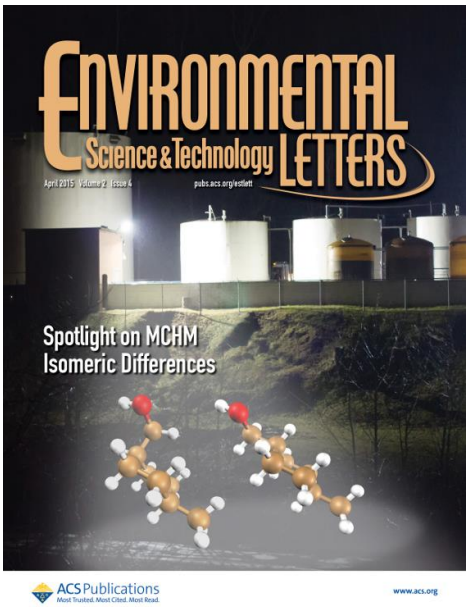
2015 Joint Southeastern/Southwest Regional Meeting 31

On the importance of conformational analysis for accurate prediction of molecular properties

William A. Alexander*, w.alexander@memphis.edu, Katherine Charbonnet, Taylor Brown, Nathan J. Deyonker. Chemistry, University of Memphis, Memphis, Tennessee, United States*

As part of the "second response" to the 2014 Elk River Chemical Spill in West Virginia, we employed various computational methods to predict physicochemical properties of the components of the spilled fluids, which mainly comprised oxidized cyclohexane derivatives. These compounds were poorly characterized and many of even the most basic of their molecular properties were unknown or unreported. In our investigation, we found that examination of only the global minimum structure was insufficient to explain observed experimental data. This disconnect with experiment hampers the ability to provide molecular property predictions with any confidence. However, with a complete accounting for all of the low lying geometric minima, we were able to reconcile our computational results with experimental fate and transport properties.[1] We will detail our methods and lessons learned from this case study, and generalize recommendations for similar efforts going forward.

(1) Dietrich, Thomas, Zhao, Smiley, Shanaiah, Ahart, Charbonnet, DeYonker, Alexander, and Gallagher, **Environ. Sci. Technol. Lett.**, (2015) ***2****,* 123–127; **DOI:** 10.1021/acs.estlett.5b00061



2015 Joint Southeastern/Southwest Regional Meeting 32

Diffusion of benzene and alkylbenzenes in *n*-alkanes

***Bruce A. Kowert**, kowertba@slu.edu, Paul M. Register. St Louis Univ, Saint Louis, Missouri, United States*

The translational diffusion constants, *D*, of benzene and a series of alkylbenzenes have been determined in four *n*-alkanes at room temperature using capillary flow techniques. The alkylbenzenes are toluene, ethylbenzene, 1-phenylpropane, 1-phenylpentane, 1-phenyloctane, 1-phenylundecane, 1-phenyltetradecane, and 1-phenylheptadecane. The *n*-alkanes are *n*-nonane, *n*-decane, *n*-dodecane, and *n*-pentadecane. Ratios of the solutes' *D* values are independent of solvent and in general agreement with the predictions of diffusion models for cylinders and lollipops. For the latter, an alkylbenzene's phenyl ring is the lollipop's candy; the alkyl chain is its handle. A model that considers the solutes to be spheres with volumes determined by the van der Waals increments of their constituent atoms is not in agreement with experiment. The diffusion constant ratios of 1-alkene and *n*-alkane solutes in *n*-hexane, *n*-heptane, and *n*-octane also are compared with the cylinder model; reasonably good agreement is found. The agreement with the cylinder model indicates that the translational motion of the alkylbenzenes is similar to that of the 1-alkene and *n*-alkane solutes in these solvents.

2015 Joint Southeastern/Southwest Regional Meeting 33

Synchrotron based infrared vibrational-rotational spectroscopic study of isobutylene

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Rotational structure in the n_{28} fundamental band of isobutylene has been examined at room temperature with synchrotron radiation at the University of Saskatchewan Canadian Light Source Facility. All of the measurements for this band were collected at a spectral resolution of 0.0009 cm^{-1}. At this level of spectral both fundamental ro-vibrational structure as well as transitions associated with internal rotational/torsional motions could be readily observed. Although the molecule is classified as an asymmetric top, the rotational structure of the band appears to possess a very regular pattern. In this talk, we will present a set of preliminary set of spectral assignments and molecular constants for this fundamental band.

2015 Joint Southeastern/Southwest Regional Meeting 34

Chemical kinetics in the processing of nuclear materials

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Irradiation of target materials is used to make actinides, such as plutonium-238, for thermoelectric generators to power deep space missions. NASA and DOE have a project to increase the stockpile of Pu-238 to power missions in 2020 and beyond. Targets are being irradiated at the Oak Ridge National Laboratory (ORNL) High Flux Isotope Reactor (HFIR). To extract the plutonium from the neptunium target material and fission byproducts, a number of chemical separations are being carried out at the ORNL Radiochemical Engineering Development Center (REDC). After dissolution of the aluminum cladding, the separations are based on control of the redox chemistry of the plutonium and neptunium, by selectively adding redox-active reagents. The chemistry of dissolution and redox state is controlled by the kinetics of the reactions involved. We have been conducting kinetics experiments and modeling reaction chemistry using Matlab in support of the process flowsheet development, and comparing these findings with published literature. We have been able to measure temperature dependent rates of reaction for the dissolution of aluminum alloy and the decomposition of hydroxylamine nitrate. The first process gives an example of an exothermic process that does not include autocatalysis, whereas the second process involves autocatalysis which requires a Semenov factor included in the rate equation. The role of minor alloying elements and fission products will be explored.

2015 Joint Southeastern/Southwest Regional Meeting 35

Adsorption studies of water and methanol on a metal phosphide surface

Heather L. Abbott-Lyon*, hlabbott@gmail.com. Chemistry and Biochemistry, Kennesaw State University, Atlanta, Georgia, United States*

The meteoritic mineral schreibersite, an iron-nickel phosphide, is hypothesized to have been the mineral source of phosphorus for prebiotic chemistry on the Early Earth. However, the mechanism of phosphorylation by schreibersite is currently unknown. In particular, the role that the mineral surface plays in these reactions is unclear. In an effort to understand the corrosion of schreibersite in aqueous organic solutions, thin films of water and methanol on a synthetic schreibersite surface (Fe_2NiP) have been studied. Schreibersite surfaces were analyzed by Scanning Electron Microscopy (SEM) before and after polishing to determine surface roughness and elemental composition. Subsequently, these samples were examined in an ultrahigh vacuum chamber using Reflection-Absorption Infrared Spectroscopy (RAIRS) and Temperature Programmed Desorption (TPD). Features corresponding to multilayers are clearly identifiable in both RAIRS and TPD spectra, while sub-monolayer peaks are more challenging to assign.

2015 Joint Southeastern/Southwest Regional Meeting 36

Real-time measurements of oxidative stress during chronic L-DOPA treatment for Parkinson’s disease

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Parkinson’s disease (PD) is a chronic neurodegenerative disorder characterized by the preferential loss of dopaminergic neurons stemming from the midbrain's substantia nigra pars compacta and innervating the dorsal striatum. The substantial decreases in striatal dopamine (DA) result in devastating hypokinetic movements and motor

disturbances. One potential contributor to Parkinsonian symptoms is increased generation of reactive oxygen species, such as hydrogen peroxide (H_2O_2). However, the precise role of H_2O_2 in the the initiation, progression, and maintenance of the disease remains unclear, as reactive oxygen species are difficult to monitor in brain tissue. Further, several lines of evidence suggest that the standard treatment strategy of dopaminergic replacement therapy via administration of Levodopa (L-DOPA; L-3,4 dihydroxyphenylalanine) may serve to increase oxidative stress and potentiate cell death. We aim to investigate how striatal H_2O_2 and DA dynamics underlie behavioral changes that result from chronic L-DOPA administration in a rodent model of PD (unilateral 6-OHDA lesion) using fast-scan cyclic voltammetry, an electrochemical technique that affords precise spatial and temporal resolution, as well as selective detection of these neurochemicals. Specifically, carbon-fiber microelectrodes are used to simultaneously quantify rapid H_2O_2 and DA fluctuations at single recording sites in the dorsal striatum over several weeks of L-DOPA administration. The chemical fluctuations are correlated with behavioral abnormalities that develop over the course of treatment. These studies will aid in our understanding of how oxidative stress modulates nigrostriatal DA signaling, and will demonstrate how these signals correspond with the development of dyskinetic movements in the treatment of PD.

2015 Joint Southeastern/Southwest Regional Meeting 37

Voltammetric method for the determination of diffusion and partition coefficients in plasticized polymer membranes

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For feedback controlled monitoring of the popular anesthetic, propofol, we used a voltammetric sensor coated with a highly-plasticized polymer membrane [1]. The sensitivity of the sensor is controlled by diffusion coefficient (D) of propofol in the membrane, while the detection limit and the selectivity depends on the partition coefficients (P) of the analyte and interfering compounds. Both D and P are strongly influenced by the composition of the membrane. To optimize the membrane composition for sub-micromolar detection limit and adequate selectivity, the diffusion and partition coefficients have to be measured in a variety of membranes.

In our contribution, we show that both D and P can be determined voltammetrically using planar electrochemical cell with a carbon fiber microelectrode. Diffusion coefficients were calculated from the steady state current recorded in membranes containing electrochemically active analyte. Utilizing aqueous extraction, a portion of the analyte in each membrane was removed, and membrane/aqueous partition coefficients were calculated from the steady state current recorded in post-extraction membranes and aqueous solution.

We report the diffusion and partition coefficient of a variety of compounds (e.g., ferrocene derivatives, propofol, acetaminophen) in membranes fabricated with a variety of plasticizers (e.g. ortho nitro phenol octyl ether, dioctyl sebacate, and octanol).

1. F. Kivlehan, F. Garay, J. D. Guo, E. Chaum and E. Lindner*, Analytical Chemistr*y, 2012, 84, 7670-7676.

2015 Joint Southeastern/Southwest Regional Meeting 38

The Stokes-Einstein equation and the diffusion of ferrocene in room temperature ionic liquids (RTILs) studied by cyclic voltammetry

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In this study, the classical Stokes-Einstein (SE) equation is used to understand the diffusion of ferrocene (Fc) molecules in room temperature ionic liquids (RTILs). Various symmetric and asymmetric RTILs are used to understand the effect of the symmetry of alkyl substitution and the role of chain length in the diffusion properties of Fc. The diffusion coefficient of Fc is determined by applying the Randles-Sevcik equation to the peak current in the cyclic voltammograms. The diffusion coefficient is found to be higher in symmetric RTILs than in asymmetric ILs with the same number of alkyl carbon atoms, which is consistent with our previous studies where we found the asymmetric RTILs to be more viscous than the symmetric ones having the same number of alkyl carbon atoms. From the SE equation, we find the effective hydrodynamic radius to be to be $(2.1\pm0.1) \times 10^{-10}$ m, which is less than the crystallographic radius (3.5×10^{-10} m) of Fc. This is consistent with previous studies of the diffusion of solutes in RTILs that show the hydrodynamic radius to be less than the van der Waals radius of the solute.

2015 Joint Southeastern/Southwest Regional Meeting 39

Quantification of some heavy metals levels in samples of edible nuts

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The concentration levels of heavy metals in edible nuts are important because they have a significant and recently increasing role in human nutrition.
Samples of several nuts were homogenized, digested (wet acidic digestion) and dissolved. The concentrations of a dozen of heavy metals in these samples were determined by flame atomic absorption spectrometry (F-AAS), graphite furnace atomic absorption spectrometry (GF-AAS) and inductively coupled plasma – optical emission spectrometry (ICP-OES). Additionally, some nut samples were also examined by ATR FTIR spectroscopy. The analytical results will be presented, summarized and compared.

2015 Joint Southeastern/Southwest Regional Meeting 40

Detection of natural product off-rates within complex matrices

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Natural products provide significant chemical diversity and phenotypic screening has been an effective approach to identify bioactive compounds. Target-based screening eliminates questions regarding mechanism that arise from phenotypic screening thus a

third drug discovery approach could effectively combine these methods. However, using target-based screening in the context of traditional bioassay-guided isolation requires methods which can evaluation complex mixtures (i.e. extracts or fractions of natural products) for binding partners. Approaches such as weak affinity chromatography have been explored as options for “ligand fishing,” but surface plasmon resonance has seen limited use. We believe that off-rates obtained through SPR can effectively support bioassay-guided isolation. Our SPR experiments are off-line using the St. Jude natural products fraction library and we are developing methods to effectively analyze sensorgrams. Analysis of off-rates has been shown to be effective in prioritizing reaction mixtures for target binding and can be useful for evaluating natural products as well.

2015 Joint Southeastern/Southwest Regional Meeting 41

Quantification of thiol Raman activity and pK_a values using Raman-based pH titration

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Organothiol and thiol-containing biomolecules are among the most important classes of chemicals used broadly in organic synthesis, biological chemistry, and nanosciences. Thiol pK_a values are key indicators of the thiol reactivity and functionality. Reported herein is an internally-referenced Raman-based pH titration method that enables reliably quantification of thiol pK_a values for both mono- and di-thiols in water. The degree of thiol ionization is monitored directly with the peak intensity of the characterized S-H stretching feature at the 2600 cm^{-1} region relative to an internal reference peak as a function of pH of the titration solution. The pK_a values were determined by curve-fitting the experimental data with two equations derived in this work on the basis of the Henderson- Hasselbalch equation. Using this Raman titration method, we determined for the first time the pK_a values for the two thiols in 1,2-benzenedithol, but only one thiol in1,4-benzenedithiol can be deprotonated in water. This Raman-based method is easy to implement and its underlying theory is easy to follow. It should therefore have broad application for thiol pK_a determinations.

2015 Joint Southeastern/Southwest Regional Meeting 42

Using water Raman intensities to determine the effective excitation and emission pathlengths of fluorophotometers for correcting fluorescence inner filter effect

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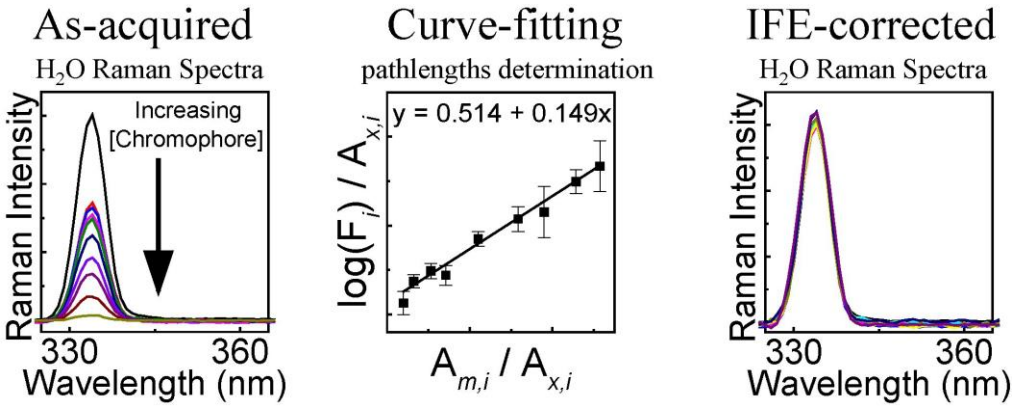
Fluorescence and Raman inner filter effects (IFE) cause spectral distortion and nonlinearity between spectral signal intensity with increasing analyte concentration. Convenient and effective correction of fluorescence IFE has been an active research goal for decades. Presented herein is the finding that fluorescence and Raman IFE can be reliably corrected using the equation $I^{corr}/I^{obsd} = 10^{d_x A_x + d_m A_m}$ when the effective excitation and emission pathlengths, d_x and d_m, of a fluorophotometer are determined by simple linear curve-fitting of Raman intensities of a series of water Raman reference samples that have known degrees of Raman IFEs. The pathlengths derived with one set of Raman measurements at one specific excitation wavelength are effective for

correcting fluorescence and Raman IFEs induced by any chromophore or fluorophore, regardless of the excitation and emission wavelengths. The IFE-corrected fluorescence intensities are linearly correlated to fluorophore concentration over 5 orders of magnitude (from 5.9 nM to 0.59 mM) for 2-aminopurine in a 1 cm × 0.17 cm fluorescence cuvette. This water Raman-based method is easy to implement. It does not involve complicated instrument geometry determination or difficult data manipulation. This work should be of broad significance to physical and biological sciences given the popularity of fluorescence techniques in analytical applications.



2015 Joint Southeastern/Southwest Regional Meeting 43

Raman spectroscopy and liquid-liquid microextractions

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The growing availability of inexpensive, compact Raman spectrometers makes them increasingly attractive for environmental analysis and teaching labs. However, the sensitivity of these instruments can limit their usefulness for liquid phase samples, particularly more dilute solutions. Colloidal substrates for surface-enhanced Raman are difficult to prepare reproducibly, and nanofabricated substrates are expensive. Dispersive liquid-liquid microextraction and cloud-point extraction can preconcentrate organic analytes from aqueous samples, and direct Raman spectroscopy of the organic extractant phase is straightforward. We present our current work on the detection of selected analytes by Raman/LLME methods, and investigation of the extractant phase itself.

2015 Joint Southeastern/Southwest Regional Meeting 44

Incorporation of benchtop NMR spectroscopy into undergraduate laboratories: An active-learning approach

Susanne Riegel*, susie.riegel@nanalysis.com. Nanalysis, Calgary, Alberta, Canada*

NMR Spectroscopy is one of the most widely used characterization techniques in chemistry. Despite pedagogical shifts towards active-learning and guided-inquiry approaches, incorporation of NMR spectrometers directly into undergraduate curriculum

has remained largely limited due to mitigating factors of size, cost and availability of high-field spectrometers. As a result, students rarely gain hands-on access to this instrumentation, particularly in the beginning stages of their programs. An emergence of a new class of benchtop NMR spectrometers (42 – 60 MHz) that are affordable, portable and do not require weekly upkeep or maintenance can facilitate the introduction of this technique at all stages of chemical education. They also offer sufficient resolution and sensitivity for structure elucidation, reaction monitoring, and basic quantitation.

Herein, we describe methods for unique incorporation of the NMReady benchtop spectrometer into undergraduate laboratory experiments and illustrate how students can learn the proper technique to use an NMR spectrometer, prepare samples, monitor and characterize reaction mixtures.

2015 Joint Southeastern/Southwest Regional Meeting 45

A multi-year analysis of commercial bleach solution

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A common oxidation-reduction titration to perform in a General Chemistry laboratory is the analysis of hypochlorite in commercial bleach solutions. Clorox® bleach, when purchased, has a listed hypochlorite mass percent of 8.25%, but it is assumed that over time the hypochlorite decomposes. A laboratory procedure has been developed in which the students analyze current bleach and then one of three previous year bleach solutions. By entering the relevant data into a google spreadsheet the students then gain some experience in working with a large data set, with analyzing data for inconsistencies and using excel to do calculations. From this data the students are then able to calculate the mass percent of the hypochlorite and see how much the bleach has decayed over time.

2015 Joint Southeastern/Southwest Regional Meeting 46

Analysis of food dyes in powdered drinks

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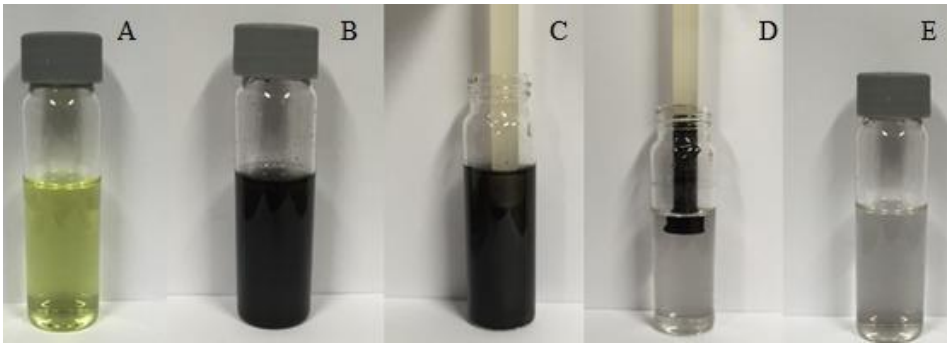
In an experiment for introductory and general chemistry labs, students can analyze dyes in different samples of powdered drinks in order to find the wavelengths of maximum absorbances for different colored solutions using a Vernier SpectraVis Plus spectrophotometer. Solutions are made both gravimetrically and volumetrically. In general chemistry labs, Beer's Law will be used to analyze a mixture of two dyes and multi-wavelength linear regression analysis (MLRA) is used in upper-level labs for more complex solutions with overlapping spectra.

2015 Joint Southeastern/Southwest Regional Meeting 47

Salicylic acid and 4-nitroaniline removal from water using magnetic bio-char: An environmental and analytical experiment for the undergraduate laboratory

Akila G. Karunanayake*, uak1@msstate.edu, Olivia A. Todd, Narada B. Dewage, Matthew Essandoh, Todd Mlsna, Deb Mlsna. Chemistry Department, Mississippi State University, Mississippi State, Mississippi, United States*

Adsorption studies of salicylic acid (SA) and 4-nitroaniline (4NA) from aqueous solutions were performed with magnetized Rinsed Ultra bio-char (MBC) in order to train students in analytical techniques such as standard calibration curves, UV-Vis spectrophotometry and separation techniques. Analysis of samples purified by MBC enhances student understanding of water purification concerns and environmental regulation while identifying the efficiency of bio-char adsorption. MBC was prepared by iron oxide precipitation onto the bio-char surface using an aqueous Fe^{3+}/Fe^{2+} solution followed by NaOH treatment. This undergraduate laboratory experiment has been developed and tested with multiple groups of students in Spring and Summer of 2015. Surveys and sample student data were utilized to refine the procedural steps and analyze the consistency of student data.



2015 Joint Southeastern/Southwest Regional Meeting 48

Making sense of the endless: Information seeking behaviors of organic chemistry graduate students

*Lindsey Cain[2], **Gautam Bhattacharyya**[1], gautamb@missouristate.edu. (1) Department of Chemistry, Missouri State University, Springfield, Missouri, United States (2) Chemistry, Anderson University, Anderson, South Carolina, United States*

A core activity of any research project involves obtaining and interpreting information from the primary literature. From the conception of a study during which researchers review extant publications to verify that the proposed work would, indeed, be of a novel nature, to the execution of the experiments wherein researchers use the literature to develop protocols, the literature tends to play a pivotal role in virtually every phase of a research project. It follows, therefore, that learning to successfully navigate the literature should be a main outcome of the training of undergraduate and graduate research students.

In recent years this navigation of the literature has been conducted by means of

electronic media – primarily SciFinder in the case of chemists. In spite of this convenience, searching for information and interpreting outputs from SciFinder involves a complex set of cognitive operations which have to be used recursively in a non-linear fashion. As a first step in understanding this process, we conducted case studies of five organic chemistry Ph.D. students about their information seeking behaviors (ISBs). Through a set of two interviews, each last 60 to 90 minutes, we elicited the students' self reports regarding their ISBs and observed these students as they worked on a task in which they were to develop a synthetic pathway for a previously-unsynthesized small molecule.

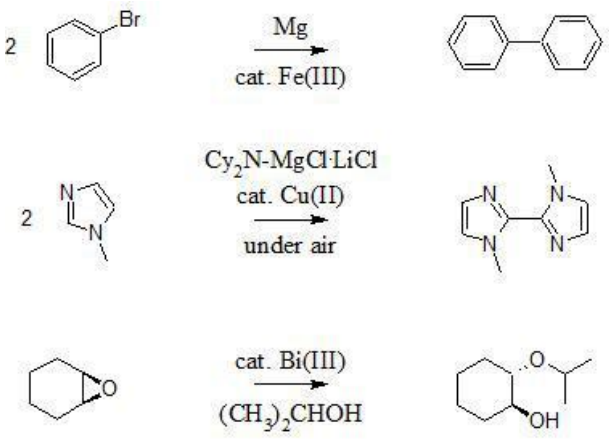
Results indicate that students spend the majority of their time evaluating information instead of searching for it. Furthermore, the database evolves from a primary tool for analysis for students in their second or third year of study to a repository of confirmatory information for students in their fifth or sixth year. Paradoxically, the students with the least experience appear to rely more on their intuition as opposed to the results from their searches; whereas, the students with the most experience used the outcomes of the searches to determine what would or would not be possible. Finally, the influence of the students' research groups was most strongly manifested in how each participant evaluated retrieved articles for their feasibility as research protocols. In addition to the results, implications for undergraduate laboratory instruction will be discussed.

2015 Joint Southeastern/Southwest Regional Meeting 49

Introducing metal catalysis in the introductory organic chemistry laboratory

***C. E. Ballard**, eballard@ut.edu. Department of Chemistry, Biochemistry & Physics, University of Tampa, Tampa, Florida, United States*

Metal catalysis continues to grow in significance as a field of organic chemistry research. Nevertheless, this topic has received little attention (with the exception of hydrogenation reactions) in most introductory organic chemistry textbooks. It is difficult to add metal-promoted reactions to the in-classroom curriculum because of the large number of topics that are already covered. The department at my institution has adopted a philosophy of using the accompanying laboratory course both to reinforce the topics discussed in the classroom and to introduce contemporary topics that cannot be accommodated in a tight course schedule. We have been adapting procedures from the chemical research literature and developing novel experiments to emphasize metal catalysis as a green approach to chemical synthesis. Iron- and copper-catalyzed homocouplings illustrate the richness of base metal redox chemistry in the context of synthesis. Another procedure is a bismuth-catalyzed solvolytic opening of an epoxide that demonstrates the utility of a relatively nontoxic metal as an acid. These experiments are practical because they require commercially available reagents and the equipment present in a typical U.S. introductory organic chemistry laboratory.



2015 Joint Southeastern/Southwest Regional Meeting 50

Instructional technology to increase student engagement and participation in chemistry

Rachel Glazener[1,2]*, rlglazener@pstcc.edu. (1) NBS, Pellissippi State Community College, Rockford, Tennessee, United States (2) Tennessee Board of Regents, Nashville, Tennessee, United States*

Like most STEM subjects, chemistry are a fast paced and complex courses. Developing content delivery methods that both assess progress and engage students can be challenging. In fact, due to the difficult nature of the course, creating an environment where students feel comfortable collaborating and participating in discussions is often more challenging than gauging their progress.

In this session, learn how Rachel Glazener of Pellissippi State Community College uses NearPod, a teaching and learning platform for BYOD, to improve student engagement and interaction with both course material and each other in her general and organic chemistry classes.

Rachel will share how she uses these platforms to create and deliver interactive lesson plans directly to student devices and pinpoint individual cognitive gaps using real-time assessments. She will discuss how NearPod has allowed her to achieve an atmosphere that encourages collaboration, active learning of material, and discussion among the entire class, not just her “A” students.

You’ll also discover how using instructional technologies helped break down common learning barriers resulting in increased confidence in course material, and directly impacted long-term retention of content and, in some cases, each student’s overall course grade.

2015 Joint Southeastern/Southwest Regional Meeting 51

Monitoring gains in visualization skills

Maria Oliver-Hoyo*, maria_oliver@ncsu.edu. Chemistry, North Carolina State University, Raleigh, North Carolina, United States*

A semester-long intervention was designed to promote visualization skills and was implemented in an inorganic course. As part of the intervention, 3D physical models were developed to help students deconstruct the visualization needed when learning symmetry. The systems provided students with physical and visual frames of reference to facilitate the complex visualization involved in symmetry and group theory concepts. The VSCS tool was administered at the beginning and end of the semester in order to monitor if changes in visual-perceptual skills could be detected. This presentation will give an overview of what the intervention entailed and will discuss the results of the scores of inorganic students on the VSCS.

2015 Joint Southeastern/Southwest Regional Meeting 52

Coupling DFT calculations with experiment in the physical chemistry laboratory

Thomas C. Devore, *devoretc@jmu.edu, Arlie Bagley, Jun Yin. Chemistry Dept, James Madison Univ, Harrisonburg, Virginia, United States*

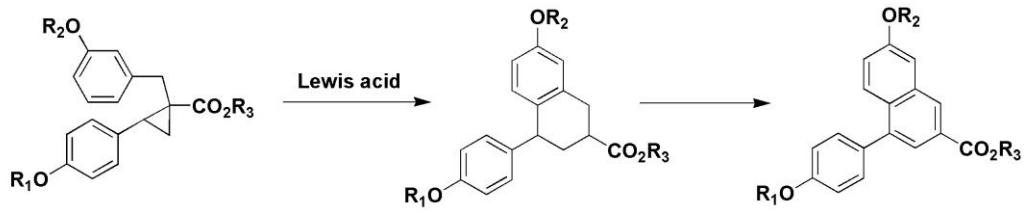
The increasing availability of relatively low cost research quality quantum mechanical software packages that will run on a personal computer enables the inclusion of these calculations into many laboratory exercises done in the P-chem lab. There are three ways to incorporate these calculations. The first is to add them on to an existing exercise. The well-known HCl-DCl experiment will be used to illustrate how this can be done. The second way is to integrate them into the experiment. Several exercises based on the NMR of methanol vapor will be used to illustrate this. The final way is to have calculations be the exercise. A discovery exercise for the Aufbau Principle and Hund's Rule will be used to illustrate this approach.

2015 Joint Southeastern/Southwest Regional Meeting 53

Synthesis of carbocyclic ring systems from donor-acceptor cyclopropanes

Radhika Reddy Nareddy[1], *nareddy.radhika@gmail.com, Keith T. Mead*[2]*. (1) Chemistry, Mississippi State University, Starkville, Mississippi, United States (2) Chemistry, Mississippi State University, Starkville, Mississippi, United States*

Carbocyclic ring systems are frequently found in biologically active natural products and their synthesis is often a significant challenge for synthetic chemists. Donor-Acceptor Cyclopropanes (DAC) in recent years have gained much attention in this respect, due to their ability to give rise to the reactive zwitterionic species upon activation by Lewis acids. This talk presents the study towards the synthesis of important carbocyclic ring systems via Lewis acid activation of Donor-Acceptor Cyclopropanes and the various synthetic routes explored for the synthesis of these Cyclopropanes.



$R_1 = R_2 = R_3 = CH_3$

$R_1 = R_2 = CH_3$, $R_3 = C_2H_5$

2015 Joint Southeastern/Southwest Regional Meeting 54

Syntheses, structures, and chemistry of a small series of isoindenone derivatives

***Markus Etzkorn**, metzkorn@uncc.edu, Victoria L. Wait, Alexander Smith, Joseph I. Franklin, Conly Strickland. UNC Charlotte Dept of Chemistry, Charlotte, North Carolina, United States*

Isoindenones are known as fleeting intermediates that may be trapped in Diels-Alder reactions or dimerized to a variety of polycyclic scaffolds. This presentation discusses the generation and fate of differnetly substituted isoindenone derivatives, the structures of their corresponding dimers, and selected chemical transformations toward novel hydrocarbons and non-classical carbocations.

2015 Joint Southeastern/Southwest Regional Meeting 55

Synthesis of substituted pyridines from dihydropyridones

***Sezgin Kiren**, sezginkiren@gmail.com. Chemistry, Winston Salem State University, Winston Salem, North Carolina, United States*

The presented research involves the studies of aromatization reactions of an adduct obtained from 1,2-addition of organocerium reagents to 2-substituted 2,3-dihydro-4-pyridones. The formation of substituted pyridines will be realized under various conditions. The advantages of this strategy will be as follows: (a) utilize the very well-established reactions, (b) employ simple, commercially available and inexpensive starting materials, (c) rapidly and efficiently generate structural complexity and diversity to reach substituted pyridines containing natural products and their analogs for drug discovery.

2015 Joint Southeastern/Southwest Regional Meeting 56

Siloxymethylamines: Methylamine transfer reagents leading to new organic chemistry

***Keith H. Pannell**, kpannell@utep.edu, Hemant Sharma, Paulina E. Gonzalez, Sanchita Chakrabarty. Chemistry, U. T. El Paso, El Paso, Texas, United States*

Transition metal-catalyzed silane, R_3SiH, reduction of amides, e.g. $HC(O)NR'_2$, to amines, $CH_3NR'_2$, an ACS Green Institute “dream” reaction, proceeds *via* the intermediacy of siloxymethylamines, $R_3SiOCH_2NR'_2$, **1**.[1] These intermediates, which may be isolated in good yields, react with a further equivalent of silane, R_3SiH, to form the corresponding methylamine and disiloxanes. We have initiated a detailed study of the reactions of **1**, R = Et, with a range of element-H species, element = O, S, N, P, etc., and unearthed a smorgasbord of chemistry often leading to previously unavailable heteroatom organics. Of particular interest are the reactions with amines, both primary and secondary, resulting in new polyamine systems, $R_2NCH_2NR'_2$, $R'_2NCH_2NRCH_2NR'_2$, etc., which themselves can be used to form new polyamine-metal complexes with interesting catalytic properties. Reactions of **1** with thiols, R”SH, and/or

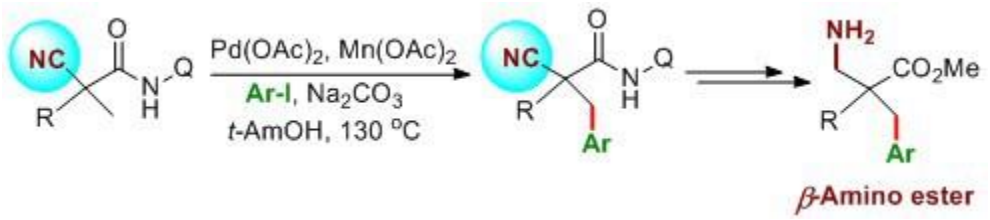
alcohols, R”OH, result in either direct substitution of the siloxy group to form $RECH_2NR'_2$, E = S or O, or in the case of aromatic R” groups involve interesting aminomethylation of the aromatic.

2015 Joint Southeastern/Southwest Regional Meeting 57

Palladium-catalyzed direct arylation of C(sp^3)-H bonds of *α*-cyano aliphatic amides

*E. Blake Watkins, **M. D. Reddy**, dreddy@uu.edu. Pharmaceutical Sciences, Union University School of Pharmacy, Jackson, Tennessee, United States*

$Pd(OAc)_2$-catalyzed arylation of C(sp^3)-H bonds in *α*-cyano-*α*-methyl aliphatic amides is achieved in the presence of 8-aminoquinoline, as a removable directing group, using $Mn(OAc)_2$ and Na_2CO_3. The current strategy enables the placement of an aryl/heteroaryl group at the *β*-position of *α*-cyano aliphatic acid derivatives for the first time. Wide functional group tolerance and easily accessible starting materials provide an efficient protocol for the synthesis of arylated *α*-cyano amides. Furthermore, the synthetic utility of the products has been demonstrated by their efficient conversions to medicinally important *α*, *α*-dialkylated acid and *β*-amino acid derivatives.

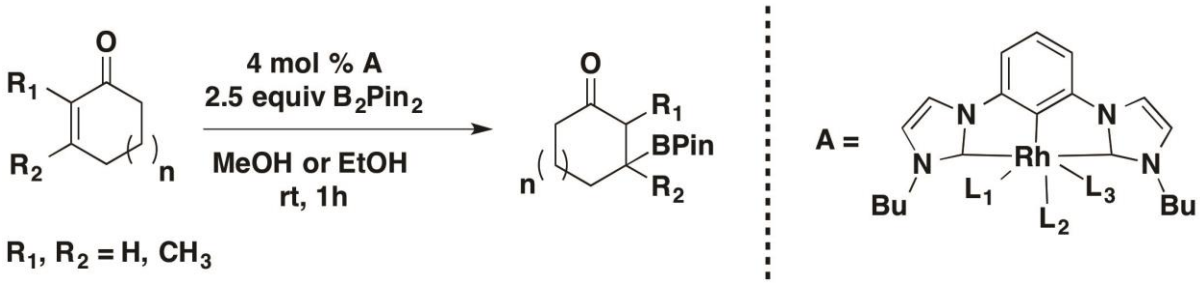


2015 Joint Southeastern/Southwest Regional Meeting 58

Synthesis and isolation of CCC-NHC pincer Rh complexes and catalytic β-boration of α, β-unsaturated carbonyl compounds

***Gopalakrishna Akurathi**, gopalaaa@gmail.com, Sean Reilly, Thedford K. Hollis. Chemistry, Mississippi State University, Starkville, Mississippi, United States*

Organoboronic acid derivatives are an important class of precursors for organic transformations. Particularly diboryl adds to alkenes and alkynes in the presence of a catalyst to generate various functionalized compounds. We in our group have synthesized air and water stable CCC-NHC pincer Rh complexes and separated them for the first time through column chromatography. Evaluation of the catalytic activity of the complexes for β-boration of α, β-unsaturated carbonyl compounds was explored using the crude CCC-NHC pincer Rh complex mixture that is initially isolated, as well as the isolated Rh amine adducts. They were found to be efficient precatalysts at room temperature in eco-friendly solvents (MeOH and EtOH). The latest results in characterization of the CCC-NHC pincer Rh crude mixture and substrate scope will be reported.

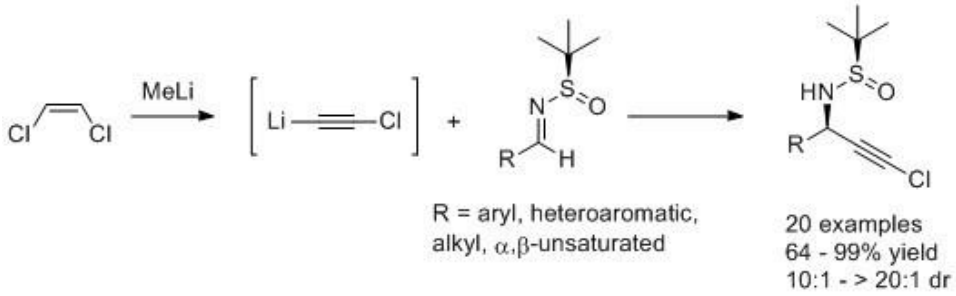


2015 Joint Southeastern/Southwest Regional Meeting 59

Highly stereoselective synthesis of terminal chloro-substituted propargylamines and further functionalization

Mark L. Turlington*, mturlington@berry.edu, Savannah Jordan, Samuel A. Starks, Michael F. Whatley. Chemistry, Berry College, Rome, Georgia, United States*

The highly stereoselective addition of lithiated chloroacetylene, derived in situ from *cis*-1,2-dichloroethene and methyl lithium, to Ellman chiral N-*tert*-butanesulfinyl imines is reported. The reaction proceeds in high yield (up to 99%) and with excellent diastereoselectivity (up to >20:1) for a variety of aryl, heteroaromatic, alkyl, and α,β-unsaturated imine substrates. Transformations of the terminal chloro-substituted propargylamine products are described in which lithium-halogen exchange yields nucleophilic acetylides that can be quenched to yield terminal alkynes or intercepted by carbon electrophiles.



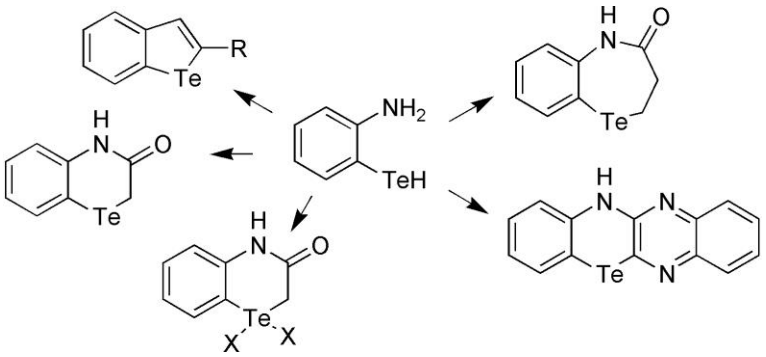
2015 Joint Southeastern/Southwest Regional Meeting 60

Organotellurium chemistry: novel Te, N-containing heterocycles

Thomas Junk*[1], txj9137@louisiana.edu, Gabrielle Sanford[1], Kaitlyn Walker[1], Frank Fronczek[2]. (1) Chemistry, University of Louisiana at Lafayette, Lafayette, Louisiana, United States (2) Chemistry, Louisiana State University, Baton Rouge, Louisiana, United States*

The chemistry of the five- six- and seven-membered Te, N-containing heterocycles remains relatively unexplored, mostly due to a lack of methods available for their preparation. Many of these compounds exhibit remarkable stabilities to heat, light and

air. Current and potential future applications include their use as antioxidants, as synthetic intermediates, in materials sciences applications and as pharmaceuticals. Improved access to novel classes of organotellurium heterocycles is expected to lead to additional applications. Recent progress will be reported in the synthesis of 2-aminobenzenetellurol and its cyclization to benzo-1,3-tellurazoles, benzo-1,4-tellurazines and benzo-1,5-tellurazepines. Their chemical properties and structural features will be discussed and differences between them and their sulfur analogs highlighted.



2015 Joint Southeastern/Southwest Regional Meeting 61

Friedel–Crafts hydroxyalkylation of N-alkylindoles with aryl aldehydes: Isolation of 1:1 adduct through a silyl triflate-mediated reaction

***Chiles W. Downey**, wadedowney@post.harvard.edu. University of Richmond, Richmond, Virginia, United States*

When N-alkylindoles are reacted with aromatic aldehydes in the presence of trimethylsilyl trifluoromethanesulfonate and an amine base, silyloxyalkylation of the indole occurs at the 3 position. The silyl group can be removed with TBAF under basic conditions to afford the hydroxyalkylation adduct. This process almost completely avoids the formation of the thermodynamically favored triarylmethane byproducts typically observed under Friedel-Crafts conditions for these reactants. The method has been expanded to include free indoles.

2015 Joint Southeastern/Southwest Regional Meeting 62

Regioselective transition metal-free 1,4-conjugate addition of Grignard reagents to dienones and thiodienoates

***Emmanuel Amoah**, eamoah@clemson.edu. Chemistry, Clemson University, Seneca, South Carolina, United States*

Conjugate additions of alkyl, aryl, and heteroaryl Grignard reagents to α,β,γ,δ-unsaturated ketones and thioates in the absence of transition metal catalysts or organo-catalysts have been investigated in diethyl ether, THF, and dichloromethane as solvents at -20^{o}C. Both dienones and thiodienoates cleanly undergo 1,4- conjugate addition reactions with alkyl Grignard reagents in the absence of any transition-metal catalysts or

organo catalysts.
While aryl and some heteroaryl Grignard reagents all exclusively added 1,4- to the thiodienoates, Grignard reagents from furan, and thiophene derivatives all gave, at best, a 1:1 mixture of both 1,2- and 1,4- adducts with the dienones as conjugate acceptors. Moreover, both methyl and alkynyl Grignard reagents gave only 1,2- additions to the dienones with yields over 80% but gave neither 1,2- nor 1,4- products with the thiodienoates.
For all the alkyl Grignard reagents investigated, only *tert*-butylmagnesium bromide gave minor amounts of 1,6-aducts for both the dienones and the thiodienoates. Control experiments conducted using catalytic amounts (0.5, 1.0, 5.0, 10.0, and 20 mol%) of zinc triflate did not show any significant difference in the regioselectivity, although zinc bromide induced 1,2- selectivity in a few of the reactions with the dienones.

2015 Joint Southeastern/Southwest Regional Meeting 63

Polysaccharide-based biomaterials for regenerative medicine

Tao L. Lowe*, tlowe4@uthsc.edu. Pharmaceutical Sciences, University of Tennessee Health Science Center , Memphis, Tennessee, United States*

Polysaccharides become increasingly attractive as biomaterials for drug delivery and tissue engineering due to their carbohydrate structure and function. In this talk, I will discuss the design and development of polysaccharide-based nanoparticles and hydrogels with tunable chemical, physical, degradation and mechanical properties for drug delivery across the blood brain/retinal barrier, cartilage repair and dental pulp stem cell growth.

2015 Joint Southeastern/Southwest Regional Meeting 64

Stimuli-responsive multilayer nanobiomaterials for controlled delivery and transplantation

Eugenia P. Kharlampieva*, ekharlam@uab.edu. Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama, United States*

Bio-inspired fabrication of biologically-active and stimuli-sensitive nanomaterials are of increasing interest in bio- and nanotechnology. This talk will focus on functional nanostructured microgels, hollow microcontainers (capsules), and nanothin coatings obtained by hydrogen-bonded layer-by-layer assembly of synthetic and biological macromolecules on inorganic templates and living cells. We will discuss volume and shape transitions in these microparticles in response to pH- and temperature variations to be used in controlled drug delivery. We will also address the application of these nanostructured materials in cell-based transplantation therapy. We will present nanothin immunomodulatory coatings with diminished inflammatory immune responses deposited on surfaces of mammalian pancreatic islet cells. These materials provide prolonged cell viability and function to be used in diabetes treatment.

2015 Joint Southeastern/Southwest Regional Meeting 65

Photo-induced release of retinoic acid from polymer micelles for cardiomyogenic stem cell differentiation

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Retinoic acid (RA) is an important morphogen that is involved in all stages of heart development by regulating cellular differentiation and proliferation of progenitor cells. To understand the effect of RA concentration gradients in cardiac tissue development and repair, we developed a RA grafted photo-cleavable polymeric nanocarrier with a capability to release RA upon UV exposure. In current design, o-nitro benzyl ester (ONB) would undergo photo-cleavage upon photo-irradiation to provide time/or dose dependent sustain release of RA from micelles thereby enabling temporal control of RA availability to direct embryonic stem cell (ESC) differentiation in cardiac lineage (**Figure 1A**). Briefly, a pendent azido functional amphipilic copolymer ($mPEG_{113}$-b-PCL_{83}-co-N_3PCL_{98}) was prepared by ring opening polymerization and coupled with alkyne end functional ONB-RA conjugate through click chemistry. The formation of polymer-RA conjugate ($mPEG_{113}$-b-PCL_{83}-co-N_3PCL_{98}-g-ONB-RA) and it precursors was confirmed by ^1H NMR and GPC (**Figure 1B**). We also prepared a pyrene-4-butyric acid grafted ONB polymer conjugate ($mPEG_{113}$-b-PCL_{83}-co-N_3PCL_{98}-g-ONB-pyrene) using similar methodology. Copolymer formed stable micelles with an average diameter of ~90 nm as confirmed by DLS (**Figure 1C**). We first confirmed the photo-cleavage of ONB through polymer-ONB-pyrene conjugate (**Figure 1D**) through UV based absorption measurements that was further replicated under similar conditions to polymer-RA conjugate at 360 nm. A detailed study about elucidating the regulatory roles of RA gradients in cardiac differentiation of ESCs will be presented.

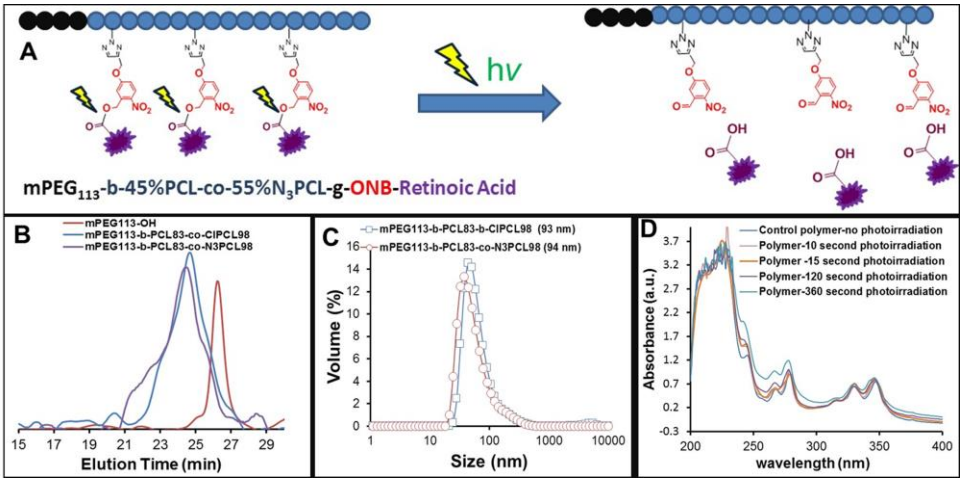

Figure 1. Synthesis and characterization of photo-cleavable polymer-RA conjugate, (**A**) Schematic for light triggered release of RA from polymer-RA conjugate, (**B**) GPC traces of $mPEG_{113}$-b-PCL_{83}-co-N_3PCL_{98} and precursor polymers, (**C**) DLS traces show $mPEG_{113}$-b-PCL_{83}-co-N_3PCL_{98} and precursor polymer forms stable micelles, (**D**) Photo-triggered release of pyrene-4-butyric acid (at 242 nm) from pyrene micelles with 360 nm light.

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Polymeric carriers for on-demand therapies and conquering the undruggable

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The Duvall Advanced Therapeutics Laboratory specializes in innovative design of smart polymer-based technologies for: (1) intracellular delivery of biological drugs such as peptides and nucleic acids, (2) proximity-activated targeting of drugs to sites of inflammation and matrix remodeling, and (3) long-term, “on-demand” drug release from localized depots. These delivery systems are designed to improve the therapeutic index of existing drugs and/or to serve as enabling technologies for manipulation of intracellular targets currently considered to be “undruggable”. To achieve optimal, finely-tuned properties for these varied biomedical applications, polymers are utilized that respond to one or more environmental stimuli including pH, matrix metalloproteinases, reactive oxygen species, and temperature. This talk will focus on the latest innovations for improving longevity of autologous vascular bypass transplants, promoting vascularization and tissue regeneration, and treating breast cancer.

Pattern-based sensing applications of hyperbranched poly(amidoamines)

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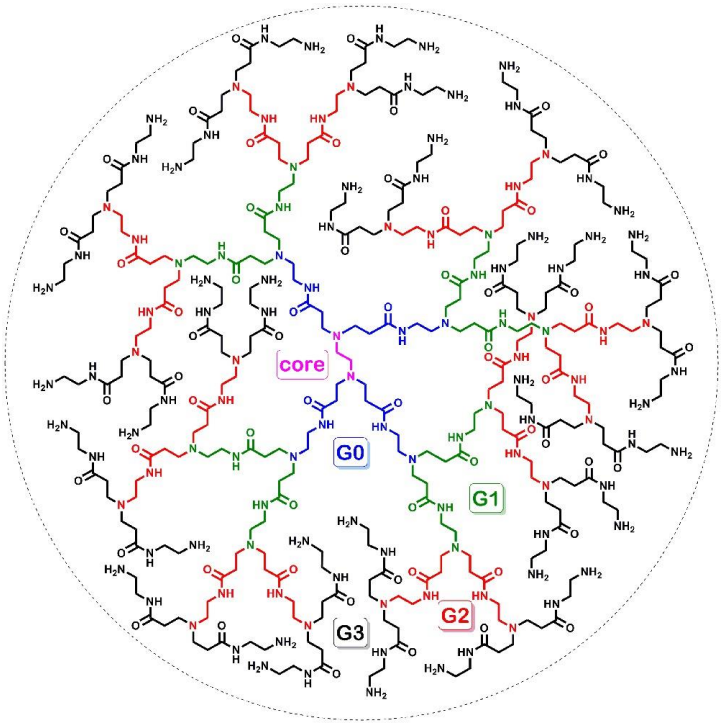
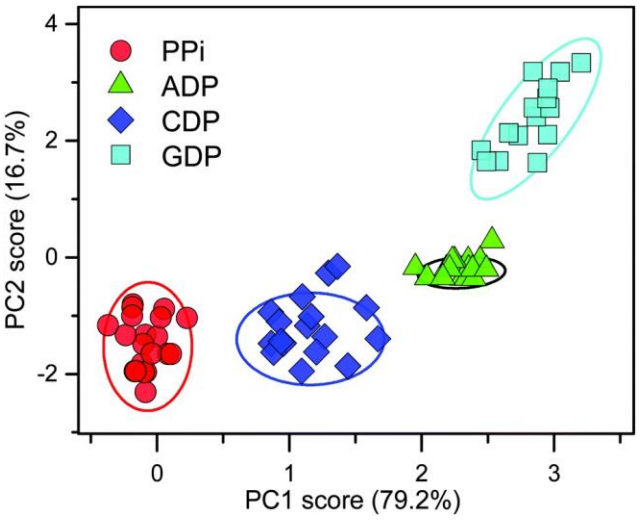
The poly(amidoamine) (PAMAM) dendrimers are large water-soluble polyelectrolytes capable of binding multiple small organic molecules through a variety of intermolecular interactions. These polymers carry multiple charges even in neutral aqueous solutions (e.g. in common physiological and environmental conditions), so they can establish strong interactions with other charged species.
Although electrostatics play a major role in determining their binding behavior, these systems display nuanced binding preferences thanks to weaker but distinctive intermolecular forces such as hydrogen bonding and aromatic-mediated interactions. These interactions are key in determining the polymers’ selectivity for small organic molecules in aqueous solution.
We have developed analytical applications of these systems based on these polymers and common fluorescent dyes that can detect anionic analytes in physiological conditions using pattern-based sensing and fingerprinting techniques. We will report on the differentiation of nucleotide phosphates and organophosphate in water solution in physiological conditions using a sensing system built from commercially available components by non-covalent interactions that require no synthetic effort.





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Preparation of lipoate-related branched polymers by two different chemistries: Utilizing radical ring-opening reaction of cyclic disulfide and thiol-ene reaction

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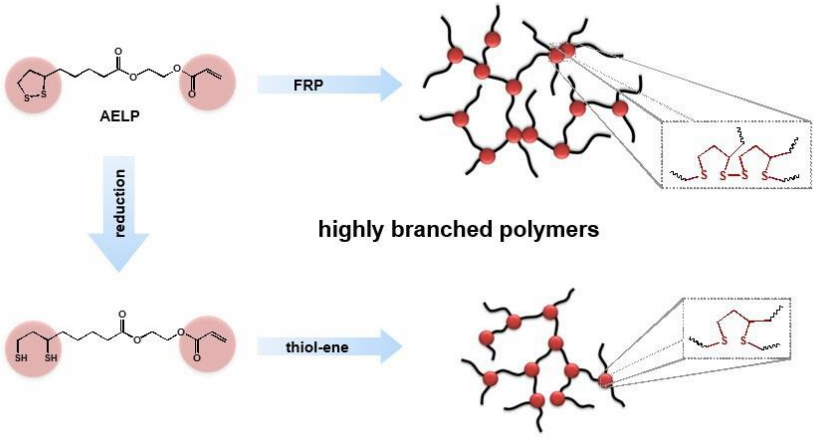
Highly branched polymers have been prepared from 2-acryloyloxyethyl lipoate (AOELp), a monomer containing two radically polymerizable moieties: a cyclic disulfide and a vinyl, which is synthesized by the esterification of 2-hydroxyethyl acrylate (HEA) and lipoic acid (LA). On one hand, since the cyclic disulfides are able to participate in radical ring-opening polymerization, they incorporate into the propagating polymer chain and

leave the vinyl sites as pendants for possible crosslinking during the free radical polymerization. The branched polymers with disulfide bonds embedded in the backbones are thus formed by at least two consecutive cyclic disulfide radical ring-opening reactions or by the radical coupling of two sulfur-centered radicals. On the other hand, the disulfide bonds can cleave into two thiols upon suitable reducing agents, and lead to the formation of a much branched architecture when treated with radicals or bases triggerring the coupling reaction between vinyl groups and thiols via thiol-ene click chemistry. These two completely distinctive mechanisms highlight the application of this monomer in the synthesis of highly branched polymers and also the design of new biodegradable materials.



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Oxovanadium(IV) carboxylates

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The standard methods of producing vanadyl acetate usually involve a significant amount of lithium hydroxide, long heating times, and several steps. After the synthesis there is still a disposal problem with the by-products. A new method has been developed that simplifies the process, shortens the time, and reduces the disposal issues. A variety of oxovanadium(IV) carboxylates have been synthesized by the hydrazine reduction of vanadium pentoxide in the presence of carboxylic acids. The synthesis procedure will be discussed along with appropriate comments to both scale-up and scale-down problems.

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Facile activation of red phosphorus through solution- and flow-chemistry methods

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Polyphosphides are negatively charged clusters of phosphorus atoms that adopt a variety of structural motifs and exhibit fascinating chemistry. Most recently, these species have been proposed as precursors for high-performance materials such as 2D semiconductors and anodes for lithium-ion batteries. Small polyphosphide clusters are routinely synthesized from their elemental constituents by high-temperature solid state reactions, whereas larger frameworks are typically produced in solution through activation of white phosphorus in complex solvent mixtures. Such methods, however, are difficult to scale up and thus limit the access to large quantities of polyphosphides, which in turn deter the exploratory chemistry, as well as the potential uses, of polyphosphides. We have recently developed a facile solution-phase route for activating red phosphorus to polyphosphides that allowed us to transition to an unprecedented flow-chemistry process to produce large amounts of soluble polyphosphides. The soluble species were characterized by 1D and 2D 31P-NMR. The product identity was further confirmed by single-crystal X-ray diffraction.

Ligand-to-ligand and host-to-guest energy transfer in hybrid crystalline scaffolds

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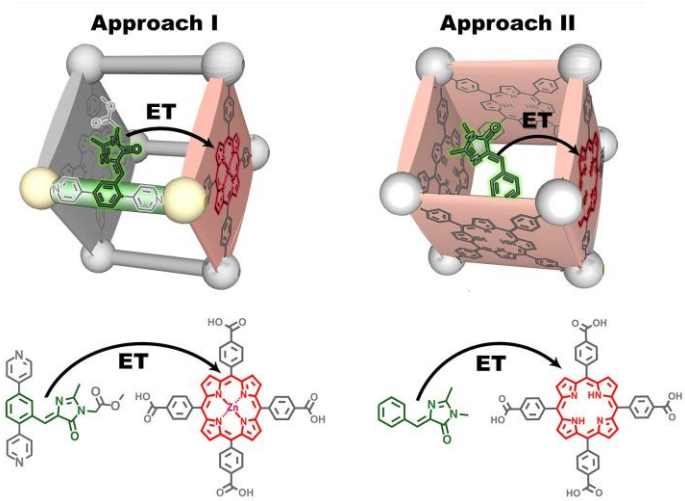
Development of new solid-state materials capable of efficient energy capture and transfer in a predesigned pathway is essential for expansion of organic solar cell utilization and evolution of catalytic systems. In the natural photosystem, the efficiency of solar energy utilization is nearly 100%, due to the hierarchical organization of hundreds of chromophores which provides a pathway for efficient directional energy transfer (ET). Therefore, to mimic the natural photosystem, artificial light-harvesting architectures should rely on the cooperative work of hundreds of chromophores possessing a predesigned pathway for efficient ET. Such complex chromophore organization can be achieved in self-assembled metal-organic frameworks (MOFs), in which the distances and angles between chromophores can be determined from single-crystal X-ray studies and tuned through ligand design or variation of experimental conditions.
Herein, we reported two different approaches to achieve high efficiency of ET through integration of chromophores with 4-hydroxybenzylidene imidazolinone (HBI) and porphyrin cores into a metal-organic scaffold. We have demonstrated that the developed approaches allowed us to achieve significant chromophore coupling, which resulted in high efficiency of ET. By coordinative immobilization of HBI- and porphyrin-containing chromophores into a MOF matrix, we were able to achieve 65% ligand-to-ligand ET efficiency. Moreover, high efficiency of ET (72%) was also obtained in the case of non-coordinative incorporation of an HBI-based molecule inside a three-dimensional porphyrin-based MOF. The presented strategy foreshadows the utilization of MOFs as a versatile platform for development of materials with a high efficiency of solar energy conversion.



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Photoswitch-directed photoluminescence of metal-porphyrin frameworks

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In the natural photosystem, high efficiency of solar energy utilization directly depends on the hierarchical organization of several hundred chromophores. Such chromophore arrangement can be achieved in self-assembled metal-organic frameworks (MOFs), crystalline materials, made from organic linkers and inorganic building blocks. One of the great advantages of MOFs for replication of the natural photosystem is that distance and angles between chromophores can be determined by single-crystal X-ray crystallography and tuned through ligand design or variation of synthetic conditions. Using MOFs as a versatile platform, we developed a novel approach which allows us to control photoluminescence of MOFs as function of excitation wavelength.[1] We were able to coordinatively immobilize light-harvesting porphyrin-based linkers and photochromic diarylethene-based linkers in a MOF matrix, and thereby, tune photophysical properties of the material through photoisomerization of diarylethene-based ligands. Moreover, the incorporated photochromic linker was still able to maintain its photoswitchable behavior after several optical cycles without degradation of MOF integrity. The described approach could be employed to control the photophysical behavior of large light-harvesting ensembles.

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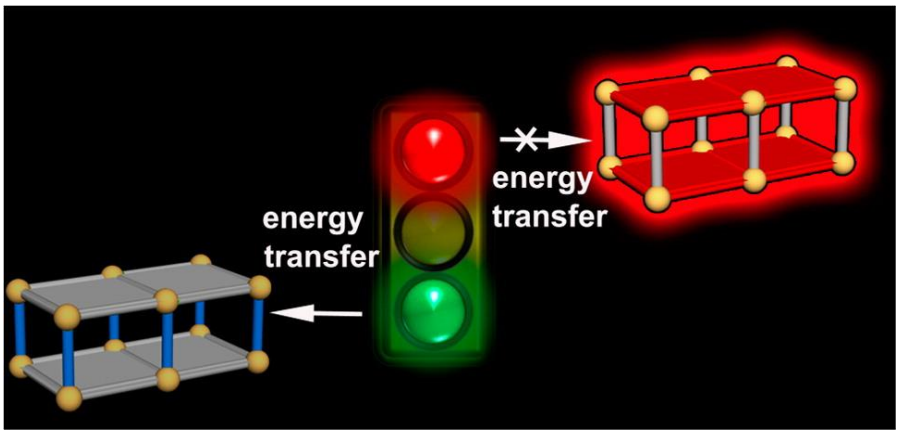

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Metal-organic frameworks with bowl-shaped ligands

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Metal-organic frameworks (MOFs) are crystalline materials made organic linkers and inorganic building blocks. Due to structural modularity and intrinsic porosity, MOFs have been already utilized for a wide range of applications including gas storage and purification, sensing, catalysis, and light harvesting.[1,2]
Herein, we report rational design and preparation of the MOFs with bowl-shaped ligands. The advantages of coordinative immobilization of the ligands inside the rigid metal-organic frameworks will be discussed. The prepared hybrid materials produced using a solvothermal approach was characterized by single crystal X-ray crystallography, powder X-ray diffraction, infrared spectroscopy, UV-vis spectroscopy, fluorescence spectroscopy, thermogravimetric analysis, and cyclic voltammetry. Upon further development, MOFs with aromatic bowl-shaped linkers could foreshadow a new avenue for the engineering of new sensors, solar cells, battery anodes, or light-emitting diodes in the future.

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Visible light active semiconductor composites for enhanced photocatalytic activity

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A clean and sustainable energy source is a basic requirement for addressing the current increase in global energy demand and environmental issues. Semiconductor-based photocatalysis has received tremendous attention in the last few decades because of its potential for solving current energy and environmental problems. In a semiconductor photocatalytic system, photo–induced electron-hole pairs are produced when a photocatalyst is irradiated by light with frequencies larger than that of its band gap (hv > E_g). The photo-generated charge carriers can either recombine with no activity, or migrate to the surface of the semiconductor, where they can be involved in redox processes. The photocatalytic efficiency depends on the number of charge carriers taking part in the redox reactions and on the life time of the electron-hole pairs generated by the photoexcitation [1]. High recombination rate of charge carriers and limited efficiency under visible light irradiation are the two limiting factors in the development of efficient semiconductor-based photocatalysts. To overcome these drawbacks, a number of chemical and design strategies have been developed [2]. Among these strategies, the design and formation of composites using two or more semiconductor catalysts is a promising approach [3]. Here, the complete study of composites of Bi_2O_3 and tantalum based compounds (Ta_2O_5/ or TaON/ or Ta_3N_5) and composite of Bi_2O_3 and WO_3 is reported and discussed. We used these two systems to demonstrate that the design and preparation of composites with proper band gaps and relative band positions can facilitate charge separation/migration and decrease the charge recombination probability, thus enhancing the photocatalytic efficiency in visible light [4-5]. On the basis of observed activity, band positions calculations, and photoluminescence data, a mechanism for the enhanced photocatalytic activity for the heterostructured composite is proposed and discussed (Fig. 1a and b).

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Codeposition and potential pulse atomic layer deposition (PP-ALD) of CdTe thin films

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CdTe thin films are some of the most promising candidates for semiconducting devices, solar energy converters, and photovoltaics. In this work, thin films of CdTe were electrodeposited onto Au substrates from an acidic, aqueous solution of CdSO4, and TeO2 at room temperature. Differing from the traditional co-deposition and electrochemical atomic layer deposition (E-ALD) methods, rectangular potential pulse electrodeposition was used to form high quality films. The pulse mode parameters were varied and the effect on the ratio of Cd/Te and crystallinity was observed. XRD patterns of the films show a sharp peak corresponding to single crystal cubic CdTe (111) (no impurity peaks from TeO2 or different orientations of CdTe). The photoelectric behavior

of CdTe films was also studied using a photo electrochemical cell (PEC). Preliminary results on the formation and characteristics will be discussed from all the respects that mentioned above.

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Amperometric detection of hydrogen peroxide and uric acid using a zinc oxide carbon nanotube composite

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The need to detect both uric acid (UA) and hydrogen peroxide (H_2O_2) in dynamic aqueous solution environments is important for municipal waste water treatment and disinfection of swimming pool environments. To achieve this end, zinc oxide nanoparticles were tethered onto carbon nanotubes to form an electrochemical sensing composite, which was characterized using transmission electron microscopy, and X-ray photoelectron and attenuated total reflectance infrared spectroscopies. The composite material was mounted onto a glassy carbon surface for use as the working electrode. Electrochemical response for selectively measuring H_2O_2 and UA peroxide was investigated using cyclic voltammetry and chronoamperometry in a dynamic, well defined swimming pool environment. A wide, linear response in the concentration range with rapid response time (<5 s) is demonstrated.

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Combinatorial/computational approach to the discovery of new intermetallics

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With the fast-paced advancement of computational capabilities, it is becoming increasingly more realistic to accelerate the discovery cycle of new materials through the use of prediction algorithms to guide synthetic efforts. In this vein, information stored in crystal structure databases remains underutilized by crystal structure prediction software, despite the wealth of knowledge they contain. In particular, we note that previous attempts at crystal structure prediction were either computationally expensive[1] or not easily applied to intermetallic compounds due to challenges associated with non-directional bonding, diverse coordination numbers, and vast compositional spaces[2,3]. To combat these issues, we have created an algorithm to determine possible crystal structures within a user-specified range of compositions using a rapid analysis of about 34,000 known crystal structures of intermetallics found in the ICSD database as connectivity templates. This approach capitalizes on the propensity of new crystal structures to adopt previously observed configurations (structure types). Atomic coordinates and unit cell parameters of predicted structures are refined using a least-squares method which minimizes the deviation of atomic pairwise distances from tabulated values. Initial tests in the Y-Co-P system show that the 3 known crystal structures (YCo_3P_2, YCo_5P_3, and $Y_5Co_{19}P_{12}$) are, indeed, among the most likely ones to be formed. Present efforts focus on applying the algorithm to 3-component systems

where one or none ternary structures have been reported so far.

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Metallocene dichlorides intercalation into the inorganic layered nanomaterial zirconium phosphate for potential cancer therapy

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Zirconium bis(monohydrogen orthophosphate) monohydrate ($Zr(HPO_4)_2 \cdot H_2O$, α-ZrP) is the best characterized zirconium phosphate (ZrP). The highly hydrated phase of the layered ZrP, known as the 10.3 Å phase or Θ-phase, is an acidic ion exchanger that has been used for the immobilization of several photo-, bio-, and redox-active compounds. Applications for these materials can range from being used as catalysts, electron transfer systems, drug carriers, and modified electrodes. Among the bioactive compounds are the metallocene dichlorides such as titanocene dichloride and molybdocene dichloride. These metallocene dichlorides have been proposed and investigated as potential anticancer drugs but have presented drawbacks of low solubility in water and instability. To overcome these drawbacks researchers are looking for ways to stabilize and deliver this drug to its intended target. Therefore, we intended to directly intercalate these anticancer drugs using ZrP.
We used the Θ-phase of ZrP as a host to intercalate by direct ion exchange these metallocene dichlorides and characterized them for possible applications in cancer nanotherapy. The intercalated materials were characterized using IR spectroscopy, X-ray powder diffraction (XRPD), and qualitative elemental analysis by energy dispersive X-ray spectroscopy (EDS) by means of SEM. The XRPD data indicate that new intercalated phases with expanded interlayer distances were obtained showing the absence of the 7.6 Å diffraction peak characteristic of the α-ZrP phase that would have resulted if the intercalation was unsuccessful and only the dehydration of the Θ-phase had occurred. UV-vis spectrophotometric analysis of the liquid phase medium was used to assess the loading ratio of the metallocene dichlorides inside ZrP. It was estimated that a 44% and 60% loading ratio was obtained for titanocene dichloride and molybdocene dichloride, respectively.
Characterization of the metallocene dichlorides and the intercalated materials will be presented.

Dynamic nanospheres for individualized, localized drug delivery of chemotherapeutics and antibiotics

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According to the World Health Organization, cancer is the second major cause of death from non-communicable diseases worldwide (8.2 million in 2012), next only to cardiovascular diseases. In addition to this, the expansion of antibiotic drug resistance is a growing menace due to the indiscriminate use of antibiotics.
Utilizing nanomedicine as a molecular scale intervention for the prevention, diagnosis, and treatment of disease, we are presenting a novel, biocompatible drug delivery platform that can be individualized to meet various oncological and anti-microbial needs by integrating metallic nanoparticles with polymer chemistry and liposomal bionanotechnology.
As a model drug, methylene blue (MB) was used to elicit the properties of our basic-labile system. MB sustained a programmable release over a 48-hour time interval in PBS simulated body fluid at 37ºC.
Ongoing research includes continuously optimizing pH-dependent release with various polymers, encapsulating the metallic nanoparticles with a lipid layer, and also performing biological studies to gain further insight into our platform.

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Quantifying the thermodynamics that define calcium selectivity: A comparison to cadmium

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Calcium is an essential biological metal that is vital for the function of numerous proteins, the regulation of numerous pathways, and cell signaling. Similar to calcium in size and charge, the toxic metal cadmium can act as a molecular mimic, disturbing the highly regulated actions of these pathways.[1] In fact, Cd^{2+} has been found to bind to the common Ca^{2+} binding domain in proteins, the EF hand loop, and cause biological function.[2] Previous research has shown Cd^{2+} binding to EF hand loops I and II in the regulatory domain of human cardiac troponin C, denoted $HcTnC_{1\text{-}89}$ (Figure 1).[4] This is of concern due to HcTnC's role as a regulatory subunit in the heterotrimeric cardiac troponin complex which essential for heart muscle contraction.[3] Loop I is termed the "defunct loop" and does not bind calcium[3], however, crystallography data[4] and ITC data from the Spuches lab reveal the presence of Cd^{2+}. Due to these findings, further questions about calcium selectivity and toxic cadmium mimicry arise, such as, "What chemical properties of loop I obstruct Ca^{2+} binding, yet enable Cd^{2+} binding?" and "How does Cd^{2+} binding to $HcTnC_{1\text{-}89}$ affect the proteins regulatory function?" To conceptualize fundamental molecular interactions with Ca^{2+} and Cd^{2+}, the equilibrium constant and thermodynamic parameters of these metal interactions with EDTA and

four EDTA derivatives have been obtained using isothermal titration calorimetry (ITC), a sensitive microcalorimetry technique. To extend studies to a model system, two 12 amino acid peptides identical to loops I and II of $HcTnC_{1-89}$ have been synthesized. Loop I and II interactions with Ca^{2+} and Cd^{2+} have been investigated using ITC.

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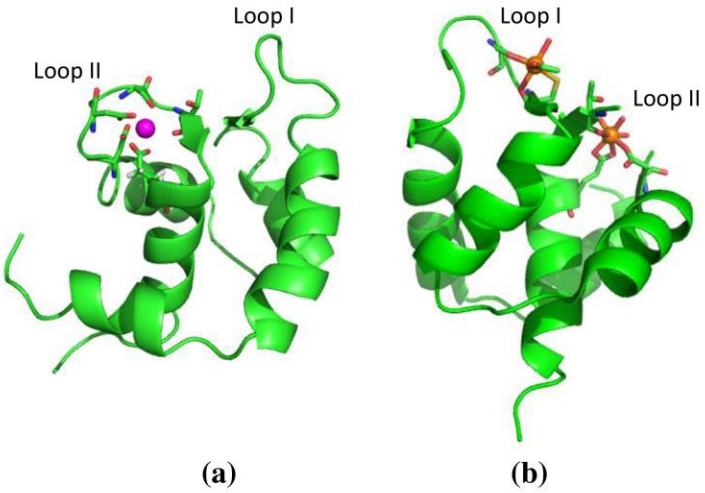

Figure 1. $HcTnC_{1-89}$ ribbon diagram with labeled EF hand Loops. **(a)** Bound Ca^{2+} ions depicted in purple. (PDB ID: 1AP4)[3] **(b)** Bound Cd^{2+} ions depicted in orange. (PDB ID: 3SD6)[4]

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Applications of luminogenic iridium azide complexes

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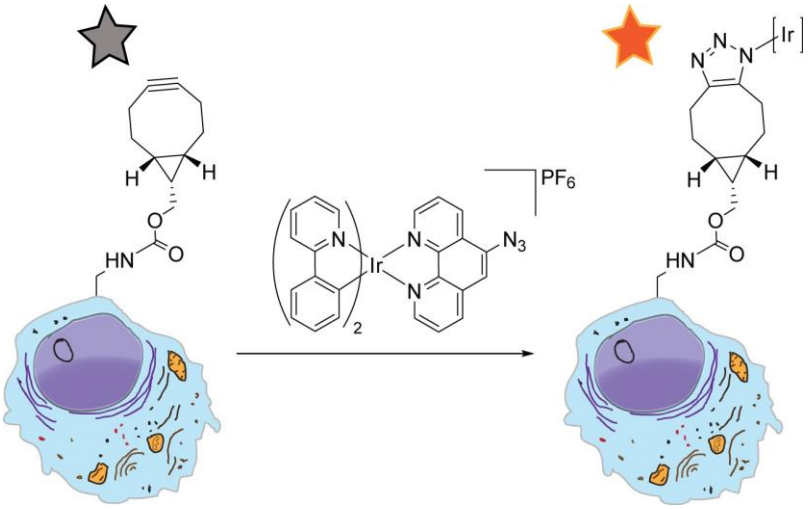
We describe facile syntheses of luminogenic iridium azide complexes. Possessing a turn-on property, emission at ~600 nm, and long lifetimes these complexes have potential in a variety of biological contexts. Applications in biomolecule labeling and cell imaging are described.



2015 Joint Southeastern/Southwest Regional Meeting 82

Incorporation of Zn^{2+} in PbS quantum dots via cation exchange

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Cation exchange provides a method to synthesize altered quantum dots (QDs) that can otherwise be difficult to produce. The introduction of transition metal ions to a system offers possibilities for manipulation of the structural, optical and magnetic properties of the QDs. With previous success in cation exchange with PbS QDs, we here experiment the reactions of Zn^{2+} cations. Temperature, ligand composition and stoichiometry serve as varying reaction conditions. Optical properties are measured via UV/Vis/NIR spectroscopy, while structural properties are analyzed via electronic spectroscopy, elemental analysis and TEM imaging.

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WITHDRAWN

2015 Joint Southeastern/Southwest Regional Meeting 84

Exploring new physics in photon-photoelectron interactions on micropatterned, zinc oxide hyper-branched nanorods

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A better understanding of fundamental physics and especially surface photoelectrochemistry can greatly benefits the advancement of science and technology especially in the field of solar energy conversion. Here, through our work, we have analyzed the characteristics of interactions of photons with photoelectrons within Zinc Oxide's hierarchically hyper-branched 3D-nanostructures on gold micropatterns that were pre-coated on a quartz substrate. By using tunable DC or AC biased voltages we have observed interesting and never-before reported phenomena between photons and photoelectrons since Einstein and Feynman days. These tunable interactions including light absorbance and current flow, appear to be functions of applied voltage, magnetic field, photonic intensity, and wavelength of light. It is our goal based on this data to gain a deeper understanding of how photonic transmission is effected by electron-flow in order to help design more efficient solar-cells and light manipulating devices and to broaden the field of electrochemical photonics.

Optical and surface studies of $Pb_{0.95}La_{0.05}Zr_{0.54}Ti_{0.46}O_3$ films deposited by chemical solution deposition method for solar cells applications

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The use of chemical-solution-deposition method (CSD) for ferroelectric thin films is attracting attention due to the ease of preparing films at low temperatures and scaling up the growth process to large wafers for solar cells applications. Ferroelectric $Pb_{0.95}La_{0.05}Zr_{0.54}Ti_{0.46}O_3$ (PLZT) thin films are of great interest for solar cells applications because photovoltaic effects can be realized without p-n junction and the existence of bulk photovoltaic effect due to internal electric field originating from electric polarization. However, the optimization of processing conditions of CSD deposited films is important to design an efficient solar cell which requires understanding of the structure, chemical reactions at the interface or within the film and its behavior with the light. In this regard, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Spectroscopic ellipsometry (SE), UV-Visible (UV-VIS) and Raman spectroscopy were performed on PLZT thin films annealed at 550 and 750 ºC to study the effect of crystallization temperature on the structural and optical properties of the films. X-ray studies demonstrated the change in crystallographic orientation and grain size with annealing temperatures. The XPS spectra of the films showed the higher binding energies of Pb, Ti, Zr, La and O for the high temperature annealed films. A small quantity of TiO_2, ZrO_2 and PbO coexisted with PLZT, observed after sputter etching the film. UV-Vis and SE showed the lower direct band gaps of the film annealed at higher temperature. The optical band gap varies in the range of 3.51-3.82 eV. The refractive index of high temperature annealed PLZT determined from SE is ~2.5 at 632 nm. The Raman spectroscopy revealed the shift in longitudinal and transverse optical modes with the change in annealing temperature.

Mesoporous materials containing heteropolyacids

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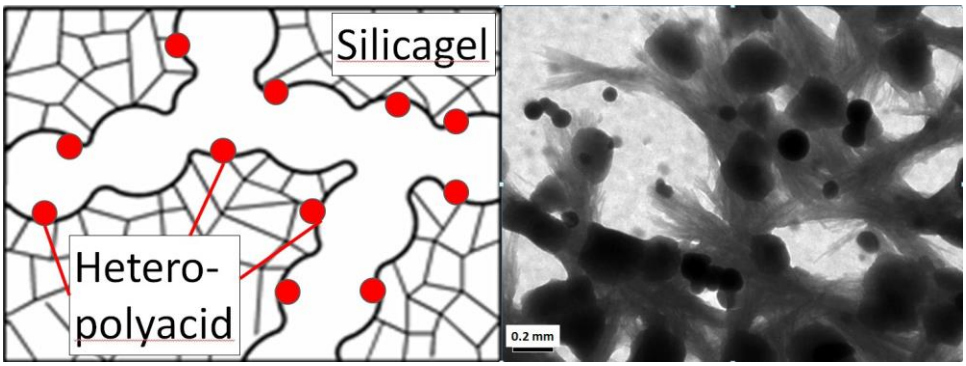
Mesoporous materials based on silica gels with incorporated heteropolyacids have unique catalytic and adsorption properties due to strong acidic sites in their structures. The present research is devoted to the systematic study of their synthesis and characteristics, including effects of various parameters on the yields and structures of the products. The materials were synthesized by co-condensation of tetraethoxysilane (TEOS) with phosphotungstic or phosphomolybdic acids using sol-gel method. Reactions were carried out in acidic media in isopropanol/water solution. The following surfactants were used as templates: sodium dodecylsulfate, dodecylamine, octadecyltrimethyl ammonium bromide, and Pluronic P123. Mesoporous products were obtained at various pH, ratios TEOS/heteropolyacid, temperatures, reaction and aging times. Chemical compositions of the materials were determined by atomic absorption and FT-IR spectroscopy. Presence of Keggin-type structures was confirmed by IR spectra of the materials, which contain characteristic bands in the region of 800-1080 cm^{-1}. All samples were amorphous with BET surface areas in the range of 424-900 m^2/g. Incorporation of heteropolyacids into silica gel reduced BET surface areas as compared with pure silica gels but not significantly. However, pore volumes of most of acid-containing samples increased in respect to unmodified silica gels. Their TEM study showed dendritic microstructures. Obtained materials may be used for adsorption of ions of radioactive isotope ^{137}Cs from contaminated soils and waters.



Copper(I) sulfide nanorods: Utilizing crystal-bound ligands and oriented attachment to create a desirable nanoparticle morphology

***Evan H. Robinson**, evanhrob@gmail.com. Vanderbilt University, Pensacola, Florida, United States*

We are investigating the use of monodisperse Copper(I) Sulfide nanocrystals as building blocks for single crystal nanorods. By design, the Cu_2S seed particles are capped with thiol ligands that are integrated into the particle surface. Under certain conditions, these crystal-bound thiol ligands can be removed from specific facets of the Cu_2S nanoparticles, allowing the unshielded faces to come into contact with one

another and attach. The oriented attachment of these seed particles creates single-crystalline nanorods. Ideally, this technique will offer an alternative to cation exchange and allow for control over the width of the nanorods.

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Synthesis, characterization, and antimicrobial studies of manganese (III) and europium (III) metal-doped ZnO nanoparticles

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ZnO, a large band gap semiconductor, has potential applications in photonic and high power electronic devices. Recently, ZnO nanoparticles have attracted significant attention in biomedical applications due to their limited-toxicity and cost-effectiveness. Electronic structure of ZnO nanoparticles promises their use in clinical applications as antimicrobial agents. Our current study is focused on doping ZnO nanoparticles with manganese (III) and europium (III) metal ions in order to explore their electronic properties and antimicrobial properties. Here, we present a synthetic method based on selective precipitation for making manganese (III) and europium (III)-doped ZnO nanoparticles. The nanoparticles were characterized using absorption and luminescent spectroscopy, X-ray powder diffraction, transmission electron microscopy, and inductively coupled plasma-optical emission spectroscopy. Antimicrobial activity of the nanoparticles were evaluated using agar diffusion, minimum inhibitory concentration (MIC), and time-dependent studies using *Escherichia coli*, *Staphylococcus aureus,* and *Staphylococcus epidermidis* bacteria species. Effects of the antimicrobial activity of the nanoparticles on metal-doping levels and particle sizes will be analyzed.

2015 Joint Southeastern/Southwest Regional Meeting 89

Using metal coordination complexes in mechanically responsive systems

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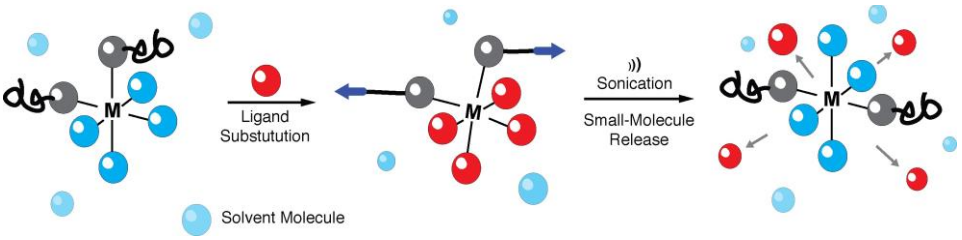
While much progress has been made towards understanding the role of mechanical forces in accelerating and directing purely covalent chemical reactivity, the behavior of coordinative complexes subjected to the same is far less understood. To probe the effect of mechanical forces on the behavior of coordination complexes we are synthesizing metallopolymers and subjecting them to mechanical shear forces in solution. This method can serve as a test-bed for future exploration of different metals, different oxidation states, and different complex geometries. We have designed and synthesized several metal-containing macromonomers that polymerize to produce polymers that contain coordinative bonds for primary structure. Our complex of interest is a known photo-activated CO-releasing molecule (CORM), which is anticipated to release CO from the mechanical distortion of the coordination-sphere of the metallopolymer. We have employed an assay to quantify the increase in photo-activated release of CO from our model complex; UV-VIS and NMR have also been used to analyze CO release from this model. Our current work has focused on using multiple

synthetic techniques to incorporate high loadings of the molecule of interest into a polymer of sufficient molecular weight for sonochemical testing and determining the best methods to monitor CO release from this metallopolymer. Future work will include investigating systems that require minimal force for small molecule release for the potential of using naturally occurring shear forces, in for example the flow of blood within the human body, for the controlled release of molecules of interest.



Cartoon of proposed process of how mechanical force may change the coordination environment at a metal center to release a small molecule.

2015 Joint Southeastern/Southwest Regional Meeting 90

Low temperature synthesis of amorphous vanadium pentoxide nanofibers and their transformation to crystalline material

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Vanadium pentoxide (V_2O_5) nanofibers have been synthesized via a low temperature, green approach. This study looks at the phase transformation from as-synthesized amorphous V_2O_5 to crystalline nanofibers upon annealing at high temperatures. Morphological studies were done on the fibers using scanning electron microscopy (SEM), which showed that as-synthesized and annealed fibers had diameters of approximately 10nm. X-ray diffraction (XRD) analysis showed that as-synthesized fibers was amorphous material; however XRD performed on annealed samples showed that at high temperature the amorphous material could be transformed into highly crystalline material. As-synthesized and annealed V_2O_5 nanofibers were also analyzed using thermogravimetic analysis (TGA), transmission electron microscopy (TEM), and Raman spectroscopy.

2015 Joint Southeastern/Southwest Regional Meeting 91

An aqueous phase synthesis of metal nanoparticles with controlled geometries

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Metallic nanoparticles offer the possibility of developing new conductive materials for electronic devices, inject printing, and nano-patterning applications due to their unique properties. Recently, considerable attention has been directed to developing conductive

metal nanoinks for printable electronics on flexible substrates. There are multiple synthesis methods have been developed for making metal nanoparticles in the presence of either surfactant or nonconductive capping agents, which prevents the aggregation and oxidation of nanoparticles. However, most synthetic methods are not economically feasible because of their low throughput. Also due to the formation of nonconductive shell of capping agents around the metal nanoparticles, there is a negative effect on the conductivity of nanoinks. There fore, here we describe a feasible and environmentally friendly synthesis to make copper and nickel nanoparticles in an aqueous phase without capping agents and explore a method to make metal-organic semiconducting hybrid nanocomposites. Our synthesis method replaces the toxic reducing agent (hydrazine) from mild reducing agent, $NaBH_4$ and prepare in large scale at room temperature. This method can be easily adapted to make other metal-organic hybrid nanocomposites.

2015 Joint Southeastern/Southwest Regional Meeting 92

Polyborafluorenes and borafluorene copolymers

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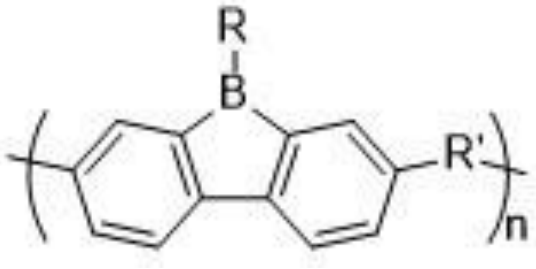
Electron deficient conjugated systems are of particular interest to the fields of novel semiconductor and sensing materials; because, when compared to the amount of electron rich systems there are relatively few. One powerful strategy to control the electronic nature of a conjugated polymer system is incorporation of inorganic elements. In addition, copolymerization of different conjugated monomers is a simple and comparable approach to tuning electronic properties. Our research is focused on the synthesis and characterization of novel borafluorene, a boron congener of fluorene, polymers and copolymers. We will be discussing our data collected on the properties of these polymers and future borafluorene synthesis.



2015 Joint Southeastern/Southwest Regional Meeting 93

Bactericidal heavy metal nanocomposites for industrial and biomedical platforms

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Transmission of pathogens and resulting biofilm growth have gained increasing importance in industrial applications like water treatment and sanitation, food packaging, and public environments, such as public transportation. In addition, reports indicate that nosocomial infections account for 2 million infections and 90,000 preventable deaths per year in the US.
Utilizing nanotechnology provides a good platform to alter physical-chemical properties of different materials compared to their bulk counterparts that can be harnessed for bio-applications. Several nanoparticles, such as silver, iron oxide (Fe3O4), titanium dioxide, zinc oxide (ZnO) and gold have been extensively studied for their antimicrobial activity. The drawback from using various nanomaterials is the lack of cost-effective methods to yield bactericidal composites for use in these niche applications.
Herein, we are reporting biocompatible, anti-microbial nanomaterials via facile, cost-efficient methods for integration in biomedical and industrial applications. Preliminary E. coli and S. aureus studies have shown inhibition of growth on brain heart infusion (BHI) media following administration and subsequent removal of the sample.
Our materials can be used for water treatment in cooling towers, bactericidal activity on orthopedic implants, and potentially reducing air-borne infection through ventilation filters. In addition to this, our materials can be reused upon UV cleaning or chemical washing which is a unique property to this disruptive product.

New chemistry in making the nonflammable graphene oxide membranes for rechargeable batteries and fuel-cells

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Graphene oxide (GO) has attracted broad interest in its great promise in large-scale production of graphene-enabled energy harvesting and conversion devices such as rechargeable battery and proton-exchange membrane fuel-cell. However, GO's high flammability may bring a great deal of fire hazard to manufacturers and consumers of these devices. In our lab, residue potassium- and sulfur-containing impurities in GO were found to be responsible to the GO's flammability, which has been seldom discussed in literature to date. In particular, a spark can cause disastrous combustion for the GO, and removing the impurities using filtration can be tedious, labor-intensive and time-consuming. Here we report a unique approach to making the new type of nonflammable GOs at ultralow-cost via a simple, one-step chemical reaction at ambient temperature and pressure, which substantially eliminates the impurities and in turn the fire hazard. Moreover, the chemical modification boosted the GO-membrane's electrical resistance up to 200MΩ/sq, which can largely broaden the new GO-membrane's applicability beyond the above-mentioned important applications.

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Dispersion study of exfoliated graphene nanoparticles

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Dispersion of exfoliated graphene nanoparticles is an important process for the preparation of graphene based coatings. We will report preliminary results of i) dispersion and stability study of graphene dispersed solutions in various organic solvents including resins, and ii) characterization study undertaken by Raman, FT-IR spectroscopy, SEM and other methods.

2015 Joint Southeastern/Southwest Regional Meeting 96

Effects of ionic liquids on stability, structure and reactivity on biological macromolecules

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Ionic liquids (ILs) show great potential as a solvent or co-solvent for many catalytic and enzymatic reactions. The use of ILs in enzymatic reactions has demonstrated that structure of the ions can dramatically alter the physical properties of the protein; in some cases stabilizing the tertiary structure of the bio-macromolecule and improving catalytic reactivity. Here we report our current efforts characterizing imidazolium based ILs, along with several new ILs based on different cationic structures (Figure 1A), to probe their ability to impact the thermal stability and reactivity associated with catalysts including zinc(II) and metal-substituted human carbonic anhydrase II (Figure 1B) and several commercially available catalytic systems. This data illuminates how solvent impacts structure, stability, and reactivity of this mononuclear metalloenzymes, which will allow us to continue to tune the solvent to support targeted bio-catalytic applications.

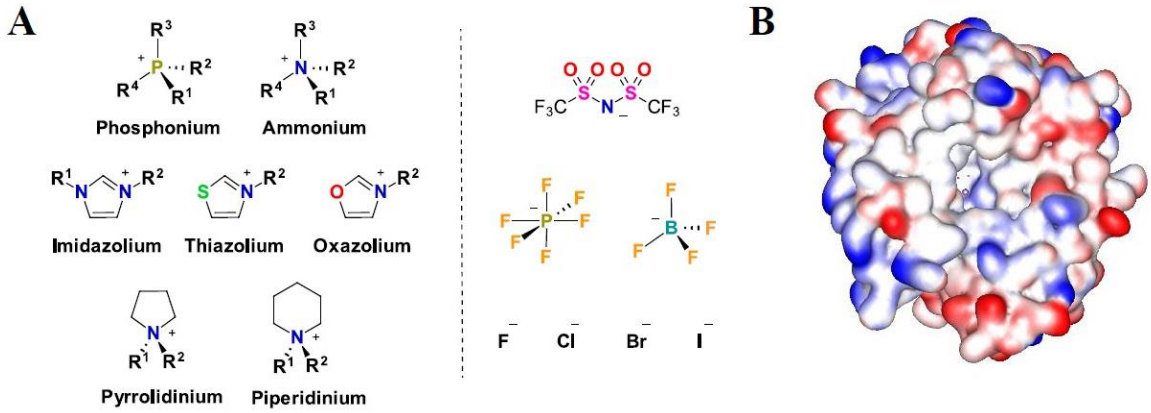

Figure 1. (A) Structural motifs commonly found in ionic liquids, the cation (left) and anions (right). **(B)** Surface charges associated with human carbonic anhydrase II.

2015 Joint Southeastern/Southwest Regional Meeting 97

The effectiveness of methods to functionalize glass-based substrates

***Aniket Maharanwar**, aam0014@uah.edu. Material Science, University of Alabama in Huntsville, Huntsville, Alabama, United States*

The research in this report is being undertaken to compare the integrity of different methods to coat glass-based substrates with silanes. A typical borosilicate glass, APEXTM glass, and quartz substrates are cleaned using different wet cleaning methods. They are functionalized
with a long-chain silane aminopropyltrimethoxysilane (APTES), a short-chain chlorotrimethylsilane (Si (CH3)3 Cl) (CTMS), and commercial SigmacoteTM. The concentration of the silane in solution is varied at constant immersion times, and the functionalized layers are immersed in water to test their stability. The nature of the clean, functionalized, and water-exposed surfaces is characterized with contact angle goniometry.
Results on the effectiveness of the different coating methods will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 98

Photochemical synthesis of silver and gold-silver alloy nanoparticles with tunable plasmonic absorption via aqueous and biocompatible media

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Metal nanoparticles have been designed and extensively studied because of the unique optical properties attributed to their surface Plasmon. In an effort to make biocompatible materials with absorption bands in the near infrared (NIR) region, many methods devised utilize the use of toxic reducing agents such as CTAB and CTAC, making them unsuitable for biological applications. In this study, we present a simple photochemical protocol utilizing light and varied concentrations of the precursors to make anisotropic silver and mixed metal silver-gold alloyed nanoparticles with tunable absorptions for applications such as sensors, Photothermal therapy, antimicrobial compositions, and drug delivery systems.

2015 Joint Southeastern/Southwest Regional Meeting 99

Sustainable green nanotechnology: Remediation of drinking water to industrial effluent treatment strategy

*Andre' L. Daniels, Maria M. Simmons, Ahkeim M. Barr, **Satish Kuriyavar**, satish124@gmail.com. Chemistry Department, Claflin University, Orangeburg, South Carolina, United States*

Nanomaterials hold the key to the development of next generation of cost effective, sustainable and highly selective remediation materials for water purification systems. This can be extended towards removal of arsenic from a multitude of consumer products ranging from rice, orange juice to baby formulas just to name a few applications. Nanometric transition metal oxides exhibit selective adsorption of heavy metal ions to treat drinking water and other food materials without contaminating them. Their synthesis and characterization will be discussed. This technology can be modified to make these aggregates from polymer matrices into magnetic beads to remove dye and other chemicals effectively from the effluents of dye industries. The traditional water treatment plants are highly expensive and need extensive treatments such as pH adjustments, color and odor removal along with sludge. This requires lot of energy and leaves a heavy carbon foot print in the process. However, nanomaterials can reduce the production costs and increase the efficiency of clean-up efforts in a more feasible and environmentally conscious manner.

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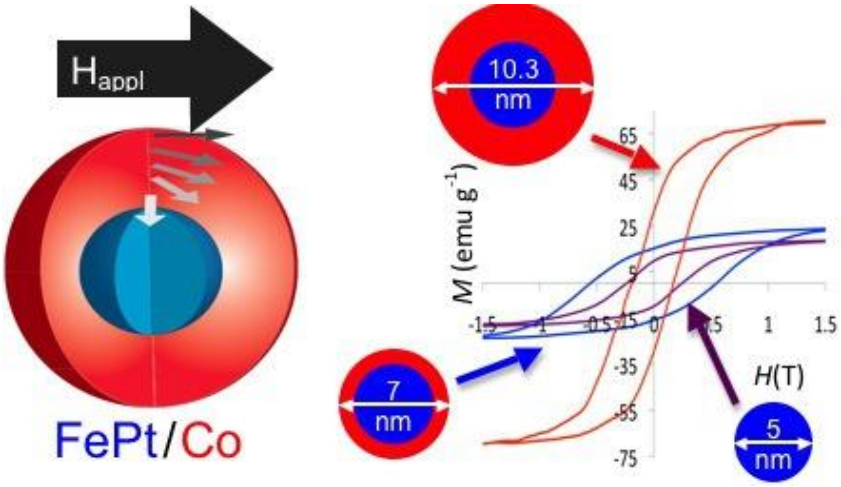
Plotting the limits of core/shell magnetic exchange

David Carnevale[2]*, dcarnevale2009@gmail.com, Michael Shatruk*[3]*, Geoffrey F. Strouse*[1]*. (1) Florida State University, Tallahassee, Florida, United States (2) Chemistry, Florida State University, Tallahassee, Florida, United States (3) Dept of Chemistry Biochemistry, Florida State University, Tallahassee, Florida, United States*

Work on the study of hard@soft exchange-spring magnetic nanoparticles over the past few decades has continually suggested that the addition of a soft magnetic shell onto a hard magnetic particle will lead to a gain in saturation moment (Ms) at the cost of coercivity (Hc) of system, compared to the pure hard magnetic core. However, our work done on the $Fe_{65}Pt_{35}$@Co system suggests that limiting the shell sizes to very small widths will lead to dual enchancement of both Ms and Hc, leading to a dramatic 4-fold increase in the energy product (BH) of the system. Further studies of this system have resulted in the clear presence of a perfect exchange-coupled regime, which quickly relaxes to the exchange-spring regime at larger shell widths, and finally leads to decoupling of the outer moments of the shell from the core.



2015 Joint Southeastern/Southwest Regional Meeting 101

Synthesis and characterization of polyphosphonates derived from polyethylene glycols and their use as ligands in styrene hydroformylation catalysts

***Timothy R. Totsch**, rosst@uab.edu, Benjamin Yancey, Gary M. Gray. Chemistry, University of Alabama at Birmingham, Birmingham, Alabama, United States*

Recently we reported that polyphosphonites (-(OP(R)-O-dodecylene)$_n$- (X = O, S, Se; R = phenyl, 2,2'-bithienyl-5-yl)) with number average molecular weights as high as 46 kDa can be efficiently synthesized via polycondensations of $PR(NEt_2)_2$ with dodecanediol. These polymers were then converted to the corresponding polyphosphonates by oxidations with either urea-hydrogen peroxide, S_8 or S. The polyphosphonates polymers with 2,2'-bithienyl-5-yl groups exhibited nonlinear optical absorption and fluorescence in the violet-blue wavelength of the visible spectrum and may have applications in sensor protection and blue organic light emitting diodes (OLEDs).

We now report the synthesis and characterization of a new series of polyphosphonites that incorporate a polyethylene glycol into the polymer backbone rather than a 1,12-dodecanediol. These new polyphosphonites show slightly more complex ^{31}P NMR spectra and also a lack of a detectable end group peak. These polymers have been converted to polyphosphonates that have been characterized by MALDI-TOF mass spectrometry and gel permeation chromatography to accurately determine their molecular weights of the polymer. The phosphorus atoms in each repeat unit of the polyphosphonates have the ability to coordinate to metal centers allowing the polyethylene oxide groups to act as a crown ether cation binding sites. Molecular versions of these groups have the ability to improve sterioselectivity in alkene hydroformlyation reactions by binding alkali metal cations, and the polyphosphonates have been evaluated as polymeric ligands for these applications.

2015 Joint Southeastern/Southwest Regional Meeting 102

SCHB is your link to success

***Joseph E. Sabol**, jsabol@chem-consult.com. Chemical Consultant, Marquette, Michigan, United States*

As the ACS Division of Small Chemical Businesses celebrates its 35th year, strong programming and member benefits abound, including free membership for the first year, discounted booth exhibit space at ACS national meetings, listing on our website business directory, discounted SOCMA membership, partnerships with local sections for programming, webinars, and other events. At the heart of it all are amazing networking opportunities for established and start-up chemical businesses. Join SCHB members and colleagues and participate in the chemical enterprise at ACS meetings and follow SCHB on social media.

2015 Joint Southeastern/Southwest Regional Meeting 103

On use of graphene to make supercapacitors with higher ampacity

***Kal R. Sharma**, jyoti_kalpika@yahoo.com. Electrical Program, San Jacinto College Central Campus, Cypress, Texas, United States*

Supercapacitors have capacitance in excess of 1000 Farads at 1.2 Volt. Single Layer Graphene sheets can be used in order to prepare supercapacitors. The ampacity of graphene supercapacitors can be expected to be twice that of current ultracapacitors. Scientists at University of Texas at Austin, TX have used graphene sheets to rapidly store and discharge electric charges. Supercapacitors can be used in conjunction with fuel cells and rechargeable batteries as reliable power sources. Chemical modification of graphene can be accomplished by exfoliation of graphite powders and reduction of graphite oxide product.
One problem area in the use of Single layer graphene in supercapacitor applications is the tendency of aggregation of graphene sheets during electrode fabrication. Vertical alignment can impede the lateral free flow of electrons. Horizontal alignment of graphene stacke may obtrude electron and ion transport. Crumbled paper ball morphology has been suggested as a preferred method of operation of single sheet graphene for use in supercapacitors. Nanostructured spacer materials may be used in order prevent stacking of graphene sheets.

2015 Joint Southeastern/Southwest Regional Meeting 104

Exploring the reactions and transition states of tungsten-pyrrole complexes

***Chris Shepard**, chris.shepard@richmond.edu. Chemistry, University of Richmond, Henrico, Virginia, United States*

Reactions and transition states of different pyrrole groups with a Tungsten based organometallic (TpW(NO)(PMe_3)) were studied using different density function theory methods. First, the possible model chemistries to be used were narrowed by testing previously studied Tungsten complexes, and determining which three gave the best results when compared to previous works. These top performing methods were then tested on a set of Tungsten-pyrrole complexes specific to our project, and the top preforming method was selected. Since little work has previously been done finding transition states with a Tungsten metal complex, multiple transition state search methods were implemented. These have yielded about 20 different transition states thus far, which are now being tested to determine which intermediates they connect and which, if any, are part of experimentally observed reactions.

2015 Joint Southeastern/Southwest Regional Meeting 105

Anomalous gel-fluid phase transition of solid-supported lipid membranes

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Solid-supported lipid bilayers are often used as a simple model for studies of biological membranes. The presence of a solid substrate that interacts attractively with lipid head-groups is expected to affect the phase behavior of the supported bilayer. Molecular dynamics simulations of a coarse-grained model are thus performed to investigate the phase behavior of supported one-component lipid bilayer membranes. Our results show that the attraction of the lipid head groups to the substrate lead to a phase behavior that is different from that of a free standing lipid bilayer. In particular, we found that the phase behaviors of the two leaflets are decoupled in the presence of a substrate. The proximal leaflet undergoes a clear gel-to-fluid phase transition at a temperature lower

than that of a free standing bilayer, and that decreases with increasaing the strength of the substrate-lipid attraction. The distal leaflet, however, undergoes a change from a homogeneous liquid phase at high temperatures to a heteregoneous state consisting of small liquid and gel domains, with the average size of the gel domains that increases with decreasing temperature. While the chain order parameter of the proximal leaflet clearly shows a gel-fluid phase transition, the chain order parameter of the distal leafelt does not exhbit a clear phase transition. The decoupling in the phase behavior of the two leaflets is due to a non-symmteric lipid distribution in the two leaflets resulting from the presence of the substrate.

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On complex fluids and diffusion law: *A capite ad calcem* in concentration

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Polymer fluids behave in a different manner compared with Newtonian fluids. “Elastic” effects have been found when the polymer fluid was made to flow. Maxwell’s viscoelastic model can be written as Eq. (3b) and seen to be an extension of Newton’s law of viscosity given by Eq. (3a). Sharma (4) has shown from heat transfer analogy that the relaxation time (momentum) is a measure of the acceleration time taken by the moving free electron before attainment of steady drift velocity. It was also shown to be a third of the collision time of the electron and obstacle. Sharma4 discussed how poor use of initial conditions can result in model
solutions that may be in dissonance with the second law of thermodynamics using Eq. (3b). A de novo equation to describe mass diffusion is derived from Gibbs chemical potential formulation for a nonrelativistic solute particle. The acceleration term eliminated between the equation of motion for the spinless particle and accumulation of chemical potential formulation leads to an equation for mass diffusion that is a capite ad calcem in concentration (Eq. (3.8)). The dC/dt, the time derivative of concentration, and dC/dx, the spatial gradient of concentration, can either be “both positive” or “both negative” but never one positive and one negative for spontaneous mass diffusion events. . Jeffrey’s equation for fluids is given in Eq. (3c).

The transient concentration in a semi-infinite medium subject to a step-change in surface concentration using the de novo diffusion equation was obtained. The method of Laplace transforms, binomial series expansion and principle of convolution were used, and an approximate solution was obtained. In Figure 3.2 is shown the side-by-side compar-isons of transient concentration profile in a semi-infinite medium subject to step-change in surface concentration from (i) parabolic Fick diffusion model, (ii) hyperbolic Maxwell-Cattaneo diffusion and relaxation model, and (iii) ballistic model for diffusion.

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Raman spectroscopic and computational analysis of the effects of noncovalent interactions on DMSO

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Dimethyl sulfoxide (DMSO) is a widely used chemical in synthetic chemistry and also has unique and important biological applications. In the pure liquid, DMSO forms chain-like structures of alternating sulfur and oxygen atoms due to its high self-association. However, it is known that DMSO/water mixtures form solutions with unique physical characteristics depending on the mole ratio. Vibrational spectroscopy allows us to study the effects of noncovalent interactions when water and DMSO interact in solution. Spectral shifts can be analyzed in order to give a clearer picture of the structure of DMSO in DMSO/water mixtures and also in solutions with other hydrogen bond donors that cannot form as extensive hydrogen bonded networks. The anomalous properties of DMSO/water mixtures have been the subject of a large number of studies. It has been previously established that the reason for the unique properties of such solutions lies in the formation of strong hydrogen bonds between water and DMSO. Despite the many studies there is still no clear picture of the structure of DMSO in aqueous mixtures. Here, the hydrogen bonding geometries of DMSO/water mixtures are studied using Raman spectroscopy and computational chemistry.

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Membrane-mediated aggregation of anistropically curved nanoparticles

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The adhesion of macromolecules or nanoparticles to lipid membranes often leads to conformational changes of membranes. For example, the complex conformations of some organelles in eukaryotic cells, such as Golgi and the endoplasmic retiuclum are due to specialized proteins known as BAR domains, which are crescent-shaped proteins. Using large-scale molecular dynamics simulations of a coarse-grained model, we investigated the binding of anisotropically curved nanoparticles, reminiscent of BAR domains, on lipid membranes and their resulting cooperative behavior on the membrane conformation and the nature of the nanoparticles aggregation. We found that the membrane morphology and the nanoparticles aggregates depend strongly on the adhesion strength and intrinsic curvature of the nanoparticles. In particular, for weak adhesion strengths, the nanoparticles aggregate into chain-like structures, forcing the membrane to accomodate a morphology that is curved on a global scale. For high adhesion strengths, the nanoparticles aggregate into a star-like clusters on a vesicle with alternating regions of postive and negative curvatures.

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Evaluation of defoamer chemistries for brown stock washing

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An effective brown stock washing process is a crucial part of the pulp mill operation due to its impact on downstream processes such as bleaching, black liquor evaporation, and

caustic recovery. An optimized brown stock washing process is necessary to remove the maximum amount of black liquor solids from the pulp while minimizing wash water usage (1). Due to the presence of soap and lignin in black liquor, a significant amount of foam is generated in the washing process. In order to combat this foam, a foam control agent is necessary in order to increase production rates, as well as optimize and continue operations (2).
The surface active components found in black liquor, such as surfactants, fatty acid soaps and other particles, create foam once energy is added to the system. Air bubbles are separated by a thin liquid-air interface called the lamella and stabilized by the surfactants. Defoamers, in the form of emulsified droplets, approach the foam surface. A three phase film consisting of oil droplets, water and air is formed. Once the defoamer droplet penetrates the lamella, it spreads into a lens at the liquid-air interface, thus destabilizing the bubble wall and disrupting the foam structure.
Several options are available to combat foam in brown stock washing applications. Water based silicone defoamers, oil based defoamers, and polymeric antifoams will be explored in this paper, including their impacts on the brown stock washing process and fundamental differences. Water based silicone defoamers are very effective but may cause deposit issues with silicone carryover in certain grades of product. Oil based defoamers are used in mills where a silicone based defoamer would have detrimental effects to the end product. In order to address these issues, Kemira has developed a novel polymeric processing aid that contains no silicone and is very effective at foam control. This study will present lab evaluations and trials to highlight the uses of these defoamer chemistries.
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The accuracy of quartic force field computations: Comparison between semi-experimental and computational results

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While quartic force field (QFF) computations are accepted as being quite accurate (to as good as 1 cm^{-1} for some vibrational frequencies), the robust accuracy of this approach as compared to experimental determination of vibrational frequencies and spectroscopic constants has not been systematically established. The focus of this to study is to provide an in-depth comparison of the so-called CcCR QFF results determined with the use of second-order vibrational perturbation theory to known gas- and condensed-phase experimental values. Percent differences between the computed values and the semi-experimental geometrical values and rotational constants of various molecular systems are reported along with the percent differences between semi-experimental harmonic frequencies and those determined from the pure *ab initio* computations. The data provided in this study show the levels of accuracy expected for CcCR QFF geometries, spectroscopic constants, and vibrational frequencies with application of these methods to aid in the detection of novel interstellar molecules.

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Investigation of the binding affinity of malachite green on magnetic colloids using surface selective spectroscopy

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Urban centers are more densely populated than ever before and the need for clean water has never been more important. Developing efficient remediation techniques to remove organic contaminants is thus necessary. Recently, the application of magnetic particles (MPs) to remove aquatic pollutants has gained popularity in comparison to the conventional methods (*e.g.* coagulation, filtration, and aeration). MPs provide a distinct advantage in removing environmental pollutants, because once adsorbed, the target species can be readily isolated from the aquatic solution by the application of an external magnetic field. Despite this unique advantage, the efficiency of MPs in removing aquatic pollutants is not well studied. Knowledge of adsorption properties (*i.e.* equilibrium constants, K_{ads}) is essential for developing better adsorbent materials. Herein, we present an *in situ* investigation of the adsorption of malachite green (MG), a prevalent aquatic pollutant, to polymer carboxylate functionalized MPs using surface selective second harmonic generation (SHG) spectroscopy. We have collected SHG adsorption isotherms of MG for both magnetic and nonmagnetic polymer particles and determined the binding equilibrium constant to be in the order 10^7. However, comparison of the magnetic vs. nonmagnetic particle data indicates that significant aggregation in magnetic particles hinders its effectiveness in removing MG from aqueous solution. Separation technique based on UV-Vis spectroscopy further corroborates the SHG results. In addition to the SHG and UV-Vis adsorption isotherms, a simple mathematical model describing the aggregation of MPs will also be presented.

2015 Joint Southeastern/Southwest Regional Meeting 112

Reinvestigation of the resonance Raman spectrum of the blue ruthenium dimer

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The blue Ruthenium dimer, *cis,cis*-$[(bpy)_2(H_2O)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$, was the first designed molecular catalyst for water oxidation. Earlier analysis of its resonance Raman spectra revealed overlapping series of absorptions which hindered quantitative analysis. Here, we reinvestigate this catalyst's resonance Raman spectra using 457.9, 465.8, 476.5, 488.0, 496.5, 501.7, 514.5, 530.9, 568.2, 632.8, 647.1, and 676.4 nm laser excitation with the goal of better describing its excited states. Multiple protonation states of the blue dimer are also observed as a function of pH and will be examined in more detail. Future work will involve the once oxidized blue dimer, the $Ru^{III}ORu^{IV}$ species.

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Investigating the effects of solvent on the surface-enhanced Raman scattering (SERS) of nitrogen containing molecules: Azabenzenes and 1H-1,2,3 triazole

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Raman spectroscopy can reveal useful structural information of molecules as well as elucidate the effects of intermolecular interactions and environment. Raman scattering signals are often weak, however, and can be overwhelmed by fluorescence emission. Surface Enhanced Raman Scattering (SERS) is a powerful spectroscopic tool that allows for the enhancement of the Raman signal and the detection and analysis of very dilute samples. Recently, we showed how conjugated nitrogen-containing molecules exhibit charge transfer with extended hydrogen bonded networks. Here, we explore the competition for charge transfer between azabenzenes and 1H-1,2,3 triazole with both silver nanoparticles and various hydrogen bonded networks both experimentally and theoretically.

2015 Joint Southeastern/Southwest Regional Meeting 114

Mucin penetrating magentic nanoparticles for therapeutic application

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The aberrant expression of mucus in various different diseased states of the epithelial lining in various organs has been exploited using mucoadhesive nanotechnology in many forms known holistically as nanoparticles. Such mucoadhesive nanoparticles allow for prolonged bioavailability of the loaded therapeutics in the body. For therapeutic applications, we are engineering a nanoparticle formulation that will effectively bind and penetrate the mucin layer. In this study, we used iron oxide based magnetic nanoparticles (MNPs) by precipitation of iron salts in the presence of ammonium. The MNPs were then coated with β-cyclodextrin (β-CD) and pluronic polymer (F127). Four different compositions of MNP formulations, plain MNPs, MNPs with β-CD only (MNP-βCD), MNPs with F127 only (MNP-F127), and MNPs with β-CD and F127 (MNP-βCD-F127) were formulated for this study. Particle size, distribution, and zeta potential of MNPs and MNP-mucin were measured using Zetasizer based on dynamic light scattering technique, mucin binding ability of MNPs was measured using SpectraMax M2e UV/Vis and fluorescence spectrophotometry, migration of MNPs in the presence of mucin were measured using Boyden chambers assay, and tissue uptake/internalization was measured by Prussian blue staining and fluorescence technique. All together, these studies suggest that because of the unique composition of MNP-βCD-F127, it binds efficiently to the mucin and migrates into the mucin layer, which suggests a unique formulation for therapeutic application and drug delivery.

2015 Joint Southeastern/Southwest Regional Meeting 115

High-resolution electronic spectroscopy of the ultraviolet bands of CaO

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Jet-cooled spectra of the ultraviolet bands of CaO are presented for the first time. Previously unobserved vibrational bands of the known $F^1\Pi^+ \leftarrow X^1\Sigma^+$ and $C^1\Sigma^+ \leftarrow X^1\Sigma^+$ electronic transitions are reported, along with refined spectroscopic constants for these states. Perturbations affecting the v=7 and 8 vibrational levels of the $C^1\Sigma^+ \leftarrow X^1\Sigma^+$ electronic transition are reported, along with transitions to a new $^1\Sigma^+$ state, which we denote as the $G^1\Sigma^+ \leftarrow X^1\Sigma^+$ transition. Molecular constants indicate that the Ca-O bond in this electronic state possess significant covalent character, uncharacteristic of previously developed models for excited electronic states of CaO.

2015 Joint Southeastern/Southwest Regional Meeting 116

An efficient Pd-Cu single atom alloy catalyst prepared by galvanic replacement for acetylene selective hydrogenation

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Selective hydrogenation of acetylene in ethylene is an important industrial process to remove traces of acetylene for the polyethylene industry. Single Pd atoms alloyed with Cu have been demonstrated to be excellent catalysts for selective hydrogenation reactions. In order to form specific single Pd atom alloy with Cu catalyst, galvanic replacement (GR) has been introduced to exchange and load 0.0338 % of Pd onto Cu nanoparticles supported on γ-Al_2O_3. This catalyst has been tested for acetylene selective hydrogenation with balance N_2 or ethylene. The results show that the catalyst prepared by galvanic replacement has much better selectivity towards ethylene and C_2H_2 conversion compared with those prepared by the impregnation method. HAADF-STEM and *in situ*-FTIR results will be discussed in relation to the formation of the single atom alloy.

2015 Joint Southeastern/Southwest Regional Meeting 117

Investigation of optical properties of gold/near IR emitting quantum dot hybrid nanoparticles

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Harvesting the sun's energy at a high efficiency and low cost is a vital step towards replacing fossil fuels. Colloidal quantum dots (QDs) are promising materials that have great potential for solar applications due to their size dependent optical properties and high-absorption cross-sections.[1] One way of developing next generation solar cells is with cheap quantum dot materials that enable multiple exciton generation (MEG). In this process a material can produce multiple excited states following the absorption of high-energy photons, potentially increasing the devices photocurrent. Lead-based QDs have a unique ability to utilize low energy photons from the solar spectrum that would be otherwise wasted. Moreover, these near IR emitting QDs can generate multiple excitons following the absorption of a blue photon, which allows solar devices to exceed 100 % efficiency! Coupling these QDs to gold nanoparticles (Au NPs) may enhance these efficiencies by increasing absorption rates above the MEG threshold. The Au/CdSe/PbSe hybrid nanoparticles were synthesized nonepitaxially, following the work of Zhang et.al.[2] The metal surface plasmon (SP) coupling with the PbSe QDs allows for MEG to occur more rapidly, which increases competition with non-radiative energy loss

processes. Transmission electron microscopy and X-ray diffraction spectra reveals the hybrid NP composition, while time resolved and steady state fluorescence studies reveals the optical response. Spectroscopic studies determines the effects of SP-exciton coupling. The NP-QD distance strongly affects the coupling strength and, consequently, the rate of PL quenching or enhancement. The aim of this research is to examine the potential of surface plasmons to increase the efficiency of MEG and ultimately improve photovoltaic device performance.

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Assembly of nanobattery array using ion beam deposition

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Deveolpment and progress in nanotechnology and nano-devices create an ever increasing demand for new components. An important component in nano-device control is a crossbar system where bars perpendicular to each other run below and above a membrane holding the item of interest. The space where the bars cross above and below can now be accessed by an external sensor/controller. Employing the ion beam deposition (or gas deposition) feature of a scanning electron microscope/focused ion beam (SEM/FIB) we are able to fabricate prototype components for such a crossbar system that accesses nanobatteries on an alumina substrate. These conductive channels used in crossbars systems we formed by controlled platinum deposition accessing nanobattery array components housed in an AAO membranes. The fabricated system will be tested by employing an Atomic Force microscope (AFM) tip in contact with the deposited metal bars allowing ac impedance spectroscopy to be conducted for investigation of the individual micro circuit and determination of nanobattery performance

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Synthesis and spectroscopic characterization of a novel Ru(II)tris(2,2’-bipyridine) templated metal organic framework derived from Zn(II) and 1,4 benzene dicarboxylate

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It has now been demonstrated that Ru(II)tris(2,2’-bipyridine) (RuBpy) exhibits a templating effect in the formation of metal organic framework (MOF) materials. In fact, several new topologies have been synthesized using Zn(II) ions and carboxylate ligands in which the encapsulated RuBpy clusters exhibit unique photophysical properties. Two such materials, RWLC-1 and RWLC-2, have been reported from our laboratory and are composed of RuBpy encapsulated in MOFs composed of Zn(II) ions and 1,3,5-tris(4-carboxyphenyl)benzene ligands (C. L. Whittington, L. Wojtas and R. W. Larsen, Inorg.

Chem., 2014, 53, 160–166). A third material, RWLC-3, was reported shortly after derived from the reaction between Zn(II) ions and 1,4-dicarboxybenzene in the presence of RuBpy (C. L. Whittington, L. Wojtas, W. Gao, S. Ma and R. W. Larsen, Dalton Transactions, 2015, 44, 5331-5337). Herein a fourth material, RWLC-4, is synthesized under MOF-5 conditions utilizing RuBpy as a templating agent. The encapsulated RuBpy exhibits biphasic emission decay lifetimes (τ-fast = 307 ns, τ-slow = 1.1 μs) and a bathochromic shift in the steady state emission spectrum relative to RuBpy in ethanol. The photophysical properties of the RWLC-4 material are quite distinct from those observed in other members of the RWLC family of MOFs. The results presented here will be discussed in relation to cavity properties and how variations in cavity composition influence RuBpy photophysics.

2015 Joint Southeastern/Southwest Regional Meeting 120

Investigating the chemical kinetics of the reaction between haloacetic acids and nicotinamide used in post-column reaction ion chromatography

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Chlorine has been used to disinfect drinking water for over 100 years resulting in a marked decreased of water-borne disease. However, chlorination produces halogenated disinfection by-products. One class of disinfection by-products are the haloacetic Acids (HAAs) which are carcinogenic. There are nine haloacetic acids that typically produced during disinfection, five of which are regulated by the United States Environmental Protection Agency (USEPA). Drinking water treatment plants and utilities are required to monitor the HAAs on a quarterly basis. Analysis for HAAs is typically carried out using USEPA method 552.3, which is labor intensive and requires highly skilled personnel. A simpler and automated alternative for HAAs analysis has been reported called post-column reaction ion chromatography (PCR-IC) with detection limits ranging from 1 – 10 μg/L for each HAAs species in drinking water. The success of the PCR- IC system relies on the HAA's reaction with nicotinamide in a basic solution which produces a fluorescent product – though details regarding this reaction are elusive. Investigation of the kinetics of the reaction between each HAAs species, nicotinamide and base could provide valuable insights that would enable further optimization. These optimizations could lead to a simpler post-column reaction system, more efficient use of reagent chemicals, or improved detection limits through increased analytical signal. In this research, seven HAAs species were investigated using systematic variation of temperature, nicotinamide concentration, hydroxide ion concentration and HAAs concentration to elucidate a chemical rate law. The results indicate the reaction is mixed second order kinetics with a possible pH dependence rather than simple first or second order. The results of the systematic variation and preliminary rate law determination will be presented.

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Using automated on-site and hourly trihalomethane concentration data to calibrate empirical models to be site-specific

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The trihalomethanes (THMs) are a class of federally-regulated, carcinogenic disinfection by-products formed during the chlorination of drinking water. Many water treatment plants (WTPs) struggle to comply with the stricter regulations that stem from the United States Environmental Protection Agency's Stage 2 Disinfection Byproduct Rule. This has triggered a demand for automated instrumentation to monitor THMs on-site. In the last five years, four commercial devices have appeared on the market for this purpose. These instruments provide an opportunity to improve the water quality and save on operating expenses for the WTP, though not all can afford them. Alternative approaches for determining THMs at WTPs have focused on development of models to predict THMs concentrations based on water quality and operational parameters. These models are numerous and primarily empirical in nature. The models can be used by WTPs to assess and optimize their day to day operations to minimize THMs as long as the model is determined to be reliable and robust.

Hourly THMs concentration data from the commercially available THM Rapid Response System is combined with water quality parameters from the Lebanon, TN WTP. The combined data set was used to evaluate and calibrate a commonly used THMs model familiar to many WTPs The calibrated model was site specific to Lebanon, TN WTP and predicted THMs concentrations to within 2 ppb when applied for prediction one year later. In this research, additional THMs models from literature will be subjected to a similar process to determine if calibration can be successful regardless of the base model. The literature and calibrated models will be rigorously compared to the measured THMs data using Bland-Altman analysis to determine its ability to predict THMs concentrations specific to the Lebanon WTP up to one year later.

Stabilization kinetics of melt processable poly(acrylonitrile-co-n-vinylimidazole) carbon fiber precursors

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Carbon fibers are one of the strongest materials by weight for high performance materials. PAN fibers are formed via solution spinning the polymer in hazardous solvents such as DMF and DMSO, then turning into the filaments during the coagulation bath of water or precipitating medium. Melt spinning of copolymers of PAN with N-vinylimidazole have been successful in the formation of carbon fiber precursors. These melt processable copolymers have been shown to create comparable strengths and moduli in the typical carbon fiber processing steps of extrusion, stabilization, and carbonization.

The conversion of PAN based copolymers to carbon fiber involves the "stabilization" of the oriented fiber then carbonizing at elevated temperatures. Even though the stabilization process is the middle step in the formation of carbon fiber, is one of the most crucial procedures. It is during this process that PAN is converted to an infusible and inflammable ladder polymer by cyclizing the nitrile groups of the polymer. The

stabilization procedure usually entails heating the fiber to 200 – 300 °C in air for at least one hour. The mechanisms of stabilization have been theorized and tested for pure PAN homopolymers, though the investigation into the copolymer systems have been limited.

By utilizing a bottom-up approach, fragments of the stabilized structures can be identified for the stabilization of poly(acrylonitrile-*co*-*N*-vinylimidazole) to be pieced together to determine the full hypothesized structure. The pieces of stabilization were determined via TGA-MS-IR along with NMR, EPR, and GCMS studies. The kinetics of stabilization for the copolymer system with N-vinylimidazole were also studied in comparison to that of pure PAN homopolymer. The kinetics showed the rate of stabilization of the copolymer system is much faster than that of the pure homopolymer with lower energies of activation.

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Discrimination of the leaf level emissions of volatile organic compounds from chestnut tree species by gas chromatography-mass spectrometry and chemometrics

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American chestnut tree is ecological and economic significance. However, it was nearly devastated by chestnut blight fungus. Many methods have been developed to restore the American chestnut trees back to natural. Breeding the blight-resistance chestnuts by crossing Chinese chestnuts with the American species via “backcrossing” is one method in use. However, to determine the resistance of one generation of breeding specie takes at least five years and the complete test requires a minimum of six generations. Researches showed that volatile organic compounds (VOCs) produced by tree leaves have a role in defense mechanisms to pathogens. Herein, we are developing a resistance test method by discriminating the VOCs profiles emitted from BC_3F_2, B_3F_3 generations, American, and Chinese chestnut tree leaves using Headspace Solid Phase Microextraction (HS-SPME) coupled with Gas Chromatography-Mass Spectrometry (GC-MS) and the pattern recognition assisted with chemometrics. Further works including dynamic headspace pre-concentration extraction method development and application of current statistical model to field samples.

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Analysis of xylitol in sugar-free gum by GC/MS with direct aqueous injection

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Xylitol is a natural sugar substitute that is found in many sugar free foods today. One popular product that contains a significant amount of xylitol in particular, is sugar free chewing gum. Gum sweetened with xylitol can be beneficial for humans as a sugar substitute, as it can help to whiten teeth, fight tooth decay, remove bad breath, and can even slow the growth of certain cavity-causing bacteria. Although xylitol serves a valid

purpose for humans, it has been found to be toxic to canines. A collaboration with the School of Veterinary Sciences of Mississippi State University lead us to develop a cheap and accurate method to analyze xylitol in sugar free gum. Our method utilizes gas chromatography with a mass detector (GC/MS) to determine the amount of xylitol in aqueous solutions by direct aqueous injection. A novel xylitol extraction method was used to extract xylitol in a fresh gum stick and gum that had been chewed for certain periods of time (5, 15 and 30 min).

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Sulfonamides and analogs in extraction-based sensing applications: Combining coordination chemistry and solvent extraction principles for selective sensing of toxic metals and other ionic targets

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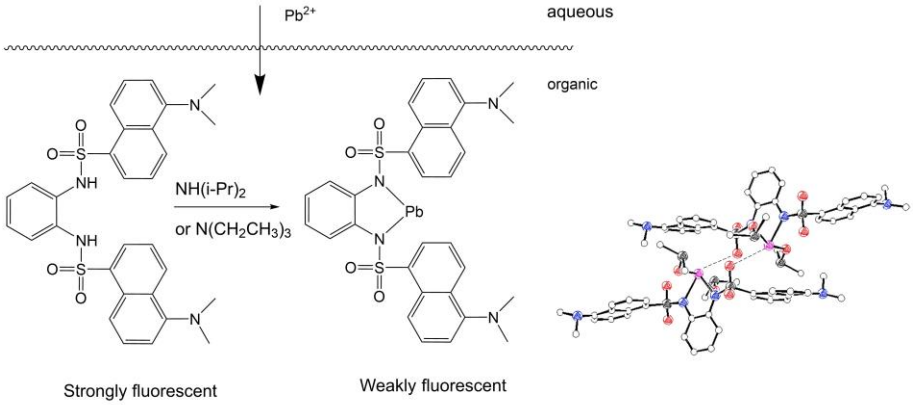
Efforts to design selective and practical sensors for larger and relatively “softer” targets, with lower charge density, such as the toxic metal species Pb(II) and Cd(II) and the anions ClO_4^- and NO_3^- still present significant challenges. Extraction from water into less polar organic solvents via the formation of complexes with distinct optical or electrochemical properties presents an opportunity for addressing sensing selectivity issues, by combining the unique coordination properties for each species (via ligand design), while taking advantage of more favorable dehydration-resolvation energetics for these targets, compared to harder more charge-dense ions (such as Ca^{2+}) which are naturally present in high concentrations and often compete for the ligand binding sites. Sulfonamides with incorporated fluorophores have been shown previously to be effective ion-exchange extractants. Herein we are expanding this approach with a variety of ligands and targets and demonstrate the combined effects of coordination and solvent extraction principles in sensor design.



Extraction-based sensing of Pb(II) by a fluorescent bis-dansylamide.

2015 Joint Southeastern/Southwest Regional Meeting 126

Electrochemical investigations into the formation of germanene

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Germanene, a two-dimensional Ge analog of graphene, does not exist in nature. The discovery of graphene and its unique properties have led some researchers to look for synthetic routes to grow germanene. The present data will demonstrate investigations into electrochemical formation of germanene structures in aqueous media. In situ Scanning Tunneling Microscopy (EC-STM) studies on Au(111) show that initial germanium electrodeposition appears to be kinetically slow and somewhat unstable. Moreover, direct electrochemical deposition of Ge is self-limited and depends not only on the potential but also on the pH of Ge precursor solution. EC-STM studies of more than a monolayer Ge coverage (pH 4.5) demonstrate a honeycomb-like structure with atomic distances of about 0.44 ± 0.02 nm. The presented data will discuss the recent progress on electrodeposition of Ge by EC-STM, voltammetry, coulometry, and micro-Raman.

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Anion sensors

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Anion sensing with synthetic receptors is an active area in supramolecular chemistry. Although, a several classes of synthetic receptors have been known showing high affinity for anions, synthetic anion sensors are still limited in the literatures. In our studies, we synthesized several types of chemical sensors using conventional synthetic protocols, and characterized by NMR, mass and elemental analysis. The new compounds were then investigated for a variety of anions in solutions by UV-Vis and fluorescence titrations, and in solid states by X-ray diffraction analysis. The results showed that the new sensors are capable of interacting several anions both in solution and solid states, displaying visual color change in the presence of certain anions.

Acknowledgements: The project described was supported by Grant Number G12MD007581 from the National Institutes of Health. The National Science Foundation is acknowledged for a CAREER award (CHE-1056927) to MAH.

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Effect of exfoliated graphene nanoparticle based coatings on corrosion-resistance, and UV spectral study of chemically modified graphene nanoparticles

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Corrosion resistance and weatherability are important properties for paint films to increase the service life of buildings, ships, marine structures, and automobiles. Graphene can be an interesting material to use in paints due to its multifunctional properties such as good UV absorption, hydrophobicity, self-assembly, barrier

properties, thermal stability, and high electrical conductivity. We will report our preliminary corrosion and weatherability study results done with the coatings prepared using graphene nanoparticles and films made with chemically treated grapheme nanoparticles.

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Rebuilding and use on rusty iron surfaces and weathered galvanized steel surfaces with a powdered zinc dust in an EPA sustainable (low carbon footprint), water-thinned acrylic emulsion paint containing barium metaborate

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This paper discusses the formulation and use of a coating based on Zinc Dust in an EPA sustainable (low carbon footprint), water-thinned, low VOC, acrylic emulsion paint containing barium metaborate for its multifunctional properties. Also reviewed are long-term durability with adhesion on weathered galvanized steel (without a sand blasted profile), corrosion resistance on rusty iron, and inhibition of microbiological growth on cement panels and shingles.

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Catalytic efficiency of hard Lewis acid metal ions on cadmium vapor generation

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Generation of cadmium vapor has not been a mature approach despite the extensive research over the last there decades. Recent publications suggest that first row transition metals ions show substantial enhancements in Cd vapor generation. In this study, we examined the efficiency of Al(III), Sc(III) and Y(III) for generation of volatile species of Cd(II) in the presence of potassium cyanide (KCN). The acidity of medium was examined from 0 to 12% HCl. Volatile Cd species were generated between 3 to 7% HCl range. Al(III) appeared more effective than Sc(III) and Y(III). Experimental evidence indicated that metal ions act as catalyst in generation of Cd vapor. An improvement up to 10-fold was achieved. The interferences from transitions metals ions were investigated on generation of Cd vapor. The method is validated by analysis seawater samples and various complex samples ranging from purely organic to inorganic by ICP-MS.

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A structural framework for how homologous recombination is stimulated by the phage T4 recombination mediator protein UvsY

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The UvsY recombination mediator protein (RMP) is critical for efficient homologous recombination in bacteriophage T4. We report here the crystal structure of UvsY in four open-barrel heptameric assemblies, and provide structural insights into its biological function. The UvsY heptamer was confirmed in solution by AUC and SEC-MALS, and ITC analyses of the UvsY-ssDNA interaction revealed two binding modes binding within the assembly. Using SPR, we examined the binding of UvsY to both ssDNA and ssDNA in complex with gp32, the T4 ssDNA-binding protein. This confirmed that ssDNA can bind UvsY and gp32 independently, and also as a ternary complex. SPR also showed that residues located on the rim of the heptamer are required for optimal binding to ssDNA, thus identifying the putative ssDNA-binding surface. We propose a model in which UvsY promotes a helical ssDNA conformation that disfavors the binding of gp32 and initiates the assembly of the ssDNA-UvsX filament.

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DNA glycosylase catalysis without base flipping enables base excision repair of bulky lesions

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Threats to genomic integrity arising from DNA damage are mitigated by DNA glycosylases, which initiate the base excision repair (BER) pathway by locating and excising aberrant nucleobases. How these enzymes find small modifications within the genome is a current area of intensive research. A hallmark of these and other DNA repair enzymes is their use of base flipping to sequester modified nucleotides from the DNA helix and into an active site pocket. Consequently, base flipping is generally regarded as an essential aspect of lesion recognition and a necessary precursor to base excision. Here, we present the first DNA glycosylase mechanism that does not require base flipping for either binding or catalysis. Using the DNA glycosylase AlkD, we crystallographically monitored excision of an alkylpurine substrate as a function of time, and reconstructed the steps along the reaction coordinate through structures representing substrate, intermediate, and product complexes. Instead of directly interacting with the damaged nucleobase, AlkD recognizes aberrant base pairs through interactions with the phosphoribose backbone while the lesion remains stacked in the DNA duplex. Quantum mechanical calculations revealed that these contacts include catalytic charge-dipole and CH-π interactions that preferentially stabilize the transition state. We show *in vitro* and *in vivo* how this unique means of recognition and catalysis enables AlkD to repair large yatakemycin adducts, which belong to the duocarmycin family of antimicrobial natural products exploited in bacterial warfare and chemotherapeutic trials. Bulky adducts of this or any type are not excised by DNA glycosylases that utilize a traditional base-flipping mechanism[4]. Hence, these findings represent a new paradigm for DNA repair and provide novel insights into catalysis of base excision.

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Structural insights into the NuRD-like SHREC complex and its mechanism of heterochromatin silencing

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Nucleosome remodeling and histone deacetylation (NuRD) complexes are essential for differentiation and development and are recruited by Methyl-DNA-Binding proteins and transcriptional regulators. The Snf2/HDAC repressive complex (SHREC) represents the fission yeast NuRD equivalent. SHREC is recruited by the HP1 proteins and unites the nucleosome remodeler Mit1, the histone deacetylase (HDAC) Clr3, and the poorly characterized subunits Clr1 and Clr2. Here we present an in-depth functional and structural description of SHREC. Clr1 forms the core of the complex, binding Mit1 with an N-terminal domain and Clr2 and Clr3 with its C-terminus (Clr1C). Crystal structures of the Mit1-Clr1 interface, of Clr2 bound to Clr1 and of the Clr3 dimer are presented. Our analysis characterizes the interaction of Clr2, Clr3 and Mit1 with the Clr1 backbone. Dissection of the complex's role in heterochromatin silencing reveals a modular architecture and new roles in recruitment of SHREC by previously unrecognized nucleic acid binding domains.

Crystal structure of a bacteriophage T7 primase-helicase DNA polymerase complex provides a molecular snapshot of replisome assembly

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Bacteriophage T7 has long served as a model system to study the processes of DNA replication, as only four proteins are required to accurately copy DNA. Our laboratory is interested in understanding how these four proteins interact and communicate in order to efficiently copy both strands of DNA in a coordinated manner. We have recently determined X-ray crystal structures of complexes of three of these proteins that are providing the first images of how these proteins interact at the molecular level. The 670 kilodalton structure shows that a helicase ring binds three copies of DNA polymerase in an asymmetrical fashion. In agreement with our structure, native electrospray mass spectrometry data reveals that a helicase ring can form a stable complex with up to three polymerases. Previous work has demonstrated that an interaction between the acidic C-terminal tail of the primase-helicase and the DNA polymerase is essential for DNA replication, and our structure provides the first clues as to where the acidic C-terminal tail of the primase-helicase specifically contacts the DNA polymerase. Current efforts are focused on generating point mutations in these proteins to attempt to disrupt the interactions observed in the crystal structures. We are testing the consequences of these mutations on the ability of these proteins to interact using a combination of biochemical approaches such as *in vitro* DNA replication assays and *in vivo* bacteriophage T7 complementation assays. Preliminary phage complementation results show the mutation of crucial contact points observed in the crystal structure are detrimental to bacteriophage survival. Our ultimate goal is to understand at the atomic

level how all four proteins assemble into a single machine to carry out coordinated DNA replication.

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Substrate specificity of MutT pyrophosphohydrolase using nucleotide analogues

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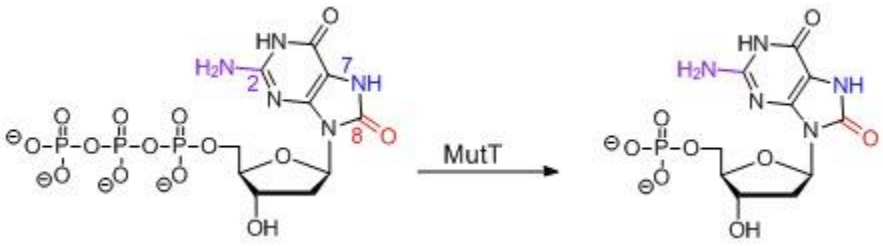
The bacterial repair enzyme MutT hydrolyzes the damaged nucleotide OdGTP (the 5'-triphosphate derivative of 8-oxo-2'-deoxyguanosine), which is a known mutagen and has been linked to antibacterial action. Previous work has indicated important roles for the C8-oxygen, N7-hydrogen, and C2-exoxylic amine during OdGTP recognition by MutT. In order to gain a more nuanced understanding of the contribution of these three sites to the overall activity of MutT, we determined the reaction parameters (k_{cat} and K_m) for dGTP, OdGTP, and nine of their analogues using steady state kinetics. Our results indicate that overall high reaction efficiencies can be achieved despite altering any one of these sites. However, altering two or more sites leads to a significant decrease in efficiency. The data also suggest that, similar to another bacterial OdG repair enzyme, MutM, a specific carbonyl in the enzyme can not only promote activity by forming an active site hydrogen bond with the N7-hydrogen of OdGTP, but can also hinder activity through electronic repulsion with the lone pair on the sp^2-hybridized N7 of dGTP.



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Insights from the crystal structure of an MCM hexamer

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In eukaryotes, the replicative CMG helicase consists of the Mcm2-7 hexamer, Cdc45, and the GINS tetramer. Mcm2-7 forms the core of this complex and assembles through the association of six unique proteins that are highly homologous. In archaea, a homologous MCM homohexamer functions as the replicative helicase at the replication fork. For this reason, archaeal MCM proteins serve as useful models for the eukaryotic Mcm2-7 helicase. The overall architecture of an MCM hexamer is two-tiered with distinct N-terminal and ATPase tiers. We have recently reported a crystal structure of an MCM hexamer that includes both tiers and is helicase-active. Our structure is a chimeric fusion of the N-terminal domain from *Sulfolobus solfataricus* and the ATPase domain

from *Pyrococcus furiosus*. Here we will discuss insights from the crystal structure and relate these to eukaryotic Mcm2-7 structure and function.

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Mapping the residues of human WRN helicase involved in unwinding G-quadruplex DNA

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Maintaining the integrity of the genome is a fundamental biological process, aberrations in which lead to tumorigenesis in higher eukaryotes. The cellular machinery that is responsible for this process has to overcome many obstacles like damaged bases or non-canonical DNA structures. G-quadruplex (G4) DNA is a specialized DNA structure that is commonly encountered by the replication machinery, and it has been shown to present a significant block for replication, and must be overcome to complete the process efficiently. G4 motifs have been shown to occur at functional regions of prokaryotic and eukaryotic genomes, like promoters of oncogenes, replication origins and telomeres. G4 sequences are also enriched at chromosomal breakpoints in multiple types of cancer. The Werner's syndrome protein (WRN) is a helicase that has been implicated in efficiently unwinding G4-DNA structures during replication. We investigated the role of the RecQ-C terminal (RQC) domain of WRN in interacting specifically with G4-DNA structures using the c-Myc G4-DNA sequence. DNA binding experiments using truncated constructs of WRN showed that the RQC domain was both necessary, and sufficient for binding G4-DNA. ^{15}N-NMR spectroscopic studies with the RQC-domain were performed in DNA titration experiments using both non-structured, and G4-DNA forming oligos to identify residues that are involved specifically in interacting with G4-DNA. Residues that showed the maximum G4-specific changes in NMR signals were considered for further studies. These residues were mutated by site-directed mutagenesis in the context of a helicase-RQC domain construct of WRN (residues 500-1092), and the resulting mutant proteins were studied in detail for their ATPase activity, ability to unwind G4-DNA and their relative affinities towards non-structured or G4-DNA substrates. All of the mutant WRN proteins showed robust ATPase and DNA-unwinding activities on non-structured substrates, comparable to the wild-type. Mutating residues T1024 and T1086 resulted in a substantial defect in helicase activity as compared to the wild-type enzyme, and this defect was only observed with the G4 substrate. The WRN$^{T1024G/T1086G}$ double-mutant protein was the most affected in this respect (only 10% G4-DNA unwinding activity compared to wild-type). Thus, we have identified residues in the WRN RQC domain that are dispensible for unwinding B-form DNA but necessary for optimal G4 unwinding activity.

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GC-MS measurement of xenon in fluids for neuroprotective applications

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Background: Neuroprotective agents are meant to slow the progression of brain damage in stroke patients by inhibiting expansion of necrotic brain tissue . Xenon's ability to antagonize NMDA receptor-mediated excitotoxicity following an ischemic attack and its ready diffusion into target tissues makes it an excellent neuroprotective candidate. We have developed a liposomal formulation of xenon (Xe-ELIP) for this purpose. The objective of this study was to develop a reliable assay to measure the amount of dissolved xenon released from Xe-ELIP in water and blood samples. **Methods:** Gas chromatography-Mass Spectrometry (GC-MS) was used to quantify 5 µl aliquots of headspace gas in 2 ml vials containing 1 ml samples of either 25 µl of 10 mg/ml Xe-ELIP mixed with 975 µl of rabbit blood or 200 µl of 10 mg/ml Xe-ELIP mixed with 800 µl of water. Rat blood samples were drawn directly from a catheterized right carotid artery during IV infusion of 6 mg Xe-ELIP lipid in 0.6 ml saline. After introduction of the samples, each vial was sealed, allowed to equilibrate to 37° C in a temperature-controlled sonicating water bath, followed by 20 minutes of sonication prior to sampling. For uniformity, headspace gas was sampled from the same vertical location in each vial. Concentrations were calculated from a gas dose-response curve and converted to percent xenon, assuming complete equilibration with the headspace. Results were normalized using the published xenon water-gas partition coefficient. **Results:** The mean corrected percent of xenon from Xe-ELIP released into water was 3.87 ± 0.56% (n = 8), corresponding to 19.3 ± 2.8 µl/mg lipid, which is consistent with previous independent Xe-ELIP measurements. The corresponding xenon content of Xe-ELIP in rabbit blood was 23.38 ± 7.36 (SD, n = 8) µl/mg lipid . Rat blood xenon concentrations after IV administration of Xe-ELIP were 0.025% and 0.016%, corresponding to 10 and 6 µM, respectively. **Conclusions:** Blood concentrations for the anesthetic dose of xenon have been established. Based on previous literature, the proposed concentration conferring xenon's neuroprotective properties is 20% of the anesthetic dose. The xenon content measured in blood after Xe-ELIP infusion is approximately one-tenth of the projected value. We have observed neuroprotective effects at these blood concentrations. More work will have to be done to determine whether greater neuroprotection can be achieved at higher blood xenon concentrations.

Biocompatible, biodegradable metal-binding cyclic peptides for heavy metal toxicity removal

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Arginine and tryptophan rich cyclic peptides, $[WR]_n$ (n = 3-5), were synthesized and evaluated for potential non-covalent coordination with Au(III), Se(IV), and Zn(II). *Ab initio* molecular orbital calculations with complete geometry optimizations were performed to study the efficiency of these peptides in heavy metal non-covalent complexation. The peptides were incubated with metals and their binding affinities were determined by monitoring UV spectrophotometry. Difference absorption spectra of free and metal-bound peptide demonstrated that the absorbance at 275-300 nm can be used to monitor peptide-metal binding. Both the theoretical results and the absorption

spectra results are in conformity with 1:1 peptide-metal complex formation and higher binding affinity to Au(III) (K_d = 0.6-1.7 nM) and Zn(II) (K_d = 3.7-11.2 nM) when compared with Se(IV) (K_d = 9.7-31.3 nM). This study provides insights about the structural requirements for generation of cyclic peptide-metal complexes with optimal binding affinity as leads for developing biocompatible drugs for heavy metal toxicity removal.

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An electrochemical platform for real-time metabolic profiling in liver-on-chip systems

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In vitro analysis of organ systems following exposure to exogenous toxins and drugs is of extreme importance in the development of novel therapeutics, particularly in regard to hepatoxicity. The liver is highly susceptible to damage based on its role as a metabolic center in the human body. For this reason, effective metabolite analysis of liver-on-chip systems is essential to accurately predict *in vivo* response to therapeutics. In the work presented here, we describe the development of an amperometric sensor platform designed to monitor changes in glucose, lactate, oxygen uptake, and pH downstream from a liver bioreactor. Based on the inherent redox activity of many bioactive drugs of interest, these measurements have traditionally been impossible with electrochemical sensors. However, the sensor platform here has been modified with a series of Os-containing redox polymers and oxidase enzymes to operate at a lower electrode bias, outside the electrochemical window of interfering drug compounds. Acetaminophen (APAP), a common pharmaceutical and liver toxin, was used herein to validate the insensitivity of the multianalyte sensor platform to background interference. Using this novel multianalyte biosensor, conditioned media from hepatocytes exposed to 10 mM APAP was analyzed. Further, the utility of this platform was extended to additional known electrochemically active liver toxins to verify the insensitivity of this sensor to these interferents.

2015 Joint Southeastern/Southwest Regional Meeting 141

Fabrication and characterization of the micro-impedance detector for enumeration of circulating tumor cell

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Currently the only FDA approved device to count Circulating Tumor Cells (CTC) is the CellSearch system. The Soper Research Group has created microfluidic devices that allow a greater clinical sensitivity for a wider range of cancers, and is working to make a mass producible system. To do this, a new impedance detector needs to be designed and tested. In this report, a new generation impedance module was fabricated and different bonding strategies for the modules were analyzed. The types of bonding that were tested includes UV-activated glue, solvent bonding, and thermo-fusion bonding. Due to a higher reproducibility, thermo-fusion bonding was chosen as the optimal route and used for the rest of this research. The new generation module was more sensitive to direct changes in solution conductance than the first generation module in approximately a 1.3:1 ratio of ΔV, and showed a larger relative response to 15 µm

beads. Proof of concept of sensing HeLa 60 cells was achieved and compared to the first generation module. This data supports the conclusion that the new generation impedance module is similar in performance to the first generation device, but more easily mass fabricated, and therefore favorable for the CTC counting device.

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Imaging of lipids in the ocular vitreous humor using matrix-assisted laser desorption ionization-mass spectrometry

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The vitreous humor (VH) of mammalian eyes makes up 80% of the ocular volume. Despite its high levels of water (~98%), it exhibits a gel-like consistency due of the network formed by the highly hydrophilic hyaluronan and collagen fibrils. Aging leads to the progressive liquefaction of the VH and may result in vitreal and/or retinal detachment. The cause(s) of liquefaction is still unknown. To address this issue, it is important to explore possible chemical changes that may contribute to liquefaction. Our hypothesis is that phospholipids (PLs) and their metabolites derived from lenticular and/or retina cell may interrupt this network. We have developed an imaging method to detect PLs using matrix-assisted laser desorption ionization-mass spectrometry imaging (MALDI-MSI). To test this approach, the VH of frozen porcine eyes were cut in half and stamped on a MALDI plate coated by dipping it in a solution of *para*-nitro aniline (PNA) (23 mg/mL of methanol) as the matrix. The plate was then dried to create a homogeneous layer of matrix. MALDI-MS was applied and the images revealed that the main PLs in the VH were phosphatidylcholines (PC), particularly PC (34:1) (see Figure 1). Sphingomyelin was also observed but in much smaller quantities. Although PNA is known to sublime under vacuum, our studies show that PNA remains attached to the sample for the entire acquisition time. This method allows for the regional detection of PLs (and other species) present in the VH and will enable the testing of our hypothesis that age-dependent lipid compositional changes contribute to liquefaction.

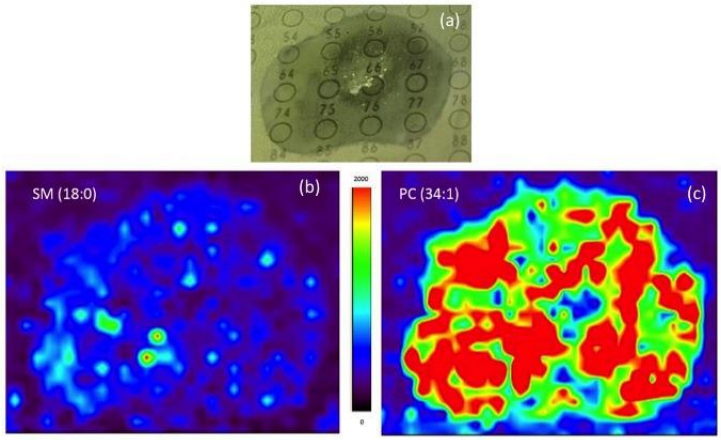

Figure 1: Frozen porcine VH stamped on MALDI plate (a) and images of the distribution of (b) SM (18:0) and (c) PC (34:1) and SM peaks shown below

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^{31}P NMR characterization of chitosan phosphorylation

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The movement towards more biocompatible and biodegradable materials has emphasized the utility of chitosan, a polymer derived from crustacean shells. As a linear polysaccharide of primarily D-glucosamine units, biodegradability is an innate property of chitosan, enabling its use as either a biomaterial or drug delivery vehicle. However, chitosan's poor solubility and net positive charge are problematic for therapeutic applications. One solution for circumventing these issues involved adding phosphate to the polymer backbone. Phosphorylation allows for fine-tuning of the overall charge (from positive to neutral or negative) while simultaneously improving solubility in aqueous solutions. Although prior work has demonstrated successful chitosan phosphorylation, such studies generally lack ^{31}P nuclear magnetic resonance (NMR) characterization. In fact, no study to date has evaluated the types of phosphates (e.g., ionically-bound, monoesters, polyphosphates) appended to the backbone and/or correlated such information to solubility or other beneficial characteristics (e.g., chelate calcium ions). In this study, we assessed the formation of phosphorylated chitosan by methanesulfonic acid and phosphorus pentoxide using X-ray photoelectron spectroscopy (XPS), and ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy. The approach and results of this work should prove helpful for other materials requiring phosphorylation.

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Effect of blood and an oxidation agent on a novel cyanide antidote

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Cyanide (CN) is highly toxic and hazardous to cells. CN inhibits the activity of the enzyme cytochrome c oxidase and therefore impairs oxygen utilization and ATP production. Antidotes for CN have been developed, such as sodium thiosulfate or hydroxocobalamin, to counteract cyanide intoxication. However, each antidote has some disadvantages. Sulfur Donor X (SDX), our novel cyanide antidote, has shown greater *in vivo* efficacy against cyanide intoxication than currently available therapies. The pharmacokinetics shows that SDX is rapidly metabolized. The aim of the research was to study the metabolites of SDX in blood with gas chromatography mass spectrometer (GC-MS) and high performance liquid chromatography (HPLC). In case of GC-MS, SDX was sampled from the head space above an aliquot of blood using solid phase microextraction. Increasing the incubation time of SDX in blood decreased its peak area. This signal lowering effect was 14 times stronger when SDX was spiked into and sampled from fresh blood versus 4-month old blood. It was hypothesized that SDX might be degraded in the blood via either oxidative or reductive process. To test the

potential for oxidative degradation, H_2O_2, a strong oxidizing agent, was applied to SDX solution. After H_2O_2 treatment, new peaks appeared at 13.1 min and 19.3 min retention time of HPLC measurement beside the main SDX peak at 9.5 min. SDX treatment with H_2O_2 time dependently reduced the peak at 9.5 min and increased the two new peaks. UV-vis absorption spectra of blood spiked with SDX were collected. These indicate that a portion of the SDX is reduced by hemoglobin, leading to the formation of methemoglobin. It can be concluded that while both oxidative and reductive processes are possible, the reduction of the sulfur donor by hemoglobin is the predominant step in the metabolism of SDX in blood.

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Surface enhanced Raman spectroscopy of cyanide metabolite 2-aminothiazolene-4-carboxylic acid (ATCA) on immersed and dried substrates

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Cyanide is a fast acting poison that interferes with the ATP synthesis. For studies of cyanide countermeasures it is advantageous to detect cyanide, cyanide antagonists, and multiple metabolites rapidly following exposure to CN. Surface enhanced Raman spectroscopy has the potential to be used for multiplexed and rapid detection of multiple analytes. Gold-coated silica nanopillar arrays have been shown to be effective SERS sensors following drop evaporation, or via gas phase exposure. It would be useful to apply them to the direct sensing of metabolytes in liquid samples. To explore that possibility we have carried out in-situ SERS experiments with gold-coated nanopillar sensors (Silmeco SERstrates) immersed in aqueous ATCA solution, and SERS experiments with sensors that have been dried, and rinsed following immersion. ATCA peaks in the SERS spectra were below our detection limit when the data was collected via immersion but reappear when the same substrate is dried. A control experiment with gold-coated nanopillar substrates that had been previously vapor coated with benzenethiol showed strong SERS signal for both immersed and dried sensors. We conclude that gold-coated nanopillar array SERS substrates have strongly differing enhancing characteristics for some, but not all, analytes based on whether the SERS spectra are collected from an immersed substrate, or from one that has been dried.

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Electrochemical detection of acetaminophen, H_2O_2, and dopamine using tapered silicon nanowires

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Tapered silicon nanowires (SiNWs), grown using chemical vapor deposition (CVD), were utilized to selectively detect and measure acetaminophen (AP), hydrogen peroxide

(H_2O_2), and dopamine (DA) in phosphate buffered aqueous solutions. The SiNWs were applied via drop-casting onto glassy carbon electrode (GCE) surfaces, which were capped with 5 wt % Nafion solution and subsequently used as the working electrode for cyclic voltammetry (CV) and chronoamperometry (CA) measurements. Voltages used on the CA/CV potentiostat for the selective detection of AP, H_2O_2 and DA were –0.055, –0.600, and –0.522 V, respectively. The maximum signal for each analyte wasfound to be pH dependent, owing to surface charge effects on the electrocatalyst surface. Effective analytical measurement ranges for AP, H_2O_2, and DA were found to be 0.5–15 mM, 1–700 nM, and 1–80 mM, respectively. Optimization of amperometric detection via selection of solution pH for each analyte will be discussed.

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Get involved with the ACS Division of Chemical Education

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Want to know more about the Division of Chemical Education, learn how you can get more involved with DivCHED, learn about educational resources for chemistry, find out how to apply for travel awards, or meet and network with people from your region, nationally, and around the world who have similar interests? The Division of Chemical Education aims to serve as a means of focusing and enhancing the interest and efforts of all constituencies involved in the teaching and learning of chemistry at every level. If you have an interest in chemistry education, we want you involved in DivCHED. Come visit our poster to learn more about the Division and all we have to offer, meet representatives from the Division, and let us know what you think the Division can do to better meet the needs of our members.

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Chromium (III) supercharging in electrospray ionization mass spectrometry of biological peptides

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The analysis of biological peptide solutions by mass spectrometry usually involves electrospray ionization (ESI), where ionization commonly occurs by the addition of protons to analyte molecules. The ability to increase the extent of ionization both improves detection limits and facilitates pBiological peptides can be identified in solution by mass spectrometry, but not as clearly as one may hope. Proteomic sequencing by radical-based techniques such as electron transfer dissociation. Scould be performed much more efficiently if peptides were more distinctly identifiable in solution by mass spectrometry. Certain solution additives can be used to increase the charge states of ions produced by ESI and also to of the sample. Additionally, additives can increase signal intensity when more peptides are encouraged to accept charge and remain at the higher charge state. Addition of acid to the solutions being electrosprayedcid addition in solution is a common method to encourage protonation of the peptide and increase its signal intensity. Our research group The has recently shown that the addition of

chromium(III) certain metal ions in solution can has been shown to “supercharge” some peptides, dramatically increasing ESI signal intensity through additional protonation. In order to further characterize ESI supercharging of peptides, tTwelve basic or neutral biological peptides were tested with additives of acid alone, Cr(III) alone, and acid plus Cr(III). ForIn most peptides, addition of acid alone decreased signal intensity. This unexpected phenomena is currently being investigated at multiple acid concentrations. Cr(III) was effective at supercharging six of these peptides, creating a signal intensity 2 to 8 times greater than the ESI signal without initial, no-additive signal. These peptides all shared one characteristic; they possess, possessing two basic residues and no acidic sites other than the C-terminus carboxylic acid group. The peptide substance P One peptide was tested in two forms, one with an amide group in place of the C-terminus carboxylic acid and one with the carboxylic acid group intact. The more neutral amine version supercharged better than its carboxylic acid equivalent, suggesting that the overall number of acidic sites may decrease supercharging. Spacing between basic residues did not appear to affect supercharging performance contrary to the thought that charges may not accumulate on basic sites in close proximity.

Solid-phase extraction-77K laser excited time resolved fluorescence spectroscopy for the analysis of benzo[a]pyrene metabolites in urine samples

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Analytical methods to elucidate the initial phase of carcinogenesis are extremely relevant to our society. Covalent binding of metabolites of PAHs to DNA appears to be the critical step in the initiation of the tumor formation process. Under this prospective, the determination of PAH metabolites prior to DNA damage fills an important niche to prevent extreme body burdens and minimize cancer risk. Urine analysis of PAH metabolites is recognized as an accurate assessment of human exposure to PAHs. Despite the sophisticated arsenal of analytical tools, monitoring PAH-metabolites via simple, cost effective and direct methods still remains a challenge. Research in our group has focused on the development of screening techniques capable to process numerous samples in short analysis time. Screening methods prevent unnecessary scrutiny of uncontaminated samples via time-consuming chromatographic procedures, reduce analysis cost and facilitate data collection from statistically meaningful population sizes. The method presented here combines solid-phase extraction (SPE) to laser excited time resolved fluorescence spectroscopy at 77K temprature. Commercially available SPE membranes serve the dual purpose of sample pre-concentration and solid substrates for fluorescence measurements. Sample freezing is performed in a matter of seconds with the aid of a fiber-optic probe directly inserted into the liquid cryogen. Wavelength time matrices (WTMs) and time resolved excitation emission matrices (TREEMs) are rapidly collected with the aid of a pulsed tunable dye laser, a spectrograph, and an intensified charged couple device. The potential of our proposition is demonstrated with the direct analysis of 3-hydroxy-benzo[a]pyrene, benzo[*a*]pyrene-*trans*-9,10-dihydrodiol, benzo[a]pyrene-r-7,t-8,c-9-tetrahydrotriol and benzo[*a*]pyrene-*r*-7,*t*-8,*c*-9,*c*-10-tetrahydrotetrol in synthetic and human urine samples. Recovery values varied from 87.54 ± 3.11% (3-hydroxy-benzo[a]pyrene) to 99.77 ± 2.98% (benzo[*a*]pyrene-*r*-7,*t*-8,*c*-9,*c*-10-tetrahydrotetrol). Limits of detection at the $pg.mL^{-1}$ concentration level were obtained with only 10mL of urine sample. The excellent analytical figures of merit demonstrate the robustness of this approach for screening

PAH metabolites in urine samples.
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Selective nano-sensing approach for the quantitative analysis of phosphate ions in biological matrixes

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Abnormal levels of phosphate ions in urine samples are indicators of potential cancer developments in thyroid, bone and other organs of the endocrine system. Although a plethora of analytical methods have been developed for the analysis of inorganic phosphate in biological systems, its determination at relevant biological concentrations remains a challenge. The need for sample clean up and pre-concentration steps prior to separation and determination via chromatographic, electrochemical or electrophoretic techniques often leads to tedious and time-consuming assays unsuited for screening purposes. As a tentative means of circumventing the shortcomings of classical methodology, a variety of bio-sensing approaches coupled to electrochemical detection have been reported in the literature. The same is true for chemical probes based on photoluminescence, chemiluminescence and spectrophotometric detection. Herein, we present a lanthanide-based luminescent probe $[Tb\text{-}EDTA]^{-1}$ utilizing synthesized gold nanoparticles (Au NPs) capped with cetyltrimethylammonium bromide (C-TAB). With this approach, it is possible to selectively determine phosphate ions at micro-molar (mM) concentration levels. Chemical species commonly found in biological systems - such as NO_3^-, NO_2^-, OH^-, CO_3^-, SO_3^{-2}, Cl^-, F^-, CH_3COO^-, creatinine and urea – cause no interference in the sensor's response. Accurate results were obtained for the determination of phosphate ions in urine samples.

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Polysaccharide-mediated formation of pigments from catecholamines

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Catecholamines like dopamine, epinephrine or norepinephrine can serve as precursors for the formation of melanin-like pigments. Polysaccharides have been observed to enhance the oxidation of these catecholamines, particularly in the presence of redox-sensitive ions like Cu^{2+}, leading to the formation of darkly colored substances. In this portion of the research, we investigated the effects of: (1) reaction time, (2) type of polysaccharide, (3) type of cation and (4) concentration of all reagents involved. These parameters were evaluated to determine the conditions that would yield the highest amount of polysaccharide-associated pigment. Following the reactions, the pigments can be centrifuged or dialyzed, washed with water and lyophilized. Pigmented materials were evaluated and characterized using UV_Sis spectroscopy, RP-HPLC, SEC, AAS and FT_IR analyses.

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Polysaccharide-mediated formation of pigments from serotonin

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Serotonin is a potent neurotransmitter affecting many aspects of human behavior or function. Copper-mediated metabolism of serotonin has been implicated in a number of neuropathologies like Wilson's disease or prion diseases. Serotonin is known to undergo enzymatic or non-enzymatic oxidation, and the oxidation products of serotonin have been postulated to be neurotoxic. We have observed that some polysaccharides, when incubated with Cu (II) cation, can induce the formation of darkly colored substances in the presence of serotonin. These observations are in line with the formation of darkly colored substances out of catecholamine like dopamine, epinephrine or norepinephrine, in the presence of polysaccharide/Cu (II) complexes. Here we report on our findings regarding the effect of different polysaccharides on this reaction and our attempts to characterize the darkly colored substances generated in these reactions.

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Optimization of a measurement system for pH measurement in tear fluid samples

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Measuring tear film composition is an essential step in the diagnosis of Dry Eye Syndrome (DES). In many cases, difficulties with sample collection—small tear volume—prevent the use of traditional analytical techniques. Microfluidic systems with integrated sensors offer an attractive solution to analyze samples with very small volume. The purpose of this project is to characterize an optical pH sensor in a microfluidic flow-through system to measure pH for small sample volumes. Optical sensors have several advantages over traditional glass electrodes; however, the sensitivity, sluggish response, and short life-time make many optical pH sensors unsuitable for many analytical applications. A high concentration of a pH sensitive dye was encapsulated into ~200 nm diameter porous nanocapsules with ~1 nm wall thickness to alleviate some of these drawbacks. The dye-loaded nanocapsules allow for rapid diffusion of small molecules and ions into the nanocapsules while eliminating the leaching of the encapsulated indicator dye. Immobilizing the dye-loaded nanocapsules into porous polyvinyl alcohol (PVA) produces a robust and versatile sensor platform. The nanocapsule-PVA gels are molded and embedded into a microfluidic system . The effect of gel geometry and nanocapsule concentration on response time and sensitivity are studied to optimize sensor performance.

2015 Joint Southeastern/Southwest Regional Meeting 154

Using fluorescent probes to study the location and interaction of disaccharides with lipid bilayers

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Certain organisms have the capability of surviving complete dehydration, freezing and/or oxygen deficiency. One such organism is the tardigrade, also known as the "water bear." The tardigrade can enter a state of self-preservation where it can withstand extreme conditions, such as high and low temperatures, high pressures and radiation. The tardigrade's ability to survive such extreme conditions is associated with a decrease in internal water content and the excess production of a disaccharide known as trehalose. Our study uses fluorescence spectroscopy to probe the location of disaccharides in model membranes and the type of interactions between these sugars and membrane lipids.

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Thermal stability of gelatin gels confined to silica gel nanopores

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This research explores the effect of nanoconfinement on the thermal stability of gelatin gels prepared inside 4, 6, 15, and 30 nm pores of a silica gel matrix. Differential scanning calorimetry and isoconversional analysis were employed to quantify the kinetic parameters associated with gel melting. It was found that nanoconfining gels decreased the heat of melting and shifted gel melting to a higher temperature with the largest effect for the 6 nm pore size and the elimination of gel formation in the 4 nm nanopores. Analysis of the effective activation energy of the gel melting revealed a surprising decrease upon nanoconfinement indicating that the enhancement of thermal stability was due to a decrease in the pre-exponential factor.

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Coronene diimide containing polymer films via electropolymerization of diphenylamine end groups

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Here we report the synthesis of a new monomer containing coronene diimide with diphenylamine end group (DCTD) and its electropolymerization. The polymer thin films of DCTD were grown onto gold, glassy carbon and ITO electrode surfaces. Cyclic voltammetry of the resulting polymers show a reversible $2e^-$ oxidation of the diphenyl benzidine unit and reversible reductions of the aromatic diimide. The spectroelectrochemical, electrochromic and electrochemical impedance properties of these films were evaluated. The polymer film morphology was characterized by AFM.

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Fluorescent assay for beta-galactosidase activity in probiotic gram-positive bacterial cells

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Measuring enzymatic activities in whole cells requires less preparation and minimizes the interruption of normal cellular activities. However, reports on measuring the enzymatic activities in gram-positive bacterial cells have been limited, which could be due to its thicker cell wall. Using two different strains of *Lactobacillus* gram-positive bacteria as our probiotic models, we optimized a protocol for measuring the activity of beta-galactosidase (β-gal) in 96 well format using a fluorescent substrate called 4-methylumbelliferyl β-D-galactopyranoside (MUG). MUG has a similar structure to D-lactose, which is β-gal's natural substrate. When MUG is used by the β-gal enzyme as a substrate, 4-methylumbelliferone is released as a fluorescent product. The optimization of the β-gal assay included reduction of background noise, testing for optimal activation time for the expression of β-gal, MUG concentration, and incubation time with MUG. The linear dynamic range and reproducibility of the β-gal assay were established with a standard curve of cell density. The optimized protocol would allow the β-gal assay to be completed in 5 hours and achieve significantly higher signal-to-noise ratios.

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Ternary metal-hydroxo complexes of Fe^{3+} and Cr^{3+} with clofibric acid (CA): A peroxisome proliferator-activated receptors-alpha (PPARα) ligand

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Fibrates are the only marketed PPARα agonists that are effective in lowering elevated serum triglycerides. Their chemical structures are characterized by the presence of the 2-phenoxy-2-methylpropanoic acid moiety. Clofibric acid (CA) is a known ligand for PPARα. Using potentiometric titrations, UV-Vis, IR and speciation diagrams, it appeared that CA binds both Fe^{3+} and Cr^{3+} in aqueous solutions in 0.1 M $NaNO_3$ at 25 ^{o}C. The potentiometric measurements indicated that for the reaction of any of these metal ions with CA a net of four protons ($4H^{+}$'s) were released into the solution; one from the carboxylic acid group and the other three from the metal-aqua ligands. The pKa value of CA is 4.32 ± 0.06. Formation of the Fe^{3+}-CA complexes cover the span of a total of 435 mV; from +222 mV to -213 mV. Both metal ions-CA reaction mixtures indicated the formation of the ternary M-CA-$(OH)_3$ complex.

2015 Joint Southeastern/Southwest Regional Meeting 159

Design of mesoporous silica nanoparticles for the delivery of platinum-acridine anti-cancer drugs

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Platinum-acridines are a class of DNA-targeted hybrid agents, which have shown promising activity in solid tumor models. To improve the pharmacological properties of these agents and reduce their systemic toxicity, we have begun designing biologically

inert nanosized carrier systems. In this study, large pore mesoporous silica nanoparticles (MSN) were synthesized by using conventional hexadecyltrimethylammonium bromide (CTAB) as soft template. Large pore sizes (> 6.5 nm) and high surface areas (> 700 m^2/g) were achieved. Grafting and coating methods were applied to enhance the aqueous dispersibility of the materials in biologically relevant media. Various characterization methods were used including Fourier-transform infrared spectroscopy (FTIR), small-angle X-ray scattering (SAXS), thermogravimetric analysis (TGA), isothermal gas adsorption, transmission electron microscopy (TEM), and dynamic light scattering (DLS). The uptake of dicationic platinum-acridines into, and release from, selected materials was studied in media mimicking physiological conditions in plasma and cells. The results suggest that optimized MSN-based materials may have utility as carriers for the safe delivery of platinum-acridines to target tissues.

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Investigation of relationship between the γ-ray absorber and polymer matrix in plastic scintillators

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High energy detection through scintillation counting is used in areas of medicine, high-energy research, and national security. Detectors based on inorganic wide band gap semiconductors are typically used for these applications. The major drawbacks of these materials are the need for the growth of large crystals, the difficulty in imparting a specific shape to the crystal, and the presence of toxic elements, such as cadmium in the state-of-the-art cadmium-zinc telluride detectors. These issues can be resolved by using plastic scintillators loaded with γ-ray absorbing components with high atomic number (Z). The efficiency and energy resolution of such systems, however, is significantly lower than that of inorganic detectors. In this contribution, we report a systematic investigation of effects the physical characteristics of the polymer and high-Z component have on the γ-ray detection efficiency. The performance of plastic detectors has been studied as a function of HOMO-LUMO gaps, high-Z component concentration, and polymer's structure. We present results of our efforts on energy gap matching and variation of the nature of high-Z component and polymer matrix.

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Pnictide mixed-aromatics

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The discovery of the aromatic diphosphatriazolate anion, $P_2N_3^{2-}$, (A. Velian and C.C. Cummins, SCIENCE, **348**, 1001-1004 (2015)) has prompted an examination of the possible existence of other pnictide mixed-aromatic anions. A theoretical study was performed on the P-, As-, Sb- and Bi-substituted compounds in cyclic aromatic rings. The SPARTAN and GAUSSIAN suite of molecular orbital programs have been employed to probe the existence and properties of pnictide-substituted aromatic ions. A

comparison for possible trends will be made with previously studied pnictide compounds.

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Seven-coordinate 18 e- complexes of tungsten (II) bearing "N_2S_2" ligands: Synthesis and reactivity

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Seven-Coordinate 18 e- complexes of [(N_2S_2[1,2])$W(CO)_3$] (N2S2:1= N,N'-bis-2-methyl-mercaptopropyl-N,N'-dimethylethylenediamine,2= N,N'-bis-2-mercaptoethyl-N,N'-dimethylethylenediamine) have been synthesized and their reactivities explored. Seven-coordinate complexes of this type have been shown to lose two carbonyl ligands and form six-coordinate complexes with 4 e- donor ligands, ie. alkynes, nitriles, and ketones. Both Complexes have been fully characterized by 1H NMR, FT-IR, XRD, UV/Vis and MALDI-TOF. The electrochemistry of these complexes have also been explored via cyclic voltammetry. To eludcidate more information about the electronic structure of these complexes density functional theory calculations have also been employed.

2015 Joint Southeastern/Southwest Regional Meeting 163

Synthesis and optical properties of phosphonate-substituted free and locked bithiophenes

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Two new series of phosphonate-substituted bithiophenes, pdP(X)(C4H2S)2H and pdP(X)(C4H2S)2P(X)pd (pd = OCH2C(CH3)2CH2O; X = O, S, Se), have been synthesized and the emission spectra, and third-order nonlinear optical absorptions have been obtained. Computational estimates of the emission spectra have been calculated and compared to experimental results of said compounds. The compounds show emission wavelengths between 380-400 nm, and depending on the choice of X, have quantum yields much greater than 2,2'-bithiophene. Calculated absorption wavelengths differ by a maximum of 10% Conformational analysis indicates two distinct S-C-C-S torsion angles within the bithiophene domain, syn and anti. Distribution between the two are nearly 2:1 over all examined conformations. When excited, energy can be dissipated via non-radiative relaxation arising from the rotation about the S-C-C-S bond. Even though the phosphonate-substituted bithiophenes have excellent emission quantum yields and good nonlinear absorptions, there is room for improvement. Therefore a locked phosphonate-substituted bithiophene was theorized to prevent non-radiative relaxation. Literature provides easy access to a conformationally locked bithiophene in the form of benzo[1,2-b:6,5-b']dithiophene-4,5-dione (BDTD). The dione bridge restricts motion about the S-C-C-S bond, preventing energy being lost to heat, and the carbonyls provide a fully conjugated backbone. Comparison of computational estimates of intrinsic fluorescence lifetimes between 2,2'-bithiophene and

BDTD show the locked bithiophene having a 105 increase. The emission wavelength of BDTD is at 577 nm; however both properties may be affected by phosphonate substitution. Synthesizing a library of phosphonate-substituted BDTD compounds, all while obtaining computational emission parameters, may give rise to new candidates for optical power limiting applications and materials for organic light emitting diodes.

2015 Joint Southeastern/Southwest Regional Meeting 164

Synthesis, characterization, and biological studies of Ru-Pt bimetallic complexes

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Bimetallic complexes consisting of ruthenium based chromophores and a cisplatin moiety are of interest as they display multifunctional interactions with DNA. Herein, we report synthesis, characterization of two mixed metal complexes, [(4-Me_2bpy)2RudppPtCl_2]$(PF_6)_2$ and [(6-Me_2bpy)2RudppPtCl_2]$(PF_6)_2$ (where dpp = 2,3-bis(2-pyridyl)pyrazine, 4-Me_2bpy = 4, 4'-2,2'-bipyridine, 6-Me_2bpy = 6, 6'-2,2'-bipyridine). These complexes exhibit Ru → dpp based metal to ligand based charge transfer transition in the visible region and ligand based π→π* transitions in the UV region. The redox, spectroscopic, and DNA binding properties of designed molecules will be presented.

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Chiral α,ω-Bis(phosphite) polyether ligands for use in the asymmetric hydroformylation of styrene: Synthesis and characterization

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Metallacrown ethers are able to bind alkali metal cations and mercury(II) chloride. This binding appears to affect their catalytic properties (activities and selectivities), especially in the hydroformylation of styrene. All of the metallacrown ethers that have been studied to date contain 2,2'-biphenol derived phosphite donor groups with flexible polyethylene glycols of various lengths as bridging groups. This research pursues the synthesis of various sterically hindered α,w-bis(phosphite)-polyether ligands that contain 1,1'-bi-2-naphthol and asymmetrically substituted 2,2'-biphenol and studies the coordination chemistry of these ligands to Rh(I) and closely related metals. The preliminary results from these studies are reported in this poster.

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Long-term, stable, and highly efficient alternatives of Z-907: Amphiphilic Ru(II) sensitizers for dye-sensitized solar cells (DSSC)

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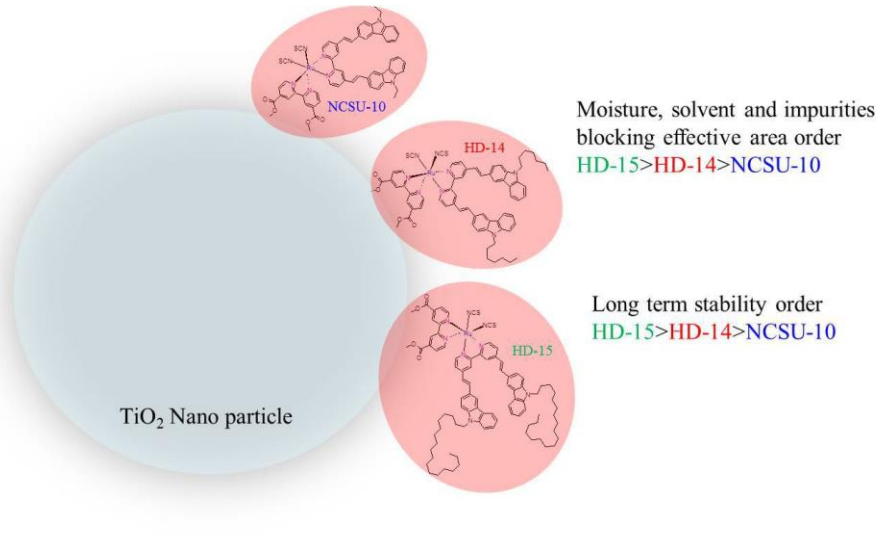
Two novel amphiphilic Ru (II) heteroleptic bipyridyl complexes HD-14 and HD-15, compared to previously reported NCSU-10 and N719 will be presented. In the simple yet robust design strategy for sensitizers, we have combined strong electron donor characteristics of carbazole and hydrophobic nature of long alkyl chains, C7, C18 and C2 (NCSU-10), tethered to N-carbazole to study their influence on photovoltaic characteristics and long term stability for dye-sensitized solar cells. Photon harvesting efficiency and electron donating characteristic of carbazole-based ancillary ligands were found to be unaffected due to different alkyl chain lengths. Under 1000 h light soaking conditions, HD-15 maintained up to 98% (only 2% loss) of initial power conversion efficiency compared to 8% loss for HD-14 and 22% loss for NCSU-10. Total power conversion efficiency (*η%*) was 9.27 for HD-14 and 9.17 for HD-15 compared to 8.92 of N719.



Demo anchoring and effective area of influence for each sensitizer

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Nitrene transfer to half-sandwich iridium(Cp*) complexes

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Oxidation of iridium(Cp*) complexes with hypervalent iodine nitrene transfer reagents is explored. Nitrene transfer to an iridium(Cp*) cation with a pyridyl-amide bidentate ligand drives an unexpected outer-sphere C-H activation and amide functionalization reaction. The mechanism likely involves a high oxidation state iridium-imido reactive species capable of hydrogen atom abstraction and a radical-based rearrangement during the formation of the ultimate iridium product.

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Photocatalytic hydrogen evolution by homogeneous molybdenum sulfide complexes

***Patricia R. Fontenot**, pfonten@tulane.edu. Chemistry, Tulane University, Kenner, Louisiana, United States*

Recent work done by several groups has focused on the synthesis of complexes containing MoS_2-type edge sites which can be exploited for their ability to electro-catalytically reduce protons to evolve hydrogen. In this work a series of complexes containing these terminal disulfide edges as well as bridging disulfide, or dithiolene ligands, were prepared and characterized not for their electrocatalytic activity, but for their ability to reduce protons from water in a photochemical system. These molybdenum complexes $[Mo_3S_{13}]^{2-}$, $[Mo_3S_7(S_2CNEt_2)_3]^{+1}$, $[Mo_2(\mu_2\text{-}S_2)(pdt)_4]$ (pdt = phenyldithiolene), and $[Mo(pdt)_3]$ were studied in a **photosystem** containing $[Ru(bpy)_3]^{2+}$ as chromophore (C), 4-N,N,-trimethylanaline (TMA) as reversible quencher in relay with triethylamine (TEA) as sacrificial reductant, and **only** H_2O as the source of protons. Using the same set of conditions it was found that $[Mo3S7(S2CNEt2)3]^{1+}$ is the most active hydrogen evolution catalyst studied in this photosystem. MALDI-TOF was used to study the photoreaction progress over time, and the $[Mo_3S_7(S_2CNEt_2)_3]^{+1}$ was found to be converted to the $[Mo_3S_{\mathbf{4}}(S_2CNEt_2)_3]^{+1}$ cluster. We now have evidence that suggests this species is the immediate precursor to hydrogen evolution. All hydrogen produced was confirmed and analyzed by gas chromatography assay.

Electronic tuning of H_2 production catalyzed by Co complexes with pentadentate ligands

***Scott R. Powers**, srpowers@memphis.edu. Chemistry, University of Memphis, Cordova, Tennessee, United States*

The potential use of H_2 as a clean and renewable fuel has attracted great interest in an effort to reduce current dependence on fossil fuels. Reduction of water to H_2, especially with visible light, has been a subject of intense study and a significant amount of efforts have been devoted towards designing metal complexes for proton reduction. Understanding the structure-function relationship in hydrogen production is important in tuning the catalytic properties such as overpotential and turnover frequency (TOF). Previous studies have shown that metal catalysts with higher redox potentials from structural modifications display little change in overpotential for H_2 evolution and require stronger acid for catalysis. To explore the electronic effects of ligand scaffold on the catalytic properties for H_2 evolution, we replaced the pyridyls in N,N-bis(2-pyridinylmethyl)-2,2'-bipyridine-6-methanamine (DPA-Bpy) with more basic isoquinoline groups. Our results have demonstrated that the replacement of pyridyls with more basic and conjugated isoquinoline groups results in positive shifts of the redox potentials of Co center and a significant improvement in catalytic H_2 evolution under neutral conditions, with lower overpotential, higher TON and TOF, as well as increased stability in electrolytic production of H_2. In order to improve the catalytic activity and efficiency, the design and synthesis of other new ligand scaffolds and their Co complexes to modify their electronic and structural features will be reported, and their effects on catalytic H_2 evolution will be discussed.

Metathesis reactivity of bis(phosphinite) pincer ligated nickel chloride, isothiocyanate, and azide complexes

***Jie Zhang**, jie.zhang@htu.edu.cn. School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan, China*

A series of nickel pincer complexes of the type [4-Z-2,6-$(R_2PO)_2C_6H_2$]NiX (R = ^{t}Bu, ^{i}Pr, Ph; Z = H, CO_2Me; X = NCS, N_3) have been synthesized from the reactions of the corresponding nickel chloride complexes [4-Z-2,6-$(R_2PO)_2C_6H_2$]NiCl and potassium thiocyanate or sodium azide. X-ray structure determinations of these complexes have shown that the thiocyanate ion binds to the nickel center through the nitrogen. A comparable Ni–N bond length (approx. 1.87 Å for the isothiocyanate complexes and 1.91 Å for the azide complexes) and an almost identical Ni–C_{ipso} bond length (approx. 1.89 Å) have been observed for these complexes. Metathesis reactivity of [4-Z-2,6-$(R_2PO)_2C_6H_2$]NiCl and ligand exchange reactions between the nickel isothiocyanate and nickel azide complexes have been investigated. The metathesis reactions with KSCN/NaN_3 are faster with a less electron rich and more sterically accessible nickel center, and the azide ion is more reactive than the thiocyanate ion. The thermodynamic stability of these nickel complexes has been rationalized using the hard-soft acid-base theory (HSAB theory); a harder ligand prefers a less electron rich nickel center. These experimental results have been supported by quantum chemical analysis of the coordinating nitrogen atoms in SCN^- and N_3^-.

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Nickel-catalyzed CO_2 reduction supported by biaryl-bridged pyridyl-*N*-heterocyclic carbenes

***Hunter A. Dulaney**, hadulane@go.olemiss.edu, Logan Bell, Ryan Higgins, Jonah W. Jurss. Department of Chemistry Biochemistry, University of Mississippi, University, Mississippi, United States*

Carbon dioxide is a greenhouse gas, but also represents a readily accessible C1 feedstock for conversion to solar fuels and value-added chemicals. However, CO_2 is relatively inert and very negative voltages or strong chemical reductants are common for its conversion. An additional challenge lies in achieving these reactions in water where aqueous protons are utilized selectively for CO_2 reduction rather than hydrogen generation. Our strategy for CO_2 reduction involves the design of new homogeneous catalysts with tunable geometries and polyaromatic frameworks with increased delocalization to lower overpotentials for catalysis. We report a family of biaryl-bridged pyridyl-N-heterocyclic carbene-based ligands and their corresponding nickel complexes. Ligand synthesis, structural characterization of complexes, and their application in electrocatalytic CO_2 reduction is discussed.

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Synthesis of a pentadentate, polypyrazine ligand and its application in cobalt-catalyzed hydrogen production

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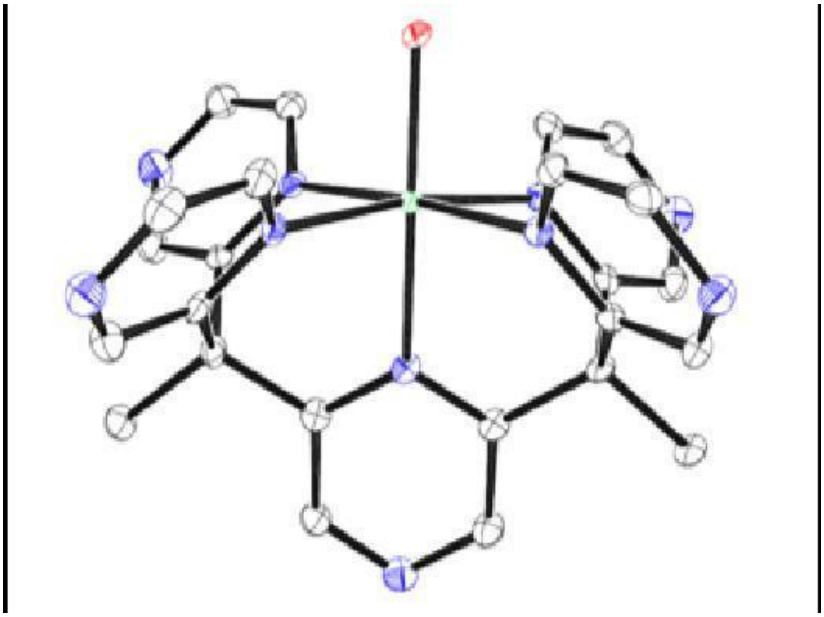
A molecular cobalt complex bearing a new pentadentate ligand, $PZ5Me_2$ (2,6-bis(1,1-bis(2-pyrazyl)ethyl)pyrazine), is studied for its catalytic activity for proton reduction to hydrogen. The polypyrazine ligand reported here is a highly symmetric analogue of the $PY5Me_2$-type frameworks that have shown promising results in both oxidative and reductive catalysis with Fe, Co, Mo, and Ru metal centers. In recently reported pyrazine-substituted cobalt complexes, ligand-centered redox activity and lower overpotentials for the hydrogen evolution reaction (HER) were observed. We sought to extend this chemistry to develop more efficient catalysts, and report on the synthesis, characterization, and electrochemical analysis of $[(PZ5Me_2)Co(OH_2)](OTf)_2$



2015 Joint Southeastern/Southwest Regional Meeting 173

Robust iron-oxo catalysts for water oxidation

Lizhu Chen[1]*, lchen9@go.olemiss.edu, Hunter A. Dulaney*[1]*, Yanbing Zhang*[1]*, Sarah Farmer*[1]*, Jonah W. Jurss*[2]*. (1) Chemistry and Biochemistry, University of Mississippi, Oxford, Mississippi, United States (2) Department of Chemistry Biochemistry, University of Mississippi, University, Mississippi, United States*

Water oxidation, a key reaction in natural and artificial photosynthesis, is responsible for supplying the protons and electrons needed in reductive half reactions that convert solar energy into chemical fuels. Inexpensive and efficient catalysts are needed for this challenging multi-electron, multi-proton reaction in order to push artificial photosynthesis forward. Recently molecular iron-oxo complexes have been reported to catalyze water oxidation, but they suffer from poor stability and high overpotentials.
To address stability problem, we have synthesized two new iron complexes with robust, tetradentate ligands that avoid weak C-H bonds. The rigid ligand frameworks afford distorted octahedral geometries with two *cis*-labile coordination sites. Crystal structures have been obtained by single-crystal X-ray diffraction. UV-Vis spectroscopy with added oxidants and electrochemical results indicate that oxidation proceeds stepwise from Fe(II)-OH_2 to high-valent iron-oxo intermediates.

Upon oxidation to iron-oxo intermediates, evolved oxygen has been measured by fluorescent lifetime measurements and gas chromatography. Catalytic water oxidation studies are ongoing.

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Synthesis and characterization of carboxylate complexes of lanthanide (III) ions

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Complexes of lanthanide (III) ions are of much interest because of their luminescence properties that make them useful in various applications such as luminescent sensors, time resolved fluoroimmunoassays, and in biological imaging. The luminescence intensity of these metal ions can be enhanced by chelating the metal ions to organic antenna chromophores that are capable of absorbing intensely in the UV region and transfer the energy to the metal ion by what is known as “antenna effect”. In this study, aromatic di- and mono-carboxylate ligands possessing large conjugated systems were used to synthesize the lanthanide ion complexes. These aromatic carboxylic acids absorb strongly in the UV region and pass the energy to the lanthanide ion. The synthesis of the complexes was achieved by reactions of $MCl_3 \cdot 6H_2O$ (M = Sm, Nd, Tb, Er) with 2, 2’-biquinoline-4-4’-dicarboxylic acid di-potassium salt ($K_2[C_{20}H_{12}N_2O_4]$) and 2,6 Diphenylisonictonic sodium salt ($Na[C_{18}H_{12}O_2N]$) in water or methanol. The metal chlorides and ligand salts in molar ratio of 2:3 for $K_2[C_{20}H_{12}N_2O_4]$ and 1:3 for $Na[C_{18}H_{12}O_2N]$ were separately dissolved in the appropriate solvent and then mixed while stirring at room temperature. The reaction resulted in an immediate formation of yellowish-white and brown powders in high yields respectively. The products were dried at 60^oC under vacuum and characterized by FTIR-, UV-Vis-spectroscopy and elemental analysis. Both elemental analysis and FTIR-spectral results suggest the formation of $M_2[C_{20}H_{10}N_2O_4]_3.4H_2O$ an eight coordinate and $M[C_{18}H_{12}O_2N]_3.3H_2O$ a nine coordinate complexes. Most of the products obtained are slightly soluble in organic solvents such as DMSO and CH_3CN but insoluble in water.

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Synthesis, characterization, and luminescent studies of europium doped $NaYbF_4$ nanoparticles

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Eu(III)-doped nanoparticles have potential applications in biomedical imaging due to their long luminescent lifetimes and narrow and well-defined emission bands with a maximum emission at 615 nm. Among appropriate crystal matrices for doping Eu(III) metal ions, LaF_3, $LaPO_4$, and $NaYF_4$ have received recent attention. Our recent research efforts are focused on doping lanthanide metal ions into a relatively new matrix, $NaYbF_4$. Recent research as shown the promise of using the NaYbF4 nanocrystal matrix for deep tissue imaging. We have developed a thermal decomposition method to synthesize Eu(III)-doped $NaYbF_4$ nanoparticles for potential

luminescent imaging applications. The nanoparticles were characterized using absorption, luminescent, and Fourier transform infra-red spectroscopy, transmission electron microscopy, powder X-ray diffraction, and inductively coupled plasma – optical emission spectroscopy. The nanoparticle surface was modified by suitable sensitizer ligands for improving the light absorption. This presentation describes the synthesis, characterization, and luminescent properties of the nanoparticles. Luminescent quantum yields will be evaluated as a function of the Eu(III) metal ion doping levels and the surface modification.

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Reliable potential energy surfaces for the reactions of H_2O with ThO_2, PaO_2^+, UO_2^{2+}, and UO_2^+

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The potential energy surfaces for the reactions of H_2O with ThO_2, PaO_2^+, UO_2^{2+}, and $^2UO_2^+$ have been calculated at the coupled cluster CCSD(T) level extrapolated to the complete basis set limit with additional corrections including scalar relativistic and spin orbit. Initially, a Lewis acid-base adduct $(H_2O)AnO_2^{0/+/2+}$ is formed, followed by a proton transfer to generate the dihydroxide $AnO(OH)_2^{0/+/2+}$. For An = Th(IV) and Pa(V), the dihydroxide is symmetric and O isotope exchange in these species can occur without a barrier. The use of an improved starting point based on density functional theory with the PW91 exchange-correlation functional or Brueckner orbitals for the coupled cluster CCSD(T) calculations is reported. The importance of including second order spin orbit corrections for closed shell molecules and the NPA analysis are also described.

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Investigating computational, structural, physiochemical and biological properties of a family of pyridoxine-lanthanide metal complexes

Arpita Saha[2]*, asaha@georgiasouthern.edu, Caitlyn E. Stouder*[3]*, Khairi Warren*[3]*, Clifford W. Padgett*[4]*, Amanda L. Stewart*[2]*, Karelle S. Aiken*[1]*, Shainaz M. Landge*[5]*, Allison Amonette*[2]*. (1) Chemistry Dept, Georgia Southern Univ, Statesboro, Georgia, United States (2) Chemistry, Georgia Southern University, Statesboro, Georgia, United States (3) Georgia Southern University, Statesboro, Georgia, United States (4) Armstrong State University, Savannah, Georgia, United States (5) Georgia Southern University, Statesboro, Georgia, United States*

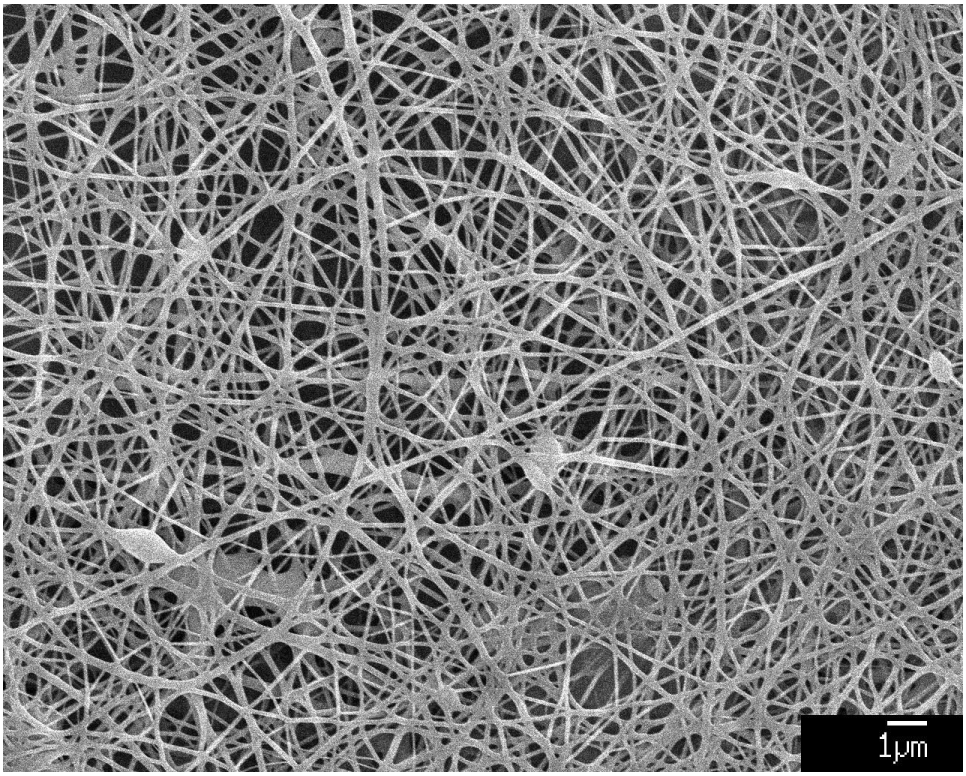
Pyridoxine is a vitamin and is often found in certain food like cereals, beans, eggs and so on and is required for proper growth and development of the brain, nerves, skin, and many other parts of the body. Medicinal usage of pyridoxine e.g. treating anemia, heart diseases, and angioplasty makes it an interesting choice to further study the interaction between this biomolecule with several metal ions. On other hand, lanthanide complexes have drawn significant attention to the medicinal inorganic chemists since, lanthanides manifest antitumor activity and lead towards the future anticancer drugs. Amalgamation of both the aspects of lanthanide metals and pyridoxine molecule promises an

interesting premise in the area of metal based anti-cancer drugs, DNA sequence-specific cleaving agents and so on. In the quest of a new class of anticancer drugs, herein, a family of pyridoxine-lanthanide metal complexes (where metals are Gd, Tb, Dy, Ho, Er) has been synthesized and reported. The complexes were further characterized by single-crystal X-ray analyses and computational structural simulations which show that they are mononuclear pyridoxine containing metal complexes. Several spectroscopic methods such as IR, ^{1}H NMR, UV-Vis spectroscopy were employed along with the electrochemical analysis using Cyclic Voltammetry to further study the composition and reaction mechanism of the aforementioned class of complexes. DNA is the primary target molecule for most anticancer and antiviral therapies according to cell biologists. Hence, in order to assay the DNA binding or cleaving ability of the synthesized complexes, UV-Vis and Circular Dichroism spectroscopy and gel electrophoresis were performed in due course.

Nanofiber based metal oxide photocatalysts for hydrogen generation through water splitting, pollution remediation, and chemical conversion

Kaniece Latimer, Ivan Thompson, Kristine Cook, Dimitrius Daniels, Phillip Elam, ***Keerthi Senevirathne****, senevirathne.k@gmail.com. Florida A&M University, Tallahassee, Florida, United States*

Conversion of abundant solar energy into chemical energy, in the form of H_2, through photocatalytic water splitting is an interesting and challenging theme that has drawn the interest of material chemists and physicists for the last 40 years. Efficient catalysts are required in order to carry out water splitting because the reaction is an energetically up-hill one. The focus of the current study is to use metal oxide nanofibers and low cost co-catalysts to effectively harness abundant solar energy in both visible and UV regions. Metal oxide nanofiber synthesis coupled with microwave-assisted co-catalyst deposition and complete physicochemical characterizations will be discussed. Additionally, synthesis of monolayer co-catalysts by galvanic displacement will also be presented. The implications for the catalytic activity, in terms of H_2 generation and organic molecule conversion, will be addressed in light of the catalyst type, co-catalyst etc.



SEM image of metal oxide nanofibers fabricated by electrospinning.

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Solventless synthesis and characterization of novel Ag(I) and Cu(I) metal-azolate complexes upon vapor-phase reaction with different substituted cyanopyridines

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The solvent-mediated and solventless reaction of cyclotrimeric azolate complexes of Cu(I) and Ag(I) with various substituted cyanopyridine ligands were studied. Most Ag(I) complexes are brightly luminescent at room temperature, whereas non-luminescent Cu(I) products were obtained that exhibited vivid visible colors. The volatility of some cyanopyridines makes solventless synthesis of these products a possibility. This presentation will give an overview of the synthesis and spectral properties of these materials. Infrared spectroscopy, nuclear magnetic resonance spectroscopy, thermogravimetric analysis, X-ray crystallography, and UV/Vis electronic absorption and luminescence data will be presented for the products of the different reactions attempted vs. the starting materials.

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Synthesis, characterization, and luminescence of CCC-NHC pincer platinum complexes

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Mississippi State University, Mississippi State, Mississippi, United States (2) Department of Chemistry, Mississippi State University, Mississippi State, Mississippi, United States (3) Department of Chemistry and Biochemistry, University of Mississippi, University, Mississippi, United States (4) Department of Chemistry, University of Alabama, Tuscaloosa, Alabama, United States

The development of the molecular organometallic compounds for organic light-emitting diodes (OLEDs) and photoluminescence applications has been rapidly expanding. Blue light emitting 2-(1,3-bis(N-butylimidazol-2-ylidene)phenylene) pincer Pt(II)-halogen complexes were reported recently. In order to replace the halogens, a series of new CCC-NHC pincer Pt(II)-X/L complexes have been synthesized and characterized, both experimentally and computationally. A variety of synthetic methodologies were employed depending on the nature of the ligand (X/L). These will be reported along with full characterization data including the photophysical and electrochemical properties of the complexes.

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Metal–tetrazolate trinuclear complexes and functional non-porous coordination polymers

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The synthesis of new trinuclear complexes or functional/fluorous non-porous coordination polymers (FN-PCPs) has been undertaken by reacting Cu(I) and Ag(I) precursors with fluorinated tetrazoles. Synthesizing new metallomacrocycles or FN-PCPs with interesting optoelectronic features is the goal of this project. Most of the FN-PCPs we synthesized are found to be insoluble in various organic solvents; conversely, the Ag(I) derivative we isolated is soluble in pyridine. This FN-PCP has been recrystallized from pyridine and characterized by IR, NMR, and single crystal X-ray diffraction. The latter highlighted the formation of the coordination polymer ($[Ag_2(FMTB)_2Py_2]Py$), (FMTB= 1-tetrazolyl-pentaflourobenzene), in which Ag_2 dimers are present; two pyridine molecules are directly bonded to the metal center, while the other one is located in the second coordination sphere. According to us, an Ag_3 trimer is present in the raw material. Hence, recrystallization in pyridine leads to the disruption of the trimer in favor of a dimeric unit. This hypothesis is supported by previous work upon the reaction of well-known cyclotrimers with imine ligands (*Inorg. Chem.* **2003**, *42*, 8612-8614). The resulting products will be deeply studied for functional/fluorous non-porous coordination polymers applications.

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Utilizing hydrophobic coatings in corrosion protection and anti-icing

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The high hydrophobic properties for fluorinated polymers and metal-organic frameworks are useful for oil spill containment, hydrocarbon storage, carbon capture, and oxygen delivery, among other applications. Other potential benefits of this material type, as coating materials to protect low-carbon steel (LCS) and aluminum substrates, are being investigated. Corrosion is one of the most expensive failures that take place to metals and other construction materials, responsible for $276 billion loss in the US alone. LCS and aluminum are commonly used metallic construction materials, possessing very favorable properties, yet they exhibit low corrosion resistance. The presentation will overview our results for the utilization of a fluorinated coordination polymer (FMOF-1) and a fluorinated copper-pyrazolate trimer (Cu trimer) as coating to prevent the corrosion of LCS and Al substrates. Ice on metals has also shown to have negative effects, especially on aluminum frames of aircraft by destroying the smooth flow of air, increasing drag while decreasing the ability of the airfoil to create lift, so the same aforementioned coatings are also being investigated for an anti-icing function on Al substrates in particular. Both the anti-corrosion and anti-icing functions will be compared for the two coatings with one another as well as with other polymer and metallic protection materials.

2015 Joint Southeastern/Southwest Regional Meeting 183

Ligand control in the photochemical generation of high-valent porphyrin-iron-oxo derivatives

Tse-Hong Chen, Ka Wai Kwong, ***Jonathan Malone****, jonathan.malone961@topper.wku.edu, Rui Zhang. Western Kentucky University, Bowling Green, Kentucky, United States*

High-valent iron–oxo intermediates play central roles as active oxidants in enzymatic and synthetic catalytic oxidations. In this presentation, a new photochemical method to generate high-valent iron–oxo model will be presented. As controlled by the electronic nature of porphyrin ligands, iron(IV)–oxo porphyrin radical cations (compound I model) and iron(IV)–oxo porphyrin derivatives (compound II model) were produced, respectively, by visible light irradiation of the corresponding iron(III) bromate complexes. These observations indicate that the photochemical reactions involve a heterolytic cleavage of O–Br in precursors to give a putative iron(V)–oxo intermediate, which might relax to compound I through electron transfer from electron rich porphyrin to the iron or undergo rapid comproportionation reaction with residual iron(III) to afford the compound II derivative.

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Local redox events at individual plasmonic nanoparticle electrodes using electrogenerated chemiluminescence microscopy

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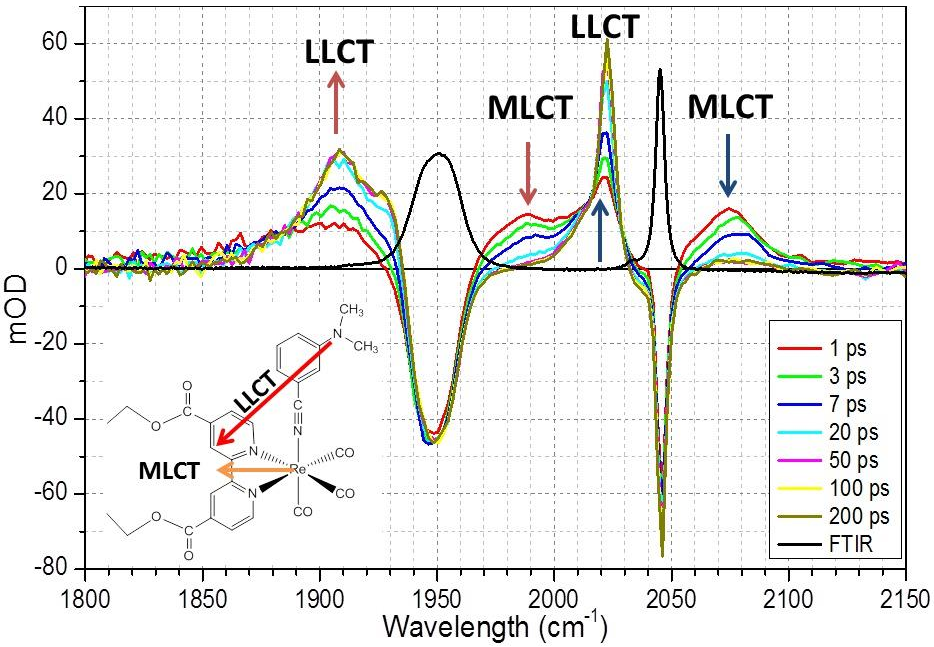
Local redox activities of single plasmonic nanoparticles are investigated using combined methods of electrochemistry (e.g., electrogenerated chemiluminescence, ECL) and spectroscopy. For example, Au NPs electrodeposited onto an indium tin oxide (ITO) electrode are found to enhance the oxidation of tripropylamine (TrPA), which is otherwise extremely sluggish at the ITO surface, enabling the detection of single Au

NPs and their local redox activities using an ECL imaging technique. Our study shows that ECL and light scattering at individual NPs increases with particle size and is affected by the shape and local environment of NPs. Quantitative agreement between calculations and experiment concerning the effect of particle size and electrode potential on spatial and transient optical profiles will be discussed.

Time resolved IR of Rhenium diimine tricarbonyl donor-acceptor complexes: Tracking events in intramolecular energy and electron transfer reactions

Yuankai Yue, Tod A. Grusenmeyer, Igor V. Rubtsov, ***Russell H. Schmehl****, russ@tulane.edu. Chemistry, Tulane University, New Orleans, Louisiana, United States*

Vibrational modes of molecules often change in ways that reflect changes in electron density distribution in molecules. Metal carbonyl complexes, for example, have CO stretching modes that are sensitive to the degree of p backbonding to the CO ligands and oxidation or reduction of the metal is clearly reflected in the CO frequencies. Intramolecular electron and energy transfer processes often yield products for which electron density distributions differ only in subtle ways. In this work we have focused on the photophysical behavior of three complexes of Re(I) in two solvents of significantly different dielectric constant : $[(LL)Re(CO)_3(n\text{-}DMABN)]^+$ (LL = 2,2'-bipyridine (bpy), 4,4'-dicarboxyethyl-2,2'-bipyridine (decb); n=3,4; DMABN= N,N-dimethylamino-benzonitrile). The complex containing the decb ligand and 3-DMABN, forms a Re-to-decb ligand charge transfer (MLCT) state upon 400 nm excitation. Over approximately 100 ps the state very clearly evolves to a 3-DMABN to decb charge transfer state (LLCT). The electron transfer reaction from the MLCT state to the LLCT state is reflected by initial increases in the frequencies of the symmetric and asymmetric CO stretching modes, indicative of the MLCT state. These give way to new CO absorption at frequencies below the ground state complex, reflecting an increase in electron density on the Re center following formation of the LLCT state.
Complexes having bpy as the diimine ligand exhibit entirely different behavior. The initially formed MLCT state of $[(bpy)Re(CO)_3(3\text{-}DMABN)]^+$ evolves to a state that appears to be a triplet state localized on the 3-DMABN ligand. In contrast, the complex $[(bpy)Re(CO)_3(4\text{-}DMABN)]^+$ forms an MLCT state upon excitation that evolves, but the CO modes continue to indicate depletion of electron density at the Re center. The results are discussed in terms of the relative energies of the ligand localized, MLCT and LLCT states and coupling of the MLCT and LLCT states.



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Characterizing the effects of noncovalent interactions on the photophysics of newly developed near infrared emissive materials

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Near-infrared (NIR) emissive organic molecules are a developing class of materials which have begun attracting attention due to their applications in optics and electronics. However, developing NIR dyes with the desired properties, large stokes shifts and high fluorescence quantum yields, is complicated by the inherent nature of low energy band gap systems. Here, the photophysical properties of a newly developed series of NIR emissive, squarine based, Donor-Acceptor-Donor (D-A-D) dyes are presented. The UV/visible absorbance, fluorescence emission and fluorescent quantum yields of these dyes were analyzed and the effects of noncovalent interactions on these properties were probed in bulk solution, in thin films and in a hybrid surface/gas phase apparatus.

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Electrochemical and spectroscopy studies of bodipy-thiophene-triphenylamine based dyes for dye-sensitized solar cells

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Due to the current increase in consumption of fossil fuels, dye-sensitized solar cells (DSSCs) have emerged as potential substitutes to traditional silicon based solar cells. In this study, a series of BODIPY-based dyes (Dye 1-5) which contain thiophene and/or triphenylamine (TPA) as redox relays of π-conjugated bridges have been synthesized and characterized owing to their potential application in DSSCs. Their electrochemical, optical and photophysical properties were investigated and exhibited incident photon-to-current conversion efficiencies (IPCE) that are still limited at a lower level. Despite their lower overall conversion efficiencies (η), they showed interesting properties in DSSC systems which promise further improvements of structure-efficiency properties.

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Correlation of atomic structure and photoluminescence of single InP/ZnX(X=S,Se) quantum dots

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Colloidal based quantum dot (QD) nano-structures display wide synthetic tunability and show great promise for applications ranging from photovoltaics to solid-state lighting and single-particle tracking. However, nano-chemists' have relied on ensemble-averaged measurement and characterization techniques that mask the divergence of individual nano-structures, limiting QD development. Indeed, single-particle measurements can facilitate further and rapid synthetic development of both workhorse and emergent QD nano-structures. In this work we synthesize emergent non-toxic, visible and near-infrared size-tunable InP/ZnX(X=S,Se) QD emitters and conduct single-particle transient photoluminescence and electron microscopy correlated measurements. Our simple correlation method allows identification of detailed structure-property relationships that inform synthetic optimization of these nano-structures.

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Evolution and dynamics of GaN-based blue laser diode emission spectra

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Efficient employment of GaN-based blue laser diodes in spectroscopy require high level of spectral and temporal stability for emitted longitudinal modes. In this talk, high resolution emission spectra of single-transverse Fabry-Perot GaN-based blue laser diode, obtained using a home-made apparatus, will be presented. A CCD camera coupled to a 0.003-nm resolution spectrometer are employed to detect and record emission spectra of the laser diode in the wavelength range between 440-450 nm as a

function of the operating current and temperature. Furthermore, the stability of the laser diode over continuous 14 hours will be demonstrated by monitoring variations in emitted power, central wavelength location and modes intensity. Furthermore, blue laser diode high resolution spectra will be shown to yield an experimental longitudinal mode spacing of 0.0548 nm which is of high agreement with corresponding calculated mode spacing that was obtained by utilizing a suitable theoretical model. An interesting trend of the longitudinal modes wavelengths location to experience a bathochromic shift with current and temperature will be exhibited and related to laser gain shift. Lastly, examples of manipulating laser diode spectra in spectroscopy, i.e. detection of infinitesimal concentrations of toxic gases and porosity of materials, will be presented and discussed.

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Elucidating quantum dot structure-function relationships one dot at a time

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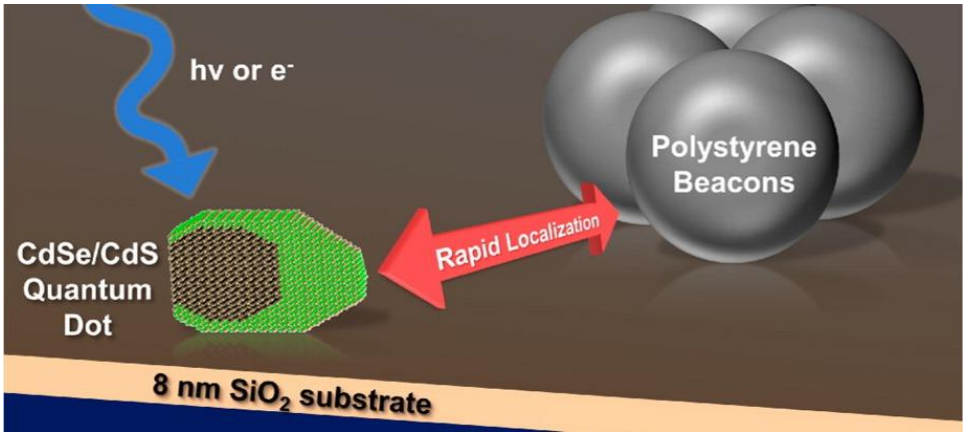
Quantum dots show great promise for application in light-emitting devices, photovoltaics, and displays. Colloidal synthesis is especially attractive, as trillions of quantum dots can easily be synthesized in one batch and implemented into the desired device. Typically when characterizing colloidal quantum dots, the chemist will collect optical spectra, such as transmission and photoluminescence spectra, that reflect the properties of the ensemble. However, unlike dye molecules, which have a well-defined chemical structure, quantum dots from the same synthetic batch display variances in chemical and structural makeup. Up until now, this heterogeneity has been visualized physically on the ensemble level *via* transmission electron microscopy. Single quantum dot spectroscopy and transmission electron microscopy uncover heterogeneous optical and physical properties, respectively, but a correlation of these two techniques is crucial to a full understanding of which optical properties correspond to specific optical behaviors.
We have developed a method by which we are able to correlate the fine atomic structure and photoluminescence properties of single quantum dots. Application of this method has led to a deeper understanding of the effects of asymmetric shell growth on core/shell quantum dots, as demonstrated on a commercially available quantum dot system. Additionally, in a collaboration with scientists at the Center for Integrated Nanotechnologies at Los Alamos National Laboratory, we have investigated a "nonblinking" quantum dot system. Using our correlation technique facilitated measurement of single quantum dot quantum yields - a measurement that has proven vital to the elucidation of the relationship between charging and photoluminescence in quantum dots. Finally, we discuss how the correlation of photophysics and structure provides potential for a highly directed approach to optimization of quantum dot syntheses.



Using ultrathin silicon dioxide as an imaging substrate and polystyrene latex beads as markers, we are able to collect single photon emission data from the same quantum dot for which we later determine precise atomic structure and chemical composition.

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Infrared photodissociation spectroscopy of early and late transition metal-acetylene complexes

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Mass-selected copper-acetylene and vanadium-acetylene cation complexes of the form Cu(C2H2)n+ and V(C2H2)n+ are produced by laser ablation and studied via infrared laser photodissociation spectroscopy in the C-H stretching region. Spectra for larger species are measured via ligand elimination, whereas argon tagging is employed to enhance dissociation yields in smaller complexes. The number of infrared active bands, their frequency positions and their relative intensities provide insight into the structure, bonding and reactivity of these ions. Density functional theory calculations are carried out in support of this work. For $Cu(C_2H_2)_n^+$, the combined data show that cation-π bonds are formed for n=1-3, resulting in red-shifted C-H stretches on the acetylene ligands. Three acetylene ligands complete the coordination of the copper cation. Additional ligands, (n=4-6) solvate the n=3 core by forming CH-π bonds. Distinctive vibrational patterns are exhibited for coordinated vs. solvent ligands. Theory reproduces these results. V(C2H2)n+ complexes form exotic metallacycles. These results are also corroborated by theory.

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Unraveling proton transfer in stepwise hydrated N-heterocyclic anions

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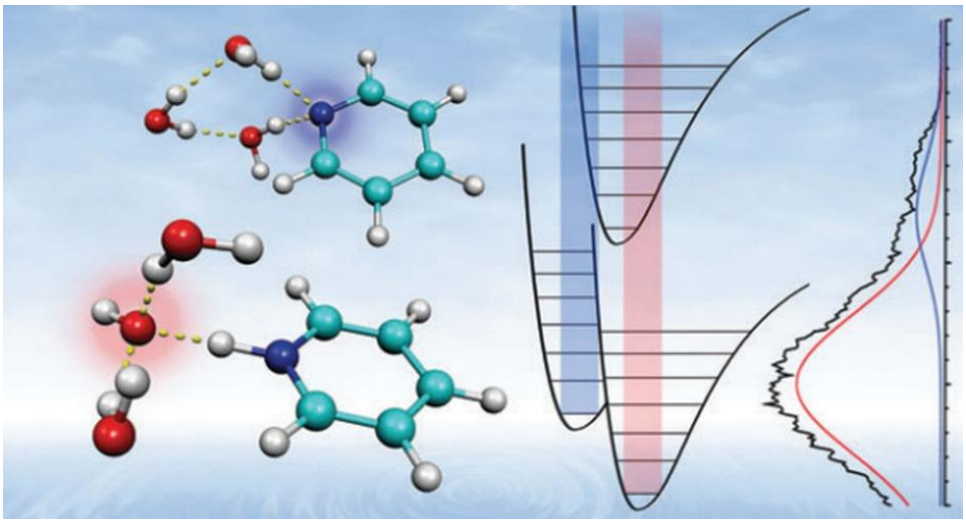
Depending upon the number and location of nitrogen atoms in a N-heterocyclic azabenzene, the addition of a single water molecule can result in a positive electron affinity. The transfer of a proton from a solvating water azine base can be induced by excess electron attachment. Here we explore this phenomenon through the use of photoelectron spectroscopy and electronic structure theory. Carefully calibrated density functional theory (DFT) computations indicate that the excess electron predominantly resides in a π* orbital of the heterocycle.



Photoelectron spectrum of hydrated pyridine cluster anion

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X-ray spectroscopy as a probe of the magnetism in cobalt benzene cluster cations

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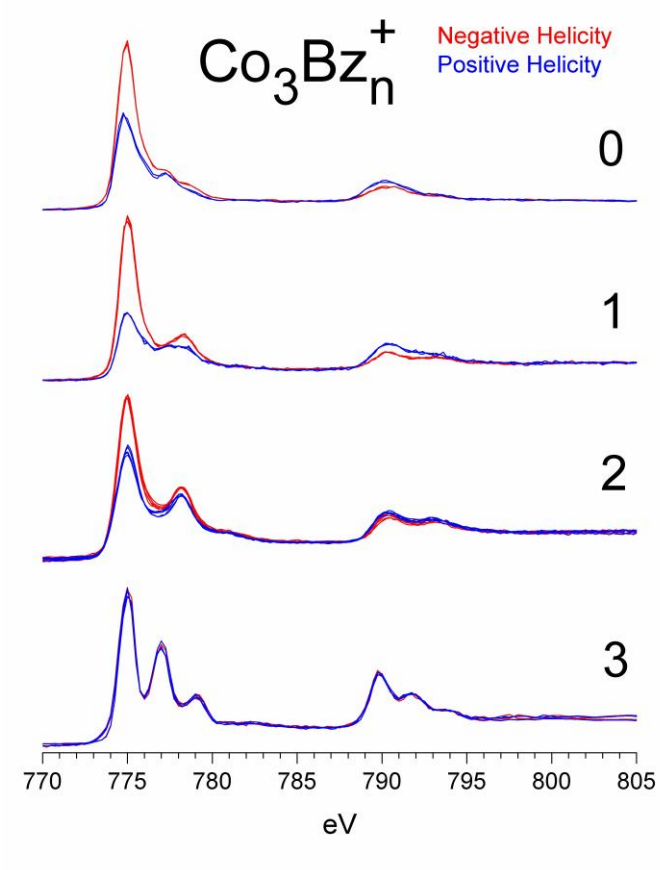
$Co_xBz_y^+$ clusters were formed using a magnetron sputtering source and investigated with x-ray magnetic circular dichroism (XMCD) at the cobalt L-edge. XMCD spectra yield magnetic moments of the clusters and the contributions from both spin and angular momentum. Dichroism of these clusters is compared to that of the free Co_x^+ clusters. In some cases the addition of benzene allows for preservation of magnetism while some clusters undergo a complete quenching of magnetism. XAS spectra of the quenched $Co_xBz_y^+$ clusters at the carbon K-edge differ from those of free benzene. This suggests a relatively strong interaction between the Co_n^+ core and the Bz ligands and may account for the quenching of magnetism.



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Mass spectrometric studies of aluminum nitrate anion complexes

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The aluminum nitrate complex, $Al(NO_3)_4^-$, was generated by electrospray ionization and studied by tandem mass spectrometry. Primary dissociation reactions of the complexes include formation of NO_3^- and elmination of $NO_2^\bullet$ by $O^{\bullet-}$ abstraction from a nitrate ligand to form $AlO(NO_3)_3^-$. Secondary dissociaiton resulted in further elimination of $NO_2^\bullet$, elmination of $NO_3^\bullet$ by electron transfer, or elmination of O_2. Secondary reactions are driven by the oxygen radical anion bound to aluminum in the $AlO(NO_3)_3^-$ fragment. Experimental generation of $AlOH(NO_3)_3^-$ demonstrated that removal of the oxygen radical site by formation of the OH bond results in a simpler fragmentation spectrum. Theoretical studies suggested several fragmentation pathways require rearragnement of a nitrate ligand on the precursor ion, and relative dissociation energies confirmed these predictions. This work shows the fragmentation of $Al(NO_3)_4^-$ is more complicated than it initially appears, but the results provide important fundamental insight related to the properties of aluminum complexes, bonding and reactivity.

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Mid-infrared signatures of hydroxyl containing water clusters: Infrared laser stark spectroscopy of OH-H_2O and $OH(D_2O)_n$ (n=1-3)

***Joseph Brice**, joebrice@uga.edu, Gary E. Douberly. Department of Chemistry, University of Georgia, Athens, Georgia, United States*

Small water clusters containing a single hydroxyl radical are synthesized in liquid helium droplets. The OH-H_2O and OH$(D_2O)_n$ clusters (��=1−3) are probed with infrared laser spectroscopy in the vicinity of the hydroxyl radical OH stretch vibration. Experimental band origins are qualitatively consistent with *ab initio* calculations of the global minimum structures; however, frequency shifts from isolated OH are significantly over-predicted by both B3LYP and MP2 methods. An effective Hamiltonian that accounts for partial quenching of electronic angular momentum is used to analyze Stark spectra of the OH-H_2O and OH-D_2O binary complexes, revealing a 3.70(5) Debye permanent electric dipole moment. Computations of the dipole moment are in good agreement with experiment when large-amplitude vibrational averaging is taken into account. Polarization spectroscopy is employed to characterize two vibrational bands assigned to OH$(D_2O)_2$, revealing two nearly isoenergetic cyclic isomers that differ in the orientation of the non-hydrogen-bonded deuterium atoms relative to the plane of the three oxygen atoms. The dipole moments for these clusters are determined to be approximately 2.5 and 1.8 Debye for ‘up-up’ and ‘up-down’ structures, respectively. Hydroxyl stretching bands of larger clusters containing three or more D_2O molecules are observed shifted approximately 300 cm^{-1} to the red of the isolated OH radical. Pressure dependence studies and ab initio calculations imply the presence of multiple cyclic isomers of OH$(D_2O)_3$.

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Injectable and degradable polymeric biomaterials for regenerative medicine

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Here I present our recent work on injectable and biodegradable polymeric biomaterials for diverse applications in tissue engineering and regenerative medicine. These photo-crosslinkable biomaterials include copolymers composed of poly(propylene fumarate) (PPF) and poly(ε-caprolactone) (PCL), PCL acrylates (PCLAs) with a wide range of molecular weights, polyethylene glycol diacrylate (PEGDA), and polymer nanocomposites containing hydroxyapatite (HA) nanoparticles and polyhedral oligomeric silsesquioxane (POSS) nanocages. These polymeric biomaterials have been fabricated via photo-crosslinking into different 2D substrates and 3D scaffolds with controllable chemistry, topology, and stiffness for different tissue engineering applications, such as bone and peripheral nerve regeneration. We have also surface tethered hydrophilic neutral or cationic polymer chains into the polymer networks and fabricated polymer network substrates with microgrooves, micro-pillars, micro-pores, nanowires, or nanopores. Growth factors such as recombinant human bone morphogenetic protein-2 (rhBMP-2) have been incorporated into the polymer scaffolds for promoting tissue ingrowth. Besides their practical applications, the networks formed using these polymeric biomaterials also serve as an excellent platform to investigate how material surface characteristics can be used to regulate the behavior and functions of mammalian cells, such as cell adhesion, spreading, phenotype, migration, proliferation, differentiation, and integrin/gene/protein expression.

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Exploring the promise of nanomedicine: Highly specific nano-scaled polymeric biomaterials for imaging and treatment of cancer

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The advent of nanomedicine within the past decade has led to the development of a number of emerging diagnostic and therapeutic avenues for the detection and treatment of cancer and other diseases. The small size and surface area of nanomedicines, including nanoparticles, makes them highly suitable for biomedical applications where their ability to be injected locally or systemically, extravasate into diseased tissue, enter cells, interact with targets at the molecular level, present surface-bound ligands to overcome physiological barriers and enable targeting, and act as carriers for delivery of active agents provides a range of opportunities. Nanomedicine open the doors to improved diagnostic, therapeutic, and theranostic technologies that offer higher efficacy, individualization, and safety compared to those currently available. While to date only a few nanoparticle-based systems have entered the market as therapeutics or biotechnological tools, it is expected that nanotechnology will revolutionize health care in the near future.

Our laboratory has focused on exploring the potential of nanomedicine in several fronts. Specifically, we have been working on the development and evaluation of (1) enzyme activatable near infrared fluorescent nanoparticles as highly specific contrast agents for optical imaging of tumors which could be used for early detection and monitoring of cancer, and for fluorescence-guided tumor therapy; (2) conductive polymer-based nanoparticles for photoablation of tumors which could provide a localized and more effective treatment strategy compared to chemotherapy alone; and (3) aptamer-modified polymeric nanoparticles as carriers for targeted delivery of chemotherapeutic agents to cancer cells. All of these materials take advantage of one of the main features of nanomedicine: the ability to integrate several functionalities into a single entity, whether it is biopolymers, synthetic polymers, fluorescent tags, or ligands, providing the means to tailored designs specific for a given application. This seminar will describe the synthesis, characterization, and *in vitro* characterization of these nanoparticle systems, and provide a glance into the enormous potential of nanotechnology in biomedicine.

Design and synthesis of supramolecular Janus-type dendrimers as efficient therapeutic carriers

Jon Williams, Lance Ezell, Ngoc Le, ***Davita L. Watkins****, watkindl@gmail.com. Chemistry and Biochemistry, University of Mississippi, Oxford, Mississippi, United States*

Asymmetric (i.e. Janus-type) dendrimers have recently been applied in the field of nanomedicine; however, reviews of their biomedical applications have been marginal. Considering the need for efficient and versatile biomaterials, the many possible

advantages of Janus dendrimers have been underutilized. This is mainly due to a demand for sophisticated synthetic and purification techniques which make Janus dendrimers less appealing. Reported is a strategic approach towards the synthesis and characterization of amphiphilic Janus dendrimers comprised of biocompatible polymeric segments of poly(L-lactic acid) (PL, hydrophobic) linked via biologically relevant cores to either polyamidoamine (PA, hydrophilic) or poly(ethylene glycol) (PE, hydrophilic). The resulting dendrimers were subjected to a series of experiments using dynamic light scattering (DLS) to characterize the self-assembly into nanoparticles in aqueous media. The principles of the self-assembly and degradation processes were then utilized to create segregated structures for the encapsulation and release of small dye molecules, which were monitored via ultraviolet-visible (UV-Vis) absorbance spectroscopy. The results highlight both the design of efficient therapeutic carriers and the synthesis of supramolecular systems for biomedical applications.

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Multifunctional polyelectrolyte complexes with embedded metal ions

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Like an old saying, “Be the salt of the earth.”, metal ions play an important role in building nature adaptive and responsive structures such as bones and proteins by interacting with biomolecules. Polymer hydrogels have great potential applications in tissue engineering because they can provide a cell-friendly environment for cell growth. Inspired by natural metal ion/biomolecule interactions, adding metal ions to polyelectrolyte complexes can not only improve the stability of polymeric hydrogels but also introduce interesting functionalities. This presentation discusses the fabrication of poly(acrylic acid) (PAA)/chitosan (CS) complexes with various metal ions, the effect of metal ions on the hydrogel properties and functionalities, and the creation of nanostructures using embedded metal ions.

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Stimuli responsive drug delivery system for curcumin to counteract radiation injuries

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Transdermal films can provide a non-invasive controlled drug release for many disorders including radiation-induced skin disorders. Curcumin (CCM) is a hydrophobic polyphenol that has excellent dose dependent radiosensitive and radio protective potential. We have developed a chitosan polymer conjugated with CCM by functionalization of CCM with an acid anhydride followed by its covalent tethering to chitosan, a biodegradable radiosensitive polymer. This conjugated polymer showed a controlled release of 0.23 ± 0.12µM CCM over 18 days (Figure 1 A). Exposure to gamma radiation, ranging from 1-6 Gy, induced cumulative burst release of 9.1 ± 3.7 µM CCM (Figure 1B). Polymer films were prepared by solvent casting and similarly displayed a gamma radiation induced cumulative burst release of 7.2 ± 0.1 µM CCM

(Figure 1D). Scanning electron microscopy characterization of the films revealed an increase in film thickness from 11.96 ± 2.09 µm with no radiation exposure to 22.33 ± 3.34 µm when irradiated at 6 Gy. Also, the FT-IR studies on radiated films indicated a selective glycosidic bond cleavage in the CCM-chitosan polymer via relatively increasing the hydroxyl band intensity (3282 cm^{-1}) in comparison to glycosidic bands (1080 cm^{-1}) with reference to the 1544 cm^{-1} chitosan peak. Overall, our investigations on this CCM-chitosan polymer/films display its unique bifacial profile comprising of a controlled drug release as well as radiation-induced burst release that could be used for skin disorder treatment.

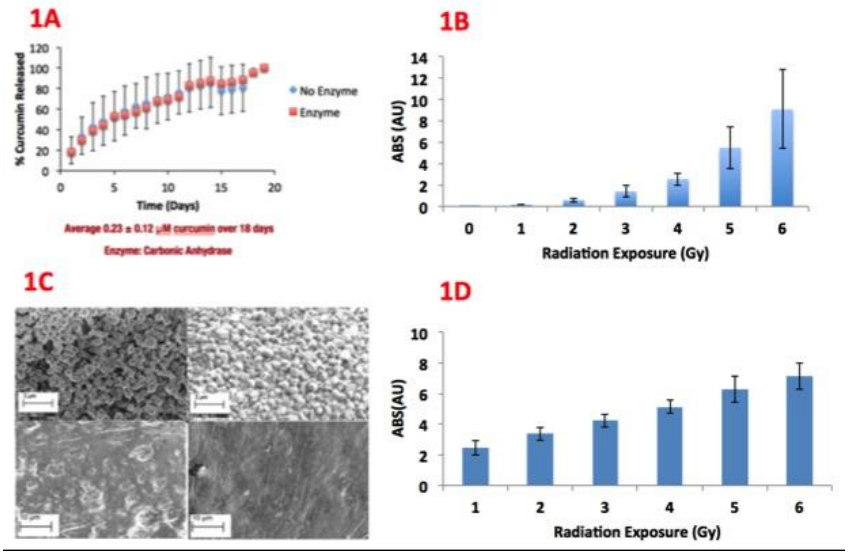

Figure 1: (*1A)* Controlled CCM release of 0.23 ± 0.12 µM from CCM-chitosan polymer over 18 days (1B) Cumulative burst CCM release from chitosan curcumin polymer after radiation exposure (*1C)* Non-radiated and 1.5 Gy radiated spray dried particles (*Top*) Non-radiated and 6 Gy radiated films (*bottom*). (*1D*) Cumulative burst CCM release from CCM-chitosan films after radiation exposure

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Synthesis and characterization of PXS based polymers for improved nanoparticle drug delivery

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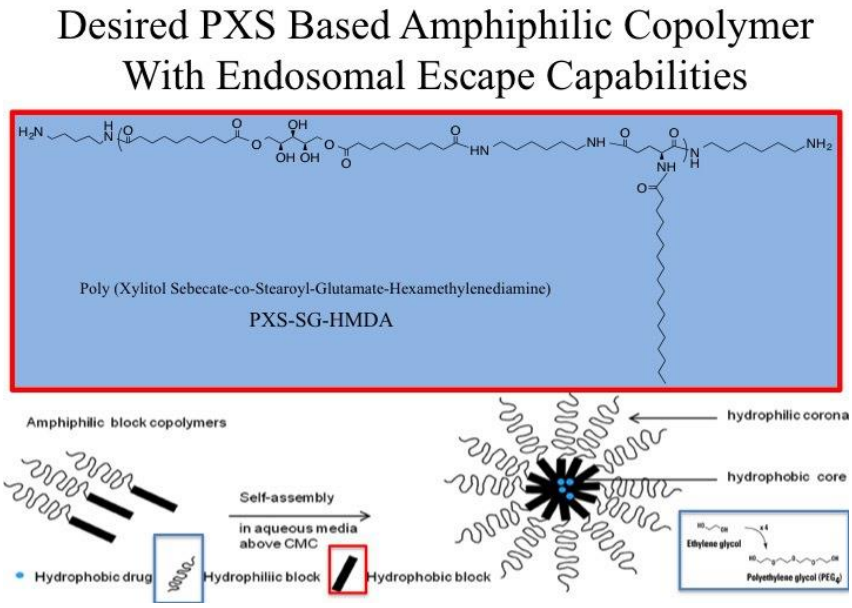
Over the years conventional drug chemotherapy has proven to be effective yet inefficient in treating cancers. With the emergence of nanotechnology, specifically focused on drug delivery, the efficacy of treatment has markedly improved. Some biodegradable polymers, such as Poly (lactic-co-glycolic) acid (PLGA), chitosan, and lactic acid have been proven to be suitable for nanoparticle drug delivery and are currently being used in medicine. These polymers are suitable for nanoparticle drug delivery due their ability to encapsulate and deliver a wide range of bioactive molecules to a specified target zone via passive and active targeting mechanisms. Also, the biodegradable polymers produce only a mild systemic response, making them optimal for nanoparticle drug delivery. On a bulk scale, PXS polymers have proven to be much more stable *in vivo*[1] than any of the aforementioned polymers. Stability is very

important because it has shown to directly correlate with the release kinetics of drug loaded nanoparticles and also determines the half-life of polymers once they've reached the site of interest, i.e. the tumor. As mentioned before PXS is an attractive base polymer due to its increased *in vivo* stability, superior biocompatibility and ability to be easily modified post synthesis. Our challenge is finding optimal block/s for synthesizing PXS-based amphiphilic block copolymers, which promote the easy self-assembly of drug-loaded nanoparticles. PXS itself is mainly hydrophilic and therefore is not suitable to make nanoparticles alone. ^{1}H NMR has confirmed the successful synthesis of PXS based on the reduced intensity of peaks at chemical shifts 11.87 ppm that correlates to the sebacic acid moiety, and 3.94 ppm that correlates to xylitol. From here, we plan to synthesize the hydrophobic monomer N-stearoyl-L-glutamic acid and conjugate that to the PXS backbone. This will allow London dispersion forces to assist in the encapsulation of poorly water-soluble Hydrophobic drugs via the Hydrophobic effect.[2]



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Highly efficient capture and accurate identification of multiple types circulating tumor cells using multifunctional biocompatible graphene oxide quantum dots decorated magnetic nanoplatform

Paresh C. Ray*, paresh10027@yahoo.com. Jackson State University, Jackson, Mississippi, United States*

Tumors metastasis is responsible for 1 in 4 deaths in USA. Though it is well documented in last two decades that Circulating tumor cells (CTCs) in blood can be used as a biomarker for metastatic cancer, due to the fact that CTCs are extremely rare cells in blood containing billions of other cells, selective capturing and identifying rare cells with sufficient sensitivity is real challenge till now. Also due to heterogeneous expression of CTC markers, it is now well understood that a single CTC marker is insufficient to capture all CTCs from the blood. Here we will discuss our recent report on

the development of multifunctional biocompatible graphene oxide quantum dots (GOQDs) coated high luminescence multifunctional magnetic nanoplatform for selective separation and diagnosis of multiple type rare tumor cells.*Our reported data demonstrate that accurate analysis of captured multiple types* CTCs *can be performed using multicolor fluorescence imaging. Our developed bio-conjugated material* has good potential for the diagnosis of early diseases that are currently being detected by means of cell-capture technologies.

2015 Joint Southeastern/Southwest Regional Meeting 203

Cancer nanotheranostics

***Xiaoyuan (Shawn) Chen**, shawn.chen@nih.gov. National Institute of Biomedical Imaging and Bioengineering, National Institutes of Health, Bethesda, Maryland, United States*

Theranostics refers to the development of molecular diagnostic tests and targeted therapeutics in an interdependent, collaborative manner with the goals of individualizing treatment by targeting therapy to an individual's specific disease subtype and genetic profile. Nanotheranostics makes use of “nanotechnology” for diagnostics and therapy of different diseases. Nanotechnology holds a great potential to be explored as a multifunctional platform for a wide range of biological and engineering applications: molecular sensors for disease diagnosis; therapeutic agents for the treatment of diseases; nanovehicles for delivering therapeutics and imaging agents for theranostic applications in cells and living subjects. Cancer nanotheranostics combines nanobiotechnology and cancer biology, aiming for early diagnosis, accurate molecular imaging, and precise treatment at the right timing and proper dose, followed by real-time monitoring of treatment efficacy. This talk provides an overview of the state-of-the-art of cancer nanotheranostics from the design of nanobiosensors for ultrasensitive biomarker detection *in vitro*, application of molecular imaging techniques for *in vivo* measurement of cancer hallmarks, image-guided cancer interventions, to nanoparticle platforms for co-delivery of imaging labels and therapeutic genes and drug molecules. The challenges of clinical translation of cancer nanotheranostic are also discussed.

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Plasmon-resonant nanorods and gyromagnetic nanostars: Multifunctional agents for nanomedicine

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Nanomaterials with near-infrared (NIR) absorption or scattering have applications as contrast agents in a wide range of biophotonic imaging modalities such as optical coherence tomography (OCT), photoacoustic tomography (PAT), and two-photon excited luminescence (TPL). However, detection limits are hampered by the intrinsic noise levels encountered in tissue. We find that coupling polarization-sensitive plasmon resonances with magnetomotive activity can generate dynamic modes of optical contrast for further gains in sensitivity. In addition, the photothermal properties of plasmon-resonant nanomaterials can be applied toward the directed thermolysis of tumor cells or hyperthermia-assisted chemotherapies *in vivo*. The scalable and

reproducible surface modification and characterization of nanomaterials is a critical factor in their future translational impact.

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RNA as a stable anionic polymer for theranostic nanoparticle construction in cancer nanotechnology

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RNA has emerged as a nanotechnology platform due to its versatility in structure and function. It can be fabricated with a level of simplicity characteristic of DNA, while possessing an adaptable tertiary structure and catalytic functions that mimic some forms of proteins. The non-canonical base pairings, base-stacking and low free energy in folding make RNA thermodynamically stable. RNA nanotechnology involves bottom-up assembly of nanometer-scale particles composed mainly of RNA. More and more evidence show that a substantial part of the 98.5% so-called "junk" DNAs in the human genome actually code for short or long noncoding RNAs. It is expected that the third milestone in drug development will be RNA drugs or drugs that target RNA. We have constructed a variety of thermodynamically and chemically stable RNA nanoparticles with different size, shape and stoichiometry. Ribozyme, siRNA, miRNA, or aptamer can be fused to the RNA nanoparticles without affecting the folding of the RNA core or each incorporated RNA modules. Systemic injection revealed that the RNA nanoparticles remained intact without showing any signs of dissociation and strongly bound to cancers without significant accumulation in other organs or tissues 3-hr after injection. The terminal half-life of RNA nanoparticles has been significantly extended as compared to the siRNA counterpart. The immune response of RNA is shape, size and sequence dependent, making it possible to design RNA nanoparticles avoiding the induction of cytokines, interferon, antibody, and toxicity; while retaining favorable pharmacokinetics and biodistribution profiles. RNA nanoparticles has a potential to serve as potential new generation drugs for cancer targeting and treatment.

Reference:
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A new interleukin-13 amino-coated gadolinium metallofullerene nanoparticle for targeted MRI detection of glioblastoma tumor cells

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The development of new nanoparticles as next-generation diagnostic and therapeutic drug platforms is an active area of both chemistry and cancer research. Endohedral metallofullerenes (EMFs) represent a unique class of nanoparticles that are highly stable and resistant to opening by most biological processes.[1] In this paper, we report a new method to functionalize trimetallic nitride endohedral fullerenes (TNT EMF). For biomedical applications, it is necessary to convert the hydrophobic fullerene cage to hydrophilic surface. We have converted the sp^2 carbon cage sites to sp^3 sites with attached amino groups providing a positively charged fullerene surface. These new nanoparticles have the general formula, $A_3N@C_{80}(OH)_x(NH_2)_y$, (A=lanthanide metal, x=~10, y=~6) with a cage surface. We will show that the $Gd_3N@C_{80}(OH)_x(NH_2)_y$ nanoparticles will bind more efficiently to negatively charged phospholipid bi-layer cellular surfaces and more readily undergo endocytosis. Previous studies have clearly demonstrated that the cytokine interleukin-13 (IL-13) effectively targets glioblastoma multiforme (GBM) cells, which are known to overexpress IL-13Rα2. We also report that this amino-coated Gd-nanoplatform, when subsequently conjugated with interleukin-13 peptide IL-13- $Gd_3N@C_{80}(OH)_x(NH_2)_y$, exhibits enhanced targeting of U-251 GBM cell lines and can be effectively delivered intravenously in an orthotopic GBM mouse model.[2]

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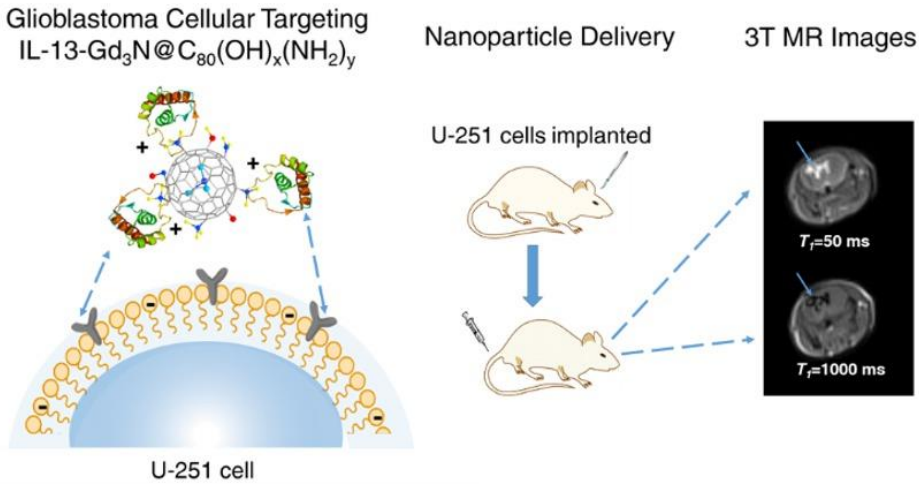

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Nanoparticles for imaging cargo delivery and cellular environments *in-vivo*

***Geoffrey F. Strouse**, strouse@chem.fsu.edu. Florida State University, Tallahassee, Florida, United States*

Nanoparticles are changing our approach to cellular biology, by acting as an optical probe, a cargo delivery vehicle, and in some cases an antagonist. Developoing new prtein transduction domain modified nanoparticles is allowing select ive targeting odf cell types and can allow co-delivery of a plethora of diverse bio-active therapeutic agents. In addition, there is no doubt that optical probe methods based upon the coupling of nanoscience to energy transfer have revolutionized bio-imaging via molecular ruler and molecular beacon techniques. The development of surface energy transfer (SET) models that describe the radiative and non-radiative perturbations to a dye in the proximity of a AuNP is now allowing complex optical probes of the changes in chemical levels within cells in real time, the reporting on molecular binding events and the induced conformational changes in biopolymers, and spatio-temporal mapping of cargo delivery into live cells. While many of these nanoparticle optical reporters merely act as passive observers of cellular environment, it can be imagined that incorporation of an active tracker of delivery and subsequent cargo processing within a cell could provide critical insight into the processing of therapeutic agents delivered by a transfection vector. We will explore the application of SET based molecular beacons for monitoring cellular environment in real time. The use of PTDs and nucleuic acid delivery on the nanoparticle will be demonstrated, as well as the spatio-temporal mapping of gene delivery and subsequent protein expression.

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Controlling nucleic acid delivery from gold nanoparticles in mammalian cells, studied via live-cell fluorescence microscopy

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There is great therapeutic potential for bio-functionalized gold nanoparticles (AuNP) to deliver genes or small interfering RNA intracellularly, especially with the ability to assemble multiple cargos on a single particle for nucleic acid therapy delivery. In order to design these dynamic systems, there must be control over cargo coupling strength and the timing of release for each therapeutic agent. By manipulating the surface chemistry for appendage of the nucleic acids to the AuNP, control over release can be achieved. Additionally, the timing and rate of cargo release from the nanomaterial can be monitored in live cells under fluorescence microscopy according to Nanometal Surface Energy Transfer (NSET) with the use of tracer and distance sensitive dyes labeled on DNA as the nanomaterial cargo. Understanding the effects of different coupling chemistries on nucleic acid delivery rates in live cell conditions will lead to better dynamic therapy design.

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Magnetic-optical hybrid nanoparticles for the capture and detection of cancer cells

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Circulating tumor cells (CTCs) are malignant cells that have exfoliated from a primary tumor and circulate in the bloodstream of cancer patients. As a hallmark of invasive behavior of cancer, CTC detection can provide a powerful tool for cancer prognosis, assessment of tumor stage, monitoring of therapeutic response and ultimately aiding in optimization of personalized treatment for patient with metastatic cancer. Sensitive and specific detection of CTCs can also help in early detection of cancer, enabling the prevention of metastasis. CTC detection, however, is extremely challenging because the number of CTCs in the blood of cancer patients is extremely low, as few as one cell per 10 million leukocytes and 5 billion erythrocytes. It requires highly specific and sensitive techniques to identify and capture rare cancer cells with high efficiency. Current techniques require multiple procedural preparations which often lead to the loss of these rare cells leading to limited detection sensitivity. Here, we report a novel method for the highly sensitive detection of rare epithelial cancer cells in blood based on surface enhanced Raman scattering (SERS) magnetic-optical hybrid nanoparticles (NPs). We developed iron oxide-gold core-shell NPs in oval shapes with combined superparamagnetic properties and SERS activities. The NPs allow on-line magnetic separation and SERS detection of cancer cells in whole blood, with the detection sensitivity down to 1-2 cells/ mL of blood. We have also demonstrated the capability of the IO-Au SERS NPs for multiplex detection by targeting different markers. Our method is a huge step forward in developing a simple, rapid, quantitative and ultrasensitive technique for CTC detection that may greatly impact the field of cancer nanomedicine.

2015 Joint Southeastern/Southwest Regional Meeting 210

Evaluation of a perturbative treatment of three-body interactions in HCP ^{4}He

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The properties of hexagonal close packed (hcp) solid ^{4}He are dominated by large atomic zero point motions, which make the primary contribution to the solid's low-temperature Debye-Waller (DW) factor. It is proposed that an accurate understanding of these zero point motions requires consideration of three-body interactions. We utilize quantum Monte Carlo (QMC) methods and either a 2-body or a 2+3-body potential energy function to calculate the DW factors for hcp ^{4}He at T = 0 K over a range of densities. We perform two sets of QMC simulations. One set of simulations incorporates the three-body interactions into the solid's potential energy function for the entire simulation; the other set of simulations treats the three-body interactions as a small perturbation, or correction, to the two-body potential energy function. At this stage, only a negligible difference between the two methods is observed, indicating that the faster perturbative approach may be sufficient for an accurate description of the system. Theoretical equations of state for each set of simulations are reported and compared to experimental data, and we observe that simulations accounting for three-body interactions show improved agreement with experiment over two-body calculations. None of our simulations reveal significant anisotropy in the DW factors for atomic motion parallel or perpendicular to the crystal's basal plane; this is in contrast to recent experimental findings of Blackburn et al. [Blackburn et al., Phys. Rev. B **76**, 024523 (2007)] where substantial anisotropy of this type was observed at temperatures near T = 0 K. Current efforts focus on extracting elastic constants from simulation results in order to further assess the importance of three-body interactions in the system.

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Three-body interactions of solid helium calculated within the Einstein model

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Three body interactions can become important in solids at higher pressures and densities as the molecules can come into close contact. At low temperatures, accurate studies of three body interactions require averaging the three-body terms over the molecules' zero point motions. An efficient, but approximate, averaging approach is based on a Taylor series expansion of the three-body term. The Taylor series can be developed in two different ways, either (1) as a function of Cartesian (x,y,z) zero point displacements of each atom from its average position, or (2) as a function of the symmetry coordinates of a triangle displaced from its average geometry. The Taylor series approach can be checked through two more accurate, but more time-consuming methods: Gaussian quadrature or Monte Carlo integration of the exact three-body function. Results are presented for solid helium, treated as an Einstein solid, for three different model three-body potential energy functions (Axilrod-Teller, Cohen-Murrell and Cencek). Certain situations cause complications for Gaussian quadrature and Monte Carlo integrations when two helium atoms undergo a close approach. A new approach will be introduced in order to reduce these complications caused by low probability triangle configurations. All results will be compared with quantum Monte Carlo simulations.

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Electrostatics, relativistic effects, and the bonding in group 12 dihalide clusters

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Abstract: The group 12 dihalides have attracted a significant degree of attention in the chemical literature because of the apparent interplay between shell effects, the d-block and lanthanide contractions and the increasing influence of relativistic effects going down the group from Zn to Hg. The reasons for these observed electronic and structural differences between Hg and Zn and Cd compounds and how those differences can be accurately modelled, understood, and exploited continues to be an area of significant interest. In this talk, we will show how the group 12 dihalide clusters (in contrast with the group 2 dihalides) provide substantial lessons for bonding in inorganic materials, and we will consider how electrostatic interactions overcome a struggle against the structural consequences of relativistic effects in certain metal dihalides, but not others. A competition between relativistic effects and electrostatics is shown to lead, for example, to a radical change in the structural preference in one particular case especially.

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Theoretical study of metal monoalkylidines

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The physical properties of metal monoalkylidine (M-CCH, where M = Sc-Zn) molecules will be evaluated using computational methods. Metal monoalkylidines are isovalent to well-studied metal monocyanides (M-CN), which suggests both will have similar electronic structures. Also, like the M-CN molecules, the M-CCH molecules likely exist in the interstellar medium and could be involved in prebiotic reactions. Different starting geometries were tested to determine the most stable shape of the structures, including linear, bent, and triangular. For low-lying electronic states of each molecule, optimized geometries were obtained via coupled cluster theory with correlation consistent basis sets extrapolated to complete basis set (CBS) limits and compared to results from multireference configuration interaction theory. The bond dissociation energies of MCCH molecules observed with coupled cluster theory were very large. The high bond dissociation energies of the MCCH 3d molecules are similar to the MCN and MNC molecules, suggesting VCCH and NiCCH will be relatively easy to isolate and characterize experimentally. The computed physical properties from this research will assist in astrochemical detection in the interstellar medium, guide synthetic routes and characterization of the compounds in terrestrial labs, and allow calibration of reliable simulated spectra for future gas phase organometallic and prebiotic research.

2015 Joint Southeastern/Southwest Regional Meeting 214

Acquiring accurate absorption intensities for HNO from *ab initio* calculations

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Experiments carried out at the University of Wyoming have synthesized HNO through the reaction, in a solid molecular hydrogen matrix, of hydrogen atoms with NO radicals. An analysis of the kinetics of this process would provide information about the role that the hydrogen matrix plays in promoting or inhibiting the H + NO reaction. This kinetic analysis can be carried out using in situ infrared absorption spectroscopy to monitor the HNO concentration as a function of time, but theoretical studies are first needed to obtain accurate absorption intensities for HNO. Over two decades have passed since the most recent (1993) study of the HNO absorption intensities; this study used a double harmonic treatment based on molecular orbital calculations that employed, by today's standard, very small basis sets. Our work shows that the assumptions established by the double harmonic approximation fail to provide accurate behaviors of energies and dipole moments of HNO. This is in part because the unusually long and weak HN bond in HNO leads to substantial anharmonic behavior. Improvements on the 1993 study will be accomplished by employing modern basis sets and by going beyond the double harmonic approximation to calculate absorption intensities.

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WITHDRAWN

2015 Joint Southeastern/Southwest Regional Meeting 216

Transition metals in astrochemistry: Which roads lead to a better understanding of astrobiology?

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New small inorganic molecules are rapidly being identified in the interstellar medium and in the radio spectra of carbon-rich stars. However, the terrestrial synthesis and characterization of this novel “library” of fragments, molecules, and binding motifs is not keeping up with data obtained via astronomical observation. The electronic structure of organic molecules and materials implicated in pre-biotic chemistry and origin-of-life reactions [for example, polyynes (HC_nH), polyaromatic hydrocarbons, and phosphates] are a substantial focus of the computational chemistry community. However, the interactions of these materials with metals that hold a crucial role in biology (such as Group IA/IIA atoms, Mn, Fe, and Zn) have scarcely been investigated. The gas phase electronic structure of many of these molecules is difficult to unravel both experimentally and theoretically. For example, the ground state electronic configuration of iron monocyanide (FeCN), a molecule that has profound catalytic and astrobiological relevance, has been heavily debated for over fifteen years. The electronic structure of FeCN and its isomer FeNC, VCN and VNC, reactions of iron cation with N_2, and characterization of the series of 3*d* metal-alkylidenes (MCCH), all computed at very high levels of *ab initio* theory, will be discussed. Elucidating the complex and challenging electronic structure of inorganic radicals has inspired development and refinement of new theoretical and spectroscopic methodologies, as well as new materials.

Quantifying electron delocalization in stretched bonds

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Electron delocalization is fundamental to chemical bonding. Covalent bonding delocalizes electrons between atoms whereas bond breaking re-localizes electrons to atoms. Our electron delocalization range function EDR quantifies the degree to which electrons at point in a calculated wavefunction delocalize over distance *u*. We apply this function to quantify the delocalization in stretched chemical bonds involving strong correlation and self-interaction errors , including H_2 and H_2^+ . The density-matrix-based EDR illustrates that, at equilibrium, covalent bonds are more localized than separated atoms, consistent with the virial theorem. The EDR illustrates the well-known localizing effects of atomic "preparation energies". The EDR also shows how simple mean-field theories over-delocalize stretched bonds, a delocalization error that is fixed in accurate multireference calculations. The role of fractional spin, a fundamental error associated with static correlation of stretched molecular systems in visible in normalization effects on the EDR. Extensions to the closed shell interactions He_2 and Kr_2, the polar covalent bonds HF and HI, and ionic and charge-shift bonds further illustrate the EDR's utility for visualizing and highlighting these concepts.

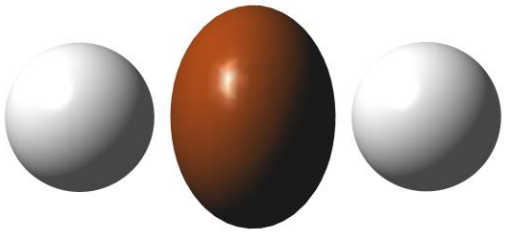

Fig. EDR (r;u=4.0 Angstrom) = 0.75 isosurface for Full Configuration Interaction calculations on H2 molecule stretched to 1.4 Angstrom. The brown color corrsponds to delocalized electrons.

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Comparison of two potential energy functions for predicting fit-for-purpose fuel properties using molecular dynamics

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The United States Navy is interested in the synthesis and use of hydrocarbon-based renewable fuels. Hydrotreated Renewable Fuels (HRFs) include aromatic, branched and linear molecules. Synthesis of these HRFs allow for compositions that differ from those of traditional fossil fuels. Due to their complexity it is not obvious which compositions are suitable for use. Two potential energy functions, the Optimized Potentials for Liquid Simulation (OPLS)[1] and the Adaptive Intermolecular Reactive Empirical Bond-Order Potential (AIREBO)[2,3] are used to predict fit-for-purpose properties such as density and bulk modulus of fuel blend candidates using computer simulations to allow experimental researchers to focus efforts on blends that meet certain criteria. Molecular dynamics (MD) simulations of individual fuel components show excellent agreement with experimental density, enthalpy of vaporization, and bulk modulus. Two binary mixtures composed of the straight-chain alkane *n*-dodecane and branched 2,2,4,4,6,8,8-heptamethylnonane as well as *n*-hexadecane and 2,2,4,4,6,8,8-heptamethylnonane are simulated over a range of mole fractions and their physical properties are compared to experimental mixtures. Finally, fuel blends containing up to twelve fuel components are investigated.

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2015 Joint Southeastern/Southwest Regional Meeting 219

Computational quantum chemistry studies of proposed reaction mechanisms for direct oxidation of melatonin

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Free radicals are connected to oxidative stress that results in aging, cancer, Parkinson's, Alzheimer's, and Sickle Cell Disease, among many other health problems. Indirect methods, such as spin trapping, are commonly used to circumvent the difficulty of direct experimental observation and identification of short-lived free radicals. Spin trapping stabilizes and lengthens the lifetime of the radical through reaction with another molecule so that it is detectable by Electron Paramagnetic Resonance spectroscopy. Recent efforts have been directed towards *in vivo* spin trapping. However, the most common nitroso and nitrone spin traps are known to be toxic at high concentrations. Further complicating the interpretation of the experimental results to establish the reaction mechanisms is that the superoxide adduct of the spin trap enzymatically degrades and decays into that of the hydroxyl adduct. Melatonin is a relatively nontoxic natural antioxidant that is directly reactive towards the hydroxyl radical and relatively unreactive towards the superoxide radical. While melatonin as an antioxidant has been experimentally well studied, its reaction mechanisms are still not well understood. This presentation will focus on computational quantum chemistry studies of proposed reaction mechanisms in the gas phase for direct oxidation of melatonin. Geometry optimizations were performed using Hartree-Fock and Density Functional Theory methods in conjunction with Dunning's correlation-consistent polarized valence-only triple zeta (cc-pVTZ) basis set. Single point energies were calculated using Møller-Plesset perturbation theory in conjunction with cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets. Stable structures and conformations of melatonin radical intermediates will help understand how melatonin functions as an antioxidant and determine if a melatonin derivative could function as a possible *in vivo* spin trap.

2015 Joint Southeastern/Southwest Regional Meeting 220

Computational investigation of linkage isomerization in sulfoxide-containing ruthenium complexes

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Materials exhibiting switchable electrochemical properties is an area of interest for the development of novel memory storage devices. Organometallic complexes that exhibit linkage isomerism are potential targets for these applications. Previous work has shown ruthenium-centered complexes with sulfoxide ligands to be preferentially either S-bound or O-bound, depending on the oxidation state of the metal center. In the current computational study employing density functional theory and continuum solvation models, a systematic investigation of the kinetics, thermodynamics, and electrochemistry of these systems is used as the basis for the interpretation of existing and design of novel systems.

2015 Joint Southeastern/Southwest Regional Meeting 221

Carbene-stabilized disilicon-based transition metal compounds

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Carbene-stabilized disilicon, L:Si=Si:L (L: = N-heterocyclic carbene), represents an intriguing silicon(0) platform that has exhibited diverse reactivity. Recently, this laboratory investigated the unusual reactivity of L:Si=Si:L with main group species such as O_2, N_2O, and CO_2. As an extension of this work, we have begun to explore the transition metal chemistry of L:Si=Si:L. We have shown that L:Si=Si:L complexes CuCl and $Fe(CO)_5$ at room temperature to give L:Si=Si(CuCl):L and L:Si=Si[$Fe(CO)_4$]:L, respectively. However, at increased temperatures, L:Si=Si[$Fe(CO)_4$]:L can react with a second equivalent of $Fe(CO)_5$ affording L:Si[μ-$Fe_2(CO)_6$](μ-CO)Si:L, through insertion of both CO and $Fe_2(CO)_6$ into the Si_2 core. The resulting compound represents the first example of transition metal-mediated cleavage of a silicon-silicon double bond. This presentation will cover the synthesis, characterization, and reactivity of these novel compounds and recent developments in our laboratory.

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Hexacoordinate polypyridylsilicon(IV) compounds for electronic and catalytic applications

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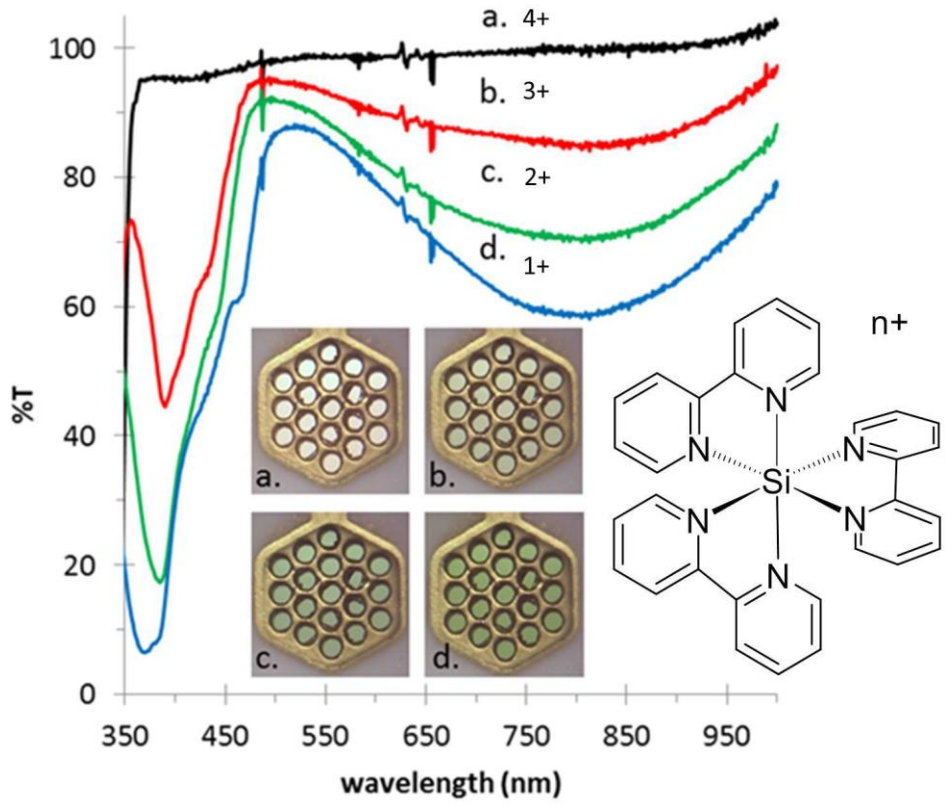
Hexacoordinate polypyridylsilicon(IV) compounds are attractive candidates for electronic and catalytic applications. They exhibit multiple, stable redox states with low-lying LUMOs. Furthermore, the lack of d-electrons precludes MLCT transitions. This increases their desirability as cathodic colorants, dyes that are colorless in the oxidized state but become colored upon reduction. The extensive ligand variability of the hexacoordinate polypyridylsilicon(IV) complexes provides endless color possibilities. Polypyridylsilicon(IV) compounds are also being developed for catalytic applications. Bis-bipyridylsilicon(IV) diols have been proven effective as dual hydrogen bond catalysts in reactions such as the addition of N-methylindole to trans-beta-nitrostyrene, and the C2 symmetry of these complexes provides further opportunity for chiral catalysis.



Transmittance and photos of various charge states of tris-bipyridylsilicon(IV) hexafluorophosphate in acetonitrile solution.

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Metallathiacrown ethers: Synthesis and characterization of transition metal complexes containing α,ω-bis(phosphite)-polythioether ligands and an evaluation of their soft metal binding capabilities

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The *cis*-$Mo(CO)_4${2,2'-$(C_{12}H_8O_2)PO(CH_2CH_2S)_nCH_2CH_2OP(2,2'-(O_2H_8C_{12}))$} (n = 2, 3) and *cis*-$Mo(CO)_4${2,2'-$(C_{12}H_8O_2)POCH_2CH_2S$-1-$(C_6H_4)$-2-$SCH_2CH_2OP(2,2'-(O_2H_8C_{12}))$} metallathiacrown ethers have been prepared as soft metal selective molecular receptors. Multinuclear NMR spectroscopy and X-ray crystallography have been used to show that byproducts formed during the syntheses of the *cis*-$Mo(CO)_4${2,2'-$(C_{12}H_8O_2)PO(CH_2CH_2S)_nCH_2CH_2OP(2,2'-(O_2H_8C_{12}))$} (n = 2, 3) metallathiacrown ethers are homobinuclear, complexes with *cis*-$Mo(CO)_4$(P-donor)(S-donor) centers. The abilities of the metallathiacrown ethers to bind $PdCl_2$ and $PtCl_2$ have been assessed using $^{31}P\{^1H\}$ NMR spectroscopy and X-ray crystallography. The complexes showed null results with $PdCl_2$, however the $PtCl_2$ experiments showed that the *cis*-$Mo(CO)_4${2,2'-$(C_{12}H_8O_2)PO(CH_2CH_2S)_nCH_2CH_2OP(2,2'-(O_2H_8C_{12}))$} (n = 2, 3) complexes formed heterobinuclear *cis,cis*-{[$Mo(CO)_4${2,2'-$(C_{12}H_8O_2)PO(CH_2CH_2S)_nCH_2CH_2OP(2,2'-(O_2H_8C_{12}))$}]$PtCl_2$} (n = 2, 3) complexes. The $^{31}P\{^1H\}$ NMR spectra of these complexes suggest a *cis*-(thioether)$_2PtCl_2$ coordination environment in each, which leads to asymmetric binding in the latter complex. Binding of $HgCl_2$ by the *cis*-$Mo(CO)_4${2,2'-$(C_{12}H_8O_2)PO(CH_2CH_2S)_nCH_2CH_2OP(2,2'-(O_2H_8C_{12}))$}

(n = 2, 3) complexes has been studied using $^{31}P\{^{1}H\}$ NMR spectroscopy. Each complex was titrated with $HgCl_2$ and the quantitative shifts in the $^{31}P\{^{1}H\}$ NMR spectra were fit to a binding mechanism. The n = 2 metallathiacrown ether binds $HgCl_2$ to form a 1:1 complex with K_a = 12.0 (0.2) M^{-1}. In contrast, interaction of $HgCl_2$ with the n = 3 metallathiacrown ether results in isomerization to the trans complex, and $HgCl_2$ binds to both isomers. A model has been adapted to fit the titration data of this complex and to extract equilibrium constants for each step in the cycle; the cis-trans equilibrium of the free, K_{free} (0.570 (0.004)), and bound, K_{bound} (0.16 (0.03)), metallathiacrown ethers as well as the association binding constants for the *cis*-, K_{cis} (4.1 (0.3) x 10^2 M^{-1}) and *trans*-, K_{trans} (1.1 (0.2) x 10^2 M^{-1}) metallathiacrown ethers. The equilibrium constants demonstrate that the *cis*-metallathiacrown ether binds more strongly to the $HgCl_2$ than does the *trans*-metallathiacrown ether and that the cis-trans equilibrium favors the *cis*-metallathiacrown ether.

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Velocity map imaging study of the photoinitiated charge transfer – dissociation of Ag^+(benzene)

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Ag^+(benzene) complexes are generated in the gas phase by laser vaporization and detected in a reflectron time-of-flight mass spectrometer. Excitation of Ag^+(benzene) at 355 nm and 266 nm results exclusively in dissociative charge transfer, leading to neutral Ag and benzene$^+$ products. Kinetic energy release in translationally hot benzene$^+$ fragments is detected using a new apparatus designed for photofragment imaging of mass-selected ion beams. Velocity map imaging and slice imaging techniques are employed. Analysis of the data provide new information on the binding energy and Ag^+(benzene).

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Studying the reactions between group 5 transition metal atoms and CX_4 molecules (X = H, F, and Cl)

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Laser-ablated vanadium, niobium, and tantalum transition metal atoms were reacted with CH_2X_2, CHX_3, and CX_4 (X = F and Cl) molecules, and the products were investigated by matrix isolation infrared spectroscopy. The major reaction products are the CH_2-MX_2, CHX-MX_2, HC-MX_3, and XC-MX_3 complexes. These species are identified by comparing their infrared spectra and isotopic shifts with predictions from theoretical calculations. The reaction pathways to form these products are investigated and will be discussed. Comparison of the properties of previously studied Group 4 and 6 analogues is also provided. The methylidyne complexes HC{}MF_3 show considerable increase in bond strength for the nominally $\sigma^2\pi^1\pi^1$(Ti), $\sigma^2\pi^2\pi^1$(V), and $\sigma^2\pi^2\pi^2$(Cr) carbon{}metal

bonds from left to right. The Group 5 HC{}MF_3 complexes have only a plane of symmetry whereas the Group 4 and 6 analogs have threefold symmetry.

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Microwave-assisted synthesis and luminescence rigidochromism for ambipolar polyimines and rhenium (I) complexes thereof

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The cause of the phenomenon *Luminescence Rigidochromism* in polyimine-rhenium(I) complexes has been well assigned to an environmental-sensitive Metal to Ligand Charge Transfer, MLCT, and π-π* radiative decays. It is well-established that, when the rigidity in the vicinity of the complexes increases, the MLCT energy level rises above or near the π-π* energy level of the corresponding diimine ligand, causing the expected emission to blue-shift. Here we present a detailed study of microwave-assisted synthesis and photoluminescence analysis for a series of ambipolar polyimines and rhenium(I) polyimine complexes thereof. Focus will be upon compounds of the formulas L and $ReL(CO)_3Cl$, where L = 4-[4,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,3,5-triazin-2-yl]-N,N-diethyl-benzenamine. Further modifications on L's functional groups produce significant photophysical property changes that include fine-tuning in not only luminescence rigidochromism but also luminescence thermochromism and solvatochromism. Detailed photoluminescence studies of the rhenium complexes in specific frozen media present a smooth luminescence rigidochromic shift near the glass transition temperature of the matrix. In addition, the achievement of remarkable fine-tuning near the glass transition temperature with 1/10 K sensitivity is discussed. Factors that are found to influence the rigidochromic shifts will be presented, including the effects of solvent polarity, concentration, and the ligand's functional group variations. Fluorescence studies of the free ligands will also be presented for comparison. Finally, methods will be uncovered for the microwave-assisted synthetic modification to include additional external cooling to improve the preparation of the ligands and complexes versus the traditional oil bath reflux systems.

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Organomanganese photochromic systems: Linkage isomerization and cage effects of bifunctional pyridine ligands substituted in the 2-position: A time-resolved infrared spectroscopic study

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The mechanism for the photoisomerization of bifunctional, 2-substituted pyridyl ligands bound to manganese in dicarbonyl(η^5-methylcyclopentadienyl)manganese was investigated using TRIR and FTIR spectroscopy on the picosecond to minute timescale in room temperature heptane. Thioamide, thiophenyl, aliphatic sulfide, cyano, and olefin side groups were selected for comparison to pyridine in dicarbonyl(functional group)(η^5-methylcyclopentadienyl)manganese. These adducts are known to be stable at room temperature and were chosen for their markedly different infrared and UV-vis

absorbance properties compared to the pyridine adduct. In a previous report, this group demonstrated that the photoinitiated conversion of dicarbonyl(3-cyanomethylpyridine-*κ*N)(η^5-methylcyclopentadienyl)manganese to dicarbonyl(3-cyano-*κ*N-methylpyridine)(η^5-methylcyclopentadienyl)manganese occurs via a bimolecular reaction involving a solvent coordinated intermediate and not by geminate cage recombination.[i] In the present study, it was found that the second functional group type and its proximity to the pyridine moiety affects the bistability of the complex and possibly the mechanism of isomerization in these photochromic systems.

[i] DeWitt, K. M.; To, T. T.; Heilweil, E. J.; Burkey, T. J. Linkage Isomerization via Geminate Cage or Bimolecular Mechanisms: Time-Resolved Investigations of an Organometallic Photochrome. *J. Phys. Chem. B* **2015**, *119*, 5531-5536.

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Metal-to-metal charge transfer in alkynyl bridged bimetallic complexes

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Charge-transfer (CT) excited states where charge is separated over a long distance are interesting from a fundamental standpoint and for applications involving solar energy conversion and photocatalysis. For example, $Ru(bpy)_3^{2+}$ based dyes have been exploited as a sensitizer for dye sensitized solar cells (DSSCs). Here, the metal-to-ligand CT (MLCT) excited state serves to inject an electron into the conduction band of the TiO_2 semiconductor. Metal-to-metal CT (MMCT) excited states have also been of general fundamental interest and for applications involving photocatalysis. In particular, several groups have begun investigating MMCT excited states in solid state M-O-M' architectures involving Ti^{IV} acceptors oxo-bridged to donors such as Fe^{II}, Cr^{III}, and Mn^{II}. Our recent interest in electron transfer through alkynyl bridged organometallic frameworks led us to investigate alkynyl bridged bimetallic systems. Herein, we report our synthetic efforts along with electrochemical and spectroscopic measurements in order to better understand the photophysics of this class of compounds.

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Oxido bridged heterobimetallic molecules containing first-row transition metals with long-lived excited states

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Photochemical transformations of organic molecules require a photocatalyst whose excited state lifetime is long-lived (≈ ns), with redox properties tuned to match the reactions of interest. We are reporting new metal-to-metal charge transfer (MMCT) chromophores derived from an unsupported, terminal M^{III} hydroxide (M = Cr, Fe, or Co) that have such properties. The protic nature of the metal hydroxides allows for the design of covalently bonded, oxido-bridged heterobimetallic complexes, which contain a Ti^{IV} electron acceptor. These molecules exhibit a charge-transfer band with significant intensity that can be tuned throughout the UV-Vis spectrum through both donor metal substitution and ligand variation. Transient absorption experiments have revealed an

excited-state lifetime on the order of nanoseconds in both the Cr^{III} and Fe^{III} derivatives at room temperature. The strongly reducing (> 2 V vs. Fc/Fc^{+}) transient Ti^{III} species, in combination with the long-lived excited state, make this class of molecules an alternative to traditional photoredox MLCT Ru and Ir-based catalysts.

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Debromination of vicinal dibromides in perfluorobenzene sulfonimide (PFSI) compounds

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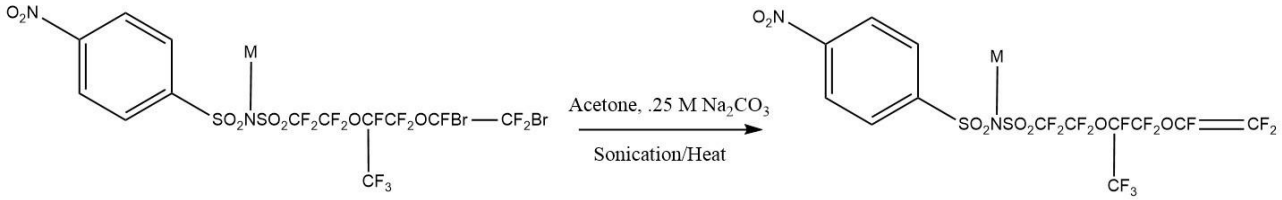
A series of facile and efficient methods were explored for debromination of vicinal dibromides in perfluorobenzene sulfonimide (PFSI) compounds. Instead of traditionally used metal zinc or sodium diiodide, recrystallization or sonication with Cs_2CO_3 solution and acetone had resulted in target perfluoroalkene product. Factors such as heating, solution concentration, UV light, and time the solution was sonicated/heated were investigated in an attempt to optimize reaction conditions. Evidence indicates that a weak base can promote such reaction via E2 mechanism, while an unwanted side reaction accompanied if a strong base was used. Attempts to debrominate *meso*-1, 2-dibromo-1, 2-diphenylethane were unsuccessful with similar methods in different organic solvents. It is concluded that this unique debromination of vicinal dibromides can only occur to PFSI compounds under weak basic conditions. The products and intermediates were characterized with ^{19}F and proton NMR.



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Developing methods for the synthesis of α-alkenyl- and α-alkynyl-phosphonates

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Alkenes and alkynes are found in nature and range in complexity from simple olefins found in petroleum sources to complex natural products and biomolecules. Phosphorus functionalized alkenes and alkynes are becoming increasingly important targets for R & D because they have unique chemical, biological and pharmacological properties. We will present our preliminary results for the synthesis of α-alkenyl- and α-alkynylphosphonates from α-acylphosphonate derivatives.

2015 Joint Southeastern/Southwest Regional Meeting 232

Highly selective oxidation of sulfides to sulfoxides catalyzed by iron (III) corroles with iodobenzene diacetate

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In this presentation, we will show that iron(III) complexes of *meso*-tri(pentafluorophenyl)corrole and *meso*-triphenylcorrole is a potent catalytic system for selective oxidation of sulfides to sulfoxides with iodobenzene diacetate, i.e., $PhI(OAc)_2$. Quantitative conversions and high selevtivities were observed for most sulfide substrates. For example, in the case of thioanisole, 100% conversion with 99% selectivity for sulfoxides was achieved within 1 hour at room temperature. Under optimal condition, quantitative conversions to corresponding sulfoxides and excellent chemoselectivities were also observed in the oxidation of a variety of thioanisoles, allylic sulfides and hydroxyl sulfides. A significant accelerating effect on the rate of sulfoxidation reactions by small amount of water was also noticed.

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The synthesis of functionalized [*n*](3,3")*p*-terphenylophanes: Precursors to funtionalized cycloparaphenylenes

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Cycloparaphenylenes (CPPs) are linearly linked benzene rings, connected at their 1 and 4 (para) positions. These macrocyclic nanohoops have been the subject of intense interest since 2008, as they represent the smallest segment of an (*n*,*n*) armchair carbon nanotube (CNT) and possible building blocks for the bottom-up chemical synthesis of CNTs. However, their application to CNT synthesis has been thwarted by the difficulty of preparing regioslectively functionalized CPPs. Our group has recently reported a non-cross coupling-based approach to CPP fragments that can be regioselective functionalized and extended into high-order nanostructures. This presentation will focus on recent work that has been developed towards synthesizing functionalized CPPs.

2015 Joint Southeastern/Southwest Regional Meeting 234

Microwave-assisted cleavage of –alloc and –oallyl protecting groups in solid phase peptide synthesis

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Orthogonal protection of amino acid side chains in Solid Phase Peptide Synthesis (SPPS) allows for selective deprotection of side chains and the formation of cyclic peptides on resin. Cyclizations are useful as they may improve the activity of the peptide or improve the metabolic stability of peptides *in vivo*. One cyclization method often used is the formation of a lactam bridge. The –Alloc/-OAllyl protecting groups are

commonly used in the formation of lactam bridges as they are compatible with Fmoc SPPS conditions. The problem with this method is that the reaction is most often performed at room temperature under argon gas. This reaction is not usually done at higher temperatures due to the fear of poisoning the palladium catalyst. As a result the reaction is long and reagent-intensive. Herein we report the development of a method in which the –Alloc/-OAllyl groups are removed in a microwave synthesizer without an inert environment. The reaction is much faster, allowing for the removal of the protecting groups before the catalyst is oxidized, as well as being less reagent-intensive.

2015 Joint Southeastern/Southwest Regional Meeting 235

New photochemical reactions and their applications

***Pengfei Wang**, wangp@uab.edu, Zhenying Ding, Dattatray Devalankar, Leyah Schwartz. Chemistry, University of Alabama at Birmingham, Birmingham, Alabama, United States*

We have recently developed a series of robust photoremovable protecting groups (PPGs) for protection of carbonyl and hydroxyl groups. For carbonyl protection, selective removal of different carbonyl PPGs has been achieved by changing irradiation wavelength. We have also demonstrated that the traditional acid-sensitive hydroxyl protecting group, *i.e*., trityl (Tr) group, can be converted to a robust photolabile hydroxyl protecting group (*i.e*., dimethyltrityl (DMATr)) by incorporating a meta dimethylamino group to one of the three phenyl rings. DMATr-based hydrophilic hydroxyl-PPGs have also been developed; their reactions in water are clean with fast photochemical kinetics. Most recently, we have developed another new benzyl-type PPG, *i.e*., diethylaminobenzyl (DEABn), for releasing alcohols and carboxylic acids. DEABn protects primary, secondary, and tertiary alcohols in ether form. Since removal of DEABn does not destroy the working chromophore, we have also developed the new diethylamino-isophthaly (DEAIP) PPG to release two substrates (alcohols or carboxylic acids) from one simple PPG chromophore. These new PPGs provide new opportunities for different applications

2015 Joint Southeastern/Southwest Regional Meeting 236

A non-cross-coupling strategy for the synthesis of biaryl bonds: Towards the synthesis of [4] cycloparaphenylene

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As the smallest possible segment of an armchair carbon nanotube (CNT), cycloparaphenylenes (CPPs) have captivated the interest of synthetic chemists since they were first reported by Bertozzi and Jasti in 2008. Our group has developed a strategy for the synthesis of CPP substructures that utilizes a non-cross-coupling-based approach to make a macrocyclic cyclohex-2-ene-1,4-diol precursor to a bent aromatic unit. The cyclohex-2-ene-1,4-diol unit facilitates the curvature necessary for macrocyclization and can be converted into a bent para-phenylene, or p-terphenyl unit, substructures of all CPPs. This method is currently being employed in the synthesis of the smallest CPP, [4]CPP, which will be difficult to prepare using known cross-coupling-based macrocyclization strategies.

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Iridium(III)-bis(imidazolinyl)phenyl catalysts for intermolecular enantioselective C–H functionalization with acceptor-only diazoacetates

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Enantioselective C–H functionalization is a powerful tool for the construction of complex molecules and materials. Besides reducing the reliance on conventional functional group manipulation, building new C–C or C–heteroatom bonds from C–H bonds often times reduces the number of synthetic steps and opens routes to classically unattainable compounds. One strategy for the enantioselective functionalization of C–H bonds exploits the inherent reactivity of metal carbenoid and nitrenoid species, which can be generated from the decomposition of the corresponding diazo- and azide-containing substrates. In particular, α-diazoacetates are attractive metallocarbene precursors due to their ease of synthesis and generation of N_2 as the only byproduct. These compounds can be further divided into donor-acceptor, acceptor-only, and acceptor-acceptor classifications. The donor-acceptor class of α-diazoacetates have proven to be remarkably useful for enantioselective C–H functionalization, however there are limitations in that further modification of certain donor groups can be difficult. Considering this limitation, expansion of the classes of diazoacetates amenable to enantioselective C–H functionalization would be highly desirable**.** However, chemistry with metallocarbenes derived from acceptor-only and acceptor-acceptor α-diazoacetates carry unique challenges, in particular the need to effectively control the enhanced electrophilicity of the carbene carbon compared to the donor-acceptor class. We have recently reported that Ir(III)-bis(imidazolinyl)phenyl catalysts are capable of affording high yields and levels of stereocontrol in donor-acceptor carbenoid group transfer, and have moved to probe this catalyst family's effectiveness with acceptor-only α-diazoacetates. An account of our studies including catalyst design, substrate scope, computation and future directions will be discussed.

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Investigation of the Tsuji-Trost variant of the Winstein-Masamune spirocyclization as a unified approach to select lycopodium alkaloids

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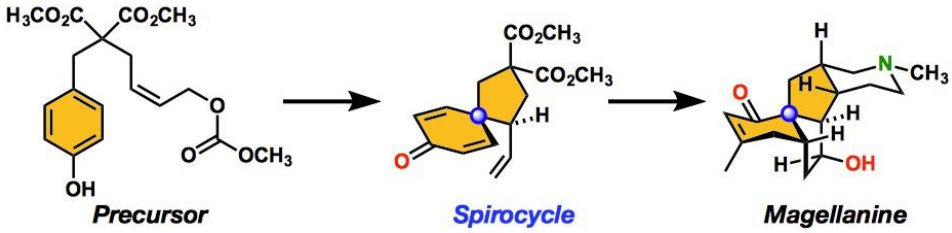
The total synthesis of natural products, especially alkaloids, remains a vigorous area of research. With the advancement of new reaction technologies even the most daunting molecular structures are being synthesized with a pace unrivaled in history. Pursuant to these endeavors we have initiated a research program aimed at transforming simple aromatic phenols into increasing complex spirocyclic compounds. The intramolecular para-alkylation of a phenol with a carbon chain bearing a suitable leaving group, known as the Winstein-Masamune reaction, results in a spiro[4.5]deca-6,9-dien-8-one. Of notable consequence of this reaction is the synthesis of a sterically congested spirocyclic quaternary carbon. This particular motif is a substructure found in the AC rings of the Lycopodium alkaloid magellanine. This natural product has captured the

imagination of many synthetic organic groups as proving ground for demonstrating new strategies and methods. In this talk, we will outline our approach to this molecule starting from 4-hydroxybenzaldehyde (A ring platform). In doing so we will define the need for the further development of the Winstein-Masamune reaction merging it with the Tsuji-Trost allylic alkylation. By employing a phenol as the nucleophilic component in an intramolecular Tsuji-Trost allylic alkylation, the resultant product contains a pendant alkene. This functional handle thereby allows for elaboration of the spirocycle. To this end, we are taking an AC to ACB approach to the construction of magellanine with the spirocyclic quaternary carbon as the focal point. Our results are supported by extensive two-dimensional NMR data and corroborated by calculations carried with Spartan 14 software.



spirocyclization reaction

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Synthesis of bis-1,4-electrophiles as linchpins in the Tsuji-Trost variant of the Winstein-Masamune spirocyclization reaction

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The Winstein-Masamune reaction of a 4-substituted phenol is an efficient reaction for the synthesis of all carbon spirocycles bearing a quaternary carbon at the ring junction. The merging of the Winstein-Masamune reaction with the Tsuji-Trost allylic alkylation represents a powerful method for constructing increasing elaborate spirocycles. We are interested in applying this reaction as a unified strategy toward the synthesis of selected lycopodium alkaloids, magellanine for example. To obtain the necessary starting materials, we have employed a Knoevenagel condensation of 4-hydroxybenzaldehyde with various active methylene species (dimethyl malonate, ethyl malononitrile, malononitrile) to give alkylidene malonate derivatives. Atmospheric hydrogenation has afforded alpha-substituted malonates that are subsequently treated with the bis-1,4-electrophiles. Our initial strategy for the synthesis of these electrophiles has been predicated on the differential protection of cis-butene-1,4-diol. To that end, mono-acylation with methyl chloroformate followed by mesylation afforded (*Z*)-4-((methoxycarbonyl)oxy)but-2-en-1-yl methanesulfonate on gram scale. Intermolecular alkylation of malonate derivatives occurs chemoselectively to displace the mesylate. The allylic carbonate then serves as the electrophilic acceptor in the intramolecular spirocyclization reaction. In order to produce more complex electrophiles with various branching patterns, we have started with the alkylation of TBS protected propargyl alcohol with aldehydes and acyclic and cyclic ketones. Subsequent reduction of the alkyne to the cis-alkene with Lindlar’s catalyst and hydrogen or the trans-alkene with sodium and ammonia has expanded the electrophile scope of the spirocyclization

reaction. The compounds produced during this research have been extensively characterize by 1D and 2D NMR and unique factors will be discussed.

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Hydrolytic catalyst selection by affinity chromatography

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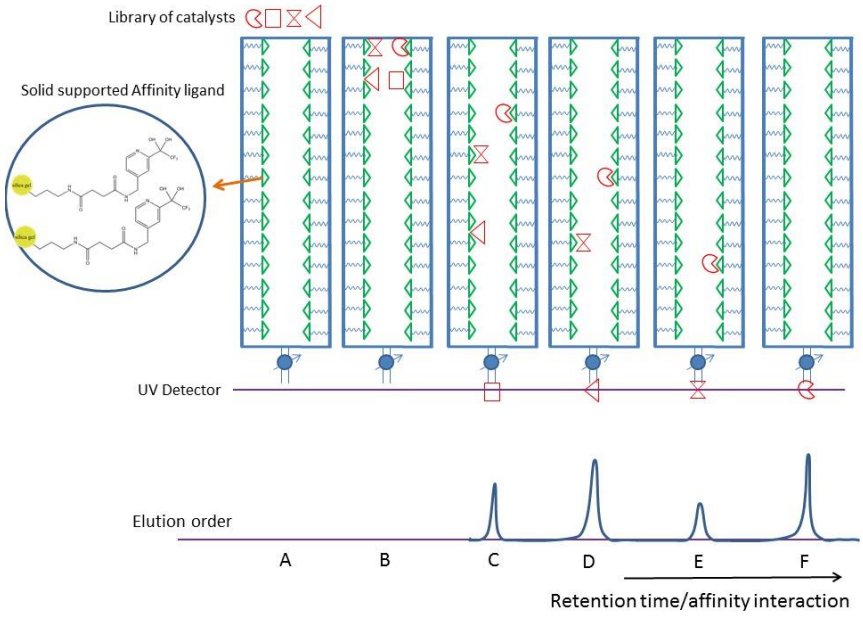
A new method of catalyst selection based on the affinity of metal complexes for solid-supported substrate and transition state analogs (TSA) will be described. Correlations between the binding affinity of Zn(imine)-complexes to a silica-tethered picolinate ester (substrate analog) and trifluoromethyl ketone hydrate (TSA) and the rate of picolinate ester hydrolysis reaction were investigated. A strong positive correlation between complex-substrate analog column retention times and complex-substrate binding affinity from kinetic measurements was found, indicating that the substrate analog mimics well the substrate-catalyst interaction. A good correlation was also observed between complex-TSA retention times and the rate of the catalyzed reactions, demonstrating that affinity chromatography with solid supported substrate and TSA analogs can be an effective tool for catalyst discovery.



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The DNA adduct N-(2'-deoxyguanosin-8-yl)-3-aminobenzanthrone gives rise to a base-displaced intercalated structure

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Mansfield, Connecticut, United States (2) Chemistry, Vanderbilt University, Nashville, Tennessee, United States

3-Nitrobenzanthrone (3-NBA) is a suspected carcinogen and an environmental contaminant. Concern about this compound arises, in part, from its high mutagenic potential coupled with likely human exposures as a component of diesel exhaust. *In vivo* reduction of 3-NBA can produce an electrophilic nitrenium ion with a resulting potential to form aminobenzanthrone (ABA) DNA adducts. The C8 position of guanine offers the attachment point for the major product, N-(2'-deoxyguanosin-8-yl)-3-aminobenzanthrone (C8-dG-ABA) with additional adducts forming at the N^2 position of guanine and the N^6 position of adenine. Development of synthetic methodologies has allowed for investigation of C8-dG-ABA in the oligodeoxynucleotide dodecamer 5'-d(GTGCXTGTTTGT)-3':5'-d(ACAAACACGCAC)-3'; X = C8-dG-ABA. We report a solution structure for this construct along with evidence of thermodynamic destabilization induced by C8-dG-ABA. The conformation of the C8-dG-ABA adduct was determined using NMR spectroscopy and was refined using restrained molecular dynamics (rMD) calculations. Experimentally determined interproton distance restraints were obtained from NMR NOE experiments. It was determined that the C8-dG-ABA adduct intercalated in the duplex which effected a transition of the adducted guanine into a *syn* conformation about the glycosidic bond. The intercalated position of the ABA moiety displaced the complementary cytosine into the major groove of the DNA. The amino and imino pattern of NOEs revealed that Watson-Crick base pairing interactions were maintained adjacent to the lesion site. While this facilitated π-stacking interactions between the adduct and the adjacent base pairs, the overall thermodynamic stability of the duplex was reduced as evidenced by a decrease in melting temperature of 11 ºC when compared to an unmodified control duplex. Major features of this structure differ significantly from those of the N^2-dG-ABA adduct, wherein the adduct was determined to reside in the minor groove leaving the adducted guanine in the *anti* conformation maintaining its capacity to base pair. Thus we concluded that regiochemistry in regards to the guanine and ABA points of attachment play a significant role in determining the structural and thermodynamic effects arising from these adducts. Supported by NIH grants R01 CA 55678 (M.P.S), R01 ES-009127 (A.B.), and R01 ES-021762 (A.B.)

Drought effects on seed composition and minerals in soybean genotypes differing in slow-wilting trait

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Soybean seed is a major source of protein, oil, and fatty acids. These constituents determine the compositional quality of seeds. Drought is an important environmental stress factor, leading to yield loss and poor seed quality. Recent advances in soybean breeding have resulted in genotypes that express the slow-wilting phenotype (trait) under drought stress conditions. However, the physiological mechanisms of this trait remain unknown due to the complexity of trait × environment interactions. The objective

of this research was to investigate the effects of drought on seed composition and mineral nutrition in seeds of slow-wilting soybean genotypes under drought stress conditions. A repeated greenhouse experiment was conducted using check genotypes: NC-Roy (fast wilting), Boggs (intermediate in wilting); and NTCPR94-5157 and N04-9646 (slow-wilting, SLW) genotypes. Plants were either well-watered or drought stressed. Results showed that genotypes responded differently under well-watered conditions. Leaf and seed concentrations of K, P, Ca, Cu, Na, and B were higher in SLW genotypes than in the checks under drought stress conditions. Seed protein, oleic acid, and sugars were higher in SLW genotypes, and oil, linoleic and linolenic acids were lower in SLW genotypes. Leaf water potential was significantly lower in checks (-2.00 MPa) than in the SLW genotypes (-1.68 MPa). The research demonstrated that homeostasis and osmotic regulation minerals such as K, P, Ca, Cu, Na, and B may be involved in SLW trait by maintaining homeostasis and osmotic regulation. Maintaining higher leaf water potential in NTCPR94-5157 and N04-9646 under drought stress could be a possible water conservation mechanism response to maintain leaf turgor pressure. The observation of higher levels of osmoregulators such as minerals, raffinose and stachyose, and oleic acid in SLW genotypes needs further research.

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Characterization of the 2,6-diamino-4-hydroxy-*N*^{5}-(methyl)-formamidopyrimidine DNA lesion

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The N7 imidazole nitrogen of guanine is the most susceptible site for DNA methylation, resulting in the formation of the cationic adduct 7-methylguanine (7MeG). Opening of the imidazole ring occurs upon exposure to hydroxide ion, producing the 2,6-diamino-4-hydroxy-*N*^{5}-(methyl)-formamidopyrimidine (MeFapy-dG) lesion. This lesion is known to convert between α and β anomers, but the possibility of additional conformational isomers cannot be ruled out. We report progress towards characterizing this DNA adduct, including the synthesis and purification of a 12mer oligodeoxynucleotide in which the CH_3 group of the MeFapy-dG is ^{13}C-labeled in the sequence 5'-CATXATGACGCT-3'; X=^{13}C-MeFapy-dG. The reverse phase HPLC chromatogram showed multiple chromatographic peaks. Two of these were suspected to be the ^{13}C-MeFapy 12mer oligodeoxynucleotide. MALDI mass spectrometry verified that these peaks exhibited the correct m/z ratio, while capillary zone electrophoresis (CZE) verified the purities of the isolated peaks. The two HPLC chromatographic peaks were thus identified as two equilibrating isomers. This corroborated work with the 12mer duplex 5'-(GCTAGTXGGTCC)-3':5'-(GGACCCACTAGC)-3'; X=MeFapy-dG. In that duplex NMR spectra showed that the A^{4}H1'-G^{5}H8, G^{5}H1'-G^{5}H8, G^{5}H1'-T^{6}H6, T^{6}H1'-T^{6}H6 NOE cross-peaks exhibited doubling, as did corresponding NOE cross-peaks in the deoxyribose H2' and H2'' region of the spectrum. These NMR data indicated the presence of two distinct chemical environments for nucleotides near the lesion. Supported by NIH Grant P01 CA-160032 (M.P.S. and C.J.R.) and the NIH Training Grant in Molecular Toxicology, T32 ES-007028 (S.N.B.).

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Parsing the structure of the 8-(deoxyguanosin-*N*^{2}-*yl)*-1-aminopyrene adduct

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1-nitropyrene (1-NP) is found in urban air particulate, coal fly ash, and diesel exhaust. It is metabolized via nitroreduction which forms aminopyrene (AP) as the major product. The adduction of 1-NP to DNA occurs at the C^8 and N^2 atoms of guanine residues, and the resultant metabolic product, AP, has been characterized as a significant DNA adduct due to its abundance after exposure to 1-NP. The N^2-AP-dG adduct, the focus of the work detailed here, is attached to the amino group of guanine that is involved in Watson-Crick hydrogen bonding which could have significant effects on base pairing. NMR Spectroscopy has been utilized to collect spectra at various temperatures to extract structural information of N^2-AP-dG within the 5'-d(GTGCXTGTTTGT)-3':5'-d(ACAAACACGCAC)-3'; X = N^2-AP-dG duplex context. COSY experiments have pinpointed the N^2-AP-dG adduct and cytosine H5-H6 scalar spin couplings. The NOESY spectra showed that all T^6, A^{19}, C^{20}, G^{21}, and A^{23} cross peaks have significantly broadened. Furthermore, at 35°C, evidence suggested a significant shift of the T^6 H1'-H6 cross peak upfield from the typical region while at 10 and 15°C the peak was not present. These observations agree with melting temperature studies that have demonstrated that the *N*^{2}-AP-dG adduct is destabilizing, lowering the melting temperature by 4°C. Cross peaks have been assigned that correlate to adduct protons H2 and H3 interacting with the H1' proton of the G^{21} sugar moiety. Weak cross peaks between H10 and H11 of the adduct and X^5 H1' proton have suggested that the adduct is oriented in the minor groove, pointed in the 5' direction of the modified strand, similar to the work by Cosman et. al. on N^2-benzo[*a*]pyrene diol epoxide. This work is supported by NIH grants R01 CA-55678 (M.P.S.), R01 ES-009127 (A.K.B.), and R01 ES-021762 (A.K.B.).

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Deltaretroviral nucleocapsid proteins display non-equivalent levels of nucleic acid chaperone activity

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RNA chaperones are proteins that direct the structural rearrangement of RNA molecules into their most thermodynamically favorable conformation. During the replication process of retroviruses, a reverse transcription step occurs where the single-stranded RNA genome is converted into double-stranded DNA prior to integration into the host cell's genome. In order to resolve stable RNA secondary structures to enable the RNA to serve as a template for reverse transcription, an RNA chaperone is required. The nucleocapsid protein (NC) from human immunodeficiency virus type 1 (HIV-1), a lentivirus, has been shown to be an effective RNA chaperone and is essential for reverse transcription to take place. In contrast, the deltaretrovirus human T-cell leukemia virus type 1 (HTLV-1) NC has been shown to be a poor RNA chaperone, owing to its acidic C-terminal domain. Bovine leukemia virus (BLV) is a deltaretrovirus that is closely related to HTLV-1, yet its NC is much more structurally similar to that of

HIV-1. To determine whether BLV NC was more functionally similar to that of HIV-1 or HTLV-1, a number of experiments were performed to provide a biophysical comparison of the three NCs. Fluorescence anisotropy was used to show that BLV NC binds to nucleic acids with an affinity much closer to that of HIV-1 NC. Analysis of data from FRET-based annealing assays reveals that the kinetic parameters of BLV NC-facilitated annealing were also very similar to results gathered using HIV-1 NC. Taken together, these results show that while BLV and HTLV-1 are from the same retroviral genus, processes that occur during replication may be different.

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HOXB9 is transcriptionally regulated by endocrine disrupting chemical, bisphenol-A

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HOXB9 is a homeobox-containing gene. HOXB9 plays critical roles in development of mammary gland, sternum as well as in regulation of renin which is associated with blood pressure control. HOXB9 is also critical for angiogenesis, cell-cycle progression and tumorigenesis. HOXB9 gene is also found to be transcriptionally regulated by estrogen (E2). Herein, we have investigated if HOXB9 expression is regulated by bisphenol-A (BPA). Our findings demonstrate that BPA induces HOXB9 expression in cultured human breast cancer cells (MCF7) as well as *in vivo* in the mammary glands of rat. Luciferase assay showed that estrogen-response-elements (EREs) at HOXB9 promoter are induced by BPA. Estrogen-receptors (ERs) and ER-coregulators such as MLL-histone methylases (MLL1 and MLL3) bind to the HOXB9 promoter EREs in the presence of BPA, modify chromatin (histone methylation and acetylation) and lead to gene activation. In summary, our results demonstrate that BPA exposure alters the epigenetic programming of the HOXB9 promoters leading to its endocrine disruption *in vitro* and *in vivo*.

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Conformational and configurational equilibria of a 2′-deoxyribosylurea DNA adduct

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2´-Deoxyribosylurea (urea) lesions form within DNA as a consequence of exposure to ionizing radiation from the cleavage of thymine by hydroxyl radicals. In addition, urea lesions may be formed from the conversion of 8-oxoguanine. Previous NMR studies of

urea lesions on the nucleoside level showed the equilibration of alpha (α) and beta (β) anomers on the 2´-deoxyribose ring. Here, we investigated a urea lesion within the single strand oligodeoxynucleotide 5´-(CTXA)-3´ (X=urea). Reversed phase HPLC revealed the presence of two species at a ratio of 1:1. NMR spectroscopy corroborated this finding along with identifying the two species. NOESY and TOCSY spectra were used to assign the resonances of the different nucleotides. NOESY spectra confirmed the identities of the two species as the α and β anomers of the urea lesion. In addition, TOCSY and one-dimensional spectra to observe coupling constants showed that the H1´ and NH amino protons of the urea lesion remained in the trans conformation regardless of the anomeric configuration. The interconversion of the α and β anomers was slow on the NMR timescale and the two configurations were observable as distinct spectral peaks. The presence of the α anomer may explain why the urea lesion blocks DNA replication. Supported by NIH grants CA-55678 (M. P. S), ES-009127 (A. K. B.), and ES-021762 (A. K. B.).

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A potentially vicious carcinogen: Profile of a cyclical reaction involving peroxochromium(IV) and glutathione

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Chromate is a carcinogen. The DNA damaging ability of chromate is considered the basis of its carcinogenicity. Oxygen and glutathione (GSH) are essential for its mutagenic and carcinogenic properties because in their absence, chromate is not able to cause DNA damage. Putative intermediates formed during the cytosolic reduction of chromate are believed to be the actual carcinogens. During the study of the potential participation of Cr(IV) in the DNA damaging process, we discovered a cyclical or catalytic behavior when the system comprised by aqua-bis-(peroxo)-ethylenediamine-chromium(IV) (**I**) and glutathione was characterized at pH 7.0.[1] Here we provide additional evidence, including, HPLC, UV, EPR, ESI-MS, and cyclic voltammetry. The stoichiometric studies revealed that for the complete reduction of **I**, nine equivalents of GSH are needed. The electrochemical experiments showed participation of intermediates with reduction potentials that shifted as the reaction progressed and were similar to the reduction potential of **I**. Hydroxyl radicals were not detected in the EPR experiments; however, the formation of glutathione thyil radicals was demonstrated using the spin trap DEPMPO. Poly glutathionato chromium(III) complexes were characterized with ESI-MS among the products. This was consistent with earlier[1] assignment of intermediates. A mechanism arises in which GSH triggers the oxidation of the Cr(IV) to Cr(VI) by one peroxo unit. The Cr(VI) species is reduced by GSH molecules to Cr(IV) via Cr(V) intermediates and the cycle repeats. The implication is for a perennial repetition of this cycle and the concomitant danger to the genetic material if the process occurs *in vivo*.

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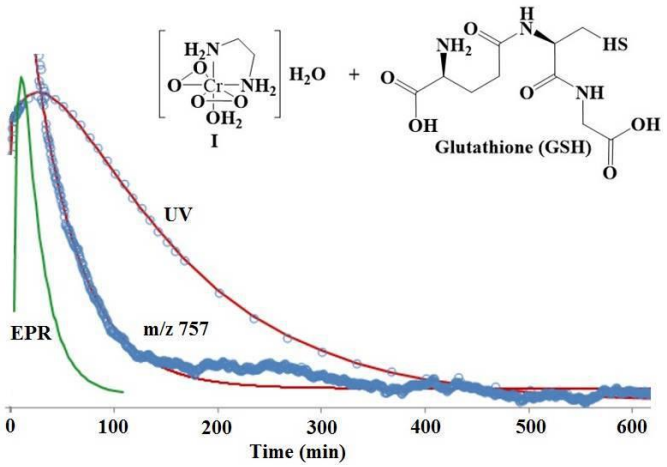

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Development of an amyloid-beta protofibril-selective antibody

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Senile plaques, composed of insoluble amyloid-β (Aβ) fibrils, are one of the most outstanding features in the Alzheimer's disease (AD) brain. Despite this prominence, many studies have indicated that soluble precursors to fibrils may be more pathologically important to the cause of the disease. Numerous reports have characterized, and established the biological activity of soluble protofibrils formed by the non-covalent oligomerization of Aβ monomers. Our own published findings have demonstrated significantly higher microglia cytokine secretion by protofibrils compared to either fibrils or monomers. Due to the importance of this soluble aggregated Aβ species, we sought to develop an antibody that selectively recognizes protofibrils over other Aβ species. Protofibrils were prepared, isolated, and characterized prior to immunization of two rabbits. Testing of the collected serum indicated a strong affinity for Aβ protofibrils. Using an indirect ELISA, antibody titers were found to be high (25,000 dilution) initially in rabbit #1 and remained so through multiple immunizations and bleeds. Serum from rabbit #2 displayed less affinity initially, but achieved significant titers over the course of the treatment (25,000 dilution). The anti-serum was highly selective for Aβ protofibrils over Aβ monomers and also displayed notable selectively over Aβ fibrils. Selectivity was confirmed using both ELISA and dot blot methodologies. The newly-developed antibody may have potential diagnostic and therapeutic uses in AD tissue and patients.

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Effects of olive metabolites on DNA cleavage mediated by human topoisomerase II

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Topoisomerase II is an essential enzyme that plays important roles in genome maintenance. To carry out its physiological functions, the enzyme generates transient double-stranded breaks in DNA. Thus, while essential to cell survival, topoisomerase II has the potential to fragment the genome. Beyond its critical cellular functions, topoisomerase II is the target for a number of widely prescribed anticancer drugs that act by increasing levels of enzyme-mediated DNA strand breaks. Many of these “topoisomerase II poisons” are derived from natural sources. Identification and characterization of topoisomerase II poisons from natural sources can provide novel drug scaffolds. Therefore, a series of water-soluble Mediterranean plants extracts were screened for activity against human topoisomerase IIα. *Phillyrhea latifolia* L., a member of the olive tree family, enhanced topoisomerase IIα-mediated DNA cleavage ~7-fold. *P. latifolia* L. contains a number of phenolic metabolites, including oleuropein, hydroxytyrosol, tyrosol, verbascoside, and caffeic acid. These compounds are antioxidants that are associated with a number of health benefits. Oleuropein, hydroxytyrosol, and verbascoside enhanced topoisomerase IIα-mediated DNA cleavage ~4-fold. In addition, several of these compounds displayed hallmark characteristics of covalent topoisomerase poisons. First, the ability of the metabolites to poison topoisomerase II was significantly enhanced in the presence of an oxidant, but was abrogated by a reducing agent. Second, the metabolites required the N-terminal region of topoisomerase IIα to enhance DNA cleavage. Third, these metabolites inhibited topoisomerase IIα activity when incubated with the enzyme prior to the addition of DNA. Finally, phenolic olive plant metabolites retained the ability to act as topoisomerase IIα poisons in complex dietary herbal formulations such as commercial olive leaf extract and olive oil. These results strongly suggest that olive plant metabolites can act as dietary topoisomerase II poisons. Studies with these compounds may provide a platform for developing new anticancer and chemopreventative therapies.

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Effect of glass color on IBU perception and IBU measured value on beer exposed to UV light

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It is generally accepted that the color of glass used to store beer can have an effect on taste as a result of isomerized hop α acids being converted to 3-methyl-2-butene-1-thiol upon exposure to UV radiation. This taste is colloquially termed “skunky” which is an appropriate term given that skunk spray also contains thiols. The purpose of this study

was to determine the relationship between bottle glass color and IBU perception via sensory judges and IBU measured value. In order to accomplish this a commercial beer was placed in green, clear or brown colored bottles and exposed to a black light for 0, 1, 5, 10, 20 or 60 minutes. Beer was then analyzed for IBU value using UV-Visible spectrometry and an organic extraction method. Sensory judges were then asked to rate some of these time exposed beers based upon overall taste and bitterness. Clear glass demonstrated the largest decrease in measured IBU which was confirmed with some sensory judge data.

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Promiscuity of CDO with alternative metals

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The mammalian enzyme cysteine dioxygenase (CDO) is a mononuclear iron enzyme that catalyzes L-cysteine to L-cysteine sulfinic acid. The iron is weakly coordinated by 3-His residues, and a thioether Cys-Tyr crosslink is located within 3.3Å of the iron center [1]. In wild-type CDO the crosslink exists in a heterogeneous mixture of crosslink and noncrosslinked species. Recent kinetic studies of rat CDO suggest the Cys-Tyr crosslink enhances catalytic activity ~10-fold [2]. In purified recombinant wild-type CDO various metals have been shown to occupy the active site [1,3]. However, there is little information on whether other metals can serve as a comparable substitute for iron.

Purification of homogeneous noncrosslinked wild-type CDO that contained a metal-free active site, was generated by adding a metal chelator during protein expression [2]. Preliminary studies show that metal-free CDO is unable to form the crosslink in the presence of L-cysteine. When the enzyme is stoichiometrically reconstituted with iron, CDO is able to form the homogeneous crosslink in the presence of L-cysteine. The ability of CDO to form the Cys-Tyr crosslink was evaluated by replacing the iron with different metals. Kinetic studies monitored the enzymes ability to utilize dioxygen correlated with the formation of the cysteine sulfinic acid product. Investigating the ability of CDO to utilize alternative metals may help in elucidating the mechanistic features of crosslink formation and product formation.

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Investigation into the potential dual role of SirC in the biosynthesis of tetrapyrroles in *Methanosarcina acetivorans* C2A

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Methanosarcina acetivorans C2A is a methanogenic archaeon that utilizes tetrapyrroles such as coenzyme F430, cobalamin, and heme for energy production. These cofactors

each contain distinct metal ions (nickel, cobalt, and iron respectively), which are thought to be inserted into the biosynthetic intermediate sirohydrochlorin by a unique chelatase. However, the genome of *M. acetivorans* C2A contains only two class II chelatase homologs. In addition, *M. acetivorans* C2A contains only a single precorrin 2 dehydrogenase (SirC) homolog, which is likely responsible for the formation of sirohydrochlorin for the biosynthesis of each of these cofactors. SirC, which is encoded within a putative alternative heme biosynthetic (*ahb*) gene cluster devoid of a chelatase homolog, is homologous to the bifunctional dehydrogenase-ferrochelatase domain of *Escherichia coli* siroheme synthase. Thus, it is possible that SirC is responsible for both sirohydrochlorin production and iron insertion during the biosynthesis of heme in *M. acetivorans* C2A. An investigation into this potential dual function of SirC is currently underway.

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Synthesis and antimicrobial studies of pyrazole derivatives as potent antibacterial agents

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Antibiotic resistance to infection has become a worldwide problem in recent years. According to the latest CDC report more than two million people are infected every year with antibiotic-resistant infections and at least 23,000 are dying as a result of these diseases in the US alone. One of the four guidelines recommended by CDC to combat antibiotic resistance is promoting the development of new antibiotics and developing new diagnostic tests for resistant bacteria. Pyrazoles (1,2-diazole) are among the privileged heterocycles in drug discovery. Many pyrazole derivatives have been approved as drugs to treat various kinds of diseases. In our efforts to get potent antimicrobial agents, we have synthesized more than 50 pyrazole derivatives to test against various bacteria. We have used efficient synthetic methods and inexpensive reagents to rapidly generate a library of new molecules. These new molecules have been tested against both Gram-negative and Gram-positive bacteria. Many compounds have shown zones of inhibition as large as 26 mm (1 micromole per disc) against *Staphylococcus aureus*, a gram-positive bacterium. Two of these compounds have shown potent activity against both gram-negative and gram-positive bacteria. Our synthetic and biological studies of these 50 compounds will be presented.

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Anti-metastatic effects of thiopurine prodrugs on prostate cancer by targeting Rac1

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Rac1 – a protein that belongs to a family of small GTPases – is involved in various cellular signaling events, such as cell migration. We showed that Rac1-dependent metastasis of DU-145 prostate cancer cells can be blocked by thiopurine prodrugs or 6-TPs (GTP analogs). We determined that this is because 6-TPs target the redox-sensitive Rac1 Cys^{18} to form a Rac1-6-TP disulfide adduct. The goal of our work is to detail the mechanism of Rac1 inhibition by 6-TPs in the presence of redox agents, so as to provide therapeutic insight into prostate cancer. By using flow cytometry, we screened an apoptotic feature of DU-145 cells associated with commercially available 6-TPs that encompass 6-TG, AZA, and 6-MP. We also used the Boyden Chamber assay to evaluate the effects of 6-TPs on the motility of DU-145 cells in the presence and absence of a redox agent such as $^{\bullet}NO_2$. We found that a concentration as low as 0.1 μM of 6-TG does not significantly cause the apoptosis of but evidently decrease the motility of DU-145 cells. $^{\bullet}NO_2$ enhances the 6-TG-mediated motility diminution of DU-145 cells. These results open a possibility of a novel therapeutic application of 6-TPs in combination with a redox agent that could potentially reduce metastasis of DU-145 cells, and thus increase survival of prostate cancer patients.

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Chemical analysis of chicken bone during diagenesis in soil

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Chicken bone consists of approximately 70% inorganic material and 30% organic material. The inorganic material, hydroxyapatite, is composite material that contains calcium and phosphate. Hydroxyapatite links to the organic material, collagen, which gives bone its strength. Collagen is the predominant organic material with other osteo-based proteins and lipids helping to support bone. When a bone is placed within soil and begins to decompose, this process is known as diagenesis. Diagenesis effectively alters the quantities of the organic and inorganic materials within bone by soil exchanging chemical components with bone and vice versa.

In this study, the diagenesis processes over a span of three months are looked at by examining the inorganic layer and organic layers by analytical techniques. Chicken samples were buried at the Southeast Texas Applied Forensic Science (STAFS) Facility in Huntsville, Texas, and one was exhumed every two weeks. Soil and chicken bone samples were analyzed for metal ions by Inductively Plasma Optical Emission Spectroscopy (ICP-OES). The organic matrix of bone was examined by an Organic Elemental Analyzer. Preliminary analyses of soil from pre-existing human burial sites at the STAFS facility found that there was a significant difference between soil in which diagenesis had occurred and virgin soil consistent existing literature. Finally, the ratio of inorganic versus organic materials in bone was examined by Infrared and Raman spectroscopy. In conclusion, this study provides preliminary analysis of diagenesis. Future studies, will identify specific organic compounds that migrate or change during diagenesis, like GC/MS of bone lipids that may migrate into soil.

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Assay development for the screening of antimicrobial peptoids

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Peptoids are a unique type of peptidomimetic consisting of an N-substituted glycine backbone. Benefits of peptoids include large chemical diversities and increased stability towards proteolysis, making them ideal as potential therapeutics. With the emergence of new strains of drug-resistant bacteria, development of quick and efficient ways to identify antimicrobial compounds becomes one of interest. The research presented here focuses on the use of solid-phase synthesis methods, combinatorial library design, and optimization of bacterial lawn based screening to find promising antimicrobial peptoids. Identication of library candidates is done by releasing the peptoid compounds in a high-throughput fashion from solid-phase Tentagel beads and visualizing zones of clearance surrounding the bead where there is an absence of bacterial growth. Mass spectrometry (MS) is then utilized to sequence the peptoid of interest from the bead, which will then be re-synthesized and tested against a variety of bacterial and mammalian cells for specificity.

Oxysterol-binding protein family (OSBP/ORP) ligand binding and natural product drug development

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A structurally-diverse class of potent anti-cancer natural product compounds – cephalostatin 1, OSW-1, ritterazine B and schweinfurthin A –exert their anti-proliferative activity through binding to members of the oxysterol-binding protein (OSBP) and OSBP-related protein (ORP) family. Based on their shared OSBP/ORP cellular targets, these natural products are referred to as the ORPphilins. The ORPphilin compounds have been shown to bind with high affinity (K_i values = 20-70 nM) to two members of the OSBP/ORP family; OSBP and ORP4. The cellular function(s) of the OSBP/ORPs are yet to be fully determined, but some of the family members apparently serve as sterol sensors and/or sterol transporting proteins. There are twelve different OSBP/ORPs in humans that show very different tissue distribution patterns. The expression levels and function of many different OSBP/ORPs have been implicated in in many disease-states, including different cancers, diabetes and cardiovascular disease. Despite their connections to disease, the OSBP/ORPs remain understudied with respect to their ligand binding and resulting biological function. The OSBP/ORP have been shown to experimentally bind oxysterols and phospholipids, but the physiological ligands for the OSBP/ORP members have not been identified. We have launched a systematic study of class-wide OSBP/ORP ligand binding, which includes understanding the binding interactions of the OSBP/ORPs with the ORPphilin natural products. Our 96-well OSBP/ORP ligand binding assay allows screening of many ligands against the complete panel of OSBP/ORP proteins, and the screen will incorporate a diverse set of oxysterols, phospholipids and ORPphilin-derived compounds. Through these comprehensive binding assays and subsequent biochemical studies, we can identify putative physiological ligands for individual OSBP/ORP family members. We are also developing natural product-derived anti-cancer compounds, based on the ORPphilin compound OSW-1, that selectively target the anti-cancer target protein ORP4.

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Characterizing the canonical macrodomain of the bat coronavirus HKU4 nonstructural protein 3 (nsp3)

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Coronaviruses are positive sense, single stranded RNA viruses that are responsible for upper respiratory diseases such as severe acute respiratory syndrome (SARS) and Middle East respiratory syndrome (MERS). While several proteins have a role in the infectious cycle of coronaviruses, we are focused on a class of proteins called macrodomains. These domains are associated in the maturation of several nonstructural proteins (nsp) and also have been known to bind ADP-ribose, a signaling macromolecule involved DNA repair and many other cellular processes. Particularly, we have predicted a conserved macrodomain fold from bat coronavirus HKU4 with the aim to characterize and compare with other known macrodomains.

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Novel exogenous agonist design for caseinolytic protease

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An emerging field for the treatment of bacteria is targeting protein biosynthesis, of which proteases play a pivotal role. The importance of energy-dependent proteases is homologous to that of molecular chaperones: they are imperative in bacteria for the “spring cleaning” needs of the cell, eradicating short-lived, improperly folded, and damaged proteins. In general, these energy-dependent proteases consist of two portions: a proteolytic chamber where proteins enter to be degraded and an ATPase gatekeeper that selectively allows the passage of proteins for degradation at the expense of ATP hydrolysis. Caseinolytic protease P (ClpP) is a highly conserved, tetradecameric chamber protease in bacteria such as *Escherichia coli*, *Bacillus subtilis*, and *Staphylococcus aureus*, responsible for a large proportion of bacterial protein degradation. Recent literature has shown that acyldepsipeptide 1 (ADEP1) binds to ClpP in the hydrophobic clefts between the monomers of the heptameric ring, doubling the size of the axial pores from ~10Å to ~20 Å, allowing unregulated protein degradation to occur within the bacterial cell. This uncontrollable protein degradation serves as a novel and promising target for an exogenous agonist to function as an antibiotic. *In silico* screening of over 100,000 compounds was done inside the ClpP crystal structure (3MT6) for *E. coli* to identify the possible lead compounds presented herein along with their devised synthetic approaches. Compounds were then ordered and evaluated.

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Association between volatile organic compounds and microbes present during the decomposition of a cadaver

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The ability to identify volatile organic compounds (VOCs) from cadavers during decomposition can lead to newer advancements in forensic science. During decomposition, larger biological macromolecules are broken down into their basic components and some VOCs are intermediates of decomposition. Once the processes of the living body stop, enzymes will go unchecked causing cells to be lysed from the inside out, a process known as autolysis. This destruction of the cells provides nutrients for the growth of microbes that are already present or are ushered in from the external environment. VOCs samples were taken from decomposing store-bought chickens and human cadavers via solid-phase microextraction (SPME) and two cotton swabs were used to collect microbes. The cotton swabs were contained in two separate tubes, one for the mouth area and one for the belly region of the cadavers. The analysis of the samples was conducted by gas chromatography-mass spectrometry for the VOCs and the cotton swabs were sent to Baylor College of Medicine for sequencing via PCR. The mass spectra of VOCs were identified and confirmed utilizing the NIST08 database, AMDIS, and Met-IDEA. Any unknown structures of these compounds that were required were identified using ChemSpider. All statistical data discussed was calculated SPSS to find the probability statistics between the two, VOCs and microbes. Using the amount of microbes present and time lapse as a basis, a comparative analysis was performed to identify a possible link between VOCs detected and microbes present during the decomposition process.

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Isothermal titration calorimetry of *Ceriporiopsis subvermispora* bicupin oxalate oxidase

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Isothermal titration calorimetry (ITC) may be used to determine the kinetic parameters of enzyme catalyzed reactions in spectrophotometrically transparent solutions. We report here the use of the multiple injection method of ITC to characterize the catalytic properties of oxalate oxidase (OxOx, E.C. 1.2.3.4) from *Ceriporiopsis subvermispora* (CsOxOx). Oxalate oxidase is a manganese dependent enzyme that catalyzes the oxygen-dependent oxidation of oxalate to carbon dioxide in a reaction that is coupled with the formation of hydrogen peroxide. CsOxOx is the first bicupin enzyme identified that catalyzes this reaction. The multiple injection ITC method of measuring OxOx activity involves continuous, real-time detection of the amount of heat generated (dQ) during catalysis, which is equal to the number of moles of product produced times the enthalpy of the reaction (ΔH_{app}). Determination of the kinetic parameters of a reaction using this method, therefore, requires two experiments 1) determination of the enthalpy of the reaction from the complete conversion of substrate to product, and 2) determination of the differential power effects from the continuous conversion of substrate to product. Steady-state kinetic constants using oxalate as the substrate determined by multiple injection ITC are comparable to those obtained by a continuous spectrophotometric assay in which H_2O_2 production is coupled to the horseradish peroxidase catalyzed oxidation of 2,2'-azinobis-(3-ethylbenzthiazoline-6-sulphonic acid) and by membrane inlet mass spectrometry.

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Liposomal encapsulation of UV filters

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The unique property of the liposomes can be used for the encapsulation of photoprotector molecules. In our study we investigated twelve different lipid compositions from L-α-phosphatidylcholine (DPPC), Cholesterol (CHOL), 1,2-Di-O-Octadecenyl-3-Trimethylammoniumpropane chloride salt (DOTMA) and 1,2-Dioleoyl-sn-glycero-3-phosphocholine (DOPC) for the encapsulation of two UV filters - octocrylene and avobenzone. The multilamellar vesicles (MLV) were prepared by thin-film hydration technique. Small unilamellar vesicles (SUV) were prepared from MLVs using extrusion through polycarbonate filters with a pore size of 400 and 200 nm.
The encapsulation efficiencies for the UV filters of the MLV and SUV samples were determined as $EE\% = (Abs_i - Abs_f)/Abs_i \times 100$, where Abs_i and Abs_f are the absorbance of the UV filter containing hydrating solution and filtered outer phase of MLV and SUV, respectively. As UV filters possess lipophilic character, the liposomal encapsulations resulted in high encapsulation efficiency values – only slightly depending on the composition and lamellarity of lipid vesicles. It can be supposed that UV filter molecules are localized between the fatty acid chains in the liposomal bilayer. As a further step we plan the co-encapsulation of photosensitive drugs with the UV filter molecules in order to increase the photostability of selected photolabile drugs.
The study was funded by the Robert A. Welch Foundation (X-0011) at Sam Houston State University

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P450BM-3 enzyme activity on acyl homoserine lactone (AHL) and thiolactone (AHTL) quorum sensing signals

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Quorum Sensing (QS) is a regulatory mechanism of gene expression performed by bacteria, depending on their population density. Acyl Homoserine Lactones (AHLs) are molecules which are produced by certain bacteria cells as quorum signals and identified by special receptor molecules (LuxR, for example). Acyl homoserine acylase and acyl homoserine lactonase are enzymes that destroy the quorum sensing activity of bacteria by hydrolyzing AHLs and this ability is known as quorum quenching. P450BM-3 (CYP102A1) is a natural enzyme produced by *Bacillus megaterium.* Its activity is quite similar to the activity of human microsomal P450 enzymes and it is capable of very efficient oxidation of AHLs. P450BM-3 enzyme has been prepared using DH5αF′IQ *E.coli* transformed with pProEX-1 vector plasmid with P450BM-3 gene. Different type of AHLs and Acyl Homoserine Thiolactone (AHTLs) molecules such as β-oxo-C12-HSL, β-oxo-C12-HCTL, β-oxo-C13-alkynyl-HSL, β-oxo-alkynyl-C13-HCTL, C11-alkynyl-HSL and C11-alkynyl-HCTL have been synthesized and enzyme kinetics characterized, calculating V_{max}, K_M and k_{cat} values to establish the efficiency of the enzyme on the

substrate molecules. The ability P450BM-3 to quench AHLs and AHTLs could potentially be used for the synthesis of novel drugs to control bacterial infections.

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Application of golden gate assembly method to combine the catalytic core of luciferase enzyme and fluorescent protein in pETDuet-1 cloning vector to detect protein-protein interactions

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Bioluminescence Resonance Energy Transfer (BRET) occurs between a bioluminescent donor molecule and a fluorescent acceptor molecule located in close proximity. Excited state energy created by the bioluminescent donor molecule is absorbed by the fluorescent acceptor and released as fluorescence. Luciferase enzyme extracted from the dinoflagellate *Pyrocystis fusiformis* acts on the substrate luciferin (a tetrapyrrole) to create blue light. The catalytic core of luciferase, which is responsible for catalyzing luciferin oxidation, is combined with Yellow Fluorescent Protein (YFP) in order to observe a BRET effect. Bioluminescent donor and fluorescent acceptor molecules can be attached to proteins and BRET can be observed when both proteins are close together, since close proximity of the donor and acceptor molecules is a requirement for BRET effect. The Golden Gate assembly method uses type IIs restriction enzymes and allows scar-less recombination. Therefore, integration of YFP and catalytic core genes into pETDUET-1 cloning vector by Golden Gate Assembly methods to express the polypeptide provide a method to detect protein-protein interactions.

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Extraction of antibacterial compounds produced by *Pseudomonas* and *Serratia* species, and induction of antibiotic production by bacterial competition

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New avenues for antibiotic drug discovery are in demand due to increasing emergence of drug-resistant bacterial pathogens. Even as multidrug resistant bacteria become an increasing threat to global health, the discovery of new antibiotics with novel mechanisms of action has slowed over the last 20 years. The use of mixed cultures of bacteria is a relatively new method shown to induce the production of cryptic antibacterial natural products, many of which may represent novel compounds that can be isolated for further research. Here, we explore how co-culturing of diverse natural bacteria may influence expression of secondary metabolite antibiotics unseen under standard laboratory conditions. Using a high throughput assay against *Staphylococcus aureus*, pure bacterial cultures isolated from pitcher plants in western North Carolina were evaluated for their ability to produce antibiotic compounds independently or in co-culture with other species. Antibiotic producers, including *Pseudomonas* and *Serratia* species, have been isolated and identified and active fractions have been extracted and

purified via preparative thin layer chromatography. Co-culture screening has identified a number of bacterial pairs with enhanced antibiotic activity, from which active fractions have additionally been extracted. Characterization of the antibacterial compounds using ^{1}H and ^{13}C NMR, IR, and mass spectrometry is ongoing.

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Investigating post-translational modifications in cysteine dioxygenase

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Cysteine dioxygenase (CDO) is a mononuclear iron containing enzyme that catalyzes the oxidation of L-cysteine to L-cysteine sulfinic acid. CDO contains a unique thioether crosslink located in the active site between Cys93 and Tyr157 adjacent to the iron center. The crosslink has been shown to increase catalytic activity ~10-fold compared to non-crosslinked wild-type CDO.[1] The role of the crosslink in catalysis has been proposed to aid in substrate binding or in stabilizing the iron center.[2] A cysteine (Cys164) residue is located ~10 Å away from the crosslink at the opening of the active site. Interestingly, the precariously placed Cys164 does not form a disulfide bond with any cysteine residues, and exists as a free thiol.
The three-dimensional structure of mammalian CDO showed electron density near the metal center that was attributed to Cys substrate coordination. However, further evaluation revealed that the excess electron density was a cystine formed between Cys164 and exogenous cysteine.[3] Substitution of Cys164 to alanine did not affect the metal content but the variant had a 20% decrease in catalytic activity.[2] Variants of Cys164 were generated to further investigate the role of this residue in crosslink formation and/or cysteine oxidation. Following purification, the metal content of each variant was quantified to determine if Cys164 plays a role in stabilizing the iron center. The ability of the Cys164 variants to form the homogenously crosslinked isoform was initially investigated, and coupling experiments were performed to correlate the amount of oxygen consumed with the amount of cysteine substrate oxidized. The results from these studies provide valuable insight on the mechanistic role of Cys164 in CDO.

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Isolation and characterization of natural product antibiotics produced by *Sarracenia purpurea* pitcher plant bacteria, and induction of antibiotic production during co-culture with *Streptomyces griseus* and other inducer strains

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The emergence of multidrug resistant bacteria has necessitated the discovery of novel antibiotics. The majority of these antibiotics are natural products, and bacterial co-culture has been shown as an effective means for stimulating antibiotic production in microorganisms. *Streptomyces griseus* strains not only produce antibiotics such as streptomycin, farinamycin, and faeriefungin, but also have been shown to induce antibiotic production in other microorganisms. Using this known species and a library of unknown bacteria isolated from *Sarracenia purpurea* pitcher plants in western North Carolina, a methodology for bacterial co-culture screening was developed to quickly identify bacteria that produce antibiotics alone or in co-culture. Then, the single and co-culture producers were scaled up to liter volumes, and the antibiotics were isolated using extraction and preparative thin layer chromatography. To date, multiple antibiotic compounds have been isolated, and work is ongoing to improve the production yield of each and to fully characterize these antibiotics by ^{1}H NMR, ^{13}C NMR, mass spectrometry, and IR spectroscopy.

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Phosphorylation of serine, threonine, and tyrosine residues of the CXCR3 receptor establish a barcode that regulates distinct downstream pathways

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GPCRS, G protein-coupled receptors, represent the largest class of cell membrane receptors targeted by drugs today. Upon agonist stimulation, these receptors are phosphorylated by intracellular kinases, including G protein receptor kinases (GRKs). Literature shows that phosphorylation of specific serine, threonine, and tyrosine residues subsequently leads to G protein and b-arrestin recruitment to serine, threonine, and tyrosine residues on the C-terminal of the receptor. A central question that remains is which specific residues are phosphorylated in response to different ligands, and how phosphorylation at distinct sites result in biased protein and b-arrestin signalling. In this research, serine and threonine residues on the C-terminus of the CXCR3 receptor, implicated in autoimmune and inflammatory diseases, were mutated to alanine to investigate the specific residues on the C-terminus that are phosphorylated upon treatment with the ligands CXCL11 (an endogenous ligand) and VUF10661 (b-arrestin biased synthetic ligand). Site-directed mutagenesis was used to create mutated receptor constructs, and b-arrestin and G-protein recruitment & receptor internalization was measured using bioluminescence resonance energy transfer-based assays. Data show that GRK phosphorylation creates a “barcode” on the tail end of the receptor, leading to differential downstream signalling. An understanding of such a barcode and its role in distinct intracellular signalling may ultimately present new opportunities for therapeutic drug screening and discovery.

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Investigating metabolic mechanisms of bacterial CDO

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Cysteine dioxygenase (CDO) is a mononuclear iron enzyme that catalyzes the oxidation of L-cysteine to L-cysteine sulfinic acid. The CDO metal center is coordinated by 3-His residues and deviates from the typical 3-His/1-Glu metal coordination motif found in many members of the cupin superfamily. The Glu is replaced by Cys in CDO resulting in a thioether crosslink formed between residues Cys93-Tyr157. A heterogeneous mixture of crosslinked and noncrosslinked isoforms are present in purified recombinant mammalian CDO. Previous studies have shown that this crosslink stabilizes the iron center and increases activity.[1] Putative CDO enzymes have been identified in several bacterial organisms. These enzymes typically have less than 30% amino acid sequence identity with mammalian CDO, and the Cys involved in crosslink formation is replaced by a Gly in bacteria.
The role of CDO in bacteria is currently not known. In mammals, cysteine sulfinic acid is either decarboxlyated to hypotaurine and then oxidized to taurine or dissimilated by aspartate aminotransferase into pyruvate and sulfite.[2] However, cysteine sulfinic acid decarboxylase has not been identified in bacteria, making it unlikely that bacterial CDO generates taurine. Therefore, the substrate specificity and inherent mechanism of bacterial CDO are not clearly defined. Mammalian CDO was modified to resemble the bacterial enzyme by substituting Cys93 with Gly (C93G CDO). The amount of iron bound to C93G CDO was determined to identify if the Cys to Gly substitution disrupted metal coordination. Coupled assays were used to correlate the amount of oxygen consumed to the amount of L-cysteine sulfinic acid formed. The metal environment of the C93G CDO variant was evaluated by EPR spectroscopy to provide insight on the native and substrate bound oxidation state. The mechanistic properties of the glycine variants were compared to bacterial CDO homologues.

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Rh(II)-catalyzed protein modification as a method for determining ligand affinity

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Recent work in our group has shown that designed Rh(II) metallopeptides can allow clean single modification of protein SH3 domains. Using this methodology, an assay for determination of ligand affinity is being developed. Titration of an inhibitor into a series of modification reactions allows production of an IC_{50} curve, and by extension, calculation of ligand K_d. This affinity assay requires only MALDI-MS as a read-out, and may offer a convenient option to complement standard techniques such as SPR and ITC. Initial studies with Src family kinase SH3 domains will be discussed.

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Towards a new class of inhibitors of cysteine proteases: Cruzain and falcipain-2

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Cysteine proteases are a group of enzymes that play an important role in the pathology caused by parasitic organisms. Cruzain is a critically-important cysteine protease found in *Trypanosoma cruzi*, the causative agent of Chagas's disease. In kind, falcipain-2 and -3 are related cysteine proteases that are important in the life cycle of Plasmodium falciparum, the protozoan that causes malaria.[1] Accordingly, the development of rational inhibitors for these cysteine proteases could potentially provide new therapeutic agents for treating diseases such as Chagas's disease,[2] also called South American trypanosomiasis and malaria [3]. McKerrow *et al* has identified a vinyl sulfone containing-compound, K777 (N-Mpip-Phe-HPhe-VSPh) as a potent inhibitor of both cruzain and falcipain-2.[4] K777 employs an electrophilic vinyl sulfone moiety in place of the scissile bond of a peptide substrate, which renders an electrophilic group that forms an irreversible covalent bond, at high potency, with the active-site cysteine residue of cruzain and falcipain-2. However, the progression of K777 as a potential drug has been thwarted by toxicity, which may arise from its irreversible action or lack of selectivity. We describe here our efforts to develop other types of peptidomimetic covalent inactivators of these enzymes which may be reversibly covalent, in which we explore other types of electrophiles by incorporating substituted heterocycles, which are conjugated to a vinyl group with a dipeptide core. The synthesis of the inhibitors and their cruzain, falcipain-2 enzymes inhibition will be discussed in this presentation.

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Chemical composition of *Blumea lacera* essential oil from Nepal: Biological activities of the essential oil and (Z)-lachnophyllum ester

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The essential oil from the aerial parts of Blumea lacera collected from Biratnagar, Nepal, has been obtained by hydrodistillation and analyzed by gas chromatography – mass spectrometry. The major component from the oil, (Z)-lachnophyllum ester, was isolated by preparative silica gel chromatography. B. lacera oil was dominated by (Z)-lachnophyllum ester (25.5%), (Z)-lachnophyllic acid (17.0%), germacrene D (11.0%), (E)-β-farnesene (10.1%), bicyclogermacrene (5.2%), (E)-caryophyllene (4.8%), and (E)-nerolidol (4.2%). Also detected in the oil were (E)-lachnophyllic acid (3.3%) and (E)-

lachnophyllum ester (1.7%). (Z)-lachnophyllum ester exhibited cytotoxic activity against MDA-MD-231, MCF-7, and 5637 human tumor cells, as well as antibacterial and antifungal activity.

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Proteins interacting with protein kinase C highlight roles in filamentous fungal cell wall synthesis

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The long-term goal of our research is to advance understanding of hyphal growth and cell wall metabolism in filamentous fungi. Recently our work has focused on proteins that localize to sites of cell wall synthesis, namely growing cell apices (hyphal tips) and forming crosswalls (septa). In our model organism *Aspergillus nidulans*, protein kinase C (PkcA) is one such protein. PkcA localizes to growing hyphal apices and septation sites and is involved in a cell wall integrity (CWI) pathway that is activated when the organism experiences cell wall stress. Here we report our work towards identifying proteins that physically interact with PkcA and to determine their roles in growth and CWI. Septum formation in fungi involves assembly of a contractile actomyosin ring (CAR) at the septation site. The formin SepA catalyzes formation of actin cables during CAR formation and, similar to PkcA, localizes to hyphal tips and septation sites. Here we used bimolecular fluorescence complementation and determined that SepA and PkcA physically interact at both hyphal tips and septation sites. In addition, a mutation in the *sepA* gene (*sepA1*) blocks PkcA::GFP (green fluorescent protein) localization to septation sites, but not hyphal tips. Overexpression of *pkcA* in the *sepA1* mutant strain does not complement the strain's hypersensitivity to CFW, but overexpression of *sepA* in a hypersensitive strain bearing a mutation in *pkcA* does. To further flesh out the network of proteins that partner with PkcA, we screened a selection of strains expressing single mutated proteins for hypersensitivity to CFW and identified three more hypersensitive strains: acyl-CoA-dependent ceramide synthase *barA1*, actin *actA1*, and the rho-like GTPase *rho4*. To date, we have determined that overexpression of PkcA complements CFW hypersensitivity in the *barA* mutant strain, and we continue to explore potential functional interactions between both actin and Rho4 and PkcA using this method.

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Optimizing expression of *Pf*PK9

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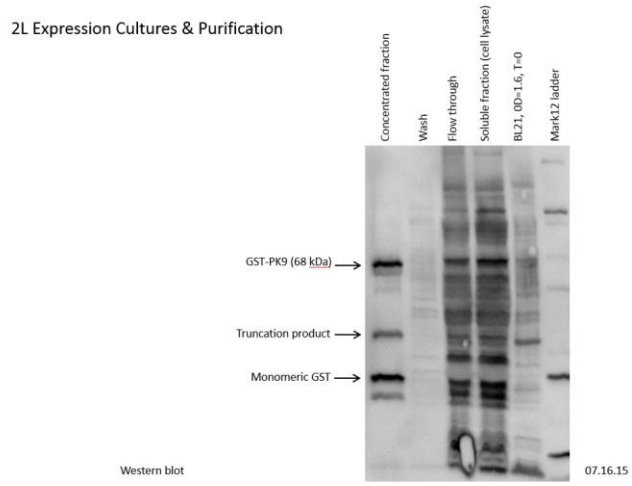
Malaria, a lethal mosquito-borne disease caused by the *Plasmodium* parasitic protozoan, afflicts hundreds of millions of people every year across the globe. In humans, the parasite goes through an obligatory liver stage, which leads to the development of blood infective merozoites. Infection of red blood cell causes the clinical

symptoms of malaria. The emergence of drug-resistance to current antimalarials such as artemisinin combination therapy warrants the discovery of novel molecular targets for developing new therapeutics. Protein kinases are attractive drug targets because they are critical proteins in the regulation of essential biological processes. Recent genetic analyses have identified several critical kinases essential for *P. falciparum* parasite, including the atypical protein kinase 9 (PK9). However, the functions of these kinases remain largely unknown. The *P. falciparum* PK9 (*Pf*PK9) is an attractive antimalarial target because it has no homology in humans. Here, I expressed and purified *Pf*PK9. Specifically, I optimize the expression of GST-tagged *Pf*PK9 in bacterial cultures by testing different conditions including bacterial strain (BL21 vs. BL21+), temperature, culture media, induction time and concentration of the protein inducer, IPTG. I then purified the expressed *Pf*PK9 for *in vitro* studies. The goal of this project is to obtain a purified *Pf*PK9 that will be used to *in vitro* studies and begin crystallization studies to further probe its biological functions.



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Analysis of amino acid residues predicted to be essential for loading of T7 DNA polymerase on to a primase-helicase ring

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Research in our laboratory is focused on understanding how genetic information is copied and passed on from generation to generation by a process known as DNA replication. Multiple proteins of specialized function must transiently assemble and communicate in order to rapidly and accurately copy DNA. We study replication in bacteriophage T7, a virus that infects *E. coli*, because it is a relatively simple model system that recapitulates all essential activities seen in more complex systems in just

four proteins. Recently our lab determined a crystal structure of an electrostatic interaction between T7 primase-helicase and DNA polymerase, with the acidic C-terminal tail of the T7 primase-helicase binding to a basic patch on the polymerase. The C-terminal tail of the primase-helicase contains a phenylalanine residue that is essential for binding polymerase, and our structure reveals that this Phe binds to a hydrophobic cleft near the basic patch. To validate our crystal structure we are making point mutations along the basic patch of the polymerase as well as the hydrophobic pocket to disrupt the observed interactions. Using *in vivo* methods such as phage complementation we are able to directly test the effects of these mutation in the virus during infection of *E. coli*. Our preliminary results show that the mutations F487A, R687A and I569A show substantially smaller plaques compared to wt, indicating that the virus is heavily impaired in DNA replication. In the crystal structure R590 of the polymerase makes a critical contact with the C-terminal tail, and in agreement with the structure mutation of R590 to alanine results in no viral plaques, suggesting that R590 serves an essential function in DNA replication. Future work will focus on studying these mutations further using biochemical assays such as rolling circle and isothermal titration calorimetry (ITC) to understand their specific role in DNA replication.

Synthesis and molecular docking of pyrollobenzodiazepine derivatives as potential non-β-lactam β-lactamase inhibitors

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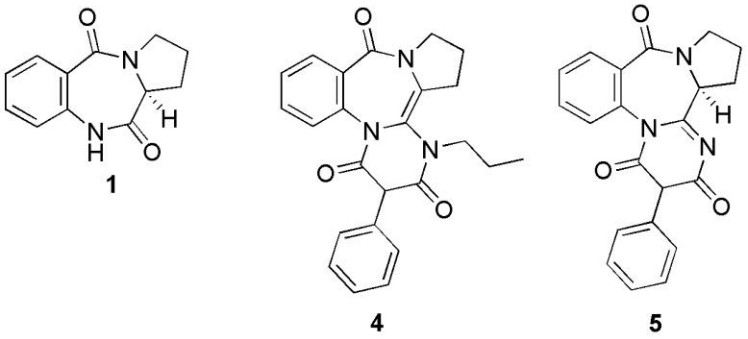
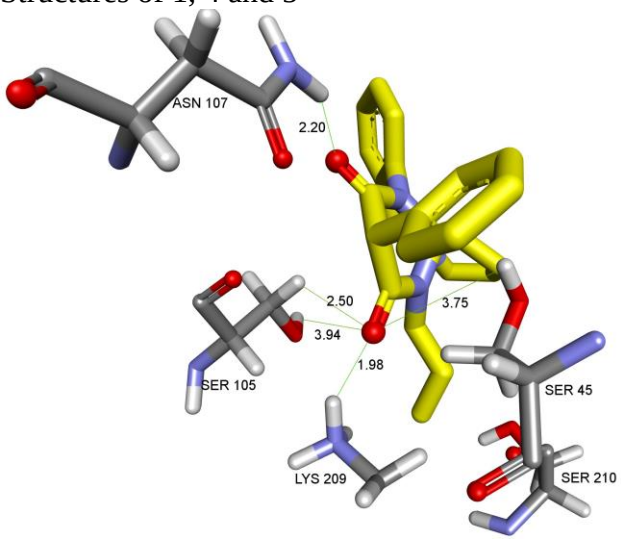
In search of novel lead compounds to serve as inhibitors for β-lactamases, novel pyrollobenzodiazepine (PBD) derivatives {*2-Phenyl-4-propyl-4b,5,6,7-tetrahydro-4,7a,12b-triazo-dibenzo[e,g]azulene-1,3,8,trione* (**4**) and *2-Phenyl-amino-4b,5,6,7-tetrahydro-4,7a,12b-triazo-dibenzo[e,g]azulene-1,3,8,trione* (**5**)} were synthesized in three step procedures from parent PBD dilactam **1** in good yield. PBDs are known to be potent anticancer and antimicrobial agents through a host of mechanisms but particularly DNA intercalation. However, PBDs have not been studied for their possible role in the inhibition of β-lactamases. Thus, this study describes the synthesis of the novel PBDs as well as molecular docking studies using TEM-1 class A serine β-lactamase. Molecular docking studies revealed possible interactions and high binding affinity energies of -7.07 and -6.86 kcal/mol for **4** and **5**, respectively. However, possible steric hindrances to more efficient interactions were thought to be encountered during docking due to the bulky nature of the PBD molecules thus limiting optimal interactions. The search for more elaborated PBD chemotypes which may have better activity as well as stronger affinity, exploiting fragment-based designing followed by synthesis and further *in vitro* evaluation against TEM-1 and P99 β-lactamases is currently under investigation.



Structures of 1, 4 and 5



4 + TEM-1 complex

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Synthesis of tethered aromatic compounds for use with fluorescence studies

Heather V. Clontz, *h.clontz@wingate.edu, Alexander Manzewitsch, James M. Gibson, Shakena Daniel. Wingate University, Wingate, North Carolina, United States*

Anthracene is a solid, polycyclic aromatic hydrocarbon consisting of three fused benzene rings. Anthracene is a precursor to dyes and is colorless, but exhibits a blue fluorescence under ultraviolet light. For this reason these types of conjugated compounds are known to be useful in the production of fiber optics or optical fiber sensors. Many times modified anthracene compounds (often called derivatives) have enhanced optical fiber characteristics. This research focuses on the synthesis of modified anthracene compounds. Our initial goal is to use model compounds, substituting a single benzene ring for the three fused benzene rings. Their characteristics and reactivity are very similar to anthracene but the molecules are much smaller. The synthesis of these compounds and their applications will be discussed.

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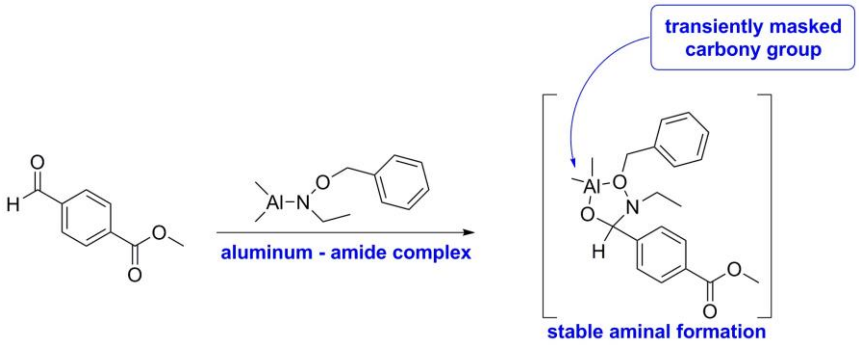
Efficient masking of carbonyl groups in the presence of nucleophiles using transient aluminum-aminals

Francis J. Barrios[1]*, fbarrios@bellarmine.edu, David A. Colby*[2]*. (1) Department of Chemistry and Physics, Bellarmine University, Louisville, Kentucky, United States (2) Department of BioMolecular Sciences, University of Mississippi, University, Mississippi, United States*

In naturally occurring compounds and in many organic molecules the carbonyl group is a prominent functional group. When synthesizing complex molecules, it is important the careful manipulation and control of their reactivity as electrophiles. The implementations of carbonyl protecting groups as well as oxidation/reduction strategies are the traditional ways of addressing these issues. It has been proven that Weinreb amides can be reacted with nucleophiles to form a stable, but transient aminal. The relevance of this methodology has led to the finding that disubstituted hydroxylamines can be synthesized and be used to form aluminum – amides complexes. These aluminum complexes were used as reagents to mask reactive carbonyl groups from nucleophiles, as aminals, similar to Weinreb amides. The stability and utility of the aminal intermediate is presented in the context of selectively controlling the reactivity of the carbonyl groups in different substrates. These new class of compounds can potentially be used as a bifunctional reagent not only masking carbonyl groups from nucleophiles but also participating in direct addition reactions.



2015 Joint Southeastern/Southwest Regional Meeting 280

TMSOTf-mediated additions of acetonitrile to aldehydes, acetals, and nitrones

Jhonmattew Santa, William M. Stith, Alice Lee, Courtney J. Botelho, ***Chiles W. Downey****, wadedowney@post.harvard.edu. Chemistry, University of Richmond, Richmond, Virginia, United States*

In the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) and amine base, acetonitrile adds to various electrophiles. (Trimethylsilyl)acetonitrile adds efficiently to acetals with just TMSOTf catalysis. Acetonitrile itself will add to electrophiles when amine base is present.

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Trimethylsilyl trifluoromethanesulfonate-mediated additions of indoles to aldehydes and nitrones

Christopher D. Poff, Alissa N. Nizinski, ***Chiles W. Downey****, wadedowney@post.harvard.edu. University of Richmond, Richmond, Virginia, United States*

In the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) and an amine base, indoles and N-alkylindoles undergo Friedel-Crafts addition to aldehydes to yield the 1:1 alcohol product. The usual decomposition to the triarylmethane is not observed if the reaction is performed in diethyl ether at -78 degrees. The reaction is general to indoles, N-methylindoles, N-allylindoles, and N-benzylindoles. Recent results suggest that nitrones are also very effecting electrophiles under similar conditions.

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One-pot enol silane-formation-aldol condensation and Mannich addition reactions mediated by trimethylsilyl trifluoromethanesulfonate and amine base

Hadleigh M. Glist, Jared A. Ingersoll, ***Chiles W. Downey****, wadedowney@post.harvard.edu. University of Richmond, Richmond, Virginia, United States*

Thioesters, amides, esters, and ketones all readily form enol silanes and attack aldehydes or N-phenylimines in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) and an amine base. Mannich products are isolated as the free, deprotected aniline without a necessary desilylation step. Aldol products depend upon the stoichiometry of the TMSOTf. When 2 equiv of TMSOTf are employed, the silylated aldol addition product undergoes dehydration to produce the derived chalcones in high yield.

2015 Joint Southeastern/Southwest Regional Meeting 283

Acyl group activation of a 4-bromopyrrole ester in Suzuki cross-coupling reactions: Application to the synthesis of rigidin E and polycitones A and B

John T. Gupton*, jgupton@richmond.edu, Andrew Harrison, Scott Yeudall, Juekun Wen, Alex Shimozono, Joe Ortolani, Veronica Moore-Stoll, Ellis Huff, Evan Crawford, Will Curry, Jon Patteson, Megan Hoerrner, Katie Lounsbury. Chemistry, University of Richmond, Richmond, Virginia, United States*

We have recently described formyl group activation of a 4-bromopyrrole ester in Suzuki cross-coupling reactions and its application to the synthesis of several important pyrrole containing marine natural products. Ongoing work in our lab has established that acyl groups confer a similar type of activation for the 4-bromopyrrole ester in Suzuki cross-coupling reactions and this work will be described along with its application to the synthesis of rigidin E and polycitones A and B.

2015 Joint Southeastern/Southwest Regional Meeting 284

Nitro and cyano group activation of a 4-bromopyrrole ester in Suzuki cross-coupling reactions: Application to the synthesis of KL-3-95, a pyrrole-containing, colchicine site inhibitor

John T. Gupton, *jgupton@richmond.edu, Scott Yeudall, Ellis Huff, Evan Crawford, Megan Hoerrner, Katie Lounsbury, Kristin Lescalleet. Univ of Richmond, Univ of Rich, Virginia, United States*

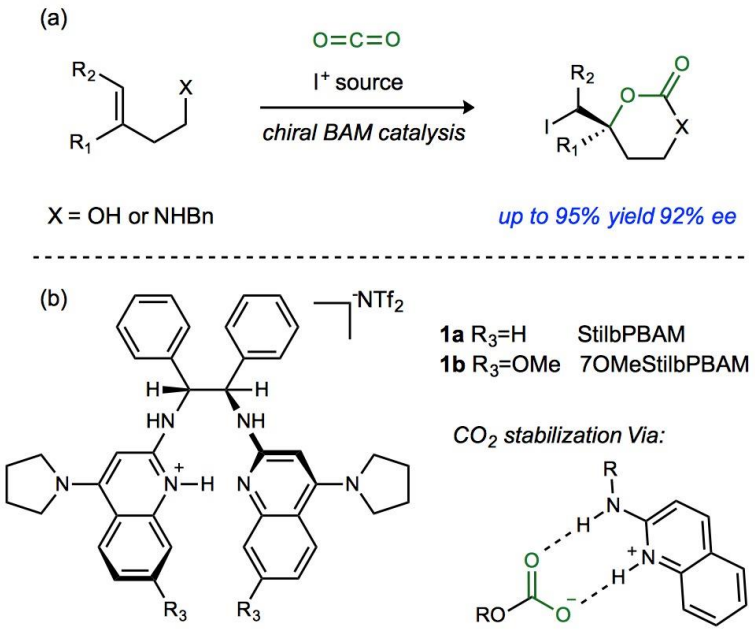
We have recently described formyl group activation of a 4-bromopyrrole ester in Suzuki cross-coupling reactions and its application to the synthesis of several important pyrrole containing marine natural products. Ongoing work in our lab has established that nitro and cyano groups confer a similar type of activation for the 4-bromopyrrole ester in Suzuki cross-coupling reactions and this work will be described along with its application to the synthesis of KL-3-95, a pyrrole-containing, cochicine site inhibitor.

2015 Joint Southeastern/Southwest Regional Meeting 285

Enantioselective carbon dioxide fixation in small molecules using a bifunctional Brønsted acid/base organocatalyst

Thomas J. Struble[2], *thomas.j.struble@vanderbilt.edu, Brandon A. Vara*[2], *Jeffrey N. Johnston*[1]*. (1) Vanderbilt Univ Chem Dept, Nashville, Tennessee, United States (2) Chemistry, Vanderbilt University, Nashville, Tennessee, United States*

Carbon dioxide possesses many characteristics that make it ideal for the use in organic synthesis; it is nontoxic, inexpensive, and plentiful. Unfortunately this valuable C_1 building block has not been used to its full potential in enantioselective synthesis of small molecules. Catalyzed by a bifunctional Brønsted acid/base, new reactivity has been uncovered for a three-component reaction between a homoallylic alcohol or amine, CO_2, and an electrophilic source of iodine. The broad applicability of this BisAmidine (BAM) catalyst is demonstrated through simple electronic tuning of catalysts when changing from homoallylic alcohol to amine CO_2 capture.



2015 Joint Southeastern/Southwest Regional Meeting 286

A divergent/convergent epoxide approach towards the synthesis of (-)-dolabriferol

Keyla Morales[1]*, keylapr13@gmail.com, Jose A. Prieto*[2]*. (1) Chemistry, University of Puerto Rico-Río Piedras, Toa Alta, Puerto Rico, United States (2) Chemistry, University of Puerto Rico, San Juan, Puerto Rico, United States*

Dolabriferol is a polypropionate natural product isolated from the Cuban anaspidean mollusk *Dolabrifera dolabrifera*. Its structure consists of a non-contiguous carbon skeleton of two stereochemically related polypropionate subunits joined by an ester linkage. This structural feature consists of an array of alternating methyl and hydroxy groups on an aliphatic chain with a particular configuration. We have developed a reiterative enantioselective epoxide-based methodology for polypropionate construction. Our approach consists of three steps: a regioselective epoxide cleavage with an alkynyl aluminum reagent, reduction of the alkyne, and the stereoselective epoxidation of the resulting alkene. This sequence could be modified to include other organometallics and epoxides structures. We have engaged in a divergent/convergent synthesis of dolabriferol in which the same precursor is used for the elaboration of the two-polypropionate fragments. Using this approach, we have successfully synthesized the enantioselective key precursor containing the C3-C9 and C12-C18 segments of dolabriferol with the correct absolute configuration. From this precursor, we have been able to synthesize the polypropionate acid and alcohol moieties of dolabriferol using our non-aldol methodology. The details and recent advances towards the synthesis of (-)-dolabriferol will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 287

Metal mediated reactions of hydrocarbons with carbon dioxide: An approach to study the mitigation of greenhouse gases

A.K. Fazlur Rahman[2,3]*, frahman@ossm.edu, Kenny M. Nicholas*[1]*. (1) Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma, United States (2) Chemistry Department, OK School of Science and Mathematics, Oklahoma City, Oklahoma, United States (3) Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma, United States*

In order to explore a possible route to mitigate Green House Gases (GHG) we reacted CO_2 with hydrocarbons (such as tetraline, dihydroanthracene, cyclohexadiene and dihydronapthalene with various catalysts ($MeReO_4$, NH_4ReO_4, V_2O_3 , $Ru(acac)_3$ to produce corresponding dehydrogenated products and formic acid. Some preliminary results of this investigation will be discussed during the presentation.

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Synthesis and characterization of *N*-alkylbenzoxazaboroles

Sobiya George[1]*, sxg062@shsu.edu, Dustin E. Gross*[2]*. (1) Chemistry, Sam Houston State University, Huntsville, Texas, United States (2) Chemistry, Sam Houston State University, Huntsville, Texas, United States*

The dynamic covalent nature of boronate esters (dioxaboroles) has been widely used for the formation of discrete oligomers and highly organized polymeric systems such as

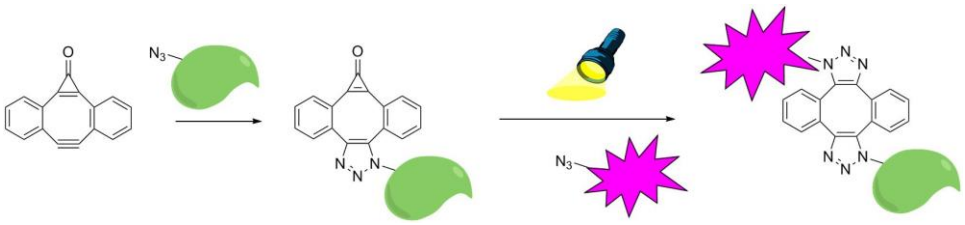
covalent organic frameworks. Oxazaboroles are structurally similar to dioxaboroles, and they may also have the potential to be used in dynamic covalent systems. We have synthesized and characterized a series of benzoxazaboroles from *o*-aminophenols and boronic acids. The results of our synthetic work and experiments concerning the reversibility of benzoxazaborole formation will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 289

Adsorption of immunoglobulin on cellulose and chitin films using surface plasmon resonance

Dewey Sutton[1]*, dasutt@uga.edu, Vladimir Popik*[2]*. (1) Chemistry, University of Georgia, Clarkesville, Georgia, United States (2) Department of Chemistry, University of Georgia, Athens, Georgia, United States*

Click chemistry and its catalyst-free variant, strain-promoted alkyne-azide click (SPAAC) have become indispensable tools for functionalization of a variety of biomolecules. A pressing need in this field is the development of a platform for sequential click ligations. We have designed a mono photo-caged dibenzocyclooctadiyne which allows for fully orthogonal, dual click functionalization. The free alkyne moiety reacts readily with azides to form triazoles which, upon irradiation, release a second highly reactive alkyne moiety. The resultant cyclooctyne possesses the fastest known rate constant with azides in organic solutions. We have utilized this platform to sequentially functionalize bovine serum albumin (BSA) with fluorescent as well as polymeric azide-tagged substrates.



2015 Joint Southeastern/Southwest Regional Meeting 290

Cationic palladium catalyzed acetylation of alcohols and carbohydrate derived polyols

Enoch A. Mensah*, mensahe@ius.edu, Franscisco R. Reyes, Eric S. Standiford. Chemistry, Indiana University Southeast, Charlestown, Indiana, United States*

The development of a new facile method for the acetylation of alcohols and carbohydrate derived polyols is described. This methodology relies on the nature of the cationic palladium catalyst to direct the acetylation reaction. This new acetylation protocol is very rapid and proceeds under mild conditions with only 1 mol% of catalyst loading at ambient temperature. This new method has been applied to a variety of different alcohols with different levels of steric hindrance as well as carbohydrate derived polyols to provide the corresponding fully acetylated products in excellent yields.

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Synthesis of 4,4-dialkoxy-BODIPYs via nucleophilic substitution

Alex Nguyen[1]*, lnguy62@tigers.lsu.edu, Petia N. Bobadova-Parvanova*[2]*, Frank Fronczek*[1]*, Kevin M. Smith*[1]*, Graca Vicente*[1]*. (1) Chemistry, Louisiana State University, Baton Rouge, Louisiana, United States (2) Chemistry, Rockhurst University, Overland Park, Kansas, United States*

Functionalization of an organic fluorophore, boron dipyrromethene (also known as BODIPY) was studied. A series of *O*-BODIPYs were synthesized via nucleophilic substitution and its spectroscopic properties were investigated. These compounds were made using three methods: a) nucleophilic addition with sodium alkoxide, b) Lewis acid mediated and addition of alcohols, c) TMSOTf-activated, followed by addition of alcohols. Seven new 4,4-dialkoxy-BODIPYs were synthesized and six crystal structures were analyzed.

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The isolation and identification of phytochemicals from the leaf extract of *Tabernaemontana longipeas*

Simira D. Carothers[1]*, simira.carothers@gmail.com, Marcus Williams*[1]*, Huaisheng Zhang*[1]*, Ifedayo V. Ogungbe*[2]*. (1) Chemistry, Jackson State University, Pearl, Mississippi, United States (2) Department of Chemistry and Biochemistry, Jackson State University, Jackson, Mississippi, United States*

Natural products have long since been utilized for their preventative and medicinal properties. The phytochemicals in plants may be effective in the treatment of many diseases. The current research is to isolate and characterize the phytochemicals in Tabernaemontana Longipeas, a neotropical plant, and to investigate the anti-trypanosomal properties of the plant. The resulting compounds are being analyzed and their structural features are being investigated using NMR and MS. The compounds will be tested for anti-parasitic activity as well as cytotoxicity using liver hepatocarcinoma cells (Hep G2). If proven effective, further research will be conducted to develop the compounds or their analogues as treatment for trypanosomiasis.

2015 Joint Southeastern/Southwest Regional Meeting 293

Library of aurone derivatives synthesized through coupling reactions

Zachary Taylor*, zet2d@mtmail.mtsu.edu. Middle Tennessee State University, Nashville, Tennessee, United States*

Aurones are a group of compounds belonging to the flavonoid family of natural products. Aurones display a wide range of biological activity against many of the world's most common health issues such as: cancer, parasites, and fungal infections, just to name a few. A library of aurones with an extended scaffold has successfully been synthesized using an iodo-substituted aurone; new moieties were introduced onto the aurone through Sonogashira and Suzuki-Miyaura couplings. The majority of the newly introduced moieties are aromatic in nature. These molecules will undergo biological assays. Two areas that are of key interest are what effect the increased conjugation and

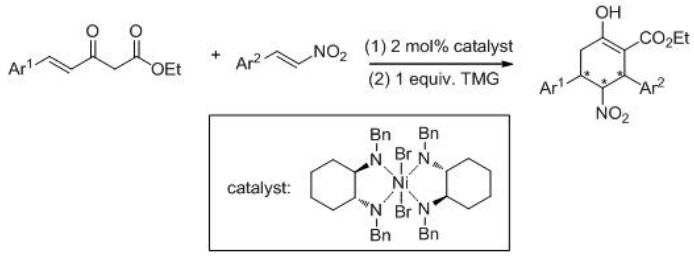
addition of such large moieties onto the aurone will have on the biological activity. The results from these assays will help guide future synthetic targets and might prove helpful in determining a mechanism of action.

2015 Joint Southeastern/Southwest Regional Meeting 294

Ni(II)-diamine complexes catalyzed asymmetric sequential Michael reactions of phenylketoesters and nitroalkenes: Synthesis of multifunctionalized cyclohexene derivatives

***Shengying Huang**, huangxixi1988@gmail.com, Karen Scherer, Bukuo Ni. Dept of Chemistry, Texas AM University-Commerce, Commerce, Texas, United States*

Mutlifunctional cyclohexene derivatives with three chiral stereocenters were synthesized via two sequential Michael reactions between phenylketoesters and nitroalkenes initiated with 2 mol% of readily prepared Ni(II)-bis[(R,R)-N,N'-dibenzylcyclohexane-1,2-diamine] complex and then with 1 equivalent of tetramethylguanidine (TMG) for cyclization. The reaction provided the desire products in good yields and high enantioselectivities as well as good diastereoselectivities under mild reaction conditions.

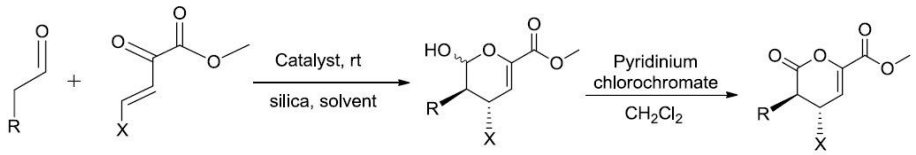


2015 Joint Southeastern/Southwest Regional Meeting 295

A highly enantioselective [4+2] cycloaddtion of aldehydes and *β,γ*-unsaturated-*α*-keto ester using enamine catalysis

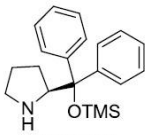
***Nanda Kumar Katakam**, knandakumar0@gmail.com. Chemistry, Texas A&M University-Commerce, Commerce, Texas, United States*

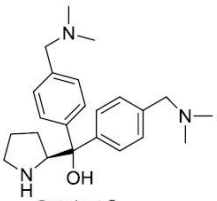
A stereoselective inverse electron demand oxo-Diels-Alder reaction between electron poor diene (*γ*-aryl-*β,γ*-unsaturated-*α*-keto ester) and electron rich dienophile has been studied in our lab. This type of cycloaddtion is extremely useful for the construction of *O*-, *N*-, *S*-centered heterocycles, which has great importance in both organic and medicinal chemistry. The [4+2] hetero cycloaddition was carried out using Catalysts **1, 2, 3.** High selectivity (enantiomeric excess 98%) was obtained using Catalyst **3**. Owing to the bulkiness of catalyst **3**, compared to Catalysts **1** and **2**, it is more efficient at catalyzing this reaction. The efficiency of Catalyst **3** to catalyze a wide scope of reactants is presently being analyzed. Reactions will be carried out using catalyst **3** and stereochemical outcome determined.

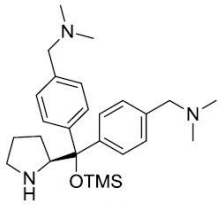


R = alkyl

X = aryl


Catalyst **1**


Catalyst **2**


Catalyst **3**

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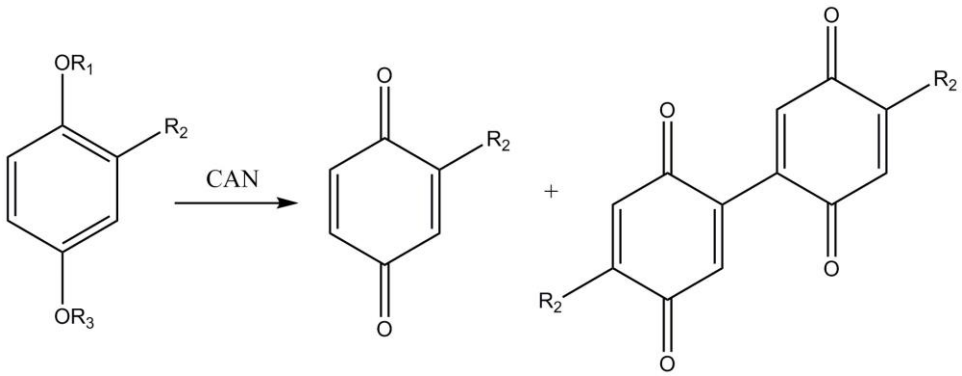
Ceric ammonium nitrate oxidations of 2-alkyl-1,4-dialkoxybenzenes

Alexander L. Simmons[2]*, simmonsa10@students.ecu.edu, Brian E. Love*[1]*. (1) East Carolina Univ, Greenville, North Carolina, United States (2) Department of Chemistry, East Carolina University, Greenville, North Carolina, United States*

Oxidation of 2-alkyl-1,4-dialkoxybenzenes using ceric ammonium nitrate (CAN) typically yields a product mixture of (mono)quinone and the symmetric dimeric quinone (diquinone). Previous work in our group has developed several protocols for altering the monoquinone to diquinone ratio by altering reaction conditions (*e.g.* solvent used, substrate concentration, mode of addition, *etc.*). Currently we are exploring the manipulation of this product ratio through modification of the alkoxy groups on the substrate. Specifically, we are investigating whether or not the hydrophobicity of these alkoxy groups affects the quinone to diquinone product ratio when these substrates are oxidized with CAN in acetonitrile/water mixtures. Results of these investigations will be reported.



2015 Joint Southeastern/Southwest Regional Meeting 297

Effective Cu-Pd dual catalyst system for direct amidation reaction from potassium organotrifluoroborates and amides

*Mohammad Al-Masum, **Mohammed Islam**, shahid_acct@yahoo.com, Wejdan Shaban. Chemistry, Tennessee State University, Nashville, Tennessee, United States*

Enamides are important synthetic intermediates and valuable topics in natural products. Many nitrogen based functionality can be created into organic systems from enamides. Potassium organotrifluoroborates are invariably showing as active cross-coupling partner for various important organic transformations. Organotrifluoroborates and their use in enamides formation by cross-coupling with amides are largely unknown. In this work, we found an interesting development of cross-coupling reaction between styryltrifluoroborates and amides in the presence of Cu-Pd catalyst system under microwave irradiation. This development and it mechanism will be discussed.

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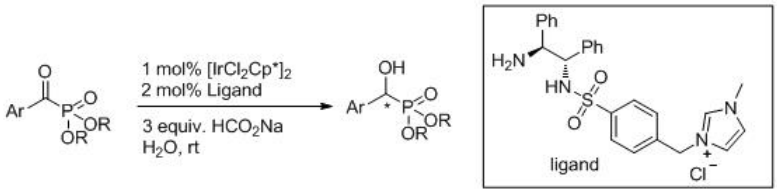
Imidazolium ion tethered TsDPENs as efficient ligands for iridium catalyzed asymmetric transfer hydrogenation of ketophosphonates in water

***Mengxia Sun**, sunmengxia1510@gmail.com, Joann Campbell, Bukuo Ni. Dept of Chemistry, Texas AM University-Commerce, Commerce, Texas, United States*

An efficient method has been developed by the use of imidazolium ion tethered TsDPENs as efficient ligands for Ir (III) catalyzed asymmetric transfer hydrogenation (ATH) of α- and β-ketophosphonates in water. The reaction provided the desire product hydroxyphosphonates in good yields and enantiomeric excess under mild reaction conditions without adding any surfactants. The enantiomeric excess were determined by 13P NMR by using (-)-cinchonicdine as chiral sovating agent, which is much more efficient method than chiral HPLC.



2015 Joint Southeastern/Southwest Regional Meeting 299

Development of new glycosylation method and synthesis of complex carbohydrates

***Pengfei Wang**, wangp@uab.edu, Dattatray Devalankar, Christopher Christian. Chemistry, University of Alabama at Birmingham, Birmingham, Alabama, United States*

Carbohydrates are ubiquitous in biological systems and are crucial to a broad spectrum of biological functions and disease processes. However, access to structurally well-defined carbohydrates is often difficult, which severely limits study of the biological roles of carbohydrates in normal and disease processes, and hinders progress in both basic and applied research in the fields of glycobiology, biochemistry, immunology and related biomedical sciences. Organic synthesis has clearly emerged as a key force in providing pure natural and unnatural carbohydrates. Development of simple, facile, and cost-effective glycosylation methods is crucial to organic synthesis of carbohydrates. We have recently developed an efficient glycosylation strategy employing only allyl glycoside building blocks. In a one-pot fashion, an allyl glycoside is isomerized to the corresponding more chemically reactive prop-1-enyl glycoside donor and its subsequent selective activation in the presence of an allyl glycoside acceptor leads to the formation of a new allyl glycoside. The new protocol can markedly simplify carbohydrate synthesis and improve overall synthetic efficiency. Its efficacy and efficiency have been recently demonstrated in the rapid synthesis of carbohydrate antigens such as the BclA tetrasaccharide of *Bacillus anthracis* exosporium, *Shigella flexneri* serotype Y O-antigen, and various saponin-based vaccine adjuvants.

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Synthesis of alpha, beta unsaturated carboxylic acids and their transformation to cyclobutane derivatives using solid state reactions

***Koushik Banerjee**, kb7071@hotmail.com, **Alexandra Hanna**, alexandra.hanna@bobcats.gcsu.edu. Chemistry, Physics, and Astronomy, Georgia College and State University, Milledgeville, Georgia, United States*

Cyclobutane derivatives have exhibited pharmaceutical uses in being anti-inflammatories, and immunosuppressant, while cinnamic acid derivatives are well known for its antidiabetic properties. We have used a newly developed green Knoevenagel condensation reaction to access cinnamic acid derivatives, for example 4-Bromocinnamic acid in 86% yield. Herein, we will disclose synthesis of several other cinnamic acid derivatives via novel green reaction condition and their subsequent transformation to cyclobutane derivatives using solid-state photochemical conditions.

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Calcium catalyzed Mukaiyama-Mannich reaction

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Mukaiyama-Mannich reaction of silyl enol ethers and nitrones is catalyzed by a commercially available calcium(II) complex.

2015 Joint Southeastern/Southwest Regional Meeting 302

Controlling the stereochemistry of new C1 substituted carbapenems

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In the past 15 years, highly antibiotic resistant strains of Pseudomonas aeruginosa, Klebsiella pneumoniae, and Acinetobacter baumannii have evolved. In our efforts to design and evaluate new carbapenems against these MDR Gram negative pathogens, we are employing new methodology to set stereochemistry at the carbapenem C1 position. We will discuss methodology that effectively controls stereochemistry at this position, assignment of stereochemistry in the preparation of intermediates useful in the synthesis of new antibiotics.

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Reactivity of bi(pyrazol-1-yl)acetic acid ligands with diiodo(η^6-*p*-cymene)ruthenium(II)

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We have previously shown that the phosphite coordinated diiodo(η^6-*p*-cymene)ruthenium(II) complex, η^6-*p*-cymene)RuI_2{$P(OCH_2)_3CEt$}, reacts cleanly with phenylmagnesium bromide at room temperature in methylene chloride to yield the phenylated ruthenium(II) complex, (η^6-cymene)RuI(Ph){$P(OCH_2)_3CEt$}. In light of this facile reactivity, we became interested in the reactivity of diiodo(η^6-*p*-cymene)ruthenium(II) with weaker nucleophiles. Reaction of bis(pyrazol-1-yl)acetic acid ($(pz)_2HCCO_2H$, pz = pyrazolyl; BPA) or bis(3,5-dimethylpyrazol-1-yl)acetic acid ($(3,5\text{-}Me\text{-}pz)_2HCCO_2H$, pz = 3,5-dimethylpyrazolyl; 3,5-MeBPA) with diiodo(η^6-*p*-cymene)ruthenium(II) in the presence of potassium carbonate at room temperature in acetonitrile (NCMe) affords the octahedral Ru(II) complexes, (η^6-*p*-cymene)(κ^3-*N*,*N*,*O*-BPA)Ru(II) (**1**) and (η^6-*p*-cymene)(κ^3-*N*,*N*,*O*-3,5-Me-BPA)Ru(II) (**2**), respectively. Increasing the reaction temperature to 80° C displaces the cymene ligand of **1** and **2** and yields cationic, *tris*-acetonitrile ruthenium heteroscorpionate complexes, [(κ^3-*N*,*N*,*O*-BPA)Ru(II)$(NCMe)_3$]I (**3**) and [(κ^3-*N*,*N*,*O*-3,5-MeBPA)Ru(II)$(NCMe)_3$]I (**4**). Compound **2** is sterically congested and displays broad and ill-defined ^{1}H NMR signals, suggesting a fluxional process most likely associated with the liberation of one of the 3,5-dimethylpyrazolyl arms of the 3,5-MeBPA ligand from the metal. All compounds have been characterized by ^{1}H, ^{13}C NMR, infrared spectroscopy and elemental analysis. Compounds **1** and **4** have also been characterized by single crystal X-ray crystallography. Notably, compounds **3** and **4** may serve as synthons for the preparation of a number of new compounds including those capable of performing olefin hydroarylation reactions.

2015 Joint Southeastern/Southwest Regional Meeting 304

A new process of synthesizing anandamide derivatives from arachidonic acid in the presence of boron catalyst

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Arachidonic acid is a polyunsaturated fatty acid useful in terms of biology, medicine and nutrition. Dennis Hall and his group recently reported a direct amidation process of carboxylic acid by *ortho*-iodo boronic acid. Applying this method we are exploring an efficient method for amidation of arachidonic acid and making various anandamide derivatives. This new development and its mechanism will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 305

Fe-catalyzed synthesis of 3-aryl-4-propenyl oxazolidines

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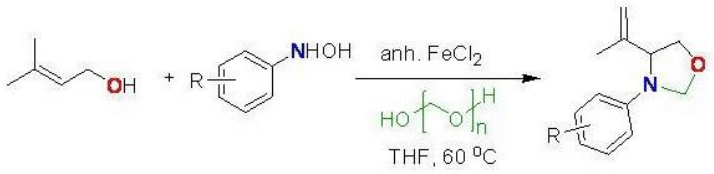
In biological systems, coenzymes catalyze a variety of group transfer reactions such as thiamine pyrophosphate (TPP), coenzyme A (CoASH), tetrahydrofolate (THF), acyl and carboxyl groups transfer. Similarly, transfer of various functional groups or fragment of a molecule from one system to another is well-known in the literature.
We have established that 3-aryl-4-propenyl oxazolidines can be obtained from the corresponding allylalcohols and arylhydroxylamines in moderate to very good yields via C-N bond formation and methylene group transfer. Oxazolidines have been utilized in organic synthesis as synthetic intermediates, protecting groups, and as ligands for metal catalysis. Oxazolidines appear in numerous medicinally active compounds and natural products of biological significance.
As a part of method development, we have screened several metal catalysts and $FeCl_2$ was found to be the most efficient catalyst for the oxazolidine formation. Steric effects of substituents seemed to be playing crucial role in methylene group transfer which determines the product whether to be oxazolidine or allyl aminoalcohols. p-Substituted arylhydroxylamines favors oxazolidines formation, but not ortho-substitutions. Interestingly, Geraniol also produced the corresponding oxazolidine in a selective manner. We have also extended the method to make allyl aminoalcohol via acid catalyzed demethylenation. Method development, substrate scope and reaction pathways will be presented.



Scheme. Catalytic synthesis of 3-aryl-4-propenyl oxazolidines

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Volume change of the random coil to folded conformational transition of *Thermomyces lanuginosus* xylanase at 24^{o}C and pH = 7.0 via application of the Clausius-Clapeyron equation.

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A partial phase diagram characterizing the conformational change that occurs in *Thermomyces lanuginosus* xylanase as it is slowly heated in 150 mM sodium phosphate (pH = 7.0) has been constructed from slow-scan-rate differential scanning calorimetry measurements. The Clausius-Clapeyron equation was applied to determine an associated volume change of -205 L mol^{-1} at 24^{o}C, the equilibrium transition temperature at 1.0 atm pressure. This value is in excellent agreement with that predicted using a previously published [1] empirical equation for calculating the hydrodynamic radius if the transition is regarded as from a random coil to a functional, folded state and with the assumption the hydrodynamic radius is a good approximation of the true random coil radius. The existence of a low-temperature random coil is confirmed by circular dichroism and dynamic light scattering measurements. Thus, at 24^{o}C and 1.0 atm pressure the enzyme appears to fold from a random coil to a functional, folded form as it is slowly heated.

2015 Joint Southeastern/Southwest Regional Meeting 307

Ensemble compactness is independent of charge and ionic strength in a multi-site phosphorylateable protein

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Intrinsically disordered proteins (IDPs) play crucial roles in cell signaling and regulation. A disordered protein's ability to preform a particular function is intimately related to the ensemble of conformations it adopts. The fraction of charged residues and their patterning within the primary sequence are currently the best predictors of compactness of IDPs. Here, we report that the C-terminal disordered region of the yeast transcription factor Ash1 falls outside the existing predictive paradigm and propose a cause in its multiple phosphorylation sites. The C-terminal 80 disordered amino acids carry 16 positively charged residues, 1 negatively charged residue, and 10 phosphorylation sites. We have determined the Ash1 size distribution with small angle x-ray scattering (SAXS) and atomistic simulations both in the non-phosphorylated and phosphorylated state and as a function of NaCl concentration. Simulations are in remarkable agreement with experimental data. Both show that the radius of gyration (R_g) is more extended than would be predicted based on charge content and patterning. Importantly, the R_g is insensitive to buffer ionic strength and phosphorylation on 10 sites, despite the strong increase in protein charge. Simulations reveal that local expansion due to phosphorylation is compensated by compaction of other sequence regions leading to an overall constant ensemble average size. Our results suggest the presence of sequence patterns that mediate insensitivity of the protein size to the charge effects intrinsic to phosphorylation. Such sequence patterning could prove essential in providing accessibility to kinases, phosphatases and binding partners, notwithstanding the protein's phosphorylation state.

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Novel reductive pathways for hydroxywarfarin metabolism

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Coumadin (R/S-warfarin) is a commonly prescribed anticoagulant for over 30 million Americans each year. While highly efficacious, the dose-response for the patient is often unpredictable and poses a therapeutic challenge. Important contributors to unpredictability are variations in R- and S-warfarin metabolism among patients. Warfarin is mainly oxidized by cytochromes P450 into hydroxywarfarins and to a lesser extent reduced by reductases to warfarin alcohols. Despite changes in structure of the parent drugs, warfarin metabolites may contribute to patient dose-responses due to residual pharmacological activity and/or roles in regulating warfarin metabolism. Clearance of primary warfarin metabolites is then likely to have pharmacological importance. Previous studies showed that some hydroxywarfarins can undergo glucuronidation for excretion in urine, but there are other possible routes of elimination for hydroxywarfarins. Like warfarin, we hypothesize that hydroxywarfarins undergo reduction to alcohols as an alternate elimination pathway. We tested this hypothesis by assessing reduction of rac-6-, 7-, 8- and 4'-hydroxywarfarin along with 10-hydroxywarfarin diastereomers using pooled human liver cytosol. We performed control experiments and confirmed reduction of warfarin. Next, we developed HPLC methods to analyze rac-hydroxywarfarin reactions and screened for specific activities. Based on those studies, all five isomeric mixtures of hydroxywarfarins underwent reduction into major and minor alcohols indicating a stereoselective preference for metabolite formation. The highest yields from those reactions were for rac-10- and 4'-hydroxywarfarin while less efficient reduction was observed for rac-6-, 7- and 8-hydroxywarfarin. The modification of the coumarin ring for the latter three hydroxywarfarins then appeared to decrease metabolic efficiency despite its distal location from the site of reduction. Future experiments will confirm the identity of metabolites by MS and reveal the kinetic mechanisms and constants for the reactions. Knowledge gained from those efforts will advance an understanding of the hydroxywarfarin clearance in patients and facilitate studies on their potential clinical relevance.

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Investigation of the catalytic mechanism of *Mycoplasma pneumoniae* L-alpha-glycerophosphate oxidase: Mutation of the proposed catalytic base

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The formation of hydrogen peroxide (H_2O_2) by the enzyme L-alpha-glycerophosphate oxidase (MpGlpO), is important for the pathogenesis of *Mycoplasma pneumoniae*. *M. pneumoniae* is a pathogen that targets the human respiratory tract, causing 40% or more of all pneumoniae infections, with the most common syndrome being

tracheobronchitis in children. MpGlpO relays electrons from L-alpha-glycerophosphate to molecular oxygen to form the products dihydroxyacetone phosphate and hydrogen peroxide. Because the formation of hydrogen peroxide is essential for *M. pneumoniae* pathogenesis, the MpGlpO enzyme has emerged as a potential therapeutic target for pneumoniae infections. Recently an X-ray crystal structure of the apo form MpGlpO was determined, and based on features of the proposed active site a model of glycerophosphate binding was proposed. Research in our laboratory is focused on mutating amino acids that are predicted from the model to bind the glycerophosphate substrate to confirm their role in the catalytic cycle. In particular we are interested in identifying the catalytic base required for deprotonation of the glycerophosphate substrate. Our preliminary results have identified histidine 51 as the acid-base catalyst in the MpGlpO reaction, as mutation of this amino acid results in a complete loss of enzymatic activity. Future work will focus on solidifying the role of His51 in the catalytic cycle as well as understanding the contribution of other residues in the active site that are predicted to bind the substrate.

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Preliminary studies of the proton induced folding of $(CCCTAA)_4$ using isothermal titration calorimetry

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We have been investigating the structures and stabilities of the unusual DNA conformations that can form from the human telomere sequence: the G-rich strand, $(TTAGGG)_x$, forms a G-quadruplex while the C-rich strand, $(CCCTAA)_x$, forms the so called i-motif. These conformations are stabilized by unusual hydrogen bonding schemes and possess either stacked G-tetrads or stacked $C:CH^+$ base pairs adjoined by TTA or AAT loops, respectively. We have demonstrated that the loop sequence context for intramolecularly folded G-quadruplexes and i-motifs influences the conformational properties of the folded structures. To deconstruct the enthalpic contributions to the proton induced formation of the i-motif for the human telomere sequence $(CCCTAA)_4$, we have been carrying out isothermal titration calorimetric studies. Here, we report the progress of these studies.

2015 Joint Southeastern/Southwest Regional Meeting 311

SPOP cancer mutations reduce protein assembly size, resulting in loss of function

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Higher-order protein assemblies play important roles in signal transduction and cell fate decisions. However, these higher-order complexes are inherently heterogeneous in size, limiting insight into how size influences function. Speckle-type POZ protein (SPOP) is a cullin3-RING ubiquitin ligase (CRL3) substrate adaptor and serves to recruit substrates to the CRL for ubiquitination and subsequent degradation degradation. SPOP self-associates into higher-order oligomers via its BTB and BACK domains. SPOP is frequently mutated in cancers (www.cbioportal.com) but the oncogenic mechanism of mutations targeting the BTB and BACK domains is not understood. Herein, we provide a link between large SPOP oligomers and their localization in nuclear speckles, higher ubiquitination efficiency, and destabilization of a known substrate, Gli3. We demonstrate that SPOP forms linear oligomers with a defined size distribution. We provide comprehensive analysis of SPOP oligomerization and how this functionality promotes its localization to nuclear speckles and ability to ubiquitinate its physiological substrate Gli3. Cancer mutations dampen SPOP self-association, resulting in reduced populations of large oligomers and functional defects. Therefore, even subtle reductions in self-association can result in loss of function, highlighting that broad size distributions of assemblies are finely tuned for physiological functions.

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Determination of the cellular levels of the oxysterol-binding proteins OSBP and ORP4 upon treatment with the anti-cancer natural product OSW-1

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Oxysterol-binding protein (OSBP) and OSBP-related proteins (ORPs) are a protein family conserved among eukaryotes and involved in sterol and lipid biology. OSBP, the founding family member, is ubiquitously expressed in mammalian cells. ORP4 is a family member most closely related to OSBP (77% sequence identity), but is only expressed in select tissue types and certain cancers. Although these proteins share high sequence similarity, OSBP and ORP4 have many differences in cellular function. OSBP is localized to ER-Golgi contact sites upon ligand binding, while ORP4 is associated with the vimentin network and ER-plasma membrane contact sites. ORP4 has recently been linked to cell survival and proliferation, suggesting this protein could be a novel and druggable target for anti-cancer drug development. OSBP and ORP4 function have also been connected to different major cellular signaling pathways. The anti-cancer natural product OSW-1 is known to exert anti-proliferative activity by targeting OSBP/ORPs. OSW-1 is known to be a high affinity ligand for OSBP and ORP4, and therefore is a powerful chemical probe to study these protein’s biological functions. This study compared cellular levels of OSBP and ORP4, including before and after OSW-1 treatment. RT-PCR and Western blotting were used to determine the transcript and protein level of both proteins. The protein half-lives of OSBP and ORP4 were determined using cycloheximide treatment. OSW-1 washout experiments were performed to determine the effect of treatment on OSBP and ORP4 levels in various cell lines. We determined that OSW-1 treatment reduced OSBP levels in cells even after washout, but had minimal effect on ORP4 levels. We also found that ORP4 has a longer half-life than OSBP. Overall, we found that these two similar proteins differ in their biology and response to OSW-1 treatment, which may be due to their different cellular roles, specifically ORP4’s importance in cell survival.

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A novel-designed heterocyclic diamidine that recognizes mixed base pair DNA sequences: NMR characterization

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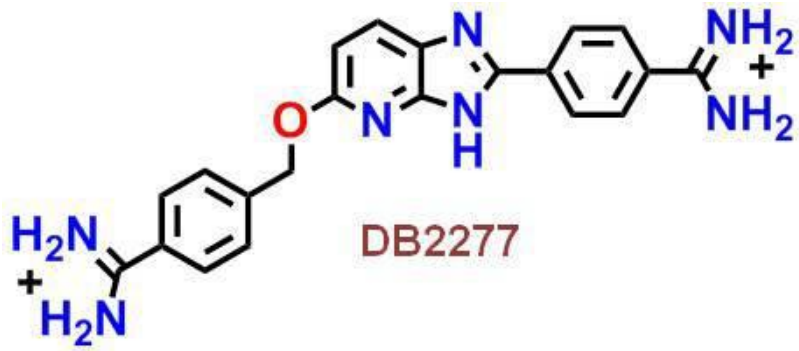
Targeting the DNA binding domain of transcription factors (TF) either for inhibition or enhancement of gene expression with designed small molecules is gaining increasing attention for the treatment of a number of different diseases. Heterocyclic diamidine minor groove binders have been successful in therapeutic targeting of DNA structures in various types of cells.
The heterocyclic diamidine, DB2277, specifically recognizes a single G•C bp in a mixed bp sequence. To understand the binding of DB2277 with mixed sequence DNA, structural information of the complex is required. DB2277 strongly binds with an AAAGTTT site, but an initial NMR experiment of DB2277 with AAAGTTT revealed the surprising result that two species are present. The two species are present even in a 1:1 complex of the compound with AAAGTTT. In order to facilitate structural NMR studies of DB2277-DNA complexes, different flanking sequences were investigated with the goal of enforcing a single ligand orientation in the complex. Binding affinities were evaluated using thermal melting and biosensor SPR studies and the binding is in sub 10 nM range. It is a major advantage to have primarily a single complex species for detailed NMR structural studies, and after evaluation of many sequences, an appropriate sequence was found.
2D EXSY provides clear evidence of slow exchange between the major and minor binding species of the complex on the NMR timescale. The comparison between macroscopic dissociation rate constant from SPR data with the total exchange rate constant from 2D EXSY for DB2277 binding with G-hp 1 shows the fast exchange between major and minor species relative to dissociation of DB2277 from the complex.
This work has been supported by NIH Grant GM111749.



2015 Joint Southeastern/Southwest Regional Meeting 314

Exploring molecular driving forces of hnRNPA1 liquid-liquid phase separation

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Cells segregate competing reactions into different organelles. In addition to membrane-bound organelles, cells contain micrometer-sized “membrane-less” organelles, which are typically spherical and include stress granules. Stress granules have liquid character and are thought to form via liquid-liquid phase separation (LLPS). hnRNPA1, a component of stress granules, is an intrinsically disordered RNA-binding protein consisting of two RNA-recognition motifs (RRMs) and a C-terminal low complexity domain (LCD) that can form condensed liquid droplets via LLPS *in vitro*. RNA is recruited to droplets and lowers the concentration of hnRNPA1 necessary for LLPS; however, the RRMs alone do not phase separate, suggesting that the LCD alone drives LLPS. However, the molecular driving forces mediating LLPS of hnRNPA1 remain incompletely understood. Importantly, a decrease of the buffer ionic strength enhances the propensity of hnRNPA1 for LLPS, suggesting a role for electrostatic interactions. The shape and size of hnRNPA1 was characterized by small-angle x-ray scattering (SAXS). Interestingly, Δhexa adopts two distinct population states, a compact state, in which the LCD may contact the RRM domains, and a more extended state. To characterize the effect of this interaction on LLPS behavior, we compared the phase behavior of full-length hnRNPA1 and the LCD alone. The removal of the RRMs increases the propensity for LLPS, suggesting the RRMs depress the proclivity for LLPS. Together, we provide insight into the molecular interactions driving LLPS of LCDs in the formation of membrane-less organelles.

Design, synthesis, and microbiological evaluation of ampicillin-tetramic acid hybrid antibiotics

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Resistance to beta-lactam antibiotics is now common in both gram-positive and gram-negative bacteria. Exploiting iron-uptake pathways by conjugating beta-lactam antibiotics with iron-chelators such as catechol and hydroxamic acid is a proven strategy to overcome permeability-related resistance in gram-negative bacteria. Since natural occurring iron chelating tetramic acids have not been previously explored for this purpose, an exploratory series of novel ampicillin-tetramic acid hybrids that structurally resemble the ureidopenicillins class was designed and synthesized. The new analogs were evaluated against a panel of clinically significant bacterial pathogens and their ability to chelate iron confirmed. The hybrids were less active than comparators piperacillin, carbenicillin and ampicillin against gram-positive bacteria. However, against gram-negative, their activity was species dependent with several hybrids displaying

improved activity against wild-type *Pseudomonas aeruginosa*. The activities of the hybrids improved in presence of clavulanic acid suggesting that they were substrate for beta-lactamases. The hybrids were also found to be efflux pump substrates and their activities improved upon the addition of efflux pump inhibitor. Unlike the catechol and hydroxamic acid based beta-lactam conjugates, the activities of the hybrids did not improve under iron-deficient condition where bacteria express increased numbers of siderophore membrane receptors and other iron-uptake transporters. We speculate that tetramic acids utilize a different set of membrane receptors than catechols and hydroxamic acids for their cellular uptake and also that our hybrids are being out-competed by bacterial siderophores that have a stronger affinity for iron compared to tetramic acids. Further studies will be needed to determine the *in vivo* potential of siderophore tetramic acids and membrane receptors to advance this class as therapeutic candidates. This study provides the first examples of natural product chelator tetramic acids conjugated with beta-lactam antibiotics.

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Investigating function of water-soluble β2 adrenoreceptor mimics using circular dichroism

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G protein-couple receptors (GPCR) make up a super family of ~800 proteins that initiate a diverse array of biological responses, gaining interest as prospective pharmaceutical targets. While the first GPCR was solved by x-ray crystallography in 2000, less than 30 different GPCR have been crystallized thus far. The long-term goal of this research is to produce a water-soluble design, transferrable throughout the GPCR family, which exhibits equivalent function to the native protein. The β2 adrenoreceptor (ADRB2) is a member of this superfamily known to form complexes with numerous ligands that stimulate a number of cardiovascular responses. Because the crystal structure of ADRB2 has previously been solved, it serves the purpose as the proof-of-principle for the water-soluble design. Mutations have been introduced to the surface of the protein to encourage the production of a water-soluble mimic and have been expressed in *E. coli*. Functional fidelity has been established by using circular dichroism as a technique to detect the changes in tertiary structure resulting from ligand interaction with known β2 adrenoreceptor agonists and antagonists.

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Cyano-nilutamide conjugates with a DNA minor groove methylating agent for selective destruction of prostate cancer cells

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Cyano-nilutamide conjugated compounds that can target androgen receptor positive cells and cause site-specific DNA-methylation in these cells have been designed and synthesized. The DNA-alkylation properties of these molecules were investigated in reactions with calf thymus DNA using HPLC analysis. These studies showed that the compounds produce predominantly N3-methyladenine adducts. Cytotoxicity studies were conducted using different cell types (LnCap (AR+), MDA-MB-231 (AR-), HEK293, and MCF-7) and the toxicity of the compounds were compared with control molecules of similar structure that were incapable of causing DNA alkylation. These studies showed that while the control molecules exhibited some toxicity, the DNA alkylating molecules were much more toxic, and that the toxicity was different in different cell types. Fluorescent analog molecules were used to monitor the uptake of these compounds in the different cells, and increased uptake was observed in androgen receptor expressing cells. These results suggest that cyano-nilutamide conjugated DNA-methylating molecules can be used for selectively targeting androgen receptor over-expressing cells such as prostate cancers.

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Novel fluorinated 9-amino acridones as covalent topoisomerase IIα poisons

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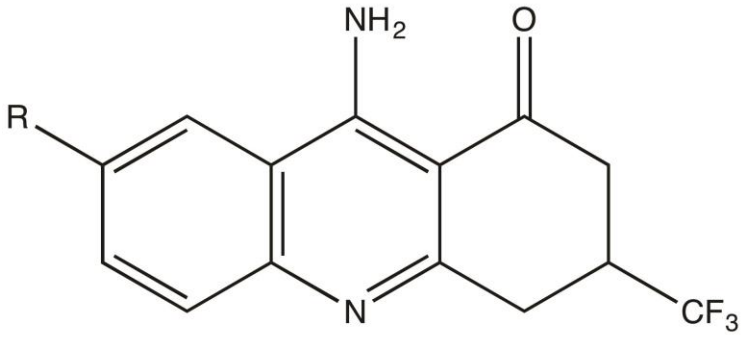
DNA topoisomerases are essential enzymes that detangle chromosomes and modulate DNA supercoiling. Type II topoisomerases act by cleaving both strands of a DNA double helix and passing another double helix through the break. The catalytic cycle of the enzyme includes a transient “cleavage complex” in which the enzyme is covalently bound to the cleaved DNA ends. Topoisomerase II poisons are compounds that stabilize the cleavage complex and lead to an increase in DNA breaks that triggers apoptosis. Two types of poisons have been identified that differ in their mechanism of action: interfacial poisons interact with the active site of the enzyme and prevent religation of the cleaved DNA, and covalent poisons adduct to sites outside of the active site and enhance DNA cleavage through a mechanism that requires the N-terminal domain of the enzyme. Several topoisomerase poisons are widely prescribed anticancer drugs.
Heterocycles containing acridone rings are common in medicinal chemistry and are found in some topoisomerase II poisons. Five novel fluorinated 9-amino acridones, differing in the functional group at C7 (compounds **1**-**5**, with R = H, CH_3, Cl, F, NO_2, respectively), were tested for the ability to increase DNA cleavage mediated by human topoisomerase IIα (hTIIα). Compounds **1**-**5** all enhanced DNA cleavage, with **4** enhancing cleavage the most (~4.5-fold over baseline levels). Several lines of evidence suggest that the acridone derivatives act as covalent hTIIα poisons. 1) Reducing agents inactivate covalent poisons, and treating **1**-**5** with dithiothreitol abolished DNA cleavage enhancement. 2) Covalent poisons require the N-terminal domain of hTIIα for activity, and **1** and **3** did not enhance DNA cleavage when incubated with an enzyme construct lacking the domain. 3) Covalent poisons inhibit enzyme-mediated DNA cleavage when incubated with hTIIα prior to the addition of DNA, and **1** and **3** inhibited cleavage under those conditions.

Due to their ability to target hTIIα, these acridone derivatives show promise as scaffolds for future drug development. Supported by NIH grants GM033944 and GM008554.



Compounds 1-5

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Inhibition of carboxylesterases by *Salvia miltiorrhiza* "Danshen" root

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Traditional Chinese medicine has been used for hundreds of years to treat a wide range of ailments and to improve health. Specifically the roots of Danshen have been used to treat hypertension, cardiovascular disease, and ischemic stroke. In fact, a specific formulation of Danshen root “Danshen dripping pill” is currently in the process of entering phase III trials. We have found that extracts of Danshen root contain potent inhibitors of human carboxylesterases (hCEs), with most of this activity being attributed to a class of compounds called tanshinones. Several purified tanshinones have been shown to inhibit both human intestinal and liver CEs with Ki values in the nM range. Since several prodrugs including irinotecan (CPT-11) and oseltamivir (Tamiflu) require CEs for activation, we assessed the effect of these inhibitors on these substrates. Incubation of hCEs with either purified tanshinones, or extracts from Danshen root resulted in reduced enzymatic activity towards these substrates. This data indicates that drug:drug interactions are likely to occur following administration of Danshen and esterified drugs, and consequently the biological activity of the latter may be dramatically impacted.

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Determination of the breakdown rate of pentobarbital in various soil types

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A growing concern is the release of organic compounds, particularly pharmaceuticals, and their breakdown products into the environment. Pentobarbital is a short-acting barbiturate that is effective as a sedative and hypnotic agent and is a common agent for euthanizing large farm animals such as horses. However, the euthanized animals become a source of contamination once they are buried since the pentobarbital residue remains in animal's tissues after injection and may leach into the surrounding soil. Experiments using LC-MS coupled to solid phase extraction were conducted to determine the breakdown rate of pentobarbital adsorbed to different soil types. In addition to facilitate bioremediation a search was conducted for a microbe strain capable of breaking down pentobarbital into its metabolites that has leached into soil.

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Chemical footprinting of secondary DNA structures within the KRAS promoter

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Non-canonical DNA structures have become a larger focus in cancer therapeutics research. From the time of their first description in the late 1960's, the G-quadruplex structure has become accepted as a targetable, therapeutic entity in many cancer types including lymphomas, colon, leukemia, and breast cancer. These secondary DNA structures can form within telomeric, 5' UTR, and promoter regions that are excessively guanine rich. In order to form, within a sequence of four sets of generally three continuous guanines, G-tetrads form through Hoogsteen base-pairing. The tetrads then stack on top of each other with interconnecting nucleotides forming loops in parallel or antiparallel configurations. Structural elucidation can be supported by DMS footprinting. This DNA sequencing polyacrylamide gel technique allows for the identification of the guanine bases involved in tetrad formation as free N7 groups on guanines are DMS-tagged and thus do not show banding. This technique has been widely utilized for G-quadruplex structure determination.

Our research focuses on G-quadruplexes forming within the kRAS promoter region, where several regions exist each with unique formations. There are three guanine rich regions within the kRAS promoter, and we focus primarily on the mid-G-quadruplex forming region. We work with single- and double-stranded DNA under various physiological conditions with co-solvents, torsional stress, and G-quadruplex stabilizing compounds for drug discovery. With co-solvents, we aim to induce dehydration and molecular crowding as they naturally occurs within the cell's nucleus using acetonitrile, polyethylene glycol, ficoll, dextran sulfate, glucose, and sucrose. We are also examining the potential to elucidate the structure formed in extracted nucleoplasm. In addition, two lead pharmacophores that selectively bind and stabilize particular conformations of the mid kRAS G-quadruplex. Several isoforms occur in a number of these conditions, and it is our ultimate goal to identify the combination of physiological stressors to be used ex vivo in order to recapitulate the higher order structures forming *in vitro* and *in vivo*. These conditions are critical for a well-positioned drug discovery program in order to

minimize false negatives and positives and provide the most optimal conditions for a successful program.

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The location and number of the amidine groups on the classic duplex minor groove binder diminazene necessary for the low nanomolar dissociation constants associated with g-quadruplex binding

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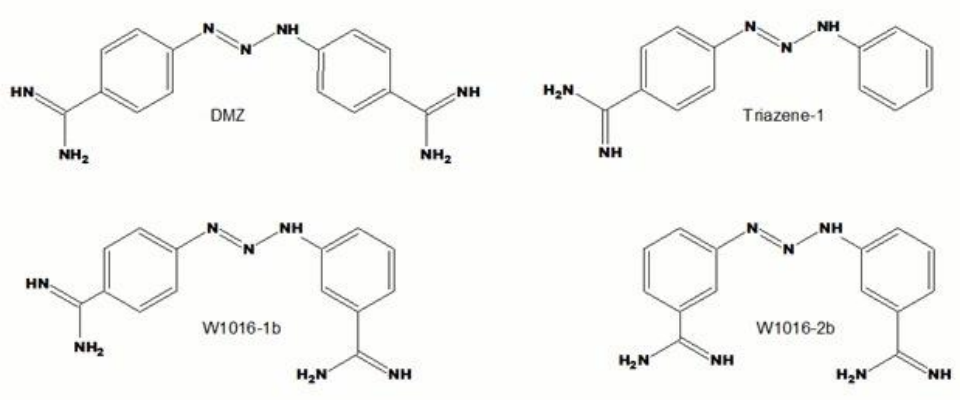
G-quadruplexes have emerged as interesting anti-cancer drug targets. The major limitations of existing G-quadruplex ligands is their low affinity and lack of specificity for quadruplex DNA. A few ligands having excellent selectivity for G-quadruplex DNA and good therapeutic windows have entered phase II clinical trials as potential cancer chemotherapeutic agents. The DNA minor groove ligand berenil (DMZ or diminazene aceturate) is used to treat the parasitic disease trypanosomiasis in animals. The known toxicological profile of DMZ makes it an ideal platform to engineer into new DNA therapeutics. We have previously determined that DMZ binds with high affinity ($K_a \approx 1 \times 10^9$ M^{-1}) to c-MYC and Bcl-2 promoter sequence G-quadruplexes while binding only weakly ($K_a \approx 1 \times 10^6$ M^{-1}) to an AT-rich duplex DNA hairpin.

In an attempt to explain the origin of the high DMZ G-quadruplex affinity, we studied the G-quadruplex binding properties of Triazine-1. The removal of one amidine group from DMZ resulted in both the loss of G-quadruplex selectivity and a significantly lower affinity ($K_a < 4 \times 10^4$ M^{-1}) for both duplex and quadruplex DNA. Having identified that both amidine groups are required for quadruplex binding, we examined the binding affinities resulting
from shifting one (W1016-1b) or both (W1016-2b) amidine groups to the meta position with C-myc G-quadruplexes. The location of amidine groups in DMZ as well as the number appears to be important for strong G-quadruplex binding as suggested by the decreased K_a.



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Biophysical investigations of c-MYC NHE-III$_1$ complementary strand forming i-Motif capped with flanking duplex ends

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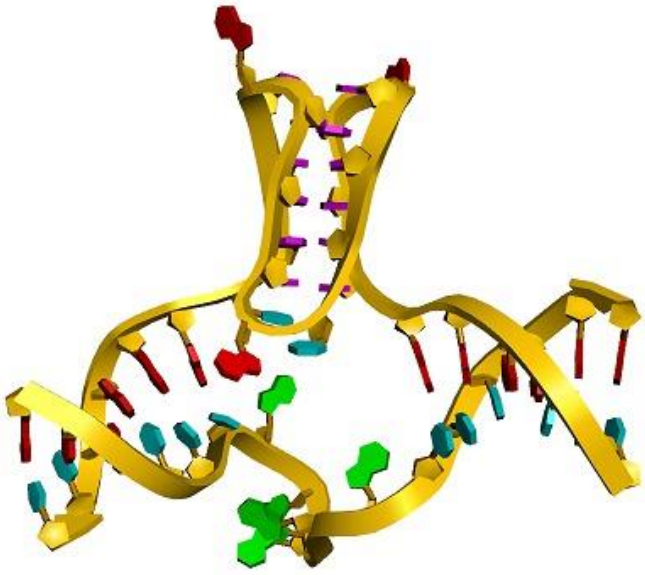
Cytosine rich DNA oligonucleotides have the potential to fold into i-Motif structures, complementary to G-quadruplex forming sequences. These structures can be found within promoting regions of several genes that can be related to cancer and are possible regulatory elements for gene expression and transcription. Currently, there is an abundance of research on single stranded i-Motif structures making it necessary for a model of c-MYC NHE-III$_1$ that caps the i-Motif forming core with flanking duplex ends. This new model is needed for a better understanding of the stability and binding of small molecules to an i-Motif core within duplex DNA. A capped i-Motif was formed by annealing a 18-mer oligonucleotide with a midsection of 6G's and tail ends of 3'-AAATTT and TTTAAA-5' to a 32-mer or 29-mer c-MYC i-Motif forming core with 3'-TTTAAA and AAATTT-5' complementary sticky ends. The wild-type sequence has the potential to fold into 1-2-1 or 1-6-1 loop isomers. Both mutants are studied alongside the wild-type to determine the folding pattern. According to molecular dynamics simulations, the 1-6-1 loop isomer appears to be more stable than the 1-2-1 loop isomer correlating with reverse ITC and CD experiments on both the single stranded and capped i-Motif oligonucleotides. TMPyP4, a common G-quadruplex binding drug, exhibits weak binding affinities with little to no disruption on the i-Motif forming core. In addition, the 1-6-1 mutant behaves similarly to the wild-type rather than the 1-2-1 mutant. Furthermore, there is an ongoing development of synthesizing a vinyl-substituted thymine able to form a cross-link with an amine group of a complementary adenine to ensure that the flanking duplex ends do not come apart. Molecular dynamics indicates that the cross-link within the flanking duplex ends makes the capped i-Motif model more stable.



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The effect of synthetic and natural compounds on tumor cell lines

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Cancer prevalence is on the rise. According to American Cancer Society, there will be an assessment 1,665,540 new cancer cases diagnosed. In 2014, about 585,720 Americans are expected to die of cancer, more than 1600 people a day. Cancer is the second most common cause of death in the US, exceeded by heart disease and chronic lower respiratory diseases. In the US, cancer is accounting for nearly 1 of every 4 deaths. Our research focuses primarily on two plants and one chemical compound never before investigated for antitumor activity. Our hypothesis is that working with Curcumin, Chamomile, and Anis compound (AS-3-39) on tumor cell lines. The ultimate goal of our studies is to improve to treat tumor cell lines like Cervical Cancer, Lung Cancer, Colon Cancer, and other forms of cancer.

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Effect of diallyl sulfide (DAS) and its commercially available analogues on *in vitro* cellular toxicity and inhibition of CYP2E1 enzyme

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Diallyl Sulfide (DAS) is a lipophilic thioether derived from crushed garlic cloves. Due to its inhibitory actions on CYP2E1-mediated metabolic activation of various chemicals and carcinogens, DAS has been shown to be protective against chemically induced hepatoxicity and to inhibit alcohol & viral protein mediated cytotoxicity in HIV model cell lines e.g. monocytes & astrocytes. However, DAS itself is metabolized by CYP2E1 to toxic metabolites diallyl sulfoxide & diallyl sulfone, which cause significant cellular toxicity. Therefore, the aim of the current project is to find an analogue of DAS from its commercially available analogues, which is stronger inhibitor but relatively weaker substrate of CYP2E1. Based on molecular docking, four different analogues are commercially available: Diallyl Ether (DE), Allyl Ethyl Sulfide (AES), Allyl Methyl Sulfide (AMS) & Thiophene (TP). Initially, we determined the cell viability and reactive oxygen species (ROS) production upon treatment with DAS & its four analogues on U937 monocytic cell lines. At 48 hour, cell viability was significantly higher in DE- & TP-treated cells than that of DAS. There were no significant changes in ROS production in all the analogues including DAS. Later, we observed that in DAS-, AES-, and AMS- treated cells, caspase-3 activity was significantly higher than that of DE- and TP-treated cells, suggesting that caspase-3-mediated apoptosis is the likely mechanism of cell death in these treatment groups. Currently, we are in the process of determining CYP2E1 inhibitory capacity of these analogues. In summary, this project will help us to find analogues of DAS with a higher CYP2E1 inhibitory capacity but with lower cytotoxicity. The most appropriate analogue from this study may further be used to develop novel compounds, which are expected to have clinical significance in terms of preventing cellular toxicity in various pathological conditions such as HIV.

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Ligand binding properties of the diheme protein in MauG

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MauG contains two c-type heme centers, a penta-coordinated high spin heme with histidine as the proximal ligand and a hexa-coordinated low spin heme with histidine and tyrosine as the axial ligands. The biological function of MauG is to catalyze the posttranslational modification of precursor methylamine dehydrogenase (Pre-MADH). The net results of this reaction are the insertion of a oxygen at the C6 position of the βTrp57 and the crosslink of βTrp57 and βTrp108 forming a tryptophan tryptophylquinone (TTQ) co-factor of mature MADH. Previous studied have indicated that it is the high spin heme that binds to exogenous ligand (such as NO) and reacts with the hydrogen peroxide to generate the unique *Bis*-Fe(IV) intermediate leading to the biosynthesis of TTQ, the protein derived catalytic cofactor of methylamine dehydrogenase (MADH).
In this research, the binding properties of MauG to cyanide and imidazole were investigaed. It was found that the high spin heme has a quite accessible distal pocket as it can bind both negatively (CN^-) and positively charged (Imidazole). Titration of MauG with either cyanide or imidazole result in a changes in the Soret absorption band. Fitting the titration data to one site specific binding model yield Kd values of 0.00073 and 0.024 M for CN^- and Imidazole, respectively. It should be noted that the cyanide titration does not has an isosbestic points indicating that more than one species were involved. This is in consistent with the resonance Raman results indicating two sun-state structures of MauG at room temperature. The titration of MauG with imidazole was characterized by a clear isosbestic point indicating that it only binds to one snstate structure, presumably a 5-coordinated high spin heme. existence of an equilibrium between the complex and free form. This work is supported by NSF Research Initiation Award under HBCU-UP program (Award number: 1505446).

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Mechanistic studies of the tyrosinase-catalyzed oxidative cyclocondensation of 2-aminophenol to 2-aminophenoxazin-3-one

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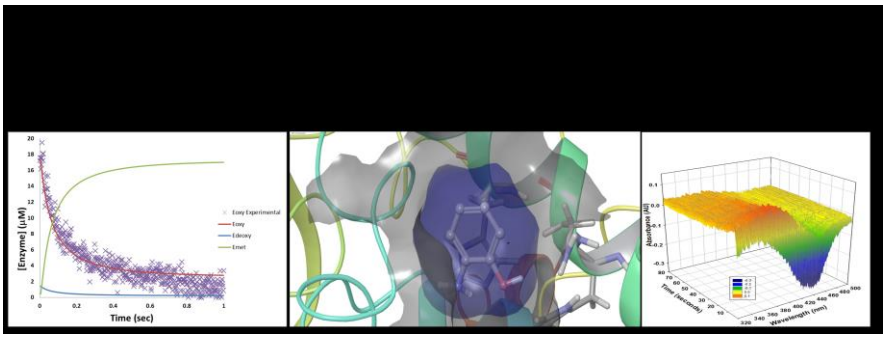
Tyrosinase(EC 1.14.18.1) catalyzes the monophenolase and diphenolase reaction associated with vertebrate pigmentation and fruit/vegetable browning. Tyrosinase is an oxygen-dependent, dicopper enzyme that has three states: E_{met}, E_{oxy}, and E_{deoxy}. The diphenolase activity can be carried out by both the met and the oxy states of the enzyme while neither mono- nor diphenolase activity results from the *deoxy* state. In this study, the oxidative cyclocondensation of 2-aminophenol (OAP) to the corresponding 2-aminophenoxazin-3-one (APX) by mushroom tyrosinase was

investigated. Using a combination of various steady- and pre-steady state methodologies, we have investigated the kinetic and chemical mechanism of this reaction. The k_{cat} for OAP is 75±2 sec^{-1}, $K_{M,OAP}$= 1.8±0.2 mM, $K_{M,O2}$= 25±4 µM with substrates binding in a steady-state preferred fashion. Stopped flow and global analysis support a model where OAP preferentially binds to the *oxy* form over the *met* (k_7>>k_1). For the *met* form, His269 and His61 are the proposed bases, while the *oxy* form uses the copper-peroxide and His61 for the sequential deprotonation of anilinic and phenolic hydrogens. Solvent KIEs show proton transfer to be increasingly rate limiting for as [O_2] ->0 µM (1.38±0.06) decreasing to 0.83±0.03 as [O_2]->∞ reflecting a partially rate limiting µ-OH bond cleavage (E_{met}) and formation (E_{oxy}) following protonation in the transition state. The coupling and cyclization reactions of *o*-quinone imine and OAP pass through a phenyl*imino*cyclohexadione intermediate to APX, forming at a rate of 6.91±0.03 $mM^{-1}s^{-1}$ and 2.59E-2±5.31E-4 s^{-1}. Differences in reactivity attributed to the anilinic moiety of OAP with *o*-diphenols are discussed.



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Effect of HPV-infected cervical cancer cells on HIV-infected monocytic cells: Clinical significance of HPV/cervical cancer and HIV/AIDS comorbidity

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Human Papilloma Virus (HPV) is the most common sexually transmitted pathogen in the United States. HPV is also the leading cause of cervical cancer worldwide, and cancer risk has been strongly correlated with immunosuppression. Cervical cancer is approximately 6-fold more prevalent in Human Immunodeficiency Virus (HIV)-infected individuals than in the normal population. It is also understood that HIV infection increases the chances for development of HPV-mediated cervical cancer, however whether HPV infection can have a reciprocal effect on HIV pathogenesis is largely unknown. It is possible that crosstalk exists between HIV-infected lymphocytes/monocytes and HPV-infected cervical cancer cells, however this interaction has not been demonstrated. This study was designed to examine the potential effect of HPV-infected cervical cancer cells on HIV pathogenesis in monocytic cells, which are one of the primary targets of HIV infection and a major viral reservoir. We hypothesize that HPV-infected cells release soluble molecules (e.g. viral proteins, cytokines, or exosomal miRNA) that reduces the expression of antioxidant enzymes (AOEs) in the blood monocytes/macrophages, leading to increased oxidative stress and

therefore increased HIV replication. In this study, we first treated the supernatant from CaSki (HPV-infected cervical cancer cells), upon growing the cells for seven days, to HIV-infected U937 monocytic cells (U1 cells), and examined viral load and AOE expression. The results showed an increase in the viral load (measured by p24 ELISA) in U1 cells upon treatment with the media from CaSki cells. We also observed a decrease in the levels of the AOEs catalase and superoxide dismutase 1 (SOD1). Our future aim is to identify the components released from CaSki cells into the media that are responsible for increased HIV replication in U1 cells. This work has implications for identifying interactions between HIV/AIDS and cervical cancer, which may eventually lead to the discovery of new potential clinical interventions for individuals with this comorbidity. [Supported by Start-up funds by College of Pharmacy, UTHSC.]

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Expression and characterization of straight α-helix concatemers for nanosheet formation

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Nanoarchitectonics is an emerging field focused on two-dimensional material assemblies and the functionalization of these materials. Self-assembling two-dimensional peptide-based assemblies capable of nanosheet formation, such as collagen mimetic peptides (CMP) and peptoids, have been created, but these peptide-based assemblies have limitations in their controllability. α-helical peptides represent enticing alternatives to CMP and peptoid building blocks due to their higher sequence flexibility and the potential to scale up assembly *in vitro*. Sheet formations from coiled-coil peptides have not been successful because the helix crossing-angle of 22° prevents tight packing between helices and assembly into two-dimensional structures. On the other hand, research in our lab has shown that straight α-helical peptides are capable of forming two-dimensional nanosheet assemblies stabilized by noncovalent interactions. Through the use of E. coli to express these peptides, the helix length can be extended to allow for the formation of thicker sheets and the peptides can be produced on a larger scale.

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Structure of an MCM double-hexamer

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The MCM helicase is an integral component of the DNA replication machinery. This ring-shaped enzyme binds double-stranded DNA (dsDNA) as an inactive double-hexamer at replication origins. Once activated, the two single hexamers proceed to unwind duplex DNA by encircling single-stranded DNA (ssDNA) during this movement. Previous studies of the N-terminal domain of archaeal *Pyrococcus furiosis* MCM (*Pf*MCM) showed ssDNA bound perpendicular to the central channel of the ring; defined as a conserved MCM ssDNA-binding motif (MSSB). Using this same model we seek to determine the mode in which dsDNA is bound within the central channel of the ring prior

to activation. Initial findings show *Pf*MCM in its double hexamer form and it is anticipated that further examination with various dsDNA substrates will reveal by what means this helicase interacts with dsDNA upon loading. These studies aim to define fundamental aspects of the DNA replication processes.

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Exploring the dynamics of polymerase switching among different DNA replication complexes

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The vital processes of DNA replication and repair require a variety of polymerases with different kinetic characteristics and various degrees of fidelity and processivity. In the model archaeon, *Sulfolobus solfataricus*, maintenance of genomic integrity at high temperatures is mediated by interactions among several polymerase complexes. Previous work revealed the formation of a highly processive PolB1 trimer complex. The binding affinity and processivity of trimeric PolB1 is enhanced at higher temperatures. This processivity is directed by active exchange within the trimer during synthesis. Formation of the DNA replication holoenzyme is directed by interactions of PolB1 with the heterotrimeric sliding clamp (PCNA123) and replication factor C (RFC), but surprisingly this complex has low processivity of synthesis. Interactions within the holoenzyme complex also play a key role in polymerase exchange during routine DNA replication through an interaction between PolB1 and PCNA2. When the replisome encounters a lesion in the template during synthesis, exchange to a lower fidelity lesion bypass polymerase (PolY) is hypothesized. Findings from kinetic and fluorescence resonance energy transfer (FRET) assays reveal an interaction between the PolB1 holoenzyme and PolY. This interaction provides for a direct switch or exchange of polymerases coupling DNA replication with lesion bypass. This exchange among PolB1 and PolY is orchestrated by several contacts with PCNA and between polymerases. Taken together, our results identify the contacts between replication and lesion bypass DNA polymerases that direct binding, catalysis, and polymerase exchange for uninterrupted, yet dynamic, DNA replication and repair processes.

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Soft interactions between model molecular crowders and the ligands of dihydrofolate reductase

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The reduction of dihydrofolate (DHF) to tetrahydrofolate (THF) by the enzyme dihydrofolate reductase (DHFR), using NADPH as a cofactor, is an essential part of the folate cycle. The product, THF, is necessary for the synthesis of methionine, purine nucleotides, thymidylate, and other compounds. Thus, the inhibition of DHFR leads to interruption of DNA synthesis and consequently cell death, making this enzyme a crucial target in the treatment of cancer and other diseases. Previous studies examined the effects of small molecule osmolytes on the substrate interactions with two non-homologous DHFRs, *E. coli* chromosomal DHFR (EcDHFR) and R67 DHFR, with vastly

different active site structures. The results indicated that DHF weakly interacts with the osmolytes in solution, shifting the binding equilibrium from DHF bound to DHFR to unbound DHF. It is hypothesized that similar weak, nonspecific interactions may also occur between cellular proteins and DHF. Weak interactions between cellular proteins and DHF would have consequences *in vivo*, where the concentration of the cellular milieu is approximately 300 g/L. Under the crowded conditions in the cell, there is a higher propensity for intermolecular interaction.
Crowding effects of macromolecules in concentrations similar to those *in vivo* were examined. Isothermal titration calorimetry (ITC) and enzyme kinetic assays were used to detect effects of molecular crowders by monitoring activity of the (DHFR)-NADPH or DHF complex and the ternary DHFR-DHF-NADPH complex in the presence of these crowders. To recreate the conditions of molecular crowding *in vivo,* the binding of the enzyme-ligand complexes in the presence of molecular weight crowding agents was examined. Analysis of the K_d's and K_m's indicated a correlation between increased molecular crowding in the solution and weakened binding of the ligands to two structurally unrelated DHFRs. These findings indicate an importance of weak, transient interactions between molecular crowding and DHFR ligands.

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Physical and dynamics studies of the AlgH protein from *Pseudomonas aeruginosa* and the AlgH protein family

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The worsening problem of resistance of pathogenic bacteria to available antibiotics encourages not only efforts towards new antibiotics and antibiotic targets, but alternate strategies to control bacterial infections. One such strategy, complementary to antibiotic therapies, is to target virulence regulation, with the rationale that targeting virulence avoids the strong evolutionary pressure normally exerted by antibiotics for selecting resistance. Along with other antibiotic resistant bacteria considered serious threats by the Centers for Disease Control and Prevention, such as methicillin-resistant *Staphyloccoccus aureus* (MRSA), vancomycin-resistant *Enterococcus* (VRE) and several others, is Multidrug-Resistant *Pseudomonas aeruginosa* (MDRPA). Some of these MDRPA strains are resistant to all known antibiotics, and comprise a high percentage (13%) of all hospital-acquired *Pseudomonas aeruginosa* infections. We are studying the AlgH protein from *Pseudomonas aeruginosa*, the namesake for a family of proteins of unknown function. Although the precise mechanism by which AlgH and its orthologues function is unknown, studies of the *algH* gene indicate that AlgH regulates production of many virulence factors, and presumably serves a global regulatory function. Thus, controlling AlgH function may help mitigate the virulence of the bacteria, and assist in controlling infections. Using NMR spectroscopy we have determined the high-resolution solution structure of the AlgH protein from *Pseudomonas aeruginosa*, and are studying the structural and dynamics properties this protein and its orthologs from other bacteria. Employing evolutionary trace analysis, hydrogen-deuterium exchange and other methods we have identified important residues in AlgH, regions of stability and instability of the protein, and how these are correlated. Using molecular dynamics simulations we are studying conformational and structural transitions of these proteins and how they might participate in AlgH function. The results should assist in understanding the underlying physical bases for AlgH function.

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Probing the energetics of proton transfer in hydrated sulfuric acid clusters: $H_2SO_4(H_2O)_{n=1-6}$, with CCSD(T) computations

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This study examines hydrated sulfuric acid clusters, $H_2SO_4(H_2O)_n$ where n = 1-6. Of the 63 minimum energy structures considered, 11 exhibit proton transfer (i.e. a solvated HSO_4^-/H_3O^+ ion pair). The structures, energetics, and harmonic vibrational frequencies of these clusters are computed for each isomer with resolution-of-the-identity second-order Møller-Plesset perturbation theory (RI-MP2) in conjunction with a series of Dunning's correlation consistent basis sets augmented with diffuse functions on all non-hydrogen atoms (cc-pV*X*Z for H and aug-cc-pV*X*Z for O, S, where *X* = D, T, Q, denoted ha*X*Z). For the energetically competitive structures near the global minimum, higher-order correlation effects are assessed with the coupled-cluster method including single, double, and perturbative triple excitations (CCSD(T)) using the same series of ha*X*Z basis sets. For clusters where $n \geq 2$, a QM:QM procedure based on the many-body expansion is used to reproduce CCSD(T) quality energetics. Although RI-MP2 and CCSD(T) binding energies are very similar for structures not exhibiting proton transfer, a larger difference is observed for structures in which proton transfer has occurred. This difference in binding energy leads to a reordering at the CCSD(T) level of theory of the closely spaced low-energy isomers in the larger clusters ($n \geq 4$) and even changes the point at which proton transfer becomes energetically favorable from n = 4 for RI-MP2 to n = 5 for CCSD(T).

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Dependence of electrostatic potential critical point values on basis set size

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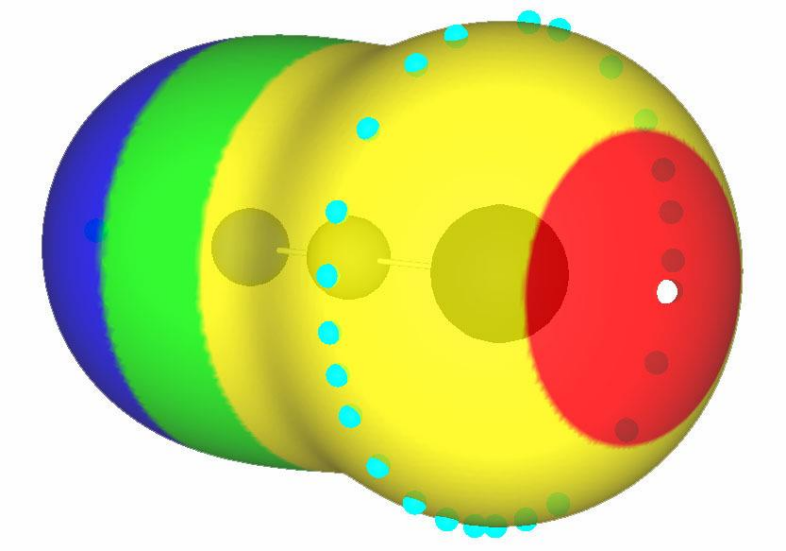
The electrostatic potential is a real physical property that can be determined experimentally by X-ray diffraction techniques. More commonly, however, the electrostatic potential is computed using computational chemistry techniques, such as Hartree-Fock (HF) or Density Functional Theory (DFT). The electrostatic potential is a one electron property, thus the use of multideterminant methods, such as MP2 or CCSD(T), provide no (or very little) improvement in the quaility of a computed electrostatic potential. The size of the basis set, however, can play a significant role in the electrostatic potential's accuracy. Here we use the values of local maxima and minima, termed $V_{S,max}$ and $V_{S,min}$, on the electrostatic potentials of several molecules computed using a large group of basis sets, varying in size from STO-3G to aug-cc-pVTZ, in order to characterize the role of basis set size on the quality of computed electrostatic potentials. Computations are carried out using both HF and DFT, which is used with two common functionals, B3LYP and M06-2X.



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Computational investigations of isoform selectivity in liver X receptor

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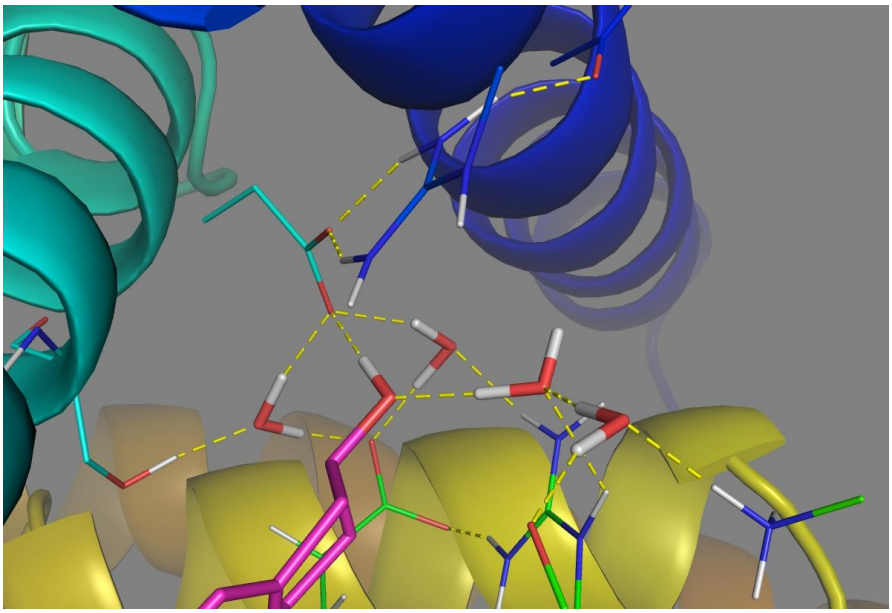
Liver X receptor occurs as two isoforms, LXRα and LXRβ, whose binding pockets are extremely similar. In recent years it has been recognized that there would be great pharmaceutical benefits to agonist ligands that selectively bind LXRβ. Several natural and synthetic ligands that selectively bind either LXRα or LXRβ have been identified, however, the mechanisms of this isoform selectivity are poorly understood. This is an especially difficult problem given the similarity of the binding pockets for these two receptor isoforms. Here we use state-of-the-art computational techniques, including molecular dynamics, docking (with inclusion of water), semiempirical PM6-D3H2 scoring, and PM6-D3H2-based glycine scanning, to elucidate the mechanisms of LXR ligand binding and investigate the distinct ligand-residue interactions that lead to isoform selectivity. It is found that LXR ligand binding often depends on hydrogen bonding networks involving waters that occur in a hydrophilic portion of the binding pocket that is open to solvent.



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DFT investigation of C-F bond activation by a low coordinate cobalt(I) complex

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A low coordinate cobalt(I) complex, $L^{tBu}Co$ [L^{tBu} = bulky beta-diketiminate ligand] was reported to be capable of cleaving the C-F bond in fluorobenzene. The mechanism of the bond activation was unclear from experiments, hence a computational study was performed. DFT calculations at the B97D/6-311++G (d, p) level of theory indicated the free energy change of C-F oxidative addition is -26.5 kcal/mol to yield a Co(III) product. A simplified ligand model (L^{Me}) with all methyl substituent was used as a guide before the full $L^{tBu}Co$ complex was calculated. Furthermore, the QM/MM (quantum mechanics / molecular mechanics) method was also employed in addition to full QM calculations for L^{tBu} model. While oxidative addition is the most stable reaction pathway studied thus far, the mode of initial cobalt binding to the arene ring of PhF defines an important intermediate, depending on the level of theory and model ligand employed. The DFT-calculated free energy changes of the transition state of oxidative addition are 10.6 kcal/mol and 14.3 kcal/mol for the $L^{Me}Co$ and $L^{tBu}Co$ supporting ligands, respectively. The binding free energies are -5.1 kcal/mol and -11.5 kcal/mol for the corresponding intermediates to form the initial cobalt-(pi-PhF) adduct. The calculations indicate a viable pathway for the activation of strong C-F bonds, as well as possible intermediates.

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Analysis of residue mutations on the enantiospecificity of CYP2C9

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CYP2C9 is in a family of enzymes, cytochrome P450s, involved in oxidation reactions in the liver that are the first steps in detoxifying foreign molecules. While many common enzymes involved in well-known pathways are largely understood, cytochrome P450s are not. An understanding of the way these enzymes function could lead to significant improvements in drug manufacturing and limitations of harmful side effects. In previous research, CYP2C9 has been shown to have significant enantiospecificity in some of its residues, notably Leu366, Phe100, and Phe476. Mutations to these residues were performed using a molecular modeling program, Sybyl-X, and molecular dynamics simulations were conducted with six NSAIDs (flurbiprofen, ibuprofen, ketoprofen, naproxen, suprofen, and zaltoprofen) with which each residue exhibiting enantiospecificity. Using previously defined parameters, the data collected from these dynamics simulations were analyzed based on intermolecular interactions between the drugs and the residues to determine if there was a difference in the results with a mutated residue. The differences in energies of interactions between the enantiomers are telling of the enantiospecificity of the residue. In some instances, the mutation caused an increase in the enantiospecificity, and in others the mutation caused a switch in the enantiospecificity. Additive effects of multiple residue mutations have also been explored and will be presented. These computational analyses will enable targeting of residues for future biochemical mutagenesis studies.

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Intrinsic energetics of proton transfer from a weak acid to water in binary $(HF)_m(H_2O)_n$ clusters

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Although hydrogen fluoride (HF) is a prototypical weak acid, estimates of the point at which proton transfer becomes energetically favorable in binary $(HF)_m(H_2O)_n$ clusters varies widely. For a single HF molecule (i.e. m=1), values at which proton transfer becomes energetically competitive ranges from n=6 to n≥10 depending on the electronic structure methods employed and structures considered. In this work, $(HF)_m(H_2O)_n$ clusters, where $m+n$≤8, are optimized with resolution-of-the-identity second-order Møller-Plesset perturbation theory (RI-MP2) with a series of Dunning's correlation consistent basis sets with diffuse functions on non-hydrogen atoms (aug-cc-pV*X*Z for O and F, cc-pV*X*Z for H where *X*=D, T, denoted ha*X*Z). More than 190 unique structures have been identified, and harmonic vibrational frequencies confirm that each one corresponds to a minimum on the potential energy surface (i.e. no imaginary frequencies, n_i=0). For the lowest-lying RI-MP2/haTZ minimum associated with each value of m and n, explicitly-correlated coupled-cluster single point energy computations that include all single and double substitutions as well as a perturbative treatment of connected triple substitutions (CCSD(T)-F12) are used to estimate the relative electronic energies of the species near the complete basis set (CBS) limit. The smallest cluster for which the lowest-energy structure exhibits proton transfer is $(HF)_2(H_2O)_4$. Most of the proton transfer structures characterized share a common hydrogen bonding topology. Specifically, the proton donor(s) tend to accept two hydrogen bonds, while the proton acceptor(s) tend to donate two hydrogen bonds.

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CDD Vision: A new reactive web platform for multidimensional drug discovery data mining and visualization

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We present a new web based data mining and visualization platform for high throughput drug discovery data called CDD Vision that makes use of a novel technology stack following modern reactive design principles. Our system is built on top of the Collaborative Drug Discovery: Vault data repository ecosystem which allows users to manipulate and visualize up to hundreds of thousands of molecules in real time. This can be performed in any browser on any platform. We will present examples of its use with datasets in CDD Public.

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A density functional theory study of novel catalysts for the “green” synthesis of aziridines

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DFT calculations were used to elucidate the mechanism of aziridination involving ethylene and model nitrenoids, Cl-M-NH-Cl (M = Ti – Zn). Aziridines are of considerable interest due to their use in the medical field to synthesize anti-tumor agents and set stereocenters in large molecules. Using the BP86/CEP-31G (d) level of theory as per prior calibrations, the change in Gibbs free energy for each step was calculated, and the majority of the steps were found to be downhill. Transition states were also found for each step of the proposed mechanisms, and the barriers (for promising metals) were calculated to be quite low, ranging from a mere 4 kcal mol^{-1} to 6 kcal mol^{-1}. Furthermore, it was established that the metal plays a key role in determining the reaction pathway. The “late” third row (3d) metals Zn and Cu undergo a two-step mechanism consisting of an initial carbometalation followed by a subsequent ring closure. The “middle” 3d metals (Ni, Co, Fe) undergo a three-step mechanism consisting of an isomerization, [2+2] addition, and reductive elimination, respectively. Moreover, these middle 3d metals exhibit two competitive pathways: the “imide” pathway and the “amide” pathway. The “early” 3d metals (Mn, Cr, V, Ti) follow the imide pathway. Overall, the study suggests that the model catalysts are promising candidates for olefin aziridination under mild conditions and worthy of experimental consideration.

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Balancing inter- and intra-molecular forces: The challenging case of dihydrogen bonding and coordinate covalent bonding in ammonia borane clusters

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Ammonia borane, BH_3NH_3, is 19.6% hydrogen by weight, a desirable characteristic for hydrogen storage. The BN bond is formed by nitrogen donating two lone pair electrons into the empty *p*-orbital on boron, an interaction referred to as a coordinate covalent, dative, or dipolar bond. In addition, ammonia borane fragments can also interact together to form dihydrogen bonds between a hydrogen attached to boron and an adjacent hydrogen on nitrogen. This investigation examines a variety of density functional theory (DFT) and *ab initio* methods to determine which can provide a balanced description of both the non-covalent interactions in ammonia borane clusters and the resulting changes in the BN dative bond. $(BH_3NH_3)_n$ clusters from n = 1 to 8 were taken from a previous study. Full geometry optimizations and harmonic vibrational frequency computations were performed using a variety of electronic structure methods for n = 1 and 2, including MP2, CCSD and CCSD(T), as well as the density functionals M06-2X and B3LYP. A correlation consistent series of basis sets with and without a set of diffuse functions (aXZ and XZ, where X=D,T,Q) were used along with two split-valence basis sets, 6-31++G(2*d*,2*p*) and 6-311++G(2*df*,2*pd*). Deviations in BN bond lengths, BN stretching frequencies, and BN frequency shifts are evaluated to determine which combination of method and basis set performs the best. For larger clusters, $n > 2$, full geometry optimizations and harmonic vibrational frequencies were computed using M06-2X with a 6-311++G(2*df*,2*pd*) basis to study the large changes in BN coordinate covalent bond length and associated BN stretching modes induced by dihydrogen bonding as cluster size increases.

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MP2 and CCSD(T) energetics for proton transfer in $(HCl)_m(H_2O)_n$ clusters, where $m+n \leq 6$

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This work investigates proton transfer in $(HCl)_m(H_2O)_n$ clusters, including those with $m \geq 2$ that have received relatively little attention. Geometry optimizations and harmonic vibrational frequency computations were performed with second-order MØller-Plesset perturbation theory (MP2) with a series of Dunning's correlation consistent basis sets with diffuse functions on non-hydrogen atoms (aug-cc-pV*X*Z for O,Cl, cc-pV*X*Z for H; where *X*=D,T,Q, denoted ha*X*Z). At this point, 50 unique $(HCl)_m(H_2O)_n$ minima have been identified, up to $m+n=6$. Higher order correlation effects were examined using the coupled-cluster method including single, double and perturbative triple excitations (CCSD(T)). A QM:QM procedure based on the many-body expansion is also used in order to reproduce CCSD(T) quality energetics. At the MP2/haTZ level, structures exhibiting proton transfer were the lowest-energy minima for $HCl(H_2O)_4$ and $(HCl)_2(H_2O)_3$. CCSD(T)/haTZ computations yield the same results for $HCl(H_2O)_4$ but invert the relative energetics of the lowest-energy dissociated and non-dissociated structures of $(HCl)_2(H_2O)_3$. It was also seen that the structures exhibiting proton transfer share a common hydrogen bonding motif, where the proton donor, HCl, accepts two hydrogen bonds from water.

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Structural identification of fibroin and cellulose: Test of monotonically decreasing local minima optimization program

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We have developed a simple computational procedure to deduce more stable structure of solid which contains large number of atoms in unit cell. The program performs local search for more stable minima by applying external stress to the solid. Tests are performed on Fibroin and Cellulose, and results are compared to X-ray crystallography results. In both cases, significantly stable structures compared to simple geometry optimization are found after extra few hours of computational effort using standard semi-empirical methods. Several potential pitfalls as well as extensions to the DFT program are discussed.

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Transparent density functional code for quantum chemistry class

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Fully functional DFT program in heterogeneous computing environment is developed specifically for educational purpose. Flow chart like Main function is kept minimal while handling standard RDFT and UDFT as well as hybrid DFT methods. Each calculation task contains both short descriptive single thread CPU code and optimized code which may utilize multi-many core CPUs and multi GPUs. All libraries are developed in C++ from scratch to make the program readable to 2nd year graduate students with minimal programming knowledge. Therefore, students will be able to follow mathematics associated with SCF and numerical integrations. Several modern programming techniques are implemented to introduce modern programming concept to chemistry graduate students. Several interesting programming exercises are discussed.

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Homology modeling of alpha viruses drug targets and virtual screening to identify their potential inhibitors

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Re-emerging and largely neglected viral infections caused by alpha viruses such as the Chikungunya, Barmah Forest, Ross River, and O'nyong Nyong currently lacks protective vaccinations or chemotherapeutic agents. A number of drug targets have identified in the viruses, and they include nsp2 protease, nsp2 RNA helicase, nsp3 adenosine binding site (nsp3) and nsp4 RNA-dependent RNA polymerase. In this work, homology modeling was used to obtain suitable structures for the nsp2 protease of the neglected alpha viruses. Virtual screening of targeted natural products and fragment libraries using the molecular dynamics based energy minimization are on-going. The top-ranked compounds will be evaluated for their protease and viral inhibitory activities.

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Water clusters in proton cancer therapy: Electron nuclear dynamics of $H^+ + (H_2O)_n$ at 100 keV

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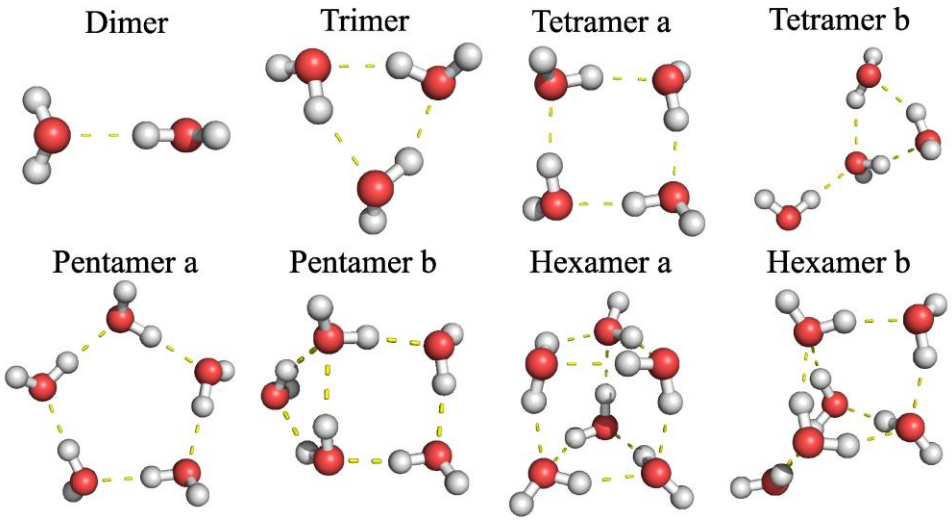
In this work, we investigate proton ionization of small water clusters at an energy relevant to the Bragg peak, a phenomenon occurring in proton cancer therapy. Utilizing a single-determinantal wavefunction and classical nuclear mechanics, we employ simplest-level electron nuclear dynamics (SLEND)—a time-dependent, non-adiabatic, direct, and variational method with electron-nuclear coupling terms. For this study, we analyze the one-electron charge transfer channel and obtain corresponding cross sections. Results are compared with available experimental data for the water monomer. The data demonstrate the ability of SLEND to provide an accurate charge transfer description and indicate the results for the larger water clusters are similarly accurate.



Water clusters studied in this work.

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WITHDRAWN

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Calculating enthalpies of formation for amino derivatives of trinitrotoluene

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Homodesmotic reactions are a subset of isodesmic reactions. Isodesmic reactions conserve bonds and bond types; homodesmotic reactions further preserve bonding environments. Homodesmotic reactions and isodesmic reactions which are almost homodesmotic can be used to compute enthalpies of formation to within one or two kcal/mol of experimental results without having to compute atomization energies. Despite the different zeros of energy, one may set the computed enthalpy of the model reaction equal to the experimental enthalpy for the same reaction. From the computed enthalpy of reaction, the desired enthalpy of formation is determined by use of reference values for all other systems in the reaction. In the current study, the enthalpies of formation of amino derivatives of trinitrotoluene (TNT) are computed. Such derivatives have been postulated to be intermediates in environmental degradation of TNT. Optimum equilibrium geometries, harmonic vibrational frequencies, and the corresponding enthalpies are computed for all of the reactants and products in each model equation using SCF and density functional theory. The DFT functionals employed are Becke's three-parameter hybrid functional using the LYP correlation functional (B3LYP), the M06-2X high nonlocality hybrid functional from Thular and Zhao, and the ωB97XD functional from Head-Gordan and coworkers which includes empirical dispersion. The basis sets employed are Dunning and coworkers' correlation consistent basis sets: cc-pVDZ, cc-pVTZ, and cc-pVQZ. We gratefully acknowledge support from the NSF (EPS-0903787) and the W.M. Keck Foundation.

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The conventional strain energies of cyclopropylborane, borirane, boretane, and the diboretanes

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In 2012, Rubina and Rubin reported the first generation and spectroscopic identification of boretane through a strain-release-driven ring expansion of cyclopropylborane. Prior to this discovery, all four-membered boracycles which had been reported were unsaturated. In the current study, we build upon this discovery by calculating the conventional strain energies of cyclopropylborane, borirane, boretane, 1,2-diboretane, and 1,3-diboretane within the isodesmic, homodesmotic, and hyperhomodesmotic models. Optimum equilibrium geometries, harmonic vibrational frequencies, and corresponding electronic energies are computed for all pertinent molecular systems using SCF theory, second-order perturbation theory, and density functional theory (DFT). The DFT functionals employed are Becke's three-parameter hybrid functional using the LYP correlation functional and the M06-2X high nonlocality hybrid functional from Thular and Zhao. Three correlation-consistent basis sets are employed: cc-pVDZ, cc-pVTZ, and cc-pVQZ. In addition, single-point CCSD(T) results are computed at the MP2/cc-pVQZ optimum geometries. Results are compared to the conventional strain energies of cyclic hydrocarbons. We gratefully acknowledge support from the NSF (EPS-0903787) and from the Mississippi College Catalysts, the alumni support group of the Department of Chemistry & Biochemistry.

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Conventional strain energies of aziridine, oxirane, phosphirane, and thiirane

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The conventional strain energies for aziridine, oxirane, phosphirane, and thiirane are determined within the isodesmic, homodesmotic, and hyperhomodesmotic models to compare the effect of third-row elements to second-row elements on the strain energies of three-membered rings. Optimum equilibrium geometries, harmonic vibrational frequencies, and corresponding electronic energies are computed for all pertinent molecular systems using self-consistent field (SCF) theory, second-order perturbation theory (MP2), and density functional theory (DFT). The DFT functionals employed are Becke's three-parameter hybrid functional using the LYP correlation functional and the M06-2X high nonlocality hybrid functional from Thular and Zhao. The basis sets employed are Dunning and coworkers' correlation consistent basis sets: cc-pVDZ, cc-pVTZ, and cc-pVQZ. In addition, cc-pV(D+d)Z, cc-pV(T+d)Z, and cc-pV(Q+d)Z basis sets are also investigated to determine the effect of the extra d function for sulfur and phosphorus on the overall results. We gratefully acknowledge support from the NSF (EPS-0903787) and from the Mississippi College Catalysts, the alumni support group of the Department of Chemistry & Biochemistry.

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Applying comparative modeling strategies and virtual docking toward deorphanization of GPR26

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G-protein coupled receptors (GPCR) are members of a large family of transmembrane proteins involved in cellular response to external stimuli. These proteins have ubiquitous roles in physiological processes and disease models of higher organisms. The largest subfamily of GPCR include several that are termed "orphan receptors" because their endogenous ligands are currently unknown. The recent rise in solved GPCR structures deposited to the Protein Data Bank has allowed for more accurate comparative models to study aspects of GPCR structure. GPR26 is an orphan receptor that has been shown to be primarily expressed in specific brain tissues and is involved in increased depression- and anxiety-like behaviors in GPR26 mouse knock-out models. Our goal is to build and validate a model of GPR26 by sequence homology comparisons and virtual docking experiments with synthetic antagonists from patent literature in orderas a tool to find potentialguide the identification of endogenous ligands. Various methods to model the conformations of the extracellular loops, which are potentially involved in ligand recognition and binding, are employed to enhance the overall model. After *in silico* screening for candidate molecules from the human metabolome database with the GPR26 homology model, we can prioritizepresent a set of high-priority compounds to be used for experimental validation.

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Role of the substituent effects on the luminescent efficiency of phenazine-based europium β-diketonate complexes: A density functional theory study

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Eu(III) metal complexes exhibit unique luminescent properties including large Stokes shifts, long luminescent decay times, and line-like emission bands. They have been proposed to be used in lasers, organic light emitting diodes, biomedical analysis/imaging, and sensing technologies. Sensitizer ligands also known as antenna ligands are used to enhance the molar absorptivity of the complexes since direct excitation of Eu(III) ions leading to *4f-4f* electronic transition are parity forbidden. Coordinated antenna ligands are responsible for energy absorption and transfer to Eu(III)-based excited states for an efficient emission process. Ligand based electronic states relative to the Eu(III)-based excited states are critical for an efficient energy transfer avoiding non-radiative decay pathways and back energy transfer processes. In this project, we have used the density functional theory (DFT) to investigate the electronic excited states of a series of $Eu(TTA)_3$DPPz-R complexes ((TTA = theonyltrifluoroacetone, DPPz = dipyrido[3,2-a:2',3'-c]phenazine). R represents methyl, carboxylic acid, methoxy, bromine, ester, nitro, and amine substituents. DFT optimized geometries will be compared with the experimental single crystal X-ray structures. Ligand-based singlet and triplet excited states of the complexes were calculated using time-dependent density functional level of theory. Comparisons will be made between theoretical absorption spectra and experimental absorption spectra. Substituent effects of DPPz ligand on the experimental luminescent quantum yields were evaluated in order to provide insight in to the design of novel antenna ligands for making highly luminescent Eu(III) complexes.

Application of surface enhanced Raman spectroscopy for distinguishing among isomeric structures of nitroanilines

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Nitroanilines are derivatives of aniline used in the manufacturing of dyes, pesticides, gasoline, certain pharmaceuticals, and poultry medications. This research shows how the three isomers of nitroaniline, namely 2-nitroanilne, 3-nitroaniline, and 4-nitroaniline, can be distinguished by Surface Enhanced Raman Spectroscopy (SERS). The SERS measurements based on colloidal silver enhance the Raman signals according to the following order of enhancement factors: 2-nitroaniline > 4-nitroaniline > 3-nitroaniline. The magnitude of enhancement factors indicates the significance of the position of the nitro group on chemisorption. Aniline gave the strongest SERS signal enhancement while nitrobenzene gave the weakest enhancement, suggesting that there might be a preferential interaction between the amino group and the silver substrate. Additional enhancement were obtained using copper foil in combination with the colloidal silver nanoparticles. Computational modeling based on Density Functional Theory (DFT) was also conducted to study the adsorption of the analytes on the silver and silver-copper substrate.

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Investigating physical properties of fuel components using molecular dynamics

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The goal of this project was to investigate physical properties of various molecules and combinations of molecules that are potentially useful in renewable fuels. The AIREBO potential is an emipirical bond-order potential that is used to model the interactions between the atoms of individual molecules using computer simulations. This work was done by modeling liquids using molecular dynamics and the AIREBO potential, and calculated the physical properties of density, viscosity, and bulks-modulus. Multiple trials for pure liquids of only one molecule and also binary systems of various ratios of isocetane and dodecane were calculated and simulation results are compared to experimental values. Individual liquid systems of pure, dodecane, dodecene, hexadecane, isocetane, isooctane, methylcyclohexane, methylnaphthalene, octadecane, tetralin, trans-decalin, toluene, and trimethylbenzene were measured. The calculated RMSD (Root Mean Square Derivative) of the twelve pure substances was found to be within 2% of the literature densities. For the binary system of dodecane and isocetane four mole fractions were calculated at two temperatures, and the RMSD of the density at 298K was 1.04% and 1.5% at 353K. The viscosities that were calculated appeared to be qualitatively correct but not quantitatively correct. The bulk modulus that was calculated for the pure systems appeared to be both qualitatively and quantitatively correct when compared to experimental values.

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Mechanism and kinetics of antioxidant activity of two recently synthesized antioxidants

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The scavenging activity of two recently synthesized antioxidants towards hydroperoxyl radical in lipid and aqueous solutions has been studied using density functional theory based methods. Several reaction mechanisms including radical adduct formation, hydrogen atom transfer, and single electron transfer were investigated to find energetically viable paths. The rate constants of these viable reaction paths were calculated using the conventional transition state theory. Similarities/differences of the reaction mechanism and kinetics based on the chemical structure and the solvent environment will be discussed.

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Computational investigation of substituent effects on guanine binding of 1-, 2-, and 1,2-substituted naphthalenes

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DNA is often a target for anti-cancer drugs due to its inherent ability to imitate such processes as transcription and replication. Intercalation, insertion of a molecule between the base pairs of DNA, is one such manner in which small molecules bind to DNA. Our group has previously focused on calculating the binding energies of benzene-substituted benzene complexes as a formative means to predict the binding strength of DNA to substituted naphthalimide intercalators. Recently the intercalation of 3-substituted naphthalimides with DNA was found to occur in guanine-rich areas. Thus, we initiated a computational study to investigate the binding of substituted naphthalenes with guanine as an improved model for understanding DNA-naphthalimide intercaltor binding.

Here we present the results of computational work focusing on the binding of 1-substiuted, 2-substituted, and 1,2-disubstiuted naphthalenes with N9-methylguanine. Specifically a series of substituted naphthalenes were studied in a parallel face-to-face orientation over guanine. The substituents included $-CH_3$, -OH, $-OCH_3$, $-NH_2$, -F, -Cl, -CN, and $-NO_2$. For each substituted naphthalene-guanine dimer four relative orientations were investigated, where the naphthalene substituents were positioned over the different guanine functional groups.

All substituted naphthalene geometries, and the N9-methylguanine geometry, were optimized and characterized via frequency calculations using the MP2(full)/6-311G** level of theory. The local binding energy minima for each substituted naphthalene-guanine dimer was determined by varying the distance between the centroids of the two molecules from 1.0-5.0 Å. All energies were calculated at the MP2(full)/6-311G** level of theory and corrected for basis set superposition error (BSSE) using the counterpoise method. In addition, Symmetry-Adapted Perturbation Theory (SAPT0) was applied to the lowest BSSE corrected binding energies for each substituted naphthalene-guanine dimer, and the energy decomposition values will be presented and discussed.

Hydrogen, ammonia borane, and carbon dioxide activation by phosphinoboranes

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The activation of CO2 and further reduction to yield hydrogenated products can be achieved by synergy between a strong Lewis acid (high capacity to accept electrons) and a strong Lewis base (high capacity to donate electrons) with the restriction that a steric effect due to their substituents precludes an optimal match for the formation of the adduct Lewis acid/Lewis base. Such frustrated Lewis pairs (FLP) containing main group elements meet these requirements and the scope of activation of inert molecules is opened beyond the use of compounds containing transition metals, with applications to hydrogen storage and the sequestration and further transformation of CO2. Three different chemistries for the activation of H2, H3NBH3 and CO2 as well as their interaction between them were studied for Y = R2P and X = R2'B. The global reaction between the four membered cyclic compound c-X2Y2 (1) in the presence of H2/CO2 to yield (OH)XYMe and water as a product is an exothermic reaction. The hydrogenation of the CO2 through the activation of H3NBH3 is also studied. Global and local reactivity descriptors derived from density functional theory (DFT) are used to rationalize the results of the different reactions paths that are predicted. The electron density response

to a change in the number of electrons, Fukui function, is compared to the frozen core approximation given by the frontier molecular orbitals. The calculations were performed with the ωB97x exchange-correlation functional and the DZVP2 basis set. The solvent is modelled as a continuum using self-consistent reaction field approaches with the dielectric constant of dichloromethane. This work was supported by the Department of Energy through Los Alamos National Laboratory.

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Automated design of small molecules with Rosetta

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The Rosetta software suite has been successful in designing proteins to interact with small molecules of given structure. We are looking to invert this process, and computationally design novel small molecules which interact with a given protein pocket. This automated protocol uses the Rosetta scoring function, reaction-based moves, and Monte Carlo optimization to produce new molecules with similar predicted binding affinities and close molecular similarity to known binders. Flexible filtering options allow selecting putative results by varied properties such as hydrophobicity, molecular weight, and synthesizability metrics, in addition to predicted binding affinity. This flexible small molecule design, paired with the capabilities of the Rosetta protein modeling framework, promises to provide a powerful tool for drug lead generation.

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Predicting ^{195}Pt NMR chemical shifts in small Pt(II) and Pt(IV) organometallic compounds with density functional approaches

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NMR is a powerful technique for gaining insight into the electronic nature of an interaction between a metal center and a ligand. A series of Pt(II)- and Pt(IV)-containing organometallic compounds have been fully characterized (i.e. full optimizations and corresponding harmonic vibrational frequency computations) with pure and hybrid non-relativistic density functional techniques. Solvent effects were included using an implicit polarized continuum model. Corresponding ^{195}Pt NMR absolute isotropic shielding constants were computed and chemical shifts were determined from $[PtCl_4]^{2-}$ and $[PtCl_6]^{2-}$ reference compounds. Previously reported results indicate a near-linear relationship between experimental and predicted chemical shifts. However, this work indicates troubling deviations and highlights the sensitive nature of the computed shielding constant with respect to the geometry or level of theory implemented. For example, elongation of the Pt-Cl bonds by 0.02 Å in $[PtCl_4]^{2-}$ changes the absolute isotropic shielding constant by approximately 600 ppm.

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Density functional theory investigation of uranyl (VI) complexes with nitrogen donor terpyridine-type ligand derivatives

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The separation of actinides from lanthanide ions in the nuclear waste products is an active area of current research. Separation of uranium species from lanthanide (III) metal ions can be achieved by choosing Lewis basic ligands which are capable of selectively coordinating to uranium metal ions forming stable metal-ligand complexes. We believe that the fundamental understanding of uranium metal-ligand bonding is essential for molecular design of uranium extracting agents with high selectivity. Exploration of suitable uranyl (VI) complexes with equatorial oxo ligands may stimulate a novel area of coordination chemistry which has shown great diversity in ligand binding. This research is focused on using density functional theory (DFT) to evaluate the bonding, electronic structure, and stability of uranyl (VI) complexes using a series of N-donor tridentate terpyridine derivatives. DFT-calculated uranyl (VI) metal-ligand bond distances are well in agreement with the experimentally determined bond distances of similar complexes using single crystal X-ray diffraction. Free energy changes of the complexes suggest that the negatively charged nitrogen donor ligands form comparatively stable metal-ligand complexes. Ligand planarity plays a crucial role in the stability of the complexes. Oxygen substitution for carbon atoms in a nitrogen donor ligand may not provide highly selective and stable complexes. Bond order analysis and the free energies of complex formation will be discussed as a means to guide selective uranyl (VI) metal complexation

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Revealing the pressure-induced breakdown pathway in WS_2 nanotubes

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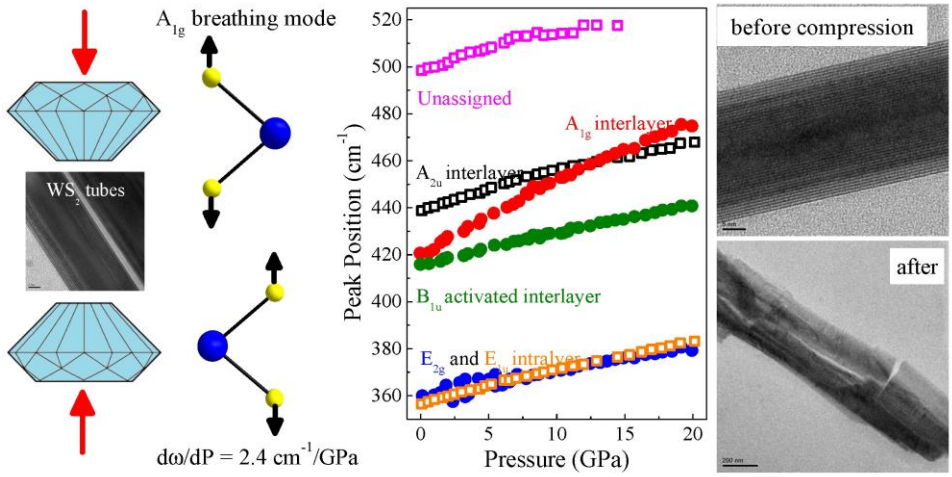
Nanoscale chalcogenides are attracting tremendous attention due to their exotic properties and demonstrated applications. These van der Waals solids form nanotubes and nanoparticles, and just like graphite, they can be cleaved into single- and few-layer sheets. The tubes and particles are well known to display superior mechanical and tribological properties, although the detailed solid state lubrication mechanism and pressure-induced breakdown under high strain rates is not well understood. In order to reveal the microscopic aspects of these processes, we measured the synchrotron-based infrared and Raman response of multi-wall WS_2 nanotubes under pressure. While most of the vibrational modes display similar compressibilities, the Raman active A_{1g} interlayer breathing mode is almost twice as responsive, suggesting that the nanotube breakdown pathway proceeds through this displacement. Suppression of this vibration, for instance with a filler or nanoscroll geometry, could prevent the breakdown and extend the range of solid state lubrication applications. At the same time, the high pressure infrared measurements provide unexpected insight into the electronic properties of the multiwall WS_2 tubes. The rising spectral background is fit to a percolation model, indicating that the nanotubes display a modest macroscopic

conductivity. Time permitting, I will also discuss the properties of chalcogenide sheets like $CrSiTe_3$ and how dichroic spectroscopy provides unique insight into their magnetic character.



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Enhancements and applications of C_{60} in energy storage materials

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Buckminsterfullerene (C_{60}) has attracted a significant amount of interest by researchers since its discovery in 1985. While there has been extensive research conducted on C_{60} and its derivatives, few applications for the molecule have been presented. Although cost is still a prohibitive factor, we present examples of applications for C_{60} in hydrogen storage materials and solid state electrolytes. Alkali-doping of C_{60} was determined to significantly reduce the conditions required for the direct hydrogenation of the fullerene cage and for the dehydrogenation of the material without hydrocarbon release. During our investigation of alkali-doped fullerenes, the first spectrometric evidence for the existence of $C_{60}H_{60}$ was acquired. It was also found that C_{60} can act as a catalyst for the dehydrogenation and rehydrogenation of $LiBH_4$. The addition of C_{60} to $LiBH_4$ resulted in a two-step desorption mechanism where the carbon nanomaterial acts as an active hydrogen storage material as well as a catalyst. Further investigation of the C_{60}-$LiBH_4$ nanocomposite revealed high lithium ion mobility. It was determined that the addition of C_{60} to $LiBH_4$ enhanced the lithium ion mobility compared to pure $LiBH_4$. This effect is believed to be due to electron density transfer to the fullerene cage from the BH_4 anion which allows for a more mobile lithium species.

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Developing spectroscopy techniques to study interaction of anticancer drugs with DNA

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Optical spectroscopy such as Raman scattering offers useful tools to study physical and chemical changes in cells and tissues, thereby providing a unique opportunity in diagnostics and therapeutics. When the Raman scattering is dramatically enhanced by the adsorption of molecules onto the surface of metal nanoparticles, it is known as Surface-Enhanced Raman scattering (SERS). SERS is an effective analytical technique due to its high sensitivity and selectivity. Our research utilizes the SERS technique to investigate how anticancer drugs modify DNA to further understand the nature of the modifications at the molecular level. In this presentation, we will discuss the SERS spectra of anticancer drugs such as cisplatin, carboplatin and oxaliplatin and SERS spectra of the DNA bases. Further studies examining modifications in the spectra of drugs and bases under various sample preparation conditions such as temperature, pH, and concentration are in progress and will be discussed in this presentation. These spectra will serve as a baseline for future studies involving drug-modified DNA under various sample preparation conditions.

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Adventures in anion photoelectron spectroscopy: CO_2 activation, water splitting, and rare earth mimics

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This talk will report on our recent progress using anion photoelectron spectroscopy to study anion complexes in which (a) carbon dioxide is strongly bound, (b) water is split by its interaction with specific transition metal atoms, and (c) the properties of rare earth compounds are imitated.

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What is so positive about negative ions?

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Negative ions play a fundamental role in chemistry as oxidizing agents. They also help to purify air and uplift mood by increasing levels of serotonin. Halogens, due to their $s^2 p^5$ valence shell, are among the most electronegative atoms in the periodic table with chlorine having the highest electron affinity, namely 3.6 eV, of all elements. To promote reactions that halogens cannot do, there is a need to go beyond the periodic table and create molecules or clusters [1] that not only mimic the chemistry of halogens but also have electron affinities much larger than those of halogen atoms. Such species called superhalogens [2] and hyperhalogens [3] have been found to have electron affinities as high as 14 eV and play an important role in a wide range of fields from hydrogen

storage to Li-ion batteries. I will discuss how such species can be created without using a single halogen atom, and how they can address some of the challenges in our pursuit of clean energy [4]. Use of simple electron counting rules to design highly stable dianions composed of organo-metallic complexes in the gas phase will also be illustrated [5].
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Spectroscopy and decomposition dynamics of nitrophenoxide anions

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We present experimental and computational results on the vibrational spectroscopy and decomposition dynamics of nitrophenoxide molecular anions. We use simultaneous infrared multiple-photon dissociation (IRMPD) and infrared multiple-photon electron detachment (IRMPED) spectroscopies to acquire the infrared action spectrum of each of the para-, meta- and ortho- nitrophenoxide species. We compare the observed experimental spectra to calculated spectra , and we compare the IR-induced dissociation pathways to those observed in a recent collision-induced dissociation experiment [1]. We examine the competition between the dissociation and electron detachment channels in detail. We build upon our earlier similar explorations of the IRMPD/IRMPED nitrobenzene radical anion [2] and a series of substituted phenoxide anions [3] in order to understand the interactions between the nitro- and phenoxy- chemical functional group moieties, particularly in regards to the role of stabilizing the negative charge and molecular structure.

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Photoelectron spectroscopy and photochemistry of ozonide cluster anions, $O_3^-(H_2O)_n$ and $O_3^-(Ar)_n$,

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Photofragmentation of ozonide solvated in water clusters, $O_3^-(H_2O)_n$, and argon clusters, $O_3^-(Ar)_n$, n ≤ 16, have been studied as a function of photon energy as well as the degree of solvation. The O_3^- acts as a visible light chromophore within the cluster, where the photodissociation cross section of the solvated anion exhibits generally the same photon energy dependence as isolated O_3^- throughout the visible spectrum. With the addition of a single water solvent, new photodissociation pathways are opened, including the production of recombined O_3^-. As the degree of solvation of the parent anion increases, recombination to O_3^--based products accounts for 40% of photoproducts for $O_3^-(H_2O)_{16}$, and nearly 90% of photoproducts for $O_3^-(Ar)_{15}$. Time-resolved photodissociation-photoelectron spectroscopy of the ionic species present following photodissociation yields information of the dynamics taking place within the evolving complexes. Finally, we report photoelectron spectra of *cis*-$HONO^-$, providing rich information on high vibrational levels of the ground state of *cis*-HONO, as well as the previously unobserved T_1 (a ^{3}A") HONO near the transition state proceeding along the *cis* Ô *trans* isomerization co-ordinate.
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Functional polycaprolactones for delivery of anticancer drugs

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The effect of the substituent on the micellar behavior of thermoresponsive amphiphilic poly(epsilon-caprolactone) diblock copolymer micelles was investigated byh a combination of experimental and computational methods. The polycaprolactone (PCL) amphiphilic block copolymers used in this study consisted of a hydrophilic poly{γ-2-[2-(2-methoxyethoxy)ethoxy]ethoxy-ε-caprolactone} block, which also gave the polymer with thermoresponsiveness, and various hydrophobic poly(γ-alkoxy-ε-caprolactone) blocks. Five different substituents have been attached to the γ-position of the e-caprolactone of the hydrophobic block, namely octyloxy, ethylhexyloxy, ethoxy, benzyloxy, and cyclohexylmethoxy, which self-assembled in aqueous media to generate the core of the micelles. Drug loading and release properties were also studied by employing Doxorubicin (DOX) as payload.

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Biodegradable three-layered micelles for efficient non-viral gene delivery systems

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Polymeric materials have found a growing interest as gene vectors due to the serious safety concerns associated with viral vectors. This study describes the development of polymeric micelles for application as systemic and localized gene delivery vectors. “Three-layered micelles” (3LM) composed of two triblock copolymers, poly(L-lactide)-b-polyethyleneimine-b-poly(L-lactide) (PLLA-PEI-PLLA) and poly(L-lactide)-b-poly(ethylene glycol)-b-poly(L-lactide) (PLLA-PEG-PLLA) are designed to combine electrostatic interaction and solvent-induced condensation of DNA. These 3LM are prepared via two consecutive steps. Step 1, DNA encapsulation is achieved through formation of an organo-micelle (OM) in tetrahydrofuran (THF). Step 2, the DNA loaded OM is stabilized for aqueous solution by enclosing within an amphiphilic triblock copolymer, PLLA-PEG-PLLA. The micelle hydrodynamic diameter of the OM and 3LM were measured to be ~100 and 200 nm respectively by DLS. The morphology of the OM and 3LM are determined to be spherical through TEM. Polyanion competition assay showed the 3LM to be highly stable at neutral pH even at high concentration of dextran sulfate. However in slightly acidic environment (ca. 4.5) we observed burst release of DNA. We attribute the observed pH dependence to the PLLA inner shell which creates a hydrophobic barrier at neutral pH preventing access to the polyplex core. At low pH however, hydrolysis of the biodegradable ester linkages leads to the destabilization of this barrier and immediate release of DNA from the polyplex. MTT assay showed >70% cell viability at the lowest concentration tested and observed gradual decrease in cell viability with increasing concentration. Furthermore, the 3LM was further developed into a temperature responsive injectable hydrogel for use as a localized gene delivery system by utilizing the stereocomplexation behavior of polylactides.

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Design of hydrogels containing alginate and modified cellulose as superabsorbent materials

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The applications of hydrogels have been a growing field of interest. These smart polymers, also known as superabsorbent polymers (SAPs), are capable to be swelled with water several times. Usually, hydrogels consist of strong hydrophilic polymers slightly cross-linked. Hydrogels have been used in hygienic products as diapers, drug delivery systems, food additives, pharmaceuticals, biomedical applications as tissue engineering and regenerative medicines, diagnostics, separation agent, and others. A particularly growing area is the use of hydrogels as additives in the agricultural and horticultural industries for the improvement of the soil's physical properties, such as nutrient and water retention, permeability, density, and structure.

Envisioned in this project is the conversion of renewable and biodegradable resources into bio-based superabsorbent polymer networks. In particular, the use of polysaccharides, such as alginate and cellulose.

In this work, we synthesized superabsorbent polymers based on oxidized cellulose and alginate and finally crosslinked with citric acid. The influence of different ratios of polysaccharides (alginate to cellulose 8:2, 6:4 and 4:6) and the weight percent of the crosslinking agent (10, 20 and 30 wt%) on the final water uptake and the structural

properties were studied by means of a Design of Experiment. In general terms, the crosslinking (amount of citric acid) yields an optimum value, below this value the crosslinking is insufficient to keep the structure of the hydrogel and above it the hydrogel decreases the availability of swelling.

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Mechanochemistry for soft, active materials and devices

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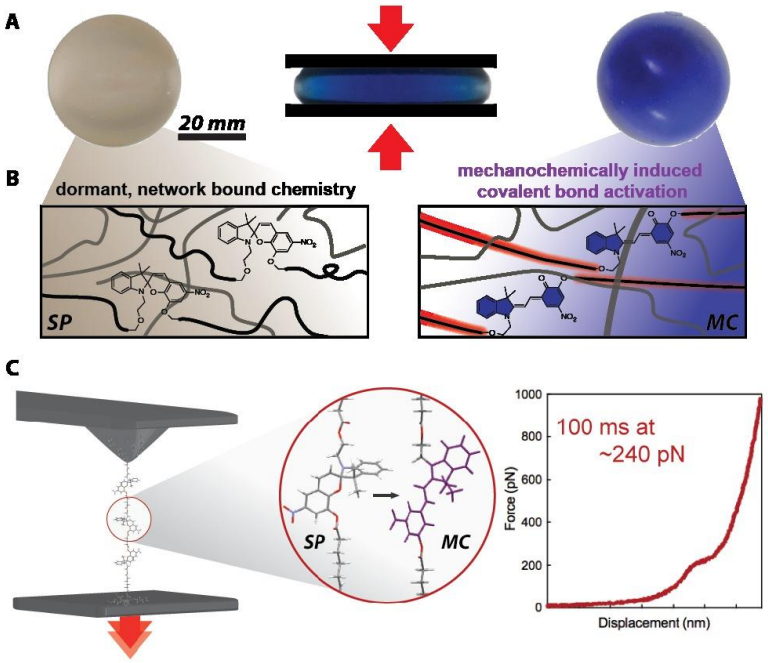
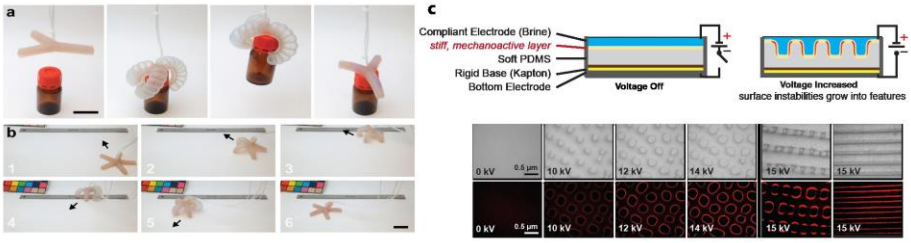
Soft polymeric materials can be made mechanically stimulus responsive when the component molecular units responsible for bulk mechanical behavior are themselves made to be mechanochemically responsive. We aim to capitalize on the hierarchy of ‘macroscopic-to-molecular’ force transmission to create chemomechanically responsive materials. Towards this end, we have: (1) Identified an elastic material platform that achieves covalent chemical reactions reversibly and repeatedly, allowing for chemical reactivity to be turned on and off with spatiotemporal resolution within an intact device. (2) Translated the material to existing dynamic soft technologies to fabricate the first chemomechanically responsive devices; first, by remotely inducing dielectric patterning of an elastic substrate to produce assorted fluorescent patterns in concert with topological changes; and second, by adopting a soft robotic platform to produce a color change from the strains inherent to pneumatically actuated robotic motion. (3) Finally, we used force spectroscopy to quantify the magnitude of forces required to activate individual spiropyran-based force-probes, and in doing so, enabled the probe behave as a “scout” of molecular forces in materials; the observed behavior of which can be extrapolated to predict the reactivity of potential mechanophores within a given material and deformation. In looking forward, we anticipate the development of new mechanophores that, like the materials, are reversibly and repeatedly activated, expanding the palate of soft, active devices and further permitting dynamic control over chemical reactivity that is otherwise inaccessible, each in response to a single remote signal.





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Using multi-step synthesis for the production of hydrogels with adhesive properties

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Hydrogels are networks of polymer chains that are highly absorbent and flexible similar to natural tissue. Currently hydrogels are being used in controlled drug delivery, fluid control, nerve regeneration and tissue engineering.[1] The production of a remote activated, polyacrylamide hydrogel system is a multi-step synthesis. The first step investigated was the formation of a copolymer via free-radical polymerization using the starting material dopamine hydrochloride reacted with sodium tetraborate decahydrate and sodium bicarbonate. This presentation will highlight the experimental design and multi-step synthesis for the production of hydrogels.

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Fast pyrolysis bio-oils as precursors of thermosetting epoxy resins

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The thermal and mechanical performance properties of organic polymers are generally linked to the presence of aromatic rings in their structures. In this context, with the objective to synthetize a high performance bio-based epoxy polymer, fast pyrolysis bio-oil (containing lignin fragments) was employed as a source of phenolic compounds in the production of a bio-based polymeric network. The bio-oil was reacted with epichlorohydrin and an aqueous solution of sodium hydroxide in the presence of benzyltriethylammonium chloride as a phase transfer catalyst. The amount of free phenolic hydroxyl groups before and after modification was quantified through P^{31}-NMR spectroscopy; and the epoxy content of the bio-oil upon chemical functionalization was measured by means of a titration using HBr in acetic acid solution. Grafting of epoxy functions onto the monomer`s structure was studied by FTIR. Likewise, α-resorcylic acid (a phenolic compound found in peanut, chickpeas, red sandalwood and hill raspberry) was also modified with reactive epoxy moieties and used as a model to study the mechanical behavior of phenolic-based epoxy polymers. The epoxidized derivatives of the bio-oil were cured in epoxy polymer with DMPA. Thermo-mechanical characterization showed that the obtained materials behave as thermoset amorphous polymers, exhibiting moduli values in the order of Giga Pascals at room temperature and glass transition temperatures above 100 °C.

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Mechanical analysis of chemically treated coir fibre polyester composites

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In this research work the mechanical and morphological behaviour of untreated and chemically treated coir fibre- polyester composites was investigated. The coir fibre content was varied from 0% to 60% by weight of the total resin. The chemical treatment of coir fibre was carried out by using chemicals; NaOH, Maleic anhydride (MA) and silane. The study revealed that untreated coir fibre- polyester composites exhibit good mechanical properties at 30% fibre loading whereas MA treated coir fibre- polyester composites exhibit better mechanical properties as compare to other two chemically treated coir fibre- polyester composites. The scanning electron microscopy (SEM) analyses revealed that good adhesion between coir fibre and polyester resin was developed in chemically treated coir fibre- polyester composites as compared to untreated coir fibre- polyester composites.

Keywords: Coir fibre, Polyester, NaOH, MA, Silane, Mechanical properties, SEM.

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Protein corona on magnetic nanoparticle

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My laboratory research attention is to enhance the therapeutic potential of synthetic or naturally occurring drug molecule(s) using nanotechnology. This can be achieved by designing number of formulation using nanoparticles, self-assemblies, hydro-/nanogels, liposomes and complexation for the sustained and efficient delivery of drug(s). We have recently developed a multi-layer approach for the synthesis of water-dispersible superparamagnetic iron oxide (magnetic) nanoparticles for hyperthermia, magnetic resonance imaging (MRI) and drug delivery applications. The interaction of serum proteins and magnetic nanoparticles leads to nanoparticle-protein complex formation that is a clinically relevant phenomenon in cancer nanomedicine. This study reports the alteration in particle size, zeta potential, hemotoxicity, cellular uptake/cancer cells targeting potential, and MRI properties of the MNPs after formation of human serum (HS) protein corona. All these superior clinical parameters potentially enable clinical translation and use of this formulation for next generation nanomedicine for drug delivery, cancer-targeting, imaging and theranostic applications.

Interdisciplinary approaches to evaluation the toxic potential of engineered nanomaterials: A regulatory perspective

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With the rapid expansion of nanotechnology in cancer therapy, there have been great concerns for the safety issues of the nano-product regulated by U.S Food and Drug Administration. Pre-clinical characterization and quality control during the manufacturing of nano-products are fundamental for understanding resulting safety issues during their wide application. All regulated products are required to submit basic physio-chemical characterization as part of Investigational New Drug (IND) Applications or New Drug Applications (NDA) submitted to the FDA for review. In regulatory science of nanotoxicology studies, these characterizations are essential to better understand the results from these toxicological studies. Recently, FDA established in-house nanotechnology core facility to support the research and detect the nanomaterials in food, drug, and cosmetics obtained from the market. Biological characterization of gold based nanomaterials and carbon nanotubes will be discussed as cases studies. The multiple characterization approaches used in these studies provided the solid basis to understand the biological responses of these nanomaterials for regulatory purpose.

Understanding the interactions of theranostic gold-based nanostructures with complex biological environment

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Gold-based nanostructures as drug delivery, bio-imaging and therapeutic agents are typically introduced to biological systems through intravenous administration. However, the potential for agglomeration of nanoparticles in biological systems could dramatically affect their pharmacokinetic profile and toxic potential. Development of rapid screening methods to evaluate agglomeration is urgently needed to monitor the physical nature of nanoparticles as they are introduced into blood. In this presentation, I will discuss the novel methods we established using darkfield microscopy with hyperspectral detection, single particle inductively-coupled plasma mass spectrometry, and confocal Raman microscopy to discriminate gold nanoparticles and their agglomerates in blood. I will also discuss the behaviors of the drug-polymer delivery system we developed in serum mimetic environment and in vesicles that model human cell membranes. These studies provide rapid determination methods of the agglomeration status of nanoparticles in blood, as well as insight of action and release kinetics of non-covalent drug delivery system in the biological environment.

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Tuning the optical-plasmonic properties of Ag/Au hybrid nanoparticles for SERS detection

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Noble metal nanoparticles (NPs) exhibit unique optical-plasmonic properties that make them advantageous for numerous applications. Gold nanomaterials in particular have been employed in imaging, sensing, and therapeutic applications due to their simple conjugation with various biomarkers as well as their biocompatibility and low reactivity. As a result of the large electric fields generated at the surfaces of gold (Au) and silver (Ag) nanoparticles (NPs) by the localized surface plasmon resonance (LSPR) of the conduction band electrons, Ag and Au NPs greatly enhance the signals of Raman scattering by adsorbed molecules. The LSPR in Ag NPs is more intense than in Au NPs and, consequently, Ag NPs typically provide stronger surface enhanced Raman scattering (SERS) signals. However, Ag NPs lack the chemical stability and biocompatibility of their Au counterparts and typically exhibit their most intense LSPR properties at wavelengths much shorter than the optimal spectral region for certain biomedical applications. To overcome these issues, various Ag/Au hybrid NPs have been synthesized. In this study, the discrete dipole approximation was employed to model the LSPR spectra and near-field enhancements of Ag-Au core-shell NPs along with Ag/Au alloyed NPs to evaluate the effects of NP composition on these properties.

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Size- and shape-controlled synthesis and properties of magnetic-plasmonic core-shell nanoparticles

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There has been a great interest in the development of nanoparticles that combine multiple functions or properties which are not obtainable in individual materials. Some of those nanoparticles combine an optical signature originating from a gold shell layer with

other physical properties such as magnetisms which originates from the magnetic core. This combined property is particularly intriguing due to its applications in biomedicine such as use in bio-separation or as magnetic resonance imaging. Our research goal is to develop novel magnetic and plasmonic hybrid nanoparticles with other related technology for cancer detection and treatment. We have developed a facile approach to prepare iron oxide-gold core-shell nanostructures in different sizes and shapes such as spheres, popcorns, and stars with integrated optical and magnetic properties. Different sizes and shapes were prepared by adjusting the amount of gold seed-adsorbed iron oxide nanoparticles and the amount of silver nitrate additives and reducing agents. By changing their shapes from sphere to star, significant red shift of the localized surface plasmon resonance peak was observed, with nanospheres at 570nm, nanopopcorns at 650 nm and nanostars at 760nm. The magnetic properties were confirmed by magnetization-field measurement and magnetic separation. The core-shell structures were confirmed the presence of both iron and gold peaks in the energy-dispersive X-Ray spectroscopy. These nanoparticles may offer next generation diagnostic and therapeutic products.

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Novel self-patented gold nanoparticles for augmented antineoplastic activity

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Phloridzin, a natural hydoxychalcone constituent obtained from fruit trees is an antidiabetic and antineoplastic agent. Phloridzin was first isolated, for clinical pharmaceutical usage, from the pear tree bark of Pyrus communis in 1838 as the first sodium-glucose linked transport 2 (SGLT2) inhibitor. Apart from its antidiabetic action, phloridzin is also reported to have anticancer activity. Phloridzin had to take an exit from the pharmaceutical market due to its side effects and poor bioavailability when compared to other antidiabetic drug competitors. This limit of phloridzin's bioavailability is primary attributed to the degradation of the glyosidic bond of the drug to result in the formation of phloretin, the aglycone of pholoridzin. Phloretin displays a reduced capacity of SGLT2 inhibition, however this nutraceutical displays enhanced antineoplastic activity in comparison to phloridzin. The mechanism of these chalcones' cytotoxic activity are primarily attributed to their ability to collapse the mitochondrial membrane potential and cause increased oxygen uptake resulting in the uncoupling of mitochondria. Nanoparticles, especially gold nanoparticles (AuNPs) have been studies for drug delivery applications for poorly bioavailable drugs. Hence, in order to tackle the side effects of phloridzin and study the unknown anticancer mechanism, we synthesized phloridzin and phloretin capped gold nanoparticles (Phl-AuNP and Pht-AuNP respectively) in single step, rapid, and biofriendly processes. The synthesized conjugated AuNPs were characterized for size and shape using transmission electron microscopy and UV-Vis spectroscopy. The presence of phloridzin or phloretin was confirmed using SEM-EDS. The percentage of organic component (phloridzin/phloretin) onto GNPs surface was characterized using thermo gravimetric analysis. The pH stability of the AuNPs was studied using UV-Vis spectroscopy. Assessment of the antineoplastic potency of the hydroxylchalcone conjugated AuNPs against varying cancerous cell lines, specifically human hepatocarcinoma cells (Hep G2), will be accomplished through anticancer assays monitored through flow cytometry. In these assays the concentration of live/dead cancerous cells shall be monitored through fluorescence. We hypothesize that functionalization of these chalcones onto the gold

nanoparticles' surface may improve the pharmacokinetic profile of phloridzin and phloretin, thereby help in regaining its lost charm.

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Multifunctional NIR light-inducible plasmonic liposomes for combination anti-cancer therapy

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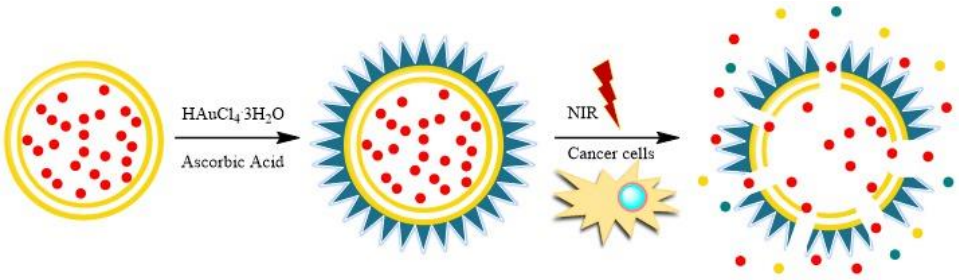
Cancer is now the second leading cause of death in the United States, with increasing incidence as the population ages. It is predicted that there will be more than 1.6m new cancer cases diagnosed and 0.5m cancer-related deaths in the U.S. in 2015. Approximately 1.1m men were diagnosed with prostate cancer in 2012, and with 307,500 deaths worldwide, prostate cancer was the most common cancer among men in the developed world and has remained so. To address this escalating human health crisis, non-toxic NIR light-inducible plasmonic gold-coated liposomes were developed for targetable, selective combined anti-cancer photothermal-chemotherapy. Rhodamine 6G-loaded plasmonic liposomes effectively released the entrapped fluorescent organic dye upon irradiation with a 671-nm NIR laser in a time-dependent manner. In addition, dye-loaded liposomes were efficiently internalized by LNCaP prostate cancer cells. *In vitro* combination photothermal-chemotherapy treatment of LNCaP cells using multifunctional plasmonic liposomes containing entrapped anti-cancer drug molecules demonstrated the great potential for this nanoscale delivery platform to be adapted easily and used as a non-toxic NIR-inducible combination cancer treatment.



Multifunctional NIR Light-Inducible Plasmonic Liposomes for Combination Anti-Cancer Treatment

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Photosensitizer-loaded gold nanorods for combined photodynamic and photothermal cancer therapy

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Photodynamic therapy (PDT) is a non-invasive cancer treatment that uses localized, non-invasive light for the treatment of certain cancers. Conventional PDT is limited by poor water solubility, non-specificity, and photobleaching. Delivery and efficacy can be improved using nanoscale deliveries, among which includes gold nanorods (Au NRs). Au NRs possess several advantages including including small size with tunable features, easy preparation, excellent stability, and immense functionalization potential. We report a Au NR-based nanocomplex as a photosensitizer-carrying photothermal agent. The silicon 2,3-naphthalocyanine dihydroxide(SiNC) photosensitizer is densely trapped in a hydrophobic pocket on the surface of the Au NRs via PEG covalently linked with an alkyl-thiol segment with a specific chain length. Highly efficient SiNC release and cellular uptake was achieved through partition between the nanocomplex and cell membrane. Additionally, we demonstrate through *in vitro* studies that the nanocomplex provides a synergistic effect upon exposure to NIR light, generating cancer cell eradication superior to photothermal therapy (PTT) or photodynamic therapy alone. With the ability to deliver high concentrations of photosensitizer and be utilized in PTT, the nanocomplex has the potential ability to completely ablate tumors, thus preventing tumor reoccurrence.

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Screening racemic catalysts in Pt-catalyzed asymmetric synthesis of P-stereogenic bis(phosphines)

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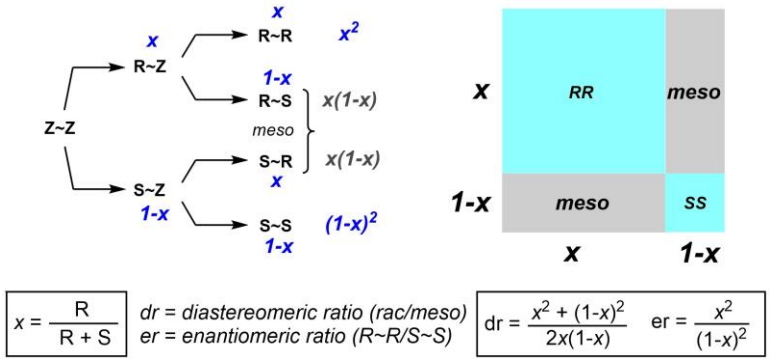
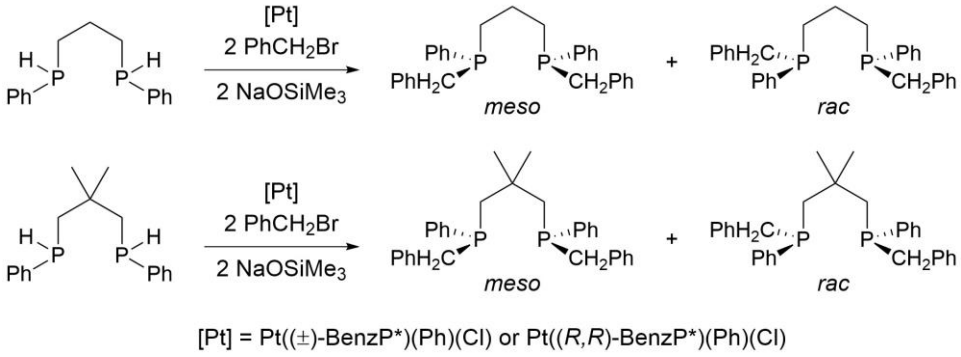
Kagan's method for obtaining selectivity information from racemic catalysts was applied to the Pt-catalyzed asymmetric benzylation of secondary bis(phosphines) and also expanded to account for cases of substrate control and substrate dissociation. The catalysts Pt((±)-BenzP*)(Ph)(Cl) and Pt((*R,R*)-BenzP*)(Ph)(Cl) were synthesized and screened in a set of reactions with the substrate $PhHP(CH_2)_3PHPh$, a variety of benzyl halides $(Y_nC_6H_{5-n})CH_2X$ (Y = alkyl, -OMe, -Br, $-CF_3$, -F, -CN, -Ph; X = -Cl, -Br), and $NaOSiMe_3$ as a base. $C_6H_5CH_2Br$ was found to be the most selective alkylating agent for this reaction, and the results were compared to those obtained by Brian Anderson using Pt((*R,R*)-Me-DuPhos)(Ph)(Cl) as catalyst. Pt((*R,R*)-BenzP*)(Ph)(Cl) (dr = 5.5 ± 0.5, er = 27 ± 13) was predicted to be a more selective catalyst than Pt((*R,R*)-Me-DuPhos)(Ph)(Cl), but some substrate dissociation was observed (positive half-alkylation test) due to ligand steric effects, and substrate control with negative cooperativity was detected by comparison with the same reaction utilizing Pt((±)-BenzP*)(Ph)(Cl) (dr 4.4 ± 0.4, predicted x = 0.92, er = 120). Lithium-mediated P-phenyl bond cleavage of $Ph_2PCH_2C(CH_3)_2CH_2PPh_2$ gave the *gem*-dimethyl secondary bis(phosphine) substrate $PhHPCH_2C(CH_3)_2CH_2PHPh$. Asymmetric alkylation of $PhHPCH_2C(CH_3)_2CH_2PHPh$ using the catalysts Pt((±)-BenzP*)(Ph)(Cl) (dr = 2.0, predicted x = 0.80, er = 16) and Pt((*R,R*)-BenzP*)(Ph)(Cl) (dr = 2.0, er = 2) confirmed that the Thorpe-Ingold effect was successful in preventing substrate dissociation (negative half alkylation test). However, the added steric demand of the two methyl groups exacerbated the negative cooperativity observed previously.



Catalyst control for an enantiopure catalyst and related Horeau diagram.



Pt-catalyzed asymmetric benzylation of $PhPH(CH_2)_3PHPh$ and $PhPHCH_2C(CH_3)_2CH_2PHPh$.

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An N-heterocyclic carbene–ruthenium complex that catalyzes the reduction of radicals in aqueous solutions

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Catalytic hydrogenation of C=O, C=N and C=C bonds is often performed using an organoruthenium complex as the catalyst and an alcohol solvent, such as *i*-PrOH, as the ultimate H_2 source. The transfer of H_2 from *i*-PrOH to an unsaturated organic substrate is analogous to the transfer of $2e^-$ and $2H^+$, thus a transfer hydrogenation catalyst should also be able to catalyze the reduction of radicals. Herein we report the catalytic reduction of 2,2'-azino-bis(3-ethylbenzo-thiazoline-6-sulfonate) radical monoanion ($ABTS^{\bullet-}$) by an N-heterocyclic carbene–ruthenium complex (**Ru1**). Non-tertiary alcohols were required as terminal reductants, wherein the C–H and O–H groups of the –CHOH– moiety were both necessary for terminal reductant function. Rate law and kinetic isotope effect studies were consistent with a transfer hydrogenation-like catalytic cycle and indicated that C–H / O–H bond-breakage occurred during the rate-determining step. In addition, **Ru1** impeded the oxidation of $ABTS^{2-}$ to $ABTS^{\bullet-}$ and then reduced all $ABTS^{\bullet-}$ formed. These findings show that **Ru1** can inhibit the oxidation of $ABTS^{2-}$ to $ABTS^{\bullet-}$ and catalyze the reduction of $ABTS^{\bullet-}$ to $ABTS^{2-}$ by a transfer hydrogenation-like process.

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Controlling dimerisation of metallo-aminoalcohol complexes for supramolecular mixed metal structures

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Amino alcohol structures have enjoyed renewed interest given the columnar motifs prevailing in supramolecular structures of these compounds. The columnar motifs rely upon stereospecific hydrogen bonding interactions consisting predominantly of O-H...O and N-H...O hydrogen bonding interactions. Hydrogen bonding interactions a kin to interactions in aminoalcohol structures prevail for architectures of metallo-aminoalcohol compounds capable of forming dimeric species. The formation of dimeric metallo-aminoalcohol compounds are of particular interest given their role as potential precursors for the synthesis of heterometallic complexes. A hexadentate amino alcohol has been previously reported to form a series of heterometallic metal complexes exhibiting novel magneto-physical properties. An aminoalkoxide dimer is identified as the precursor species for these mixed metal structures. This presentation reports the spectroscopic and solid state investigation of the role of ligand reinforcement, as a controlling factor in the dimerization of suitable copper aminoalcohol complexes as precursors for heterometallic structures.

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Coordination chemistry of versatile N-heterocyclic thione (NHT) and related ligands

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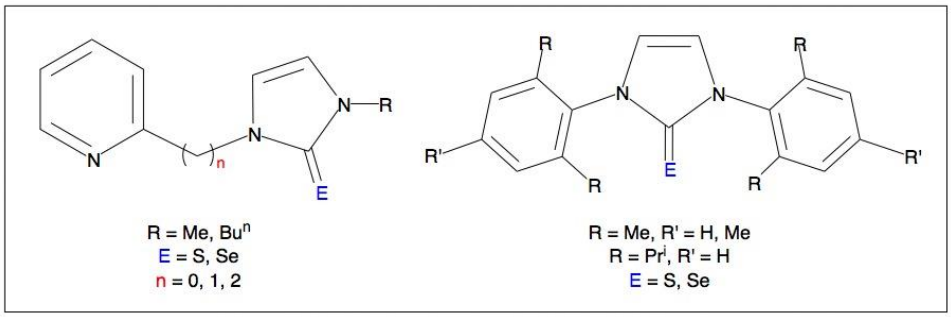
We have used a range of nimble bidentate ligands that contain pyridine and either N-heterocyclic thione (NHT) or N-heterocyclic selone (NHSe) donor groups to prepare synthetic analogues of methanobactin (mb), a fascinating small protein that plays a key role in the acquisition and transport of copper ions in methanotrophic bacteria. This presentation will describe recent advances in the synthesis and characterization of metal complexes supported by such [NS] or [NSe] mixed-donor ligands, including some that mimic the metal center in mb. In addition, the syntheses and coordination chemistry of new monodentate NHT or NHSe ligands bearing large aryl substituents, including the preparation of copper(I), mercury(II), and halogen derivatives, will also be outlined in this presentation.



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The role of steric factors in hydrogen activation: Incorporation of bulky N-heterocyclic carbene ligands into the coordination sphere of Bu^t_3Sn-Pt complexes leads to novel reactivity and catalysis

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A series of Pt(II)-Sn bimetallic complexes of the type $Pt(SnR_3)_2(CNBu^t)_2$ (R = Bu^t, Mes, Ph, Pr^i) have shown that sterics factors are importantant for H_2 activation and H_2-D_2 catalysis. The reaction of $Pt(COD)_2$ and one equivalent of Bu^t_3SnH at room temperature yielded Pt(COD)($SnBu^t_3$)(H), **1**. Replacement of the COD group in **1** with the N-Heterocyclic carbene ligand, N,N'-di-*tert*-butylimidazol-2-ylidene, (IBu^t), gives an unsaturated diplatinum complex $[Pt(SnBu^t_3)(IBu^t)(H)]_2$, **2**. In spite of its having a dimeric structure, complex **2** provides a ready source of the reactive fragment "$Pt(SnBu^t_3)(IBu^t)(H)$" and its reactions with CO and C_2H_4 are rapid. The reactivity of **2** with small molecules extends to dihydrogen, where the novel trihydride complex is formed in a rapid and reversible addition of H_2. Replacing the IBu^t group in **2** with IPr, N,N'-bis-(2,6-(diisopropyl) phenyl)imidazol-2-ylidene, the mononuclear 14 electron complex $Pt(SnBu^t_3)(IPr)(H)$, **3**, was isolated and characterized crystallographically. Complex **3** reacts with H_2 at room temperature to afford $Pt(SnBu^t_3)(IPr)(H)_3$. Complex **3** is an active hydrogenation catalyst at room temperature. The synthesis and reactivity of these complexes will be discussed.

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The next experiment: Some successful applications of computational chemistry

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Scientific truth is determined by experiment. Theory and simulations are most useful when they can motivate new and interesting experiments. I discuss three collaborations where computational chemistry motivated experiments on bimetallic complexes, phosphinylidenes, and triazine-based drug delivery platforms. These results help illustrate modern computational chemistry's value as a tool to explore hypotheses, rationalize results, and ultimately help design "the next experiment".

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Carbene-stabilization of elusive main group oxide

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This laboratory has been interested in the stabilizing influence of N-heterocyclic carbenes (L:) for some time. One of our early discoveries was the synthesis of carbene-stabilized disilicon, L:Si=Si:L, where the silicon atoms reside in the formal oxidation state of zero. We recently began to explore the reactivity of this compound. For

example, we have recently reported the synthesis of elusive silicon oxides Si2O3 and Si2O4. This presentation will concern the synthesis and molecular structure of these molecules and place them in context with other novel results in this laboratory.

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The activation and functionalization of strong carbon-hydrogen bonds: A computational perspective

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The catalytic functionalization of small, inert alkanes with strong C-H bonds has seen renewed interest arising from the abundance of natural gas, which is primarily comprised of methane, with not insignificant amounts of ethane and propane. To this end, we have used quantum chemical modeling - closely integrated with experimental research - to understand the salient features needed to both activate and functionalize strong C-H bonds. Typically, disparate electronic demands are placed upon a metal-ligand active site to accomplish these two chemical tasks. This paper will discuss recent research in our group on multiply bonded complexes that yield new insight on novel systems by which these reactions may be accomplished, and thus aid in the identification of viable, Earth-abundant catalysts for the functionalization of small alkanes.

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Synthesis of functionalized purine analogs for antibody conjugation

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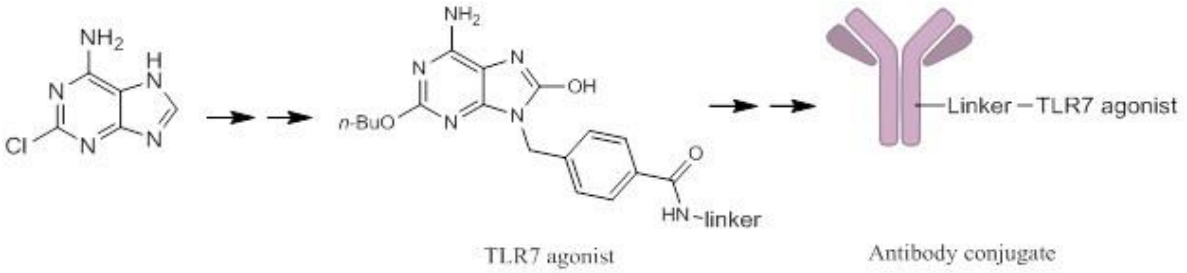
The recognition of pathogen-associated molecular patterns (PAMP) by transmembrane proteins initiates an effective immune response. The toll-like receptors (TLRs) are one family of PAMP receptors and includes TLR7, which has double-stranded viral RNA as its natural ligand. Several small-molecule TLR7 agonists have been discovered including a family of purine derivatives. Conjugation of the TLR7 agonists to antibodies could potentially lead to localized delivery of these potent immunostimulatory molecules, avoiding systemic activation of the immune system. The synthesis of new purine analogs with a variety of mechanistically distinct linkers for protein conjugation will be described, as well as results from in-vitro assays evaluating the IFN-inducing activity of the synthesized compounds and their antibody conjugates.



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Synthesis of ascarylose diphosphate nucleotides

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Ascarosides, a 3,6-dideoxysugar, are used by both free-living and parasitic nematodes in chemical signaling. *Caenorhabditis elegans* (*C. elegans*) is a 'free-living' model organism which secretes ascarosides to mediate its behaviour and development, including gender-specific attraction, repulsion, aggregation and entry into dauer (a stress-resistant life stage). De-coding the chemical language of *C. elegans* will improve our understanding of the biochemistry of nematodes could lead to new chemical methods to control parasitic species.
In *C. elegans*, the ascarosides are connected *via* an α-glycosidic bond to a fatty acid side chain. It is known that the biosynthesis of the fatty acid-derived side chains occurs through peroxisomal β-oxidation pathways; however less is known about the biosynthesis of the ascarylose moiety.
Nucleoside diphosphate sugars are important intermediates in glycoconjugate biosynthesis, however, sugar-nucleotides contain a number of different functional groups and are both water-soluble and relatively stable; this makes them difficult targets for synthesis. In particular, sugar-nucleotides typically contain a 1,2-*cis*-glycosidic bond, which can be especially challenging to install. To date, no examples of the synthesis of ascarylose diphosphate nucleotides have been reported in the literature.
We describe herein, our recent work to synthesis ascarylose diphosphate nucleotides. This work will help to uncover mechanisms by which *C. elegans* produces ascarosides.

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Unsymmetrical ketone synthesis using a heterocyclic tosyl hydrazone and aromatic aldehydes for synthesis of STAT3 inhibitors

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A high throughput screen at Scripps Florida performed under the auspices of the MLPCN program was performed to identify potential STAT3 inhibitors. One of the most potent compounds (**SR-3-0982)** after initial rounds of SAR optimization contained an unsymmetrical ketone moiety that was critical for potency. A method has been developed to access analogs of this compound in one step from a common intermediate

by utilizing the reaction of the derived tosyl hydrazone and aryl aldehydes (**Figure 1**). The synthesis of unsymmetrical ketones functionalized with a heterocycle and a variety of substituted aryl rings has been achieved. This methodology provides efficient access to many compounds that would be difficult to synthesize by our first generation synthesis, and provides an excellent platform for conducting SAR studies in this STAT3 inhibitor series.

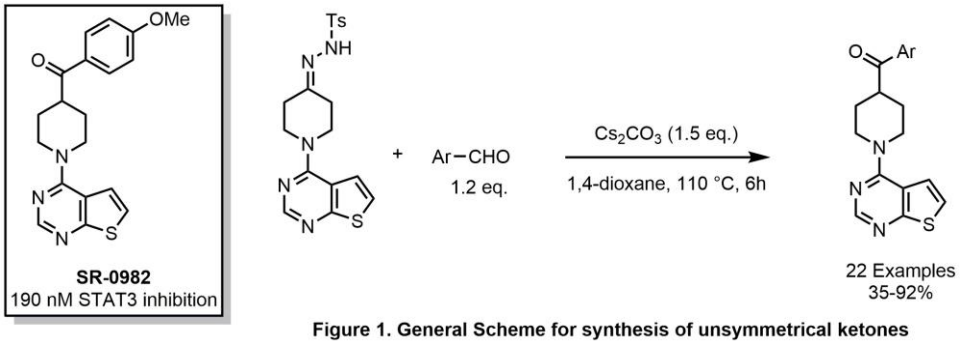

Figure 1. General Scheme for synthesis of unsymmetrical ketones

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Chemoselective conversion of biologically sourced polyols into chiral synthons

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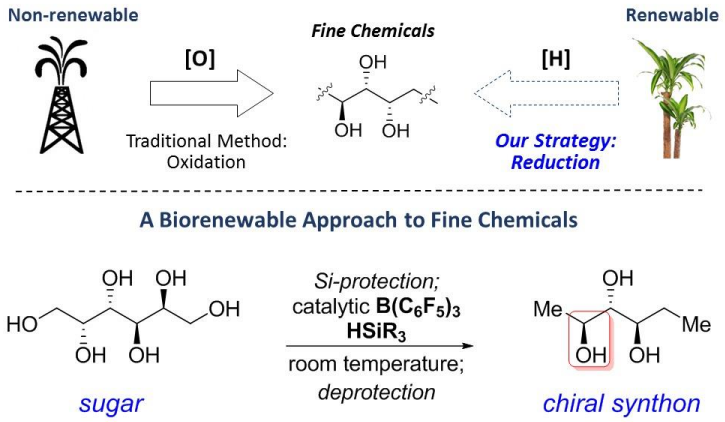
Recent attention has been given by scientists and consumers alike to the source of chemicals in commodity products. Traditionally, petroleum sources have been utilized to access fine chemicals; however, use of *renewable* feedstocks is in high demand. Towards this end, we have developed a transition metal free method utilizing a catalytic amount of $B(C_6F_5)_3$ and a stoichiometric tertiary silane reductant to controllably deoxygenate biologically sourced polyols. Generation of stereo-defined chiral synthons occur in one or two synthetic steps to afford many previously undescribed triols and tetraols of varying structure. Key to controlling the selectivity is the involvement of neighboring group participation and cyclic intermediates en route to the products.

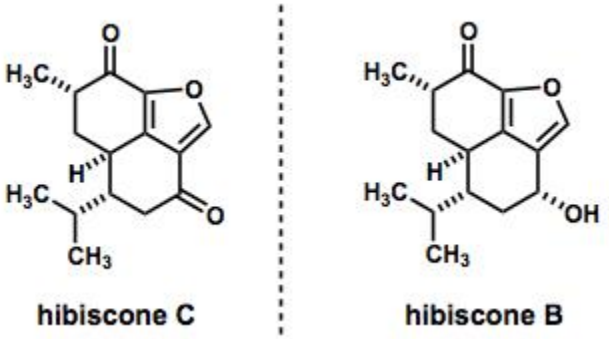


2015 Joint Southeastern/Southwest Regional Meeting 396

Total synthesis of hibiscone B

Brian C. Goess, *brian.goess@furman.edu. Dept of Chemistry, Furman University, Greenville, South Carolina, United States*

The first synthesis of (+/-)-hibiscone B, one member of the furanosteroid family of natural products which also includes wortmannin, is described. The synthesis relies on a regio-, chemo-, and stereoselective reduction of hibiscone C, a related furanosteroid. The challenges associated with achieving this selective reduction will be discussed.



2015 Joint Southeastern/Southwest Regional Meeting 397

Progress of the total asymmetric synthesis of antascomicin B

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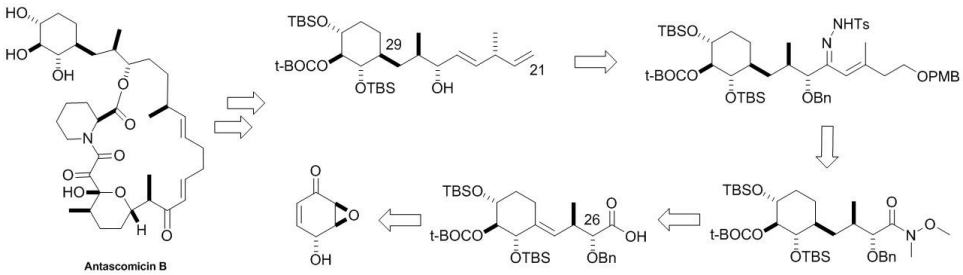
The purpose of this work is to describe the progress of the total asymmetric synthesis of antascomicin B. The antascomicins are among a few naturally occurring molecules that have been identified to bind FKBP12, similar to FK506 and rapamycin, but do not show immunosuppressive tendencies. The construction of the C(34)-C(22) fragment of antascomicin B is prepared from a mono-reduced epoxide intermediate and includes an Ireland-Claisen rearrangement to afford the anti-relationship at the C(27)-C(26) stereocenters and directed Hydrogenation of the C(29) *exo*-cyclic double bond. Synthetic strategies and additional details to complete fragment by an allylic diazene rearrangement will be discussed.



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Combretastatin and chalcone B-ring analogues via indole aldehydes

*Benjamin J. Shields, Caitlin M. Bridges, **Herman Holt**, hholt@unca.edu. UNC Asheville, Asheville, North Carolina, United States*

Indole analogues of combretastatin A-4 (CA-4) and chalcones were prepared. Both CA-4 and some chalcones are effective tubulin binding agents which ultimately disrupts vascular function. The Hemetsberger-Knittel method was used to successfully prepare substituted indoles from α-azidocinnamates in good yields. Oxidation state adjustment generated a highly diverse indole aldehyde that can be used in a variety of ways. One carbon homologation provided ethynyl indoles as functional dipolarophiles in catalyzed 1,3-dipolar cycloadditions to produce a 2-(1,2,3-triazolyl)indole. In addition, the synthesis of indole chalcone and α-halo substituted indole analogs of CA-4 were performed. The synthesis of some indole aldehydes and their utility will be described.

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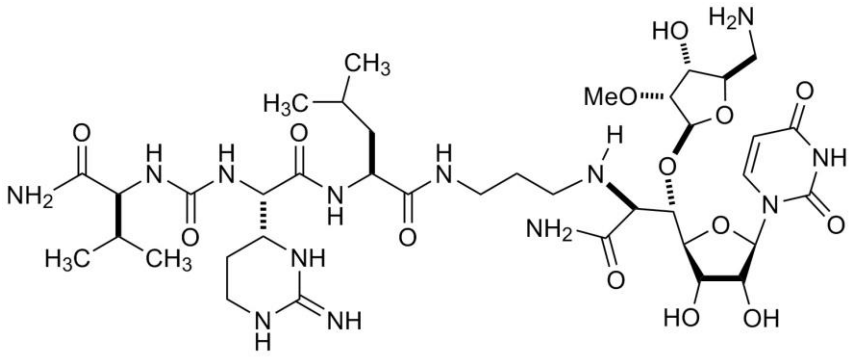
Synthetic studies on muraymycin antibiotics for Gram-negative bacterial infections

***Katsuhiko Mitachi**, kmitachi@uthsc.edu, Michio Kurosu. Department of Pharmaceutical Sciences, College of Pharmacy, University of Tennessee Health Science Center, Memphis, Tennessee, United States*

Muraymycins exhibited strong antibacterial activities against Gram-positive and -negative bacteria by inhibiting an early peptide glycan biosynthesis enzyme, translocase I. In our program towards the expansion of spectrum activity of muraymycins, we have established efficient syntheses of ribosamino-uridine antibiotics including muraymycin

D_1. Our synthesis of muraymycin D_1 includes stereoselective ribosylation and Strecker reaction. We will present the detailed synthesis of a muraymycin D_1 analog in this meeting.



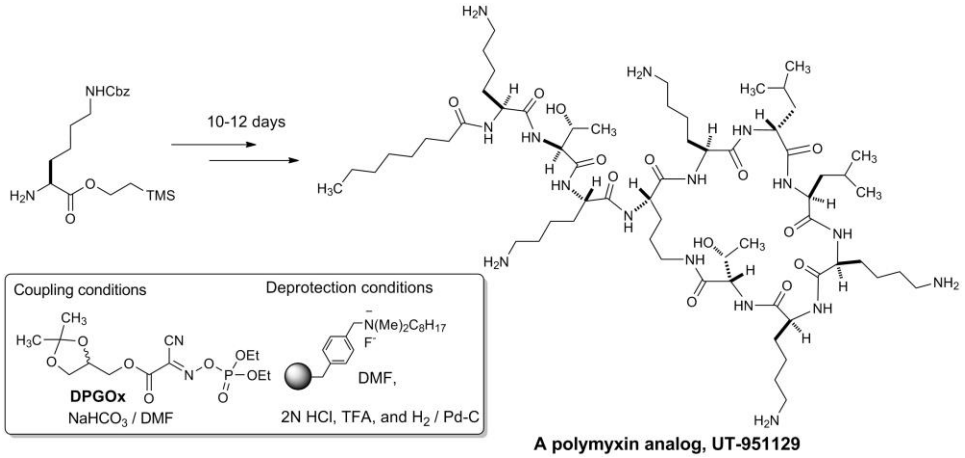
A muraymycin D_1 analog
retaining the antimicrobial activity of the parent molecule

2015 Joint Southeastern/Southwest Regional Meeting 400

Practical synthesis of novel polymyxin analogs for *in vivo* studies

Yuki E. Kurosu*, ykurosu@umich.edu, Michio Kurosu. Department of Pharmaceutical Sciences, College of Pharmacy, University of Tennessee Health Science Center, Memphis, Tennessee, United States*

Polymyxin (colistin) is considered to be the drug of last resort for the treatment of MDR Gram-negative bacterial infections. However, clinical use of polymyxin is limited due to severe nephrotoxicity. Thus, development of clinically relevant novel polymixin analogs with improved therapeutic index is an important objective. In order to perform systematic analog syntheses followed by *in vitro* and *in vivo* evaluations, we have developed an efficient synthetic method for oligopeptides in solution that is amenable to gram-scale production without multiple time-consuming chromatography steps. We present the details of our synthesis of polymyxin analogs (e.g. UT-951129) using diethylphosphoryl-glyceroacetonide-Oxyma (DPGOx) and polymer-supported ammonium fluoride.



A polymyxin analog, UT-951129

2015 Joint Southeastern/Southwest Regional Meeting 401

Synthesis of human milk trisaccharides en route to functionalized galacto-oligosaccharides

Dorothy L. Ackerman*, dorothy.l.ackerman@vanderbilt.edu, Steven D. Townsend. Chemistry, Vanderbilt University, Nashville, Tennessee, United States*

Breastfeeding is the most cost effective public health strategy used to combat infant illness and mortality. In addition to ideal nutrition for infants, breast milk also contains important carbohydrates that act as prebiotics and assist in providing immunological benefits. Known as human milk oligosaccharides (HMOs), these highly branched carbohydrates significantly regulate and direct the development of an infant's intestinal microflora. Due to their complex nature, no synthetic substitute has been developed to date. Instead, infant formula contains galacto-oligosaccharides (GOS), which fail to mimic the complex branching native to HMOs. We have synthesized several human milk trisaccharides and related glycoconjugates from a protected lactose core. With this pool of glycoconjugates in hand, we will explore their chemoezymatic polymerization to generate functionalized GOS that are structurally similar to large HMOs. Our goal is to measure whether it is possible to generate compounds that are superior to commercially available, unfunctionalized GOS in influencing the composition of the infant microbiota.

2015 Joint Southeastern/Southwest Regional Meeting 402

Method for the synthesis of difluoroglucosides for incorporation into anti-oxidant natural products

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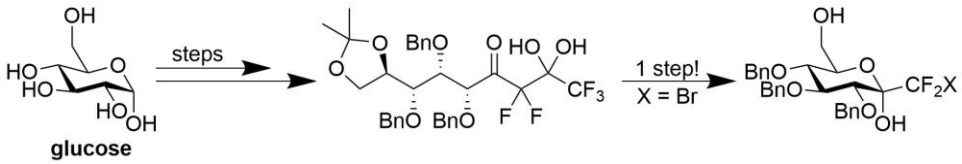
Strong evidence suggests that oxidative stress plays a causal role in many neurodegenerative diseases, such as Alzheimer's, Huntington's, Parkinson's, and Amyotrophic Lateral Sclerosis (ALS). Anthocyanins, such as cyanidin-3-O-glucoside, delphinidin-3-O-glucoside, and malvidin-3-O-glucoside are powerful, naturally occurring antioxidants that have shown potential as neuroprotective agents *in vitro*, but are quickly metabolized, primarily through cleavage of their weak glycosyl linkage *in vivo*. Typically, the aglycones have a poor distribution into the central nervous system and, as a result they are unable to elicit their anti-oxidative effects at the target site. Therefore, in order to investigate their potential as antioxidants for the treatment of neurodegenerative disorders, metabolically stable derivatives are needed. We hypothesize that bioisosteric replacement of the oxygen of the labile glycosyl linkage with a stable difluoromethylene group will prevent this hydrolysis of the sugar. Of the few synthetic methods available to install a difluoromethylene unit, the most straightforward approach is the generation of an α,α-difluoroenolate and its subsequent addition to an electrophile. Recently our lab developed a mild and efficient way to produce α,α-difluoroenolates by the release of trifluoroacetate from α-keto pentafluoro *gem*-diols. The method will be used to prepare

α,α-difluoro glucosides from α,α-difluoroenolates derived from an α-keto pentafluoro *gem*-diol glucose derivative.

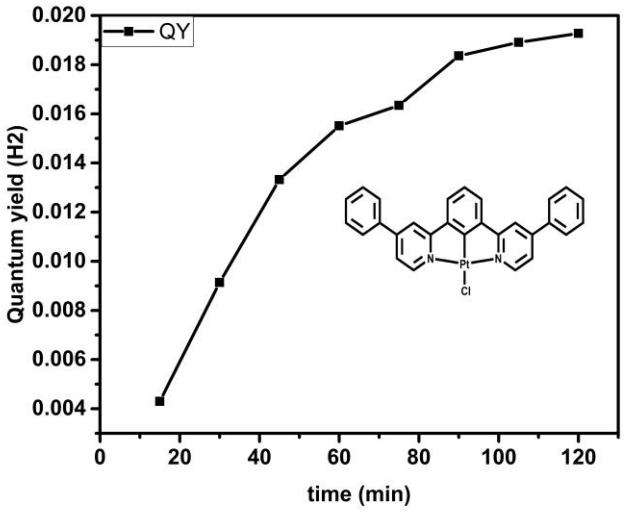


2015 Joint Southeastern/Southwest Regional Meeting 403

Hydrogen generation using single component Pt(II) NCN system

Aditya D. Kulkarni*, akulkarn@tulane.edu, Russell H. Schmehl. Chemistry, Tulane University, New Orleans, Louisiana, United States*

Single component systems that produce H_2 are relatively rare with long term studies uncommon. Some of the examples of H_2 photocatalysts that operate both as a photosensitizer and a catalyst in one structural motif are $[Rh_2^{0,0}(dfpma)_3(PPh_3)(CO)]$ (dfpma = $MeN(PF_2)_2$), [PtCl(tpy)]Cl (tpy = 2,2':6' ,2''- terpyridine) etc.. The former system uses a hydrohalic acid (HX) and splits it to produce H_2 and the latter carries out hydrogen production from photoinduced reduction of water in the presence of a sacrificial electron donor like EDTA in aqueous medium at pH 5.
Using recently sysnthesized Pt(II) NCN type complexes by us, hydrogen generation was observed in a 9:1 DMF:water mixture in the presence of only triethylamine (sacrificial electron donor). The quantum yield of hydrogen generation was ~2 % after 2 hours of irradiation. 18 moles of hydrogen were produced after 2 hours of irradiation. The NCN ligand was synthesized using Michael addition type condensation reaction of an aromatic acetyl oxime and an a,b-unsaturated aldehyde. The platinum complex was synthesized by refluxing a mixture of the ligand and K_2PtCl_4 in acetic acid.
Further studies include determination of the exact mechanism followed by the platinum complex to reduce water and produce hydrogen. Transient absorption studies along with control studies in the presence and absence of mercury (a trap for colloidal Pt(0)), the quencher, the chromophore etc. will help to rule out the formation of hydrogen by any other process other than the chromophore-catalytic activity of the platinum complex itself.



Quantum yield of hydrogen generation.

2015 Joint Southeastern/Southwest Regional Meeting 404

Increased efficiency and oxygen resistance of Ru,Rh,Ru water reduction photocatalysts in air-saturated aqueous solutions containing polyelectrolytes

Theodore Canterbury, *canterbu@vt.edu, Shamindri M. Arachchige, Robert B. Moore. Virginia Tech, Blacksburg, Virginia, United States*

Production of renewable fuels to replace dwindling natural resources is one of the greatest challenges in the scientific community. The production of hydrogen fuel from water is a promising strategy that has sparked a vast amount of research. Supramolecular photocatalysts of the molecular architecture $[\{(TL)_2Ru(BL)\}_2RhX_2]^{5+}$ (BL=bridging ligand, TL=terminal ligand, X=halide) demonstrate efficient hydrogen production in deoxygenated organic solvents, but are limited by poor performance in aqueous solutions due to efficient quenching of the triplet metal to ligand charge transfer excited state (^{3}MLCT). We investigate the impact of water soluble polyelectrolytes on the excited state dynamics of supramolecular photocatalysts in order to improve catalyst efficiency in aqueous solutions.

2015 Joint Southeastern/Southwest Regional Meeting 405

H_2 production catalyzed by Co complexes with pentadentate ligands

Xuan Zhao[1], *xzhao1@memphis.edu, Ramana Mittapalli*[1], *Scott Powers*[1], *Kristin Knight*[2], *Kandria Driskill*[3], *Tiffany Rice* [4], *Christian Lyons*[4], *Yacine Gueye*[5]. *(1) Department of Chemistry, University of Memphis, Memphis, Tennessee, United States (2) Department of Chemistry, University of Tennessee at Chattanooga, Chattanooga, Tennessee, United States (3) Department of Chemistry & Environmental Biology, Arkansas State University, Jonesboro, Arkansas, United States (4) Department of Chemistry, Christian Brother University, Memphis, Tennessee, United States (5) Division of Science and Math, Rust College, Holly Springs, Mississippi, United States*

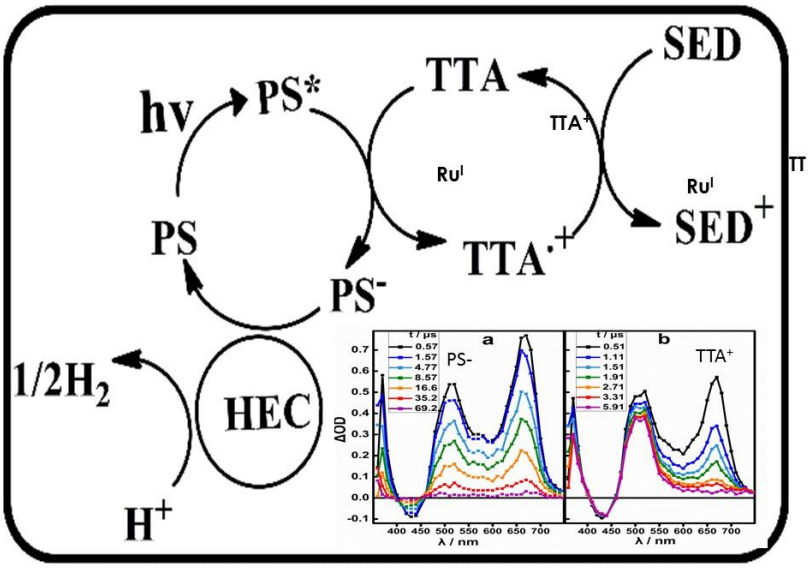
In order to explore the electronic and steric effects of ligand scaffold of cobalt complexes on the catalytic properties of H_2 evolution, pentadentate ligands derived from N,N-bis(2-pyridinylmethyl)-2,2'-bipyridine-6-methanamine (DPA-Bpy) by replacing the pyridyls with various groups were synthesized and characterized. Our study demonstrates that the activity of H2 production depends strongly on the relative positions of substitutions on pyridyl rings, and its implications on the mechanisms of H2 production will be discussed.

2015 Joint Southeastern/Southwest Regional Meeting 406

Tracking catalyst intermediates in photoinduced generation of hydrogen with transient spectroscopic and mass spectral methods

*Bing Shan[3], Patricia R. Fontenot[4], Jim P. Donahue[1], **Russell H. Schmehl**[2], russ@tulane.edu. (1) Tulane University, New Orleans, Louisiana, United States (2) Chemistry, Tulane University, New Orleans, Louisiana, United States (3) Chemistry, University of North Carolina, Chapel Hill, North Carolina, United States (4) Chemistry, Tulane University, New Orleans, Louisiana, United States*

The photolysis of Ru(II) diimine complexes in the presence of a reversible reductant and sacrificial electron donor results in the formation of strongly reducing Ru complexes having potentials ranging from -1.2 to -1.4 V vs. SCE. These photosystems are used to reduce catalysts for water reduction to H_2 ; generation of H_2 is followed by GC and evolution of the catalyst is followed using MALDI mass spectroscopy. Intermediates formed on the nanosecond and microsecond time scale are tracked using ns/ms laser flash photolysis. Efficiencies for the photoinduced electron transfer reaction, charge separation to form the strong reductant (Ru(I) complex) in solution and the subsequent one electron reduction of catalyst are determined with transient spectroscopy. In some cases the reactivity of the one electron reduced catalyst could be followed. Details of reduction for systems involving a Ni(II) catalyst with chelating phosphine ligands and a Mo(IV) complex with a $Mo_3S_7^{4+}$ core.



2015 Joint Southeastern/Southwest Regional Meeting 407

Using theory to guide design: Development of hydrogenase inspired Ni and Fe H_2 oxidation catalysts

Monte Helm[1]*, monte.helm@pnnl.gov, Simone Raugei*[1]*, Jonathan Darmon*[1]*, Neeraj Kumar*[2]*, Ryan Stolley*[1]*. (1) Chemical Materials Sciences Division, Pacific Northwest National Laboratory, Richland, Washington, United States (2) Pacific Northwest National Laboratory (PNNL), Richland, Washington, United States*

Recent advances in bio-inspired catalysts obtained in the Center for Molecular Electrocatalysis, an Energy Frontier Research Center, EFRC, at the Pacific Northwest National Laboratory demonstrated the electrocatalytic oxidation and production of H_2 using inexpensive, abundant metals such as Ni, Mn and Fe. A key feature in our studies is incorporation of a pendant amine as a proton relay into the ligand, generally at a distance that will preclude formation of a M-N bond. In these catalysts the oxidation of H_2 proceeds via an interplay between hydrogen binding, followed by proton, hydride and electron transfer steps. The careful use experimental data and computational work to identify rate determining steps in the catalytic cycle, used to guide the design of catalysts with enhanced activity, will be discussed in this presentation.

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Micellar effects on photoinduced electron transfer in aqueous solutions: Dramatic enhancement of cage escape yields in surfactant Ru (II) diimine complex / $[Ru(NH_3)_6]^{2+}$ systems

Rebecca E. Adams*, radams6@tulane.edu, Russell H. Schmehl. Chemistry, Tulane University, New Orleans, Louisiana, United States*

In a typical photocatalytic scheme, an excited state can transfer oxidizing or reducing equivalents to a catalyst to drive chemical reactions. In order to maximize the efficiency of a photocatalytic cycle, the initial redox products must be produced in high yield. The yield of products that escape from the geminate ion pair is dependent upon the exergonicity of back electron transfer and the changes in the reactants' spin states. Repulsion between cation or anion pairs within the cage is also a large factor that affects charge separation. Cationic micelles in aqueous solution allow for compartmentalization of reactants and provide a highly charged barrier which can repel other cationic species. Relative to their initial states, products of light-induced electron transfer reactions may exhibit a change in hydrophobicity. If the reactants are positively charged, an oxidized product will become more hydrophilic, while a reduced product will become more hydrophobic. When one reactant associates with a cationic micelle, its effective positive charge increases, thus decreasing the probability of encounter with another positively charged reactant. Utilizing a series of ruthenium(II) tris-diimine chromophores, modified with alkyl chains of varying lengths, rates of electron transfer and cage escape yields were measured. Chromophores bearing carbon chains of 13 or greater are less effectively quenched by the electron donating $[Ru(NH_3)_6]^{2+}$ in CTAB solutions relative to non-micellar solutions. When reduced by $[Ru(NH_3)_6]^{2+}$ in the presence of micelles, the amphiphilic chromophores exhibit increased charge separation yields and recombine with $[Ru(NH_3)_6]^{3+}$ with a decreased rate. Ionic strength increases are shown to diminish the electrostatic effects of the micelles. A reversible

scheme is presented in which both hydrophobic and electrostatic effects are used to produce a strongly reducing species in high yield.

2015 Joint Southeastern/Southwest Regional Meeting 409

Structure-property relationships: Ancillary ligand molecular design for Ru (II) complexes and how it leads from 5% to 10% efficiency in dye-sensitized solar cells

***Hammad Arshad Cheema**, hcheema@ncsu.edu, Ahmed El-Shafei. College of Textiles, North Carolina State University, Raleigh, North Carolina, United States*

Bipyridyls (bpy) are well known for their rich coordination chemistry towards transition metal complexes. Their use in the field of electron, energy transfer and energy harvesting has increased exponentially during the last two decades especially due to the huge interest in Ru (II) metal complex compounds for dye-sensitized solar cells (DSSC). In this talk I will summarize our research and learning on molecular design of bipyridyl ancillary ligands for Ru (II) metal complex sensitizers. By careful design of ancillary ligands, we were able to achieve not only highly efficient but also highly stable sensitizers outperforming benchmark N719. Electrochemical (cyclic voltammetry, impedance), photoelectrochemical (I-V, EQE or IPCE) and optical (photoluminescence, sub-pico second transient absorption) measurements established the underlying structure-property relationship as dictated by design of ancillary ligand with similar Ru-metal core. The design strategies that will be discussed for Ru (II) metal sensitizers are mono vs. bis ancillary ligand for carbazole and benzodioxan based electron donors, influence of alkyl chain length on efficiency and stability of DSSC, influence of isomerism and steric effect of ancillary ligand on photocurrent and photovoltage of DSSC.

2015 Joint Southeastern/Southwest Regional Meeting 410

Designing a family of long lifetime copper(I) phenanthroline complexes

***Catherine McCusker**[2], cemccusk@ncsu.edu, Felix N. Castellano[1]. (1) Chemistry, North Carolina State U, Raleigh, North Carolina, United States (2) Department of Chemistry, North Carolina State University, Raleigh, North Carolina, United States*

Earth-abundant copper(I) *bis*-phenanthroline complexes are potential alternatives to the more familiar 2nd and 3rd row transition metal containing photosensitizers for solar energy or photocatalytic applications. Copper(I) diimine complexes have metal-to-ligand charge transfer (MLCT) absorptive properties similar to $[Ru(bpy)_3]^{2+}$, without the deactivating ligand field states found in other first row transition metal complexes. However, upon excitation, Cu(I) diimine complexes undergo a significant structural rearrangement, leading to low energy excited states possessing very short lifetimes, thereby limiting their usefulness as photosensitizers. In our parent Cu(I) complex, methyl groups in the 3,4,7,8- positions of the phenanthroline ligand, combined with bulky *sec*-butyl groups in the 2,9- positions cooperatively restrict the degree of structural distortion in the Cu(I) MLCT excited state thereby extending its lifetime to the microseconds time scale. Varying the substituents in the 4,7- positions of the phenanthroline ring allows for tuning the spectroscopic and electrochemical properties of the Cu(I) *bis*-phenanthroline complex while maintaining the long excited state lifetime

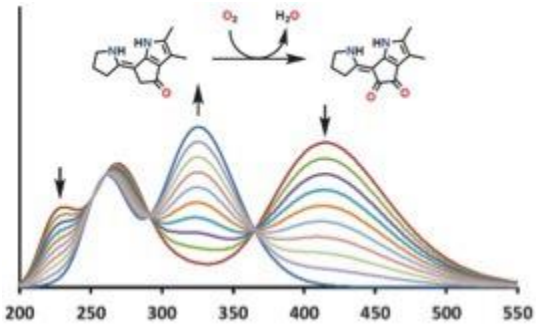
of the parent Cu(I) complex. The synthesis and photophysical properties of this new series of Cu(I) sensitizers will be discussed.

2015 Joint Southeastern/Southwest Regional Meeting 411

The mechanism of dinoflagellate bioluminescence: A computational approach to elucidating the structure of the luminophore of dinoflagellate luciferase

***Phong Ngo**, phong@auburn.edu, Steven Mansoorabadi. Department of Chemistry and Biochemistry, Auburn University, Auburn, Alabama, United States*

Dinoflagellates are an important group of marine microorganisms that are photosynthetic and capable of bioluminescence induced by physical agitation. The bioluminescence reaction, which is regulated on a circadian rhythm, involves the oxidation of a luciferin substrate by the enzyme dinoflagellate luciferase. Of all the major classes of luciferase (i.e., firefly, bacterial, and dinoflagellate), the least is known about the mechanism of light production by dinoflagellate luciferase. Time-dependent long-range corrected density functional theory (TDLCDFT) was utilized in the calculation of excited state energies of distinct luminophores from three proposed reaction mechanisms in an effort to garner theoretical support in favor of a single mechanism.



2015 Joint Southeastern/Southwest Regional Meeting 412

Comprehensive prediction of drug-protein interactions and side effects for the human proteome

***Jeffrey Skolnick**, skolnick@gatech.edu. Georgia Inst of Technology, Atlanta, Georgia, United States*

Identifying unexpected drug-protein interactions is crucial for drug repurposing. We develop a comprehensive proteome scale approach that predicts human protein targets and side effect of drugs. For drug-protein interaction prediction, FINDSITE^{comb}, whose average precision is ~30% and recall ~27%, is employed. For side effect prediction, a new method is developed with a precision of ~57% and a recall of ~24%. Our predictions show that drugs are quite promiscuous, with the average (median) number of human targets per drug of 329 (38), while a given protein interacts with 57 drugs. The result implies that drug side effects are inevitable and existing drugs may be useful for repurposing, with only ~1,000 human proteins likely causing serious side effects. A *killing index* derived from serious side effects has a strong correlation with FDA

approved drugs being withdrawn. Therefore, it provides a pre-filter for new drug development. The methodology is free to the academic community on the DR. PRODIS (DRugome, PROteome, and DISeasome) webserver at http://cssb.biology.gatech.edu/dr.prodis/. DR. PRODIS provides protein targets of drugs, drugs for a given protein target, associated diseases and side effects of drugs, as well as an interface for the virtual target screening of new compounds. Successful applications of the methodology to treat Chronic Fatigue Syndrome, to identify novel antibiotic leads and promising anti-seizure drugs are described.

Predicting and characterizing protein functions in the "big data" era

***Natarajan Kannan**, kannan@bmb.uga.edu. Biochemistry and Molecular Biology & Institute of Bioinformatics, University of Georgia, Athens, Georgia, United States*

The massive amounts of data ("Big Data") generated by "omic" efforts posses major challenges in predicting and characterizing protein functions in the post-genomic era. Consider, for example, the protein kinase gene family. There are over quarter million protein kinase related sequences from diverse organisms, thousands of crystal structures and tens of thousands of published articles. The difficulty in integrating and analyzing these existing data poses major bottlenecks in investigating protein kinase functions in normal and disease states. In this talk, I will describe a computational framework for integrating and conceptualizing diverse forms of protein kinase data in a machine and human readable format. I will describe the application of this framework in integrative data mining and in generating new hypotheses for functional studies. Specifically, I will describe how quantitative comparisons of diverse protein kinase sequence and crystal structures from diverse organisms has provided new insights into the evolution of allosteric regulation in the protein kinase domain and a conceptual framework for predicting the residue networks associated with the functional specialization of kinases in signaling pathways. I will also describe our ongoing efforts to combine long-time scale molecular dynamics simulations with mutational analysis to predict and characterize disease-causing mutations in the protein kinase core.

Selected Publications:

1. McSkimming DI, Dastgheib S, Talevich E, Narayanan A, Katiyar S, Taylor SS, Kochut K, **Kannan N***. ProKinO: a unified resource for mining the cancer kinome. *Hum Mutat.* 2015 Feb;36(2):175-86. PMID: 25382819

2. Oruganty K, Talathi NS, Wood ZA, **Kannan N***. Identification of a hidden strain switch provides clues to an ancient structural mechanism in protein kinases. *Proc Natl Acad Sci U S A*. 2013 Jan 15;110(3):924-9. PMID: 23277537

3. Oruganty K, **Kannan N***. Design principles underpinning the regulatory diversity of protein kinases. *Philos Trans R Soc Lond B Biol Sci*. 2012 Sep 19;367(1602):2529-39. PMID: 22889905

4. Ruan Z, **Kannan N*.** Mechanistic Insights into R776H Mediated Activation of Epidermal Growth Factor Receptor (EGFR) Kinase. *Biochemistry*. 2015 Jun 23. PubMed PMID: 26101090.

2015 Joint Southeastern/Southwest Regional Meeting 414

Concepts of protein dynamics in drug design

***Jeremy C. Smith**, a2a@ornl.gov. Center for Molecular Biophysics, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

The design of drugs using protein structures is undergoing a renaissance. Now, internal motions of proteins have begun to be incorporated into structure-based drug development. We examine the variety of motions in proteins, demonstrate entropy-driven vibrational softening on the binding of a cancer drug to its target and show that inter-domain motion can be described by the principle of De Gennes Narrowing. Curiously, over the typical biological lifespan of a protein internal motions remain out of equilibrium, obeying a self-similar (fractal) time dependence over thirteen decades in time. Metastability analysis can be used to produce a thermodynamically reigorous representation of the conformational transitions involved. Finally, we show how the incorporation of protein dynamics into virtual high-throughput screening has permitted the successful generation of lead compounds to combat hypophosphatemia, antibiotic resistance and thrombosis.

2015 Joint Southeastern/Southwest Regional Meeting 415

Molecular dynamics simulations of the NF-κB inducing kinase

***Michael R. Jones**, mrj0089@unt.edu, Joshua Yue, Angela K. Wilson. Department of Chemistry, University of North Texas, Denton, Texas, United States*

Improper signaling of the nuclear factor-κB (NF-κB) pathway plays a critical role in many inflammatory disease states, including cancer, stroke, and viral infections. Although the signaling pathways are known, how these molecular mechanisms respond to changes in the intracellular microenvironment (i.e., pH, ionic strength, temperature) remains elusive. Molecular dynamics simulations were employed to determine how changes to the intracellular ionic strength alter the structure-property relationships of the NF-κB Inducing Kinase (NIK), a protein kinase responsible for invoking the non-canonical NF-κB pathway. Analyses of structure-activity and conformational-activity relationships suggest that the protein-protein interactions and the binding of small molecules are sensitive to changes in the ionic strength.

2015 Joint Southeastern/Southwest Regional Meeting 416

The dynamics of GCN4 facilitate DNA interaction: A model-free analysis of an intrinsically disordered region

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NMR spectroscopy is a powerful experimental approach for characterizing protein conformational dynamics on multiple time scales from picoseconds to seconds. The intramolecular dynamics of the basic leucine-zipper (bZip) domain of GCN4, whose DNA binding domain is intrinsically disordered in the absence of substrate, have been characterized by NMR spin relaxation measurements at four static magnetic fields. The amplitudes of motion are in excellent agreement with earlier NMR studies [Bracken, *et*

al. (1999) *J. Mol. Biol*., 285, 2133–2146] and with molecular dynamics (MD) simulations [Robustelli, *et al.* (2013) *J. Chem. Theory Comput.*, 9, 5190–5200]. Joint analysis of molecular dynamics (MD) simulations and the NMR data allow detailed assessment of atomistic mechanisms linking bZip conformational dynamics with recognition of DNA. In addition, the data at multiple static fields allows the time scales of internal dynamics of the GCN4 bZip domain to be reliably quantified. Dynamic fluctuations in the DNA-binding region have correlation times ($\tau_S \approx 1.4–2.0$ ns) consistent with a model in which initial encounter complexes of partially ordered GCN4 bZip domains with DNA rapidly rearrange to the high affinity state with fully formed recognition helices.

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Functional activation of the pro-apoptotic BAX by the intrinsically disordered N-terminus of p53

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The tumor suppressor p53 performs pro-apoptotic functions in the cytosol independently of its transcriptional activity. Under conditions of genotoxic stress, such as UV-induced DNA damage, p53 can directly activate the pro-apoptotic protein BAX. Active BAX forms oligomers that permeabilize the outer mitochondrial membrane, provoking the release of cytochrome c, a critical signal towards caspase activation and apoptosis. We investigated the mechanism by which cytosolic p53 interacts with BAX using NMR spectroscopy in combination with a variety of biochemical assays to track BAX activation. Our findings demonstrate that BAX activation is mediated by the cis-trans isomerization of a proline within the intrinsically disorderded N terminal region of p53. Surprisingly, to effectively take place in cells, this process requires a catalytic engagement of the prolyl isomerase Pin1. The molecular mechanism by which p53 activates BAX therefore exhibits a novel and intriguing mode of regulation to tightly control a signaling outcome that will result in the life or death of a cell. This mechanism is mediated by the structural plasticity of a disordered protein segment.

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Non-Fourier methods for improving multidimensional NMR

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Intrinsically disordered proteins (IDPs) and proteins with intrinsically disordered regions (IDRs) present a nearly perfect storm of challenges to NMR. Proton chemical shift dispersion is low, leading to spectral crowding. Although rapid motion leads to motional line narrowing, motion on slower time scales can result in broadened spectral lines that reduce resolution and sensitivity. Hydrophobic surfaces, persistently or transiently exposed in IDPs and IDRs, lower solubility and sample lifetimes, presenting challenges to sensitivity as well as experiment times. Non-Fourier methods offer a number of opportunities for improving sensitivity and resolution and reducing experiment time for

multidimensional NMR experiments to address these challenges. Examples involving nonuniform sampling and partial multidimensional deconvolution will be described.

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Exploring the thermodynamics of the Pin1-histone interaction

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Pin1 is an essential Peptidyl-prolyl isomerase (PPIase) that catalyzes cis-trans prolyl isomerization in peptides containing pSer/Thr-Pro motifs. It has an N-terminal WW domain and a C-terminal PPIase domain. Pin1 targets pSer/Thr-Pro motifs by its WW binding domain and catalyzes isomerization through the PPIase domain. The Pin 1/histone H1 interaction plays a key role in pathogen response in bacterial infected host cells. This makes anti-Pin1 therapeutics important target for treating infections as well as cancer. The H1 histones (H1.0-H1.5) each contain several potential Pin1 recognition (pT/pS)-P motifs. For example H1.1 has two (pT/pPS)-P sites and H1.5 has five sites. It is presently unknown whether Pin1 interacts with a subset or all of these possible sites. To understand this interaction fully, it is important to determine how both the WW and PPIase domains bind to these H1 histone substrates. NMR studies can be used to measure the thermodynamics of biopolymer binding. This technique probes the dissociation constant (K_d) and monitors the residues involved in substrate binding. Here, we investigate the binding affinities of several H1 peptides that have been designed directly from the histone proteins. We observe different K_d values depending on the histone binding site, suggesting that energetics plays a role in guiding the Pin1-histone interaction. In the future, this information may be useful in determining how Pin1 may be involved in regulating histone and therefore chromatin structure.

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Molecular recognition by disordered protein regions

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Upwards of 30% of eukaryotic proteins exhibit disordered regions that mediate remarkably diverse biological functions. In some cases, disordered protein regions fold upon binding their partners and exert their functions after assuming order. However, in others, disordered regions interact transiently with one or more partners and exert their functions while retaining a high degree of disorder. We are interested in understanding the basis of molecular recognition in these latter types of systems and how dynamic interactions mediate diverse functions, ranging from signal transmission to the assembly of cellular structures termed membrane-less organelles. Gaining detailed insights into molecular recognition in dynamic systems is challenging, however, and we will discuss how information from NMR, computations and other methods can be combined to understand disorder-function relationships for proteins with disordered regions.

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Profiling chemical fingerprints of lead-free gunshot residue analogs

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Modern analysis of inorganic gunshot residue (GSR) relies on the use of three key ingredients; barium nitrate, antimony sulfide, and lead styphnate. However, recent environmental concerns are trending toward an industry-wide shift in the manufacture and distribution of lead-free ammunition. Consequently, this change will require new methods that can be used to fully characterize the composition of lead-free GSR. This study uses laser-induced breakdown spectroscopy (LIBS) and scanning electron microscopy/energy-dispersive x-ray spectroscopy (SEM-EDX) for characterizing simulations of lead-free gunshot residues. Chemical fingerprints for simulated lead-free GSR were used to identify statistically significant analytical markers present in each composition. Rates of error associated with each simulation are determined by leave-one-out cross validation. LIBS proved to be an effective and rapid screening method in the analysis of simulations of lead-free gunshot residues.

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Analysis of biogenic amines as quality indicators of three fish species commonly consumed in Kuwait

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Biochemical analyses of three fish species commonly consumed in Kuwait - silver pomfret (*Pampus argenteus*), orange-spotted grouper (*Epinephelus coioides*), and grunt (*Pomadasys kaakan*), were performed in relation to the overall quality of fish during normal commercial activities at the fish markets using HPLC. Parameters analyzed included the total volatile basic nitrogen (TVBN), biogenic amines (histidine, cadaverine, and putrescine), trimethylamine (TMA), and protein degradation patterns. TVBN values increased in all fish species on each day of sampling. Fish samples collected in the morning had lower levels of TVBN ranging from 25.9 ± 0.20 mg/100 g to 30.2 ± 0.58 mg/100 g for all three species compared with the range of 31.2 ± 0.39 mg/100 g to 40.9 ±0.19 mg/100 g for samples collected in the evening. Among all three fish species studied, the silver pomfret (*Pampus argenteus*) showed the least levels of TVBN, ranging from 25.9 ± 0.20 mg/100 g to 31.2 ± 0.39 mg/100 g, while grunt *(Pomadasys kaakan*) had the highest levels of TVBN (33.0 ±0.79 mg/100 g - 40.9 ± 0.19 mg/100 g). Biogenic amine levels were also low in the fish species. Electrophoregram of the fish species showed no visible evidence of protein degradation in all the samples during the day. The data from the current study indicate that fish handling practices at Kuwait fish markets do not result in significant abuse of fish temperatures, and that volatile and non volatile amine levels do not rise to levels indicating fish decomposition during normal commercial activity.

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Investigating pyrene levels in water and sediment samples in presence of bioturbators

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Pyrene is one of the polycyclic aromatic hydrocarbons, PAHs. This group of pollutants is found naturally in the environment. They are usually associated with oil spills. Exposure to pyrene as one of the PAHs target organs like kidneys, liver and fat, causing kidney and liver damage. Benzo(a)pyrene is the most common PAH to cause cancer is formed from pyrene. In the present study, greenhouse mesocosms containing field-collected clean water and sediment. Controlled in-lab sediment pyrene dosing was done in presence of bioturbators (the ghost shrimp Lepidophthalmus louisianensis introducing it on the sediment surface of the mesocosms. These marine bioturbators are abundant; they move a lot of sediment, and initiate the exchange of water within the sediment and between the sediment and the water column. Pyrene concentrations were determined or the razor clams Tagelus plebeius) the most-abundant bioturbators on the Gulf Coast. Liquid-liquid extraction was used to monitor the concentration of pyrene in overlying water. Microwave Extraction was used to determine the pyrene concentration in sediments (surface & subsurface) was extracted; finally samples were analyzed using gas chromatography with flame ionization detector (GC-FID). The ghost shrimp and razor clams affect the distribution and biodegradation of pyrene. It was observed that the presence of such type of marine animals, especially the ghost shrimp enhanced the rate of decline in pyrene concentration in the surface sediment.

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Construction of a semiconduction-biological interface for solar energy conversion: P-doped silicon/photosystem i/zinc oxide

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The interface between photoactive biological materials with two distinct semiconducting electrodes is challenging to both develop and analyze. Building off our previous work using films of Photosystem I (PSI) on p-doped silicon, we have deposited a crystalline zinc oxide (ZnO) anode using confined-plume chemical deposition (CPCD). We demonstrate the ability of CPCD to deposit crystalline ZnO without damage to the PSI biomaterial. Using electrochemical techniques, we were able to probe this complex semiconductor-biological interface. Finally, as a proof of concept, a solid state photovoltaic device consisting of p-doped silicon, PSI, ZnO, and ITO was constructed and evaluated.

2015 Joint Southeastern/Southwest Regional Meeting 425

The simple approach to measuring calcium via ICP-MS

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Several methods for the determination of Ca via ICP-MS have been developed throughout the years, including the use of “cold” plasma, isotope dilution ICP-MS and multi-collector ICP-MS. These methods have proven to measure Ca accurately however they require complicated sample preparation or additional equipment for the analysis to be performed. We present a simple approach to measure Ca via ICP-MS without complicated sample preparation by calibrating the instrument with a Ca standard and shifting the mass balance towards 51 instead of the center point of 60. A NIST 1640a calibration standard was used for repeated measurements throughout several runs (n=6) to confirm the accuracy, reproducibility and repeatability of the method. The standard value for Ca in NIST 1640a was 5.615 ± 0.021 mg/L compared to an average 6.17 ± 0.55 mg/L measured. Considering that the general mode at mass balance of 60 gives a percent yield of 13 ± 2%, the mass balance shift and the use of a Ca standard to calibrate proves to be an improvement in the measurement of Ca (percent yield 114 ± 10 %).

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Digital imaging and fluorescence characterization of Langmuir films of quantum dots

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We report on an analytical study to quantify the uniformity of Langmuir and Langmuir-Schafer (LS) films of quantum dots (QDs) using digital image analysis and fluorescence spectroscopy. Gradient-core QDs were selected for creating the thin films because of their growing popularity for use in industries. The QDs were cast as Langmuir films on a water subphase, and the Langmuir films were deposited onto substrates using the LS technique. Images were taken using a digital optical microscope of both the Langmuir and LS films with white light and black light sources. Agglomerations, voids, islands, and ridges were some of the artifacts found when surveying the Langmuir films. These artifacts were seen to template directly to the LS films. Emission spectra of the LS films were mapped using fluorescence spectroscopy. Variations in the brightness on the optical images was proposed to be due to changes in the topography in films. Image processing software was used to quantify the intensities of the variations at different spatial locations across the films. A direct correlation was made between the spatial variations in image brightness and the intensities of fluorescence spectra at the same given point on the LS films.

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Using thermogravimetric analysis to differentiate between ethylene bis-stearamide and polyamides in paper machine deposits where FTIR results are inconclusive

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Ethylene bis-Stearamide (EBS) is a common component of paper mill defoamers. The chemistries used in paper making are complex and can cause deposits on paper and paper making equipment. Paper machines use felts to transport wet pulp. Water is removed through the felts by drainage, pressure or heat. During these processes, deposits may form on the felts. If EBS is present, it may become part of the deposit. Felts are constructed of polyamide. Aggressive solvents, like dichloromethane, and heat are used in deposit analysis. These solvents can not only remove paper mill deposits from the felts but also dissolve polyamide from the felt. FTIR is commonly used for identification of paper mill deposits. The spectra of EBS and amide from felts are similar. TGA will differentiate, qualitatively, amide from EBS and amide from Felts.

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The determination of inorganic and organic compounds in kombucha

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Kombucha is a fermented tea produced from the modification of sweetened tea by a symbiotic culture of bacteria and yeast (S.C.O.B.Y.). Kombucha by-products include nutraceuticals, aroma, and flavor compounds. Nutraceuticals of interest in kombucha include pseudoalkaloids, anions, metals, and catechins. Aroma and flavor compounds of interest include esters, aldehydes and ketones. In addition to their medicinal value, anions, metals, aroma, and flavor compounds are also responsible for the taste, quality, and stability of kombucha.

The purpose of this research project was to develop and perform kombucha quality analysis methods for a regional company. Inorganic ions and metals, and a variety of organic compounds were determined in finished kombucha and raw materials. Sample treatment assays and instrument methods were developed.

Anion and metal concentrations in 10 different flavors of kombucha have been determined. Ion Chromatography (IC) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) were used for analysis. Analysis showed the concentrations of metals were relatively consistent among the ten flavors tested. Calcium, magnesium, and sodium concentrations varied. This is typical in fermented consumer beverages. The analysis showed variability among the anions in each brand with acetate having the highest concentration. This is expected since acetic acid bacteria convert ethanol to acetic acid during fermentation.

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Amperometric determination of aurocyanide for hydrometallurgical gold processing

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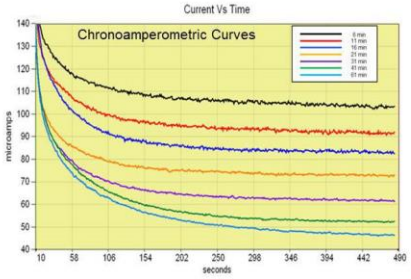
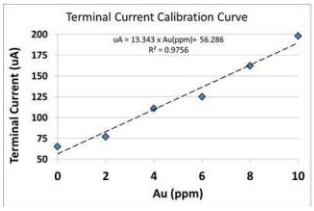
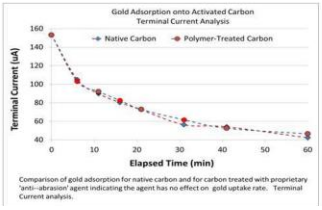
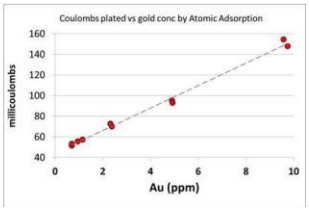
Determination of dissolved gold concentration is a fundamental need in hydrometallurgical gold extraction. An analytical method suitable for on-line measurement was developed that can enable more frequent gold analysis compared to

standard batch AA methods; enabling more rapid response to changing conditions within the gold mill. DC amperometry was used to measure aurocyanide, $Au(CN)_2^-$ according to a modified Levich equation. A three-electrode glass cell with gold working, carbon counter and calomel reference electrodes was filled with 100 mL of a 0.05M borate-buffered, 50 µM $Au(CN)_2^-$ pH 12 solution adjusted to 0.02M CN^- and 14 µM Pb^{2+} with NaCN and $PbCl_2$ respectively. Pb^{2+} was used to cathodically polarize hydrogen reduction, minimizing interference with the $Au(CN)_2^-$ reduction. The solution was aggressively sparged with nitrogen for ten minutes prior to analysis to eliminate oxygen and sparging was continued throughout the test to maintain diffusion-limited conditions. The potential was stepped to -1.2 V_{sce} using a potentiostat and current was recorded over an eight minute period. The analytical signal both as terminal current and total coulombs was linear in response to gold concentration with a detection limit of 0.5 mg/L. The rate of gold uptake onto activated carbon used in gold processing was determined for native carbon and for carbon that was treated with a polymeric material to reduce carbon abrasion. A 110 mL volume of 10 mg/L gold solution was tumbled in glass jars containing borate buffer and 4.5 g/L native or polymer-treated carbon. At intervals over 90 minutes, the solution was sampled, amended with CN^- and Pb^{2+} then analyzed. The treatment had no effect on gold uptake indicating compatibility with the gold adsorption process. Concentrations were in excellent agreement with separate analysis by atomic adsorption.









2015 Joint Southeastern/Southwest Regional Meeting 430

Method development for portable HPLC as a tool for onsite accurate analysis of THC in oral fluid

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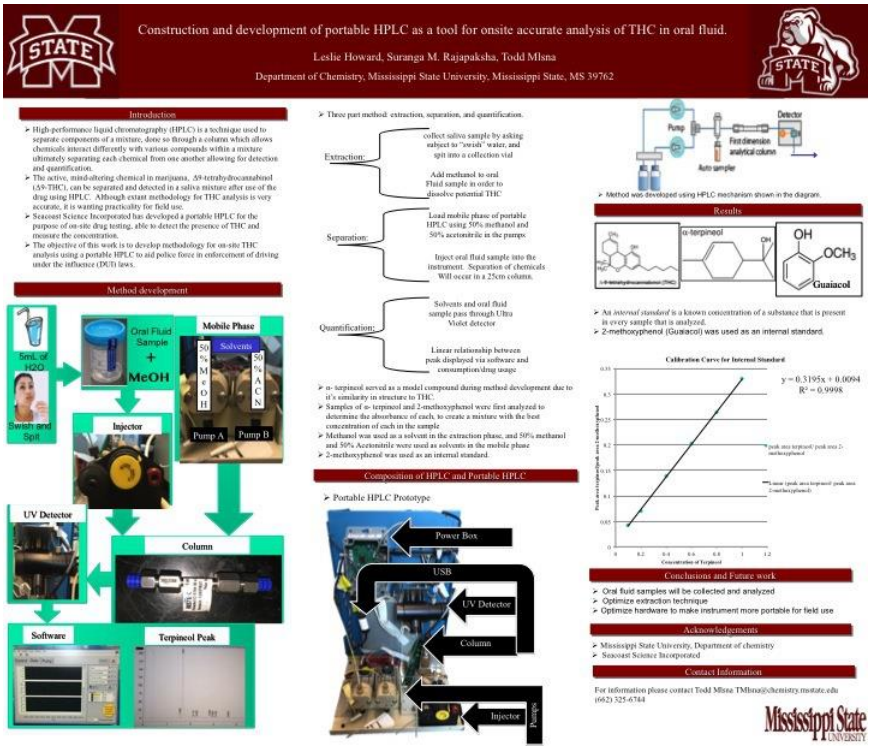
The legalization of marijuana is becoming increasingly popular in many states, resulting in a growing and unmet demand for onsite, law enforcement testing devices that can quantify recent use. Driving under the influence of marijuana can greatly impact ones driving ability by slowing the users' reaction time, thus detection hardware is needed to keep the our roads safe. Δ9-tetrahydrocannabinol (THC) is the main chemical in

marijuana responsible for producing the drugs mind-altering effects or creating a “high.” Past studies have created methods in which the presence of THC can be detected onsite. With current methodology, if THC is detected in saliva onsite, a second oral fluid sample must be collected and sent to a lab in order for the concentration to be measured. This is not compatible with field sobriety tests. We are working towards the development of a portable high-pressure liquid chromatography (HPLC) instrument that will be able to detect and quantify THC in oral fluid on site within 10 minutes. Model compounds are being tested in order to develop methods for measuring THC with the portable HPLC. In addition an HPLC/MS method has already been developed as a reference method to compare performance with the portable HPLC.



2015 Joint Southeastern/Southwest Regional Meeting 431

Forensic identification and differentiation of visually indistinguishable fiber pairs using excitation-emission fluorescence microscopy paired with multi-way chemometric analysis

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Non-destructive techniques that can discriminate between similar fibers or match a known to a questioned fiber and still preserve their physical integrity for further court examination are highly valuable and advantageous in the field of forensic science.

When fibers cannot be differentiated by non-destructive methods, the next reasonable step is to extract these fibers for dye analysis with a more selective technique. Unfortunately, dye extraction destroys the evidence and the possibility for fiber court examination no longer exists. Here, we investigate the potential of excitation-emission fluorescence microscopy as a non-destructive technique for differentiating textile fibers pre-dyed with dyes having similar molecular structures and absorbance spectra. Four different dyed fiber pairs were chosen, including Nylon 361 dyed with Acid Yellow 17 and Acid Yellow 23, Polyester 777 dyed with Disperse Red 1 and Disperse Red 19, Acrylic 864 dyed with Basic Green 1 and Basic Green 4, and Acetate Satin 105B dyed with Disperse Blue 3 and Disperse Blue 14. Excitation-emission matrices (EEMs) were obtained via fluorescence spectroscopy, from all the studied fibers, by using a spectrofluorimeter connected to an epifluorescence microscope via a bifurcated fiber-optic probe, and were processed by several multi-way chemometric methods, such as second order unsupervised parallel factor analysis (PARAFAC), and supervised further by linear discriminant analysis (LDA), and discriminant unfolded partial least squares (DU-PLS). This allows using the complete discriminating information contained in the EEMs of the corresponding pair of dyes, which is given an enhanced discrimination power than first-order approaches, which only use the emission or the excitation spectrum for the analysis. These supervised algorithms were able to classify the investigated pairs of single fiber dyes, allowing for a proper differentiation between visually identical fibers with no need of dye extraction, by the proposed non-destructive analytical approach.

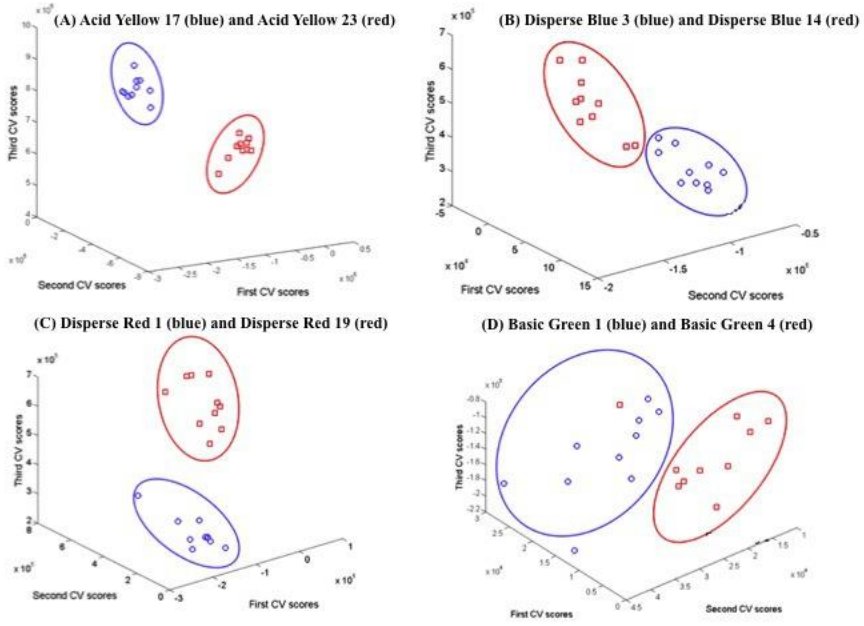

Figure: Results from LDA scores from different and indistinguishable pairs of dyed fibers

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Humic acid's influence on surfactant toxicity as measured by *Artemia franciscana*

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Surfactants are amphiphilic compounds that are routinely introduced into aquatic environment via a variety of pathways, and many are known to be toxic to aquatic species. Humic acids (HAs) are present in both soil and natural water environments, and are known to play a significant role in the binding, transport, and change of bioavailability of pollutants, including surfactants. It is important to understand their ability to bind and change the bioavailability of a range of chemically distinct surfactants. In this study, *Artemia Franciscana* were used to measure the toxicity of three different surfactants. It was found that, depending on the type of surfactant (nonionic, cationic, or anionic), HAs from differing sources had different binding abilities. The polarity of the HA played a strong role in determining HA binding with the nonionic surfactant, while electrostatic interactions and aromatic-moieties were implicated in the binding of anionic and cationic surfactants, respectively.
To further understand which HA moieties interacted with the surfactants, chemical modifications were performed to remove individual components in the HA, namely: Soxhlet lipid extraction to reduce lipid components, acid hydrolysis to reduce O- and N-alkyl groups, and bleaching to reduce aromatic moieties. Lipid moieties were found to be a significant binding component with the nonionic surfactant, while aromatics were found to play a role in binding with the cationic surfactant. The anionic surfactant had nonspecific electrostatic binding to all HAs and their moieties.

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Studies of electronic cigarette emissions for assessing human exposure to harmful chemicals

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Electronic cigarettes (ECs) has gained popularity partly because of the perception that ECs are less addictive and safer compared to the traditional cigarettes. This research aims to evaluate the validity of this perception. Supporters of ECs usually point out that E-liquids used in ECs are made up of nicotine and harmless components such as propylene glycol, glycerol, and flavoring agents that are generally regarded as safe (GRAS). By analyzing the vapor and aerosol fractions of EC emissions, it is shown additional compounds besides the GRAS constituents can be produced or inhaled. Emissions from ECs are characterized for eleven commercially available E-liquids in two models of EC devices and as a function of different EC voltage settings. Compositions of aerosol particles of different size fractions are analyzed to assess the extent of human exposure to specific chemicals. Deviation of nicotine and other E-liquid constituents from their labelled concentrations are also observed.

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Entropic and enthalpic correlations in S_N2 reactions between dianions and alkyl halides by mass spectrometric techniques

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The purpose of this study is to identify the relationships between entropy and enthalpy with respect to temperature change in substitution and elimination reactions by using dianion species, or doubly-charged anions. The dianions that were used are 6-(3-sulfonatopropoxy)-2-naphthoate (also called naphthoate) and 3-((4'-oxido-[1,1'-biphenyl]-4-yl)oxy)propane-1-sulfonate (also called biphenoxide). A series of reactions between dianions and alkyl halides were carried out to determine the relative rate constants of the reactions through the usage of mass spectrometry. We are especially interested in the reactions between dianions and the aromatic halides with special variations in their substituents. From the mass to charge ratio of the product formations, the rate constants of individual substitution and elimination mechanisms are determined from the pseudo first order reactions. With some modifications between Arrhenius and Eyring-Polanyi equation, we were able to compute the experimental values of entropy and enthalpy for substitution reactions from relative rate constants collected from the mass spectra. The experimental barriers or activation energy will then be compared to ones computed values in our previous quantum mechanical studies. Overall, the data shows that S_N2 transition states are surprisingly flexible and allow for much compensation between enthalpy and entropy effects than expected.

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Investigation of speciation of Cu^{2+} in the synthesis of HKUST-1 using UV-visible spectrophotometry

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Metal Organic Frameworks (MOFs) are 1D, 2D, and 3D crystalline compounds that are composed of metal ions or clusters as a center and organic molecule ligands as linkers, often varying in porosity. HKUST-1 (also called MOF-199, Cu-BTC) is a copper based MOF forming blue crystals under solvothermal conditions. HKUST-1 is synthesized using Cu^{2+} and Trimesic acid (TMA) dissolved in Dimethylformamide (DMF). The investigation of speciation is observed using UV-Visible Spectrophotometry. The speciation of the Cu^{2+} ion is attained through pre-heated samples of Copper/TMA solutions (at various time intervals throughout heating), the mother liquor of the synthesized MOF, and HKUST-1 itself. The primary parameters of investigation is the ratio (in grams) of Cu^{2+} to TMA and heating time. After the data is obtained comparisons will be made to spectrum of the copper precursor ($Cu(NO_3)_2$-$2.5H_2O$) in DMF and Trimesic acid in DMF.

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Magnetic enhancement in powerchip LIBS microplasmas

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Laser-induced breakdown spectroscopy (LIBS) uses a laser to ablate and simultaneously excite sample atoms, creating an emissive plasma. Powerchip lasers (a derivative of microchip lasers) achieve kilohertz repetition rates and subnanosecond pulse lengths with low M^2 values. Their pulse energies are modest, on the order of ~50 µJ, resulting in very fast-evolving plasmas. The passive q-switching employed in commercial powerchip models results in microseconds of jitter, making time-resolved measurements difficult, as the plasmas persist for only ~100 ns. Because these plasmas are particularly fast-evolving, they should benefit from magnetic field confinement/enhancement. Magnetic fields have been shown to improve limits of detection with conventional flashlamp-pumped LIBS, making the plasmas hotter and longer-lasting. This study presents time-resolved measurements of powerchip LIBS plasmas formed with and without magnetic fields produced by rare-earth ring magnets.

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Radiocarbon dating rock paintings at Eagle Cave, TX

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Our laboratory determined age estimates for three Pecos River Style paintings in Eagle Cave, a rock shelter in southwest Texas, using a combination of oxidative plasma and accelerator mass spectrometry. For the paint layer samples, we utilized low-temperature oxygen plasma reactions which oxidize the organic binders present in the paint to carbon dioxide which was collected for radiocarbon measurement. We also sampled overlying and underlying accretion layers to be dated separately in order to determine minimum and maximum dates. The accretion layers contain calcium oxalate, which was identified using Fourier Transform Infrared spectroscopy, isolated using acid treatments, and then cleaned using plasma oxidation. The calcium oxalate samples were then sent for combustion and accelerator mass spectrometry radiocarbon dating. The dates for the three paint layer samples are all statistically indistinguishable giving a weighted average of 3280±70 years BP. The accretion layer dates also agreed with the paint layer dates with the outermost layer being younger and the underneath layer being older. This agreement suggests that both dating methods are producing valid results. With more excavation in the Eagle Cave area underway, rock paintings can now give us a better understanding of the hunter-gather society of the time.

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Rapid LC-MS/MS analysis of chlorogenic acid, phlorizin, epicatechin, and catechin in apple juice

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Apple juice contains several antioxidants that may provide health benefits. A quantitation method for four antioxidants in apple juice was developed. Chlorogenic acid, phlorizin, epicatechin, and (+)-catechin were chromatographically separated using

a UHPLC method coupled to a ultraviolet/visible photo diode array detector (UV-vis PDA) and a triple quadrupole mass spectrometer (LC-MS/MS). Chromatographic separation was carried out with a UHPLC column (2.6 micron, 5 X 2.1 mm C18 stationary phase) with a 6.5 minute cycle gradient elution time program. The flow rate was 0.75 mL/min; the mobile phase consisted of 0.1% TFA in water and 0.1% TFA in acetonitrile. Chlorgenic acid and phlorizin were quantified at the 320 nm wavelength using UV-Vis spectroscopy. The LC-MS/MS was used to quantify epicatechin and (+)-catechin to provide more sensitivity than the UV-Vis PDA detector could provide for catechins. A set of standards were prepared for the analytes. Calibration curves were either linear fit or quadratic fit with 1/C weighting. The fresh apple juice sample contained 40.40 µg/mL of chlorogenic acid, 17.91 µg/mL of phlorizin, 1.03 µg/mL of epicatechin and 0.29 µg/mL of (+)-catechin. In comparison, pasteurization reduced the amounts of antioxidants in the bottled juice. The pasteurized bottled apple juice contained 2.89 µg/mL of chlorogenic acid, 1.88 µg/mL of phlorizin, 0.16 µg/mL of epicatechin, and 0.16 µg/mL of (+)-catechin.

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Comparison of two analytical methods for the measurement of nitrate concentrations across different concentration ranges of standard solutions and environmental samples

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Preliminary analysis of river water samples collected on the Little Shoe Heel Creek for nitrate ion concentrations using two different analytical techniques indicated that the methods were giving statistically different results. A UV/Visible Spectroscopic method outlined in the 16th edition of Standard Methods: For the Examination of Water and Wastewater and an ion selective electrode method using the Horiba B-34X Compact Nitrate Ion Meter were used to analyze the water samples. Preliminary results indicated that concentrations found in collected environmental samples showed statistically different outcomes between the two methods. In order to determine if the two methods were in fact giving statistically different results across a range of concentrations, a controlled set of samples were prepared both at lower concentrations and higher concentrations. Standardized nitrate ion samples, standardized mixed nitrate-nitrite ion samples and environmental water samples were prepared or collected and analyzed using the two methods. Statistical analysis using both the t-test and the f-test of the resulting paired data sets will be presented and discussed.

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Analysis of ambient air pollution at natural gas production facilities by GC/MS and FTIR

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Natural gas is known for its clean-burning characteristic compared to coal or oil. However, natural gas production is often associated with the emission of volatile organic compounds (VOCs) into the atmosphere. For this project, canisters were used to collect grab samples at multiple locations in Karnes County, Texas, where many oil and gas production facilities are in operation. The samples were analyzed for VOCs using gas chromatography-mass spectrometry (GC/MS) with a cryogenic pre-concentrator and the low molecular weight pollutants including carbon monoxide were analyzed using Fourier Transform infrared spectrometry (FTIR) with a 10-meter gas cell. Both selective ion monitoring (SIM) and scan modes of GC/MS analysis were used to improve the detection limits and accuracy of identification for the VOCs, respectively. Selected samples show high levels of C3-C8 hydrocarbons including benzene, toluene, ethylbenzene, and xylenes. Likely sources of these pollutants can be deduced using meteorological and Toxics Release Inventory data.

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Developing a reliable approach for surface-enhanced Raman headspace sampling and kinetic studies within a cuvette

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Surface enhanced Raman spectroscopy (SERS) is a sensitive, cost-effective method that has long-term potential for multiplexed, portable headspace sensing. In developing headspace sensing methods, it is useful to measure the temperature dependent analyte binding kinetics to the sensor. Temperature controllers for cuvettes are common. To use a SERS sensor for headspace binding studies in a cuvette the following challenges must be met: a reliable method for positioning the sensor relative to the Raman excitation beam and signal collection optics; a method for pre-exposing the sensor to the solvent; a method for rapid introduction of the sample; a method for maintaining a good vapor seal. A novel sensor holder has been designed to overcome these challenges. We present the detailed design of the holder and preliminary SERS experiments that employ the holder for headspace sampling and kinetic studies within a cuvette mounted in a temperature controller.

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Immobilized redox active substrates on indium tin oxide surface modeled as immunosorbent assay device

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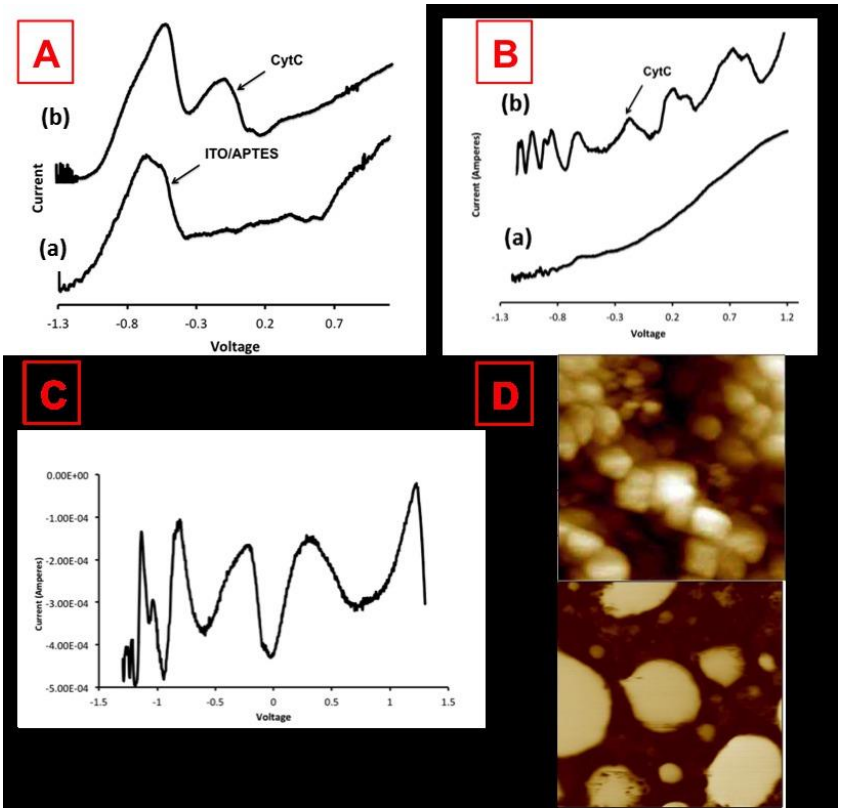
The modification of Indium-Tin-Oxide (ITO) electrode surfaces with monolayers designed to capture potential analytes was investigated as a diagnostic tool for detection of surface bound redox active proteins. Firstly, the ITO surface was modified with (3-Aminopropyl) triethoxysilane (APTES) followed by the passive adsorption of recombinant protein G (ProG), a bacterial protein known to strongly bind the Fc regions of antibodies. This was done in hopes of orienting the antibodies with their antigen binding regions away form the ITO surface to enhance specificity and binding potential

of the surface towards analytes. The ITO/APTES/ProG surface is exposed to anti-cytochrome C (cytC) antibody, followed by exposure to cytC analyte. This lead to enhanced detection of cytC via squarewave, cyclic voltammetry and atomic force microscopic techniques, Figure 1A, 1B and 1D. Alternatively, the ITO/APTES surface was modified with electrochemiluminscent probe *cis*-dichlorobis (2,2′-bipyridine)ruthenium(II), with redox potentials at -250 mV, 250 mV and -800 mV, Figure 1C. The similar exposure to anti-cyt C antibody leads to its tethering at bipyridine ligand centers of ruthenium complex followed by detection of cyt C at the electrode surface. These two strategies will be used towards engineering the electro active-integrated optical waveguide platform for ultrasensitive detection of surface bounded proteins.



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Solid phase extraction Cd(II) from environmental samples using a novel ion imprinted polymer and determination by ICP-MS

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A new Cd(II)-imprinted sorbent was syntesized using *N*-methacryloyl-L-histidine (MAH). First, Cd(II)-MAH complex was synthesized, which was then copolymerized in the presence of ethyleneglycol dimethacrylate cross-linker via bulk polymerization. The resulting Cd(II)-imprinted polymer (IIP) was characterized by FT-IR. The ion imprinted

polymer (IIP) extracted Cd(II) in aqueous solutions quantitatively between pH 6.0 and 7.0. The experimental conditions for effective sorption of Cd(II) were optimized using a minicolumn of IIP. A volume of 5 mL sample solution was loaded onto the column at 2.0 mL min^{-1} followed by elution with 1.0 mL of 0.5 mol L^{-1} HNO_3. The IIP also exhibited excellent selectivity for Cd(II) against competing metal ions, including Cu, Co, Ni, Pb and Zn. Computational calculations indicated that the selectivity of IIP was from the stability of Cd(II)-MAH complex. A limit of detection (LOD, 3s) 0.004 µg L^{-1} was achieved. The method was successfully applied to determination of Cd(II) in seawater (CASS-4) and estuarine water (SLEW-3) samples.

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Chemical vapor generation for determination of transition metals: Preliminary studies on manganese and cobalt

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Chemical vapor generation (CVG) is a classical but powerful approach for determination of hydride forming elements. Attempts on transition metals have shown mostly poor results. Here, we present evidence for formation of volatile species of manganese (Mn) and cobalt (Co). A number of chelating agents, including 1,10-phenanthroline, 8-hydroxyquinoline, diethyldithiocarbamate (DDC) and dibenzyldithiocarbamate (DBC) were examined to boost signals. The effects of mineral acids, including HCl, HNO_3, H_2SO_4 and acetic acid were examined. HCl and HNO_3 appeared effective for generating volatile species of Mn and Co. HCl was suitable for both Mn and Co vapor generation. A concentration of 3 to 4% (v/v) was used. DDC and DBC showed enhancement in signals. DBC was the most effective reagent. A cooled spray chamber afforded smooth generation and transport of volatile species to ICP-MS. The analytical potential of the method was verified by determination of Mn and Co by vapor generation ICP-MS in seawater reference samples.

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Biophysical characterization of pathological tau oligomers

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Alzheimer's disease (AD) is the most common form of dementia, and the sixth leading cause of death in the United States. Last year AD cost the US economy 450 billion dollars. By 2050 the inflation-unadjusted Medicare costs *alone* will explode to an estimated 1.2 trillion dollars as the American demographic ages. AD is a neurodegenerative disorder. Symptoms begin with mild memory impairment, progressing to mood and behavior changes, confusion, serious memory loss, and difficulty with motor control and language. At the biomolecular level, AD pathology arises from misfolding and aggregation of two specific proteins: amyloid-β (Aβ), and tau. The biochemistry of AD is *exceedingly* complex; different aggregation states induce different cellular responses, and therefore influence different aspects of AD pathology, including direct neuron death, changes in neuron signaling and metabolism, and

activation of the neuroinflammatory response. The process by which Aβ forms aggregates is better understood than tau, yet tau is more closely tied to the cognitive decline in AD.
The presented work represents a biophysical study of tau aggregation. A seeded oligomerization method was used, where pre-formed tau oligomers initiate templated aggregation upon addition to a solution of monomeric tau. Monomeric 2N4R and 2N3R tau isotype solutions were used, and the effect of chemically crosslinking the seeds was also investigated. Solutions were purified via size exclusion chromatography (SEC) with in-line multi-angle light scattering (MALS). Further characterization included electron microscopy (EM), circular dichroism spectroscopy (CD), and conformation-specific fluorescent dye binding assays. Oligomer fractions had molecular weights consistent with trimeric tau oligomer, while monomer fractions were smaller. Interestingly, based on dye-binding assays, oligomer and monomer fractions both had significant hydrophobic surface exposure. EM images of the oligomer fractions suggested that multiple aggregate species were present. This study provides a promising groundwork for our future exploration of tau biophysics.

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Structural studies of HIV-1 and HTLV-II long terminal repeat substrates

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Retroviral Integrases (IN) recognize different viral LTR sequences, allowing them to process a variety of substrates. Common to all viral DNA 3’ processing substrates is a conserved CA dinucleotide motif and corresponding GT pairing nucleotides. This indicates the CA sequence motif may contain or impart a unique structural or dynamic feature to the DNA duplex that serves as a recognition marker. Previous studies have shown the CA motif does not impart gross structural perturbations to the substrate; however, an investigation of conserved features of different substrates has not been possible due to inherent variations and differences in structure generation processes. Here we have systematically characterized the global and local features of different retroviral integrase substrates using identical procedures. This allows for the comparison of even subtle details that would be otherwise biased by individual investigatory procedures. Analysis of our DNA substrate structures reveals conserved but also different helical features of the CA motifs in these substrates. Our study suggests that the local DNA structure at the CA motif is not the main determinant for retroviral recognition. Comparing our results to published structures of Integrase - DNA complexes yields insight into the retroviral recognition process. Interestingly, the G residue of the CA motif is exclusively implicated in specific interaction. We are currently investigating modified substrates to improve our understanding of the recognition process. Based on our biophysical results and an analysis of previous literature we propose a model to rationalize how retroviral Integrase enzymes locate the cleavage site used for integration of the viral DNA.

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Chronic exposure of benzo(a)pyrene and benzo(b)fluoranthene, tobacco constituents, induces oxidative stress, apoptosis, and cellular toxicity in U937

monocytic cells, perhaps through CYP pathway: Implications with HIV pathogenesis

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Cigarette smoking is a major form of substance abuse among HIV-infected population. Smoking enhances HIV-1 replication and pathogenesis, and also leads to decreased responses to antiretroviral therapy (ART). However, the exact mechanism by which smoking enhances HIV pathogenesis has yet to be explored. Polyaryl hydrocarbons (PAHs) are carcinogens present in cigarette smoke. Among the hundreds of PAHs known, we explored the effects of five specific PAHs: Benzo(a)pyrene (BaP), Naphthalene (NPh), Phenanthrene (Phe), Benzo(a)anthracene (BeA) and Benzo(b)fluoranthene (BeF) on expression of cytochrome P450 (CYP) enzymes and oxidative stress response in U937 human monocytic cells. These compounds are reported to exert their tumorigenic actions in their parent form or after metabolic activation through CYPs. In our study, we demonstrated that only BaP and BeF have a significant effect on CYP-mediated oxidative stress in monocytic cells.
First, we determined the effect of these PAHs on the mRNA and protein expression levels of CYPs (CYP1A1 and CYP3A4) and antioxidant enzymes, (AOEs) superoxide dismutase-1 (SOD1) and catalase. Acute (24 hour) exposure of BaP (100nM) and BeF (100nM) led to ~ 17 and ~2.8 fold increase in CYP1A1 mRNA expression, respectively, but there was not much change in CYP1A1 at the protein level. No significant effect was observed on the mRNA and protein expression of CYP3A4 or AOEs following acute treatment with either compound. A similar increase in CYP1A1 mRNA expression was observed with chronic treatment of BaP (100nM) and BeF (100nM). However, the elevation in reactive oxygen species (ROS) level was observed only with the chronic treatment of BaP, while cellular toxicity was observed with both compounds. Furthermore, elevation in caspase-3 activity following BaP or BeF treatment indicated that the cell death occurred via apoptosis.
Our results suggested that BaP and BeF induced apoptosis and cell toxicity in monocytic cells, perhaps through CYP1A1-mediated activation of BaP and BeF. To confirm the effect of BaP- and BeF-mediated oxidative stress on HIV pathogenesis, we are in the process of conducting similar studies *in vitro* using HIV-1-infected primary macrophages and U1 cells (HIV-infected U937 cell lines).

Uncovering the forces driving higher-order SPOP self-association

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Higher-order oligomers carry out critical functions in signal transduction because of their ability to scaffold signaling complexes, confer non-linearity and filter noise. However, their biophysical analysis is hampered by their inherent size heterogeneity, preventing insight into the dependence of function on the size of higher-order oligomers. Here, we present the self-association mechanism and size distribution of the speckle-type POZ protein (SPOP), a substrate receptor of the Cullin3-RING ubiquitin ligase. Misregulation of SPOP has been implicated in breast, kidney, and prostate cancers because it leads to aberrant levels of its substrates, some of which can drive oncogenesis. SPOP self-associates into higher-order oligomers, which have increased ubiquitination activity. However, the sizes of higher-order SPOP oligomers are unclear, limiting insight into their enhanced activity. Here, we employ biochemical and biophysical techniques to uncover the inter-molecular interactions that drive SPOP self-association. We show that SPOP dimerizes via two domains; the bric-a-brac, tramtrack and broad complex (BTB) forms dimers with nanomolar affinity while the BTB and C-terminal Kelch (BACK) domain forms dimers with micromolar affinity. Together these domains mediate the formation of higher-order SPOP oligomers via an isodesmic self-association mechanism, in which each addition of a building block occurs with the same affinity. Our analysis quantifies the size-distribution of SPOP in solution, demonstrating that a considerable fraction of SPOP monomers is sequestered in large oligomers. We further show that SPOP self-association becomes stronger with increased buffer ionic strength; we therefore conclude that SPOP self-association is driven by hydrophobic, rather than electrostatic, interactions. This work lays the foundation for investigating how the size distribution of SPOP oligomers impacts SPOP function and how it may relate to cancer pathogenesis.

Structure and activity relationship studies of a highly endosomolytic fluorescently labeled dimer of the cell penetrating peptide TAT (dfTAT): Effects on cytosolic cellular penetration

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The plasma membrane acts as a barrier to hydrophilic molecules and hinders delivery of cell-impermeable macromolecules into the cytosolic space of live cells. Cell-penetrating peptides (CPPs) have been used to aid in the internalization of macromolecules inside cells utilizing the endocytic pathway. However, endosomal entrapment severely limits the efficiency of macromolecular delivery into the cytosolic space of cells. Achieving efficient release of macromolecules from endosomes could increase the potential of this technology in medicine as well as in biomedical research. In our laboratory we have generated a peptide dfTAT, derived from the prototypical CPP TAT, which penetrates live cells by escaping from endosomes with a particularly high efficiency and no noticeable impact on cell physiology. Understanding the molecular features that confer the high endosomolytic activity of dfTAT is crucial and has not yet been identified. Therefore this project focuses on establishing the structure activity relationships that will help in identifying the molecular properties required for this efficient endosomal escape. In this study, a focused library of peptide analogues based on the prototype dfTAT was synthesized and characterized for cellular penetration and endosomolytic activity. This knowledge is critical since it will aid in the understanding of

molecular features that are essential to achieve efficient endosomolytic activity. This project also lays a foundation for the design of cellular delivery agents with improved therapeutic value.

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Pursuit of an inhibitor for MAGE-B2, a novel oncogene restricted in expression to the testis and cancers

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MAGE-B2 is a member of the melanoma antigen (MAGE) family of proteins with no previously identified function. It is a cancer-testis antigen that has restricted expression to the male germline but is aberrantly expressed in many tumors. Our lab has recently determined that MAGE-B2 is both necessary and sufficient for tumorigenesis: expression of MAGE-B2 in immortalized, non-tumorigenic human colonic epithelial cells (HCEC) drives robust xenograft tumor growth in mice, transient knockdown of MAGE-B2 in cell lines reduces viability, and cancer lines with stable MAGE-B2 knockdown exhibit significantly slower tumor growth *in vivo*. Furthermore, our lab has determined that MAGE-B2 modulates its pro-tumorigenic effects by altering the stability of specific mRNAs with AU-rich elements in their 3' UTRs, dramatically shifting the transcriptome towards a pro-growth, pro-survival, and de-differentiated profile.

We have screened 200,000 compounds for toxicity against MAGE-B2-expressing human colonic epithelial cells, and by cross-screening against control HCEC-vector cells, we have narrowed down our hits to 17 compounds that are specific to MAGE-B2-expressing cells. 4 of the compounds have a similar core structure. We aim to further assay these top 17 hits in MAGE-B2-positive and MAGE-B2-negative cancer lines to determine specificity and also test their ability to inhibit MAGE-B2 action *in vitro* and *in vivo.* This will serve as a proof-of-concept study for targeting the function of MAGE proteins as a viable strategy to specifically target cancer cells.

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Examination of creatine kinase-B's role in triple negative metastatic breast cancer

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Creatine kinase (CK), an enzyme responsible for catalyzing the transfer of a high energy phosphoryl group from ATP to convert creatine to phosopho-creatine, is often upregulated in solid tumors. Creatine Kinase brain isoform (CKB) has been indicated as a possible key molecular driver in the metastasis of solid tumors. Previous studies in PyMT CKB KO mouse model showed a decrease in metastatic lesions compared to PyMT WT. To further explore the role of CKB in the metastasis of triple negative breast cancer, cyclocreatine (cCr), a substrate analogue and known inhibitor of CK was used to treat several different cell lines expressing CKB: DU145, MDA-MB 453, and MDA-468. The effects of cCR on cell cycle, migration, invasion and cellular signaling in both apoptotic and cellular metabolism pathways were examined. Consistent with published

research for other cancer types, inhibition of CKB results in a general cell cycle arrest, primarily G2 arrest, but some cell lines did show G0 and cell death for sensitive cell lines at the maximum soluble dose of 50mM. Protein CKB levels are not changed by treatment with cCR, but other key molecular signaling changes.

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Wet-laid soyfiber reinforced scaffold: Fabrication, mechano-morphological, and cell proliferation studies

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Among the materials used in biomedical applications such as tissue engineering, regenerative medicine, and drug delivery, hydrogels have received a consistent linear growth in interest over the past decade. The use of hydrogels as a biomaterial in these applications is optimal due to their large water volume and saliency to the natural extracellular matrix but is often limited due to their sub-optimal mechanical properties. To improve the mechanical weaknesses inherent of hydrogels, chemical or physical crosslinking is often performed. While chemical crosslinks form consistent crosslinks among polymer chains, they typically require the use of toxic reagents that must be subsequently removed. Physical crosslinking procedures are more temperamental to environmental changes during the crosslinking process but can be formed without the application of toxic reagents. In this study, we have utilized a fiber-reinforcement method to increase the mechanical robustness of a poly(vinyl alcohol) (PVA) hydrogel formed through successive freezing-thawing cycles by incorporating a non-woven, multi-directional microfiber mat formed by the wet-lay process. By reinforcing the hydrogel with a rapid-cycle time wet-laid fibrous mat, the mechanical properties can be increased isotropically due to the multi-directionality of the fiber mat. This approach to hydrogel-reinforcement presents a facile, tunable method by which hydrogel systems can attain increased mechanical properties without sacrificing their inherent biologically favorable properties.

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Nanofiber bioscaffold sensor for cancer cell detection

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A simple, sensitive, and reliable method that can distinguish cancer cells from normal cells is critical for cancer screening and treatment, in which little has been reported in literature on turning a bioscaffold into an electrochemical sensor. Here we present some preliminary results from the development of a label-free electrochemical biosensor on a bioscaffold for direct detection of cancer cells in, hopefully, both qualitative and quantitative manners. In the present work, a sensory nanobioscaffold was incubated with two types of human cancer cells and one type of corresponding normal human

cells, respectively. These three types of cells showed significant differences on the bioscaffold-sensors, suggesting that these cells upon bounding on the scaffold have altered the surface charge-density on the nanobioscaffolds. This new method can be potentially used in various important applications in cancer screening and monitoring, which are doable *in vivo* at ultralow-cost and in real-time.

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Late endosomes and its unique anionic lipid bis(monoacylglycero)phosphate act as doorways for the endosomal escape and cytosolic entry of the fluorescently-labeled dimeric cell-penetrating peptide dfTAT

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Endosomal entrapment is one of the key challenges and a multibillion dollar issue in the field of delivery of biologics/therapeutics inside live cells. Currently, there is an urgent need to define cell penetration and endosomal escape mechanisms in order to improve existing delivery strategies. We have shown that dfTAT, a recently identified delivery tool, can circumvent this hurdle. In this work we describe the use of dfTAT, a dimeric peptide found to promote endosomal leakage extremely efficiently and without deleterious effects to cells, as a model cell-penetrating peptide that can reveal the cellular organelles and factors involved in endosomal escape. By modulating the trafficking of dfTAT within the endocytic pathway, we identify late endosomes as the unique organelles rendered leaky by dfTAT and as the exit point for dfTAT endosomal escape. dfTAT binds bis(monoacylglycero)phosphate (BMP), a negatively-charged phospholipid found in late endosomes and, consequently, causes the leakage of bilayers containing BMP but not bilayers containing two other negatively-charged lipids, phosphatidic acid (PA) and phosphatydilglycerol (PG), *in vitro* (PG being a structural isomer of BMP). Finally, we establish that an anti-BMP antibody is capable of blocking leakage *in vitro* and endosomal escape in cellulo. Together, these data not only identify late endosomes as the cellular gateways utilizable for efficient delivery protocols, but also sheds light on a mechanism that may provide a fundamental basis for the rational design of future cell-permeable molecules.

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Engineering CRISPR/Cas9 system for diagnostic application

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Clustered Regularly Interspaced Short Palindromic Repeats (CRISPR) associated system (Cas) is used as a defense mechanism in bacteria to silence foreign nucleic acid sequences. The bacterial CRISPR II associated system is capable of inducing DNA double strand break (DSB) with the help of RNA guided endonuclease Cas9. Cas9 needs to be directed by CRISPR RNA (crRNA) and trans-activating crRNA (tracrRNA) to bind and cleave the target DNA sequence, thereby creating a DSB. The crRNA and tracrRNA are duplexed to form a guide RNA (gRNA), which can be designed to

recognize target DNA complementary to the gRNA. Molecular beacons (MB) are short hairpin RNA (shRNA) loops that contain a sequence complementary to the target DNA in the middle of the loop and a quencher and fluorophore at the ends. No fluorescence is observed when the quencher and the fluorophore are in close proximity with each other. However, a spontaneous fluorescence is observed on hybridization of the MB with the target DNA due to the separation of the quencher and the fluorophore. The combination of engineered CRISPR/Cas9 and molecular beacons can be used as a novel diagnostic tool for the detection of pathogens, leading to new application of CRISPR/Cas9. Herpes simplex virus (HSV) is a double-stranded DNA virus that affects a large population of people in the United States. It usually remains asymptomatic for a long period of time. Hence, sexually transmitted disease caused by HSV requires early diagnosis and treatment in order to prevent it from spreading. Here, we employed CRISPR/Cas9 system along with molecular beacons to develop a simple and fast diagnostic method to detect the presence of HSV.

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Synthetic studies of colletoic acid, a selective 11β-hydroxysteroid dehydrogenase inhibitor

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Colletoic acid is a novel acorane sesquiterpenoid isolated from the fungus *Colletotrichum gloeosporioides*, and exerts remarkable selective inhibition against 11β-Hydroxysteroid Dehydrogenase type 1 (11β-HSD1). 11β-HSD isoforms maintain homeostasis in the cell by regulating the conversion of cortisone to cortisol which is involved in various biological processes such as metabolism and cell growth. This biological profile renders colletoic acid a potential molecular probe to study important mechanisms mediated by 11β-HSD1 action. An efficient synthetic route to (+)-colletoic acid analogs has been developed in our laboratory. We hypothesized that a diversity-oriented strategy, featuring a modified palladium mediated-Heck reaction could provide the all-carbon spirocenter in multi-gram scale to access other acorane family members, and synthetic analogs. Compounds were purified and characterized utilizing column chromatography, HPLC-MS, and NMR techniques. Our convergent synthetic strategy afforded gram quantities of the fully functionalized colletoic acid core, which can be utilized to develop other acorane family members. Our preliminary structure activity relationship (SAR) studies highlighting analogs synthesized via alpha-hydroxylation, chemoselective epoxidation, and halogenation will be disclosed.

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Synthesis and anti-melanoma activity of the marine alkaloid calothrixins

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In spite of the recent scientific advances and the promise of alternative drug discovery strategies, natural products continue to serve as a significant source of drug candidates leading to clinical trials for various diseases. We are currently exploring the potential of the marine natural product, calothrixins to be used in the treatment of melanoma. Indolo[3,2-*j*]phenanthridine alkaloids, calothrixin B and its *N*-oxide derivative, calothrixin A are two bioactive metabolites isolated from the cyanobacteria *Calothrix*. Both these alkaloids have been synthesized in our laboratory using a novel oxidative free radical reaction as the key step. Calothrixin B is generated from the commercially available 2,4,5-trimethoxybenzaldehyde in only 7 steps. The key step in this synthesis is the $Mn(OAc)_3$ mediated oxidative free radical reaction of 9-(benzylamino)phenanthridine-7,10-dione with cyclohexenone to form 12-benzyl-12*H*-indolo[3,2-*j*] phenanthridine-7,13-dione. Calothrixin A is achieved by the N-oxidation of calothrixin B. We have demonstrated that calothrixin A has the ability to inhibit the growth of melanoma cells at nanomolar IC_{50} values. Treatment of human melanoma cells (A375 and Hs294t) with calothrixin A significantly inhibited the activity of class I histone deacetylases (HDACs) while enhanced the activity of histone acetylation (HAT) in melanoma cells. Thus, our study demonstrates for the first time that calothrixin A has the ability to inhibit the growth of melanoma cells and it is mediated through targeting class I HDACs.

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Characterizing protein adsorption to gold nanoparticles

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The utilization of gold nanoparticles (AuNPs) for drug delivery to tumors is limited by the stoichiometry and activity of the protein adsorbed to the surface. The size of the AuNPs can be determined with the use of dynamic light scattering (DLS) and transmission electron microscopy (TEM). When proteins are added to AuNP solutions, they spontaneously adsorb to the nanoparticle surface, creating a protein corona and therefore increasing the apparent size of the AuNP. This increase can be used to estimate the number of protein layers bound to the sample. Additionally, by comparing this change in diameter to the radius of gyration of the folded protein, we can predict whether the proteins have remained globular upon adsorption. Each protein has its own characteristic physicochemical properties, and therefore individual proteins bind in different ways to the AuNP surface. We have tested the binding behavior of several globular proteins, including wild type GB3, chemically methylated GB3, and bovine carbonic anhydrase (BCA). In addition, we have investigated binding on several differently-sized AuNPs with diameter of 15 nm, 24.5 nm, 41 nm, 97.5 nm. Our results support previously recorded NMR measurements, which suggest that a singular layer of globular protein is bound to the AuNP surface. By using DLS and TEM, an accurate approximation of the size of the AuNPs was determined with and without the added protein; therefore also determining the number of adsorbed protein layers and predicting whether or not they have remained globular on the surface. Our results are in good agreement with previous NMR data, strengthening the case that proteins are generally compact and globular on the AuNP surface. This principle may be useful for optimizing nanoparticle-based therapeutics in the future.

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Analysis of site-directed mutants of sphingosine kinase-1 by LC-MS/MS and bi-substrate kinetics

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Sphingosine kinase 1 (SK1) mediates the phosphorylation of sphingosine (SPH) to form sphingosine 1-phosphate (S1P). S1P is a bioactive phospholipid involved in cellular apoptosis, proliferation and survival. The SK1/S1P system plays a role in several human diseases, including cancer and cardiovascular diseases. SK1 inhibitors are proposed to reduce metastasis, induce apoptosis and to sensitize tumor cells to radiation and chemotherapeutics. The identification of novel SK1 in would benefit from a deeper understanding of the SK1 mechanism. This work describes the development of an LC-MS/MS assay that allows direct quantitative analysis of S1P levels. This assay has been applied to the characterization of more than 20 SK1 site directed mutants using bi-substrate kinetics.

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Identification and characterization of a novel chlorophyll catabolite from the bioluminescent dinoflagellate *Pyrocystis fusiformis*

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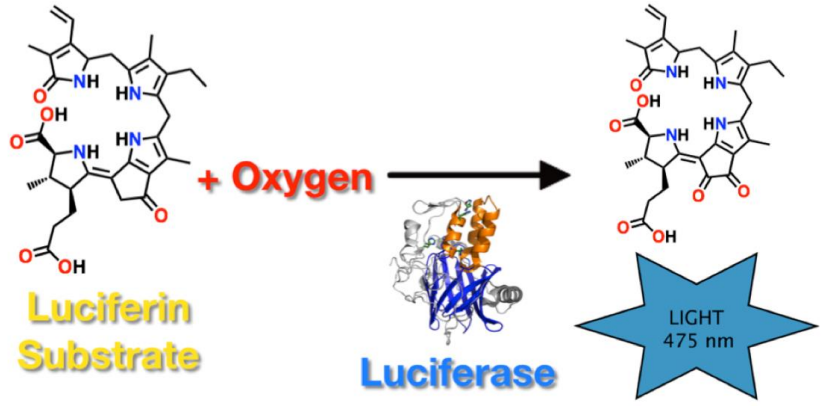
Dinoflagellates are an important group of marine microorganisms and the causative agents of red tides. Certain species are photosynthetic and capable of bioluminescence induced by physical agitation. The bioluminescence reaction, which is regulated on a circadian rhythm, involves the oxidation of a luciferin substrate by the enzyme dinoflagellate luciferase. Dinoflagellate luciferin is derived from chlorophyll in an unknown pathway. A proteomic investigation is underway to elucidate the biosynthetic pathway of dinoflagellate luciferin, which may aid in the development of algicides for the remediation of coastal seawaters and the use of dinoflagellate luciferase as a reporter gene and cellular imaging agent.



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Examples of alternate antibody conjugation strategies

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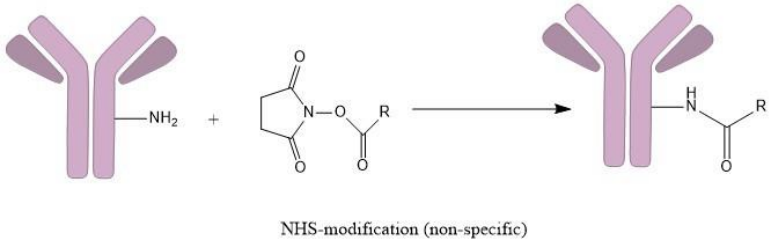
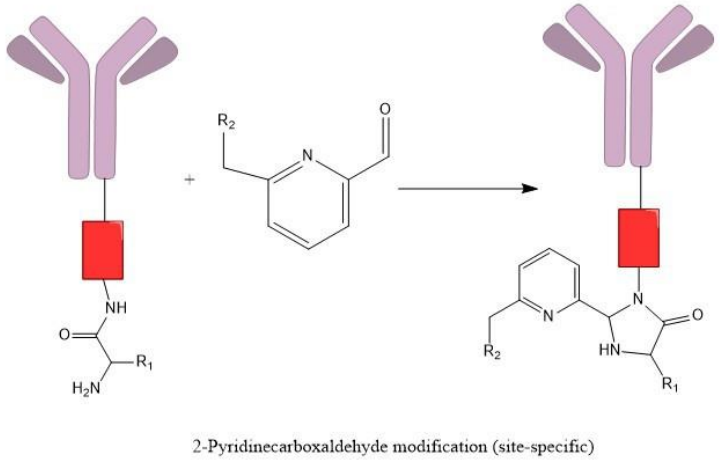
As antibody-drug conjugates have become a popular topic in the field of cancer therapy, the need for new methods of antibody conjugation has grown rapidly. The most common method currently used to conjugate small molecules to antibodies is through the reaction of N-hydroxysuccinimide esters with lysine residues on the antibody. This method has the drawback of being non-site-specific and may potentially modify the antibody binding region and thus inhibit binding with the target. Our research has focused on creating small molecule-antibody conjugates using site-specific modification techniques, including the use of 3-Indolebutyric acid crosslinking, transglutamination, and pyridinecarboxaldehyde reactions with the N-terminus of proteins. These methods have been tested using a variety of antibodies which target receptors found on dendritic cells, with the intention of using these antibody conjugates to stimulate an immune response through the Toll-like Receptor 7 pathway.





Antibody modification strategies

Excess sodium ion concentrations: The plight of the peptide chemist

*Russell L. Lewis, Erin Seal, Ryan C. Fortenberry, **Amanda L. Stewart**, amanda_stewart1@yahoo.com. Department of Chemistry, Georgia Southern University, Statesboro, Georgia, United States*

Water quality is an important consideration in many different fields due to health and environmental concerns, but it is also significant in the daily research experiments of chemists and biochemists because of the effects of ion concentrations on chemical structures and reactions. Ion concentrations in aqueous solutions are particularly critical in biochemistry research due to their effects on protein structures. A well-studied peptide known to be soluble and highly structured in aqueous solutions was determined to be insoluble in aqueous solutions from a local water source. Subsequent studies of this peptide and other proteins indicate that ion concentrations in this water affect multiple peptide and protein structures. After analysis of various water samples via ICP-MS, high sodium ion concentrations in the water are thought to be the cause of these anomalies in protein structure and function. Quantum chemical computations provide evidence that sodium ions disrupt stabilizing cation-pi interactions and unfold peptides. Circular dichroism experiments also give insight into the structural effects of high sodium concentrations in peptides and proteins. These results demonstrate the significance of water quality during experimentation and point to broader implications in peptide chemistry.

Charge distribution influences conformational properties and signaling efficiency of the intrinsically disordered cell cycle inhibitor p27

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p27 is a member of the Cip/Kip family of intrinsically disordered Cdk inhibitors that controls progression through the mammalian cell cycle. The inhibition of Cdk2/cyclin A by p27 is relieved by a sequence of signal transduction events culminating in proteosomal degradation of p27. A key step in this signal transduction cascade is intracomplex phosphorylation of p27 at T187 by Cdk2/cyclin A, mediated by intrinsic disorder of p27's C-terminus in the context of the p27/Cdk2/cyclin A ternary complex. Recent work has shown that the conformational properties of intrinsically disordered proteins (IDPs) depend on the distribution of charged residues within the protein sequence. Here we have used a sequence permutation strategy to probe the impact of charge patterning on conformational properties of p27 and the impact, if any, on the efficiency of T187 phosphorylation. We find that the conformational properties of the p27 permutants, as measured by SAXS and NMR, are well predicted by computational models but that their efficiencies as kinase substrates did not correlate with these conformational properties. Strikingly, kinase activity through intra-complex and inter-complex mechanisms are strongly correlated, demonstrating that the substrate efficiencies of the various permutants is an intrinsic property of the chain, and revealing an unappreciated auxiliary motif that affects the accessibility of the T187 substrate to

the kinase active site. We propose that due to their lack of sequence conservation such regions may be more abundant in IDPs than previously appreciated.

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On electrophoretic methods used in gene mapping and finite speed diffusion

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Genomic mapping is a method in order to obtain the distance between two repeats that appear in DNA. DNA barcoding, optical mapping, electropherogram, fluorescent burst using flow cytometry, and high-throughput sequencing are different methods of sizing the oligonucleotide sequences. Phenotype disease states can be determined from genomic rearrangements. The size of restriction fragments can be determined using the method of gel electrophoresis. Electrophoretic mobility of DNA in free solution depends on the molecular weight of the oligonucleotide. Electrophoresis technique is lower in cost, not laborious, and can be used for both analytical and fractionation purposes. Limitations of the method are long-time needed, semiquantitative nature, and hurdles of automation. Finite speed diffusion models can be used in order to reduce the time taken for analysis.

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Design and optimization of simple sensing ensembles using multivariate analysis

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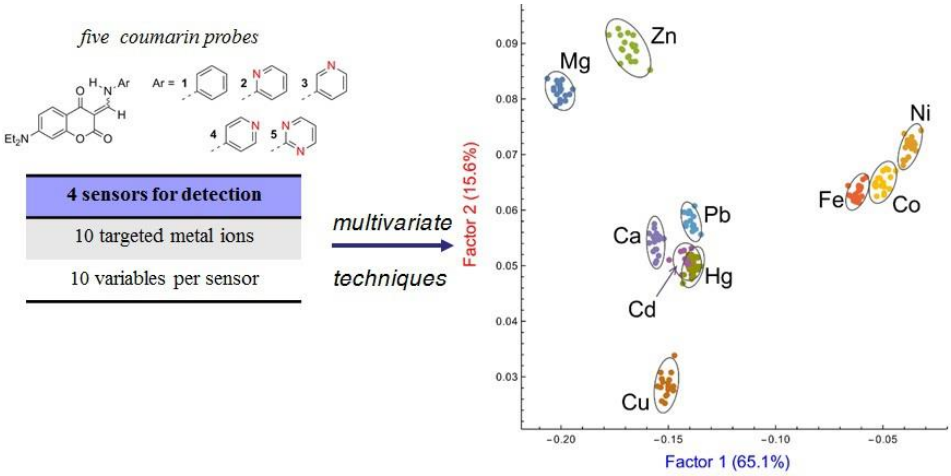
We have developed a pattern-based recognition approach in designing a general method for the construction of self-assembled optical sensor arrays using simple components. By utilizing charged, fluorescent molecular probes we gain insight into the structure of the spontaneously formed aggregates through spectroscopic properties, specifically absorption and fluorescence techniques. We present the design and implementation of cross-reactive optical sensor arrays built from simple components to discriminate various analyte classes including biological diphosphates and metal anions. We employ multivariate pattern recognition approaches in probing structurally similar analyte classes. We illustrate multivariate analysis achieves what an univariate approach cannot: full differentiation of series of analytes.



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Repeated and folded DNA sequence optically switch silver cluster adducts

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DNA strands form specific Ag cluster chromophores (≲30 atoms) and we consider a DNA scaffold that transforms silver clusters. This ~20-nucleotide strand has two components - a cluster domain (S1) that stabilizes silver clusters and a recognition site (S2) that hybridizes with complementary oligonucleotides (S2C). The composite S1-S2 exclusively develops a violet cluster with low emission. This conjugate hybridizes with S2C, and the violet chromophore transforms to a fluorescent cluster with ~100 fold stronger emission. Furthermore, the fluorescence spectra are tuned by the S1 cluster domain, and our studies focus on the DNA s*equence* and *structure* that develop a cluster with I_{ex}/I_{em} = 490/550 nm. Repeating C_4X sequences with X = adenine, thymine or guanine favor this cluster, and three factors direct the violet→blue-green cluster conversion: the number of C_4X repeats, the identity of the X nucleobase, and the number of contiguous cytosines. Electronic spectra with these different DNA hosts identify the optimal S1 sequence C_4AC_4T, and the different nucleobases have distinct roles in this aggregate binding site. This C_4AC_4T sequence intramolecularly folds, and two factors guide its conformation: hybridization with the S2C complement and folding by the cluster adduct. S2C hybridizes with C_4AC_4T-S2 forms a dangling, single-stranded C_4AC_4T. Thermal and isothermal spectroscopic studies and alternate S2C complements suggest that these unpaired nucleobases coordinate the blue-green cluster. Chromatography studies and DNA constructs with restrained conformations show that the blue-green adduct reciprocally condenses its C_4AC_4T host. We propose that DNA sequence and structure are linked because the cluster crosslinks the repeated C_4X components.

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Understanding the structural properties of the C-terminal domain of Alb-3 from *Pisum sativum*

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The goal of this research project is to determine and explain the binding ability of C-terminal Albino3 to the chloroplast signal recognition subunit, cpSRP43. To achieve this objective, production and purification of C-Alb3 protein must be optimized. The source of the C-Alb3 clone under current study is from the chloroplasts of *Arabidopsis thaliana* and belongs to the Alb3/Oxa1/YidC protein family (Dünschede 2011). It is an independently duplicated protein from that of its relatives, with some unique modification in its conformation. Previous studies have shown that this family of proteins facilitates membrane insertions in wide variety of membrane proteins (Kuhn 2003). While Oxa1 and YidC's ability to mediate membrane protein insertion has been demystified, that of C-Alb3 is still unclear (Funes 2011). It has been suggested that this family acts as membrane chaperones which in turn facilitates the newly synthesized proteins to properly fold into the lipid membrane bilayer. It has also been determined that C-Alb3 binds to cpSRP43 and this project will focus on specifics of C-Alb3 binding. While very little has been revealed about this protein, C-Alb3 is directly involved in the insertion specific (LHCP) light harvesting complex proteins (Kuhn 2003). The map of cpSRP43 binding sites on C-Abl3 will provide essential information on the interactions of C-Alb3 with cpSRP43.

Mode of action and biomarker discovery for anti-cancer natural products

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Natural products have provided a rich source of anti-cancer therapeutic leads that act through diverse modes of action. Key challenges to developing natural products for therapeutic use include incomplete understanding of anti-cancer modes of action, heterogeneity of patient responses, and toxicity. We have integrated experimental and computational methods to address these challenges, first by mapping natural products to their cellular mechanisms of action on a library-wide scale, and second by identifying biomarkers capable of predicting best responders to specific anti-cancer natural products. Within the experimental setting of human HCT116 colon cancer cells, we measured quantitative expression-based cellular responses to marine-derived natural products and to siRNA-mediated genetic perturbations. We then used unbiased similarity matrices to match similar responses, thus enabling target prediction at the pathway level. In this way, we matched several novel and known compounds to their cellular mechanisms of action. One key example is discoipyrrole A, a novel compound that targets the DDR2 collagen-sensing pathway and selectively kills lung cancer cells harboring oncogenic driver mutations in the DDR2 kinase. Another key example is the previously-studied depsipeptide didemnin B, which we found induces rapid apoptosis in sensitive cancer cells from various tissues of origin through a dual mechanism of action, targeting both the translational elongation factor EEF1A1 and the lysosomal hydrolase PPT1. We then used the elastic net machine learning algorithm to identify a multi-

feature expression biomarker capable of predicting sensitivity to didemnin B and to an analog that is currently in clinical trials for oncological diseases. Improved mechanistic understanding combined with enhanced ability to predict response has the potential to improve and expand therapeutic utility of anti-cancer natural products.

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Development of adjuvant therapeutics for leukemia: Potent and selective AKR1C3 inhibitors based on a natural product scaffold

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Acute myeloid leukemia (AML) is a blood cancer characterized by uncontrolled proliferation of poorly differentiated myeloid cells within the bone marrow. Current drugs non-selectively damage DNA in rapidly proliferating cells, resulting in high levels of toxicity. Pediatric and geriatric patients have reduced tolerance to high dose chemotherapy and poor prognosis. If the efficacy of chemotherapeutic agents can be enhanced, this will have a high clinical impact on leading to lower dosing of chemotherapeutic agents and reduced chemotherapy-related toxicity.
The aldo-keto reductase 1C3 (AKR1C3) enzyme is overexpressed in leukemia cells. The enzyme converts the prostaglandin (PG) PGD_2 to $PGF_{2\alpha}$. $PGF_{2\alpha}$ functions to arrest myeloid differentiation by antagonism of peroxisome proliferator-activated receptor γ and by stimulating mitogen activated protein kinase(s) via occupying the FP1 receptor. Inhibition of AKR1C3 thus prevents the formation of $PGF_{2\alpha}$ and results in potentiation of myeloid differentiation.
Baccharin (Benzenepropanoic acid, 4-[(*E*)-2-carboxyethenyl]-2-(3-methyl-2-buten-1-yl)phenyl ester), a structurally distinct natural product, demonstrates potent inhibition coupled with a high selectivity for AKR1C3 (IC_{50}: ~100 nM) over the other human AKR isoforms. Baccharin however, possesses several structural alerts; an ester bond, crucial for activity, is metabolically unstable, and a Michael acceptor is a known toxicophore. Preliminary structure-activity relationship studies for baccharin-mediated AKR1C3 inhibition have identified multiple regions of the baccharin scaffold that are amenable to modification. Modeling of the scaffold within the AKR1C3 active site has identified critical interactions between functional groups on the hit structure and amino acid residues unique to the AKR1C3 isoform.
We show that hydrolytically stable non-toxic AKR1C3 inhibitors based on the natural product scaffold exert an adjuvant effect on AML cell lines, enhancing the cytotoxicity of etoposide by up to six-fold.
Etoposide (0.5 μM) provides approximately 20% reduction of cell viability in a human AML cellular model. Application of 0.5 μM etoposide with 1.0 μM of our non-toxic lead compound resulted in significant synergism between the two agents resulting in 60% reduction of leukemia cell viability: an adjuvant effect far greater than reported pan-AKR1C inhibitors.

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Marine alkaloid synthesis as a platform for chemical and biological discovery

***Joshua G. Pierce**, joshuapierce6@me.com. Dept of Chemistry, North Carolina State Univ, Raleigh, North Carolina, United States*

Natural products bearing complex structures and potent biological activities have long been the target of chemical synthesis and have served as successful lead molecules for drug discovery. As part of our program centered on the synthesis and chemical biology of marine natural products we have achieved a rapid synthesis of synoxazolidinone A and structural analogs. Through these efforts we have developed not only a novel reaction for the preparation of 4-oxazolidinones, but also stereoselective routes to other heterocyclic scaffolds. Additionally, the 4-oxazolidinone core has inspired the synthesis of two classes of compounds that are active antimicrobial agents. These molecules are exciting leads for infectious disease research going forward. The story of discovery resulting from our synthetic and chemical biological efforts on marine alkaloid natural products will be presented.

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Development of spectinamides as new anti-tuberculosis drug candidates

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Spectinomycin is a potent bacterial protein synthesis inhibitor yet has poor antimycobacterial activity. By using structure based drug design a pyridyl side chain was introduced to Spectinomycin, which generated a novel series of 3'-substituted spectinamides. Spectinamides are promising new semisynthetic anti-tubercular agents, which blocks native efflux from the tuberculosis cell. From the 140 spectinamides synthesized, a clear structure activity relationship has been established with respect to antitubercular activity and protein synthesis inhibition. From this panel, the most potent compounds showed M. tuberculosis MICs that are far superior to the MIC of Spectinomycin and comparable to Streptomycin. Lead spectinamides are potent against MDR/XDR-tuberculosis and are not cross resistant to any current tuberculosis therapeutics. based on pk study, murine infection models and synthetic scalability, 1599 was choosen as the preclinical candidate and 1810 as a backup candidate.

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Marine natural products as powerful molecular tools for the control of cancer and infectious disease

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Mammals have complex biological systems and are constantly prone to infections by a wide array of bacteria, fungi, viruses, and parasites, a significant challenge to the constant development of disease-strains resistance to current drugs. As a result, there

is always a need to identify new anti-infective agents against these organisms. My research group explores the NMR structure, synthesis, pharmacology, ecological roles and pharmaceutical utility of marine natural products.
This presentation will highlight several case studies to demonstrate the power of natural products as molecular tools to understand disease related mechanisms, and eventually lead to potential pharmaceuticals. Natural products will continue to provide an excellent source of new leads and combat antidrug resistance, long drug-development processes and sometimes toxic side effects.

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Natural products inspired synthesis

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Thiamine is an essential cofactor for all living things. The mechanism of thiamine action proposed by Ronald Breslow in 1958 has inspired the invention of a wide variety of chemical transformations catalyzed by thiamine and other N-heterocyclic carbenes (NHCs). We will described mechanistically novel stoichiometric transformations of NHCs that provide biomedically relevant azoles.

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Identification and characterization of an allosteric inhibitory site on dihydropteroate synthase

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The extensive global presence of antibiotic resistant bacteria dictates an urgent need for novel classes of antibacterial chemotherapy. Dihydropteroate synthase (DHPS) catalyzes a vital step in the bacterial folate biosynthetic pathway, a pathway that is absent in higher organisms. DHPS has a highly successful history as the target of the sulfonamide class of antimicrobials that transformed our ability to treat infections. We report the discovery of the first known allosteric inhibitor of DHPS, identified through a fragment-based screen. Crystal structures reveal that it engages a novel site at the dimer interface. Kinetic data show that this inhibitor exerts its effect post substrate binding at a subsequent step in the catalytic cycle. Molecular dynamics simulations and quasi-harmonic analyses show that the effect of inhibitor binding is transmitted from the dimer interface to the active-site loops that are known to form an obligatory ordered sub-structure during catalysis. Together with the kinetics results, these structural and dynamics data suggest an inhibitory mechanism in which binding at the dimer interface influences loop movements that are required for product release. These results potentially provide a novel target site for the development of new pharmaceuticals.

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Glucosamine analogue inhibitors of *Trypanosoma cruzi* glucokinase

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Chagas' disease is a neglected tropical disease caused by *Trypanosoma cruzi* protozoa and new drugs are in need because the current treatments have major issues, such as toxicity and unpleasant side effects. Glucokinase as well as hexokinase from the organism are potential enzyme drug targets for antiparasitic chemotherapy. These enzymes are found in essential metabolic pathways, including glycolysis and the pentose phosphate pathway that allow for the phosphorylation of glucose with co-substrate ATP to yield glucose-6-phosphate. It has been well known that trypanosomal drug targets reveal that *T. cruzi* cells are highly susceptible when glycolysis is inhibited. The goal of this study was to test for inhibition of *T. cruzi* glucokinase (*Tc*GlcK) and hexokinase to thereby inhibit the glycolytic pathway. Glucosamine analogues were synthesized, characterized, and analyzed in enzyme-inhibitor assays against *Tc*GlcK and *H. sapiens* glucokinase. The same compounds were tested against *T. cruzi* amastigotes co-cultured in NIH-3T3 mouse cells for *in vitro* biological activity. X-ray crystal structures of *Tc*GlcK complexed with potent glucosamine analogues and their corresponding key enzyme-inhibitor interactions were also examined. These results will be presented along with a discussion about the long-term objective, in which modified analogues of glucosamine will be tested based on a structure-activity relationship study, which stems from the most biologically active compound identified from this work.

Development of chemical biology probes of the pro-apoptotic Bcl-2 effector protein BAK

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The BCL-2 family proteins regulate mitochondrial apoptosis, the most common pathway of programmed cell death. Deregulation of mitochondrial apoptosis is one of the hallmarks of cancer. This pathway is triggered when the BH3-only protein BID directly activates BAK, one of the BCL-2 effectors of mitochondrial outer membrane permeabilization (MOMP). BAK-mediated MOMP releases cytochrome *c* from the mitochondria to initiate downstream caspase activation and the execution of apoptosis. We aim to develop small molecule chemical probes that mimic the activity of BID and serve to trigger mitochondrial apoptosis by activating BAK. We screened 4,000 fragments with recombinant BAK using 1D ligand-based NMR to find over 200 BAK

binders. We identified over 3 dozen hits through functional and binding orthogonal secondary screen validation assays and summarize the structure-function analysis for several hits, which are derivatives of a common scaffold. Our future work involves structure-based hit-to-lead optimization and the development of small molecule BAK direct activators as chemical probes for apoptosis and cancer biology.The BCL-2 family proteins regulate mitochondrial apoptosis, the most common pathway of programmed cell death. Deregulation of mitochondrial apoptosis is one of the hallmarks of cancer. This pathway is triggered when the BH3-only protein BID directly activates BAK, one of the BCL-2 effectors of mitochondrial outer membrane permeabilization (MOMP). BAK-mediated MOMP releases cytochrome c from the mitochondria to initiate downstream caspase activation and the execution of apoptosis. We aim to develop small molecule chemical probes that mimic the activity of BID and serve to trigger mitochondrial apoptosis by activating BAK. We screened 4,000 fragments with recombinant BAK using 1D ligand-based NMR to find over 200 BAK binders. We identified over 3 dozen hits through functional and binding orthogonal secondary screen validation assays and summarize the structure-function analysis for several hits, which are derivatives of a common scaffold. Our future work involves structure-based hit-to-lead optimization and the development of small molecule BAK direct activators as chemical probes for apoptosis and cancer biology.

Structure and function studies of conserved residues in the bacterial fatty acid binding protein family

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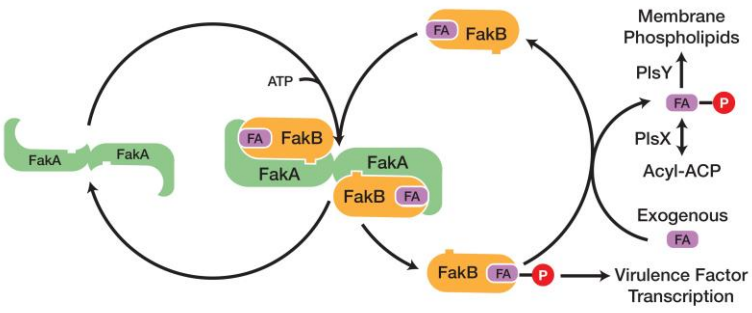
The fatty acid kinase pathway in *Staphylococcus aureus* functions in exogenous fatty acid incorporation into membrane phospholipids and virulence factor transcription. Fatty acid kinase forms a complex made up of an ATP binding protein, FakA, and a fatty acid binding protein, FakB. Analysis of the 1.2 Å crystal structure of the FakB2-oleic acid complex and sequence alignments determined five conserved residues to interrogate. These residues were critical for protein stability, complex formation, kinase activity, exogenous fatty acid incorporation and virulence factor transcription. This work defines the key residues of the FakB protein family, Pfam02645.



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The crystal structure and mechanism of a bacterial phospholipid remodeling acyltransferase

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Acyltransferases are key integral membrane enzymes, present in both prokaryotes and eukaryotes, which catalyze the transfer of a fatty acid chain from an activated intermediate to a hydroxyl group of glycerol. Despite the importance of the acyltransferases in biology and their potential for medicine, almost nothing is known about their structures and catalytic mechanisms. PlsC is an acylglycerol-PO_4 acyltransferase that transfers an acyl chain from acyl-CoA (ACP) to the 2-position. The protein was expressed in *E. coli*, purified from the membrane fraction, crystallized using a detergent screen, and solved using selenomethionine SAD methods. The final structure at 2.9 Å reveals the active site architecture in which a histidine is activated by a neighboring aspartate residue within a conserved HxxxxD motif, and there are several apolar grooves that appear to accommodate the acyl chains of the substrates. Most intriguingly, a pair of exposed hydrophobic helices is well positioned to 'surf' the membrane and help search for and extract the substrate into the active site. A suitably located basic surface patch for the phosphate head group is also apparent.

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Targeting translesion DNA polymerases for inhibition in cancer

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Tumor cells rely on translesion DNA polymerases (TLS pols) to mitigate the destructive effects of oncogene induced replication stress in order to maintain viability and proliferate. TLS pols can also render genotoxic anti-cancer therapies ineffective through the efficient bypass of DNA damage. Moreover, TLS pols are mis-regulated and mutated in many cancers, including brain, breast, and ovarian cancer. As such, they represent a potential target for improving cancer treatments as an adjuvant to existing drugs. As central mediators of TLS, human Y-family pols are especially promising targets. We have investigated *N*-substituted indole barbituric acid (IBA) and indole thiobarbituric acid (ITBA) chemical scaffolds as inhibitors of Y-family pols in an effort to improve existing chemo- and radio-therapies. Through extensive structure-activity studies, we identified several *N*-naphthyl-substituted IBA/ITBA derivatives with IC_{50} values against pol eta and Rev1 near or below 10 micromolar. Two of these

compounds, PNR-7-02 and PNR-9-59, were found to inhibit Y-family pols eta and Rev1 activity around five- to ten-fold more effectively than either A- or B-family pols. Kinetic analysis revealed that PNR-7-02 appears to follow a partial competitive mechanism of inhibition, further validating previous experiments from our group with a different ITBA analog (PNR-3-51). In cell culture experiments, we observe a synergistic relationship when triple-negative breast cancer cells are exposed to a combination of PNR-7-02 and doxorubicin. A similar effect is observed when ovarian cancer cells are treated with PNR-7-02 and cisplatin. Additional experiments will be required to ascertain whether the synergy observed in cell culture is dependent upon the activity of individual TLS pols and to test if these effects are carried over into animal models. However, our results are consistent with the idea that inhibiting TLS pol activity in cancer improves the action of genotoxic drugs by inhibiting DNA damage tolerance.

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Influence of electrostatic interactions at the sliding clamp interface on clamp loading and stability

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Ring-shaped sliding clamps serve as processivity factors for DNA polymerases enabling the polymerases to incorporate thousands of nucleotides in a single DNA binding event. Clamp loaders assemble these ring-shaped proteins onto primed template junctions where DNA synthesis will begin. The *E. coli* sliding clamp is a dimer of two crescent-shaped monomers that oligomerize in a head-to-tail fashion. The protomer interfaces are stabilized by a group of hydrophobic amino acid residues at the center as well as charged amino acid residues that are arranged asymmetrically with positively charged residues on one side of the interface and negatively charged residues on the other. These charged amino acid residues contribute to the stability of the oligomer, which in turn influences the clamp loading reaction. High concentrations of NaCl (0.5 – 1M) or mutation of an arginine residue destabilize the clamp increasing dissociation into monomers. Mutation of the Arg residue in the b-sliding clamp and high salt affect the activity of the clamp loader to increase the rate of clamp opening and the affinity of the clamp loader for the clamp.

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HDX-MS used to validate interactions with the excluded DNA strand during hexameric helicase unwinding

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The archaeal MCM helicase from *Sulfolobus solfataricus* (*Sso*) is a model for understanding structural and mechanistic aspects of DNA unwinding. Although interactions with the encircled DNA strand within the central channel have been unambiguously characterized, any interactions with the excluded strand have been

difficult to discern. We have previously proposed an extension of the tradition steric exclusion model (SE) of unwinding to also include significant contributions with the excluded strand during unwinding, termed steric exclusion and wrapping (SEW). The SEW model hypothesizes that the displaced single strand tracks along exterior patha on hexameric helicase external surface to protect ssDNA and stabilize the complex in a forward unwinding mode. Now, using hydrogen/deuterium exchange (HDX) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR), we have probed the binding sites for ssDNA using multiple substrates targeting both the encircled and excluded strands. In each experiment, we have obtained greater than 98.5% sequence coverage of *Sso*MCM from more than 650 peptides (5-30 residues in length) and are able to identify interacting residues on both the interior and exterior of *Sso*MCM. The strongest HDX signals from positively charged regions on the exterior surface were targeted for mutagenesis studies. Mutation of these external positively charged residues generally lowered DNA unwinding rates but had unaltered ATPase activities. The combined data globally identifies binding sites for ssDNA during *Sso*MCM unwinding as well validates the importance of the SEW model for hexameric helicase unwinding.

Medulloblastoma-associated mutations in DDX3X drive stress granule assembly and impair protein translation

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Next-generation sequencing has revealed frequent driver mutations in DDX3X in pediatric and adult cases of medulloblastoma (MB). DDX3X regulates multiple aspects of RNA metabolism, but the impact of cancer mutations is unknown. Here we show that MB-associated mutations drive hyperassembly of stress granules (SGs) *in vitro*, in *Drosophila*, and in tumors. Comprehensive analysis of endogenous DDX3X targets with CLIP-seq revealed that this helicase binds a large spectrum of mRNAs where it is enriched in the 5’UTR and supports their translation. MB-associated DDX3X mutants retain the ability to bind RNA, however, these mutations do not result in productive translation of DDX3X targets but shift targets to SGs and impair translation. Surprisingly, broad translation inhibition extends to non-DDX3X targets since these mRNAs are recruited to SGs and are inhibited in trans. Assessment of translation efficiency with single cell resolution reveals that SG assembly correlates precisely with impaired global translation. Importantly, the SG hyperassembly and impaired translation driven by MB-associated mutations in DDX3X is significantly rescued by genetic manipulation of SG assembly, suggesting that impaired global translation in cells expressing mutant DDX3X is a consequence rather than a cause of SG assembly. Taken together, this work provides crucial mechanistic insights into the normal function of DDX3X and reveals the consequences of one of the most common mutations contributing to MB. Moreover, our data suggest that inhibition of DDX3X-mediated SG

hyperassembly may modulate protein translation in tumor cells, leading to new avenues for cancer treatment.

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Structural basis for RNA-mediated regulation of lysine specific demethylase-1

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Lysine specific demethylase 1 (LSD1) is an essential epigenetic regulator in metazoan and influences chromatin structure by catalyzing the removal of mono- and dimethyl functional groups from H3 proteins at lysine positions 4 and 9 (H3K4/K9). LSD1 interacts with over 60
regulatory proteins and also associates with lncRNAs (TERRA, HOTAIR), suggesting a regulatory role for RNA in LSD1 function. We report the first structure of an RNA bound to a chromatin remodeling enzyme complex, revealing the mode of a TERRA binding element by LSD1. Conserved residues of LSD1 are involved in nucleobase recognition and this interaction is located on the opposing face of the H3 peptide-binding cleft. Base specific contacts of the AG dinucleotide region of the RNA with LSD1 reveal a network of hydrogen bonds and a salt-bridge across the RNA-protein interface. We demonstrate that an intramolecular G-quadruplex representing TERRA RNA [UUAGGG]4U binds with high affinity to full-length LSD1 and LSD1-CoREST (Kd ≈ 40 and 42 nM, respectively), in contrast to a DNA G-quadruplex of analogous sequence or an unstructured single-stranded RNA. These data indicate that LSD1 can distinguish between RNA and DNA as well as structured vs. unstructured nucleotide motifs. Further, kinetic assays show that a G-quadruplex forming RNA serves as a potent noncompetitive inhibitor of LSD1-catalyzed demethylation. The identification of a novel RNA binding site on LSD1 coupled with kinetic data suggest that a structured RNA can function as a negative allosteric effector in LSD1-mediated regulatory pathways.

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MCM ring hexamerization is a prerequisite for DNA-binding

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The hexameric Minichromosome Maintenance (MCM) protein complex forms a ring that unwinds DNA at the replication fork in eukaryotes and archaea. Our recent crystal structure of an archaeal MCM N-terminal domain bound to single-stranded DNA (ssDNA) revealed ssDNA associating across tight subunit interfaces but not at the loose interfaces, indicating that DNA-binding is governed not only by the DNA-binding residues of the subunits (MCM ssDNA-binding motif, MSSB) but also by the relative orientation of the subunits. We now extend these findings by showing that DNA-binding by the MCM N-terminal domain of the archaeal organism *Pyrococcus furiosus* occurs specifically in the hexameric oligomeric form. We show that mutants defective for hexamerization are defective in binding ssDNA despite retaining all the residues observed to interact with ssDNA in the crystal structure. One mutation that exhibits

severely defective hexamerization and ssDNA-binding is at a conserved phenylalanine that aligns with the mouse *Mcm4(Chaos3)* mutation associated with chromosomal instability, cancer, and decreased intersubunit association.

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Capped G-quadruplexes flanked by duplex DNA photochemically cross-linked using psoralen: A model for human c-MYC NHE-III1

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In vitro studies of intramolecular G-quadruplex structure and function have typically been restricted to single strand G-rich DNA constructs. We report here on the biophysical characterization of double stranded intramolecular G-quadruplexes that model the human c-MYC NHE-III_1. The model NHE-III_1 was assembled by annealing a 17-mer oligonucleotide, having a mid-sequence run of 5 cytosines and tail sequences of 3'-AAATTT and TTTAAA-5', to a 32-mer oligonucleotide having a 20-mer c-MYC G-quadruplex forming core and a complimentary tail sequences of 5'-TTTAAA and AAATTT-3'. The single stranded c-MYC and model NHE-III_1 contain at least two folded G-quadruplex conformations (e.g. 1:2:1 and 1:6:1 isomers). In the model NHE-III_1, this conformational equilibrium is shifted, with the 1:6:1 loop isomer becoming the predominant G-quadruplex species. Additionally continued work is being done on this construct using psoralen as a thymine to thymine duplex cross-linker, where irradiation with long wavelength UV light forms covalent adducts. Although this NHE-III_1 model may still yet be too simplistic, it appears to provide a new perspective for drug targeting G-quadruplexes formed in the c-MYC NHE-III_1 or G-quadruplexes formed in other oncogene promoters.

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Development and therapeutic potential of clamp-mediated stabilization of G-quadruplex DNA3

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The prolific transcription factor MYC, with more than 30,000 bindings sites across the genome, is upregulated or amplified in up to 80% of all cancers and has been well-validated as an molecular anti-cancer target. While most research focuses on modulation of protein function, several groups have focused on targeting *myc* promoter secondary DNA structures to regulate MYC expression. Of those groups, the majority have worked on developing small molecules to stabilize the unique promoter G-quadruplex (G4); however, we have taken an alternate approach and have optimized linked nucleic acid clamps that specifically recognize the *myc* promoter structure and shift the dynamic DNA structural equilibrium to favor higher order formations. From the several clamps tested by electrophoretic mobility shift assay and electronic circular dichroism, each recognizing unique structural isoforms, a lead was selected that stabilized the G4 formed from the first four runs of continuous guanines. This was further examined *in vitro* and demonstrated transcriptional downregulation of *myc*

promoter activity. Works are ongoing to develop nanomaterials to couple with the clamp for selective delivery into cancer cells.

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Linking pH, temperature, and conformation for the DNA i-motif

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DNA is higly polymorphic and the conformation a particular DNA segment assumes depends upon its sequence context and the environment under which it is prepared. We have been investigating the pH induced transitions for all permutations of the DNA sequence $(CCCXXX)_4$, where X = A and/or T, from a single stranded structure at pH 7.0 to the i-motif at pH 5.0 using spectroscopic approaches. All DNA sequences studied undergo the pH induce transition as evidenced by circular dichroism (CD) studies. The pH at the midpoint of the transition varies slightly with sequence. Optical melting studies by CD scans were used to determine the van't Hoff enthalpies of the transitions. The temperature at the midpoint of the transition is highly dependent upon sequence context. Currently, we are investigating the effects of temperature as well as pH on the transition of $(CCCTAA)_4$. We have carried out titrations of $(CCCTAA)_4$ from pH 7.0 to pH 5.0 at seven different temperatures (15 ^{o}C, 20 ^{o}C, 25 ^{o}C, 30 ^{o}C, 35 ^{o}C, 40 ^{o}C and 45 ^{o}C). DNA samples were prepared in phosphate buffer with least 12 different pH values from 7.0 to 5.0. Circular Dichroism (CD) spectra were determined at different temperatures to monitor the transition. Preliminary analysis of the data indicates that the transition is favored by higher temperatures. These results will be discussed from a thermodynamic point of view.

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On the road to controlling gene expression with DNA minor groove binders

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It is now well established that, although only about 5% of the human genome codes for protein, most of the DNA has some function. These functional sequences open immense possibilities in both biotechnology and therapeutics for the use of cell-permeable small molecules, such as DNA minor groove binding agents, that can bind specific base pair sequences of DNA for regulation of genomic functions. Unfortunately, most established minor groove binders bind well only to A•T sequences and generally have insufficient binding specificity. Only polyamides have been designed to recognize mixed DNA sequences and for future progress in targeting specific genes, it is essential to have additional classes of compounds that can be rationally designed from established modules and which can bind strongly to mixed base pair sequences. Based on extensive experience in design of antiparasitic minor groove agents for A•T recognition, we have designed and prepared a small compound library based on rational principles for introduction of G•C recognition modules. New compounds that bind to specific DNA sequences with sub-nanomolar K_D, very slow dissociation kinetics,

and 100 times selectivity over the related sequence without a G•C base pair have been designed and will be described.

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DNA damage by one-electron oxidants: Implication of charge transfer in DNA

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Free radical damage to DNA by reactive oxygen species (ROS) overproduced in living organisms due to a number of exogenous and endogenous factors has been unequivocally linked to such debilitating conditions as cancer, cardiovascular and neurodegenerative diseases. Until recently, research in this area has been mostly focused on hydroxyl radicals and on their reactions with DNA: hydrogen abstraction from DNA sugar and double bond addition to DNA bases. However, there is growing evidence that other biologically important ROS may also play a significant role in *in vivo* DNA damage. Of special interest are naturally produced and model one-electron oxidants (OEO) such as singlet oxygen, superoxide and peroxyl radicals, and carbonate, sulfate, and dibromide radical anions.
We have demonstrated in model *in vitro* studies by using HPLC-based analysis that oxidation of native DNA by a number of OEO results in nonlinear kinetics of 8oxoG accumulation, with the yields of 8oxoG maximizing in the range of ~ 2.0 % of the total concentration of guanine regardless of the nature of OEO studied. Kinetics of accumulation of 8oxoG during the reaction of DNA with hydroxyl radicals shows a nearly linear dependence, in sharp contrast with OEO. This contrast is attributed to different mechanisms of DNA damage by $^{\cdot}OH$ and by OEO. While $G^{\cdot+}$ centers formed in DNA as a result of guanine oxidation by OEO are mobile and can migrate along DNA strand and, in turn, act as oxidizers, hydroxyl radicals add to double bonds of DNA bases to form immobile addition complexes. This hypothesis is further supported by our experimental finding that 2-amino-5-[(2-deoxy-b-D-*erythro*-pentofuranosyl)amino]-4H-imidazol-4-one (dIz), a product of 4-electron oxidation of guanine, is produced in large amounts in native DNA by a number of OEO, while negligibly low amounts of dIz are produced by hydroxyl radicals.

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Nuclease biodegradable poly(ethylene glycol) hydrogels prepared by copper-free click chemistry

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Significant research has focused on investigating the potential of hydrogels in various applications and, in particular, in medicine. Specifically, hydrogels that are biodegradable lend promise to many therapeutic and biosensing applications. This

research was performed in order to demonstrate that DNA molecules could be integrated into a hydrogel network using copper-free click chemistry, and that such hydrogels could be biodegradable.

Poly(ethylene glycol) hydrogels cross-linked with single stranded DNA were prepared using copper-free click chemistry. Specifically, 4-Arm-PEG-Dibenzocylclooctyne (4-Arm-PEG-DBCO) was prepared by reaction of 4-arm-PEG-NH_2 with paranitrophenyl-DBCO. The 4-Arm-PEG-DBCO was reacted with ssDNA functionalized on both 3' and 5' ends with azide groups in phosphate buffered saline. Hydrogels were characterized by optical and scanning electron microscopy. The degradation of the hydrogels upon interaction with nucleases was monitored by microscopy and quartz crystal microbalance. The degradation of a 0.3-µL DNA-crosslinked-hydrogel exposed to Benzonase® solution (5 U/mL) occurred over a period of 45 minutes. In contrast, controls of DNA-crosslinked hydrogels not exposed to nuclease, or PEG-crosslinked hydrogels exposed to enzyme or buffer did not degrade. These data indicate that the endonuclease cleaves the DNA, effectively disrupting hydrogel crosslinking. In addition, the ability of the hydrogels to act as depots for nuclease-triggered delivery of model therapeutic agents was investigated. The nuclease-dependent release of fluorescently labeled bovine serum albumin (BSA-FITC) was demonstrated with the physiologically relevant DNase I enzyme via fluorescence microscopy and spectroscopy .

In this work, we present a method for the facile preparation of hydrogels that are made from branched hydrophilic polymers that are crosslinked with single stranded DNA. Specifically, copper-free click chemistry was utilized to prepare hydrogels from 4-Arm-PEG-DBCO and azide-functionalized DNA strands in saline solutions at room temperature. Degradation of these hydrogels was demonstrated using non-sequence specific endonucleases Benzonase® and DNase I. This work demonstrates the potential of DNA crosslinked hydrogels as biodegradable systems that could have applications in drug delivery.

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Ionic strength-specific, photo-oxidative DNA cleavage by a 9-aminomethylanthracene dye

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In past decades, cancer researchers have been focused on developing therapeutic agents that specifically affect diseased cells and thus decrease adverse, systemic side effects. Temperature, pH, and recently substrate-specific agents have been widely studied. Ionic strength is also another factor that can determine specificity of drug interactions. Towards this end, our laboratory has been interested in the development of ionic strength-specific agents. Here we show that increasing concentrations of NaCl and KCl intensify DNA photo-cleavage by a 9-aminomethylanthracene dye, whereas fluoride, bromide, and iodide salts of Na(I) and K(I) exhibit an inhibitory effect (350 nm, pH 7.0). Using fluorescence and circular dichroism spectroscopies, we consider explanations for the observed enhancement. According to CD experiments, KCl and NaCl untwist the DNA double helix. When compared to NaF and KF, quantum yield estimations show that the Φ_F of the anthracene decreases in the presence of high NaCl and KCl concentrations. This points to the involvement of an intersystem crossing

pathway that eventually increases the population of reactive oxygen species generated by the excited anthracene triplet state. Our findings are significant in light of the high Na^+ concentrations found in certain cancer cells.

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A potent new class of drugs for treating human African trypanosomiasis revealed by phenotypic screening

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Human African trypanosomiasis (HAT) can occur in 36 countries in sub Sarahan Africa and is caused by the protozoan, *Trypanosoma brucei*, through the bite of the infected tsetse fly. After only a few months, the disease can progresses to the late-stage where the parasites enter the central nervous system and, if left untreated, the patients eventually succumb to the neurological effects of the disease and die. Better drugs are needed for late-stage HAT due to severe side-effects and difficult administration of current therapies. A phenotypic screen of a compound library for activity against *T. brucei* led to the identification of a handful of scaffolds with drug potential, including a 4-phenylthiazole-2-ethylbenzamide and a 1-benzylindole-3-vinyl pyrimidinone. Over 200 compounds were synthesized in order to optimize these scaffolds for efficacy against *T. brucei*, as well as solubility and ability to penetrate the blood brain barrier. One compound has shown antiparasitic activity *in vitro* with an EC_{50} of 35 nM. In addition to a high selectivity index, this compound has shown to be stable to both mice and human microsomes and has displayed a good plasma to brain ratio in mice. This compound also cured 5/5 mice infected with early stage T. brucei when dosed orally. More research is ongoing, but this compound has potential to be a new drug in the fight against HAT.

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Synthesis and antibiotic activity of azabicycle compounds

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A rise in antibiotic resistant bacteria due to the overuse of antibiotics has led to a deficit in potent antibiotics. Thus, research into new compounds that exhibit novel modes of action will aid in the development of antibiotics that are active against drug-resistant strains. Based on the promising activity of ficellomycin, which contains the a unique and highly strained azabicyclo[3.1.0]hexane ring system, this project utilizes an intramolecular reductive amination, via Lewis acid catalysis and subsequent imine hydrogenation, as a viable method of azabicycle synthesis. Current work is focused on optimizing a synthetic route towards less strained 5,5 and 5,6 azabicyclic rings and then synthesizing analogs of the 5,3 ring present in ficellomycin. One possible route utilizes an alkylation reaction of protected pyrrolidine and piperidine methanols followed by the cyclization step. Another route begins with methyl acetoacetate and uses an alkylation followed by epoxidation and aziridination to form the molecule needed for cyclization.

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Discovery and characterization of the choline transporter inhibitor: N-((3-isopropylisoxazol-5-yl)methyl)-4-Chloro-3-((1-methylpiperidin-4-yl)oxy)benzamide, VU6001221

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Existing chemical probe ML352 was identified through high-throughput screening and chemical optimization as a potent and selective inhibitor for the high affinity choline transporter (CHT). Additional SAR was done around ML352 aimed to improve clearance, brain-to-plasma ratio, and potency while still maintaining selectivity, protein plasma binding, and solubility. Alternative ethers and amides were explored as well as modifications to the central core. VU6001221 was discovered via a replacement of the methoxy group on ML352 with chlorine. VU6001221 displayed a 100-fold improvement in clearance, 2 hour increase in half life, and 10% greater brain penetration. This structural modification has maintained equal potency, selectivity, and solubility while improving pharmacokinetics, thus producing a more advantageous probe for CHT inhibitors.

2015 Joint Southeastern/Southwest Regional Meeting 495

Comprehensive access to apoptolidin-derived chemical probes to study cancer cell metabolism

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Natural products contain novel scaffolds and further our understanding of biological phenomena through their use as selective chemical probes. Glycosylated natural products have long been explored for their excellent antitumor activity. We have found apoptolidin to have sub-nanomolar activity against tumor cells when glycosylated. When the sugars are removed, the aglycone loses activity (> 10 μM, H292 cells, human lung cancer). Accessing variants of apoptolidin as a function of glycosylation state will enable us to examine the role deoxy sugars play in the cytotoxicity profile of the apoptolidins against varying cancer cell types. As each cancer cell type displays a unique metabolic profile, and notably distinct from healthy cells, we hope to use our toolbox of apoptolidin glycovariants in the quantification of cellular uptake, localization, and subsequent activity as a function of glycosylation state of the apoptolidins and metabolic state of each cancer line. To access our apoptolidin glycovariants, we aim to combine techniques utilizing chemical total synthesis, precursor directed biosynthesis, and biosynthesis.

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Determining the most effective peptoid submonomer mimic of arginine and aspartic acid

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Peptides identified through natural product or high-throughput screening are becoming attractive therapeutics. However, many potential peptide therapeutics have poor proteolytic stability and short *in vivo* half-lives. To address these issues, many researchers use peptoid compounds, which are peptides mimics, as therapeutics. Because they are completely resistant to proteolysis, peptoids make excellent candidates for a range of different biomedical applications. The present study supports the growing field of research into peptoid therapeutics by developing peptoid submonomer mimics of common amino acids. The peptide that was used in this research is the affinity tag AviD, which has unique amino acids that can be studied by peptoid submonomer substitution. The main focus of this work is on two amino acids, arginine and aspartic acid. The overall goal of this study is to determine which peptoid submonomer best mimics these amino acids and maintains peptomer secondary structure in AviD. The present research will aid researchers in developing peptoid mimics of useful peptide therapeutics.

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A greener coupling of silicon and boron compounds

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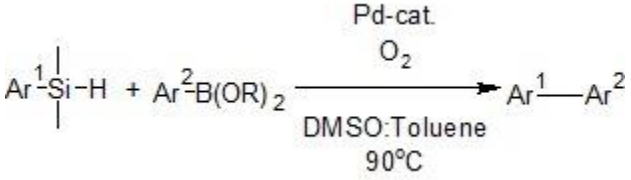
Cross-coupling methods have revolutionized chemistry, resulting in facile formation of Csp^2-Csp^2 bonds and biaryl compounds. This is reflected in the variety of areas in which biaryl units are found-- helical polymers, pharmaceuticals, and fungicides. However, current methods require air-sensitive substrates and/or ligands. The work described involves easily accessible boron and silicon compounds coupled under ambient-air conditions using simple palladium catalysts. The optimization and scope of the reaction will be described.



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Synthesis and biological evaluation of novel HER2 inhibitors for the treatment of trastuzumab-resistant breast cancer

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Overexpression of the human epidermal growth factor receptor 2 (HER2) is responsible for nearly 15-30% of breast cancers, and is associated with aggressive metastasis resulting in poor patient survival. Current treatment options including the monoclonal antibody targeted therapy, trastuzumab (Herceptin®), usually results in acquired resistance within a year. The dual EGFR/HER2 kinase inhibitor lapatinib (Tykerb/Tyverb®) showed promising phase II results, but a recent phase III trial found no significant advantage to single-agent lapatinib treatments over trastuzumab treatments alone. Recently our group developed four novel naphthoquinones highly effective at auto-phosphorylation inhibition of the HER2 Y1248 residue in breast tumor cells, as well as growth inhibition of trastuzumab resistant oncogenic isoform HER2Δ16 cells. In the initial high-throughput assay, all four compounds showed significant growth inhibition of the MCF7-HER2, MCF7-HER2Δ16 breast cancer cell lines.

2015 Joint Southeastern/Southwest Regional Meeting 499

Identification and development of novel casein kinase 1 inhibitors

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Alzheimer's disease (AD) is a progressive neurodegenerative disorder associated with the accumulation of the neurotoxic peptide Amyloid β (Aβ). Casein kinase 1 family comprises of eight isozymes, two of which CK1δ and CK1ε are predominantly expressed in the brain. CK1δ plays a critical role in AD through phosphorylation of tau, a protein associated with microtubules, which precedes neuritic lesion formation, implicating CK1δ in the tau fibrillization reaction pathway. CK1δ has been reported to be associated with pathological accumulation of tau in several neurodegenerative diseases including AD, Down syndrome, progressive supranuclear palsy, and parkinsonism dementia complex of Guam. Inhibition of CK1δ has been shown to reduce fibrillar lesions and to inhibit Aβ production. Our recent work investigating quinones as kinase inhibitors revealed a quinone compound that inhibited CK1δ and Pim1 kinase preferentially over CK1γ2 and 98 other human protein kinases. Similarity search and preliminary in-vitro CK1δ kinase inhibition assay have yielded a few compounds with good potency.

2015 Joint Southeastern/Southwest Regional Meeting 500

Synthesis of clinical tools for detecting G-proteins in cancer cells

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The aim of our proposed research is to develop clinical tools for detecting and studying G-protein coupled receptors (GPCRs) in cancer cells. A peptide binding to one of these receptors initiates a signaling network within the cell that regulates the expression of growth-promoting genes. We have designed and synthesized a potential useful clinical tool for detecting these proteins. The essential feature of our design is the attachment of an easily detectable fluorescent probe molecule to a peptide substrate that specifically binds to G-protein receptors. To meet the design criteria, we have selected a lanthanide based chromophore to serve as our fluorescent tag and will use a PEGO linker to attach this to the MSH-4 peptide ligand. The synthesis of this ligand and the MSH-4 peptide will be discussed.

2015 Joint Southeastern/Southwest Regional Meeting 501

Screening and identification of inhibitors of *T. brucei* cathepsin L with antitrypanosomal activity

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Current treatment options for Human African Trypanosomiasis (HAT) are ineffective, and they have several well-known clinical limitations. In our continued efforts to identify chemotypes that can be developed into clinically useful drugs, we screened a targeted compound library against the major cathepsin L (rhodesain) in T.brucei. The antirhodesain activity and antitrypanosomal activity of a series of compounds are reported. The identified compounds can serve as a starting point for structure- and/or phenotype-based lead optimization strategy against Trypanosoma brucei.

2015 Joint Southeastern/Southwest Regional Meeting 502

Synthesis and characterization of a novel series of pyrrolo[2,1-c][1,4]benzodiazepine derivatives with potential biological activity

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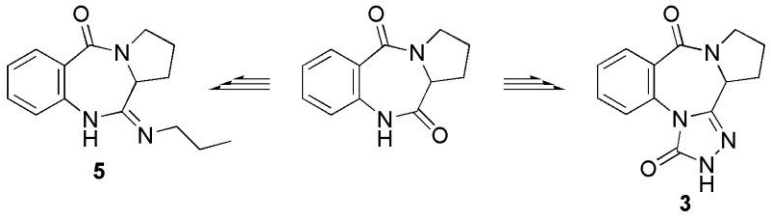
Pyrrolo[2,1-c][1,4]benzodiazepines (PBDs) have been known to form a class of biologically active compounds capable of recognizing and binding to specific sequences of DNA resulting in a wide variety of potential biological responses. PBD derivatives possess cancerostatic and antiinfective properties thus making them candidates of possible antibacterial agents in the exploitation of organic compounds. Therefore, current research has been focused on the synthesis and characterization of a novel series of Pyrrolo[2,1-c][1,4]benzodiazepine derivatives (PBDs). Compound **3** {*11-propylamino-1,2,3,11a-tetrahydro-5H-Pyrrolo[2,1-c][1,4]benzodiazepin-5-one*} and **5** {*11,12,13,13a-tetrahydro-9H-Pyrrolo[2,1-c]-1,2,4-triazolo[4,3-a][1,4]benzodiazepin-3,9-dione*} were synthesized from the parent PBD in a multi-step reactions approach and characterized using ^{1}H , ^{13}C-NMR and GC-MS. The biological activities of these

compounds are yet to be investigated for *in vitro* anticancer drug screening in a panel of human cancer cell lines.



General synthetic steps for 3 and 5

2015 Joint Southeastern/Southwest Regional Meeting 503

Extraction and characterization of an antibiotic- like molecule produced by *Rhodococcus* sp. MTM3W5.2

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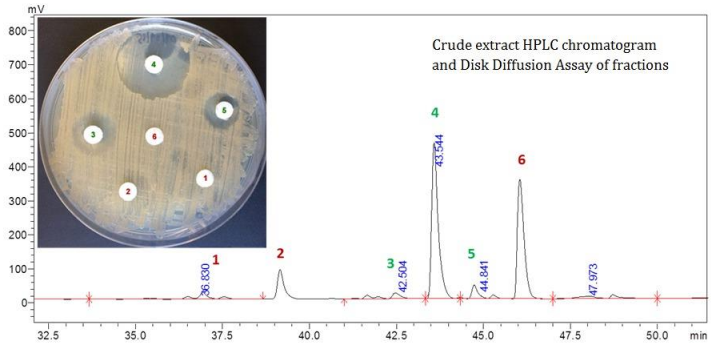
The increasing resistance of bacterial pathogens to antibiotics was the first problem derived from the widespread and uncontrolled application of antibiotics. To curb this rise in resistance, there is an urgent need for discovery of novel effective antibiotics. Recently a new *Rhodococcus* strain MTM3W5.2 isolated from a soil sample collected from Morristown in East Tennessee was found to produce an inhibitor compound which is active against *R. erythropolis* and closely related species. This research aims to accomplish the bioactivity-guided isolation, purification and identification of secondary metabolites from *Rhodococcus* strain MTM3W5.2. To achieve this goal, solvent extraction of a Rich Medium (RM) broth culture was performed using n-butanol. The butanol extract of RM broth was fractionated by chromatographic separation techniques including Sephadex LH-20 column chromatography using 100% methanol and preparative/analytical high-performance reversed-phase liquid chromatography. In each step, activity was tested using a disk diffusion assay and the stability of desired compound was monitored by UV absorption spectroscopy. Structure elucidation of inhibitory molecules using recent spectroscopic techniques, especially 2D NMR and mass spectrometry analysis is being investigated.



Crude extract HPLC chromatogram and Disk Diffusion Assay of fractions

2015 Joint Southeastern/Southwest Regional Meeting 504

Design and synthesis of ORP4-selective compounds

***Anh T. Le**, quynhanh18@gmail.com. Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma, United States*

A class of structurally-diverse natural product- cephalostatin 1, OSW-1, ritterazine B and schweinfurthin A- has shown potent anti-proliferative activities through targeting the oxysterol binding protein (OSBP) family. Based on their shared targets, these compounds have been name ORPphilins. The oxysterol binding protein (OSBP) and OSBP-related proteins (ORPs) are a class of cytosolic proteins present in all eukaryotes with a poorly defined cellular function. Recent results suggest that OSBP and ORPs could serve as master sensors for sterols and/or lipid molecules. Multiple OSBP protein family members have been related to the pathologies of different types of cancer, including pancreatic and blood cancers. ORP4, an OSBP family member, was shown to be overexpressed in blood cancer cells and to drive cancer cell proliferation. Our research goal is to develop compounds that specifically target ORP4 over the other OSBP protein family members. These ORP4-targeting compounds will be used to further study ORP4 cellular function and be explore as potential personalized anti-cancer lead therapeutic compounds.
OSBP and ORP4 have been shown to bind OSW-1 (NCI-60 GI_{50} average = 0.78 nM), 25-hydroxycholesterol and phosphatidylinositol 4-phosphate (PI4P). Therefore, our research focuses in designing and synthesizing derivatives of OSW-1, 25-hydroxycholesterol and PI4P. Multiple synthesis approaches will be developed to allow for rapid generation of analogs. These compounds will be evaluated for binding affinity with OSBP and ORP4. The project will result in compounds that possess high specificity for ORP4.

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Synthesis and characterization of new 5,7-dibromo-3-phenyl-3,4-dihydroacridin-1 (2H)-one derivatives: Potential anticancer compounds

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Acridone-based compounds are naturally occurring alkaloids in plants, which can be considered as aza-analogs of anthrones and xanthrones. Literature reports indicate that many acridone compounds display potent antimalarial and antibacterial activities. Moreover, many also exhibit potent antitumor activities *in vitro* and *in vivo* against a range of tumors in murine and human. Some have also been reported as small molecule inhibitors of telomerase and breast cancer resistant protein ABCG2. NSC753758 (figure 1) was synthesized using one-pot MCR method and was then submitted to NCI 60 cancer cell line screening. It showed antiproliferation in a wide range of cancer cell lines. Further testing in collaboration with Chen's laboratory at Meharry Medical College indicated that NSC 753758 decreased EZH2 levels in C4-2B cells, as well as caused a decrease in H3K27me3 in PC3 cells. The objective of this study is to synthesize a focused set of analogs in order to establish structure activity relationship (SAR). The synthesis and properties of analogs of the lead compound will be presented.

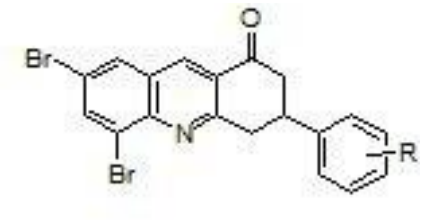

Figure 1: R = H

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Bis-naphthylcycloprenone a metal free source of carbon monoxide

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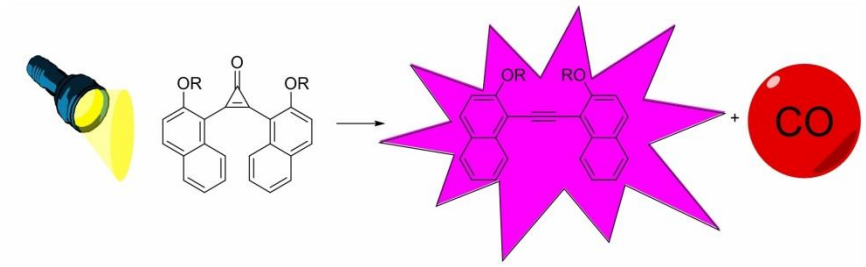
Carbon monoxide, which is generated endogenously from the breakdown of hemoglobin by heme oxygenase (HO) is an important signaling molecule. The signaling effects of carbon monoxide include anti-inflammatory response and regulation of apoptosis. Carbon monoxide releasing molecules (CORMs) have been developed as a potential therapeutic and a way to study carbon monoxide as a signaling molecule. Photochemically activated CORMs (PhotoCORMs) allow for the spatiotemporal control of CO release. The majority of PhotoCORMs are using photolabile transition metal complexes. A few organic photo-CORMs that have been developed so far avoid using toxic metals, but suffer from low quantum yield and low stability. We have developed a very efficient photoCORM platform based on the photodecarbonylation of bis-naphthylcyclopropenone. This cyclopropenone is stabile in biological systems, contains no toxic metals, and has a high quantum yield of decarbonylation (Φ= 0.42). Since this cyclopropenone is not fluorescent, but the resulting acetylene has a high quantum yield of emission, this platform permits quantification of carbon monoxide released.



2015 Joint Southeastern/Southwest Regional Meeting 507

Conjugation of bicyclol-polymer conjugates for protecting liver from injury

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Bicyclol, a novel anti-hepatitis drug originated from Chinese Herb Fructus Schizandrae, was used to treat chronic hepatitis B. It would boost immune system by increasing hepatic activity. However, it is insoluble in water, resulting in poor absorption. The purpose of this work is to increase bicyclol water solubility and bioavailability. Our strategies include conjugation of bicyclol to water soluble N-(2-hydroxy propyl) methacrylamide (HPMA) polymer through pre-polymerization and post-polymerization modifications. Two series of bicyclol-conjugated copolymers are prepared in this work. First, the bicyclol copolymer was synthesized by conventional radical polymerization from N-(2-hydroxy propyl) methacrylamide and functionalized hydrophobic monomer. The coupling reaction between primary amine and carboxylic group was employed to construct the monomer.1 Alternatively, using a post-polymerization modification strategy, the bicyclol moieties were appended to poly(N-(3-amino propyl) methacrylamide) copolymer with controllable attachment at room temperature. The monomer and bicyclol conjugated copolymers were purified by column chromatography and dialysis and characterized by 1H NMR spectroscopy and FT-IR. The toxicity of bicyclol conjugation polymer at 0.5, 2.5, 25 μM to Huh7-SJR12 replicon cells was measured by Firefly luciferase activity experiments. The appearance of the resonances characteristic ester protons (–OCOCH_2–) was observed at ~2.60 ppm along with the resonances of methylene protons (–CH_2NHCO–) at 3.20 ppm in the ^{1}H NMR spectra, which indicated the successful coupling between amine and carboxylic group in the monomer. The appearance of the resonances characteristic methyl protons (–PhOCH_3–) in the bicyclol copolymers was observed at ~4.90 ppm in ^{1}H NMR spectroscopy, indicative successful incorporation of bicyclol moieties in the final water soluble copolymers. The solubility of the bicyclol conjugated on HPMA polymer in water at room temperature was 60 mmol·L^{-1}, which was much greater than that of the bicyclol alone. The bicyclol-HPMA conjugates induced the similar Firefly luciferase activity in Huh7-SJR12 replicon cells as the control medium. The bicyclol containing water soluble copolymers were prepared by radical polymerization and polymerization modification

approach and the solubility of bicyclol was significantly improved by conjugating to the HPMA polymer. The future study will focus on bicyclol conjugated polymer protection from liver injury.

2015 Joint Southeastern/Southwest Regional Meeting 508

Synthesis of novel, anti-inflammatory *N*-arylpyrazolo[3,2-*c*]-based molecules and applications in treating type 1 diabetes mellitus

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Type 1 diabetes mellitus (T1DM) can be characterized as an immune-mediated disease caused by β-cell inflammation and autoimmune-mediated death, which results in a subsequent decrease in insulin. Research exploring the interaction between glucocorticoids (GCs) and β-cells, along with the development of an immunosuppressive GC-based molecule, could greatly contribute to the prevention and treatment of T1DM. Previously reported GCs have shown a reduction in β-cell inflammation accompanied by an unwanted decline in insulin production. In this study, a series of structurally diverse N-arylpyrazolo[3,2-c]-based molecules have been synthesized in order to determine the structural features that lead to dissociative activity in order to synthesize a molecule that suppresses inflammation without reducing insulin production. Bioreporter assays based on the chemokine ligand 2 (CCL2) promoter-luciferase promoter and glucocorticoid response element (GRE) promoter-luciferase promoter along with measures of glucose stimulated insulin secretion (GSIS), were used to monitor repression of IL-1β-induced inflammation, activation of pro-inflammatory genes, and the affect on insulin production, respectively. Repression of IL-1β-induced inflammation by two arylpyrazoles at 1M were comparable to dexamethasone at 10 nM while also having comparable GRE activation. For one (**16**), the reduction in insulin secretion was comparable to dexamethasone. The other (**17**), however, did not show an appreciable decrease in insulin production.

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Preparation and antitubercular properties of novel *p*-aminosalicylic ester thioureides

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Despite the mobilization of considerable resources since the declaration of tuberculosis as a global public health crisis some twenty years ago, the disease continues to claim upwards of two million lives per year. The situation has been made even more complex by the emergence of new strains of *Mycobacterium tuberculosis* (Mtb) that are resistant to all of the current front-line chemotherapeutic agents, threatening to return treatment to the pre-antibiotic era and underscoring the need for research in antitubercular drug discovery. We now report on the preparation and antitubercular properties *in vitro* and *in vivo* of thioureides of *p*-aminosalicylic esters. In a representative preparation, *p*-

aminosalicylic acid phenyl ester reacted smoothly with phenyl isothiocyanate (1.05 equiv) in refluxing ethanol to produce the thioureide in pure form (65%): mp 140-142°C; IR γ 3204, 1677, 1625, 1589 cm^{-1}; 1H-NMR δ ppm 10.4-10.2 (3 overlapping br s, 3H), 8.0-7.1 (m, 13H). *Anal*. Calcd for $C_{20}H_{16}N_2SO_3$: C, 65.92; H, 4.43. Found: C, 65.73; H, 4.44. Against the standard laboratory strain of Mtb $H_{37}R_v$, the new thioureide had a minimum inhibitory concentration (MIC) of 0.20 ug/mL (positive control rifampicin MIC 0.25 ug/mL), selectivity index 35, EC_{90} 0.203 ug/mL, EC_{99} 0.92 ug/mL. The thioureide maintained its *in vitro* activity against Mtb organisms resistant to the current front-line drugs isoniazid, rifampicin, ethambutol and ethionamide. In a short-course therapy study in Mtb infected mice, administration of 25 mg/kg of the thioureide for two days led to a reduction in the bacterial burden by 0.5 log CFU. These results suggest that new agents against Mtb may be found among the thioureides of *p*-aminosalicylic esters and will warrant further investigation.

2015 Joint Southeastern/Southwest Regional Meeting 510

Synthesis of phthalimides and indazolones as selective CDK inhibitiors

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Cyclin-dependent kinases (CDKs) are serine/threonine kinases that play key roles in the regulation of cell cycle progression. Alterations in CDK activity are associated with cancer, proliferative renal diseases, and neurodegenerative disorders making them prime targets for therapeutics. CDK1, 2, 4, and 6 are directly involved in the cell cycle regulation, while CDK7 and 9 control processes such as transcription. CDK5 is highly expressed in the nervous system and is deregulated in several neuronal diseases. Inhibition of CDK activity can be achieved through blocking the binding of cyclin to their cognate CDK proteins, preventing the binding of ATP to the protein using small molecule competitive inhibitors and modulation of upstream kinases. Our project involves the synthesis of indazolones, phthalimides and their derivatives as potential ATP-competitive inhibitors of CDKs. The synthesis and characterization of indazolones and phthalimides derivatives are described.

2015 Joint Southeastern/Southwest Regional Meeting 511

Synthesis and evaluation of electronic and steric depsidone analogs for use as antibiotics

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Depsidones are tricyclic molecules with a wide range of antibacterial properties (MIC = 0.0825-8 ppm). This research involves the synthesis of B ring analogs with varying size and electronic profiles, and their effects on depsidone antibiotic activity. Modifications to the central ring through ester, thioester, and amide intermediates have been successfully synthesized with yields ranging from 3-70% using a 2 to 3 step synthetic sequence involving first esterification and then copper catalyzed ring closure. Due to low yields new procedures inverting the reaction sequence are underway to improve overall yield for each analog. Once synthesized, each depsidone analog will be

evaluated for antibiotic activity against both Gram-positive and Gram-negative bacteria. The assays will probe how changes to the central ring affect biological activity. Modifications to the ester and/or ether functional groups will show whether ionic or polar interactions are present between the molecule and inhibition sites are at play, whereas lengthening carbon chains of the starting materials will enlarge the central ring and show whether changing the size of the molecule strongly affects its activity.

2015 Joint Southeastern/Southwest Regional Meeting 512

Synthesis and antibiotic evaluation of heterocyclic a and c ring depsidone analogs

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Depsidone natural products are potent inhibitors of Gram-positive bacteria, with MIC values ranging from 0.1–8.0 μg/mL. Here, we have exchanged the A and C benzene rings on the tricyclic depsidone core for sulfur and nitrogen based heterocycles to probe the role of these functional groups on the natural products antibiotic activity. Each heterocyclic derivative was initially synthesized using a two-step method involving esterification (3% - 62% yield) and an intramolecular copper catalyzed ring-closing reaction. Due to low yields, the synthetic strategy was modified to perform the copper catalyzed ether formation first, followed by the intramolecular esterification. Although the second strategy requires an additional protection/deprotection sequence, the overall yield of each analog has increased. These analogs will allow us to probe the electronic effects of the A and C rings on the natural products antibiotic activity using a biossay against S*taphylococcus aureus* while also improving the solubility and pharmacokinetics of the molecules.

2015 Joint Southeastern/Southwest Regional Meeting 513

Synthetic studies toward metabolically stable puromycin analogs

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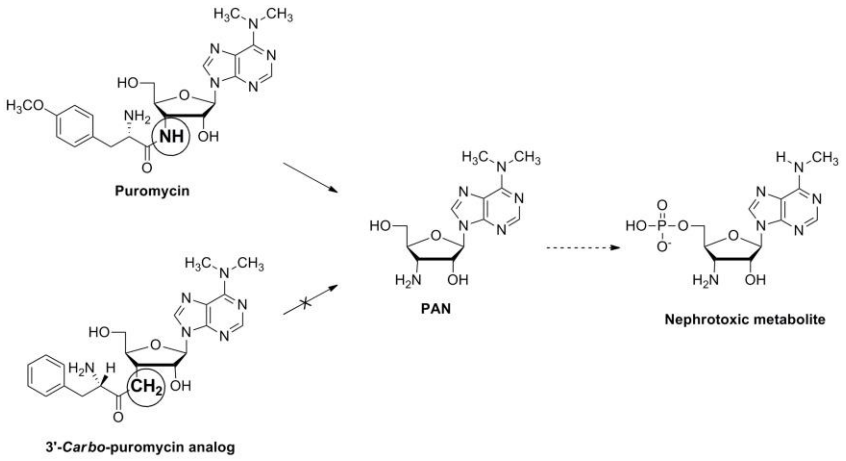
Puromycin is a peptidyl nucleoside antibiotic produced by *Streptomyces alboniger* that inhibits peptidyl transfer on both prokaryotic and eukaryotic ribosomes. Widely used as a basic tool in biochemistry and molecular biology, puromycin has been evaluated as antimicrobial and antitumor agent with disappointing results. As an anticancer, the major drawback of puromycin is the nephrotoxicity of the metabolite puromycin aminonucleoside (PAN). In the attempt to improve the toxicity profile of puromycin, we have replaced the amide NH of puromycin with a methylene group, thus generating a “metabolically” stable analog incapable to undergo metabolism to PAN. The target molecule was synthesized in 9 steps starting from D-xylose. The key steps were a regio-and stereoselective Horner-Wadsworth-Emmons olefination and the stereoselective reduction of the resulting alkene. In preliminary studies, the target compound showed antimicrobial activity on *Staphylococcus Epidermidis* and multi-drug resistance *Staphylococcus Aureus* cells. Unfortunately, although biologically active and

“metabolically” stable, the target compound is not chemically stable and seems to equilibrate to a mixture of isomers.



2015 Joint Southeastern/Southwest Regional Meeting 514

Isolation and characterization of phytochemicals from the leaf extract of *Tapirira mexicana*

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Plant-derived natural products have long been used as starting chemotypes in drug discovery. They are particularly useful in the treatment of infectious diseases. In this work, *Tapiria Mexicana* of the Anacardiaceae family, endemic to Central America was investigated for antitrypanosomal properties. The compounds isolated from the leaf extract of *Tapirira Mexicana* are being characterized using NMR and MS, and their antitrypanosomal activities are being evaluated, and will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 515

2,6-bis-hydrazinopyridine hydrazones: Potential metal ligands

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Hydrazinopyridines have remarkable promise as platforms for the construction of new transition metal ligands. Previous work has demonstrated that 2,6-bis-hydrazinopyridine (BHP) gives access to a wide variety of 2,6-bis-pyrazolylpyridines. However, hydrazones of BHP have hardly been reported and have not been evaluated as metal ligands. We undertook the preparation of hydrazones from 2-hydrazinopyridine and BHP for evaluation as metal ligands. We report the synthesis and characterization of these readily prepared, stable compounds.

2015 Joint Southeastern/Southwest Regional Meeting 516

Synthesis of novel norcantharimide derivatives

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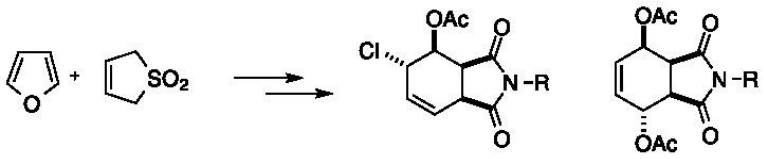
Cantharidin and its analogues show anticancer effects. These compounds are playing role as protein phosphatase 1 and 2A inhibitors. Currently, syntheses of norcantharimide derivatives in the discovery of lead compounds for early drug discovery have attracted the scientific community. We have synthesized several norcantharimide having functional group on cyclohexene ring and nitrogen. Biological activities of the synthesized norcantharimide derivatives here tested against PC3 and A549 cell lines.



R = Me, Et, Ph, Bn, $(CH_2)_2OAc$

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Stereoselective bora-Wittig olefination of ketones with a diazaborolane - acetonitrile enolate

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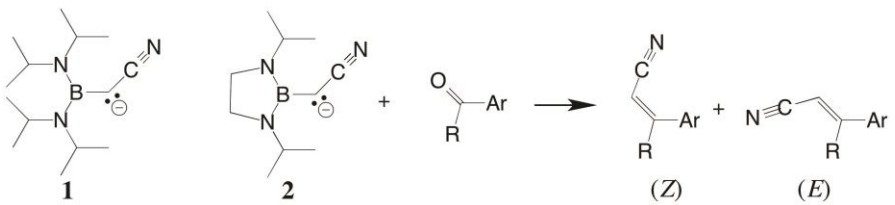
We have reported the (*Z*)-stereoselective olefination of aldehydes with **1**, an acetonitrile enolate stabilized by an acyclic bis(dialkylamino)borane, to give β-substituted acrylonitriles. **1** is unreactive or gives poor yields with most ketones, however, presumably because of steric hindrance. A less-hindered, cyclic bis(dialkylamino)borane reacts with lithioacetonitrile to give the diazaborolane enolate **2**. **2** reacts with ketones to give β,β-disubstituted acrylonitriles in good or excellent yields. The reaction is stereoselective for (*Z*) alkenes; with ortho-substituted acetophenones, the stereoselective ratio is typically > 3:1.



1 **2** (*Z*) (*E*)

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Synthesis of the azabicyclo[3.1.0]hexane ring core of ficellomycin

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Ficellomycin, originally isolated from the Gram-positive bacteria *Streptomyces ficellus,* has been shown to have antibiotic properties, but due to its instability shows poor efficacy *in vivo.* The core of ficellomycin contains a unique azabicyclo[3.1.0]hexane ring system, and this moiety has been hypothesized to be the source of ficellomycin's antibiotic activity as with the closely related azinomycin natural products. Unfortunately, it has also been implicated in ficellomycin's chemical instability. To improve ficellomycin's stability and efficacy through chemical modifications a simplified derivative of the azabicyclic[3.1.0]hexane ring core was synthesized using a convergent synthetic scheme that culminates in a Lewis Acid promoted double cyclization modeled after the work of Shipman et al. Starting from glyoxylic acid monohydrate, methyl-2-(((benzyloxy)carbonyl)amino)-2-(dimethoxyphosphoryl)acetate was produced in three steps in 67-80% yield. The phosporylacetate was then reacted with pent-4-enal under basic conditions to produce methyl-(*E*)-2-(((benzyloxy)carbonyl)amino)hepta-2,6-dienoate with an overall yield of 53%. Epoxidation and subsequent azide addition resulted in methyl-(*E*)-7-azido-2-(((benzyloxy)carbonyl)amino)-6-hydroxyhept-2-enoate in 30% yield. Finally, the azide-alcohol was treated with triphenylphosphine in toluene to first produce the aziridine, and then to promote aziridine cyclization onto the alkene producing the azabicycle in a single step. Cyclization trials and synthesis and evaluation of ficellomycin amino acid derivatives are ongoing.

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Tris(3,5-dimethylpyrazol-1-yl)methane and 1,1,1-tris-(3,5-dimethylpyrazol-1-yl)-2-(trimethylsiloxy)ethane platinum compounds: Synthesis, reactivity and structure

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Cationic platinum (II) complexes bearing substituted bipyridyl ligands ($[bipyPt(L)Ph]^+$, L = labile ligand) have been shown to be efficient and selective olefin hydroarylation catalysts. To expand this genre of chemistry, we became interested in studying neutral tris(pyrazol-1-yl)alkane ligands on platinum to examine how a third proximal donor ligand within the coordination sphere of platinum would affect the catalytic olefin hydroarylation reactivity. Herein, we present our preliminary results and progress. Reaction of $Ph_2Pt(SEt_2)_2$ with tris(3,5-dimethylpyrazol-1-yl)methane ($HC(3,5\text{-}Me\text{-}pz)_3$, pz = pyrazolyl, Mp) or 1,1,1-tris-(3,5-dimethylpyrazol-1-yl)-2-(trimethylsiloxy)ethane ($((CH_3)_3SiOCH_2C(3,5\text{-}Me\text{-}pz)_3$, pz = pyrazolyl, Sp) yields the square planar complexes, (κ^2-*N*,*N*-Mp)$PtPh_2$ (**1**) and (κ^2-*N*,*N*-Sp)$PtPh_2$ (**2**). Complex **1** reacts rapidly with hydrochloric acid in diethyl ether to form an isolable, cationic Pt(IV) intermediate, [(κ^3-*N*,*N*,*N*-Mp)$PtPh_2$(H)]Cl (**3**), then slowly transforms into (κ^2-*N*,*N*-Mp)PtPhCl (**4**), after reductive elimination of benzene under prolonged heating at reflux. Complex **2** reacts cleanly with hydrochloric acid to produce (κ^2-*N*,*N*-Sp)PtPhCl (**5**) with no observable formation of a cationic Pt(IV) intermediate, which we believe is due to the steric profile

of the trimethylsiloxy group that prevents coordination of the free 3,5-dimethylpyrazolyl arm. Compound **5** cleanly reacts with silver tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (AgBArF′, [B{3,5-$CF_3(C_6H_3)$}$_4$]) in acetonitrile to produce [(κ^2-*N*,*N*-Sp)PtPh(NCMe)][BArF'] (**6**). All compounds have been characterized by ^{1}H NMR and/or single crystal X-ray crystallography. Compound **6** is notable as it may show promising olefin hydroarylation reactivity in our future studies.

2015 Joint Southeastern/Southwest Regional Meeting 520

A surface science study on the reaction of carbon monoxide and methanol with a meteoritic mineral analogue

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The focus of this research is to better understand the nature of the surface of the meteoritic mineral, schreibersite $(Fe,Ni)_3P$, as it is hypothesized to be the ultimate source of phosphorous in life. The reaction of CO and CH_3OH with a synthetic schreibersite sample was investigated. Temperature programmed desorption (TPD) and reflection-absorption infrared spectroscopy (RAIRS) experiments, which provide information about chemical structure changes on the surface, will be presented along with SEM/EDS and XPS characterization of the geometric structure and the composition of the surface.

This work was jointly supported by NSF and the NASA Astrobiology Program, under the NSF Center for Chemical Evolution, CHE-1004570.

2015 Joint Southeastern/Southwest Regional Meeting 521

On use of graphene oxide dispersions in electrorheological fluid applications

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GO, Graphene Oxide dispersion can be used in order to prepare ER, electro rheological fluids. Over a 1 microsecond, time interval, rapid microstructural transition from fluid state to a solid-like state when electrical field is applied can be expected in the case of smart fluids. ER fluids are used in automatic transmission sytems in automobiles, torque transducers, vibration attenuators, control systems and ER polishing. RLC, inductance, resistance and capacitance meter was used to characterize the rheological properties of GO based ER fluids. The viscoelastic property seen in the fluids can be explained by particle chain formation. Hummer's method is used in preparation of GO. Particle chain formation was confirmed using optical miscroscopy. Interparticle forces play a role in the increase of storage and loss moduli.

2015 Joint Southeastern/Southwest Regional Meeting 522

Aggregation of spherical nanoparticles on lipid membranes

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Aggregation, bending, penetration, and encapsulation of synthetic nanoparticles by cellular membranes creates stresses that lead to biocompatibility problems in pulmonary and cerebral systems. To better understand the effect of nanoparticles on lipid membranes at a molecular level, a coarse-grained implicit solvent molecular dynamics was used to investigate interactions between a model biomembrane and solid spherical nanoparticles. The model is used to derive effective two-body and three-body interactions between nanopartciles as a function of their size, their adhesion strength to the membrane and the membrane tension. Our study shows that the nanoparticles either aggregate into lateral linear chains for relatively weak adhesion strength or linear culsters protruding normal to the membrane in the case of relatively strong adhesion strength.

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Non-covalent interactions between trimethylamine N-oxide (TMAO) and urea in water

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Trimethylamine N-Oxide (TMAO) and urea are two common osmolytes found in nature, both responsible for maintaining cell volume and responding to cells under thermodynamic stress and pressure. Their main significance to the biophysical field, however, is how they interact with proteins. Urea is a strong protein destabilizing agent, whereas TMAO is known to counteract its effects. More specific information on these cosolvents' interactions would be advantageous to the biotechnology and pharmaceutical industry, giving a better understanding of protein folding and unfolding mechanisms. More specifically, this can help to better isolate proteins, dissolve and stabilize them, and extend protein shelf life. The exact mechanism by which urea destabilizes folded proteins is still highly debated in the literature. Although some evidence has shown that urea binds directly to amino acid side chains to make protein folding less thermodynamically favored, it has also been suggested that urea acts indirectly to denature proteins by destabilizing the surrounding hydrogen bonding water networks. TMAO is also known to counteract the effects of urea. Here, Raman spectra of saturated urea, saturated TMAO, and saturated TMAO-urea solutions were obtained using a scanning Raman spectrometer. Experimental data shows that the addition of TMAO into a solution of saturated urea causes an 11 wavenumber blue shift of the HNH urea symmetric bending mode, indicating interactions between the two cosolvents. Density Functional Theory calculations were performed on a number of urea-water and TMAO-urea-water clusters in order to elucidate the origins of the vibrational energy shifts.

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Quantum chemical rovibronic data for *c*-C_3H with application to the interstellar medium

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C_3H is a known interstellar neutral radical detected in both its linear and cyclic isomers. The *c*-C_3H neutral radical has a known low lying excited state in the 1 eV range that has not been observed in the interstellar medium (ISM). Electronically excited states of known interstellar molecules are viable avenues for exploring their potential role in the diffuse interstellar bands, a series of ultraviolet to near-infrared molecular absorption peaks observed towards multiple stellar objects. Coupled cluster singles, doubles, and perturbative triples is used to compute the geometries and energies of the ground state. Equation of motion (EOM) computations at the CCSD level are used for the excited state. Highly-accurate quartic force fields, fourth-order Taylor series expansion of the potential of the internuclear Hamiltonian, can then be constructed. These provide structural data, vibrational frequencies, and spectroscopic constants. Even though the ground electronic state is known, the new advances in our methodology allow us to provide rovibronic data for the $1\ ^2A_1$ excited state in addition to the $1\ ^2B_2$ ground state. These data may be useful in the detection of this radical in its multiple states in the ISM.

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WITHDRAWN

2015 Joint Southeastern/Southwest Regional Meeting 526

Equilibrium and photo-kinetic properties of *p*-nitrophenolate at the air-water interface

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Phenols are a class of organic compounds that are prevalent in agricultural, industrial, and petroleum products. Due to their toxicity, when introduced to the aquatic environment, these compounds pose a health risk to the ecosystem. In addition, upon exposure to solar radiation these compounds photo-degrade. This impacts their transport and fate throughout the environment – which includes the air-water interface. An interface is the boundary between two different phases. Molecules bound to an interface possess unique characteristics as they have specific orientation and different electronic properties than those in the bulk liquid. Thus, they can exhibit unique surface chemical reactivity. It is therefore critical to understand the changes that these compounds undergo at the air-water interface. Second harmonic generation (SHG) has been shown to be a powerful tool in the exploration of chemical surfaces since this process is only permitted in regions that lack center of inversion symmetry, such as at the air-water interface. Using SHG, it has been demonstrated that *p*-nitrophenolate (*p*NP^-, *p*H 13) adsorbs at the air-water interface. We have also shown that the average molecular orientation of *p*NP^- at the surface, relative to the laboratory coordinate, is dependent upon the surface population. Furthermore, we have compared the kinetics of UV photodegradation of *p*NP^- in aqueous solution to that process occurring at the surface. In the bulk solution, the kinetic is slow, in the order of a few days. At the surface however, the kinetic process is found to involve changes in molecular orientation and surface population. SHG based equilibrium and kinetic data will be

presented and the applicability of SHG in probing chemical reactions at an interface will be highlighted.

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Using spectroscopy to engage students in STEM and physical chemistry

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The study of physical chemistry concepts at the high school level would help fill a void that is currently present in high school chemistry curricula. Specifically, the introduction of spectroscopy would help students gain a fundamental understanding of many facets of physical chemistry. The study of light emission from various sources in their own classroom using a portable spectrometer helps students learn the properties of light and what color is and how it originates from different sources such as the sun, incandescent lights, fluorescent lights, handheld laser pointers, and computer display monitors. Such a physical chemistry project was presented to three different schools in Northern Mississippi. High school students first listened to a brief lecture on the properties of light and an introduction to spectroscopy. Using laser pointers, students were shown the relationship between color and wavelength; students were then shown the relationship between wavelength and energy by using the Planck equation and the wavelengths of the laser pointers to calculate the energy. Students also learned the difference between discrete and continuous emission spectra; students analyzed spectra of sunlight and incandescent bulbs to learn about continuous spectra and analyzed the spectrum of a fluorescent bulb to learn about discreet spectra. Students were also taught about the different phenomena that give rise to each type of spectra. After the completion of the demonstration, students were allowed to analyze spectra of their choosing to encourage engagement and critical thinking of the concepts taught. To analyze the effectiveness of the demonstration, students were given Likert scale type questionnaires with eleven questions on the material before and after the demonstration. Two schools showed statistically important self-reported gains in knowledge in all categories while the third school showed statistically important gains in all but three categories.

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Complete basis set limits for the Hartree-Fock and second-order Møller Plesset energies for DMPO, EMPO and their hydroxy-radical adducts

*Hayden B. Short, **Scott J. Kirkby**, kirkby@etsu.edu. Chemistry, East Tennessee State University, Johnson City, Tennessee, United States*

Free radicals, and the characteristics exhibited by free radicals, have become a topic of much interest in chemical research recently. Carcinogenic effects have been linked to a number of free radicals produced in the human body. However, the study of radicals in solution is a very difficult task due to the high reactivity and extremely short lifetimes. Spin traps have been found to posses the ability to stabilize radicals thus more easily allowing their study. Thus, much research and effort has been put towards the design and production of novel spin traps. This research aimed to calculate the reaction rate constants for the reaction of 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) and 2-ethoxycarbonyl-2-methyl-3,4-dihydro-2H-pyrrole-l-oxide (EMPO) with the hydroxyl radical (•OH) using chemically accurate energies (errors ~1kcal/mol or less) using

composite quantum chemistry methods. DMPO and EMPO spin traps are commonly used to study radical reactions in biological systems and have been the focus of much computational and experimental research, but accurate rate constants have not been previously obtained using computational methods. On the route to obtaining chemically accurate energies, the complete basis set limit for Hartree Fock and second-order Møller Plesset energies were calculated using the density functional theory optimized geometry will be presented.

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Comparison of laboratory evaluation methods for defoaming chemistries

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Brown stock washing is critical in papermaking, as it is extremely important to the final product quality as well as overall optimization of the process. Brown stock washing greatly impacts downstream processes such as caustic recovery, black liquor evaporation, and bleaching. The primary objective of brown stock washing is to remove the maximum amount of black liquor solids from the pulp while using as little wash water as possible (1). In this process, soap and lignin are present generating a significant amount of foam. In order to reduce and control this foam, a foam control agent is necessary to operate as well as to improve production rates and optimize operations (2).

Traditionally, silicone defoamers are used in brown stock washing applications and the primary laboratory testing method is a foam cell test to evaluate these chemistries. Kemira utilizes a FEAT (Foam and Entrained Air Test) unit instead of a traditional foam cell test. The FEAT unit aids in the evaluation of the performance of antifoam and defoamer chemistries in a laboratory setting. The apparatus measures the change in the density of the liquor/filtrate as the chemistry is introduced and for a determined amount of time. While traditional defoamer foam cells test only the effects on the surface foam, FEAT evaluates the change in density as a direct measurement of the change in entrained air.

This paper will focus on FEAT and laboratory evaluation techniques as well as how these methods relate to field recommendations. It will explore data on a cost basis (varying dosages on equal cost) and head to head (identical dosages). It will highlight the analysis used when these comparisons yield varied trends, and how to further study the pulp process. Additional analysis can include washer design, application points, and chemistry type. This paper will highlight the importance of the testing method and technique for this type of analysis and how to perform a relevant evaluation for full scale recommendations.

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Handbook for Pulp and Paper Technologists, 3rd Edition, G. Smook
Emulsions, Foams, and Suspensions: Fundamentals and Applications, L. Schramm

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Investigating the chemical reactions with naphthalenium in the interstellar medium

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In the interstellar stellar medium (ISM), neutral and charged polycyclic aromatic hydrocarbons present are assumed to be present within the same ISM. Research has pointed out to the formation of a naphthalenium with acetylene, propylene or isobutene complex within the medium. This reaction is unusual because it is slow under interstellar conditions, yet the ion-molecule reaction is orders of magnitude faster. These reactions also have similar chemistries to flames on earth. Understanding the formation conformations of both weakly bound and covalent products opens up the possibility of a better understanding of flames.

The focus of this project is to investigate further understand the reactions between naphthalenium and acetylene within interstellar space. After studying the naphthalenium and the acetylene complex and two sample covalent adducts under different ab initio and DFT model chemistries, we have determined that Truhlar's M062X functional combined with the Dunning's aug-cc-pVTZ basis set was the most effective as well as least expensive model for us to use. All complexes with naphthalenium have been tested and as a result there was a steady increase in binding energy when changing between acetylene, propylene and isobutene. There is yet more to be tested and to determine which specific complex is the most stable.

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Spectroscopic and computational study of chlorine dioxide/water interactions

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Chlorine dioxide, a relatively stable free radical, plays important roles in water purification. It is a strong oxidizing agent that is used to oxidize harmful metals in unpurified ground water. Chlorine dioxide also possesses strong antimicrobial properties and is currently emerging as a choice disinfectant for medical equipment. Despite its useful properties, little is known with regards to how it interacts with water. Here, the electronic and vibrational spectra of chlorine dioxide are analyzed in detail using UV/visible absorption and Raman spectroscopy. Experimental spectra are compared to the results of electronic structure computations performed on discrete micro-solvated clusters.

2015 Joint Southeastern/Southwest Regional Meeting 532

Synthesis and characterization of carbon quantum dots with varying amounts of nitrogen

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Carbon quantum dots (CQDs) represent a new class of quantum dots with unique properties. Doping CQDs with heteroatoms provides an attractive means of effectively tuning their intrinsic properties and exploiting new phenomena for advanced device applications. Herein we report a simple microwave assisted hydrothermal approach to

luminescent CQDs with nitrogen-rich functional groups. The effect of nitrogen content and nitrogen location on chemical and physical properties is investigated using a variety of spectroscopic techniques.

Carbon quantum dots are a class of graphene quantum dots synthesized by a “bottom-up” approach. In a typical approach, a carbon source, usually a carbohydrate, carboxylic acid, or ketone, is dehydrated to produce a carbon nucleus that grows due to carbonization until it become self-passivated. By carefully choosing the carbon source, CQDs with different amounts of heteroatoms can be produced. By varying the nitrogen content and size of a CQD, the emission wavelength of the quantum dot can be tuned to a variety of colors. The high solubility and benign starting materials make CQDs excellent candidates for cellular imaging.

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Deep ultraviolet stimulated Raman scattering crystal calcium borate

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As an important branch of nonlinear optics, stimulated Raman scattering of solid state material has been an effective method to change laser wavelength. Up to now, except diamond, no Raman laser crystal can work at deep ultraviolet waveband (200~300 nm), because of the limitation of the transmission cutting edge. Here we reported a broadband stimulated Raman scattering crystal, $Ca_3(BO_3)_2$. It simultaneously possesses strong Raman response, short ultraviolet cut-off wavelength (180 nm), and outstanding anti laser damage threshold. Other benefits include easy growth, low cost, and no pollution. All of these advantages make $Ca_3(BO_3)_2$ a powerful, practical SRS material available for various wavelength, especially for deep ultraviolet (DUV) and vacuum ultraviolet (VUV, < 200 nm) lasers. It supplies a precious chance to develop rare, wavelength tunable DUV and VUV laser sources, which will be simple, cheap, and reliable.

Figure 1. The $Ca_3(BO_3)_2$ single crystal grown by Cz method along crystallographic *c* axis

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Effects of nanoscale surface curvature on the adsorption and desorption of thiolated ligands on gold nanoparticles

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Nanoscale surface curvature has profound impacts on the interactions between thiolated ligands and gold nanoparticles. We use a combination of surface enhanced Raman scattering and ICP mass spectrometry to gain quantitative insights into the kinetics and thermodynamics associated with the adsorption and desorption of thiolated ligands onto gold nanoparticle surfaces. The knowledge gained from this work will ultimately enhance our capabilities to rationally optimize the ligand-nanoparticle interactions for widespread applications in biomedicine and energy conversion.

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The thermodynamic properties of recyclable plastics with exposure to UVB light

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Plastics such as polyethylene terephthalate (PETE), polyethylene high density (PEHD), and polyethylene low density (PELD) are used in all forms of consumer products. These plastics are found in soda bottles, chemical containers, plastic bags, etc. The purpose of this research was to see if continuous exposure to UVB light for weeks would have an effect on the physical properties of the plastics. Ten samples of each type of plastic were placed inside a box, where adjustments were made to prevent any source of outside light to reach the samples, and left with constant exposure of UVB light. Each week, a sample would be taken out of the box and placed inside a Differential Scanning Calorimeter (DSC), where it would undergo heating and cooling cycles. The data of interest were the values for melting point, enthalpy of fusion, and glass transition phase. Results showed that the longer the plastics were exposed to UVB light, the more energy that was required to melt the sample. Plastic samples were also studied using thermogravimetric analysis (TGA) to determine if the melting behavior differed in the samples.

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Determination of rate constant, binding constant, and binding number by fluorescence measurements of $Gd_3N@C_{80}(OH)_{20}$ in D_2O

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Today MRI imagining techniques are capable of discerning between abnormal and normal complex tissues by providing contrasting images of these tissues. One drawback of using MRI imagining is its low sensitivity. However, this sensitivity can be greatly enhanced by introducing contrasting agents who can provide a new pathway for water molecules to significantly relax faster and hence generate the desired “contrast” between healthy and unhealthy tissues. We report the first ever recorded fluorescence

emission spectrum of $Gd_3N@C_{80}(OH)_{20}$; where -$(OH)_{20}$ is the average number of hydroxyl groups. Our emission data indicates that the H_2O- $Gd_3N@C_{80}(OH)_{20}$ interactions lead to fluorescence quenching via a static quenching mechanism. The binding constant, K_b, on the other hand, was found to be of the same magnitude as interactions between human serum albumin and small organic acid but quite different, several orders of magnitude smaller, than protein nanoparticle complexes. Interestingly, the binding number, n, was found to be approximately 0.5, which in cases like this, is rounded to a whole number of one. The data also indicated an extremely fast rate constant on the order of 10^{12} L mol^{-1} s^{-1} which is outside of the diffusion-control regime. These results are presented within this report.

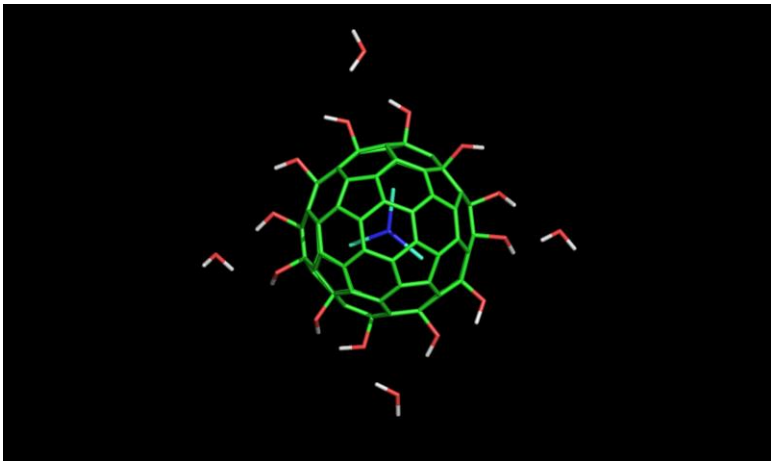

Figure of $Gd_3N@C_{80}(OH)_{20}$

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Investigation of hydrothermal conversion of methylosinus trichosporium to bio-oil

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Methylosinus trichosporium is a bacterium that feeds on methane from the environment. Utilization of this bacterium has a great potential to help solve the global warming issue while generating large amount of biomass for other uses. Further conversion of generated biomass to everyday products would balance the carbon outputs and leaving no carbon footprints in the environment. Research on the hydrothermal conversion of methylosinus trichosporium biomass into bio-oil had never been done before. It is hypothesized that reasonable yield of bio-oil will be produced by the hydrothermal conversion process. In this study, methylosinus trichosporium is hydrothermally converted with different temperature and time, extracted, and isolated to obtain bio-oils. The energy contents of the methylosinus trichosporium biomass and the resulted bio-oils are determined via bomb calorimetry. Thermo gravimetric analysis (TGA) is performed to determine the water content in the biomass and its decomposition behavior. In addition, FT-IR and GC-MS will be used to obtain the composition info of the bio-oil products.

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Hematite coated gold thin films for enhanced photocatalytic water splitting

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The photoactivity of semiconductor photocatalysts are limited by its poor absorptivity and a limited carrier diffusion length. Coupling the semiconductors with plasmonic metal nanostructures of Au, Ag, and Cu which are known to concentrate and scatter broad range wavelengths of incident light and hold the promise on enhancing the light absorption cross-section of a semiconducting material. Engineering the semiconductor plasmonic metal configuration in order to obtain the optimum performance without compromising the stability of metal nanoparticles by corrosion at high potentials is necessary. Herein we report photoelectrochemical characteristics of a smooth hematite photocatalytic layer embedded with sputter deposited Au thin films. The photoactivity of hematite films were enhanced by the plasmonic activity of Au films. The enhancement observed was much higher as compared to Au nanoparticles.

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Surface enhanced titanium based electrode for efficient oxygen evolution reaction

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Developing high efficient oxygen evolution reaction (OER) catalyst for water splitting is one of the most promising solutions for addressing the challenge of renewable energy conversion. However, the major obstacles to widespread application are the low efficiency of catalysts and the high capital costs of electrode materials. In this study, we developed an efficient, durable and low-cost OER electrode based on earth-abundant elements of Ti and C to reduce the costs of noble metals for water electrolysis. The carbon modified titanium oxide electrodes with nanostructured surface were synthesized by facile hydrothermal reaction and followed carbon thermal modification of in an atmosphere of methane and hydrogen. The OER performance of carbon modified titanium oxide electrode exhibited much higher catalytic activity than that of IrO_2 or Pt electrode.

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Platinum based binary electrocatalysts supported on carbon for a single compartment direct ethanol fuel cell

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Virtually all research published in the area of ethanol fuel cells to date has involved the study of proton exchange membrane cells, which typically include costly components such as a proton exchange membrane, gas diffusion layers, bipolar plates with flow fields, platinum electrocatalysts, etc. This work investigates two methods of reducing these costs and therefore improving the overall effectiveness of the cell: (1) alloying a second metal to platinum in order to improve electrocatalytic properties and reduce the necessary platinum content in the electrocatalysts and (2) utilizing a simple single compartment ethanol fuel cell that does not require as many expensive components. Bimetallic platinum-based electrocatalysts were synthesized and studied via cyclic voltammetry. Cyclic voltammograms showed that a platinum-palladium alloy supported on carbon was ethanol tolerant during the oxygen reduction reaction, whereas a commercial platinum catalyst exhibited poisoning effects in the presence of ethanol. These results indicate that a PtPd/C electrocatalyst can catalyze the oxygen reduction reaction in a single compartment fuel cell. A platinum-tin alloy supported on carbon was found to be active towards the ethanol oxidation reaction via cyclic voltammetry. The two electrocatalysts deposited onto glassy carbon electrodes developed an open circuit voltage of ~90 mV in an ethanol containing electrolyte solution of H_2SO_4 with O_2 bubbled in, as the oxygen was reduced at the PtPd/C cathode and the ethanol was oxidized at the PtSn/C anode. These results support the hypothesis that a single compartment ethanol fuel cell can be effective when electrocatalytic properties are tuned properly.

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Catalytic bio-oil upgrading using a Mo/Co/K catalyst with addition of water gas shift active metals with bio-syngas

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The conversion of biomass to bio-fuel has received considerable attention due to continued depletion of non-renewable fossil fuels. One problem with raw bio-oil, from pyrolysis, is that it contains high amounts of oxygenated compounds which reduce its fuel quality. Our work uses a catalytic approach to upgrade this oxygenated bio-oil, by utilizing hydrodeoxyganation (HDO) and Fischer-Tropsch reactions, into transportation grade liquid hydrocarbons. A catalyst system using a ZSM-5 zeolite support with molybdenum, cobalt, and potassium metals was prepared with different ratios of known water gas shift catalytic metals, copper and iron. Since water is a large component in bio-oil, water gas shift metals are used to promote conversion of water and CO into hydrogen. This serves to decrease water content while producing more hydrogen gas that is subsequently utilized in upgrading reactions. Bio-oil upgrading was done within a batch autoclave using gases at 500-1400 psi. To optimize conditions, guaiacol, a model compound found in bio-oil, is used. After optimization, simulated bio-oil is used to test the upgrading reactivity of the best catalyst under optimal reaction conditions. Bio-syngas, from gasified biomass, a 50/50 mixture of hydrogen and carbon monoxide, and hydrogen gas, which is traditionally used in upgrading, were all used in the upgrading reactions to provide comparisons. The reaction temperatures were 250 or 300°C. Liquid and gas samples of each reaction were collected and analyzed. Good conversions, 70-99%, where found for the model compounds. For each catalyst similar conversions, deoxygenation, and selectivities were observed for a given temperature. Quantitative GC was used to calculate the CO and gas conversions. A GC/MS was used to analyze

the liquid products from the reaction, and to calculate the heats of combustion for the products. Liquid products have higher heat of combustion (kJ/g) than the model compounds. This, and product selectivity, suggests there is good HDO and incorporation of C from CO in the syngas.

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Earth-abundant materials for renewable energy catalysis

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Hydrogen and oxygen evolution reactions for water splitting and oxygen reduction reaction for fuel cell application all play important roles in the general field of renewable energy catalysis. Due to their nature of multiple electron transfer, these reactions are kinetically sluggish under ambient conditions. It remains a grand challenge in developing low-cost, efficient, and robust catalyst materials to accelerate these reactions for large-scale application. We are interested in exploring 1^{st}-row transition metal-based catalysts for overall water splitting and oxygen reduction under benign conditions. Facile electrochemical and microwave-assisted synthetic approaches were employed to produce various nano-structured catalysts with low energy cost. Various surface characterization and electrochemical techniques were utilized to study the composition-structure-activity relationship of obtained catalysts. Coupled with theoretical computation, our work provides a guidance for the rational design and development of improved catalysts for renewable energy catalysis.

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Microwave assisted nanocarbonization of conducting polymers for battery applications

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Three well-established approaches; namely, conducting polymer (CP) nanofiber (NF) synthesis by NF seeding, CP nanoclip (NC) synthesis by oxidative template and microwave (MW) energy assisted nanocarbonization were systematically combined to prepare active nanocarbons from CPs, with great potential as the anode material, for lithium ion battery applications. Polypyrrole (PPy), as one of the most well-known and commonly studied members of the CP family, was prepared in both NF and NC forms, as the sacrificial carbonization precursor, for electrochemical property comparison purposes. Due to PPy's highly electromagnetic active nature, both its NFs and NCs had vigorously interacted with MWs and the as-generated energy from such interactions was transformed into a large amount of heat leading to a drastic temperature increase, which was simultaneously used for the instant decomposition and carbonization of PPy via preserving its morphological features. Furthermore, the as-obtained samples from this process exhibited good thermal stability and electrochemical cyclic performance, which are crucial as an active lithium ion battery material. The process offers significant advantages such as; (i) being facile, straightforward and affordable, (ii) being applicable at ambient conditions without the need of any extra equipment or chemical protection, and also (iii) being able to provide functional nanocarbons, without causing any distortion or physical alterations in the sacrificial nano-CP structure. Thus, it is believed

that, this well-established and well-studied combination will dominate the large scale manufacturing of the next generation carbon-based battery materials from CPs.

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Hydrated titanium phosphates as promising materials for rechargeable batteries

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In the light of the gradual depletion of conventional energy resources and the resulting environmental crisis from the heavy usage of fossil fuels, developing advanced energy storage systems for renewable energy resources is essential for the sustainable supply of energy to society needs. In this respect, rechargeable lithium (Li)-ion batteries (LIBs) have been considered as the most successful energy storage device due to their high energy densities and long cycle lives. The limited resource of Li, however, will face concerns of the future cost. Thus, developing alternative energy storage systems using abundant elements is highly desired. Sodium (Na)-ion batteries (NIBs) are the most promising alternative of LIBs due to the abundance of Na-containing precursors. Not all of the electrode materials that show Li storage, however, can be used for Na storage due to the steric limitation caused by the larger ionic radius of Na^+ compared to that of Li^+. Therefore, expanding the range of materials that have potentials for sodium storage with fast kinetics is an important subject.
Hydrated titanium phosphate, of a formula $Ti(HPO_4)_2 \cdot H_2O$, is built on a two-dimensional structure of layers comprised of $PO_3(OH)$ tetrahedra and TiO_6 octahedra. The structure incorporates interlayer water molecules that involve hydrogen bonding with acidic protons on the phosphate groups. These acidic protons can be exchanged with various metal cations such as Li^+, Na^+, and Ca^{2+}. In addition, the interlayer space can be tuned by organic molecules intercalation. $Ti(HPO_4)_2 \cdot H_2O$, thus, is an attractive candidate material for rechargeable batteries due to its interlayer water and the amenable interlayer properties. In this work, $Ti(HPO_4)_2 \cdot H_2O$/carbon nanotubes composites were synthesized via a solvothermal route. As-synthesized composites formed well connected cathode films for NIB without additional binders and conductive additives. Interestingly, while the hydrated form showed reversible Na^+ intercalation and de-intercalation, the dehydrated form did not store Na^+ electrochemically. This result reveals that the critical role of interlayer water molecules which expand the interlayer spacing, enabling intercalation of such large Na ions. The experimental details and results will be discussed.

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Synthesis of diazonium (perfluoroalkyl) benzenesulfonimide (PFSI) monomer from perfluoro (3-oxapent-4-ene) sulfonyl fluoride for proton exchange membrane fuel cells

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Perfluoroalkyl benzenesulfonimide (PFSI) polymers are proposed as new electrolytes in Proton Exchange Membrane Fuel Cells (PEMFCs) due to their better thermal stability, inertness to electrochemical conditions, and lower susceptibility to oxidative degradation

and dehydration. For a better integration between the electrode and the electrolyte, the PFSI polymers can be grafted onto carbon electrode by diazonium moiety. It is expected that the PFSI polymers can enhance electrolyte stability, increase the proton conductivity and improve the catalyst efficiency in PEM fuel cells compared with the traditional perfluoroalkyl sulfonic acid (PFSA) polymers. 4-diazonium perfluoro(3-oxapent-4-ene) bezenesulfonimide **(I)** zwitterionic monomer has been synthesized from perfluoro(3-oxapent-4-ene) sulfonyl fluoride through a 6-step reaction scheme. All the reaction intermediates and the final product were characterized using ^{1}H NMR, ^{19}F NMR and IR.

Figure 1. The Structure of 4-diazonium perfluoro(3-oxapent-4-ene) Benzenesulfonimide Zwitterionic Monomer

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The enhanced physical properties of a nanostructured $LiCoO_2$ cathode utilized in a nanoengineered all-solid-state lithium ion battery

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Batteries with high operating voltages, energy densities and cyclabilities are needed to power several electronic devices. Over the past few decades, applying nanotechnology to Li ion battery chemistries has helped to lessen the technological divide between battery performance and electronic device capabilities. Nanostructuring electrode materials is a unique engineering technique employed to drastically increase the active surface area of the material. Using a nanoporous Anodized Aluminum Oxide (AAO) membrane with nanopores of 200nm in diameter as a template, high surface area nanostructured $LiCoO_2$ cathodes can be created. Using RF magnetron sputter coating, these AAO templates can be sputter coated with a $LiCoO_2$ source to a thickness of 300nm. The line of sight deposition of sputter coating will deposit the $LiCoO_2$ nanoparticles on the surface of the AAO substrate, depositing on the honeycomb-like nature of the nanoporous surface while leaving the pores still exposed. This process effectively templates the underlying nanoporous nature of AAO substrate with a layer of $LiCoO_2$, creating an extremely high surface area $LiCoO_2$ cathode. The surface area generated from the nanostructuring results in about six times the surface area compared to a more traditional thin film with no nanostructuring. The additional surface area is generated from the added lateral surface area of the cylindrical-like nature of the nanopores. This added surface area leads to more electrolyte-electrode contact, the ability to intercalate Li ions into and out of the material faster, store more capacity and ultimately make better batteries. In addition to added surface area, nanostructured $LiCoO_2$ cathodes appear to exhibit a unique crystalline orientation that has been investigated by X-Ray diffraction and Raman spectroscopy. This orientation lends itself to promote ionic conduction and shorten diffusion distances. Nanostructuring both electrode materials as well as the electrolyte can lead to a novel all-solid-state Li ion battery. Nanostructured SnO_2 anode and $LiCoO_2$ electrodes have been generated along with a polyethylene-oxide (PEO) based electrolyte nanoconfined in an AAO membrane, to generate a functioning nanostructured all-solid-state full cell. The full cell was investigated using AC impedance and galvanostatic cell cycling. The unique characteristics of a nanostructured $LiCoO_2$ cathode along with some preliminary results from the all-solid-state cell will be discussed.

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Exploring the insertion mechanism of SVS-1 β-hairpin peptide into an anionic lipid bilayer

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Antimicrobial peptides (AMPs) are ubiquitous in many biological systems and act as host defenses against microbial pathogens. Existing theories on how AMPs insert and cause pore formation still lack mechanistic detail. In this study, we characterize the insertion mechanism of SVS-1, a beta-hairpin peptide, into an anionic lipid bilayer using atomistic molecular dynamics (MD) simulations. There is an energy barrier needed to overcome the strong electrostatic interactions of peptide side-chains and charged lipid head groups. Our studies show that the hydrophobic portions of the peptide are needed to facilitate insertion into the bilayer. By comparing the folding of SVS-1 in charged and uncharged lipid bilayers, we found that folding occurs at different rates and may lead to different secondary structures. Simulations at non-zero surface tension were conducted to expand the bilayer such that the hydrophobic side-chains of the peptide can interact with the hydrophobic tails of the bilayer. The introduction of one valine side-chain site into the bilayer promotes a cascading (twist) event of the hydrophobic peptide surface into the bilayer. Surface tension mimics the stress induced by multiple peptides binding to the surface of a bilayer leaflet, so we propose the insertion mechanism of SVS-1 strongly favors a cooperative effect that thins the bilayer and promotes insertion of peptides via the hydrophobic groups. Insight gained from our studies can potentially aid in design of novel AMPs as therapeutic or cancer targets and classify the mechanisms of insertion and membrane disruption.

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Conceptually simple approaches to complex structural problems: Ligand migration in myoglobin

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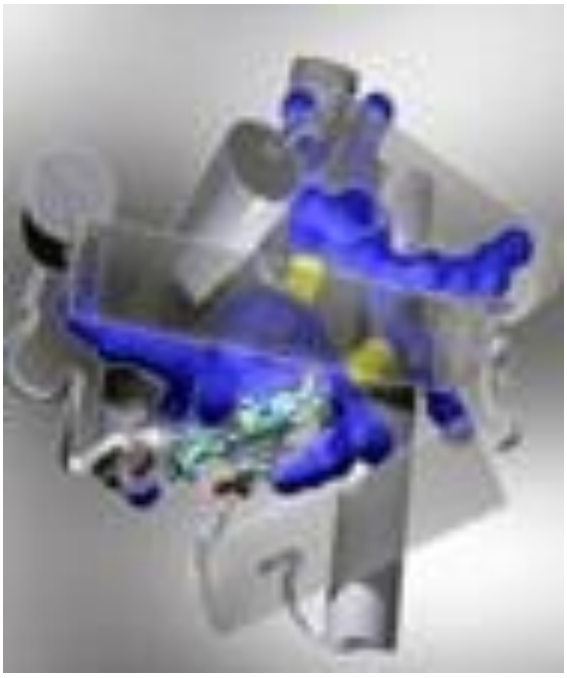
Myoglobin -- the "hydrogen atom" of molecular biology -- is a globular protein involved in oxygen storage and transport. Key to its function is the ability of small non-polar molecules such as O2 or CO
travel from the outside of the protein to the deeply buried binding site in myoglobin. We use a combination of conceptually simple, but computationally intense methods to reveal complete, atomic-level picture of ligand migration pathways in myoglobin. We show how local structural fluctuations lead to the existence of a global network of pathways that occur in the "softer" regions of the protein
matrix in-between its helices.



Ligand mygration pathways in myoglobin

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Proteins under pressure

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The discovery of “extremophilic” microbes that are able to withstand remarkable extremes of temperature, pressure, and chemical composition leads to the question of how the macromolecular structures comprising the microbes are preserved. Our focus is on effects of high pressure, which are much less understood than temperature effects. The effects are likely to differ; for instance, pressure-induced protein unfolding appears to be qualitatively different from thermally-induced unfolding. In addition, some microbes appear to use certain osmolytes to protect against pressure. Here, the effects of different osmolytes on protein stability under pressure are investigated using simulations of the B1 domain of streptococcal protein G

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Hydrogen-bonding networks dictate conformational sampling of a *Pneumococcal* fibronectin-binding adhesive protein

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We study the effect of networks of non-covalent interactions on the conformational dynamics of the *Streptococcus pneumoniae* virulence factor, PfbA. Multi-microsecond molecular dynamics simulations of the apo, Ca^{2+}-bound and Mn^{2+}/Ca^{2+}-bound surface – binding protein in water and sugar solutions help identify potential glycan recognition sites and develop a hypothesis for the mechanism of surface binding. We find that while

residues in the β-domain of PfbA remain rigid over the course of microseconds, residues in the α/β domain undergo a bending movement akin to a swinging pendulum. Surprising, metal ion binding has a limited effect on the conformational dynamics of the protein. We identify networks of non-covalent interactions including hydrogen bonds and π-π stacks motifs that are maintained over the course of our simulations. We further model the entire protein to develop a hypothesis of how the α domain is involved in signaling and protein recognition. Our quantum mechanical calculations determine that a strong cooperative effect is present in hydrogen bonding pathways that accounts for an almost 20% increase in hydrogen bond strength. A Ramachandran analysis finds that residues in the region connecting the two domains alternated between β-sheets and α-helix like conformations. Our analyses find the α-helical regions around Gly184 and Gln185 to undergo conformational changes that may play a role in plasminogen binding. Our simulations further find support for a putative carbohydrate-binding site. Conformations of PfbA docked against plasminogen expand our understanding of the interaction at this interface. Overall, our study provides insights that will help develop a pharmaceutical means to inhibit *S. pneumonia* virulence.

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Protein solubility to aggregation and structure

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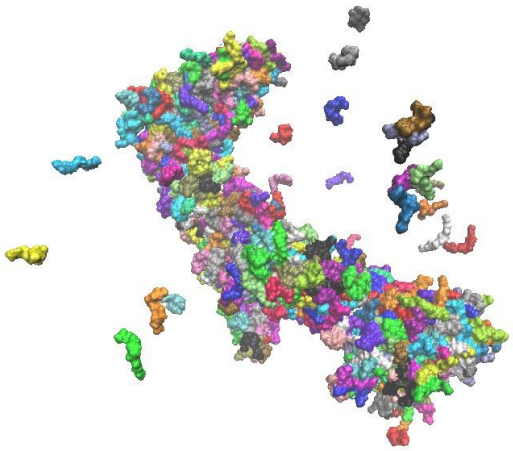
The mechanism of protein folding is often described in terms of hydrogen bonding, side chain packing and the hydrophobic effect. In this study we consider a finite concentration of peptides as a model of the behavior of protein molecular recognition, both self as in collapse of intrinsically disordered proteins and intermolecular as in dimerization. Aggregation often manifests as a liquid-liquid, phase separation. We simulate oligopeptides in water at varying concentrations in order to understand the structural and thermodynamic changes that occur during aggregation of these short peptides. Thermodynamic signatures of this aggregation of short oligoglycines is remarkably similar to the thermodynamics of folding or collapse of longer oligoglycines in water. We compare the thermodynamics of aggregation of short peptides with the collapse of longer peptides in water in order to understand the thermodynamics of collapse of proteins. We find a common dipole driven mechanism, which needs no hydrophobic groups or hydrogen bonds, promotes collapse.



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Protein-protein docking and molecular dynamics simulations suggest potential mechanisms of electron transfer between ferredoxin and cyanobacterial photosystem I

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Photosystem I (PSI) is a thylakoid membrane-bound protein that is involved in the process of cyanobacterial photosynthesis. The protein complex is involved in the transfer of electrons from cytochrome c6 or plastocyanin from Photosystem II and ultimately to transiently-bound Ferredoxin (Fd) or Flavodoxin in the stroma of the chloroplast. Based on the X-ray structure of photosystem I, obtained from the Protein Data Bank, residues of potential binding sites have been identified using state-of-the-art bioinformatics software based on energy landscape theory as well as the conservation of residues. The Protein Frustratometer (www.frustratometer.tk) identified highly “frustrated” residues on the potential energy surface of PSI, which could be involved in protein-protein interactions or ligand binding. The Evolutionary Trace method (http://mammoth.bcm.tmc.edu/ETserver.html) performed a multiple sequence alignment of PSI protein sequences to determine the conservation of residues across analogous proteins in the phylogenetic tree. The bioinformatics data from these two methods was combined to determine potential binding sites for Fd on PSI. Three docked complexes of Fd and PSI were simulated using the NAMD molecular dynamics software package (www.ks.uiuc.edu/Research/namd/) for 1 microsecond each. The simulations show several important movements in protein structure of both PSI and Fd that improve the quality of the docked complexes and suggest possible mechanisms of electron transfer. An understanding of the structure and dynamics of this system at the atomic level is useful for the modification of these proteins and the design of a biologically-based photovoltaic energy cell for alternative energy.

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Role of intrinsically disordered proteins in cellular signaling and regulation

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Intrinsically disordered proteins (IDPs) mediate critical regulatory functions in the cell, including regulation of transcription, translation, the cell cycle, and numerous signal transduction events. In keeping with their regulatory function, the cellular abundance of intrinsically disordered proteins is tightly controlled. The lack of stable globular structure confers numerous functional advantages on IDPS, allowing them to exert an exquisite level of control over cellular signaling processes. IDPs frequently function in dynamic regulatory networks, where their propensity for posttranslational modifications, their rapid binding and dissociation kinetics, and their ability to interact with multiple target proteins makes them well adapted for precise transduction of cellular signals. Many viruses hijack their host cells by making extremely effective use of intrinsic disorder to mimic key cellular regulatory proteins that are themselves intrinsically disordered. The role of IDPs in dynamic cellular signaling will be illustrated by reference to pathways regulated by the general transcriptional coactivators CBP and p300, the tumor suppressor p53, and the adenovirus E1A and human papillomavirus E7 oncoproteins. CBP and p300 are central nodes in eukaryotic transcriptional regulatory networks and transcription factors must compete for binding to the limiting concentrations of CBP/p300 present in the cell. Many intrinsically disordered proteins contain multipartite interaction motifs that facilitate the assembly of higher-order complexes and the integration of complex signaling networks. The presence of multiple binding sites in IDPs enables allosteric regulation of cellular signaling.

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NPM1 facilitates assembly of nucleolar components through phase separation

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The nucleolus, the site of ribosome biogenesis and a cellular stress sensor, is a membrane-less organelle with liquid-like properties, comprised of thousands of proteins and various forms of nucleic acids. Nucleolar components are internally organized into three compartments: the fibrillar centers (FCs) and dense fibrillar component (DFC) are engulfed in the largest nucleolar region, the granular component (GC). Nucleophosmin (NPM1) is a highly abundant protein within the GC, with roles in stress sensing, ribosome biogenesis and tumor suppression and is often used as a nucleolar marker. Here we describe a previously unrecognized role of NPM1 in facilitating the assembly of ribosomal RNA (rRNA) and nucleolar proteins through phase separation into heterogeneous liquid-like structures. Using a novel combination of approaches that spans atomic to light microscopy length-scales, we characterize the structural features of liquid-like droplets that arise from phase-separation of NPM1 with other nucleolar components. Our results provide a unique foundation for future studies into the

structural organization of the nucleolus and the molecular mechanisms that control ribosome biogenesis and the nucleolar stress response.

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The role of IDPs in aggregation associated with Parkinson's disease

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Intrinsically disordered proteins (IDP) are involved in human disease and particularly in neurodegenerative diseases such as Parkinson's and Alzheimer's. Understanding the molecular mechanism of protein aggregation from IDPs is critical for drug development against these devastating diseases. We explore the relationship between the nature of the IDPs and their transient low affinity interactions with their aggregation or inhibitory properties using different variants of synuclein involved in Parkinson's disease.

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The role of protein disorder and self-association in the formation of membrane-less organelles

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Cells confine competing reactions into different compartments to enrich function. In addition to typical membrane-bound organelles, cells mediate multiple critical processes within bodies known as "membrane-less organelles", which are typically µm-sized, spherical structures with a clear boundary from the surrounding cytoplasm or nucleoplasm. Notable membrane-less organelles include the nucleolus, stress granules, and nuclear speckles, and respectively function in ribosome assembly, mRNA sequestration upon stress, and RNA splicing. To carry out their critical functions, membrane-less organelles are required to concentrate specific components of the cytoplasm or nucleoplasm of cells in a defined area without membrane enclosure. Some membrane-less organelles have been demonstrated to possess properties of liquid droplets. Liquid demixing phase separation (LDPS) was suggested as the biophysical basis for the formation of this second liquid phase. Critical constituents of membrane-less organelles can mediate LDPS *in vitro* via transient interactions. Such interactions involve either intrinsically disordered low-complexity sequence domains, or a pair of interaction partners, one with repeats of binding domains and the other with linear binding motifs. For both types of interactions, intrinsic disorder may play a role in mediating LDPS under physiological conditions. We will report molecular architectures mediating LDPS *in vitro* and recruitment to membrane-less organelles in cells and discuss implications for function. Further, we will consider the role of a change in dynamics of organelles as molecular driving force for disease states. We will report on the role of SPOP-mediated ubiquitination in nuclear speckles and cancer pathogenesis and the role of hnRNPA1 in stress granule formation and neurodegenerative diseases.

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Decoding functions and phase behavior of IDPs using sequence design

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Decoding functions and phase behavior of IDPs using sequence design.

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Ion issues in physical chemistry

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This talk will highlight experiments where ions had a central role in experiments of fundamental importance in physics and chemistry. Whenever my group worked on ion issues of fundamental importance, we always seem to have been preceeded by work from Bob Compton. Issues of cluster ions and absolute ion solvation thermodynamics as well as multiply charged ions will be reviewed and related to Bob Compton's work.

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Photofragment imaging studies of metal-ligand charge transfer

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Metal cation-molecular complexes are produced and cooled in a pulsed supersonic molecular beam, followed by mass analysis and mass selection in a time-of-flight spectrometer. Selected cation complexes are decelerated and then photodissociated at various UV-visible laser wavelengths. Velocity map imaging (VMI) and slice imaging techniques are employed in a newly designed instrument to detect the kinetic energy release (KER) distributions in the photofragment cations. These methods are employed for charge-transfer dissociation processes in ion-benzene complexes and dication-water complexes of the transition metals. Analysis of the KER data provides new determinations of bond dissociation energies that are difficult to obtain by other methods.

2015 Joint Southeastern/Southwest Regional Meeting 560

Laser experiments for chemistry and physics

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In recognition of the International Year of Light, this talk will describe a number of experiments which are included in a new textbook on the application of lasers in graduate and undergraduate education[1]. The properties of light will be discussed with respect to historical estimates of the speed of light as well as using the capacitance of a

capacitor and timing lasers pulses over known distances. Precise measurements of the Faraday effect is used to demonstrate the interaction between light and a magnetic field in a medium. Experiments in non-linear optics involve the generation of harmonics (SHG, THG) as well as resonantly-enhanced multi-photon ionization (REMPI) of atoms and molecules. Raman spectroscopy of dry ice will be used to introduce the Fermi Resonance. Also, lasers are employed to determine the speed of sound in matter as well as to estimate the size of blood cells. Finally, the profound impact of lasers in analytical chemistry will be illustrated through experiments in laser induced break down spectroscopy (LIBS) and laser desorption mass spectroscopy.

[1]R.N. Compton and M.A. Duncan, Oxford University Press (in press).

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Chiroptical spectroscopy: An emerging tool for chiral molecular structural determination

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Three dimensional structural determination of chiral molecules is gaining increasing importance in recent years. While x-ray crystallography has been one of the main techniques used for this purpose, the need for growing good quality crystals limits the use of this method. Recent developments in spectroscopic instrumentation for measuring chiroptical spectra and quantum theoretical developments for predicting chiroptical spectra have revolutionized the field of chiroptical spectroscopy. The number of applications reported using chiroptical spectroscopy has increased exponentially in recent years. In this presentation, I will give an overview, and present the unique applications as well as limitations of chiroptical spectroscopy.

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Detecting the surface sum frequency generation signal from noncentrosymmetric crystal

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Second-order nonlinear spectroscopies, such as second harmonic generation (SHG) and sum frequency generation (SFG), are well-established surface-sensitive techniques, which have been limited mainly to centrosymmetric materials. Here, we use femtosecond broadband SFG spectroscopy to first observe strong bulk-surface interference from the archetypical non-centrosymmetric semiconductor GaAs (001). Azimuthal angular dependence studies in reflection geometry under eight possible polarization configurations reveal more structural information compared to corresponding SHG studies. The experimental results demonstrate that SFG with non-identical photons and over band-gap excitation can significantly improve the surface sensitivity. Additionally, carbon monoxide is employed as a molecular marker to examine the sub-monolayer surface sensitivity on GaAs. The resonant carbon monoxide stretching mode is clearly observed in the vibrational SFG spectra on top of a

non-resonant signal from the GaAs crystal. These results suggest that this technique can be generally applied to surface and interface studies of other noncentrosymmetric crystals.

2015 Joint Southeastern/Southwest Regional Meeting 563

The Compton effect

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While most scientists are aware of the Compton effect in physics, which deals with inelastic scattering of a photon with a charged particle, the chemical physics community has experienced it's own "Compton effect", the effect that Robert N. Compton has had on our field. In this talk, I will highlight the impact that Bob has had on my career, on chemistry and physics at the University of Tennessee and Oak Ridge National Laboratory, and ion chemistry in general.

2015 Joint Southeastern/Southwest Regional Meeting 564

Member benefits and business resources from the ACS Division of Small Chemical Businesses (SCHB)

***Joseph E. Sabol**, jsabol@chem-consult.com. Chemical Consultant, Marquette, Michigan, United States*

The ACS Division of Small Chemical Businesses Division (SCHB) was founded in 1978 and has provided valuable member benefits, resources, and programming at ACS national, regional, and local section meetings. SCHB member benefits include: business listing in the SCHB on-line members' directory of products and services; deeply discounted expo booth space at ACS national meetings; scholarship to attend ACS Leadership Courses; periodic newsletters; advance notice of meeting abstracts and events; lunch with speakers at national meetings; the opportunity to shape and direct SCHB by holding office or chairing a committee; and - the best of all - amazing networking opportunities, including in-person at ACS meetings and 24/7/365-virtual through SCHB's myriad of social media platforms, including ACS Network, Linked-In, Twitter, and Facebook. Patron [corporate] membership is also available. Get involved! See what SCHB can do for you - and what you can do for SCHB!

2015 Joint Southeastern/Southwest Regional Meeting 565

From academic laboratory to commercial plant: The ThruPore story

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Many academic researchers believe that their work has the potential to make a significant impact in the chemical market place. With the steady dwindling of federal support and ever greater pressures from reviewers to "demonstrate impact" commercializing inventions generated in a research lab is becoming a more attractive option for many in academia. However taking inventions from the bench, through the

patent process to market entry, is a path that few chemists are routinely trained for. We will present our journey from a regular NSF grant, through NSF's I-Corps program, SBIR Phase I, Phase Ib, and a pending Phase II, discussing some of the issues we encountered and lessons we have learned.

2015 Joint Southeastern/Southwest Regional Meeting 566

Findings on blending hemp with thermal coal for power generation or gasification

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The findings of a whitepaper published in 2014 and in process of being updated on the use of industrial hemp as a torrefaction material that is to be blended with coal, as well as potential syngas production and other applications to reduce harmful emissions while maintaining Btu of thermal coal to create hybrid energy centers for power generation, bio-chemical production, and renewable and alternative fuel production.

2015 Joint Southeastern/Southwest Regional Meeting 567

Out of the frying pan, into the fire, and swimming upstream

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Most people are familiar with being an employee, but know little about being an employer. What if you want to start your own company? How do you start? What do you do? Cash is oxygen - how do you generate sales? Start-up and existing small businesses are a major source of economic growth and scientific, technology, and engineering advances in the commercial sector are measured by their utility in the broader community. Successful small businesses leverage their entrepreneurial skills to overcome the barriers that revolve around large and established competitors. Small entities are characteristically nimble, innovative, and accept a higher level of risk with their perspective for building success.

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Dissociation pathways, rearrangement reactions, and relative stabilities of O-sulfated amino acids and small peptide

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Tyrosine sulfation, which was first reported in 1954,[1] is a post-translational modification (PTM) which has been implicated in various biological processes, including hemostasis and leukocyte adhesion.[2] The O-sulfation of serine and threonine were reported relatively recently, in 2004.[3] Given the scope of their known roles in biological function and disease states thus far, the importance of discovering sites of sulfation and their respective roles is critically necessary, and yet their analysis is not trivial. The “extreme lability” of this modification has been noted as a key challenge for mass spectrometric analysis.[2] However, this lability has not yet been explored at a fundamental level. This work aims to investigate the dissociation pathways and rearrangement reactions that

are at play in sulfated model systems.

The ion-trap CID fragmentation pathways of the modified amino acids, sulfoserine and sulfotyrosine, were recorded in both the positive and negative ionization modes. Sulfoserine underwent abundant neutral loss of SO_3 and H_2SO_4 in the positive mode and gave rise to a single fragment ion, deprotonated sulfuric acid, in the negative mode. Sulfotyrosine produced more varied mass spectra, with, for instance, the M-CO_2H_2 peak dominating the positive-mode spectrum. However, the neutral loss of SO_3 was still indeed an observed fragmentation pathway. The loss of SO_3, in both cases, would correspond to a complete loss of sulfosite memory during sulfopeptide analysis.

PTM rearrangement reactions, which have been previously reported for phosphorylated systems,[4, 5] are another potential source of error in PTM analysis. We have recently observed the intermolecular transfer of H_2SO_4 and SO_3 between the sulfopeptide sSE and triarginine upon CID of a heterodimer. This reaction has been characterized by MS^n, energy-resolved CID, and isotope labelling.

Ongoing experiments aim to directly compare the stability of sulfation to phosphorylation using energy-resolved CID.

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Effects of acidic peptide sequence on metal attachment and electron transfer dissociation tandem mass spectrometry

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Biological compounds with long series of acidic residues are difficult to protonate in positive mode electrospray ionization (ESI) because they preferentially form negatively charged ions. Therefore, analysis by electron transfer dissociation (ETD), which requires multiply positively charged precursor ions, is not possible by protonation alone. Adduction with di- and trivalent metal ions facilitates formation of multiply positively charged precursor ions. Previous work done by our group which involved mixing fibrinopeptide b (pEGVNDNEEGFFSAR) with trivalent lanthanide metal ions produced abundant $[M+Met+H]^{4+}$, $[M+Met]^{3+}$, and $[M+Met-H]^{2+}$. The current study will investigate how the sequence of the acidic peptide affects its ability to bind metals and the effects of metal attachment on fragmentation by ETD. Fibrinopeptide b, a 14 amino acid peptide, has a mix of different types of amino acid residues including a residue with a basic side chain. Hirudin(54-65) (GDFEEIPEEYLQ) and epidermal growth factor(985-996) (DVVDADEYLIPQ) both contain 12 amino acid residues with a variety of residues. The 18 amino acid residue ACTH(22-39) (VYPNGAEDESAEAFPLEF) also has a variety of amino acid residues. Peptides mentioned above formed abundant

$[M+Met+H]^{4+}$, $[M+Met]^{3+}$, and $[M+Met-H]^{2+}$ at a lower abundance. ETD spectra of the multiply charged positive precursor ions produced extensive sequence informative fragmentation and complete sequence coverage in many cases. In contrast, low-molecular-weight chromium-binding peptide clip (EEEGDD) contains 7 amino acid residues with one non-acidic residue. No metal adducted precursor ions were observed with this peptide. Seven residue AAADAAA, however, produced $[M+Met]^{3+}$, and $[M+Met-H]^{2+}$ in lower abundance. No metallated precursor ions were observed for acidic peptides with less than 7 amino acid residues. Preliminary results indicate that metal adduction is favored when acidic peptides contain a variety of the types of amino acid residues and have a sequence greater than 7 amino acid residues. In addition, metallated product ions appear from the halfway point of the peptide sequence. Further goals involve systematically varying the types of amino acid residues present in the acidic peptide's sequence to determine the effects of sequence on ETD fragmentation and site of metal attachment.

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Structural analysis of 9cUAB30 methyl derivatives and coactivator peptide GRIP1 on rexinoid X receptor by hydrogen deuterium mass spectrometry

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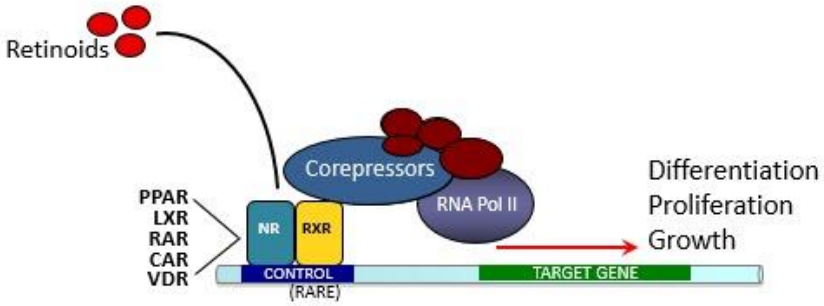
RXR, a ligand dependent nuclear receptor is involved in many signaling pathways of transcription initiation that regulate cellular proliferation, differentiation, growth, and homeostasis. Due to RXR's unique involvement as a heterodimer partner it has become a target for therapeutics. We previously established that 9cUAB30 is a potent and selective agonist for the RXR's and have proven to be non-toxic. To probe the ligand binding pocket of RXR, methyl derivatives were synthesized and tested. Recently published data on biological studies of 9UAB30 methyl derivatives show that 4-methyl 9cUAB30 and 7-methyl 9cUAB30 both significantly increase triglyceride levels in mouse models up to 420% and 642%, respectively when compared to 9cUAB30[1]. Gene arrays done with 4-methyl 9cUAB30 show an increase of mRNA key enzymes for lipogenesis through signaling of RXR: LXR heterodimers [1]. Our preliminary 4-methyl HDX data indicate that the four methyl derivative has closer interactions with helices three and helices seven when compared to 9cUAB30. The HDX data of 4m9cUAB30 also indicate increased deuterium suppression of helix three and a decrease in dynamics of helix 12 when compared to 9cUAB30[2]. X-Ray crystal structures for 4m9cUAB30 and 7m9cUAB30 also indicate a significant increase in contacts with residues in helix 7 (V_{342}, I_{345}, F_{346}) [3]. The seven methyl derivative was responsible for the highest increase of triglyceride levels in rat studies [1]. We hypothesize that dynamics of hRXRα-LBD homodimers in the presence of 7m9cUAB30 will result in similar or exaggerated results when compared to 4m9cUAB30. We will provide the dynamics for RXR homodimers in the presence of methyl derivatives with and without coactivator peptide GRIP-1 and establish what dynamics are associated with toxicity.



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Gas-phase acidities of the phosphorylated amino acid and their amides

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Many amino acids prevalent in nature contain post translational modifications (PTM), such as phosphorylation. To better understand the acidity of larger biomolecules with PTMs, the gas-phase acidity (GA) values of the phosphorylated amino acids need to be examined. Also, as amino acid amides give a better representation of the acidity of an amino acid residue in a peptide, these phosphorylated amino acid amides will be determined. Ion/molecule reactions can determine the GA value of the phosphorylated amino acids/amides. Computational results will be compared for the GA values and to obtain deprotonated ion structures.

Ion/molecule reactions were performed in a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS). The amino acids and their corresponding amides that were studied are capable of being phosphorylated and commonly have a hydroxyl group on their side chain. These amino acids are: serine, threonine, and tyrosine. Once phosphorylated, the acidity of the molecule is increased significantly. For example, serine has a calculated GA value of 325.7 kcal/mol, however, after phosphorylation has a calculated GA value of 308.9 kcal/mol. (A lower GA value indicated a more acidic molecule). Phosphorylated amino acids/amides were reacted with neutrals of well-known GA values. Computational studies have shown that the phosphate group is involved in strong hydrogen bonding networks, and generally, deprotonation at the phosphate is the lowest in energy, with the exception of phosphotyrosine. The range of the computational GA values for the phosphorylated acids is from 308.9-306.7 kcal/mol and for the amides is 314.2-307.0 kcal/mol. The experimental and computational GA values are in excellent agreement.

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Competitive binding of copper(I) and zinc(II) by methanobactin from *Methylosinus trichosporium* OB3b and analog methanobactin peptide

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Methanobactin (1154 Da) is a class of copper binding peptides identified in methanotrophic bacteria. These copper binding peptides are thought to mediate the acquisition of the copper cofactor for the enzyme methane monooxygenase, which catalyzes the oxidation of methane to methanol. The methanobactin (mb-OB3b) from *Methylosinus trichosporium* OB3b with the primary structure 1-(N-[thio-(5-oxo-2-(3-methylbutanoyl)oxazol-(Z)-4-ylidene)methyl]-Gly_1–Ser_2–Cys_3–Tyr_4)-pyrrolidin-2-yl-(thio-[5-oxo-oxazol-(Z)-4-ylidene]methyl)–Ser_5–Cys_6–Met_7 primarily binds to Cu(I) but will also bind Zn(II). The research presents a study of the competition between Cu(I) and Zn(II) binding by mb-OB3b and an analog methanobactin peptide (amb, 1481 Da) that has a similar primary structure of ac-Leu_1-His_2-Cys_3-Gly_4-Ser_5-$[Cys]_6$-Tyr_7-Pro_8-His_9-Cys_{10}-Ser_{11}-$[Cys]_{13}$-Met_{14} as mb-OB3b but replaces the bi-dentate enethiol oxazolone rings of mb-OB3b with two His-Cys for comparison. Ion mobility-mass spectrometry, fluorescence, and UV-Vis were used to monitor the competitive titrations of mb-Ob3b and/or amb with $ZnCl_2$ or $CuCl_2$ to study the relative binding affinities for each of these metal ions. Collision cross section measurements of Zn(II)- and Cu(I)-bound mb-OB3b showed the size of the complex decreased from 256 to 245 $Å^2$ as the molecule rearranges to accommodate Cu(I), indicating a tighter bound conformation for the Cu(I) complex.

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Fragmentation of lanthanide-adducted oligosaccharides by collision-induced dissociation and electron transfer dissociation

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Oligosaccharides are an important sub-class of carbohydrates that participate in many biological processes. They contain three to ten monosaccharides linked by glycosidic bonds to form highly branched structures. Mass spectrometry techniques are important in the structural analysis of oligosaccharides. Five non-derivatized oligosaccharides (maltotetraose, 3α,4β,3α-galactotetraose, stachyose, nystose and maltoheptaose adducted with 14 lanthanide metal salts. The mixtures were subjected to electrospray ionization (ESI) and the resulting multiply-charged metallated carbohydrate ions were isolated and fragmented by CID or ETD. Analysis was performed on a Bruker HCTultra PTM Discovery System high capacity quadrupole ion mass spectrometer. This research further explores metals that have not yet been examined as cationizing agents for oligosaccharide structural analysis. High signal intensity, extensive precursor ion dissociation, glycosidic bond cleavage, cross-ring cleavage, and internal cleavages were observed for all metal-adducted oligosaccharides without permethylation. The results in this study indicate fragmentation patterns and efficiency depend on sequence of the oligosaccharide, identity of metal, and dissociation method. In previous work studying alkaline earth metals, alkali metals , and transition metals, it was found that the fragmentation observed depended greatly on the identity of the metal being studied. The fragmentation patterns seen with the lanthanide metals vary from the previous metals studied, but do not vary significantly amongst the lanthanide group. The reducing structures exhibit different fragmentation patterns and yields compared to the non-reducing structures. Both ETD and CID of the reducing sugars, generally provided

complete glycosidic-bond fragmentation, however the cross-ring cleavages seen varied between the dissociation methods, with ETD producing more cross-ring cleavages than CID. There were some oligosaccharide fragments that were only seen in either CID or ETD, suggesting that these two methods could be used complimentarily to achieve more structurally informative information.

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Desorption by impulsive vibrational excitation (DIVE): Ultrafast/ultrasoft laser ablation for mass spectrometry and biodiagnostics

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The development of mass spectrometry systems capable of reaching the long sought, fundamental limit of single protein identification has been made possible by our group's recent developed of a novel picosecond infrared laser (PIRL). The PIRL delivers high power, ultrafast infrared laser pulses to selectively excite water under the conditions of desorption by impulsive vibrational excitation (DIVE). DIVE ablation produces intact gas phase molecules faster than the thermal and acoustic relaxation time of the excited water and nucleation growth to avoid cavitation as well as thermal and shock wave induced analyte damage. We have recently applied the method to achieve near scar free surgery in animal models, intact extraction of functional biological entities from tissue for precision laser biopsy and dramatically enhanced proteome preservation through laser tissue homogenization. Here we further demonstrate the efficient production of gas phase ions of intact small molecules, peptides and large proteins from water for ultra-high sensitivity mass spectrometry using DIVE in combination with a novel mass spectrometry interface. The system was further applied to atmospherically coupled mass spectrometry using a recently designed and nanofabricated dynamically wetted, self-localizing pico-liter array in conjunction with custom image processing base fiducial registration software.

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Negative electron transfer dissociation mass spectrometry of acidic peptides

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Electron transfer dissociation (ETD) is a tandem mass spectrometry technique in which reagent radical anions, generated via a chemical ionization source, are let into the ion trap with the precursor cation. The reagent radical anion then transfers an electron to the precursor cation, which initiates fragmentation of the precursor cation. This method is useful for sequencing peptides that readily protonate to produce positive ions. However, highly acidic peptides cannot be sequenced by this method. Recently, negative ion mode ETD (NETD), where a precursor anion transfers an electron to a reagent radical cation, has been studied as a method for peptide sequencing. In the present study, the ability of NETD to sequence highly acidic peptides was explored. Nine peptides, containing at least four acidic residues and fewer than three basic residues, were studied. The peptides ranged in size from 12 residues to 33 residues. Samples were analyzed at a concentration of .001 mg/mL in a solvent system of

acetonitrile (ACN): water (H_2O): ammonium hydroxide (NH_4OH) at 50:50:0.1 (v/v). Experiments were performed on a Bruker HCTultra PTM Discovery System high capacity quadrupole ion trap (QIT) mass spectrometer equipped with an electrospray ionization (ESI) source. For NETD, precursor anions ranged from $[M - 3H]^{3-}$ to $[M - 6H]^{6-}$ depending on peptide sequence.
For all peptides, dominant cleavage observed in the NETD spectra is at the Cα-CO bond of the peptide backbone, and both N-terminal and C-terminal product ions are observed. As the charge state of the precursor anion increases, more extensive fragmentation is observed for each peptide. Complete, or nearly complete, sequence informative fragmentation is observed for peptides with fewer than 20 residues. Observed fragmentation is less extensive for peptides with 20 or more residues, but is still informative. Overall, NETD is shown to provide extensive sequence informative fragmentation for highly acidic peptides.

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Determination of the structure of steroid and saccharide molecules in solution using residual dipolar couplings (RDCs)

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Residual Dipolar Couplings (RDC) have been used to determine the three-dimension structure of biomolecules and small organic molecules. RDC can be observed by NMR spectroscopy when molecules are oriented in the anisotropic media. Dipolar Coupling (Dij) can provide powerful structure information and it depends on A) the distance between two nuclei i and j and 2) the angle of the inter-nuclear vector (rij) regarding to the direction of magnetic field (B0). In this study we used lyotropic solution and Poly methyl methacrylate (PMMA) as anisotropic media to respectively study the best possible structure of sucrose and progesterone in solution.

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Determining the structure of metal ligand complexes in solution by nuclear magnetic resonance (NMR) spectroscopy using residual dipolar couplings (RDCs)

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Residual Dipolar Couplings (RDC) have traditionally been used in the structure determination of Biomolecules, Pharmaceutical molecules and small organic molecules. Determining the structure of metal-ligand complexes is an area of interest that may also benefit from the application of dipolar couplings. In solid state Metal Ligand complexes, X-ray crystallography can be used in determining the structure. Many applications of metal-ligand complexes are in solution and so structural determination in solution is of direct interest for these complexes.

This study focuses on determining the structure of Metal (1R, 2R)-N, N′-1, 2-Cyclohexanediylbis (2-pyridinecarboxamide) OR (R, R)-DACH-pyridyl TROST ligand complex and Metal Acetyl Pyrazine Benzyl Thio Semi Carbazone (APZ-BTSC) complex

in its solution form using anisotropic media. An anisotropic media of PMMA gel and PVAC gel is used to align the ligands and metal ligand complexes. Based on this anisotropic media the RDCs are determined in solution by NMR spectroscopy and used to find the three dimensional structure of these complexes.

2015 Joint Southeastern/Southwest Regional Meeting 578

It's easy being green: Budget-friendly, safety-conscious chemistry labs for the science classroom of today

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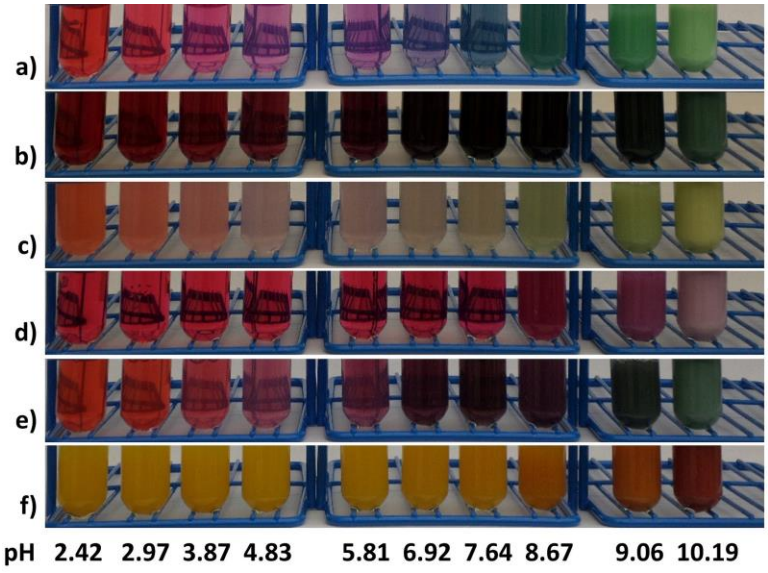
Concerns for student safety, limited access to a variety of chemicals and lab equipment, access to chemical disposal services, and disposal budgets can often be severely limiting factors in creating an environment of hands-on learning in the science classroom. Access to practical, environmentally friendly, low-budget labs that can address multiple curriculum standards provide science teachers with the opportunity to incorporate more lab-based explorations into their lessons. *Spice Up Your Chemistry Lab with Neutralization Reactions* was the pilot workshop for the *It's Easy Being Green: Budget-Friendly Safety-Conscious Chemistry Labs for the Science Classroom of Today* workshop series offered by the Department of Chemistry and Physics at Belmont University. This pilot workshop focused on using neutralization reactions (performed using only combinations of baking soda, milk of magnesia and vinegar) to explore limiting reactants, gas laws, natural indicators and acid-base titrations. Teachers attending the workshops were provided with a series of detailed instructions regarding experimental preparation for the instructor and both instructor and student versions of pre-lab questions, data analysis and post-lab questions for each laboratory experiment. The workshops were attended by over 40 middle and high school science and chemistry teachers from 14 counties in the Middle Tennessee area. The workshops afforded classroom teachers the opportunity to network among their peers. They also provided the teachers with connections to the scientific community and a support network of university faculty willing to answer questions and help develop programs addressing the needs in their science classrooms.



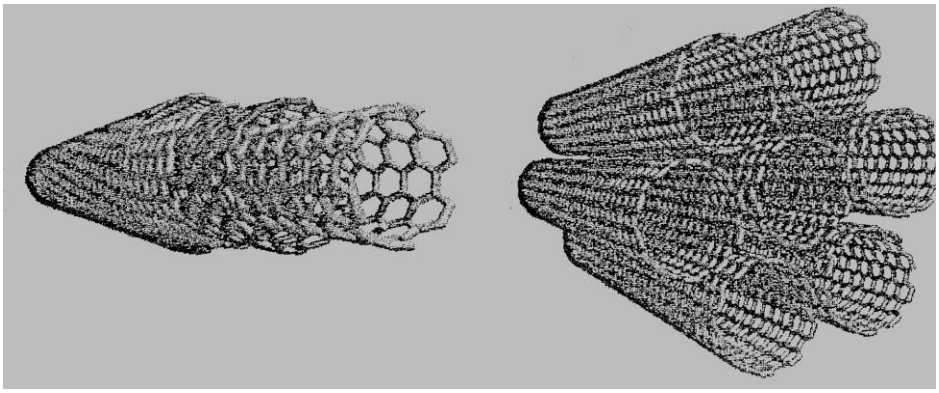
Natural indicators over various pH ranges: a) red cabbage leaves, b) blueberries, c) red apple peels, d) beets, e) cranberries and f) turmeric.

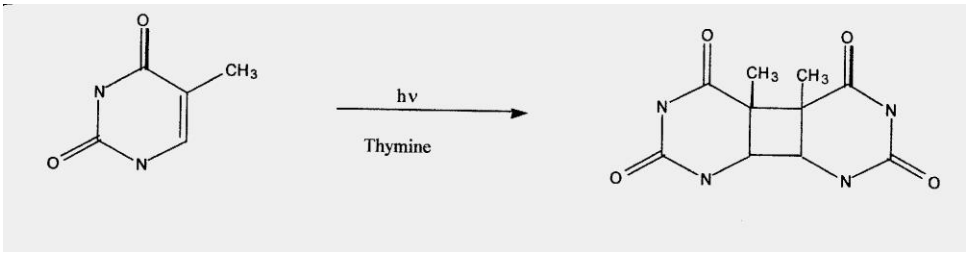
2015 Joint Southeastern/Southwest Regional Meeting 579

Progress towards solutions to diseases: Developing new materials and alternative energy with heterocyclic amines

***Juliet M. Hahn**, JulietHahnPHD@yahoo.com. Chemistry, Francis Marion University, Columbia, South Carolina, United States*

Various heterocyclic amines with multiple applications will be discussed. Carbon nanotubes have been functionalized by heterocyclic amine bioorganic molecules to increase the electrical conductivity of the carbon nanotube thin films. The functionalization has been characterized by spectroscopy and electrical conductivity measurements. Electrically conducting thin films have many applications as novel materials, including solar energy and light weight electrically conductive materials with armor like properties. Photodimerization of thymine is implicated in skin cancer. A study of the simple bioorganic heterocyclic amine eliminates the complications of the real biochemical system. The photodimerization is studied under different reaction conditions to simulate the effect of skin cancer lesion sensitive DNA segments. The heterocyclic amine, Tropanes are in a class of some 200 natural product molecules, including cocaine, which have neurobiological effects. The research is limited to developing synthetic methodology using a zwitterionic effect and organoaluminum catalysis. The synthetic methodology can be used for synthesis of a wide variety of pharmaceuticals. Progress towards the synthesis of an organometallic catalyst with heterocyclic amine ligands with potential application in developing synthetic gasoline will also be discussed.





2015 Joint Southeastern/Southwest Regional Meeting 580

Poly-functional porous-organic polymers: Structure-function relationships in CO_2 sorption

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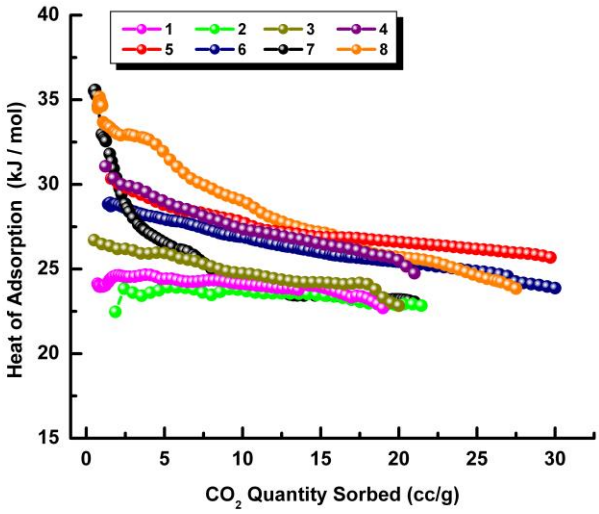
Herein, we report a facile approach towards construction of POPs with a range of functional groups simultaneously present in the porous solid. The functional groups employed were selected to span the range of Lewis-base to neutral to Lewis-acid character. Our results clearly indicate that the nature of chemical functionality affects the observed Q_{st} for CO_2 adsorption inside the material, being largest for N-containing Lewis base sites.

In this report, we demonstrate the versatility of a Sonogashira-Hagihara cross-coupling reaction to construct a family of porous solids with wide range of functional groups, namely pyridine, phenol, pyrimidine, and aromatic carboxylic acid. This approach utilizes the nearly similar reactivity of several brominated aromatic molecular building blocks in C–C heterocoupling reactions, constructing a family of POPs containing one or multiple types of chemical functionalities simultaneously integrated in the backbone of the solids.

we are presenting a facile approach to construct functionalized POPs with functional groups spanning the range of Lewis-base to neutral to Lewis-acid character. We have also demonstrated the effect of the nature of chemical functionality on the observed Q_{st} for CO_2 adsorption inside the material. In addition, it is demonstrated that increasing the dimensions of the pores inside the material, while maintaining the chemical composition, resulted in decreased enthalpy of interactions. It is suggested that incorporating the above factors, Lewis-base functionality and small pores system, into designer materials can potentially result in materials with favorable CO_2 uptake energetics. Materials with high chemical and thermal stability (preferably all-organic) that simultaneously incorporate Lewis-base sites and small pore volumes are of particular potentials to address current challenges in CO_2 separation and capture.



Isosteric heat of adsorption for CO_2 in the studied POPs.

2015 Joint Southeastern/Southwest Regional Meeting 581

Fabrication of alginate nanoparticles using microfluidics, effect of flow rate on dispersity of particle diameters

Sumit P. Jamkhindikar[2]*, spjamkhind42@students.tntech.edu, Holly A. Stretz*[1]*, John Massingill*[3]*. (1) Dept of Chemical Engineering, Cookeville, Tennessee, United States (2) Tennessee Technological University, Cookeville, Tennessee, United States (3) Chemtor, L.P., San Marcos, Texas, United States*

Use of microfluidic flow regimes for large scale production of nanoparticles is important in the emerging fields of personalized and targeted drug delivery, fuel cell catalysis, LEDs, environmental remediation of spills, etc. Formulation of droplets with uniform diameters is a challenge which microfluidic devices have been reported to achieve, but not at high throughput. One approach to high throughput involves the use of a fiber-packed reactor, a platform patented by our partners, Chemtor. The fluid mechanics of such environments has been studied in microfluidic “T” junction system for production of droplets of cross-linked alginate. We report a relation between the ratio of volumetric flow rates of the two phases or Capillary number and the standard deviation of the diameter of the droplets/particles formed.

2015 Joint Southeastern/Southwest Regional Meeting 582

An improved synthesis of fulgenic acid and its use in constructing metal organic frameworks and coordination polymers

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Fulgenic acid is a potentially interesting ditopic ligand for use in the creation of metal organic frameworks (MOF’s) and coordination polymers. Literature methods for the synthesis of fulgenic acid were difficult to reproduce, occurred with low yields and required difficult purification steps. We developed a new synthetic strategy which is a significant improvement over reported methods. A crystal structure of fulgenic acid was obtained and its solid-state behavior studied. The creation of a number of co-crystals as well as metal organic frameworks were attempted by combining fulgenic acid with a variety of metal acetates. The synthesis and structure of these complexes will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 583

Synthesis of novel graft-interpenetrating polymer networks

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Highly transparent and tough graft-interpenetrating polymer networks (graft-IPNs) were synthesized using an elastomeric polyurethane phase (PU) and a highly stiff acrylate-base copolymer phase, which is capable of undergoing both free radical and poly-addition polymerization. The thermo-mechanical properties, fracture toughness properties as well as network and surface phase morphology of the graft-IPNs synthesized were evaluated in this work. Data obtained suggested that the minimization of the phase separation was succesfully achieved by the generation of crosslinking points between both networks. High transparency was obtained in all samples as an indication of the high level of interpenetration achieved. The relative high values obtained for the fracture toughness tests suggest that generating chemical crosslinks between networks is a good approach for increasing the tougheability of polymeric materials.

2015 Joint Southeastern/Southwest Regional Meeting 584

Synthesis of two candidate donor-sigma-acceptor molecular rectifiers with anionic donors and a quinolinium acceptor

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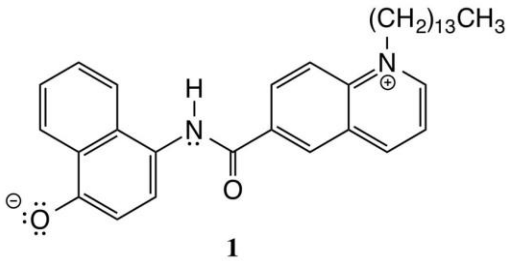
We have prepared many Donor-Sigma-Acceptor molecules with moderate donors like ferrocene and moderate acceptors like perylenebisimide. Monolayers of these molecules are capable of rectifying electrical current, as measured by R. M. Metzger's group at the University of Alabama. We are now seeking stronger donors and acceptors, to improve rectification ratios. We have prepared two zwitterionic compounds that include a cationic quinolinium acceptor that should have a low-energy LUMO, paired with anionic donors that should have high-energy HOMOs. **1** has a phenoxide donor, and **2** has an aryltrifluoroborate donor. The tetradecyl tails are included to aid in orienting the monolayers. We will report the details of the syntheses of **1** and **2** from quinoline-6-carboxylic acid.



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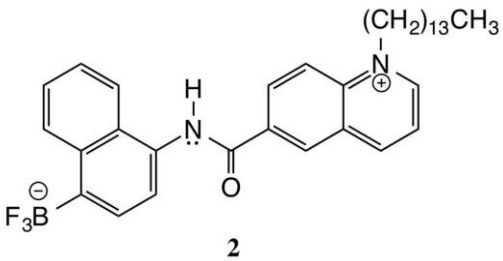

2

2015 Joint Southeastern/Southwest Regional Meeting 585

The dynamic nature of benzodiazaborole formation and the synthesis of benzodiazaborole based oligomers

Chamila P. Manankandayalage*, cxp032@shsu.edu, Sanjaya D. Lokugama, Dustin E. Gross. Chemistry, Sam Houston State University, Huntsville, Texas, United States*

The reversible nature of dioxaborole formation has been widely used for the synthesis of macrocycles as well as 2D and 3D covalent organic frameworks. We have found that diazaborole formation is also dynamic under certain conditions. Based on the above reaction, we were able to synthesize discrete diazaborole based oligomers from *o*-phenylenediamine and boronic acid based monomers. Efforts towards more soluble *o*-phenylenediamine derivatives and macrocycle formation will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 586

Beta-sitosterol/polyethylene glycol water soluble complexes as drug delivery vehicles for cancer therapeutics

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b-sitosterol is a plant sterol that has been well documented to exert an inhibitory effect on tumor cell growth. However, b-sitosterol is hydrophobic and difficult to be delivered into aqueous systems. Aqueous system delivery is required for effective blood circulation. In this report water soluble, b-sitosterol/polyethylene glycol (PEG) complexes were prepared by solution blending in 1,2-dichloroethane, which is a good solvent for the two components. Polyethylene glycol was used because it is amphiphilic and biocompatible. The complexes were studied by nuclear magnetic resonance (NMR) spectroscopy and differential scanning calorimetry (DSC). Proton NMR (^{1}HNMR) of the complexes shows that the methylene (CH_2) protons of the PEG are slightly shifted because of its non-covalent interaction with b-sitosterol. The complex formation was supported by 2-D NMR (NOESY) spectroscopy. NOESY spectra show cross peaks, indicating interaction between the two components. DSC of the complexes shows thermal characteristics that are different from the individual components. In particular, the PEG in the complexes shows a lower melting point and decreased crystallinity compared to the pure PEG. The NMR and DSC studies suggest the formation of stable water soluble b-sitosterol/polyethylene glycol complexes. These complexes have the possibility to reduce the swelling of benign prostatic tumors.

2015 Joint Southeastern/Southwest Regional Meeting 587

1,2,3- triazoles as controlled molecular switches

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A 1,2,3-triazole based molecular sensor has been utilized for the application of selective switching processes homogeneous mediums. The molecular sensor presented in this study was synthesized using “click chemistry” which is a simple one step process, and is a 1,4-diaryl-1,2,3-triazole containing a phenol moiety. The switch ON process was characterized by a fluorometric response which is displayed when the sensor binds to anions such as Fluoride, Acetate, and Di-hydrogen phosphate . The turn OFF

sequence, which is displayed by the quenching of the fluorescence, is triggered by the addition of metal cations such as Cu(II), Zn(II), etc. the characterization and monitoring of this process is done by UV spectroscopy, Fluorescence spectroscopy, and Nuclear Magnetic Resonance spectroscopy (NMR).

2015 Joint Southeastern/Southwest Regional Meeting 588

Synthesis and application of novel initiators in atom transfer radical polymerization techniques

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Initiators play a crucial role in Atom Transfer Radical Polymerization (ATRP), one of the most important living radical polymerization techniques. ATRP provides polymers with exquisite control over molecular weight, dispersity, and morphology, but its use as a method for the preparation of polymer-supported catalysts is limited. An ongoing project in our laboratory involves in the synthesis and application of novel ester bromide initiators, such as salen and imidazolium salts, in ATRP reactions for the preparation of novel, polymer-supported catalysts.

2015 Joint Southeastern/Southwest Regional Meeting 589

The development of porphyrin-thiazolothiazole donor-acceptor materials for solar energy conversion

Keming Ren[1]*, kren@uncc.edu, Dawn M. Marin*[2]*, Nicholas G. Grubich*[3]*, Justin M. Kolesar*[4]*, Sara J. Hall*[3]*, Michael G. Walter*[5]*. (1) Chemistry, UNC Charlotte, Charlotte, North Carolina, United States (2) Chemistry, UNC Charlotte, Charlotte, South Carolina, United States (3) UNC Charlotte, Charlotte, North Carolina, United States*

Porphyrins have demonstrated promising solar conversion efficiencies in devices such as dye-sensitized and organic bulk heterojunction solar cells. The inspiration of studying porphyrins comes from natural photosynthesis where chlorins absorb light and efficiently transfer energy. Porphyrins can be tuned to enhance visible light sensitivity and their excited state energy formation can be modified to improve exciton diffusion in thin film optoelectronic devices. In this study, new porphyrin materials have been pursued to elucidate how donor-acceptor materials affect exciton diffusion. Thiazolo[5,4-d]thiazole was chosen as a strong acceptor unit and bis(2,6-dioctoxyphenyl)porphinato zinc (II), was chosen as the donor material. Thiazolothiazole (TTz) has shown high free charge carrier mobilities and is readily accessed by condensing dithiooxamide with aromatic aldehdyes. TTz materials with ethynyl groups were coupled at the meso position of the dioctoxyphenylporphyrin to ensure effective conjugation between the porphyrin donor and TTz acceptor unit. Density functional theory (DFT) modeling of the donor-acceptor system shows that the highest occupied molecular orbital (HOMO) resides on the porphyrin unit while the lowest unoccupied molecular orbital (LUMO) is centered on the thiazolothiazole unit. Presented are several synthetic strategies and spectroscopic characterizations of these new donor-acceptor porphyrin materials.

2015 Joint Southeastern/Southwest Regional Meeting 590

Harnessing solar energy using poly(3-hexylthiophene) and a buckyball

***Phillip R. Pulley**, prp2p@mtmail.mtsu.edu, Dwight J. Patterson. Chemistry, Middle Tennessee State University, Chapmansboro, Tennessee, United States*

Survey of poly(3-hexylthiophene), P3HT, using chain-growth condensation polymerization and a buckminsterfullerene as the electron accepting end groups. It is common practice to use a Phenyl-C61-butyric acid methyl ester, PCBM, and P3HT blends in solar cells. The survey will characterize different molecular weights of P3HT using buckminsterfullerene as the electron accepting end groups. In the future, one will compare the results with different molecular weights of P3HT with PCBM electron accepting species. This survey will help to determine, if chain coupling the electron accepting molecule, buckminsterfullerene, without spacer units will change the electron transport properties of the composition, such as the power conversion efficiency.

2015 Joint Southeastern/Southwest Regional Meeting 591

Understanding thermal behavior and morphology of long chain alkylated porphyrins in excitonic solar devices

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Porphyrins are known for their useful photochemical properties due to their broad absorption spectrum and tunable optical properties. Long chain alkyl derivatives of carboalkoxyphenyl porphyrins show interesting thermal behavior upon heating solution-cast thin films. A detailed spectroscopic comparison study of carboalkoxyphenyl porphyrins containing methyl, butyl, hexyl, and octyl alkyl chains was performed using techniques such as UV-vis spectroscopy, photoluminescence emission, and time-correlated single photon counting (TCSPC). TCSPC measurements were performed on heated and non-heated films to observe the effects of thermal treatment on the emission lifetime (τ), exciton diffusion length (L_d), and quenching efficiency (Q). Exciton quenching studies were performed on thin film samples of long alkyl chain porphyrin derivatives by doping the porphyrin solution with 0.06% and 0.2% volume fractions of [6,6]-phenyl-C61-butryic acid methyl ester (PCBM). Differential scanning calorimetry (DSC) heating as well as cooling cycles were performed to observe the phase transition, while X-ray diffraction studies were performed on heated films and non-heated films to examine crystallinity and porphyrin film morphology. An understanding of self-organization (stacking), crystallinity, and phase changes in the porphyrin materials with thermal treatments has been pursued to link molecular orientation to exciton generation and diffusion. These studies provide useful insights into the relationship of porphyrin structure to thin film molecular orientation and will aid in engineering higher efficiency porphyrin-based solar cell devices.

2015 Joint Southeastern/Southwest Regional Meeting 592

Preparation and characterization of polylactic acid (PLA) nano-cellulose composites

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Polymer Matrix composites (PMCs) are comprised of a variety of short or continuous fibers bound together by an organic polymer matrix. PMCs use reinforcers to provide high strength and stiffness. There has been a growing interest and use of bio-derived and biodegradable polymers for the use in plastics, adhesives, coatings, and composites which would require a reinforcing or toughening phase in the systems. The use of a bio derived nanomaterial as a reinforcing phase would allow the production of a 100% bio derived PMCs. The development of renewable PMCs provides an alternative to composites created utilizing nonrenewable resources and address the issue of disposal. Trees and plants are an excellent source of bio derived nanomaterial for such PMCs. Trees and plants are nature's composites which rely on cellulose for their reinforcing phase. The cellulosic fibers are comprised of amorphous and crystalline regions which can be isolated by a number of processes leading to nanomaterials with an array of dimensions and accentuate properties. Cellulose Nano Crystals (CNCs) have modulus and tensile properties slightly higher than Kevlar^{TM}. However, the hydrophilic surface of the cellulose makes compatibility with many polymer systems difficult. Current research studies proved that coating the CNCs with lignin leads to a more thermally stable product. Lignin, also found in trees and plants cell walls, allows favorable interaction with a polymer leading to homogeneous dispersions by allowing lignin and cellulose to work together to provide stiffness and rigidity. Lignin coated cellulose nanocrystals (L-CNCs) have been introduced into many polymer systems by high torque melt mixing and radical polymerizations. Dynamic mechanical analysis (DMA) has shown a significant increase of modulus using L-CNCs as a nanofiller in bioderived polymers such as Polylactic acid (PLA), Polyhydroxybutirate (PHB), and polyolefins.

Structure-property relationship of ancillary benzyl containing ionic compounds: Insight for development of low melting organic salts

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A series of imidazolium based salts containing systematic variations in the attached benzene containing side-group were synthesized. The physico-chemical properties of the compounds were examined using a variety of methods including NMR, infrared spectroscopy (IR), dynamic scanning calorimetry (DSC), thermogravimetric analysis (TGA), and single crystal X-ray diffraction. Substitution of halogens in the ortho-, meta-, and para- positions on the benzene ring were found to dramatically change the melting point of the salts while maintaining equivalent thermal stability across the related series. Further, variations on the linking carbon chain between the imidazolium to benzene group were examined. It was observed that restricting thermal motion of these groups was found to increase the melting point of the salts likely due to steric interactions as observed in the solid-state. Anions were also varied in an effort to determine structure-property relationships of these new set of compounds. Finally, electrochemical

properties of the compounds were examined as a preliminary screening methods for potential use as electrolytes.

2015 Joint Southeastern/Southwest Regional Meeting 594

Structure and properties of a highly strained [2.2]naphthalenophane

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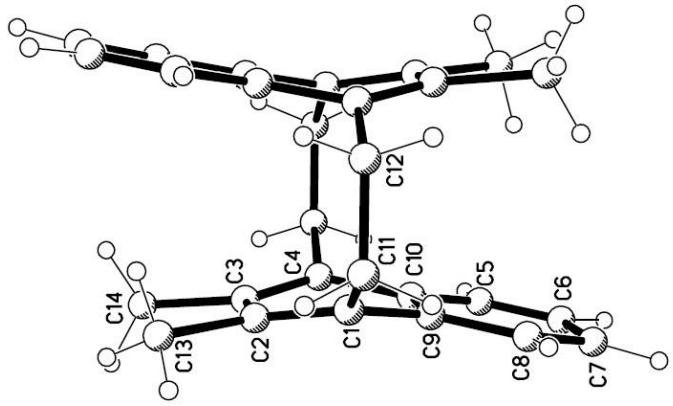
Strained organic molecules are of continuing interest for storing energy on a molecular level in a variety of applications, ranging from fuels and explosives to solar energy conversion. [2.2]Paracyclophanes are strained molecules, and in [2.2]naphthalenophanes some of this strain manifests itself in a significant distortion of the naphthalene moieties. Reductive elimination of 1,4-bis(bromomethyl)-2,3-dimethylnaphthalene (1) under Finkelstein conditions gave anti- and syn-[2.2](1,4)-2,3-dimethylnaphthalenophanes (2 and 3). Fractional crystallization has allowed the anti-isomer 2 to be isolated and a crystal structure obtained. The Me groups in 2 are located directly over the opposing naphthalene rings, which are held together closer than their normal Van der Walls distances. As a result, the naphthalene rings are even more distorted than in the parent [2.2]naphthalenophane. The effects of the unique structure of 2 on its spectroscopic and physical properties, and its reactivity, will be discussed.



2015 Joint Southeastern/Southwest Regional Meeting 595

Photocatalytic reduction of CO_2 to CO with Re-NHC complexes

Aron Huckaba, ***Emily A. Sharpe****, eaxsharpe@gmail.com, Jared H. Delcamp. Chemistry, University of Mississippi, University, Mississippi, United States*

The ability to transform CO_2 into a useable fuel source by energy efficient methods would have a remarkably positive impact on the global carbon economy. Solar energy is an ideal, renewable power source for this process. This project involves the synthesis and testing of air and water stable Re (I) pyridyl N-heterocyclic carbene (NHC) compounds for the photocatalytic reduction of CO_2 into CO using a simulated solar spectrum. The catalysts NHC ligands are known to be strongly bound to the catalyst center to promote long catalyst lifetime when compared with prior examples using pyridine ligands. The Re-NHC catalysts were quickly synthesized through three synthetic steps, stable under ambient conditions and were purified by standard silica gel chromatography. The presence and absence of two components, a photosensitizer *fac*-$Ir(ppy)_3$ and a strong electron donor BIH, were tested along with several catalyst to determine the photocatalytic system stability based on turnover number (TON) measurements for the conversion of CO_2 to CO. It was found that each of the five catalysts worked to reduce CO_2 to CO under conditions with the photosensitizer and BIH; however, the catalyst with the strongest electron withdrawing group substituted on the NHC aryl achieved high TONs with and without the use of the photosensitizer. TONs for this catalyst where shown to be higher than that of the benchmark photocatalyst $Re(bpy)(CO)_3Cl$.

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The reactivity of propargyl alcohols and propargyl acetates in the presence of trimethylsilyl trifluoromethanesulfonate

*Danielle N. Confair, **Chiles W. Downey**, wadedowney@post.harvard.edu. University of Richmond, Richmond, Virginia, United States*

Trimethylsilyl trifluoromethanesulfonate (TMSOTf) activates the propargyl positions of propargyl alcohols and propargyl acetates, allowing attack by various nucleophiles. Reactivity has been observed with triethylsilane, thiols, and ketones. If amine base is present, a ketone nucleophile can be converted to the enol silane, which will then attack the propargyl cation generated by the TMSOTf.

2015 Joint Southeastern/Southwest Regional Meeting 597

SAR studies directed at optimizing the anti-tumor activity of NT-7-16: Functional group changes at the 5-position of the pyrrole scaffold

***John T. Gupton*[1]*, jgupton@richmond.edu, Andrew Harrison[1], Scott Yeudall[1], Juekun Wen[1], Nakul Telang[1], Michael Wormald[1], Kristin Lescalleet[1], Susan Mooberry[2], Glen E. Kellogg[3], Cristina Rohena[2]. (1) Univ of Richmond, Univ of Rich, Virginia, United States (2) Science Center- Dept of Pharmacology, University of Texas Health, San Antonio, Texas, United States (3) Medicinal Chemistry, Virginia Commonwealth University, Richmond, Virginia, United States*

For some time our research group has been investigating highly substituted pyrroles as potent anti-tumor agents and inhibitors of microtubule formation. SAR studies directed at improving intrinsic bioactivity of this class of compounds by functional group modifications at the 5-position of the pyrrole will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 598

Effect of cooking methods on polyphenol content and antioxidant activity of kale

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The objective of this research was to determine the effects of three cooking techniques (boiling, steaming and baking) on polyphenol content and antioxidant activity of kale as measured by four analytical assays: the Folin-Ciocalteu method, Trolox equivalent antioxidant capacitiy (TEAC), ferric reducing antioxidant power (FRAP), and high performance liquid chromatography (HPLC). The results follow similar trends found in studies done on vegetables of the same species, *Brassica oleracea*. They support the most common method of preparation, steaming, to be the best method for preserving polyphenols and potentially increasing antioxidant activity as shown by FRAP, Folin-Ciocalteu, and HPLC data.

2015 Joint Southeastern/Southwest Regional Meeting 599

Synthesis and characterization of thermochromic pyridinium salts

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Isomeric cyanomethylpyridinium hexafluorophosphate salts were synthesized and characterized by microsopy, DSC, FTIR, UV/vis, and single crystal X-ray diffractometry. All isomers are found to exhibit a bathochromic shift in visible absorbance corresponding to an observed change in color from white or yellow at room temperature to red upon heating. Experimental methods, characteristic spectra, physical properties, and crystal structures of these interesting compounds will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 600

A prebiotic source of glyoxylic acid

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Glyoxylic acid, an alpha-keto acid, is a crucial molecule in multiple hypotheses regarding the chemical origins of life. For example, it has been suggested as a feedstock for a pre-citric acid cycle proto-metabolism. Although glyoxylic acid has been detected in interstellar space, and in electric discharge experiments, it is a strong electrophile and thus quite reactive. A demonstration of a renewable synthesis of glyoxylic acid in a prebiotic environment would make its inclusion in these hypotheses more viable. A potential autocatalytic synthesis of glyxolate from hydrogen cyanide polymer will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 601

Development of an active learning: General chemistry laboratory experiment on the identification of unknown halide salts for use as a recruiting tool during the first UNC Asheville NSF S-STEM “Chemistry First Prospective Scholars and Teacher Day”

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The goal of this project was to develop a general chemistry laboratory experiment to be used as a recruiting tool for high merit, first generation students from western North Carolina during the inaugural *Chemistry First Prospective Scholars and Teachers* (CFPST) *Day* at UNC Asheville. This laboratory experiment was designed to allow prospective scholars to experience what a typical general chemistry laboratory is like at UNC Asheville while providing regional high school teachers with an easily reproducible experiment that they could implement at their home institution. The experiment integrates quantitative and qualitative analysis through the use of three different experimental tests: precipitation, halogen exchange, and titration, to identify 3 unknown halide salts and a single unknown mixture. From these results the students are able to identify the chemical formula for each unknown by comparing the experimentally determined formula mass with that calculated for each group 1 and group 2 salt and devise a method for identifying which salts are in their mixture. To assess the effectiveness of the experiment on recruiting and teacher development pre-surveys and post-surveys were provided to all participants, which were analyzed to improve the experiment for the following years.

2015 Joint Southeastern/Southwest Regional Meeting 602

Involving high school students in summer chemistry research

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Three high school students performed summer research in chemistry on a local college campus. The goal was to give high school students a chance to participate in an authentic chemistry research experience. Over the course of two weeks, students were able to make progress in research that we plan to publish in a peer-reviewed research journal in due course. Students were assigned a project at the beginning of their research experience. One of the projects involved development of a modified Ritter reaction to prepare hindered amides. The other project involved development of a procedure using catalytic transfer hydrogenolysis of aldehyde derivatives to prepare amines.

2015 Joint Southeastern/Southwest Regional Meeting 603

Biosorption of cadmium from aqueous solutions using highly characterized peats

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The purpose of this research was to investigate the cadmium (Cd) biosorption potential of highly characterized peats from aqueous solutions. Six peat types were mixed with Cd solutions. Samples were tested unaltered, and after HCL treatment. Additional parameters tested include sample dose, contact time, mixing temperature, and the concentrations and pH of the Cd solutions. Desorption studies were performed to determine if the removed Cd could be recovered. In addition, tests were done to determine if the peats could be reused for additional Cd biosorption cycles. The results demonstrate that all six peat types worked well at biosorbing Cd from aqueous solutions

(36-100% removal). As sample dose increased, the percent of Cd removed increased (16-31% increase). As contact time increased, the percent of Cd removed increased slightly (1-10% increase). As the Cd solution concentration increased, the percent of Cd removed decreased for 2 of the 6 peats (19-23% decrease), while increasing slightly for 3 of the 6 peat types (1-4% increase). As the mixing temperature increased, the percent of Cd removed decreased slightly for 3 of the 6 peat types (1-5% decrease), while increasing slightly for the other 3 peat types (1-12% increase). As the pH of the Cd solution increased, the percent of Cd removed increased (16-56% increase). Desorption results showed a 34-71% Cd recovery rate. Reused peats were also highly effective at removing Cd (with or without going through desorption). Hence, these peats may be reused repeatedly for this purpose without becoming a hazardous waste disposal problem. Two of the 6 HCL-treated peats worked slightly better at removing Cd than did the untreated peats (4-7% better), while the other 4 peat types worked better in the unaltered state (3-18% better). Overall, the peat types tested demonstrated a great potential for biosorption of Cd from aqueous solutions.

2015 Joint Southeastern/Southwest Regional Meeting 604

Incorporation of titania into porous PMMA for photocatalytic applications

***Justin D. Glover**, jglover@erskine.edu, Joel E. Boyd. Department of Chemistry, Erkskine College, Due West, South Carolina, United States*

Porous poly(methyl methacrylate) infused with commercially prepared titania nanoparticles has been previously developed for photocatalytic applications. This material has been made in the past by mixing PMMA, acetone, and Tween surfactant together, and then spraying a titania-water dispersion onto the PMMA-acetone solution to coagulate the porous PMMA matrix. Incorporation of the titania directly into the PMMA-acetone solution prior to coagulation with distilled water, produces porous composite photocatalytic materials with a higher titania to PMMA ratio and reduced titania loss during sample preparation and initial photocatalytic use. Photocatalytic activity was evaluated by the decolorization of the organic dye methyl orange. Samples prepared by adding the titania directly to the PMMA-acetone solution have 50% greater photocatalytic degradation rates than those prepared with titania incorporated into the water spray when comparable amounts of titania are used. These new materials are thus more photocatalytically active and possess a higher titania retention ability than the previous materials, and will enable the production of more efficient photocatalytic reactor systems.

2015 Joint Southeastern/Southwest Regional Meeting 605

Synthesis and antimicrobial evaluation of an α-methylalanine analog of puromycin

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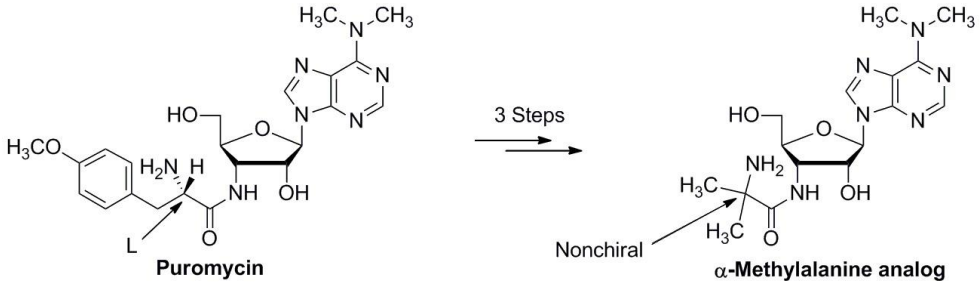
The peptidyl nucleoside antibiotic puromycin has been used to probe the active conformation of peptidyl transferase, the catalytic core of the ribosome. It is generally accepted that ribosomes catalyze the incorporation of L-amino acids into proteins in

stereospecific fashion, and puromycin analogs bearing the natural configuration at the aminoacyl moiety are generally active, whereas a D-like configuration produces inactive analogs. However, chiral discrimination during translation is not uniquely associated with the geometry of peptidyl transferase, and recent studies point to an unexpected plasticity of its catalytic center. In order to probe this plasticity, we designed and synthesized a nonchiral α-methylalanine analog of puromycin where a methyl group replaces the α-hydrogen of alanine. Evaluation of the title compound on *Staphylococcus Epidermidis* and multi-drug resistance *Staphylococcus Aureus* cells is in progress and results will be presented.



2015 Joint Southeastern/Southwest Regional Meeting 606

Effectiveness of various visual cues included in video instruction on pre-laboratory preparation in the general chemistry laboratory

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The increased use of video instruction in introductory laboratories requires understanding how students use the videos to prepare for the laboratory. Video can be watched passively, so strategies to increase engagement are expected to improve pre-laboratory preparation. A control/treatment experimental design was implemented to determine whether visual cues embedded within the videos increase the number of key terms and ideas that are recorded in the laboratory notebook. Qualitative examination of the notebooks was also implemented to assess whether the recorded information was expected to be useful in the completion of the laboratory. Three visual cues were implemented throughout the term: no visual cue, a simple icon, and a text box. Differences in the quality of pre-laboratory notes recorded in student laboratory notebooks were scored according to a rubric and compared based on which version of the video they were assigned for the week. This poster will present the results of the statistical analysis and will aim to increase knowledge on best practices for video instruction.

2015 Joint Southeastern/Southwest Regional Meeting 607

A comparison of interaction energies in 2-cyano-1-methylpyridinium salts

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A series of 2-cyano-1-methylpyridinium salts was synthesized. Following crystal growth, their crystal structures were determined using single crystal X-ray diffraction. In order to learn more about how different types of non-covalent forces contribute to the various architectures observed in these compounds, the interaction energies between ions in each salt were calculated using density functional theory with GAUSSIAN09. These energies were further analyzed using Symmetry Adapted Perturbation Theory (SAPT) calculations. Computationally optimized vs. experimentally observed ion pair geometries, along with other interesting results across the family of compounds, will be presented. Anions studied to date include halides, nitrate, tetrafluoroborate, perchlorate and hexafluorophosphate.

2015 Joint Southeastern/Southwest Regional Meeting 608

GPR88 modeling and antagonist discovery

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GPR88 is an orphan GPCR that is emerging as a therapeutic target for the treatment of schizophrenia and bipolar disorder. Studies have shown that inhibiting GPR88 is a possible way of treating schizophrenia and bipolar disorder. Currently there are no known antagonists that act on GPR88 to be tested as treatments for schizophrenia and bipolar disorder. Current treatments for these diseases have proven to not be fully effective and also produce unwanted side effects in patients. Using GPR88 as a target for treating schizophrenia and bipolar disorder would provide a more targeted treatment with potentially fewer side effects because GPR88 is only found in the striatum. A homology model of GPR88 using the PDB entry 2VT4 as a template was created and displayed interactions with known synthetic agonists that were consistent with potency trends. Because of the length of time to get a new pharmaceutical on the market in the absence of prior studies in humans, approved pharmaceuticals for other indication were examined for potential repurposing for the treatment of schizophrenia and bipolar disorder. A set of 187 approved pharmaceuticals was docked into the GPR88 homology model to test for binding to the receptor. Pharmaceuticals with the best results were then examined for potential side effects as well as their current use. A prioritized list based on computational screening results was created to guide future experimental screening for GPR88 antagonists.

2015 Joint Southeastern/Southwest Regional Meeting 609

Analysis of telomere fragments from various apoptotic cancer cell lines

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In this study, magnetic bead capture was used to determine whether differences exist in the telomere fragmentation pattern of various breast cancer cell lines ranging from normal healthy cells to precancerous stage 1- stage 4 during apoptosis. Streptavidin coated magnetic beads, in conjunction with biotin labeled PNAs, were used to measure

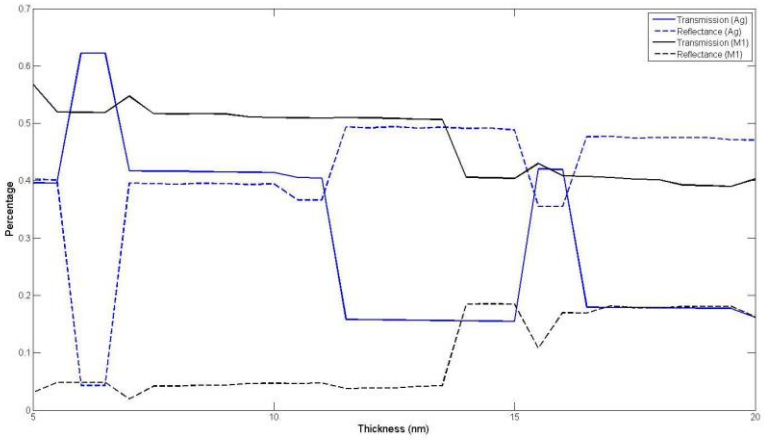
the amount of telomeric DNA captured. In addition, fragment lengths and sequencing were analyzed using a sequencing facility. The results of these procedures will provide both qualitative and quantitative characteristics of the telomeric fragments released from the various cancer stage cell lines. This information could eventually give insight into disease progression and possible stage diagnosis for breast cancer. Furthermore, this study could be conducted with different types of cancer cell lines to determine whether the findings can be generalized to all types of cancers.

Heat-reflecting window coatings: Improved design with novel materials

***Jennifer Zou**, zou16j@ncssm.edu. North Carolina School of Science and Mathematics, Chapel Hill, North Carolina, United States*

Optical filters for window coatings, composed of alternating layers of dielectric and metallic materials, are designed to achieve heat-reflecting properties, through the reflection of infrared light (>750 nm) while maintaining high transparency of visible light (380-750 nm). The performance of a 7-layer structure composed of alternating materials, indium tin oxide (ITO) and silver (Ag), was simulated using a finite-difference time-domain (FDTD) solver in the range of 300 to 1500 nm. Comparison to experimental optical filter performance demonstrated great agreement, validating our model [1]. We then substituted the silver layers with an idealized metal (M1)—a material with an electron concentration of $5x10^{14}$ electrons/cm^2—and analyzed the performance of the two optical filters. The 7-layer structure with the new material (M1) attained an integrated visible transmission value 38% higher than the traditional filter in the visible spectra (380-750 nm). Furthermore, we optimized the performances of 5-layer ITO/Ag and ITO/M1 optical filters by varying the metal layer thicknesses. We found that the ITO/M1 device displayed higher visible transmission values and comparable infrared reflection values across a wide range of layer thicknesses, suggesting that the ITO/M1 is more reliable. Similarly, optimized 3-layer ITO/Ag and ITO/M1 optical filters demonstrated significantly higher and more consistent visible transmission values across various metal thicknesses. We demonstrate the improved performance of heat-reflecting window coating structures by substituting traditional silver with our idealized metal.

[1] Hood et al, Color-Corrected Heat-Reflecting Composite Films and Glazing Products Containing the Same. U.S. Patent 5,071,206, Dec 10, 1991.



Plot of integrated visible transmission (380-750nm) and IR reflectance (750-1500nm) for 5-layer ITO/Ag and ITO/M1 structures across a thickness range of 5 to 20 nm for Ag and M1.

2015 Joint Southeastern/Southwest Regional Meeting 611

Protein modeling using 3D printing

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In an effort to help illustrate abstract concepts to students, an increasing number of schools and universities are incorporating commercial 3D printers into course curriculum to bolster the development of teaching tools. Due to a steep learning curve and the often complex multi-step file conversions required, however, users can be disappointed with the initial results of 3D printing.
At Texas Wesleyan University, High school students—supported by the American Chemical Society's Project SEED program—developed a single-step procedure to convert Protein Data Bank (.pdb) files into 3D-printed objects. Using Chimera[1], a structure describing dihydrofolate reductase (DHFR) was prepared and successfully printed.[2] This simple process is a vast improvement over other published, multi-step protocols.
DHFR is a focal point of biochemistry curriculum at Texas Wesleyan University, used to convey vital biochemical concepts in both the lecture and lab environments. DHFR is an essential enzyme found in all organisms. It is necessary for cell proliferation, growth and replication.[3] DHFR catalyzes the conversion of dihydrofolate to tetrahydrofolate—an important precursor in purine, thymidylic acid and amino acid synthesis. DHFR is an active drug target with prescriptive antibiotic and chemotherapy agents to treat bacterial infections and cancer, respectively.

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2015 Joint Southeastern/Southwest Regional Meeting 612

Synthesis and characterization of novel polyamide thin film composite reverse osmosis water desalination membranes

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The synthesis and characterization of Novel Polyamide Thin-Film Composite (TFC) Reverse Osmosis Membranes using various synthesized and purchased diamines is described in this presentation. Purchased amines used in this research included m-Phenylenediamine (m-PD) and melamine, while synthesized monomers were prepared from the reactions of m-PD with cyanuric chloride (3-TAPTT) as well as m-aminophenol (mAP) with dichlorodiphenylsulfone (DCDPS). Each amine compound was dissolved in water and reacted via interfacial polymerization with trimesoyl chloride (TMC) in dodecane to form the desired TFC membrane. ^{1}HNMR showed the successful synthesis of 3-TAPTT monomer by the appearance of the peaks at 4.0 ppm and 5.77 that correlates to the proton on the N-H group and on the carbon adjacent to the N-H group. ATR-FTIR showed successful synthesis of the all polyamide membranes with the appearance of peaks between 1638 -1685 cm^{-1}. Water permeation and salt rejection of the membranes will be determined via crossflow filtration at the University of Texas at Austin.

2015 Joint Southeastern/Southwest Regional Meeting 613

Synthesis of phosphonated biphenol precursors for polymer composite membranes for fuel cell applications

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The current study describes the synthesis and characterization of a phosphonated biphenol precursor (PBP) to be used in poly(arylene ether sulfone) copolymers for application as proton exchange membranes in fuel cells. PBP was synthesized by reacting biphenol with triethylphosphite in the presence of bromine and zinc bromide followed by acid hydrolysis. The successful synthesis of PBP was confirmed using ^{1}H NMR and ^{31}P NMR through the appearance of peaks at 12 ppm (^{1}H NMR), signifying the O-H proton of the phosphonic acid moeity, and 2.6 ppm (^{31}P NMR) for the phosphorous in the phosphonic acid moeity of the PBP molecule.

2015 Joint Southeastern/Southwest Regional Meeting 614

Synthesis and characterization of novel polyamide thin film composite reverse osmosis water desalination membranes

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Polyamide thin film composites (TFC) are the most widely used membranes in desalination. TFCs for reverse osmosis (RO) desalination are multilayered membranes comprised of ultra-thin skin polyamide top layer (20-100 nm) on top of a polysulfone porous support and reinforced by a non-woven fabric. The polyamide top layer is formed via interfacial polymerization of a diamine (e.g. *m*-phenylene diamine, MPD) in aqueous phase and di- or –tri- chloride (e.g. trimesoyl chloride, TMC) in organic phase. TFC membranes offer additional advantages such as high selectivity and fluxes, enhanced stability over larger pH range and higher temperatures, and reduced fouling. The major limitation of polyamide TFC membranes is their sensitivity to chlorine which has been proposed to degrade by chlorination first undergoing N-chlorination through chlorine attack on amidic nitrogen followed by ring chlorination through intermolecular rearrangement.
The purpose of this research was to prepare various TFC membranes using both purchased and synthesized diamine monomers and trimesoyl chloride (TMC) with improved water performance. The synthesized monomers prepared included: 3,3 Disulfonic acid – bis[4-(3-aminophenoxy)phenyl]sulfone (SA-DADPS) and 4 – aminophenyl – 1,3,5 – Triazine – 2,4,6 – Triamine (4-ATT) interfacial polymerization occurred at room temperature. Infrared Attenuated Total Reflectance (IR ATR) verified polymer synthesis by the appearance of the amide peak at 1580-1585 cm^{-1}, salt rejection and chlorine tolerance tests will be carried elucidate the water performance characteristics of the membranes.

2015 Joint Southeastern/Southwest Regional Meeting 615

Synthesis and characterization of biphenol based monochloro-1,3,5-triazine (BP-TT) monomer precursors for disulfonated poly(arylene ether sulfone) hybrid copolymer preparation

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Fuel Cell is a device that converts the chemical energy of a substance into electrical energy. Fuel cell's advantage over the conventional types of energy is that it does not produce carbon dioxide as a byproduct. Hydrogen is most often used as a source of chemical energy and therefore the only products of the reaction are water and heat. Currently the most widely used membranes is Nafion®, a perfluorinated sulfonic acid copolymer. Perfluorinated membranes are costly to produce and perform the most efficiently at temperatures 100℃ and above. Poly(arylene ether sulfone) copolymers can be place in the membrane as a better alternative. Our research consists of the synthesis of monochloro-1,3,5-triazine (BP-TT) hybrid monomer using biphenol and cyanuric chloride. BP-TT monomer will be used to polymerize. The successful synthesis of BP-TT monomer was demonstrated using 1HNMR due to the appearance of intense peak at 7.25 ppm, which shows that there is a linkage between the cyanuric chloride and biphenol.

2015 Joint Southeastern/Southwest Regional Meeting 616

Synthesis of hydroquinone based poly(arylene ether sulfone)-2,4,6-monochloro-1,3,5-triazine hybrid coploymers

***Jazmin Ewers**, jaz014min@yahoo.com, Natalie Arnett. Fisk University, Nashville, Tennessee, United States*

The future of clean energy relies on innovative, efficient, and inexpensive technology such as the fuel cells. Currently the polymer electrolyte membrane or proton exchange membrane (PEM) fuel cell is the most commonly used fuel cell despite its high cost and limited operational temperature. The purpose of this research was to synthesize hydroquinone monochloro-1,3,-triazine (HQ-MT) novel hybrid monomer to be used in the preparation of poly(arylene ether sulfone) (PAES) hybrid copolymers. The objective of incorporating the HQ-MT monomer into the PAES backbone is to have available site for post modification to increase its efficiency in fuel cells. Under current investigation, HQ-MT was synthesized by reacting hydroquinone and cyanuric chloride by a slurry method. ^{1}H NMR showed the successful synthesis of HQ-MT monomer by the appearance of peaks at 7.5 and 6.4ppm that signifies the carbon-carbon connection between hydroquinone and cyanuric chloride.

2015 Joint Southeastern/Southwest Regional Meeting 617

pH and salinity dependence of copper leaching from anti-fouling marine paints

***Donald W. Carpenetti**, carpenettid@cravencc.edu, Aaliyah C. Martin, Christian Rust. Math & Science, Craven Community College, New Bern, North Carolina, United States*

Anti-fouling paint or bottom paint is a specialized coating applied to the hull of a ship or boat to slow the growth of organisms that attach to the hull and can affect a vessel's performance and durability. One method used to discourage the growth of barnacles, mussels, algae and other marine organisms, is the incorporation of biocides into the paint. Paints containing the biocide tributyl tin were outlawed in the 1990's due to the tin being highly poisonous to underwater ecosystems. Tin based anti-fouling paints have since been largely replaced by copper based paints. Copper based bottom paints actively leach into the surrounding water to deter the growth of marine organisms, but potentially similar to tin, if the copper levels in the water column reach high enough levels there can be a toxic effect on marine organisms in the water or in bottom sediments. Washington State has passed a ban on the use of copper-based anti-fouling paints on private recreational boats to take effect January 1, 2020. This study evaluates the extent to which copper leaches from a painted surface into surrounding water by analyzing copper concentration over time in a water sample in contact with a painted surface. Also addressed will be how the rate of leaching is influenced by other environmental factors such as the water pH and salinity levels.

2015 Joint Southeastern/Southwest Regional Meeting 618

Investigating the effects of disaccharides on bacteria

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Colonies of e-coli were treated with various concentrations of disaccharides and stored at -20 °C. After thawing the survival rate of colonies was determined and the effect of varying sugar hydrophobicity on the survival rate will be discussed. The results of these

experiments and experiments to examine bacteria growth at 37°C in varying concentrations of sugars will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 619

Creation of an ELN for quantitative analysis

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Using LabArchives an electronic lab notebook (ELN) was created and tested for use in Quantitative Analysis. The advantages and disadvanteges of using an ELN for Quantitative Analysis will be discussed. This includes information into the preparation of the notebook prior to student use and the ease of use by students performing the labs.

2015 Joint Southeastern/Southwest Regional Meeting 620

ASU ACS chapter community outreach: Educating local students

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The Aranksas State University ACS chapter is dedicated to spreading the understanding and joy of chemistry to the local college population. Our secondary mission, is dedicated to educating and exciting local highschool and elementary students about chemistry and science. Our goal is to excite students to become future scientist and innovators. Several community activities and their sucssess are disscussed.

2015 Joint Southeastern/Southwest Regional Meeting 621

Toxic chemical emissions in smoke produced via burning of scrap tires, firewood, and liquefied petroleum gasoline as fuel sources for singeing meat

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This pilot study was conducted to determine the presence (or lack thereof) and concentrations of toxic chemicals emitted through smoke produced via burning of scrap tires, firewood, and liquefied petroleum gasoline (LPG), which are commonly used as fuels for singeing meat intended for human consumption in Ghana. Benzene, carbon monoxide (CO), and other selected pollutants were characterized through longitudinal analysis. The concentrations of these pollutants were quantified over time, using a Chip Measurement System (a multichannel, analyte-specific, colorimetric quantification technique). This system is field-practical and provides immediate results at time of sampling.

Analysis was conducted at six different locations in Ghana, where animal carcasses are processed for human consumption. Four locations (slaughterhouses) use tire-derived fuel, and the fifth (mechanized abattoir) uses LPG, while the sixth uses firewood to singe the meat. The levels of pollutants from the tire-based smoke were compared with

data from the LPG-derived smoke (control) and WHO standards. Weather conditions such as temperature and humidity were also measured using a hygrometer to determine their potential effect(s) on the chemical composition of the smoke. Other factors that were examined include: the estimated number of tires used at each site per day, the tire brands or sources at each location, the number of operators at each slaughterhouse/abattoir, and the number and species of animals processed at each location per day. These variables were determined by worker surveys, which allowed for field-practical data collections.

Overall, the average benzene levels in smoke produced from burning of scrap tires and firewood were 3.536 and 1.243, respectively. CO concentrations were 128.667 and 130.857 for scrap tires- and firewood-derived smoke, respectively. The pollutant levels of the LPG derived samples were below detectable limits.

The detectable presence of benzene and CO in tire-derived smoke indicates the need for further research and policy. The goal is to create a solid, data-driven policy and generate viable alternatives regarding meat processing in affected countries.

2015 Joint Southeastern/Southwest Regional Meeting 622

Flipping pre-labs for organic chemistry

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Three hour organic chemistry labs seem daunting to the student and laborious for the instructor. If the pre-lab assignment is given a week beforehand, students often forget key details or forget the entire lab. On the other hand, if pre-lab is given immediately before lab, students tend to be much less prepared. With both scenarios, too much time is wasted in figuring out what is going on in lab. Students are already turning to YouTube® and the internet for lab videos but are confused when the instrumentation and experiment setup doesn't look exactly the same in lab. This year, we decided to maximize lab time and flip the pre-lab. Short videos were made to introduce lab techniques and to highlight where the experiment might go "wrong" and what to "look" for. The videos are available all year and students can access them multiple times. We are assessing the use and usefulness of the videos through online surveys and pre-lab quizzes.

2015 Joint Southeastern/Southwest Regional Meeting 623

Investigating the effect of the dispersant Corexit 9500A on the movement of an oil-in-water emulsion through an Alabama beach sand

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A majority of Alabama's 60 miles of beaches were exposed to the crude oil released from the massive 2010 Deepwater Horizon oil spill. To help remediate the spill, BP sprayed the dispersant, Corexit 9500A, over the floating oil in the Gulf and at the subsurface damaged Macondo wellhead. This dispersant could have promoted an oil-in-water emulsion which infiltrated deeper into the exposed beach sand than the oil

alone. A series of short column tests of packed beach sand in glass columns simulated the arrival of an oil-in-water emulsion at the beach. Prior to the tests, the oil was subjected to two conditions to volatilize the light hydrocarbons. Fraction 1 (F1) was the crude oil fraction that did not distill below 70 degrees C at 0.86 atm. Fraction 2 (F2) was the crude oil fraction that did not distill below 250 C and 0.86 atm. Using these two fractions, 10 mL of 21% oil-in-water emulsions were loaded on columns containing 20.0 g of dry beach sand. The columns were washed with either 100 mL of salt water or 100 mL of salt water containing Corexit at its critical micelle level of 2%. The emulsion formed from the F2 fraction penetrated deeper into the sand as compared to the F1 fraction. Salt water alone removed only negligible amounts of oil from either fraction. Salt water with Corexit removed 0.14 g of oil from the F1 treatment column and 0.70 g from the F2 column. These results indicate that Corexit would not be an effective agent for beach remediation following a crude oil release.

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The development of 3D printed materials for selective growth of ZnO nanorods with applications in photovoltaics

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The development of solar energy has become increasingly popular over the last few decades with an intense focus to decrease the cost of manufacturing while simultaneously increasing the power conversion efficiency. Our project uses novel approaches to accomplish these goals such as low temperature growth of ZnO nanorods as an n-type material grown on indium tin oxide (ITO). However, ordered growth in localized regions of ITO can be difficult to control. Both carbon tape and photolithography had their advantageous, yet they both left residues and caused concern for contamination. Therefore, we utilized 3D printing to solve the issues of localized growth with minimal contamination. Various filaments printed using the Makerbot Replicator 2X were tested and the results showed promising applications. The structures made from the different materials were tested to withstand heat, high pH, as well as maintain shape during the chemical bath deposition of ZnO nanorods. EDX was used to test for contaminants on the surface of the printed materials as well as the grown rods with the results pointing to zero interference from the printing filament. The design of the sample holders were also shown to somewhat prevent Zn that is sputtered onto the substrate, as well as growth of nanorods, on sections that were masked. Overall, this 3D structure is an improvement over carbon tape and photolithography methods we employed. It is anticipated that using 3D printing to aid in fabricating solar cell devices will expedite their future development.

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Nature of metal ion mediated second shell hydrogen bonds

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We investigate the role of induction effects in a zinc ion mediated second-shell hydrogen bond that plays a critical role in the mechanism of allosteric regulation in the paradigm sensor protein *Staphylococcus aureus* CzrA. These effects have been observed at other metal binding sites (MBSs). Natural Bond Order (NBO) and Symmetry-Adapted Perturbation Theory (SAPT) calculations on MBSs adopted from various proteins find that charge transfer (CT) effects withdraw greater charge from atoms participating in hydrogen bonding in the presence of Zn(II) than in the apo state. Polarization may play a significant role in helping strengthen the metal ion mediated hydrogen bond in CzrA and other metal sensor proteins. Furthermore, we find that ligand identity has an effect on second-shell hydrogen bonds.

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Structural perturbations induced by aflatoxin adducts in DNA

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Aflatoxin B_1 (AFB_1) is the predominant mutagenic fungal metabolite produced by *Aspergillus flavus*. Dietary exposures to AFB_1 are strongly implicated in the etiology of human hepatocellular carcinomas. AFB_1 is metabolized in the liver to AFB_1-exo-epoxide, which alkylates DNA regioselectively at N^7-dG, yielding the N7-deoxyguanosine adduct trans-8,9-dihydro-8-(N7-guanyl)-9-hydroxyaflatoxin B_1 (AFB_1-N7-Gua). This adduct can undergo base-catalyzed hydrolysis to yield the persistent and highly mutagenic formamidopyrimidine (AFB_1-FAPY) adduct. The structural biology of the AFB_1-FAPY DNA adduct is complex. It equilibrates between α and β deoxyribose anomers. While the β anomer is favored in duplex DNA, this equilibrium shifts toward the a anomer in single-strand DNA. The β anomer is associated with the high levels of G to T mutations caused by this lesion, whereas the α anomer blocks DNA replication. The AFB_1-FAPY adduct also equilibrates between *E* and *Z* rotamers of the formyl moiety. The position of this equilibrium depends upon the identity of the 3′-neighboring nucleotide. With the Y-family Dpo4 polymerase, error-free bypass and extension is observed for AFB_1-N7-Gua. In contrast, error-prone bypass involving mis-insertion of dATP and extension is observed for the AFB_1-FAPY adduct. The misinsertion of dATP correlates with the characteristic G to T mutations arising from cellular AFB_1 exposures. For both AFB_1-N7-Gua and the AFB_1-FAPY derivative, the 5'-intercalation of the AFB_1 moiety relative to the alkylated dG is maintained during DNA replication, as is the b deoxyribose anomer; however, the geometries of the lesions differ within the active site of the polymerase. The structural data provide an explanation as to why the AFB_1-N7-Gua adduct is replicated successfully but the AFB_1-FAPY adduct is replicated in an error-prone manner. Supported by NIH grant CA-55678 (M.P.S.).

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Structure and dynamics of DNA containing single ribonucleotide damage

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Ribonucleotide monophosphates (rNMPs) represent the most common nonstandard nucleotide in genomic DNA. Although the ribonucleotide excision repair is efficient in removing rNMPs, mutations in the repair enzyme ribonuclease H2 (RNase H2) and the subsequent accumulation of ribonucleotides in the genome has been linked to the immune diseases Aicardi-Goutières syndrome (AGS) and recently systemic lupus erythematosus (SLE). The presence of a reactive hydroxyl group in the ribose ring of the embedded rNMP can contribute to genomic instability through backbone cleavage or structural perturbation, consequently impeding DNA replication or transcription and leading to mutagenesis. We are interested in characterizing the structural effects of this damage on short DNA sequences using Nuclear Magnetic Resonance (NMR) spectroscopy and molecular dynamics (MD) to better understand the underlying molecular basis of these and other associated diseases. While the lesion is well tolerated, we show by ^{1}H and ^{31}P NMR asymmetric localized deviations in the rNMP containing DNA 3' of the lesion; this results in altered sugar conformations and backbone torsion angles in nearest and next-nearest neighbors. Additionally, the degree of perturbation varies with sequence, as seen in the ^{31}P Δδ, where the largest shift is 1.3 ppm for one sequence and 0.4 ppm for a different sequence, both containing single rGMPs at the core, suggesting an important sequence dependence effect which may impact recognition and repair.

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H NMR solution structure and biophysical characterization of aminoglycoside interaction with Sp1 transcription factor consensus sequence 5'-d[(G/T)GGGCGG(G/A)(G/A)]

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As a transcription factor, specificity protein 1 (Sp1) and its consensus sequence hold promise as therapeutic medicinal targets.[1-3] While the Sp1 protein's NMR solution structure and the X-ray crystal structure for the Sp1 consensus sequence; 5'-d[(G/T)GGGCGG(G/A)(G/A)], have been published, an NMR solution structure for 5'-d[(G/T)GGGCGG(G/A)(G/A)] has not yet been determined.[4, 5] Tangentially, aminoglycosides have been shown to be major groove binders that exhibit higher affinity for A-form nucleic acid structures.[6] In accord, Sp1's consensus sequence's G-C rich A-form global structure presents an opportune target for the identification of potential aminoglycoside-conjugate therapeutic agents. With these principles in mind, the ^{1}H NMR solution structure determination of four Sp1 consensus sequence mimics (5'-dG4CG3A, 5'-dG4CG4, 5'-dTG3CG3A, and 5'-dtG3CG4) , ^{1}H NMR structural analysis of their respective paromomycin complexes, and accompanying biophysical interaction data are presented.

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A repeated and folded DNA sequence and its fluorescent silver cluster adduct

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Silver clusters with ≲30 atoms are molecules with diverse electronic spectra and wide-ranging emission intensities. Specific cluster chromophores develop within DNA strands, and we consider the DNA scaffold for one such chromophore with blue-green spectra. The ~20-nucleotide strand has two components - a cluster domain (S1) that stabilizes silver clusters and a recognition site (S2) that hybridizes with complementary oligonucleotides (S2C). The hybridized S1-S2:S2C forms an emissive species with I_{ex}/I_{em} = 490/550 nm via a precursor cluster, and our studies focus on the *sequence* and *structure* of the S1 cluster domain. From the sequence perspective, the cluster binding site is organized into repeating C_4X sequences with X = adenine, thymine or guanine, and three factors shape the DNA environment: the number of C_4X repeats, the identity of the X nucleobase, and the number of contiguous cytosines. Distinct environments are reflected in the electronic spectra of their cluster adducts, and these studies identify the optimal S1 sequence C_4AC_4T with two C_4X repeats and X = adenine and thymine. From the structure perspective, two factors direct the DNA conformation: hybridization with the S2C complement and folding by the cluster adduct. C_4AC_4T-S2 hybridizes with S2C and retains a single-stranded C_4AC_4T component. Thermal and isothermal spectroscopic studies and alternate complements suggest that these exposed and unpaired nucleobases coordinate the blue-green cluster. However, the secondary structure of the DNA changes. Chromatography studies and constrained DNA constructs show that the blue-green adduct condenses its C_4AC_4T template. The overall conclusion from our studies is that DNA sequence and structure are linked. We propose that the 2 C_4X components are crosslinked by the intervening blue-green cluster. We discuss this crosslinking in relation to near-infrared clusters.

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Construction of diverse synthetic antibody library for therapeutic antibody optimization

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Antibody libraries are typically obtained from pathogen stimulation of a host system, such as mouse or disease human B-cells. The pool of antibodies is used to isolate antigen-specific antibodies after a long tedious process. The obtained antibodies suffer

from problems of low affinity of binding, thus poor specificity and selectivity. Various mutagenesis methods have been introduced to expand the diversity of antibody pools by introducing DNA sequence variations for antibody genes. We have developed an efficient work flow for creating synthetic monoclonal antibodies with precisely controlled CDR sequences and thus designed antigen binding sites. This allowed the use of the abundant sequence information of antibodies with known high binding affinity and specificity. We overcome the difficulties that the exceedingly large designed CDR oligonucleotides would be expensive and slow to obtain by introducing a new generation of microchip based parallel synthesis technology. Which allow parallel synthesis of millions of oligonucleotide of designed sequences on a single microchip. i.e., traditionally, a single oligo nucleotide is made at one location of a microchip. In the second generation microchip for oligonucletoide technology, multiple oligonucleotides (upto 1,000 different sequences of designed context) are synthesized at one location. The resultant CDR oligonucleotides are incorporated into mAb antibody expression plasmid for construction of antibody library reaching diversity in tens of millions. The method has been used to construct anti ERBB2 (HER2) libraries. The screening experiments generated new antibodies of improved properties compared to herceptaine, which is clinically prescribed therapeutic antibody for treatment of HER2 expression breast cancers. The efficient generation of rationally designed antibody libraries allowed possibilities of improving the effectiveness and the biosafety of the existing antibody therapeutics in short amount of time.

Using NMR combined with molecular dynamics to link structural and dynamic effects of the universal base 8-aza 7-deaza N8-linked adenine analog

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A truly universal nucleobase enables a host of novel applications such as simplified templates for PCR primers, randomized sequencing, and DNA based devices. A universal base must pair indiscriminately to each of the canonical bases with little or preferably no destabilization of the overall duplex. In reality, many candidates either destabilize the duplex or do not base pair indiscriminatingly. The novel base 8-aza-7-deazaadenine (pyrazolo[3,4-d]pyrimidin- 4-amine) N^8-(2'deoxyribonucleoside), a deoxyadenosine analog (UB), pairs with each of the natural DNA bases with little overall destabilization or sequence preference. We have utilized NMR complemented with molecular dynamic calculations to characterize the structure and dynamics of a UB incorporated into a DNA duplex. The UB participates in base stacking with little to no perturbation of the local structure yet forms an unusual base-pair that samples multiple conformations. These local dynamics result in the complete disappearance of a single UB proton resonance under native conditions with little to no impact on any other resonances in the UB or flanking residues. Accommodation of the UB is additionally stabilized via heightened backbone conformational sampling. Surprisingly, despite the multiple base-pair sampling and heightened backbone dynamics, the local and global structure of the DNA oligonucleotide are remarkably unperturbed. This combination of NMR with various computational techniques has allowed for a comprehensive

characterization of both structural and dynamic effects of the UB in a DNA duplex and underlines that the UB as a strong candidate for universal base applications.

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Site-specific DNA methylation targeted to androgen receptor-positive cells

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In our ongoing effort to design new alkylating molecules that can selectively target specific cancers, we have been developing compounds that can bind to specific proteins in the targeted tumors, and cause site-specific, cytotoxic, DNA damage in those cells. These molecules have the potential to improve the efficacy and minimize the side-effects currently seen in clinically used DNA-alkylating chemotherapy drugs. We recently reported the design and properties of molecules targeting breast-cancer cells. We now present the development of novel compounds that can target the androgen receptor which is over expressed in prostate cancer cells. These new compounds produce predominantly N3-methyladenine DNA adducts, show increased uptake and selective toxicity in prostate cancer cells. The design, synthesis, characterization of the chemical reactivity with DNA, and cellular toxicity of these compounds will be presented.

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A proaromatic thienothiophene building-block for dye-sensitized solar cells

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Dye-sensitized solar cells (DSCs) are a promising, low-cost technology for the generation of electricity from solar energy. Power conversion efficiencies (PCEs) have benefited tremendously from the development of building blocks for the common donor-π bridge-acceptor (D-π-A) dye design with this design now giving the top efficiency dyes. The development of building blocks for this configuration that allow extended solar access is critical to improving PCEs. Proaromatic building blocks are known to stabilize excited-state oxidation potentials of small molecule systems used in DSCs, thus reducing their optical band gap and allowing absorption farther into the NIR region of the solar spectrum. One such building block, 3,4-thienothiophene (3,4-TT), has experienced limited use in DSCs due to a drastically low excited-state potential, leading to poor open-circuit voltages (V_{OC}). Through judicious physical organic-based dye designs incorporating 3,4-TT, prohibitively low excited-state potentials have been raised to operative energy levels and PCEs were significantly increased from 3.7% to 7.4% when compared to prior uses of 3,4-TT.

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Thieopyrazine as a proaromatic building block for NIR organic dyes and their use in DSCs

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Metal-free dyes in dye-sensitized solar cells (DSCs) have shown great improvements in the past two decades. Because of these improvements, DSCs are a promising technology to overcome future energy challenges. The dye plays a critical role in DSCs and is ideally responsible for absorbing photons throughout the visible and near-infrared (NIR) regions. In metal-free sensitizers, the donor-π-acceptor (D-π-A) based sensitizer design has gained increasing popularity and is present in nearly all power conversion efficiency record-setting dyes in recent years. Importantly, this dye design boosts performances while potentially keeping the dye size small. Recently, the performances of D-π-A dyes have been increased substantially by incorporating quinoidal building blocks such as benzothiadiazole into their structures. Proaromatic building blocks are known to promote excited-state quinoidal character in dyes and have low exited-state oxidation potentials. The lowered excited-states are a result of local competing aromaticities in the ground- and excited-states of the dye and lead to increased absorption breath allowing for access to the NIR region. Despite these broad absorptions, these dyes have found limited use in DSC dye design. We introduce for the first time thieno[3,4-b]pyrazine (TPz) as a promising proaromatic building block for DSCs. Palladium catalyzed C-H activation reactions to desymmetrize the parent TPz building block were employed. Using this methodology a series of TPz based dyes were synthesized and through judicious structural modifications dye band gaps were reduced to 1.48 eV (840 nm) allowing access to the NIR spectral region with relatively low molecular weight dyes. An achievement of ~6% power conversion efficiency was observed for this first generation series.

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Design, discovery, thin-film preparation, and characterization of lead-free perovskites

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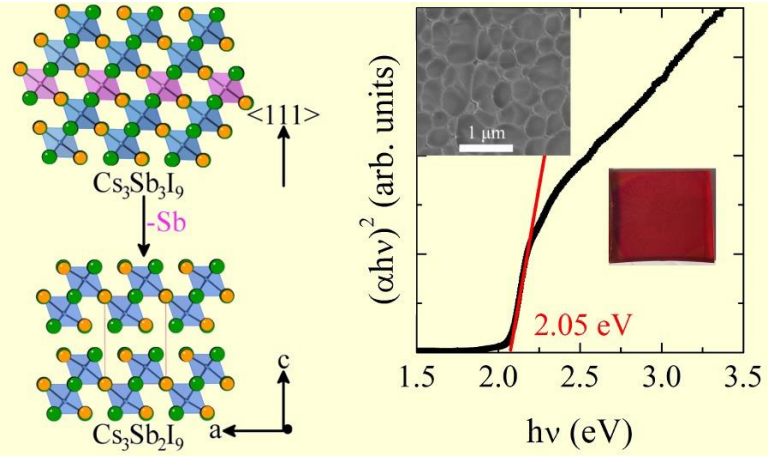
Solar cells based on perovskite absorbers have attracted worldwide interest due to their remarkable light-harvesting properties, high efficiencies above 20% and low-temperature, low-cost processing. However, these materials suffer from the toxic element Pb and device stability issues. First, we discuss design strategies for perovskites that are free of toxic lead by proposing a series of mixed-cation and mixed-anion compositions. Our experimental and DFT work on these mixed-cation and mixed-anion compositions indicate presence of high-stability impurities featuring low dimensional defect perovskite structures. Next, we discuss our computational and

experimental results for one of these high-stability impurities, the layered semiconductor $Cs_3Sb_2I_9$. $Cs_3Sb_2I_9$ is a one-third Sb-deficient derivative of the perovskite structure, and is a potential candidate for high band-gap photovoltaic applications. We describe a two-step thin-film deposition method that enables the preparation of large grain (>1 μm) and continuous thin films of the layered $Cs_3Sb_2I_9$. By changing the thin-film deposition and post-annealing conditions, films that are *c*-axis or randomly oriented can be fabricated. The films exhibit an optical band gap of 2.05 eV, and demonstrate enhanced stability in air (20-50 % relative humidity), compared to $CH_3NH_3PbI_3$ films stored under similar conditions. However, the photoluminescence peak intensity of $Cs_3Sb_2I_9$ is considerably lower compared to that of $CH_3NH_3PbI_3$. The theoretical studies of defect properties confirm the presence of deep level defects that result in non-radiative recombination, including I_i, I_{Sb}, and V_I. Therefore, in order to employ $Cs_3Sb_2I_9$ as a photovoltaic material, a careful control of defects and defect passivation will be necessary. Importantly, this work highlights the heterovalent substitution of Pb^{2+} and Sn^{2+} in $CH_3NH_3(Sn,Pb)I_3$ with trivalent pnictogens such as Sb^{3+} in $Cs_3Sb_2I_9$ as another route for preparation of perovskite PV materials. Because these substitutions are isoelectronic, the advantageous features of the band structures of lead halie perovskites are expected to be preserved.



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Growth of ZnS nanofilm by pulse potential atomic layer deposition

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The ability to control growth at the atomic level is highly desirable in the formation of high-quality thin films. This study focuses on atomic layer-by-layer deposition of ZnS nanofilms – an *n*-type photovoltaic window material that has a wide direct band gap of 3.54 - 3.77 eV[1]. Conventional ZnS electrodeposition is difficult because of the material's low hydrogen overpotential and its tendency to catalyze hydrogen evolution[2]. The method used in this study to grow ZnS is referred to as Pulse Potential Atomic Layer Deposition (PP-ALD[3]) – a variant of the well-established technique Electrochemical Atomic Layer Deposition (E-ALD). Both E-ALD and PP-ALD are electrochemical analogs of condensed phase ALD. Their principle is to use surface-limited

underpotential deposition (UPD) to grow only a sub-monolayer amount material per cycle. PP-ALD needs only a single solution containing all precursors, and it can achieve ALD-level control by selectively depositing different elements using different potentials. This affords higher deposition rate, compared to traditional E-ALD, because changing the electrode potential can be achieved on a much shorter timescale than changing solutions. The deposition solutions consisted of ZnO and $Na_2S_2O_3$ as precursors. Cyclic voltammetry (CV) was used to study the electrochemical behavior of the individual elements. The compositional, structural, and optical properties of the ZnS nanofilms were characterized using EPMA, XRD, and photoelectrochemistry (PEC). Subsequently, the chemistry for growing ZnS will be combined with those for CuSe[3] and SnS to form a superlattice structure of $Cu_2ZnSn(S,Se)_4$ (CZTS) - a PV absorber material.

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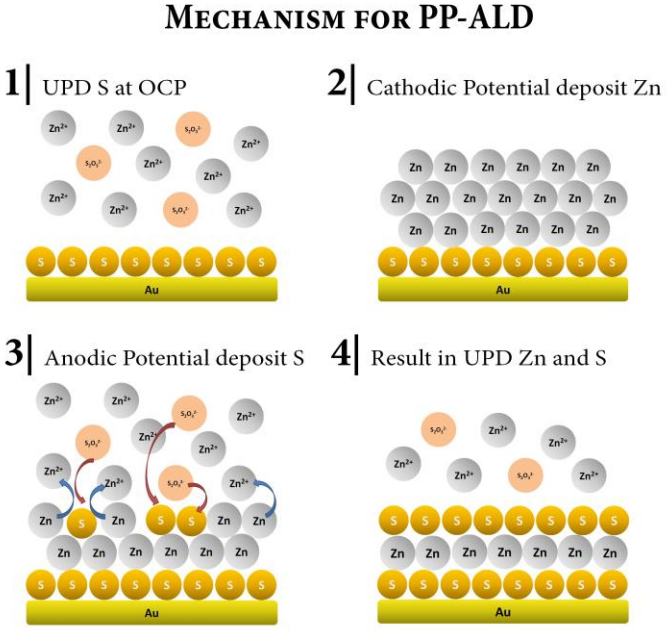

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Doping Ge quantum dots for solar applications

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Several methods of doping germanium quantum dots were investigated for future use in solar cell applications. Doping the area surrounding the quantum dots in a silica matrix was not successful, and neither was modifying the outside layer of the quantum dot.

Doping the quantum dot during synthesis was successful with phosphorus but was unsuccessful with boron or gallium. Further investigation indicates that the phosphorus is on the surface rather than inside the particle. Efficiency testing shows that the position of the dopant does not affect its ability to enhance the photoresponse of the quantum dots.

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Photocatalytic conversion of CO_2 to fuels and electricity generation with solar energy

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The use of photonic energy to provide directly usable energy is a crucial step forward in securing humanities energetic future. Solar-to-electric conversion systems are great avenues toward electric production. However, the development of catalysts for efficient energy usage from photovoltaic systems or the direct use of photocatalysts is necessary to meet our solar-to-fuel needs. Re-*N*-heterocyclic carbene-based photocatalysts will be discussed as potential systems for the conversion of CO_2 to more readily usable carbon-based fuels and fuel precursors directly from sunlight. Additionally, the development of a novel proaromatic organic donor building block (indolizine) for NIR dye-TIO2 sensitization in dye-sensitized solar cells may be discussed. This component has a host of applications as a NIR material in fluoresence imaging, TiO2 sensitized photocatalytic CO2 reduction, and telecommunications. In general, proaromatic building blocks offer a unique platform for accessing relatively low molecular weight small molecules with substantial absorption breadths. Dyes based on indolizine have demonstrated excellent device performances in DSCs for a low-molecular weight dye (8% power conversion efficiency).

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Routes to improving polymer solar cells: Improving crystalline polymer diffusion and reducing spontaneous charge transfer to TiO_2 nanostructures

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In contrast to fullerene-based polymer solar cells, alternative metal oxide acceptors incorporate nanoscale-morphological control and cost-effective materials, while maintaining mechanical flexibility and roll-to-roll processability. These metal oxide-polymer solar cells depend on forming a high density of donor-acceptor interfaces. The heterojunction formation process is crucial for two reasons: 1) infiltration of polymer aggregates is restricted by nanostructured TiO_2 films to achieve the high density of donor-acceptor interfaces, and 2) spontaneous electric dipoles can create electric fields (~10^7 V/m; ~10^{-1} eV) promoting or preventing charge transfer.

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WITHDRAWN

2015 Joint Southeastern/Southwest Regional Meeting 641

Electrochemical atomic layer deposition of CdS on Au and tin-doped indium oxide

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The CdTe based solar cell is a very promising product in the solar cell market. The CdS/CdTe/Au substrate configuration and ITO/CdS/CdTe superstrate configuration were studied in this report. The II-VI compound semiconductor CdS was electrodeposited onto Au substrates using electrochemical atomic layer deposition (EALD). A 1:1 stoichiometric ratio of the two elements in the deposit was verified by electron probe micro-analyzer (EPMA). The thickness of the deposits was found to be linearly related to the number of electrodeposition cycles. In the device fabrication step, CdTe thin films was codeposited onto Au before the deposition of CdS. XRD results showed a good separation of CdS cubic (111) and CdTe cubic (111) structure. This method was transferred to ITO surfaces, with CdS EALD followed by CdTe codeposition. The deposits were found in good stoichiometric ratio, but with a rougher surface morphology.

2015 Joint Southeastern/Southwest Regional Meeting 642

Coatings with improved eco-profile enabled by EVOQUE™ pre-composite polymer technology

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In the United States approximately 700 million gallons of house paint are produced each year. The environmental impact of these paints has been reduced consistently since the 1940's when 70% of a gallon of paint applied was released into the atmosphere as volatile organic compounds (VOC). Far from the solvent borne paints of the past, many waterborne architectural paints of today are Low or Ultra-Low VOC (Often containing <5g VOC/Liter of paint). The replacement of white lead with Titanium Dioxide (TiO_2) as the primary opacifying pigment also greatly improved the eco-profile of paints. However, life cycle analysis shows that TiO_2 is often the most energy intense raw material used in white and pastel paints today.

Practical adsorbing latex polymer technology is a new innovation in the coatings industry which offers the ability to improve the eco-profile while lowering the cost of paint making by reducing dependence on TiO_2. This novel technology replaces the conventional polymeric paint binder with a pre-composite material which does everything the conventional binder does while additionally improving pigment efficiency. By employing pre-composite binders during the standard paint making process, polymer-pigment composites self assemble which result in a more ordered distribution of TiO_2 in the paint film, helping to improve not only hiding but barrier properties as well. Pre-composite polymers offer a powerful advantage by combining improvements in sustainability, performance and economics. This innovative technology provides cost-efficient improvements in key sustainability metrics as demonstrated by a third-party validated life cycle assessment following ISO14040 standards. This technology, which was awarded a Presidential Green Chemistry Challenge Award by the Environmental Protection Agency (EPA) in 2013, has now been produced in commercial quantities well

over several million pounds.

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2015 Joint Southeastern/Southwest Regional Meeting 643

Studying the melt processibility of carbon fiber precursors towards high strength fibers

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Carbon fiber is predominantly made from polyacrylonitrile (PAN) based precursor where the fibers are wet spun in the presence of hazardous solvent that also adds to the cost of production because of expensive solvent recovery and solvent recycling process. Use of melt processable precursor for carbon fiber has long been suggested as a solution for this problem for both environmental and economic perspective. Here, in this study a successful method for carbon fiber preparation from melt processable acrylonitrile-co-1-vinylimidazole (AN/VIM) carbon fiber precursor is presented. Free radical solution polymerization conditions of AN/VIM with a molar feed ratio of 82/18 were optimized for scalability. The copolymers of different molecular weights were synthesized and used for extrusion, annealing, stabilization and carbonization. Positive correlations were observed when the mechanical properties of as spun, annealed, stabilized and carbonized fibers were compared with molecular weights of copolymers. A carbon fiber having a high tensile strength of 1.9 GPa with modulus of 196 GPa was prepared from a copolymer having a weight average (Mw) molecular weight of 37 KDa. These mechanical values met the current requirement by automobile industry (TS = 1.73 GPa, YM = 173 GPa).

2015 Joint Southeastern/Southwest Regional Meeting 644

Production of soluble, homogeneous protein for structural studies

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The ability to express and purify soluble/homogeneous protein is a critical prerequisite for successful NMR, EM or crystallographic structural studies. Advances in experimental techniques such as protein expression and purification, incorporation of novel additives, and protein engineering have improved our ability to produce purified protein for structural studies. This presentation will review some of the more successful approaches in each of these areas. The presentation will describe application of an emerging technology, high-throughput self-interaction chromatography (HSC™), for

rapid identification of solution conditions that maximize protein solubility and physical stability. An instrument has been developed that enables high-throughput quantitative study of weak protein-protein interactions. The approach integrates three innovative technologies into a single instrument that has a small footprint, is easily operated by technician-level personnel. The primary technologies featured by the instrument include microfluidics handling, a diagnostic for measuring the osmotic second virial coefficient (B) for a protein solution, and a predictive algorithm with data-mining capability. Other applications for this technology including stabilization of protein-protein interactions and screening for protein-peptide interactions will be reviewed.
In addition, initial results will be described for a NASA-sponsored experiment involving the crystallization of a large number of challenging proteins using the International Space Station (ISS). Finally, Dr. DeLucas, a former NASA astronaut, will briefly describe his personal experiences flying on the Columbia Space Shuttle, STS-50 in June, 1992.

2015 Joint Southeastern/Southwest Regional Meeting 645

Clinically important parameters that influence sensor design and utility

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Electrochemical sensors play a critical role in clinical medicine, and both amperometric (e.g., blood glucose determination) and potentiometric (e.g., ion-selective electrodes) devices are used to guide clinical decisions daily. This talk will discuss how physicians evaluate the utility of a new sensor and how this can guide the development and “validation” of new sensors. In particular, statistical means of evaluating new devices will be examined and critiqued.

2015 Joint Southeastern/Southwest Regional Meeting 646

Nitric oxide-releasing mesoporous silica nanoparticle dopants for polyurethane-based glucose sensor coatings

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The foreign body response (FBR) is a significant impediment to the analytical performance of subcutaneous glucose biosensors. Local generation of nitric oxide (NO) from sensor coatings has been shown to lessen the FBR, encourage neovascularization, and improve *in vivo* sensor accuracy. However, the optimal NO-release durations and surface fluxes remain unknown. To this end, we have developed a series of NO-releasing mesoporous silica nanoparticles (MSNs) for use as sensor membrane dopants. To prepare *N*-diazeniumdiolate-modified MSNs capable of NO release, we first synthesized bare particles under basic conditions using the structure-directing surfactant cetyltrimethylammonium bromide (CTAB). The particles were next functionalized by addition of aminosilane directly to the particle sol and commensurate ion exchange reaction between the cationic aminosilanes and CTAB. Following synthesis, *N*-diazeniumdiolate NO donors were formed on the secondary amines to yield NO-releasing silica MSNs. Nitrogen porosimetry, small-angle X-ray scattering, ^{29}Si nuclear magnetic resonance spectroscopy, dynamic light scattering, elemental analysis,

and transmission electron microscopy were used to characterize both the particle physical structure and aminosilane incorporation. Nitric oxide-release characteristics of the MSNs were measured in physiological buffer using chemiluminescent NO analysis and correlated to specific physicochemical properties (*e.g.*, surface area, pore ordering, aminosilane modification). The ion exchange-based MSN modification approach was adapted to prepare four distinct sizes of monodisperse particles: 30, 150, 450, and 1100 nm. The NO-releasing MSNs were characterized as having large, tunable total NO storage (0.4–2.3 μmol mg^{-1}) and diverse NO-release durations (1–50 h). The wide range of MSN sizes and NO-release properties obtained demonstrates the flexibility of this methodology for macromolecular NO donor synthesis. Preliminary work on the incorporation of the NO-releasing MSNs into the outer diffusion-limiting polyurethane membrane of a multilayer glucose biosensor will also be described to demonstrate the ability to fabricate functional NO-releasing sensors.

2015 Joint Southeastern/Southwest Regional Meeting 647

Monitoring urine carbon dioxide in septic shock

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Since 2001 intensive care doctors have used “early, goal directed therapy” for the management of shock. The protocol’s essence is careful monitoring of metabolic parameters (hematocrit, venous carbon dioxide (CO_2) and adapting treatment to their changes. Emanuel Rivers demonstrated mortality decrease from 47 to 31% by following this protocol.
We hypothesized that urine carbon dioxide may also indicate septic shock prognosis and therefore provide benefit to monitoring. Scientists have shown large differences in urine CO_2 between healthy controls and hemodynamically unstable patients. Increased CO_2 production and decreased CO_2 clearance may contribute to the difference. Detecting urine carbon dioxide is almost prohibitively impractical, so we needed to determine if urine carbon dioxide as a prognostic indicator in septic shock has enough promise to justify the efforts for us to improve the detection system. To investigate the utility of urine CO_2 as a prognostic tool for septic shock we validated a sampling protocol and we collected samples in an IRB approved pilot study to know if developing a more refined sensor system is justified. During the initial phase of our project we built a wall-jet flow through manifold for measuring urine carbon dioxide and we have established that our system accurately detects urine carbon dioxide. We validated it for varying pH, ionic strength, and temperature. During the second phase of our study we used a syringe with acceptable CO_2 impermeability characteristics to collect samples from patients’ Foley catheter. In an IRB approved study, we successfully monitored urine for carbon dioxide levels in 12 intensive care unit patients both during and after shock. Patients were sampled at shock onset, 12 hours, 24 hours, and after recovery from shock. During analysis of our data we recognized the need for more continuous urine CO_2 monitoring (more data points). The study would also benefit from a sensor placed directly into Foley catheter. In the second phase we establish that urine CO_2 may indeed correlate with patient hemodynamic status and have the justification for the third phase of our project, fabricating a better urine CO_2 sensor.

2015 Joint Southeastern/Southwest Regional Meeting 648

Ion-selective electrodes with PEDOT(PSS) on platinum, gold and glassy carbon – equilibration time

***Marcin Guzinski**, mgzinski@memphis.edu, Jennifer M. Jarvis, Bradford D. Pendley, Erno Lindner. BME, University of Memphis, Memphis, Tennessee, United States*

Solid contact ion-selective electrodes (ISEs) are multilayer structures, which have an intermediate layer between the ion-selective membrane and the electron conductor. The intermediate layer is used to improve reproducibility and stability of these electrodes compared to the coated wire electrode in which the ion selective membrane is in direct contact with the electro conducting substrate electrode. The influence of composition of the intermediate layer and/or the electron conductor on the first equilibration time so far has not been studied systematically. The equilibration time is especially important for single use sensors and sensors implemented in point-of-care devices.

In this work we report equilibration times for solid contact ISEs prepared with (Poly(3,4-ethylenedioxythiophene) Polystyrene sulfonate – PEDOT(PSS)) conduction polymer as intermediate layer. The equilibration time is defined as the time interval from the first solution contact of the electrode and the time when the potential drift drops below a threshold value (0.3 mV/min). We have found that the second and third equilibration time is shorter for electrodes, which were kept dry between experiments. In addition, we found significant differences between the equilibration times of solid contact ISEs built on Platinum, Gold and Glassy Carbon substrates. The equilibration times were longer using Pt substrate. To trace the source of the unexpected differences in the equilibration times the structure of PEDOT(PSS) on Au and Pt surfaces were studied by X-ray photoelectron spectroscopy, and scanning electron microscope and the potential – time traces of PEDOT(PSS) coated Au and Pt electrodes were recorded.

Immobilization of biomolecules on multiple-branched DNA structures

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Biosensors can rely on biomolecules, such as enzymes, for target recognition and signaling. Immobilizing these biomolecules on surfaces helps preserve enzyme activity and prevents leaching into the testing solution. Unfortunately, current immobilization methods do not readily allow controlled distance separation between the surface and enzyme or between multiple enzymes to optimize placement. To address this limitation, we are interested in exploring DNA structures for the immobilization of biomolecules. DNA is stable under a variety of conditions and is easily modified for attachment to various surfaces, including electrodes, making it an attractive material for many applications. A specific type of DNA structure we are studying is called comb-branched DNA. The ability to place multiple biomolecules in a controlled fashion on a surface will allow for higher density and potentially multiplexing. Comb-branched DNA is an ideal structure for organizing one or more biomolecules while maintaining distance control between the biomolecule and the surface or between multiple biomolecules.

Catalytic DNA, also known as deoxyribozymes or DNAzymes, is used to attach adenylated substrate DNAs at specific riboadenosine (rA) locations within a foundation strand, creating branches emanating from the parent strand and resulting in comb-

branched DNA. Previously, single branched structures were used to immobilize single enzymes for amperometry studies [Hausmann et. al., J. Electrochem. Soc. 161, H3001 (2014)]. Currently, we are expanding studies to use multi-branched structures. Each branch strand can be modified for attachment, so multiple biomolecules can be arranged on a single foundation strand. The distance between multiple branches can be adjusted to optimize separation.

Studies presented will focus on the testing of different biomolecule attachment chemistries for directed multi-enzyme immobilization and subsequent modified electrode evaluation.

2015 Joint Southeastern/Southwest Regional Meeting 650

The development of a microfluidic conductivity sensor to detect evaporation from gas permeable PDMS organ-on-a-chip devices

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The use of PDMS for Organ-on-a-Chip (OoC) devices is ideal for its gas permeability, and ability to create microenvironments similar to *in vivo* conditions. However, as devices become smaller and are run for longer periods of time, the risk of evaporation grows resulting in the circulation of hypertonic or hyperosmotic media. Cells exposed to such conditions could experience apoptosis, irreversible DNA damage or inhibition of integral enzymatic pathways. When water evaporates from microfluidic chambers, the subsequent increase in salt concentration result in an observable conductivity change. Here a microfluidic conductivity detection method has been optimized using a screen printed electrode and a nanoelectrode array. The single platform allows for real-time monitoring of changes in conductivity and cellular bioenergetics in a submicroliter chamber.

2015 Joint Southeastern/Southwest Regional Meeting 651

Nanoporous polysulfone fabrication and performance in redox flow batteries

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Nanoporous membranes are attractive as ion exchange membranes (IEMs) in batteries and fuel cells due to channels they have for ion transport. Here we are particularly interested in IEM usage in vanadium redox flow batteries (VRFBs) and how nanoporous membranes can be used to overcome current membrane limitations to improve VRFB performance and cost effectiveness. A promising avenue of production of nanoporous materials involves the bottom-up approach exploiting a self-assembled block copolymer membrane with a degradable block that can be selectively removed. Triblock copolymers that consist of polylactide (PLA) and polysulfone (PSU), PLA-PSU-PLA were synthesized with tailored volume fractions. These polymers were then solvent cast into robust phase separated membranes followed by subsequent crosslinking. The

membranes were introduced into an aqueous alkaline solution to induce solid phase hydrolysis of the polyester block. The complete hydrolysis of PLA did not cause the membrane to lose integrity and shape in spite of the stoichiometric weight loss of the molar fraction of PLA. The resulting porous membrane demonstrated sufficient mechanical properties for VRFB applications as well as hydroxyl lined pores left over from complete removal of PLA in which the PSU and PLA fractions had a hydroxyl group interface. These membranes were characterized and cycled in a vanadium redox flow battery.

2015 Joint Southeastern/Southwest Regional Meeting 652

Ionic liquid and polymer blends for solid state battery electrolytes

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In the future the most popular energy source for portable electronic devices will be solid state lithium ion batteries because of improved storage densities, cycle life and improved battery safety. For instance, lithium ion incorporated polymers are used to make battery electrolytes due to their high mechanical strength, flexibility and stability (safety) compared to liquid electrolytes. Gel polymer electrolytes are generally composed of polymer matrix and a liquid electrolyte and are used in lithium ion batteries due to their excellent ionic conductivity. In this project, a polymer electrolyte, poly(ethylene oxide) complexed with $LiSO_3CF_3$ salt, will be blended with an ionic liquids. Ionic liquids will be used to enhance the conductivity further because of their high ionic conductivities at room temperature. This polymer electrolyte/ ionic liquid electrolyte combination is a good choice for room temperature batteries.In an attempt to further increase ion conduction, this ionic liquid/polymer blend is nanoconfined in alumina nanopores, which also increase the mechanical and thermal stability. Nanoconfinement of polymer helps to increase the ionic conductivity of polymer due to the changes in crystallinity and alignment of polymer chains. Scanning electron microscopic images will be used to confirm the formation of solid polymer nanostructures and AC impedance will be used to calculate specific conductivity values. Further, DSC and XRD can be used to find the changes in crystallinity and TGA can be used to find the thermal stability.

2015 Joint Southeastern/Southwest Regional Meeting 653

Synthesis and characterization of comb polysiloxane polyelectrolyte containing polyethers and sulfonate-terminated side chain

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Comb shape polymer electrolytes were synthesized by co-coupling a poly(methyhydrosiloxane)-PMHS backbone with oligoether ($MPEG_7OCH_2CHCH_2$) and sulfonate terminated alkyl side chains. These polyelectrolytes were prepared to study the effects of the polymer structure on the hydrogen-ion conductivity. We have varied the mole fraction of the two different side chains and mixed the polyelectrolyte with additional $MePEG_7SO_3H$ acid. We have used AC impedance spectroscopy to measure the anhydrous ionic conductivity of the polymer. The oligoether side chain provide H^+

coordination sites, while the alkyl sulfonic acid contributes mobile H^+ for the conductivity. The results show that Fractional Free Volume and the ionic conductivity increase with increasing percentage of the sulfonate group with a maximum ionic conductivity in 90% PEG and 10% alkyl sulfonate polymer of 1.20×10^{-5} S cm^{-1} at 80 °C. When we plot the data as a Walden plot, the data points appear below the ideal Walden line, indicating that the sulfonic acid attached to the polymer likely behaves as a weak acid in the polymer.

2015 Joint Southeastern/Southwest Regional Meeting 654

Optimizing the properties and performance of polystyrene based anion exchange membranes via structural modification of the polymer

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Anion exchange membrane (AEM) is the key component of alkaline fuel cells which conducts hydroxide ions from anode to cathode. An ideal AEM must possess the proper transport properties like high ionic conductivity and low gas/fuel permeability and should have acceptable mechanical, chemical and thermal stability. The performance of an AEM can be optimized by tuning these properties through the modification of the chemical structure and the morphology of the polymer. To study the structural effect on the membrane's properties, durable AEMs which were differed by the amount of crosslinkers and ion contents, have been synthesized by chemical crosslinking between azide and alkyne functionalized polystyrene. These AEMs demonstrated high hydroxyl ion conductivity along with longer durability, low swelling and slow degradation and we have found that the degree of crosslinking and ion contents greatly affect the water uptake, conductivity and durability of the membranes. Since the selection of the crosslinker with appropriate structure and properties was crucial for the stability and flexibility of the membranes, further structural modification was performed. Hydrophilic and hydrophobic di-alkyne crosslinkers of different chain length were used for membrane fabrication to study the insight of ion transport mechanism. AEMs were also prepared from block copolymer as separating the ion-conducting phase from hydrophobic phase in block copolymer enables independent modification of the ion conductive, water swelling and mechanical properties of the membrane. By analyzing the local structure, physical properties, and performances of these series of membranes, we can summarize the effective chemical modifications on polystyrene based AEMs.

2015 Joint Southeastern/Southwest Regional Meeting 655

Evolving electrical conductivity in the matrix of cross-linked PDMS

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Polydimethylsiloxane (PDMS) is a polymer whose ubiquity comes from its low glass transition temperature, conformal lithographic properties, and biomedical applications. Typically an insulating material, PDMS has been doped with rhodamine and anthracene

silica derivatives in order to evolve conductivity within the matrix of PDMS. After the addition of dopants, a microbubble oil-in-water emulsion of PDMS is made, cross-linking is induced, and the emulsion is heat-cured into a solid, high surface-area material. Even after washing in various solvents, fluorescence from anthracene and rhodamine confirms their chemisorption within the PDMS lattice as materials are illuminated with UV radiation (340 nm). The materials are cast onto a glass/ITO substrate and aluminum electrodes are thermally evaporated onto their surface in order to measure conductivity. The successful integration of organic pi-conjugated systems is a critical step in transforming PDMS into a conducting material for biocompatible, low-cost, scalable thermoelectric devices.

Exploring enzymatic reaction pathways using QM/MM methods

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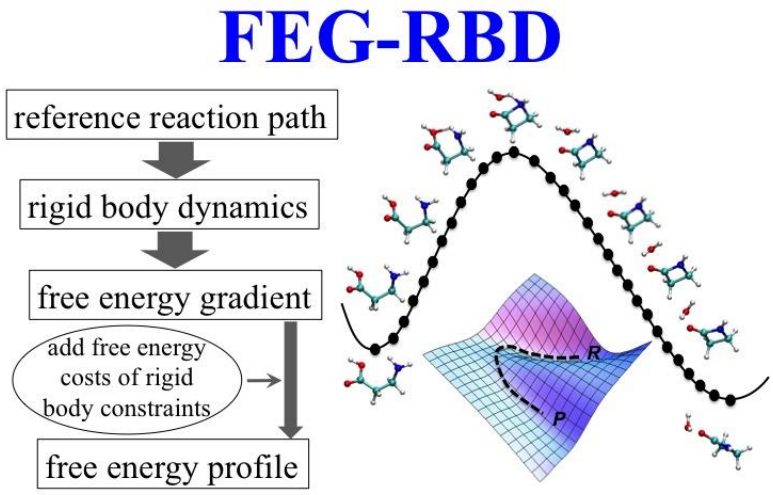
The hybrid quantum mechanical and molecular mechanical (QM/MM) methods have been very effective tools to characterize enzymatic reaction mechanisms. The enzymatic reaction mechanisms are normally represented as minimum energy pathways (MEP) including reactants, products, and transition states (TS) as saddle points. There are three commonly used methods to characterize reaction pathways: eigenvector following, reaction coordinates (RC) scan, and chain-of-states methods. In this presentation, a series of reaction pathway studies about various enzymatic systems using QM/MM and different reaction pathway methods will be reviewed. In an early study of matrix metalloproteinase 2 (MMP2) inhibiting mechanisms, the reactants, products, and TS were identified before the intrinsic reaction coordinates (IRC) calculations were carried out to complete the reaction pathways. In another study of 3-deoxy-D-manno-octulosonate 8-phosphate synthase (KDO8PS), RC scan calculations were carried out to construct potential energy surfaces (PES) to compare different catalytic mechanisms proposed for KDO8PS. Using an intra-molecular condensation reaction and MMP2 as model systems, chain-of-states methods implemented in CHARMM program package were demonstrated to have better efficiency but comparable accuracy with eigenvector following methods to obtain MEPs, and are highly recommended for future enzymatic reaction mechanism studies. After obtaining MEPs, free energy profiles are normally desired to further evaluate reaction mechanisms. Using a new rigid body dynamics integrator implemented in CHARMM, referred as SHAPE, we developed an efficient free energy sampling method, free energy gradient from rigid body dynamics simulations (FEG-RBD), to sample free energy profile for a given MEP. Preliminary results demonstrated that FEG-RBD method has faster convergence rate and better accuracy than commonly used umbrella sampling method.



2015 Joint Southeastern/Southwest Regional Meeting 657

Numerical studies of the electron polarization effects in QM and QM/MM calculations

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We will dicuss the electron polarization effects in QM and QM/MM calculations. For QM calculations, we perform a decomposition of the molecular polarizability into the fluctuating charge (FQ) and induced atomic dipole (IAD) contributions, and show that the FQ contribution is rather substantial. For QM/MM calculations, we will present several methods for estimating the QM/MM polarization energy of a fixed-geometry neutral QM region and a flexible MM region: MESS-E (Roothaan-step extrapolation), MESS-H (Newton-Raphson correction), and PAC/PAD (force-field approaches). MESS-E and PAC/PAD methods are also applied to the computation of hydration free energies of small solute molecules.

2015 Joint Southeastern/Southwest Regional Meeting 658

Hybrid nanoparticles: Synthesis and applications

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The recent emergence of advanced applications for nanomaterials has created a demand for novel hybrid nanoparticles and synthetic fabrication techniques thereof. Recent advances in hybrid nanoparticles preparation are discussed. The diversity of synthetic strategies which provides the ability to simultaneously control the chemical composition, structure, and properties of the hybrid nanoparticles enabled the development of new advanced materials. Much effort has been devoted to the characterization of nanosized particles with an emphasis on synergetic properties in

hybrid particles with well-controlled size and shape. The surface modifications of the particles further allowed additional derivatization by incorporation of functional agents. Different shape nanomaterials including semiconductor, magnetic particles have been studied with much interest with reference to many potential applications. The tremendous application potential of hybrid nanoparticles is highlighted.

2015 Joint Southeastern/Southwest Regional Meeting 659

On-surface redox chemistry to control well-defined oxidation states of transition metal single-site centers

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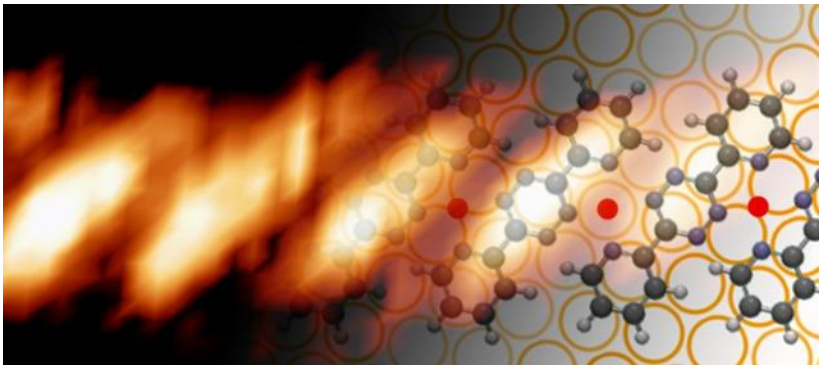
Programming the specific chemistry of single-site transition metal centers at surfaces by organic ligand design is a promising route to improve selectivity in surface catalysts. Our group has recently demonstrated the formation of structurally ordered and chemically uniform single-site centers at surfaces by on-surface redox chemistry of metallic precursors including platinum, chromium, iron, and vanadium with organic ligands on a gold surface (*J. Am. Chem. Soc.* 2014, **136**, 9862-9865; *J. Chem. Phys.* 2015, **142**, 101913; and *J. Am. Chem. Soc.* 2015, **137**, 7898-7902). New results probe the extent of oxidation state control in these systems using tailored tetrazine-based ligands and platinum or vanadium metal. The oxidizing power of the tetrazine species is tuned by peripheral functional groups to access two and three electron oxidation processes, as determined by X-ray photoelectron spectroscopy (XPS). Molecular-resolution scanning tunneling microscopy (STM) reveals well-ordered metal-ligand chain complexes (see figure), which reinforce the chemical uniformity of the system as almost all of the metal atoms are in identical quasi-square-planar coordination sites. This strategy is also applied to earth-abundant metals such as iron and chromium using commonly available phenanthroline ligands. Recent experiments with reactant adsorption probe the potential of these sites for chemical activity and catalysis. These studies develop our understanding of how to control and program single-site metal centers on surfaces for next-generation catalysis.



Scanning tunneling microsopy image (left) with schematic overlay of a one-dimensional chain of single site platinum(II) centers stabilized by bis-pyridinyl tetrazine ligands on a Au(100) single crystal surface. Molecular resolution images, like this, allow detailed structural characterization,

while complementary X-ray photoelectron spectroscopy measurements allow chemical characterization. Image adapted from J. Am. Chem. Soc. 136, 9862-9865 (2014), DOI: 10.1021/ja504850f.

2015 Joint Southeastern/Southwest Regional Meeting 660

Activation of the molecular nanocluster FeMoC-EtOH in growth of carbon nanotubes

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Chirality controlled growth of carbon nanotubes (CNTs) is of interest for numerous applications due to the superlative properties they exhibit as consequence of their chirality. A possible route for chiral specific growth is the use of uniform critically-sized catalysts under tightly controlled reaction conditions. Here we systematically investigate the hydrogen gas concentration and growth temperature influences on the “activation” of the molecular nanocluster catalyst FeMoC-EtOH $[H_xPMo_{12}O_{40} \subseteq H_4Mo_{72}Fe_{30}(O_2CMe)_{15}O_{254}(H_2O)_{98-x}(EtOH)_x]$ (where is x is calc. to be 30) in the growth of carbon nanotubes. The FeMoC-EtOH catalyst was demonstrated to be “activated” when the hydrogen gas concentration and growth temperature were sufficient enough to completely reduce the catalyst nanoparticles. The observations from prior work with FeMoC will be discussed with respect to these results in the aim of optimizing CNT growth.

2015 Joint Southeastern/Southwest Regional Meeting 661

The effects of colloidal C_{60} particle size on zeta potential

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Multiple methods are used to synthesize C_{60} to what is believed to be its most environmentally and biologically relevant form, an aqueous colloidal suspension (nC_{60}). Stability of the suspension is attributed to a relatively large negative zeta potential that has been shown to develop upon the formation of nC_{60}. Investigations of the spontaneous development of this negative surface charge have provided partial explanations towards the identification of its origin, but a mechanism that completely identifies the origin has yet to be actualized. A relatively uncontrollable variable in nC_{60} formation, size, is investigated to help elucidate this mechanism. Six different synthesis methods were evaluated to determine the effects, if any, that particle size has on zeta potential. Aqueous suspensions from each method were subjected to a particle-by-particle zeta potential analysis using NanoSight Model NS500HSB. Zeta potential as it relates to particle size will be discussed.

2015 Joint Southeastern/Southwest Regional Meeting 662

Epoxidation of cyclohexene on Ag catalysts supported on hierarchically porous SiO_2 and Co_3O_4 monoliths

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In this work, the synthesis of silver (Ag) supported on hierarchically porous silica (SiO_2), and cobalt oxide (Co_3O_4) monoliths and the catalytic activity of these monoliths for the oxidation of cyclohexene is reported. The SiO_2 monoliths were synthesized using a sol-gel technique. The Co_3O_4 monoliths were prepared by nanocasting, using the SiO_2 monoliths as template. Loading of Ag nanoparticles on the SiO_2 and Co_3O_4 monoliths, was done by a solution infiltration method using aqueous silver nitrate ($AgNO_3$) solution followed by reduction with hydrazine hydrate. Structural characterization of these materials was carried out by various techniques including scanning electron microscopy (SEM), N_2 adsorption, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The catalytic activities of powdered and monolithic Ag/SiO_2 and Ag/Co_3O_4 for the oxidation of cyclohexene were studied and the impact of parameters such as catalyst loading, temperature, oxidant, and substrate to oxidant ratio determined. The catalysts were found to be suitable for the oxidation of cyclohexene to cyclohexene oxide accompanied by formation of cyclohexenone as a minor product, and the catalysts could be reused several times without affecting the catalytic activity.

2015 Joint Southeastern/Southwest Regional Meeting 663

Mitigation of ionospheric scintillation by chemi-ionization: Benefits of fundamental chemical physics

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The Air Force has long considered ways of creating enhanced plasma density as a method of mitigating the detrimental effects of ionospheric density irregularities. Numerous easily photo-ionizable molecules have been released for study in this regard, yet this approach is inherently limited to daytime use. Recently attention has turned towards chemi-ionization. Several lanthanide metal oxides have bond strengths greater than their IP, such that $M + O \rightarrow MO^+ + e^-$ becomes energetically accessible. In 2013 the Metal Oxide Space Cloud (MOSC) mission released vaporized samarium in the lower ionosphere to study its potential as a chemi-ionization agent with atomic oxygen. While successful at producing enhanced densities, several results created questions about the underlying chemistry. This talk will focus on our lab's efforts supporting these releases, both in analysis of the principal thermochemistry and its effects on assessment of previous results, as well as ongoing experiments considering the potential of other chemi-ionization systems for future experiments.

2015 Joint Southeastern/Southwest Regional Meeting 664

Visualizing and quantifying the nonvalence character of excess electrons: Multipole-bound states and clusters

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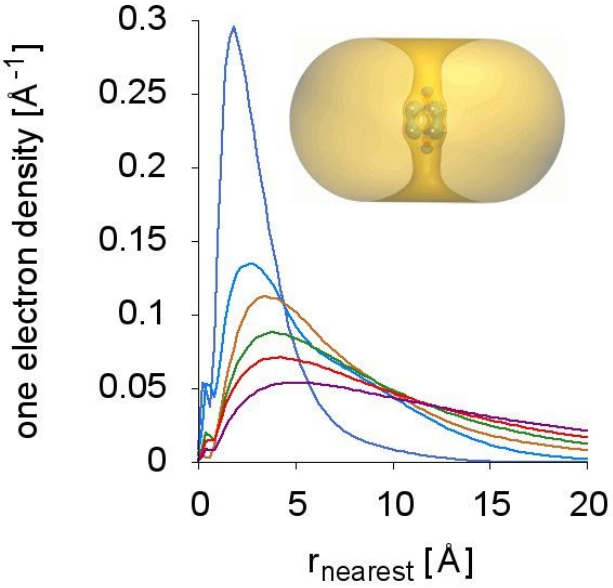
States formed by attachment of an excess electron to molecules or clusters can be broadly classified into valence and non-valance states, but many of these states do

have both, some valence and some non-valence character. Here an analysis scheme for this type of state is presented based on considering the density of the excess electron as a function of the distance to the nearest atom, and this vantage point yields, in the first place, an intuitive picture akin to the well-known atomic radial distribution function, and, in the second place, a distance-from-the-atoms measure that is directly related to the non-valence character of the excess electron. The analysis scheme will be applied to various typical nonvalence anions: water clusters, dipole-bound states, and quadrupole-bound states.



2015 Joint Southeastern/Southwest Regional Meeting 665

On the role of anharmonic effects on the vibrational spectra of $X^{\pm}$ $(H_2O)_n$ clusters

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Vibrational spectra of $X^{\pm}(H_2O)_n$ clusters often display very large red shifts and many more transitions than predicted in the harmonic approximation. In this talk, I present several such systems including $CH_3CO_2^-\bullet(H_2O)$, $NO_3^-\bullet(H_2O)$, $H^+(H_2O)_n$, and $[\text{pyridine}\bullet(H_2O)_n]^-$. Emphasis will be placed on the use of reduced degrees of freedom model Hamiltonian approaches for analyzing the spectra in these systems.

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2015 Joint Southeastern/Southwest Regional Meeting 666

The development of a comprehensive platform for the on-demand synthesis of peptide natural products containing unusual α-amino amides

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Organic synthesis has always measured itself by how quickly and inexpensively complexity in small molecules can be obtained using established methods. Chiral molecules present unique challenges that further restrict the number of tools appropriate to achieve their total chemical synthesis. With the importance of peptides in biology and therapeutic development as a backdrop, this lecture will describe the development of Umpolung Amide Synthesis (UmAS) as a technology to enable the efficient synthesis of peptides. Recent developments in the chiral proton-catalyzed aza-Henry reaction have been leveraged to deliver an increasingly diverse group of UmAS donors to effect peptide homologation with α-aryl and α-alkyl substituted α-amino amides. Each homologation is achieved in only three steps from commercially available aldehydes. The preparation of an aryl glycine-rich peptide and a depsipeptide will illustrate the key role that enantioselective catalysis is playing to render peptide synthesis increasingly general and on-demand for peptides containing unusual α-amino amides.

2015 Joint Southeastern/Southwest Regional Meeting 667

High throughput plant phenotyping at the plant imaging consortium

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Manual phenotyping requires a great deal of resources and is typically not feasible for detection of subtle plant phenotypes. Therefore, there is a growing need to develop quantitative and automated phenotyping systems to analyze large numbers of plants. Recognizing this need the Arkansas Center for Plant Powered Production (P3) acquired a Scanalyzer HTS. This instrument is equipped with visible, fluorescence, near infrared, and laser cameras allowing unbiased, non-invasive and automated screening of plant phenotypes. Additional funding from the National Science Foundation has recently allowed the establishment of the Plant Imaging Consortium (PIC, http://plantimaging.cast.uark.edu). One of the missions of PIC is to expand access to this powerful phenotyping tool to other plant scientists in the region. In order to developed and validate phenotyping protocols we have used known Arabidopsis lines with enhanced growth and tolerance to stress. After extracting information contained in the high resolution images we have acquired, a high correlation between the digital readouts measured with the LemnaGrid software (e.g. leaf area and caliper length), and the manual readouts measured for these lines (e.g. aerial dry weight) has been found. The power of the fluorescence and near infrared cameras has become evident after analyzing the response of these lines to stresses such as drought and salinity, where novel digital readouts of stress have been identified. Additional applications for detection of specialized metabolites with unique color and fluorescence properties will be discussed as well.

2015 Joint Southeastern/Southwest Regional Meeting 668

Which chamomile is which? Taxonomy, chemistry, biology, and safety implications: Exploring all directions

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The 'wonder' plant chamomile is one of the most widely used medicinal plants in the world. In the form of herbal teas, over one million cups of this natural product are consumed each day. Chamomile is preferred for its pleasant taste and calming, sedative effects, as well as its long established medicinal properties such as anti-inflammatory, anti-spasmodic, anti-allergic and anti-bacterial. Commercial chamomile products include beverages, cosmetics, hair dyes, perfumes, massage oils, soaps and shampoos among others. Chamomile flowers are considered as an official drug in the pharmacopoeia of 26 countries. The three most common types of chamomile observed in commercial products are German chamomile (*Matricaria chamomilla L.*), Roman chamomile (*Chamaemelum nobile L*) and Juhua (*Chrysanthemum morifolium R.*). The similarity of medicinal practice of different types of chamomile and lack of a clear definition of 'chamomile' lead to significant issues with respect to the quality control and safety of products purported to contain chamomile as an active ingredient. To differentiate the three most chamomiles, the details of the taxonomy, chemical diversity, secondary metabolism, biological activities and safety studies will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 669

Residue analysis of archaeological smoking pipes from the southeastern US

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Chemical analyses of organic residues from smoking pipes excavated from archaeological sites in the southeastern United States provide insight into ritualistic smoking traditions of indigenous peoples. This study examined residues scraped from pipes and pipe sherds in collections at the Fernbank Museum of Natural History in Atlanta, Georgia, and the McClung Museum of Natural History and Culture in Knoxville, Tennessee. One of the primary goals was to determine whether nicotine was present in the residue, thereby expanding our knowledge of when and where tobacco was first used in the southeast. For the analyses, residues were extracted by ultrasonicating the samples in methanol/chloroform. An aliquot of the extracts were analyzed directly using GC-MS and GC-FID; another aliquot was derivatized using BSFTA with 1% TMCS and also analyzed using GC-MS and GC-FID. While nicotine was present in only two of the residues studied, the results suggest a complex and diverse tradition in which smoking pipes were used to smoke a wide array of natural materials.

2015 Joint Southeastern/Southwest Regional Meeting 670

Analysis of organic residues from Native American noded vessels using GC-MS and GC-FID

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Analysis of organic residues in ceramic vessels from archaeological excavations have the potential to identify the substances Native Americans stored in pots of various shapes, sizes and designs. In this study we analyzed residues extracted from noded ceramic pots, a particular type of vessel that has unique designs covering the outer surface of the vessels. It was recently proposed that noded pots were used specifically to process *datura* for religious ceremonies. *Datura* contains various tropane alkaloids that have pharmacological properties, but also makes the plant extremely dangerous if ingested. In this preliminary study, two pots were analyzed non-destructively by ultrasonicating the whole pots directly in a methanol:chloroform solvent mixture. The volume of the extracts were reduced under vacuum using a rotary evaporator, and the extracts were derivatized using BSFTA with 1% TMCS before analysis using gas chromatography/mass spectrometry (GC/MS) and gas chromatography with flame ionization detection (GC-FID). One compound of particular interest was atropine, which could indicate storage of jimson weed (*Datura stramonium*), and standards of this compound were used to determine the instrument LOD and MDL. Our results indicate that atropine was below the detection limit but other alkaloids were present.

2015 Joint Southeastern/Southwest Regional Meeting 671

Neurotransmitter quantification to understand alcohol tolerance in non-mammalian organisms

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Model organisms are often used in place of humans to study the effects of alcohol upon the brain. *Drosophila melanogaster* and other non-mammalian organisms utilize many of the same neurotransmitters as humans. Here we investigated the effects of alcohol on behavior in *Drosophila* and developed separation methods to measure the changes in neurotransmitter concentrations using high performance liquid chromatography with electrochemical detection. As alcohol volume increases flies become sedated faster in single alcohol exposures, while in exposures to alcohol data (five day exposures) flies experienced increased in sedation time indicating increased exposure. Brains were then dissected from flies, homogenized, and separated to compare the effectiveness of separation methods. The procedures and methods established from studying *Drosophila* will aid in preparation for the introduction of other model organisms *Danio rerio* (zebra fish) and *Tribolium castaneum* (flour beetles)and ultimately a better understanding on how the brain changes when under the effects of drugs of abuse.

2015 Joint Southeastern/Southwest Regional Meeting 672

Preliminary analysis of the molecular distribution of polyhexamethylene biguanide using equilibrium dialysis and gel filtration chromatography

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In recent years, bacteria have become increasingly resistant to traditional antibiotics, necessitating the development and characterization of new compounds with biocidal activity for a broad range of personal care products. Among biocides currently in use is polyhexamethylene biguanide (PHMB), a polycationic and polydisperse ingredient found

in multipurpose contact lens solution (MPS) and other anti-bacterial solutions. Previously in our lab, we have utilized ultra-performance liquid chromatography (UPLC) and mass spectrometry (MS) to collect fractions of PHMB and determine if there is a correlation between elution time and molecular weight size. In order to better investigate the molecular distribution of this polymer, we have employed a variety of techniques including equilibrium dialysis and gel filtration chromatography (GFC). Using a wide variety of molecular weight pore sizes in equilibrium dialysis we are able to better understand the molecular weight cut offs in comparison with the chromatogram patterns acquired from UPLC. In addition, preliminary GFC results combined with equilibrium dialysis have allowed for an understanding of separation based on molecular weights. In the future we hope to better characterize the structure and activity of these polymer particles in solution, and work to determine if certain molecular weight sizes are more efficient against bacteria.

2015 Joint Southeastern/Southwest Regional Meeting 673

Synthesis and characterization of *cis*-[Cr(TMP)(DPPZ)(1-MeImid)]$^{3+}$

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Our lab group has previously shown that octahedral chromium(III) tris(diimine) complexes of the type [Cr(diimine)$_2$(DPPZ)]$^{3+}$ non-covalently bind very strongly to DNA due to intercalation by the dipyridophenazine (DPPZ) ligand. These complexes are capable of DNA photo-oxidation, and as a result may have potential applications in the area of photodynamic cancer therapy. In the present study one of the bidentate diimine ligands has been replaced by two monodentate 1-methylimidazole ligands (1-MeImid). This substitution opens up the possibility of an additional DNA binding mode involving direct covalent binding between Cr(III) and a DNA nucleobase. Such systems may therefore exhibit DNA binding characteristics somewhat similar to the widely prescribed antitumor agent cisplatin. The target complex, [Cr(TMP)(DPPZ)(1-MeImid)$_2$]$^{3+}$, was synthesized in a 5-step process where the DPPZ ligand was attached first and the 3,4,7,8–tetramethyl–1,10–phenanthroline and 1-MeImid ligands were attached in subsequent steps. The purity of the isolated complex was established via elemental analysis, electrospray mass spectroscopy, and capillary electrophoresis studies. The interaction of the complex with DNA was then investigated using a variety of analytical techniques. Isothermal titration calorimetry with CT-DNA was used to determine enthalpic and entropic values as well as to estimate the DNA binding constant. Subsequently spectrophotometric titration was used to confirm the K values determined from isothermal titration calorimetry. Additionally, the binding affinity relative to other compounds as well as enantiomeric specificity was determined via equilibrium dialysis studies in conjunction with UV-vis and circular dichroism spectroscopy.

2015 Joint Southeastern/Southwest Regional Meeting 674

Optimization of an analytical method to determine the KCN antidote (SDX) in blood by HPLC

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Cyanide (CN) is a poison that prevents cells from utilizing oxygen by blocking the mitochondrial respiration chain. The present therapies in the US are the Cyanokit and the Nithiodote, but each of them has disadvantages. There is a need to find a novel CN antidote with a better profile. A potential candidate being developed in our lab is the sulfur donor X (SDX).Our aim was to develop a detection method for SDX from blood that could be used for future pharmacokinetic studies. An HPLC was used and the SDX was measured with a UV detector at 215 nm. Sample preparation and HPLC instrument methods were optimized. Different organic solvents (ethanol, methanol, and acetonitrile) were added to facilitate the partitioning of the SDX into the supernatant following centrifugation of the blood sample. Cold acetonitrile yielded the best SDX recovery and the smallest inter sample standard deviation. The effect of sodium chloride addition and sonication to blood samples were also tested, but they did not measurably improve the SDX recovery. Different mobile phases were applied to find the best elution and of those tested a blend of 65% acetonitrile and 35% water was found to yield by best isolation of the SDX peak. Dissimilar liquid injection volumes (10-50 µl) were tested to the column, which showed 40 µl as the preeminent injection volume. A calibration curve was prepared with a best-fit line that showed an R^2 = 0.9984 and a limit of detection = 0.725 µg/ml. Validation is ongoing. This method shows promise for future pharmacokinetic studies.

The study was funded by the Robert A. Welch Foundation at Sam Houston State University (x-0011) and the USAMRICD (Contract No.W911NF-11-D-0001).

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Determining purity of ginkgo biloba extract in the presence of non-native flavonol aglycones and isoflavone glycosides using HPLC and mass spectral analysis

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Standardized Ginkgo biloba leaf extract has long seen use as an herbal remedy and dietary supplement, for treatment and prevention of various conditions including cognitive impairment, venal insufficiency and tinnitus. As with many herbal medicines and nutraceutical formulations, ensuring the purity for Ginkgo products can be a difficult task, and opportunities exist for adulteration with components or extracts from other plant sources for various purposes including economic advantage. In addition to testing for terpene lactones (ginkgolides and bilobalide) content, current methods of analysis for Gingko biloba product quality measure the total flavonol glycoside content extrapolated from the content of the three main aglycone (free) flavonols (quercetin, kaempferol and isorhamnetin) after hydrolysis. By testing for the presence of added aglycone flavonols before hydrolysis, as well as for compounds from potential adulterants not native to Gingko (e.g., the isoflavones genistein, genistin, and sophoricoside), we developed a reliable indicator for the purity of commercial samples. Using High Performance Liquid Chromatography (HPLC) combined with both UV and mass spectral (MS) detection, we separated and quantified flavonols and isoflavone in

both authentic and adulterated Ginkgo biloba samples in a blind assay format. Samples with isoflavones present, and/or containing free flavonols prior to hydrolysis, were consistent with previously reported adulteration with other materials, including extracts of Sophora japonica. It is noteworthy that extracts from the fruit of this plant have been strategically selected as an adulterant because of its high content of the main Ginkgo flavonol aglycones, kaempferol and quercetin, which may be added to diluted Ginkgo extract to boost the total flavonol content.

2015 Joint Southeastern/Southwest Regional Meeting 676

Analysis of a potassium ferrocyanide based pyrotechnic material as forensic evidence

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Potassuim ferrocyanide has historical use in pyrotechnic materials and has potential to be used as an ingredient in the emerging market of lead-free small caliber firearm ammunition. Elemental profiling of the ferrocyanide based combustion reaction products by laser-induced breakdown spectroscopy (LIBS) and scanning electron microscopy/energy-dispersive x-ray spectroscopy (SEM-EDX) establish emission lines as analytical markers for potential forensic applications. Data shows that the iron and potassium emission lines are statistically significant markers for potassium ferrocyanide based lead-free ammunition simulations. Rates of error associated with each simulation were determined by leave-one-out cross validation and show promising results in the ability to identify individuals who have been exposed to ferrocyanide based pyrotechnic materials.

2015 Joint Southeastern/Southwest Regional Meeting 677

Reaction kinetics of low molecular weight carboxylic acids with carbonate aerosols

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Low molecular weight carboxylic acids like formic acid, acetic acid and glutaric acids are ubiquitous in the atmosphere. Theyare found in aqueous and gas phases environments as well as in aerosol particles and are thought to play an significant role in controlling the acidity of the aerosol environment. The mechanisms and reactions of these acids with basic aerosols like carbonates, and how they influence acidty/basicity of atmospheric aerosols have not been studied as closely. This study investigates the reaction of these low molecular weight carboxylic acids with sodium carbonate and using gas chromatorgraphy and infra red spectroscopy. Preliminary results show an abundance of gases being produced, with IR spectra indicating the presence of carbon dioxide, possibly from the decomposition of the acids.

2015 Joint Southeastern/Southwest Regional Meeting 678

Manufacturing of anticancer drug fluorouracil loaded polycaprolactone nanoparticles using emulsion solvent evaporation

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Anti-cancer drug (5-Fluorouracil, 98% [FU]) loaded, Polycaprolactone (PCL) (MW 80,000) based nanospheres were manufactured through a novel double emulsion solvent evaporation method and correlation between solution, processing parameters and nanoparticles' morphology was investigated. Four samples (two single and two double emulsions) were produced. All samples were produced using a 0.5% (by wt. %) PCL (avg. mw 80,000) into Dichloromethane (DCM) solution as the polymer solution. Both of the double emulsion samples used a 0.5% FU into Deionized water mixture as the aqueous solution. All samples were stabilized by a 1% polyvinyl alcohol (PVA) into Deionized water solution. Scanning electron microscopy (SEM) was used to determine the morphology of all obtained nanoparticles which showed that through the single emulsion technique, nanoparticles of approximately 400 nm in diameter were produced with few oblong formations. The results of both of double emulsion samples also showed that nanoparticles formed. One sample produced rigid dispersed spheres of approximately 500 nm while the other sample produced smoother less dispersed spheres of approximately 300 nm. Energy Dispersive X-ray Spectroscopy (EDS) showed no presence of drug on the outside of nanoparticles. Transmission Electron Microscopy (TEM), drug release tests will be performed to determine encapsulation efficiency and drug release characteristics of nanoparticles.

HPLC UV-Vis and MS analysis of endocrine-active compounds in the symbiotic relationship between algae and sea anemones

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Aiptasia pallida, the pale sea anemone, form symbioses with intracellular photosynthetic algae. It is assumed that this symbiosis primarily offers food to the host. However, anemones maintained in the dark have been found to lack functional gonads. We hypothesized that symbiotic algae may produce compounds that modulate the reproductive performance of their hosts. Phytoestrogens such as isoflavones are known to affect reproduction of marine organisms, and symbiotic algae may be capable of producing these endocrine-active chemicals. A method using high performance liquid chromatography with UV-Vis detection was developed to measure these endocrine-active chemicals, and three isoflavones, diadzein, genistein, and biochanin A, were identified as potential candidates from sea-water samples containing anemones grown with and without algae. Separations were developed from a 0.1 % formic acid/acetonitrile gradient method previously used to measure isoflavones in waste water samples. The separation system was then adapted for use with high performance liquid chromatography with mass spectrometry to attempt to confirm whether diadzein, genistein, and biochanin A were indeed present in anemone water samples.

Method development for the determination of isoflavones in *Aiptasia pallida* using SPE and GC-MS

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The pale sea anemone, *Aiptasia pallida,* is a powerful model system to study symbiosis due to its ability to survive both with and without its intercellular algae. Typically symbiotic algae provide energy to their hosts, converting light in to usable sugar, while the anemone provides protection for their symbiont. Algae might also play a larger role in the anemone's reproductive cycle. Anemones reproduce both sexually and asexually. Preliminary evidence shows anemones that have had their algae removed fail to develop gonads and are capable of only reproducing asexually. Free-living microalgae produce bioactive compounds including alkaloids, saponins, and flavonoids, many of which are nuclear receptor agonists potentially making them capable of interacting with estrogenic receptors. These species might be used by algal symbionts in sea anemones to produce the observed reproductive changes. Using solid phase extraction (SPE) of water samples used to grow anemones with and without algae, GC-MS was used to investigate what species are released these by intracellular algae and the role algae play in the anemones' reproduction system.

Characterization of citrate-acetate mobile phases for high performance liquid chromatography with electrochemical detection

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Non-mammalian model systems offer significant advantages to the neurochemist - small sizes, relatively short life cycles, ease of molecular and genetic manipulation, and similar molecular make-ups to humans. For example dopamine, serotonin, and estrogen which are present in the mammalian central and peripheral nervous systems, also function as neuromodulators in non-mammalian model systems and mediate the same physiological functions. Some differences do exist however. Insect systems contain octopamine and tyramine which act as analogs to norepinephrine and epinephrine, while biogenic amines undergo metabolism via N-acetylation rather than carboxylation of the amine and O-methylation. A mobile phase of 110 mM citrate, 90 mM acetate, 0.45 mM 1-octanesulfonic acid, 25 µM EDTA, 0.1% triethylamine, at pH 4.5 was developed for HPLC with electrochemical detection. Compared to typical phosphate buffers used in the literature, this citrate-acetate mobile phase showed improved resolution and sensitivity of 20 neurotransmitters due to a more favorable pH range, particularly for octopamine and tyramine. Cyclic voltammetry was then used to further probe why this system works more effectively.

Identifying fertilizer origin using portable FT-IR and handheld Raman spectroscopy

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Calcium ammonium nitrate (CAN) and ammonium nitrate (AN) fertilizers are oxidizers that are often used to make home-made explosives and roadside improvised explosive devices (IEDs). Previous forensic analysis studies have reported the use of benchtop instruments such as inductively coupled plasma–mass spectrometry (ICP–MS) and isotope-ratio mass spectrometry (IRMS) to determine the manufacturer of CAN and AN samples. One disadvantage of using these instruments is that they are time-consuming and samples cannot be analyzed in the field. Currently, there are no published studies on field analysis of fertilizers using handheld or portable instruments. So, the main objective of this research was to determine whether or not it is possible to identify the country of origin of CAN and AN samples using portable FT-IR spectroscopy and handheld Raman spectroscopy.
Our study analyzed eight batches of CAN and four of AN using a handheld Raman (Thermo Scientific Ahura FD) and a portable FT-IR (Smiths Detection HazmatID 360), respectively. Seven of the CAN batches were from countries B, C, and D; the eighth batch—batch A—was of unknown origin. Three of the AN batches were from unknown sources and were referred to by their batch names: E, F, and G. The fourth AN batch was from country H. Solid samples were crushed and scanned using both instruments in clear vials, and data was produced in less than ten minutes. Partial least squares discriminant analysis (PLS-DA) models were built in Matlab's PLS Toolbox based on 54 CAN samples and 36 AN samples using Raman and FT-IR spectroscopy, respectively. PLS-DA model for AN contained two levels: the first level determined whether a sample was from batch E or not; the second level determined whether the sample was from batch F, batch G, or country H. Finally, unknown samples were analyzed for both types of fertilizer. PLS-DA models accurately predicted 13/13 (100%) of the unknown CAN samples and 11/12 (91.7%) of the unknown AN samples with no unclassified strict or probable predictions. This study clearly demonstrated that it is possible to determine the origin of calcium ammonium nitrate and ammonium nitrate fertilizers using a handheld Raman and a portable FT-IR for field applications.

Voltammetric detection of silver ions using carbon paste electrodes for nanosilver oxidation studies

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Silver nanoparticles (Ag^0 NPs) are now widely used in consumer goods, raising concerns about the environmental impact of their use due to the know oxidative dissolution of Ag^0 NPs to release toxic silver (Ag^+) ions. Current analytical methods are unable to measure Ag^+ ions in the presence of Ag^0 NPs at low, environmentally relevant concentrations without a separation step. To address this, we have developed a method that utilizes differential pulse stripping voltammetry (DPSV) with carbon paste electrodes (CPE) to detect nanomolar Ag^+ concentrations. Various parameters have been optimized for this method including deposition time, deposition potential, and scanning technique. Because this method responds to Ag^+ ions and not Ag^0 NPs, the oxidative dissolution of Ag^0 NPs can be monitored without a separation step, greatly simplifying analysis. We have applied this method in a study of the pH-dependence of

nanosilver oxidation. This technique will be further utilized in future studies that examine how other solution conditions like salinity, dissolved oxygen, sulfide and organic material influence the release of Ag^+ ions from Ag^0 NPs in conditions and at concentrations representative of natural waters.

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Synthesis and characterization of surface-enhanced Raman scattering gold nanoparticle probes for detection and capture of circulating tumor cells

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Due to their exceptional properties, gold nanoparticles have been the subject of exponentially increasing levels of research interests during the last decade. They have found use in many areas, from energy generation to medicinal treatment. In this work, we aim to develop anisotropic gold nanoparticles, gold nanorods for multicolor detection of cancerous cells in the bloodstream. Due to the unique localized surface plasmon resonance, gold nanorods strongly enhance Raman scattering of adsorbed molecules, allowing for highly sensitive detection of circulating tumor cells via surface enhanced Raman scattering spectroscopy. In this study, gold nanorods of different aspect ratios were synthesized via a seed-mediated method. They were tagged with four different Raman tags: QSY-21, IR-783, IR-820, and BHQ-3 to make four-color surface enhanced Raman scattering nanoparticles. Systematic studies were conducted to examine the effects of aspect ratio of the nanorods and the density of Raman tags on the surface enhanced Raman scattering sensitivity. We found that gold nanorods with aspect ratio around 4.00 – 4.15 (localized surface plasmon resonance around 800 – 815 nm) gave the highest SERS sensitivity for all Raman tags. For each Raman tag, an optimal coating was achieved to give the highest SERS sensitivity without causing particle aggregation. Continued studies on bioconjugation with monoclonal antibodies will lead to four-color gold nanorod surface enhanced Raman scattering probes for identification and detection of circulating tumor cells.

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Crystallization kinetics of salts from aqueous solutions

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This study explores the possibility of using DSC to measure the kinetics of crystallization of salts from aqueous solutions. The saturated solutions of potassium nitrate, rubidium nitrate, and ammonium perchlorate have been studied at several cooling rates. It has been found that crystallization of the salts is accompanied by a significant heat release that becomes detectable above 0^oC. The DSC peaks demonstrate a shift to lower temperature with an increase in cooling rate. The DSC data have been analyzed by means of an advanced isoconversional method [1] which permitted estimating dependencies of the effective activation energy (E_a) on the conversion (a). The E_a values are negative which has been the case [1] for a number of

other nucleation driven processes measured on cooling such as the melt crystallization, gelatin solution gelation, and solid-solid phase transition. The negative values reflect anti-Arrhenian temperature dependence of the process rate, i.e., acceleration with decreasing temperature. All three salts appear to demonstrate similar E_a dependencies that include a maximum. It is proposed that a switch from the increasing to decreasing portion of the Ea dependencies may be associated with a change in crystallization mechanism from primary (homogenous) to secondary (heterogenous) nucleation.

[1] S. Vyazovkin, Isoconversional kinetics of thermally stimulated processes. Springer: 2015.

2015 Joint Southeastern/Southwest Regional Meeting 686

Identifying the polyphenols present in green, black, and herbal teas

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This study attempted to see which polyphenols were present in a variety of teas using cyclic voltammetry. Different teas were first brewed and diluted while cold. After these results were gathered, we explored how heat might affect the molecules present. We found that most of the cold brewed teas contained catechin, while a few teas contained catechol or unidentified molecules. With heat, the teas were shown to have many of same molecules as the cold, with a higher concentration of catechin. However, some heated teas contained completely different polyphenols than the cold brew. This paper examines under what conditions different anti-oxidants appear.

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Kinetics of phenolphthalein color fading experiment via a small footprint diode array spectrometer

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Phenolphthalein is a common indicator used is acid base titrations. In acidic solutions, phenolphthalein is colorless, while in basic solutions it has a pink color. An interesting fact is that the pink color fades with time. The rate law for this reaction is second order but by increasing the concentration of base significantly the reaction becomes a pseudo-first order reaction. This experiment employs a small footprint visible-near-infrared spectrometer (Vis-NIR) with diode array detector. The absorbance at 555 nm of phenolphthalein in high concentrations of base as a function of time was collected employing using the software that operates the spectrometer. The results contained in the data collection file are exported to a spreadsheet for further processing. The order with respect to phenolphthalein and base can be determined. This experiment with its small foot print spectrometer (easily portable) is well suited to educational settings.

2015 Joint Southeastern/Southwest Regional Meeting 688

Equatorial and axial ligation of Ru2(dpf)3(O2CCH3)Cl where dpf = N,N'-diphenylformamidinate anion

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In this work, we report the reaction of Ru2(dpf)3(O2CCH3)Cl (dpf = N,N'-diphenylformamidinateanion) with Cu(TriPC) (TriPC = carboxyphenyl triphenylporphyrin dianion), 4-cyanopyridine (CNpy) and1,4-phenylene diisocyanide ((CN)2Phen). The reaction between the diruthenium complex and theporphyrin proceeds via a replacement of one acetate by the Cu(II) porphyrin and yields a compoundisolated as Ru2(dpf)3(Cu(TriPC))Cl on the basis of mass spectral and electrochemical data. The reactionproducts of Ru2(dpf)3(O2CCH3)Cl with 4-cyanopyridine and 1,4-phenylene diisocyanide were both in-situcharacterized by UV-visible spectroscopy and cyclic voltammetry in coordinating and/or non-coordinating solvents. Analysis of the data suggests formation of mono and/or bis adducts in the case of4-cyanopyridine while compounds of the type Ru2(dpf)3(O2CCH3)((CN)2Phen)(dpf)3(O2CCH3)Ru2 and chaincomplexes such as [Ru2(dpf)3(O2CCH3)(CN)2Phen)]n are proposed to exist in solution in the case of 1,4-phenylene diisocyanide.

2015 Joint Southeastern/Southwest Regional Meeting 689

Reactions of some hydroxy carboxylic acids with Cu^{2+} and Cr^{3+} in aqueous solutions

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Over the past decade we have studied variety of low-molecular-mass ligands with many metal ions in aqueous solutions using various spectrophotometric techniques (IR and UV-Vis) and electromotive force measurements. Herein, we are reporting the interaction of lactic acid, malic acid, and citric acid as examples of hydroxy carboxylates with Cu^{2+}, and Cr^{3+}. We are reporting the equilibrium behavior for newly discovered metal-complexes as well as their spectroscopic absorption spectra in aqueous solution at room temperature.

2015 Joint Southeastern/Southwest Regional Meeting 690

Copper and iron glycine complexes in aqueous solutions

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Glycine is the simplest amino acid (AA) among all known AAs. Because Glycine is a neurotransmitter as well as Iron(III) and Copper(II) are found in neurological fluids, we propose that these metal ions and Glycine would interact in aqueous solutions, but we didn't know how. One of the aims of this work is to determine the complex(es) formed between these ions and Glycine under ambient conditions. Potentiometric titrations and spectroscopic measurements were used to address this hypothesis. It appeared that the one to one complex (which was identified in literature before) along with other Copper/Iron and Glycine complexes were formed. Both the UV-Vis Spectroscopy and IR Spectroscopy were utilized to address this research point.

2015 Joint Southeastern/Southwest Regional Meeting 691

Investigating metal-to-metal charge transfer in bimetallic Fe-Ti complexes through spectroelectrochemistry

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Alkynyl bridged Fe-Ti complexes could be useful in solar energy conversion and photocatalysis due to their metal-to-metal charge-transfer (MMCT) excited states. It is believed that an electron is initially being transferred from Fe^{II} to Ti^{IV} to oxidize Fe^{II} to Fe^{III} and reduce Ti^{IV} to Ti^{III}, creating the MMCT excited state. For such compounds to be applied to solar cell technology, it is important to understand the decay process of the MMCT excited state. The decay of the MMCT excited states of these systems has been investigated through time resolved transient absorption spectroscopy. The spectroelectrochemisty of these molecules was also studied in order to obtain a spectrum of the reduced Ti^{III} species. Herein, we explore the spectroelectrochemistry of alkynyl bridged Fe-Ti complexes to compare to the transient absorption spectra and to further understand the decay of the MMCT excited state.

2015 Joint Southeastern/Southwest Regional Meeting 692

Redox potentials of ruthenium complexes to understand catalytic ability in water

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In attempt to help better understand the catalytic ability of ruthenium (Ru) complexes in the Aldehyde Water Shift (AWS), the hydricity of the Ru complex must be determined in aqueous solution. This is quite difficult to accomplish, both experimentally and computationally. Hence, we are exploiting the fact that hydricity is contained within a thermochemical cycle with pK_a and redox potentials in order to help simplify the process. Our research involves computationally determining redox potentials, in volts (V), of these Ru complexes. We are working with a variety of complexes. Density functional theory (DFT) was used, with multiple levels of theory utilizing three (3) functionals (B3LYP, B3P86, and M11) and two (2) basis sets. Ultimately, the goal is to determine the best level of theory to suit a wide array of applications for which hydricity is a key catalyst property. Our research has discovered that basis set was least important in determining redox potentials among the computational parameters investigated with an average of a 0.07 V difference. Changing functionals made a notable difference of 0.50 V on average in predicted redox potentials. The largest contributor to the accuracy of the calculations was ensuring that the complexes are appropriately solvated with a continuum water model, which had an average impact of 6.14 V between the gas state and SMD-water.

2015 Joint Southeastern/Southwest Regional Meeting 693

Steps toward a mechanically active gadolinium chelate

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Mechanical energy is often destructive to synthetic materials. Mechanophores, or functional groups activated by mechanical force, are designed to reroute destructive force into a constructive response. Current mechanophores produce color change, small molecule release, or cross-linking within a polymer network, functions that are useful in sensors, data displays, and self-strengthening materials. These systems are normally organic, whereas metal chelates are much less explored as mechanophores, but present several potential advantages: (1) The nature of a chelating macrocyle is such that parts of the ligand should stay coordinated to the metal center even when another part is pulled off, which bodes well for reversibility; (2) Dative bonds are weaker than normal covalent bonds, requiring a lower force for activation; (3) Many metal complexes are water tolerant and even incorporate water molecules into their coordination spheres, offering opportunities for applications in functional hydrogels. One such chelate is gadoteric acid, a gadolinium (Gd) based magnetic resonance imaging (MRI) contrast agent. With some modifications to its synthesis, this compound can be functionalized with alkene-terminating arms, allowing its incorporation as a load-bearing cross-linker in a polymer network We hypothesize that force applied to bulk material will transfer from polymer chains to the chelate, causing parts of the ligand to dissociate from the metal. This in turn should alter the MRI contrast and photophysical properties of the complex. Steps towards the synthesis of the target chelate will be presented, along with possible applications as a pressure sensor and self-strengthening hydrogel.

2015 Joint Southeastern/Southwest Regional Meeting 694

Photochemical and oxidative degradation of Fe-Ti complexes

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Research has shown that titanium dioxide can be combined with a light-absorbing dye to produce a system that can capture solar energy—a technology called dye sensitized solar cells. Typically, these dyes are made of ruthenium complexes. Ruthenium, however, is a very rare and expensive transition metal. Our lab is researching bimetallic complexes comprising first row transition metals, chiefly titanium and iron, to be used as these dyes. In order for these bimetallic dyes to be applied to solar cells, it is essential to know their photochemical and oxidative stability. Herein, we report our findings on the photochemical and oxidative decomposition of bimetallic complexes between iron and titanium. Mechanistic implications of the photochemistry will be discussed.

2015 Joint Southeastern/Southwest Regional Meeting 695

Synthesis, characterization, and reactivity of tris(2,2,2-trifluorethyl)phosphite complexes of ruthenium(II) with electron-rich arene ligands

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Ruthenium(II)-phosphite complexes of the type [Ru(*p*-cymene){$P(OCH_2CF_3)_3$}$(Cl)_2$] (**1**), [Ru(hexamethylbenzene){$P(OCH_2CF_3)_3$}$(Cl)_2$] (**2**), and [Ru(Cp*){$P(OCH_2CF_3)_3$}$_2$(Cl)] (**3**) have been prepared and characterized by multi-nuclear NMR and UV-vis spectroscopy in addition to single-crystal X-ray diffraction. Complex **1** was further reacted to produce [Ru(*p*-cymene){$P(OCH_2CF_3)_3$}(Ph)(OTf)] (**4**) as a potential catalyst for olefin hydroarylation. Olefin hydroarylation involves the formation of a new C-C bond via addition of an aromatic C-H bond across an olefin. In the presence of **4**, catalytic olefin hydroarylation attempts involving benzene and either ethylene or 1-hexene were completed. New directions involving an *N*-heterocyclic carbene (NHC) complex of the type [Ru(*p*-cymene)(C^OH)$(Cl)_2$] (**5**), where C^OH = 3-methyl-1-(3,3-dimethyl-2-butanol)imidazolin-2-ylidene, will be described where the tris(2,2,2-trifluorethyl)phosphite has been replaced with a proposed hemilabile hydroxyl functionalized NHC ligand. The structural effects of **1**-**3** with different neutral and anionic aromatic ligands, catalytic C-H functionalization attempts with **4**, and future directions with hemilabile hydroxyl NHC ligands will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 696

Building a nanothermometer for localized magnetic induction heating

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Magnetic nanoparticles can be heated by an external radio frequency ac magnetic field thereby providing local heating on a nanoscale. For their use to be fully realized, accurate surface temperatures must be obtained. Building a nano-sized thermometer that can be directly attached to the surface of magnetic nanoparticles is one way to obtain an accurate temperature of the particles at their surface during magnetic induction heating. To achieve this goal, rhodamine B, a compound with temperature dependent fluorescence, was attached the surface of the particles. Rhodamine B isothiocyanate (RITC) was reacted with 3-aminopropyltrimethoxysilane (APTMS) to give the corresponding thiourea. Alternatively rhodamine B N-hydroxysuccinimde was reacted with 3-aminopropyltrimethoxysilane to give the correspnding amide. The product was reacted with magnetite nanoparticles, where the trimethoxysilane group formed a covalent bond to the surface of magnetite. A dispersion of the magnetite-APTMS-RITC System (MARS) particles in ethanol was heated in a fluorometer and the fluorescence spectrum was measured at different temperatures. The excitation wavelength was 485 nm and there was a peak in the fluorescence emission at 573 nm. The fluorescence intensity at 573 nm decreased linearly with increasing temperature, thereby giving a calibration curve. From there, the MARS particles were used to accurately test the efficiency of heating magnetite nanoparticles by magnetic induction.

2015 Joint Southeastern/Southwest Regional Meeting 697

Rhodium and iridium complexes of a fused N-heterocyclic carbene as catalysts in hydrosylation reactions

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Since the isolation of the first stable N-heterocyclic carbene (NHC) by Arduengo in 1991, diaminocarbenes have emerged as an important class of ligands in catalysis. The development of new NHCs is an area of intense current research. A series of rhodium and iridium complexes of type [M(COD)Cl] and [$M(CO)_2Cl$] bearing a new polycyclic heteroaromatic carbene were synthesized and fully characterized by spectroscopic and crystallographic methods. The preliminary studies on the catalytic activity of these metal complexes in the hydrosilylation of acetophenone derivatives will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 698

Investigate the interface of amino acid on graphene surface

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Graphene has attracted much interest in recent years due to its unique properties and characteristics. It is considered to be the strongest, flexible, conductive and most transparent material known. Noncovalent functionalization of graphene with peptides is a promising method for producing novel biochemical sensors with high sensitivity and selectivity. In this study, graphene was synthesized using Hummers/Offeman method and peptides are then selected as possible binding candidates on graphene sheets. Both graphene and complexes were characterized with IR, NMR, and UV spectroscopy. In order to better understand the binding mode of peptides on the graphene surface, the amino acids E (Glutamic Acid), K (Lysine), L (Leucine), M (Methionine), P (Proline), and Q (Glutamine)) are modeled by Gauss View and Python and further simulated by VASP. The objective of this project is to understand the relationship between peptides and graphene host and locate possible binding parameters such as the distance and conformation. The investigation on the interaction of peptides with graphene can also provide insight into the binding behavior of larger biomolecules. This knowledge could facilitate the development of tailored peptide-functionalized graphene for sensitive biochemical sensors..

2015 Joint Southeastern/Southwest Regional Meeting 699

Stabilizing ligands for highly active water oxidation catalysts used in renewable energy conversion

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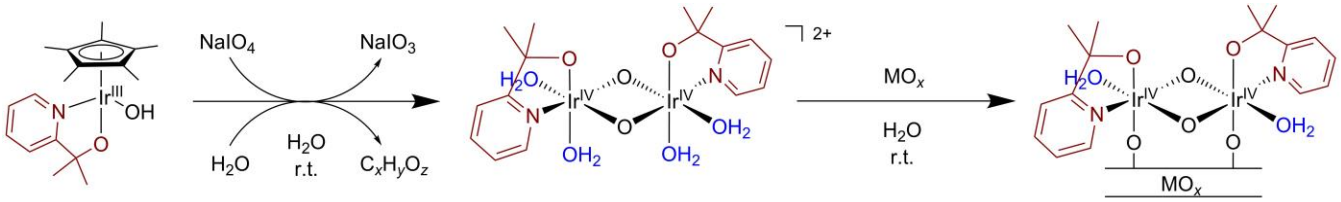
Burning fossil fuels for energy is unsustainable and has been proven to be harmful to the environment. Thus, a key challenge for scientists is to find a more sustainable source of energy supplies and conversion schemes. One option is to use hydrogen gas, produced via water splitting driven by renewable electricity from wave, wind, or solar

power. One of the main stumbling blocks for this is the challenging water oxidation step which requires the development of extremely efficient catalysts.
The iridium complex shown below is currently one of the best water oxidation catalysts. An in-depth study revealed that the Cp^* compound is a pre-catalyst, and that oxidative activation gives the dimeric species indicated which is believed to be the active catalyst. The literature has confirmed the structure of the dimer using a range of spectroscopic tools, but the multiple conformations of the dimer in solution have so far prevented capturing an accurate X-ray crystal structure. The activated form has been shown to bind to metal oxide surfaces, yielding exceptionally active O_2 evolution electrodes.
The synthesized polyoxometalate (POM), potassium decatungstosilicate ($K_8[\gamma\text{-}SiW_{10}O_{36}]\bullet 12H_2O$), is being tested to determine if it can act in a similar manner to a metal oxide surface that will trap the activated catalyst into one confirmation in order for us to obtain an X-ray crystal structure. So far, the POM has been synthesized, the identity has been confirmed using IR spectroscopy, and the POM has been tested with the iridium compound.
Oxidatively rugged, chelating phosphine-oxide ligands have also been synthesized in order to further lock the activated catalyst into one confirmation. The phenyl-substituted ligand has been synthesized and confirmed using NMR spectroscopy. The next step in this project is to complex the OPNPO ligands to a water oxidation catalyst, and to investigate their activity for this important and challenging step in obtaining hydrogen gas for a renewable energy source.



Oxidative activation of a pre-catalyst into a dimeric water oxidation catalyst that can be bound to metal oxide surfaces.

2015 Joint Southeastern/Southwest Regional Meeting 700

N-heterocyclic carbenes based on a triazine backbones: Synthesis and complexation to transition metals

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The chemical industry relies heavily on the use of metal catalysts for the economical production of a wide variety of petrochemicals in use today. Metal-catalyzed reactions can be both economically and environmentally advantageous because catalysts allow transformations to be carried out under mild conditions with high selectivity and yield. As a result, it is extremely important to develop new catalyst systems that offer increased activity with inexpensive materials under mild conditions. Due to their functional and synthetic diversity, air and moisture stability, nontoxicity, as well as a high affinity toward a wide range of main group and transition metals, nucleophilic carbenes, namely N-heterocyclic carbenes (NHCs), have shown remarkable utility as ligands for organometallic catalysts and as organocatalysts. Vital to the advancement of NHC-based catalysts has been the design and synthesis of new mono- and multitopic NHCs

that display an array of electronic and steric properties. The synthesis and properties of a new class of NHCs derived from a triazine backbone will be presented. These ligands have the potential to find tremendous utility as building blocks for homo- and heterometallic transition metal complexes**.** Complexes of catalytically relevant metal centers (rhodium and iridium) of these carbenes will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 701

Synthesis and chemical analysis of KP1019–(poly)lactic acid nanoparticle

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Platinum-based chemotherapeutic agents are widely used to combat malignant, non-metastatic cancers including testicular cancer, lung cancer, and lymphoma. These drugs have had success in treating these diseases, but come with a variety of harmful side effects due to their inability to target cancer cells exclusively. Indazolium *trans*-[tetrachlorobis(1H-indazole)ruthenate(III)], or KP1019, is a possible alternative to the current platinum-based anticancer drugs and is theorized to have a strong specificity towards cancer cells and is known to have no dose-limiting toxicity like its platinum-based counterparts. Although KP1019 appears to be promising, its effectiveness may be limited due to its low solubility in aqueous solutions. To combat this problem, synthetic drug carriers such as polylactic acid (PLA) can be used to form nanoparticles containing KP1019. To synthesize these nanoparticles, KP1019 and PLA were dissolved using nonpolar, organic solvents and combined with an aqueous surfactant solution to aid in formation of the nanoparticles. The organic solvents were then evaporated from the solution and chemical analysis was conducted on the product. After synthesis, it was observed that KP1019/PLA nanoparticles did not appear to precipitate out of solution. UV-visible spectrophotometry was conducted over time to determine if KP1019, PLA, and the surfactant (Tween 80) were indeed interacting. Over time, the characteristic KP1019 absorbance peaks increased, indicating an interaction was occurring. A closer look at KP1019 and its interaction between the PLA or surfactant solution individually showed that there was a strong interaction with KP1019 and the surfactant. The chemical properties of the KP1019/PLA nanoparticles will be described.

2015 Joint Southeastern/Southwest Regional Meeting 702

Synthesis and toxicity studies of C_{12}EDMAB coated gold nanorods: A comparison to CTAB

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Over the last 15 years the number of publications centered around nanoparticles has increased significantly. Gold nanoparticles have been the subject of many investigations owing to their interesting optical properties, long-term stability, and minimal cytotoxicity. Gold nanorods are often synthesized following a seed-mediated protocol in the presence of the cationic surfactant hexadecyltrimethylammonium bromide (CTAB) with great success. CTAB forms a micelle bilayer on the side faces of the gold promoting rod-like growth. Though effective, CTAB possesses properties that are hazardous to the environment. In the current study we have investigated the alternate cationic surfactant,

dodecylethyldimethylammonium bromide (C_{12}EDMAB), as a possible growth-directing alternative. C_{12}EDMAB has been found to have similar capabilities as those of CTAB with respect to gold nanorod synthesis yet pose a smaller threat to environmental safety and overall health based on reported MSDS data. In addition to successful gold nanorod growth as measured by UV-Vis spectroscopy and transmission electron microscopy, evidence of aspect ratio control from added $AgNO_3$ has been found and is consistent with the well-documented CTAB approach. Furthermore, preliminary cell studies suggest that at specific concentrations rods coated with C_{12}EDMAB are less toxic in HEp-2 cells over 48 hours as measured by MTT.

2015 Joint Southeastern/Southwest Regional Meeting 703

Amyloid beta (Aβ) peptides and the exposure of their hydrophobic residues upon copper(II) complex formation: Probing mechanisms of amyloid plaque formation in human and rat peptide with fluorescence spectroscopy

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Alzheimer's Disease (AD) is a progressive, neurodegenerative disease that affects 35 million people worldwide and is the 6th leading cause of death in the United States. AD is characterized by neurofibrillary tangles and amyloid plaques in the brain. The plaques are formed when amyloid beta (Aβ) peptides aggregate at their hydrophobic residues. Elevated concentrations of essential metals, copper, iron, and zinc, have been detected in the plaques and research indicates that the presence of metals speed up the formation of the plaques. Previous binding studies have determined that metal binding occurs within the first 16 amino acids of the Aβ peptide, which are usually 40 or 42 amino acids long. The rat Aβ peptide does not aggregate to an appreciable extent and differs by only 3 amino acid point substitutions (R5G, Y10F, and H13R). Based on previous thermodynamic binding studies from the Spuches lab, the exposure of the peptides' hydrophobic residues when bound to Cu(II) are hypothesized to be more accessible in the human peptide than the rat. To test this hypothesis, rat and human Aβ28 peptides in the presence and absence of Cu(II) are probed with hydrophobic fluorophore 1,8-ANS. A decrease in fluorescence is expected if the hydrophobic residues of the peptide-copper complexes become buried upon Cu(II) binding. Interesting results shed light on potential structure of both peptides in the presence and absence of Cu(II).

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2015 Joint Southeastern/Southwest Regional Meeting 704

Synthesis of chromium(III) nutritional supplement

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Nutritional supplements containing chromium(III) and a particular amino acid metabolite individually have varied reported effects on the body. While Cr is no longer considered an essential trace element, the nutritional versus pharmacological effects in the human body, specifically concerning insulin resistant conditions such as type 2 diabetes, are still unclear. In an effort to combine the purported enhanced high-intensity exercise performance associated with the amino acid metabolite and the effects of Cr into one supplement, chromium(III) salts and the amino acid metabolite acid have been combined in solvents of varying polarity and in the presence or absence of stabilizing ligands to form a trinuclear compound of the target composition. Spectroscopic and mass spectrometric studies have been utilized to establish the composition and properties of the product. A.G.M. was supported by an NSF REU award to J.B.V. and S.A. Woski.

2015 Joint Southeastern/Southwest Regional Meeting 705

Iron-catalyzed hydrophosphination

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Hydrophosphination reactions are widely considered an ideal way of creating carbon-phosphorus bonds because they allow for an easy way to achieve molecular complexity from simple, commercially available starting materials and also have the potential to be 100% atom economic reactions. We describe our attempts at catalyzing these reactions with the cheap, iron centered complexes $Fe(N(SiMe_3)_2)_2$ and $Fe(N(SiMe_3)_2)_3$.

2015 Joint Southeastern/Southwest Regional Meeting 706

Fate of dietary copper: Is the form of copper in the diet key to prevent it from becoming toxic?

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While copper is an essential trace elements for humans, copper in the form of copper(II) salts in the diet has been proposed to be associated with the increased rate of Alzheimer's disease, a disease of increasing loss of cognition leading to dementia with age. Most notably, recent studies have linked the use of copper plumbing and free copper levels (copper(II)) in the body with Alzheimer's disease. However, the fate of dietary copper in the gastrointestinal tract is poorly understood. Most foods contain copper in the form of copper(I), as the copper is bound to proteins and other biomolecules; however, in the presence of air and water, copper(I) can rapidly be converted into copper(II). In the presence of the appropriate chemicals to bind the copper, the reverse reaction can also potentially take place. The extent to which this

interconversion can take place in the gastrointestinal tract is unknown. Starting with artificial gastric juice and intestinal fluid and building to an artificial meal exposed to the fluids, the fate of copper(I) and copper(II) species in simulated gastric and intestinal environments will be determined using a variety of spectroscopic and magnetic techniques. Establishing conditions that can lead to the generation of copper(II) salts could lead to changes in diet that could minimize risk for the development of Alzhemier's disease and related conditions.

2015 Joint Southeastern/Southwest Regional Meeting 707

Luminescent enhancement of europium (III)-doped GaF_3 nanoparticles by surface modification

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Lanthanide fluoride-based nanoparticles have attracted attention due to their unique luminescent characteristics and potential use in biomedical applications. Eu(III)-doped LaF_3 nanoparticles have been extensively studied for luminescent applications where Eu(III)-centered red luminescence at 615 nm is promising for cellular imaging. Recent literature promises the use of GdF_3 as an alternative matrix for doping Eu(III) metal ions where the electronic structure of Gd(III) ions may promote energy transfer between Gd(III) and Eu(III) excited states. Notwithstanding the current progress, the use of Eu(III)-based nanoparticles in cellular imaging is limited by their low absorption coefficients due to the parity forbidden nature of 4f-4f electronic transitions. With such recognition, we are in the process of developing a sensitization process where the nanoparticle surface is functionalized with organic chromophores capable of strong light absorption. We have synthesized citric acid coated Eu(III)-doped GdF_3 nanoparticles via a water-based co-precipitation method and the nanoparticles were functionalized with ligands capable of strong light absorption. The nanoparticles were characterized using absorption and fluorescence spectroscopy, Fourier transform infra-red spectroscopy, powder X-ray diffraction, and transmission electron microscopy. The luminescent quantum yield measurements of the nanoparticles will be discussed in terms of the degree of Eu(III)-doping and surface modification.

2015 Joint Southeastern/Southwest Regional Meeting 708

Synthesis of phosphorus containing ligands for cobalt complexes for hydrogen production

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By modifying different ligands derived from 'N,N-bis(2-pyridinylmethyl)- 2,2'-bipyridine-6-methanamine (DPA-Bpy) by replacing nitrogens with phosphorus we can determine the electronic effects of ligand scaffold of cobalt complexes on the catalytic properties of H_2 production. Our study shows that not only does the placement of substitutions on pyridyl rings affect the H_2 production, but also the substitution of nitrogen with a softer element does too.

2015 Joint Southeastern/Southwest Regional Meeting 709

Ligand exchange or polymerization of an enzyme-mimic Schiff-base copper(II) complex? A kinetic study

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The synthesis, purification and characterization of a Copper(II) Schiff-base complexe is presented. The [CuLN4]$(ClO_4)_2$ complex (LN4 = N,N'-bis-(1-pyridin-2-yl-ethylidene)-propane-1,3-diamine) is highly soluble in acetonitrile, and moderately soluble in water, and exhibits Beer's Law behavior. The compound is unreactive in the presence of strong oxidizing agents, but does react slowly with oxalic and ascorbic acid. The reactivity of the complex in aqueous solvent in the presence of oxalic acid and ascorbic acid is investigated. Rapid mixing of various concentrations of [CuLN4]$(ClO_4)_2$ and oxalic acid monitored by UV-visible spectroscopy suggest an overall second order rate law. At greater time resolution, however, there is underlying complexity, suggesting an intricate mechanism. The reaction seems to be unaffected by exposure to the atmosphere. Potential structures of the product(s) will also be introduced, and various mechanisms discussed.

2015 Joint Southeastern/Southwest Regional Meeting 710

Structural and chemical biology of fosfomycin resistance in Gram-positive pathogens

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The Gram-positive pathogen *Staphylococcus aureus* is a leading cause of global morbidity and mortality. Like many multi-drug-resistant organisms, *S. aureus* contains antibiotic-modifying enzymes that facilitate resistance to a multitude of antimicrobial compounds. FosB is a Mn^{2+}-dependent fosfomycin-inactivating enzyme found in *S. aureus* and other Gram-positive pathogens that catalyzes nucleophilic addition of bacillithiol to the antibiotic, resulting in a modified compound with no bactericidal properties. Kinetic analyses and high-resolution X-ray structures of FosB from *S. aureus* and its homologue from *Bacillus cereus* have provided a clear picture of the mechanism of thiol addition and subsequent inactivation of fosfomycin. In addition, fosfomycin-treated disk diffusion assays involving *S. aureus* Newman and the USA300 JE2 methicillin-resistant *S. aureus* (MRSA) demonstrate a marked increase in the sensitivity of the organism to the antibiotic in either the FosB or bacillithiol null strains, indicating that both are required for survival of the organism in the presence of the antibiotic. This work identifies FosB as the primary fosfomycin-modifying pathway of *S. aureus* and establishes the enzyme as a potential therapeutic target for increased efficacy of fosfomycin against Gram-positive pathogens.

2015 Joint Southeastern/Southwest Regional Meeting 711

Pathogen selective antibiotic minimizes disturbances to the microbiome

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Broad spectrum antibiotics is one of the most significant medical achievements in the 20th century, reducing the mortality rates of bacterial caused infections by greater than 99%. However, recent research have found that the damage caused by broad spectrum antibiotics to the commensal microbiome is linked to reduced colonization resistance and increased chances of obesity and autoimmune diseases. Therefore, one area of active interest in antibiotic research is developing antibiotics that are selective for the pathogens and minimize the collateral damage to the microbiome. AFN-1252 is an antibiotic designed against the *Staphylococcus aureus* enoyl-ACP reductase that has passed phase II clinical trials, with nanogram per milliliter potency against *Staphylococcus aureus*. The gut bacterial abundance and composition of mice treated with AFN-1252 was compared to mice treated with broad spectrum antibiotics. Whereas broad spectrum antibiotic treatments caused up to a 4,000 fold reduction in the bacterial abundance of the gut, AFN-1252 does not affect the gut bacterial abundance. The changes to the gut microbiome composition are selective and transient during AFN-1252 treatment, with only the uncultured Bacteroidetes family S24-7 significantly decreased by day 10 of AFN-1252 treatment. S24-7 recovers to normal levels by 2 days after AFN-1252 treatment is stopped. In contrast, broad spectrum antibiotics caused severe changes to the gut microbiome composition during treatment, with many rare species still lost by 27 days after the treatment has stopped. Together, our results show that AFN-1252 is a pathogen selective antibiotic that minimizes gut microbiome disturbance.

2015 Joint Southeastern/Southwest Regional Meeting 712

Chemical control of cullin neddylation

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Ubiquitin (UB) and ubiquitin-like protein (UBL) modification pathways have emerged as important targets for oncology drug discovery based on the successes of proteasome inhibitors (e.g. bortezomib or carfelzomib), E3 inhibitors, and the NEDD8 E1 inhibitor

MLN4924. Toward this end, we have pursued approaches to target NEDD8 ligation to the cullins, through developing small molecule inhibitors of the DCN1-UBC12 protein-protein interaction. The *DCN1* gene was discovered as undergoing frequent chromosomal amplification in squamous cell carcinomas and other cancers and is associated with poorer patient survival rates. DCN1 activity is dependent on its interaction with UBC12. I will discuss our structure-based drug discovery efforts toward this target. To date, we have conducted a high-thoughput screening campaign of 600,000 compounds and identified three unique chemical series for optimization. All three series effectively disrupted the DCN1-UBC12 protein-protein interaction and neddylation in biochemical assays. Biophysical studies showed that the binding constants of the molecules to DCN1 were equivalent to inhibitory constants and the proposed binding modes were validated by crystallography. I will focus on the structure-based optimization of one of the three series that has yielded a 100-fold increase in potency and improved solubility and permeability. Our current goal is the continued optimization of this lead series to provide compounds with sufficient potency, selectivity, and bioavailability to allow the study of the consequences of inhibiting this interaction in cells and animals. Ultimately, these preclinical studies will set the stage for long-term efforts to dissect DCN1-dependent signaling pathways involved in tumorigenesis and the development of novel therapeutics for squamous cell carcinomas and other cancers.

2015 Joint Southeastern/Southwest Regional Meeting 713

Evaluation of colletoic acid: from structure to function

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Obesity-related metabolic syndrome (MetS) is a group of conditions that include insulin resistance, glucose intolerance, and type 2 diabetes to name a few. Its global rise over the past decade calls for the development of chemical tools to better understand and potentially treat it. Glucocorticoids (GCs) are endocrine hormones involved in metabolism and have been associated with MetS. GC action depends on its circulating levels as well as intracellular concentrations, which are regulated by the 11β-hydroxysteroid dehydrogenases (11β-HSD).
Colletoic acid, a natural product, is a selective and potent 11β-HSD1 inhibitor. As part of our program focused on the synthesis and chemical biology of natural products, we have developed an efficient total synthesis of colletoic acid to study its biological properties. The co-crystal structure of colletoic acid with 11β-HSD1 as determined by X-ray crystallography will be presented. Colletoic acid is a constrained molecule that effectively utilizes its functional groups to influence its binding mode. The findings highlight the close interphase between chemical biology and biomolecular crystallography to study basic mechanisms of disease.

2015 Joint Southeastern/Southwest Regional Meeting 714

Identification and characterization of influenza variants resistant to a viral endonuclease inhibitor

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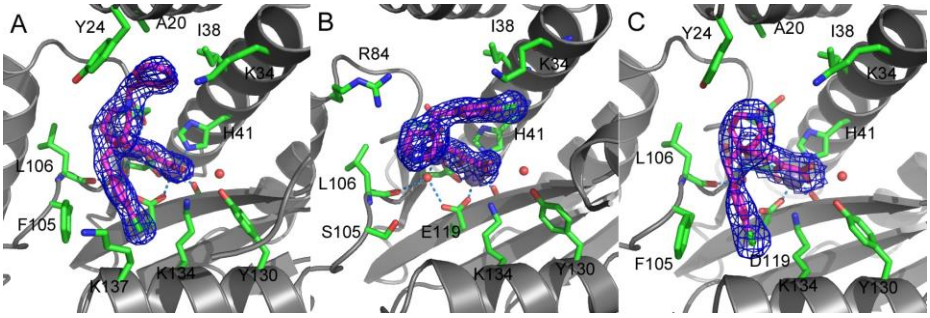
The influenza endonuclease, an essential subdomain of the viral RNA polymerase, processes host pre-mRNAs to serve as primers and is an attractive target for anti-influenza drug discovery. Compound L-742,001 is a potent endonuclease inhibitor, and we report here the generation of point mutants with reduced sensitivity to L-742,001 using a random mutagenesis approach. Each mutation mapped to the catalytic site locale where they can directly impact inhibitor binding. Engineered viruses containing the mutations showed resistance to L-742,001 both *in vitro* and *in vivo* and they displayed only a modest reduction in fitness. Introduction of the mutations to the pandemic H1N1 2009 virus also increased the resistance of this virus to the inhibitor. Using the wild type and mutant isolated H1N1 2009 endonuclease domains, we characterized the binding properties, kinetics and structural interactions of L-742,001. These analyses revealed the structural basis of resistance of the two most significant mutations, F105S and E119D. These studies will guide ongoing efforts to endonuclease inhibitors as influenza therapeutics while avoiding the emergence of resistance.



L-742,001 in complex with wtPA$_N$, F105S and E119D mutants.

2015 Joint Southeastern/Southwest Regional Meeting 715

Using NMR spectroscopy to understand the thermodynamics of gold nanoparticle-protein interactions

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When exposed to a solution containing gold nanoparticles (AuNPs), proteins spontaneously bind to the nanoparticle surface, leading to the formation of a stable surface coating, or biocorona. The composition of this biocorona in biological fluids depends on various factors, and it is currently impossible to predict whether an adsorbed protein will retain its function on the AuNP surface. AuNPs are potentially useful in a variety of diagnostic and therapeutic applications, but it is necessary to understand the physical interaction with host proteins before any of these applications can be realized. Using biophysical NMR spectroscopy, we are investigating the structural consequences and thermodynamic determinants of protein-nanoparticle interactions. Using a dataset of six globular proteins, we have found that all of them

appear to remain globular upon binding, forming a single layer on the nanoparticle surface. Protein hydrogen-deuterium exchange rates are not perturbed upon addition of AuNPs, suggesting that at least some native structure is retained on the surface. Our observations hold for a broad range of nanoparticle sizes, suggesting that surface curvature may only play a minor role in protein binding. Most recently, we have investigated protein binding as a function of pH, and, assuming moderate shifts in protein p*K*a values, we have derived a thermodynamic model for the electrostatic contribution to binding. This model can be used to interpret competition experiments where two proteins are exposed to the same nanoparticle. From our results, we conclude that binding is a complex, electrostatically-driven process with multiple discrete steps. Future investigations will focus on whether the principles derived here can be used to design functional protein-based nanoconjugates.

2015 Joint Southeastern/Southwest Regional Meeting 716

Measuring the kinetics of ground-state motion in disordered proteins and how it is influenced by small-molecule binding

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Intrinsically disordered proteins (IDP) are abundant within the human proteome and are capable of influencing a variety of cellular functions. For many IDPs, their conformational promiscuity allows for interactions with a variety of binding partners. Although the heterogeneity of these structural states has been described by NMR-based ensemble approaches, their kinetics and thus thermodynamic properties have eluded direct experimental analysis. Here, through a use of low temperature and high power NMR relaxation dispersion, we show with atomic resolution that aromatic clusters within $p27^{Kip1}$ (p27), a disordered cell cycle regulator, samples discrete conformational substates. These conformational fluctuations at 1°C occur on the timescale of 10s of μs implying low barrier motion within the ground-state of p27. The temperature-dependence of these motions exhibited non-Arrhenius behavior indicating that the motions may involve rearrangements of hydrophobic surfaces of p27 residues that interact with water. Importantly, a recently discovered small-molecule that binds and inhibits p27 (termed “SJ403”) specifically depopulates part of the ground-state ensemble, suggesting that this small-molecule interacts with specific structural states of p27. Our results provide the first-ever detailed insights into the structural mechanism and kinetics of small molecule/disordered proteins interactions. Importantly, our studies have required the development of high-powered NMR relaxation dispersion methods to study the dynamics of ^{13}Cα backbone atoms within an IDP. We will present this new methodology and the exciting results we have obtained using it for p27, a prototypical IDP.

2015 Joint Southeastern/Southwest Regional Meeting 717

Structure and binding studies of the bi-functional *Chlamydia trachomatis* protein, Scc4

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Chlamydia trachomatis causes the most common, sexually transmitted bacterial disease with an estimated 2.8 million infections occurring annually in the United States. In the body, the pathogen goes through an essential developmental process triggered by global regulatory switches. During the process infectious elementary bodies (EBs) enter host cells, differentiate into actively dividing, reticulate bodies (RBs), and then differentiate back into EBs. This unique cycle depends on the virulence-associated type III secretory system (T3SS), where class I T3SS homodimer chaperones are required to secret virulence factors that allow *C. trachomatis* to infect and multiply within host cells as EBs. Scc4 is a unique, cytosolic *C. trachomatis* enzyme that functions as both a class I T3SS chaperone and a transcription factor. Scc4 is the first class I T3SS chaperone/transcription factor shown to directly alter gene transcription by binding the β subunit (RpoB) and the primary sigma subunit σ^{66} (RpoD) of the RNA polymerase (RNAP) holoenzyme, globally inhibiting σ^{66}-dependent transcription and regulating the transition from RB to EB in the developmental cycle of *C. trachomatis*. Scc4 is also an unusual class I T3SS chaperone because it functions as a heterodimer with Scc1 to bind CopN, an essential T3SS regulator and effector. Nuclear magnetic resonance (NMR) spectroscopy, analytical gel filtration chromatography, and surface plasmon resonance (SPR) were used to investigate the binding kinetics of Scc4, Scc1, and CopN. The Scc4:Scc1 heterodimer is a very tight binding complex and can be purified directly after co-expression in *E. coli*. In contrast, the *in vitro* association rate of Scc4 and Scc1 is slow, suggesting either a change in the Scc4 and/or Scc1 structure(s) *in vitro* or the assistance of an unknown chaperone to form the heterodimer. We are using NMR to study the structure and dynamics of the Scc4:Scc1 complex to compare to the structure and dynamics of Scc4 and Scc1. Understanding the association mechanism of Scc4:Scc1 may provide a model for the release of Scc4 to function as a transcription factor.

Solution NMR refinement of a metal ion bound protein using metal ion restrained molecular dynamics methods

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Correctly calculating the structure of metal coordination sites in a protein during the process of nuclear magnetic resonance (NMR) structure determination and refinement continues to be a challenging task. In this study, we present an accurate and convenient means by which to include metal ions in the NMR structure determination process using molecular dynamics (MD) constrained by NMR-derived data to obtain a realistic and physically viable description of the metal binding site(s). This method provides the framework to accurately portray the metal ions and its binding residues in a pseudo-bond or dummy-cation like approach, and is validated by quantum mechanical/molecular mechanical (QM/MM) MD calculations constrained by NMR-derived data. To illustrate this approach, we refine the zinc coordination complex structure of the zinc sensing transcriptional repressor protein *Staphylococcus aureus* CzrA, generating over 130 ns of MD and QM/MM MD NMR-data compliant sampling. In addition to refining the first coordination shell structure of the Zn(II) ion, this protocol benefits from being performed in a periodically replicated solvation environment including long-range electrostatics. We determine that unrestrained (not based on NMR data) MD simulations correlated to the NMR data in a time-averaged ensemble. The accurate solution structure ensemble of the metal-bound protein accurately describes

the role of conformational dynamics in allosteric regulation of DNA binding by zinc and serves to validate our previous unrestrained MD simulations of CzrA. This methodology has potentially broad applicability in the structure determination of metal ion bound proteins, protein folding and metal template protein-design studies.

2015 Joint Southeastern/Southwest Regional Meeting 719

Computational and experimental studies of mono- and poly-ADP-ribosylation of peptides

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Poly(ADP-ribosyl)ation is a widespread post-translational modification that affects a large number of biochemical pathways. Molecular dynamics studies were employed to investigate the structural effects of PARylation of peptides and proteins. Force field parameters were developed to model mono-ADP-ribosylated Asp and Glu residues in Amber 12 and PARP-1 was modeled with mARylation at 4 different sites. The results showed that mARylation led to changes in secondary structure content.

We also investigated a family of mono- and poly(ADP-ribose) binding proteins, the macrodomains. Divergent macrodomains from coronaviruses were cloned, expressed and tested for biochemical functions. Five proteins were shown to be stable and independently folded. Two proteins showed unexpected nucleic acid binding affinity. NMR studies, computational predictions and biochemical experiments for studying the binding of nucleic acids and NAD^+ metabolites will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 720

Discovery of small molecules that inhibit the disordered protein, $p27^{Kip1}$

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Disordered proteins are highly prevalent in biological systems, they control myriad signaling and regulatory processes, and their levels and/or cellular localization are often altered in human disease. In contrast to folded proteins, disordered proteins, due to conformational heterogeneity and dynamics, are not considered viable drug targets. We challenged this paradigm by identifying through NMR-based screening small molecules that bound specifically, albeit weakly, to the disordered cell cycle regulator, $p27^{Kip1}$ (p27). Two groups of molecules bound to sites created by transient clusters of aromatic residues within p27. Conserved chemical features within these two groups of small molecules exhibited complementarity to their binding sites within p27, establishing structure-activity relationships for small molecule:disordered protein interactions. Finally, one compound counteracted the Cdk2/cyclin A inhibitory function of p27 *in vitro*, providing proof-of-principle that small molecules can inhibit the function of a disordered

protein (p27) through sequestration in a conformation incapable of folding and binding to a natural regulatory target (Cdk2/cyclin A).

2015 Joint Southeastern/Southwest Regional Meeting 721

Using neutrons to study fluid-rock interactions

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Recovery of hydrocarbons by hydraulic fracturing depends on complex fluid-rock interactions that we are beginning to understand using neutron imaging and scattering techniques. Organic matter is often thought to comprise the majority of porosity in a shale. In this study, correlations between the type of organic matter embedded in a shale and porosity were investigated experimentally. Selected shale cores from the Eagle Ford and Marcellus formations were subjected to pyrolysis gas chromatography (GC), Differential thermal analysis/thermogravimetric analysis (DTA/TGA), and organic solvent extraction with the resulting affluent analyzed by GC-mass spectroscopy (MS). The pore size distribution of the microporosity (~1 nm to 2 µm) in the Eagle Ford shales was measured before and after solvent extraction using small angle neutron scattering (SANS). Organics representing mass fractions of between 0.1 to 1 wt.% were removed from the shales and porosity generally increased across the examined microporosity range, particularly at larger pore sizes, approximately 50 nm to 2 µm. This range of pore sizes reflects extraction of accessible organic material, including remaining gas molecules, bitumen molecules, and kerogen derivatives, indicating where the larger amount of organic matter in shale is stored. An increase in porosity at smaller pore sizes, about 1 to 3 nm, was also present and could be indicative of extraction of organic material stored in the inter-particle spaces of clays. Additionally, a decrease in porosity after extraction was attributed to swelling of pores with solvent uptake that occurred in a shale with high clay content and low maturity. The extracted hydrocarbons were primarily paraffinic, although some breakdown of larger aromatic compounds was observed in toluene extractions. The amount of hydrocarbon extracted and an overall increase in porosity appeared to be primarily correlated with the clay percentage in the shale, with the results being complicated by solvent interactions with the pore matrix. This study complements fluid transport neutron imaging studies, to explain the physics and chemistry of fluid-rock behavior.

2015 Joint Southeastern/Southwest Regional Meeting 722

In-situ soil carbon analysis using inelastic neutron scattering

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In situ soil carbon analysis using inelastic neutron scattering (INS) is based on the emission of 4.43 MeV gamma rays from carbon nuclei excited by fast neutrons. This *in-situ* method has excellent potential for easily measuring soil carbon since it does not require soil core sampling and processing needed by the standard dry combustion method. The INS system was developed over the last decade at Brookhaven National Laboratory with recent system improvement and field testing at the USDA-ARS National Soil Dynamics Laboratory.
Conducting soil carbon analysis using the current INS system requires a 1 hour measurement per site area (2.5 m^2). The system was calibrated over pits containing carbon-sand mixtures with different carbon contents. After data processing using the calibration line, the average weight percent in a soil layer of ~10 cm thickness is determined by the INS system computer. The average weight percent in this soil layer can be used with no *a priori* knowledge of carbon distribution within the soil profile. Since comparisons of INS results to dry combustion sample analysis demonstrated good agreement, the *in-situ* INS method can be recommended as a time-saving alternative means for measuring carbon in the upper soil layer.

2015 Joint Southeastern/Southwest Regional Meeting 723

Spectroscopic monitoring of atmospheric methane near the Craighead County landfill

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From anthropogenic sources to natural oceanic emissions, the concentration of methane in the atmosphere has more than doubled in the last 200 years. Since methane represents a global warming potential 23 times an equivalent mass of carbon dioxide, monitoring this species is of great interest. In terms of anthropogenic emissions, landfills represent a significant source of atmospheric methane. We have developed an in-house algorithm for extracting methane concentrations directly from FTIR spectra for gas samples. In this work, we will describe the algorithm and present some preliminary measurements on samples collected at a local landfill.

2015 Joint Southeastern/Southwest Regional Meeting 724

Sorptive removal of Pb^{2+} and mechanisms of adsorption on chitosan-modified biochar

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In this study, Pine wood biochar prepared at 698 K with a residence time of 20-30 s in an auger-fed reactor was used to synthesize chitosan-modified biochar to produce a low cost adsorbent to remove Pb^{2+} from aqueous solution. The characterization of both chitosan-modified and non-modified biochars were studied using Fourier transform

infrared spectroscopy, scanning electron microscopy,scanning electron microscopy/energy dispersive X-ray spectroscopy, surface area measurement, elemental analysis, thermogravimetric analysis, and ζ-potential measurements. Charaterization results showed that the application of chitosan on biochar surface could improve its performance as an adsorbent. Batch sorption studies were performed at pH values from 2 to 5, and temperatures from 298 to 318 K.The total amount of Pb^{2+} adsorbed was determined quantitatively using atomic absorption spectrophotometry. Batch sorption experiments indicated that, compared to the unmodified biochar, the chitosan-modified biochar showed enhanced removal of Pb^{2+} from solution, suggesting that the modification of biochar with chitosan generates different adsorption sites on their solid surface for metal adsorption. Pseudo-second order kinetics provided the best fit with regression coefficients of 0.998 or greater. Sorption was evaluated from 298 to 318 K using the Freundlich and Langmuir isotherm models. The mechanisms of Pb^{2+} adsorption on chitosan-modified biochar were studied by using the Fourier transform infrared spectroscopy and X- ray photoelectron spectroscopy. This work proves that combination of biochar and chitosan, which are both very cheap and largely available green materials, can be used as an effective adsorbent to remove Pb^{2+} from aqueous solution.

2015 Joint Southeastern/Southwest Regional Meeting 725

Assessment of down-hole membrane-diffused hydrogen for stimulating uranium reduction and immobilization

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The most common technology currently used for restoring groundwater at In-Situ Recovery (ISR) uranium mining sites is Reverse Osmosis (RO) and reinjection of the permeate. However, this practice does not restore the formation to its original reduced state, and in many cases groundwater uranium concentrations are not restored to pre-mining baseline levels. This study was performed to evaluate the effectiveness of introducing dissolved hydrogen into a post-mined formation at an ISR mining site to stimulate reduction and immobilization of residual soluble uranium. The main objectives of this research project were: 1) to develop and optimize a system for minimizing air entrainment during water injection when employing a membrane gas-transfer device for down-hole hydrogen infusion; 2) to assess whether injecting dissolved hydrogen using the membrane gas-transfer device can promote immobilization of dissolved uranium in groundwater to near or below pre-mining concentrations. Approximately 30,000 gallons of groundwater were pumped to the surface and then re-injected into the subsurface while being supplied with dissolved hydrogen using the down-hole membrane gas infusion device. The groundwater was pumped back to the surface after several months to evaluate the extent to which dissolved uranium had been removed. Initial results indicate an approximately 80% reduction in soluble uranium concentration was achieved. Microbial analyses indicated a significant increase in iron-reducing bacteria, but less significant increases in sulfate-reducing bacteria. A bromide tracer study was performed concurrently with the hydrogen injection study so that the effective zone of influence of the push-pull test could be estimated, while pump tests were performed before and after the hydrogen injection study so the effect of the injected hydrogen on the formation permeability could also be assessed.

2015 Joint Southeastern/Southwest Regional Meeting 726

Fabrication and characterization of nanoscale pillar arrays for planar chromatography

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This work evaluates silicon nano-pillar arrays for use in planar chromatography. Electron beam lithography (EBL) and Dewetting (DW) protocols are used to create nano thin layer chromatography platforms. The pillar heights for all systems investigated are 1-2 micron. The pillar diameter/pitch is 400/550-700 nm for the EBL arrays and 230/640 nm for the DW. A porous silicon oxide layer is added to each of the pillar arrays and then a C18 stationary phase created. Wicking flow was studied with permeability being markedly higher than for traditional planar platforms. The plate height using Sulforhodamine test dye was as low as 0.1 micron and reproducible. Separations of fluorescent dyes, environmentally significant derivatized-amines, and anti-tumor drugs are illustrated. Current efforts include adding a centrifugal force component to enhance and optimize flow rates. Since the pillar platforms are diminutive and driven by wicking flow they are suitable for mobile, in field use.

2015 Joint Southeastern/Southwest Regional Meeting 727

Ion transfer stripping voltammetry for the detection drugs in real samples

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The ion transfer stripping voltammetry (ITSV) technique is used to detect selective serotonin reuptake inhibitors (SSRIs) such as fluoxetine (Prozac®), citalopram (Celexa®), and sertraline (Zoloft®) in drinking and river water. These are common antidepressants that become highly toxic contaminants when they get into the drinking water. In this work we applied ITSV to detect the SSRIs in their cationic form at nanomolar concentrations using a sensitive, inexpensive, and disposable pencil lead electrode with a lower limit of detection of 35, 45, and 25 nM for fluoxetine, sertraline, and citalopram, respectively. The pencil lead was modified by an electrochemically deposited 3, 4-ethylenedioxythiophene (PEDOT-C_{14}) conductive polymer layer and then dip coated with a plasticized poly(vinyl chloride) (PVC) membrane. The PVC/PEDOT-C_{14}-modified electrode was operated in the stripping voltammetric mode. It had a linear current response between 100 nM and 1000 nM for fluoxetine, sertraline, and citalopram, respectively, in tap and river water samples. Importantly, the measurements with the membrane-coated electrode provided information on the lipophilicity of these antidepressants, thus contributing to a better understanding of their environmental toxicity and the risks they pose to humans.

2015 Joint Southeastern/Southwest Regional Meeting 728

Electrochemical detection of TNT using vanadium dioxide particle films

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Vanadium dioxide (VO_2) undergoes a first-order phase transition at 68ºC from an insulating phase (M) to a conducting phase (R), resulting in increases in the conductivity and optical absorption. Thin films of VO_2(M) have been used in electronic and electro-optic applications, but often require expensive precursors or instrumentation to synthesize; due to this, the applicability of VO_2(M) in other areas, such as catalysis and sensing, has remained relatively unexplored. Hydrothermal methods, however, offer the capability of inexpensively synthesizing relatively large quantities of VO_2(M). 2,4,6-trinitrotoluene (TNT) is an explosive compound that is widely used in both the military and civil sectors. In addition to being explosive, TNT and its derivatives are also known to be mutagenic, leading to the need to be able to both detect and eliminate TNT from the environment in a rapid and cost-effective manner. Electrochemical methods have been shown to allow for rapid and sensitive detection of TNT and TNT derivatives. Recent work in the Cliffel lab has shown that thin films of VO_2(M) deposited on ITO glass can electrochemically detect TNT in solution at concentrations as low as 1 ppb. In this work, we use hydrothermally synthesized VO_2(M) nanoparticles and drop cast them onto glassy carbon electrodes to use as the working electrode. The VO_2 particle films are approximately five times more sensitive than the VO_2(M) thin films at TNT concentrations greater than 1 ppm.

2015 Joint Southeastern/Southwest Regional Meeting 729

Predictive models of aqueous organic contaminant binding properties on carbon surfaces: QSPR and QM computations applied to emerging contaminants of concern

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A compound's affinity for activated carbon surfaces is an important factor to consider in various environmental analysis, filtration, and remediation technologies. We highlight efforts and success in developing a model that can be used to predict adsorption isotherm behavior over a range of compounds with varying physicochemical properties. The important influence of accounting for conformational complexity, as revealed by exhaustive stochastic searches of the conformational space, when obtaining relevant molecular descriptors cannot be understated. The resulting QSPR is based on a training set of 62 neutral organic molecules for which isotherm data was available and it's utility is illustrated by predicting a host of representative contaminants of emerging concern, including endocrine disrupters, flame retardants, and pharmaceuticals, as well as components of the spilled fluids implicated in the 2014 Elk River Chemical Spill in WV.

2015 Joint Southeastern/Southwest Regional Meeting 730

Comparison of teratogenic and toxic effects of ortho-phthalate esters in xenopus embryos

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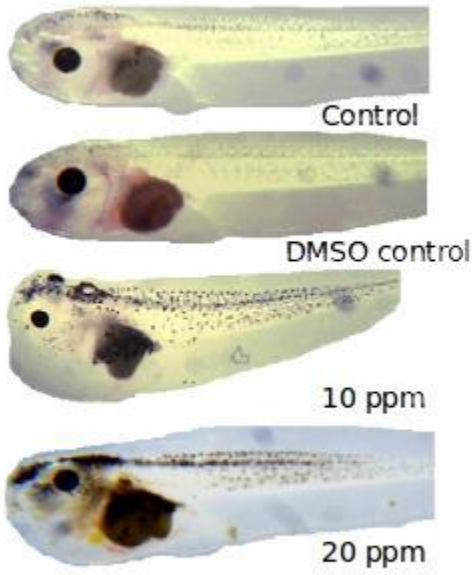
Phthalates, compounds used to add flexibility to plastics, are ubiquitous in the environment. These compounds have been shown to cause detrimental effects in organisms, with toxic effects that vary according to alkyl chain length. Embryos of *Xenopus laevis*, the African clawed frog, have been used to assess toxicity and teratogenicity of diethyl, di-n-propyl, and di-n-butyl phthalate, and could serve as model for assessing the toxic and teratogenic effects in ortho-phthalate esters. These phthalates showed increasing toxicity with increasing ester length. Developing *Xenopus laevis* exposed to Diethyl, Di-n-Propyl, and Di-n-Butyl phthalate showed similar malformations that also occurred at lower concentrations with increasing alkyl chain length. Teratogenicity did not increase with alkyl chain length, with the assay showing only Di-n-Butyl phthalate to be teratogenic.



Xenopus laevis embryos from a representative Di-n-propyl phthalate, (DnPP), experiment at 96 hours. Both DMSO and FETAX control embryos, shown in the top two panels, show normal development. DnPP embryos exposed to 10 ppm, shown in the third panel from the top showed increased melanization, and dark pigmentation, as well as some edema, gut coiling, and brain abnormalities. Embryos exposed to 20 ppm DnPP showed more drastic gut coiling abnormalities, as well as edema.

2015 Joint Southeastern/Southwest Regional Meeting 731

Interactions of fluoroquinolones and MGIs with *Mycobacterium tuberculosis* gyrase: Enhancing drug activity against wild-type gyrase and resistant mutants

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Mycobacterium tuberculosis is a significant source of global morbidity and mortality and is second only to HIV/AIDS as the most prolific killer due to a single infectious agent. Moxifloxacin and other fluoroquinolones are important therapeutics for the treatment of tuberculosis, particularly multi-drug resistant infections. Therefore, it is critical to understand the basis of quinolone action against *M. tuberculosis* gyrase and how mutations in the enzyme cause resistance. To address these issues, we characterized interactions of quinolones and related drugs with wild-type gyrase and enzymes carrying mutations at A90 and D94. *M. tuberculosis* gyrase lacks a highly conserved serine that anchors a water-metal ion bridge that is critical to quinolone function against other bacterial type II topoisomerases. Despite the fact that the serine is replaced by an alanine (A90) in *M. tuberculosis* gyrase, the bridge still forms and plays an important role in mediating quinolone-gyrase interactions. Clinically relevant mutations at A90 and D94 cause quinolone resistance by disrupting the bridge interaction, thereby decreasing drug affinity. Quinolone activity against wild-type and resistant enzymes can be enhanced by the introduction of specific groups at the C7 and C8 positions. Alterations at the C8 position of moxifloxacin were especially effective and produced a compound that induced high levels of stable cleavage complexes with wild-type gyrase and two common resistant enzymes, $GyrA^{A90V}$ and $GyrA^{D94G}$. C8-modified moxifloxacin was ~5 times more potent than moxifloxacin against wild-type *M. tuberculosis* gyrase and displayed higher activity against the mutant enzymes than moxifloxacin did against wild-type gyrase. In addition to drug structure, the handedness of supercoils in DNA substrates had a profound effect on gyrase-mediated DNA cleavage and drug efficacy. Finally, a novel class of *Mycobacterium* gyrase inhibitors (MGIs) induced gyrase-mediated single-stranded DNA breaks and were active against quinolone-resistant mutant enzymes. This chemical biology approach to defining drug-enzyme interactions has the potential to identify novel drugs with improved activity against tuberculosis. Supported by NIH grants CA09582 (KJA), AI87671 (RJK), GM007628 (EGG), CA077373 (JMB), and GM033944 (NO), VA Merit award I01 Bx002198 (NO), NSF Graduate Research Fellowship DGE-0909667 (REA), and a European Molecular Biology Organization Long-Term Fellowship (TRB).

2015 Joint Southeastern/Southwest Regional Meeting 732

Iron mediates catalytic function of nucleic acid processing enzymes

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Life originated and proliferated in an anoxic environment where iron was benign, abundant and soluble. We hypothesize that for the first 2 billion years of life on earth Fe^{2+} was a ubiquitous and generally useful cofactor for nucleic acids, with roles in folding, catalysis and processing by proteins. In this model, Fe^{2+} was replaced as the primary cofactor for nucleic acids by Mg^{2+} in parallel with other metal substitutions of metalloproteins, driven by the great oxidation event. To test this model, we assay the ability nucleic acid processing enzymes to use Fe^{2+} in place of Mg^{2+} during catalysis. We have substituted Fe^{2+} for Mg^{2+} in a thermostable DNA polymerase and in a T4 DNA ligase. The results show that Fe^{2+} can indeed substitute for Mg^{2+} in initiation and elongation by the DNA polymerase, as well as in ligation of DNA oligonucleotides by the T4 DNA ligase. Early earth conditions facilitate Fe^{2+} to Mg^{2+} substitution in two enzymes

and are consistent with a more general model in which modern biochemical systems retain latent abilities to revert to primordial Fe^{2+}-based states when exposed to pre-GOE conditions.

2015 Joint Southeastern/Southwest Regional Meeting 733

Elucidating the mechanism of charge transport in human DNA primase

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DNA polymerases responsible for synthesizing new complementary strands during replication are incapable of initiating synthesis on their own and require the presence of an 8-10 ribonucleotide primer initially laid down by DNA primase. Eukaryotic DNA primases are composed of two subunits: a smaller catalytic subunit (p48) and a larger regulatory subunit (p58). p58 is responsible for binding and positioning the template DNA strand over the active site of p48 and contains an 4Fe-4S cluster. A primary goal of our research is to understand the role of the 4Fe-4S cluster in DNA primer initiation and handoff to polymerase α. Our hypothesis is that it is involved in redox-active electron charge transport across the DNA substrate to communicate with other 4Fe-4S cluster containing proteins. However, the 4Fe-4S cluster in p58 is not near the surface of the enzyme. Instead, it is buried in the core of the C-terminal domain (p58C), approximately 20 Å from the accepted DNA binding location of p58C. A bridge of three tyrosines (Y309, Y345, and Y347) link the 4Fe-4S cluster to the DNA binding domain and could serve as an electron transport conduit in a protein radical transfer mechanism. To probe the mechanism of the 3-tyrosine pathway, we mutated each to a phenylalanine. Indeed, each of the Y to F mutants is charge transfer deficient relative to the WT enzyme. Circular dichroism and electronic absorption spectroscopy indicate that the three mutants are folded and cluster-loaded similar to WT p58C. Fluorescence anisotropy analyses indicate that each mutant binds DNA with similar affinity to WT p58C, and a crystal structure of Y347F shows that the overall structure of the mutant is the same as WT P58C with the phenylalanine ring oriented in the same position as the tyrosine ring in the superimposed structures. These results support a protein radical transfer mechanism from the 4Fe-4S cluster to the DNA through p58C. Elucidating the role of charge transport in DNA primase could transform our understanding of other DNA damage and repair pathways.

2015 Joint Southeastern/Southwest Regional Meeting 734

Using restriction endonuclease activity assays to examine cooperativity and competition in the binding of small molecules to DNA

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The binding of a variety of types of small molecules, e.g., actinomycin, netropsin, heterocyclic diamidines, porphyrins, to DNAs has been shown to produce changes in

the structure of the DNA. Such structural alterations subsequently produce alterations such as cooperativity in the further binding of these molecules to the target DNA. The exact nature of the structural alterations and the effects on binding vary depending upon molecular structure. We have previously used restriction enzyme activity assays to probe the binding of the molecular types listed above to relaxed and supercoiled phiX174 DNA. In addition to the observed sequence specificity of binding, these molecules produced enhancement of cleavage by certain restriction enzymes at certain locations. Enhanced cleavage likely arises from the binding and DNA structural alteration near but not at restriction enzyme reaction sites. With [N-methylpyridyl]porphines and with diamidines, altering molecular structure changed enhanced cleavage into inhibited cleavage, suggesting that altering the ligand structure changes the effect of binding on DNA structure. To probe this, we have examined the effects of binding mixtures of either the porphines or the diamidines [provided by D. W. Boykin and W.D. Wilson, Georgia State University] to phiX174 DNA using restriction enzyme activity assays. For example, using the restriction enzyme Nru I [TCGCGA], separately the diamidine DB75 produced inhibition of cleavage and DB818 produced enhancement. The combination produced inhibition. Using Stu I [[AGGCCT], DB293 produced enhancement and DB818 had no effect. The combination produced inhibition. With Alw44 [GTGCAC], DB75 and DB818 separately produced enhancement. The combination produced inhibition. Ortho [N-methylpyridyl]porphine and meta[N-methylpyridyl]porphine separately produced inhibition of cleavage by Dra I [TTTAAA] but the mixture yielded enhanced cleavage. With Bssh II [GCGCGC], the ortho isomer produced inhibition and the meta had no effect. The mixture yielded enhancement. These studies suggest that, while related molecules may bind to the same sites on DNAs, the exact nature of the binding depends on the structure of the binding species.

Bypass and misincorporation of DNA polymerases at DNA-peptide crosslinks

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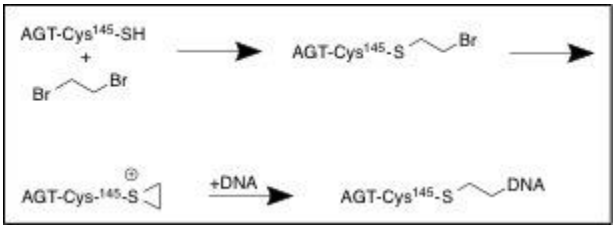
The preservation of DNA replication is requisite for cellular integrity and prevention of tumor formation and cell death. The Y-family DNA polymerases (Pol *h*, *k*, *i*, and REV1) are crucial in this process because of their roles in the replication and bypass of DNA lesions and adducts. DNA-peptide crosslinks (DPCs) are formed through the bioactivation of *bis*-electrophiles such as ethylene dibromide and butadiene diepoxide. These electrophiles can bind both peptide and polypeptide targets such as glutathione and alkylguanine DNA-alkyltransferase (AGT) and DNA. Evidence has shown that these DPCs are mutagenic as well as cytotoxic to cells. Mutations can arise from the translesion DNA polymerases replicating past the DPCs. However, this notion is enigmatic because it is assumed that AGT crosslinked to DNA would prevent DNA polymerase replication due to protein size. Therefore, we believe that AGT crosslinks undergo proteolysis to smaller peptides before replication, and our central hypothesis is that select translesion DNA polymerases are capable of replicating through DNA-peptide crosslinks. We synthesized peptide adducts from the active site of the AGT protein and crosslinked them to an oligonucleotide. Replication studies show that Pol *h*, *i*, and *k* are capable of bypassing through smaller crosslinked peptides (3-7 aa) when bound to DNA complexes. This bypass has also been shown to mutagenic in the bypass of Pol *h* and *i* but not Pol *k*.



2015 Joint Southeastern/Southwest Regional Meeting 736

Investigating different metal ion concentrations for *in vitro* selection of DNA aptamers for pesticide targets

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Functional nucleic acids, including aptamers, ribozymes, and deoxyribozymes, have become important in a variety of applications, particularly sensors. Aptamers, with their ability to bind to targets with high selectivity and affinity, are useful for recognition and can be paired with catalytic DNA sequences (deoxyribozymes) to form signaling aptazymes. One challenge when developing aptazymes is that the *in vitro* selection conditions used to identify the aptamer can vary greatly from the reaction conditions necessary for optimal deoxyribozyme activity. Aptamer selections commonly mimic physiological conditions, while deoxyribozyme selections are conducted under a wider range of pH and divalent metal ion conditions. We are particularly interested in understanding the effect of divalent metal ion concentration on aptamer selections. Isolating aptamers under conditions that match deoxyribozyme reaction conditions should ease the development of aptazymes and facilitate the activities of both the binding and catalytic components. We targeted the herbicides alachlor and atrazine in our selection efforts using different divalent metal ion conditions. Each set of conditions yielded aptamers that were unrelated to aptamers identified under the other selection conditions. Our efforts to characterize these aptamers and the implications for aptazyme development will be discussed.

2015 Joint Southeastern/Southwest Regional Meeting 737

Exploring the origins of RNA: Spontaneous formation and assembly of plausible proto-nucleotides

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The ‘RNA world’ remains one of the most influential hypotheses regarding the origin of life. Nevertheless, a plausible prebiotic synthesis of RNA has not been demonstrated. Early attempts to synthesize nucleosides in model prebiotic reactions demonstrated that adenosine can be formed by drying and heating adenine with ribose, but analogous reactions have not been found to produce the three other canonical nucleosides of RNA [1]. We are investigating the hypothesis that different nucleobases came before those of contemporary RNA [2], and that the ancestral nucleosides (or proto-nucleosides) readily formed glycosidic bonds with ribose. As part of these studies, we have recently

discovered that 2,4,6-triaminopyrimidine (**TAP**) forms nucleosides with dried and heated with ribose [3]. The spontaneous formation of **TAP** nucleosides is also of interest because, unlike the free bases and mononucleosides of RNA, **TAP** nucleosides form ordered assemblies when mixed in water with a complementary heterocycle (i.e., cyanuric acid), even as the crude products of a **TAP**+ribose reaction. We are now exploring model prebiotic reactions for the synthesis of nucleosides that pairs with **TAP** nucleosides, as well as the synthesis of the nucleotides of these model proto-nucleosides.

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2015 Joint Southeastern/Southwest Regional Meeting 738

Mechanism of action of N-hydroxylating flavin-dependent monooxygenases

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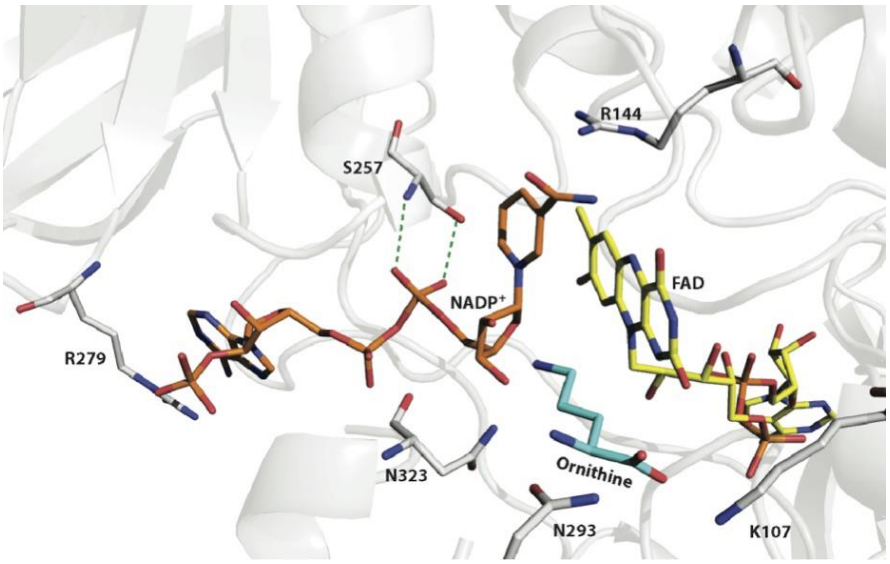
Flavin-dependent monooxygenases catalyze the NADPH-and O_2-dependent hydroxylation of a variety of substrates. At the center of the chemical mechanism of these enzymes is the formation and stabilization of the C4a-hydroperoxyflavin intermediate, which is the hydroxylating species. Siderophore A (SidA) is a flavin-dependent monooxygenase that catalyzes the hydroxylation of ornithine at the N5-position in the biosynthesis of siderophores in *Aspergillus fumigatus*. Because the function of SidA is essential for virulence, this enzyme has been identified as a target for drug development. We present results from biochemical, DFT and molecular dynamics simulations, and structural approaches that have allowed the detailed characterization of the mechanism of hydroxylation and the role of key residues in catalysis. The results support a mechanism of coenzyme-assisted catalysis in SidA, where NADP(H) plays a dual role, flavin reduction and stabilization of oxygenated flavin intermediate. The results are relevant to other flavin-dependent enzymes and have implication for drug design.



2015 Joint Southeastern/Southwest Regional Meeting 739

Methods for the identification of potential therapeutics from combinatorial peptoid libraries

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Previous work has demonstrated the utility of peptoids, peptide mimics with backbone shifted R groups, as potential therapeutics. Given their ease of synthesis and modular design, peptoids are well suited for combinatorial synthesis and high-throughput screening. Our research focuses on the design and synthesis of combinatorial libraries of peptoids and the development of high-throughput methods to screen these libraries. Current work is focused on methods to identify antimicrobial peptoids and peptoid antagonists of the leptin receptor as potential therapeutics for triple-negative breast cancer. Peptoid synthesis and sequencing, biological target purification, and library screening will be discussed.

2015 Joint Southeastern/Southwest Regional Meeting 740

E-4-Hydroxy-3-methylbut-2-enyl diphosphate reductase (IspH): An isoprenoid synthesis enzyme

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Isoprenoids are a large group of biomolecules that are essential for the survival of organisms. Most eubacteria and protozoan parasites use the 1-deoxy-D-xylulose 5-phosphate (DOXP) pathway for the synthesis of the isoprenoid building blocks, isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMAPP). The DOXP pathway is not used in humans hence the enzymes involved in this pathway can be specifically targeted, making this an attractive pathway in the search for novel antibacterial and antimalarial drugs. To achieve this an in depth knowledge of the

reaction mechanisms of these enzymes is needed, including understanding the role of cofactors and conserved amino acid residues in the active site of the enzymes. IspH catalyzes the last step in the pathway, the conversion of E-4-hydroxy-3- methylbut-2-enyl diphosphate (HMBPP) into IPP and DMAPP. Colorimetric assays and EPR-spectroscopy-based-kinetics studies were used to probe the active site 4Fe-4S cluster and the conserved amino acid residues H124 and E126 of wild type and mutant IspH. The H124Fvariant has very low activity whereas the E126Q mutant has no activity. Rapid Freeze quench experiments with WT IspH showed two signals with different g values. A transient intermediate with EPR g values 2.176, 2.008 and 2.000 (E.coli) or 4.668 and 3.384 (A.aquifex). This signal denoted as FeS-I is proposed to be an intermediate where the cluster is a $[4Fe\text{-}4S]^{3+}$ based species and directly bound to the HMBPP. A second signal with g values 2.082, 2.006 and 1.991 that represents cluster-product species, FeS-II. Both FeS-I and FeS-II species are observed for the H124F variant. The E126Q mutant shows a species,FeS-III, with g values 2.117, 2.003 and 1.964 which is different than the FeS cluster bound to substrate or product. The kinetic and spectroscopic analyses suggest that the H124 participates in correct orientation of the HMBPP and the E126 residue is involved in stabilizing the HMBPP C4-OH and dehydroxylation. Although the FeS-III has been proposed to resemble a transition intermediate, the formation of this form does not appear to be catalytically competent.

2015 Joint Southeastern/Southwest Regional Meeting 741

Novel approaches for the biosynthesis and diversification of polyketides

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Many polyketides are biosynthesized in a modular fashion by the selection and condensation of small molecule building blocks, catalyzed by polyketide synthases (PKSs). Chimeric PKSs can be constructed in an attempt to produce analogues for drug discovery. Yet, the scope and utility of this combinatorial approach is limited by the inherent substrate specificity and poor functional modularity of most PKSs. Here, we show that several PKS components are more tolerant towards non-natural building blocks than has been previously recognized. Such promiscuity forms a platform for constructing new biosynthetic parts with substrate specificities orthogonal to those found in Nature. Accordingly, we describe a comprehensive program of enzyme engineering, directed evolution, and synthetic biology aimed at constructing artificial bacterial strains capable of producing complex polyketides that are regioselectively modified with non-natural chemical functionality. Our synthetic biology approach expands the synthetic capabilities of polyketide diversification strategies, and provides an improved understanding of the molecular basis for specificity in complex molecular assemblies.

2015 Joint Southeastern/Southwest Regional Meeting 742

The role of the S-loop of human glutathione synthetase

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The second step in the biosynthesis of the cellular antioxidant glutathione is catalyzed by human glutathione synthetase (hGS), a negatively cooperative homodimer. Experimental point mutations to three active site residues (R267, D268, Y270) and molecular dynamic simulations show the S-loop not only binds the negatively cooperative substrate γ-glutamylcysteine (γ-GC) through a salt bridge and multiple hydrogen bonds, these residues also modulate allosteric communication in hGS. By elucidating the role of S-loop residues in active site structure, substrate binding, and allostery, the atomic level sequence of events that leads to the detrimental effects of hGS mutations in patients are more fully understood.

2015 Joint Southeastern/Southwest Regional Meeting 743

Molecular structure and oxidation of methionyl dipeptide

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Methionine (Met), one of the two sulfur containing amino acids, is readily oxidized by reactive oxygen species. Oxidation of Met, free as well as protein-bound, has been implicated in numerous inflammatory, age-related diseases. We suspect that the oxidation of Met in peptides and proteins may depend on the position of Met within the biomolecule. In order to understand the mechanism of biochemical oxidation, we have taken three Met-containing (Met-Gly, Gly-Met, and Met-Met) and reacted them with either peroxynitrite or hypochlorite. The reactions were carried out in phosphate buffer at pH 7.0 and monitored using UV/Vis spectrophotometry. The products formed in these reactions were analyzed by RP-HPLC. When stoichiometric equivalents of PN was added, about 50% of Met was consumed in the reaction. In the case of Met-Gly, the extent of oxidation was 74 %, about 24% higher than that was found when free Met was employed in the reaction. With stoichiometric amounts of hypochlorite, all three dipeptides were completely oxidized. The UV-Vis analysis of the product peaks for both peroxynitrite and hypochlorite oxidation showed peaks between λ_{200nm} to λ_{220nm} which varied depending on the peptide sequence. In addition, we also elucidated the crystal structure of all three dipeptides. The absolute configurations were confirmed by the X-ray data. All peptides were zwitterionic, and the amino acid residues are linked to each other in a *trans* orientation. The findings from these experiments will support ongoing studies on the role of methionine in oxidative stress pathways, and the stability of proteins in degenerative diseases such as Alzheimer's and Parkinson's disease.
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Global metabolomic profiling of cuprizone-induced demyelination in the central nervous system

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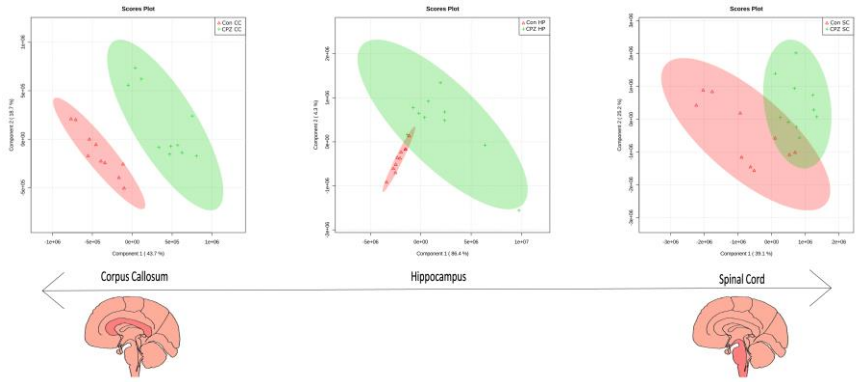
The emerging field of mass spectrometry-based metabolomics offers information on metabolic alterations predictive of disease phenotypes as well as biomarkers for inflammation and tissue damage. Our work investigates the copper chelator cuprizone (CPZ) as a platform to test the predictive power of global metabolomics. CPZ has been used for almost 50 years to study pathways involved in white matter damage that occurs in multiple sclerosis. Administration of CPZ to mice results in reproducible and selective damage to the myelin-producing cell, the oligodendrocyte. Despite the extensive use of this model to test neuroprotective therapies, little is known of its structure or its mechanism of action. Our preliminary metabolomic work, utilizing an oligodendrocyte cell line, showed elevated dysregulation in CPZ treated cells. Tissue was then collected from different areas of the CNS after mice were exposed to CPZ for 6 or 2 weeks and comprehensively analyzed. The corpus collosum, hippocampus, and spinal cord were all compared, as they are uniquely affected. Meta-analysis of the tissue revealed many analyte overlaps, including metabolites associated with folate, and arachidonic acid. The spinal cord (an area clear of lesions) revealed unique dysregulations that were time-point dependent. Analysis of CPZ-induced pathology in oligodendrocytes indicates that this compound perturbs multiple tissue specific pathways and that its *in vivo* toxicity may involve more than its ability to chelate copper.



The PLS-DA analysis of varying tissue samples comparatively analyzing CPZ treatment versus the vehicle. A trend is evident correlating to demyelination among tissue regions.

2015 Joint Southeastern/Southwest Regional Meeting 745

Principles of transition metal selectivity and transport in transmembrane ion pumps

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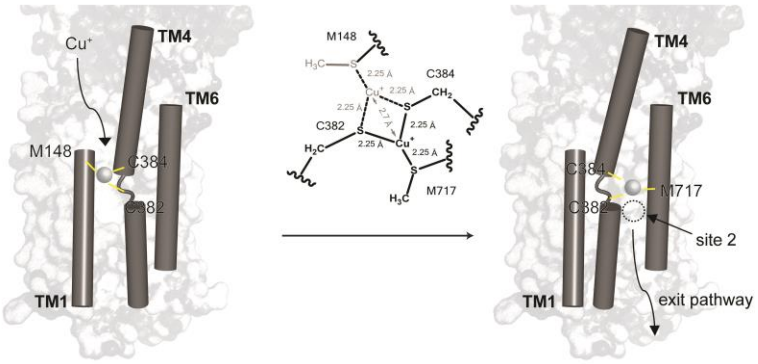
P_{1B}-type members of the P-type ATPase superfamily of ion pumps evolved as a principal transport system for the selective translocation of essential and toxic transition metal ions across the cell membrane. The molecular mechanisms by which these nanomachines select transition metals and how the energy stored in ATP is converted into the directional flux of metal ions across the membrane are not completely understood.
A multidisciplinary structural and biochemical strategy is developed to obtain a molecular understanding of the principles of transition metal selectivity and transport in P_{1B}-type ATPases.
By utilizing a bioinorganic chemistry approach, we investigate how transition metal and oxidation state selection are achieved. We are characterizing the metal binding and transport properties of targets belonging to different P_{1B}-type subfamilies which show different ion selectivity patterns, including Cu^{+}/Ag^{+}, Cu^{2+}, $Zn^{2+}/Cd^{2+}/Pb^{2+}$ or Co^{2+}. By using structural and spectroscopic techniques, we have determined the metal transport pathways in Cu^{+}/Ag^{+}, $Zn^{2+}/Cd^{2+}/Pb^{2+}$ and Cu^{2+} ATPases purified in detergent micelles or reconstituted in artificial lipid bilayers. These studies are revealing differences in the nature of the coordinating ligands, the geometry of metal binding in their transmembrane binding sites, and the coordination chemistry and mechanism underlying metal selection and translocation. Together with the biochemical characterization of the pumps catalytic transport cycle we are providing new highlights into the peculiar bioinorganic chemistry involved in metal transport across biological membranes.



A sulphur-based transport pathway in Cu^{+} ATPases

2015 Joint Southeastern/Southwest Regional Meeting 746

Synthesis and pharmacology of a radioiodinated δ-opioid selective agonist based on the [$_{D}$Ala^{2}]deltorphin II template

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The deltorphins are a group of peptides isolated from skin secretions of the Giant Monkey Frog, (*Phyllomedusa bicolor*), which are potent δ-opioid receptor selective

agonists. Halogenated derivatives of [$_D$Ala^2]Deltorphin II were synthesized and tested for agonist activity. It was found that there was a linear correlation between binding affinity and the size of the halogen. Additionally, the iodinated compound (Figure 1) was δ-selective over the μ and κ receptors and a full agonist in the [^{35}S]GTPγS functional assay. This compound was analgesic when given supraspinally in mice, with ED_{60} values over three times more potent than morphine. This analgesia was blocked by the δ-opioid receptor antagonist naltrindole, indicating that the analgesia is mediated through the δ-opioid receptor. An ^{125}I radioligand of this compound was successfully synthesized via a modified Sandmeyer reaction and tested in Chinese Hamster Ovarian (CHO) cells expressing the δ receptor, resulting in a compound with a K_D of 0.1nM. This compound may be an interesting ligand for use in probing δ-opioid receptor pharmacology.

2015 Joint Southeastern/Southwest Regional Meeting 747

Investigation of polymethine cyanine dyes: Oxidation and thermal DNA cleavage

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Cyanine dyes have been extensively investigated for use *in vivo* as fluorescent probes for biomolecular labeling and imaging, and as photosensitizers in photodynamic therapy (PDT) for cancer. In general, these dyes consist of two terminal aza-heterocyclic rings connected *via* a polymethine chain. With current synthetic methods, the electron-deficient π systems of the compounds can be altered to render optical properties optimized for *in vivo* applications. Cyanines can possess planar ring components that promote binding with DNA between the base pairs. A number of cyanine dyes are currently under consideration or being evaluated in FDA trials for clinical use. Recently we found a series of cyanine dyes that oxidatively degrade DNA to various extents in the absence of light and/or an external reducing agent. It becomes crucial to investigate this property, because dyes that thermally damage DNA without selectivity may be detrimental when used *in vivo*. Herein, we have synthesized a series of cyanine compounds and have proposed a preliminary summary of structural features that contribute to thermal DNA cleavage.

2015 Joint Southeastern/Southwest Regional Meeting 748

Uptake of fluorescently-labeled amyloid-β42 by primary murine microglia

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Amyloid beta (Aβ) is a 42-residue peptide that can aggregate in the brain, eventually leading to the formation of the intercellular plaques associated with Alzheimer's disease. These plaques are composed of insoluble Aβ fibrils, yet data from our laboratory and others has shown that the soluble forms of Aβ42 provoke activation of, and the subsequent proinflammatory response from, microglial cells. Since the interaction between protofibrils and microglial cells leads to an inflammatory response, we sought to understand the fate of Aβ monomers and protofibrils upon interaction with murine primary microglial cells. Current studies employ monomers and protofibrils of Aβ42 prepared in artificial cerebral spinal fluid, conjugated to an Alexa Fluor 488

tetrafluorophenyl ester (A488-TFP) fluorophore, and separated by size exclusion chromatography. The labeling stoichiometry was much higher for monomers than for protofibrils. Labeled Aβ42 (A488-Aβ42) protofibrils have a curvilinear structure less than 100 nm in length and have an average hydrodynamic radius centered around 16 nm (range of 5-50 nm).

The interaction of A488-Aβ42 with microglia was similar to unlabeled Aβ as determined by immunofluorescence. In both concentration- and time-dependent studies, A488-Aβ42 monomer uptake was minimal based on fluorescence intensity. Protofibrils of A488-Aβ42 were taken up quickly by microglia in a concentration-dependent manner. Time dependent studies showed that protofibril uptake correlated with the production of tumor necrosis factor α and interleukin 1β. Competition experiments showed that uptake of unlabeled Aβ42 did not diminish uptake of fluorescent Aβ42 up to 20 μM total Aβ42. In our studies, A488-Aβ42 did not substantially colocalize with lysosomes, which was unexpected given results from other researchers that do show colocalization. Using A488-Aβ42 instead of immunofluorescence allows treatment with lower, more physiologically relevant concentrations of Aβ monomers and protofibrils. These studies help refine understanding of the process and mechanism of Aβ interaction with, and uptake by, microglia.

2015 Joint Southeastern/Southwest Regional Meeting 749

Study membrane protein structure by neutron scattering

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The structure and function of membrane protein in native membrane or membrane-like environment is of great interest. However such study poses as a challenge due to the complexity of protein-membrane or protein-membrane-mimic complex. Because of the naturally different contrast in neutron scattering between different molecules such as proteins, lipids, detergents etc., small angle neutron scattering (SANS) affords researchers an excellent tool to study individual components in such complex biological systems. Further, the high penetration power of neutrons and the lack of radiation damage make SANS well-suited to the study of large, multi-component biological complexes both in-situ and in-vivo, by using neutron contrast variation techniques with selective deuterium labeling. Here I will present a few strategies for studying membrane protein in a membrane-like solution environment with SANS with examples on ExbB-ExbD complex, Photosystem I, etc. Also I will give a brief introduction to an open access user facility named Bio-SANS, a high neutron flux and low experimental background SANS instrument dedicated for biological research.

2015 Joint Southeastern/Southwest Regional Meeting 750

Preparation of Au_2S—$Cu_{2-x}S$ hybrid nanoparticles via cation exchange

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The growing significance of the copper sulfides as a nontoxic alternative to commercially significant quantum dot materials such as PbS and CdS has led to a proliferation of work studying these materials. However, Au_2S, a material with potential

for many of the same applications as Cu_2S, remains relatively ignored. The inherent difficulty of direct synthesis of gold (I) sulfide in the nanocrystalline form as well as the metastable nature of the material once synthesized are significant obstacles to the study of Au_2S. We report an indirect synthesis of Au_2S nanocrystals and Au_2S—$Cu_{2-x}S$ hybrid nanoparticles via cation-exchange, and the insights into this material transformation gained in this study.

2015 Joint Southeastern/Southwest Regional Meeting 751

Simple synthesis of luminescent graphene quantum dots using acetone and their facile incorporation into polymer matrices

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Graphene Quantum Dots (GQDs) are two-dimensional semiconducting crystals comprised of carbon in a hexagonal lattice with lateral dimensions of just a few nanometers across. GQDs exhibit a strong photoluminescence (PL) which makes GQDs useful as fluorescent biomarkers for bioimaging due to their photostability, low cytotoxicity, and their ability to be easily functionalized. GQDs have also been shown to be excellent materials for light emitting diodes, photovoltaics, fuel cell anodes, electrochemical cells, and photocatalysts for photobatteries. This work demonstrates a novel and low-cost method to mass produce GQDs with a high quantum yield. Furthermore, a new facile technique was found to diffuse the as-produced GQDs in various polymers without the need to initially melt the polymer. The PL of the GQDs diffused into several consumer polymers was investigated and reported. This new simple method to produce GQDs and the technique to incorporate GQDs in polymers as reported opens the doors for various applications and devices.

The as-produced graphene quantum dots under visible light (left), and the same sample under UV-A light (365 nm) showing blue photoluminescence (right).

2015 Joint Southeastern/Southwest Regional Meeting 752

Electron transport in nanocomposites of silver telluride and naphthalene-diimide–bithiophene co-polymer films.

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Thermoelectric materials convert thermal energy into electrical power by extracting electrons from an n-type layer and holes from a p-type layer. In general, a thermoelectric material must be a good electrical conductor and a poor thermal conductor. In addition, the voltage generated across the hot and cold ends of the materials must be large, which is called by the Seebeck coefficient. It is difficult to optimize each of these parameters in a single-phase material. An alternative approach is to make a composite material. In the past few years a new paradigm has emerged in the design of thermoelectric materials, namely the combination of inorganic nanostructures with high Seebeck coefficients and conducting polymers with low thermal conductivity. To date, most of these composites have been p-type materials. As a result, this work was focused on the development of n-type composites. In this talk we describe the synthesis of silver telluride whiskers from Te nanowires. The Te nanowires were synthesized by reducing tellurium dioxide with ascorbic acid in diethylene glycol. Transmission electron microscopy (TEM) revealed the Te nanowires were highly crystalline with a length of ~ 5 microns and ~ 70 nm in diameter. The Te nanowires were stirred with excess silver nitrate and converted into silver telluride. TEM images of the silver telluride whiskers revealed a significant geometric transformation. The silver telluride whiskers were shorter in length and curved. The whiskers were mixed into the poly{[N ,N′ -bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis-(dicarboximide)-2,6-diyl]-alt -5,5′ -(2,2′ -bithiophene)} or P(NDI2OD-T2), a well-known n-type conducting polymer. The principle goal of this work was to increase the electrical conductivity of the composite. Dispersions were made by adding various amounts of the silver telluride whiskers to the P(NDI2OD-T2) polymer in various solvents, such as toluene, dichlorobenzene and chloronaphthalene. Films were made by drop-casting the dispersions onto glass substrates and evaporating the solvents. We found that the films with the highest electrical conductivity resulted from dichlorobenzene with subsequent thermal annealing. We characterized the thin films by FTIR, Raman, UV-Vis, and fluorescence spectroscopy to assess the degree of P(NDI2OD-T2) packing and orientation.

Area specific atomic layer deposition enabled by microcontact printing

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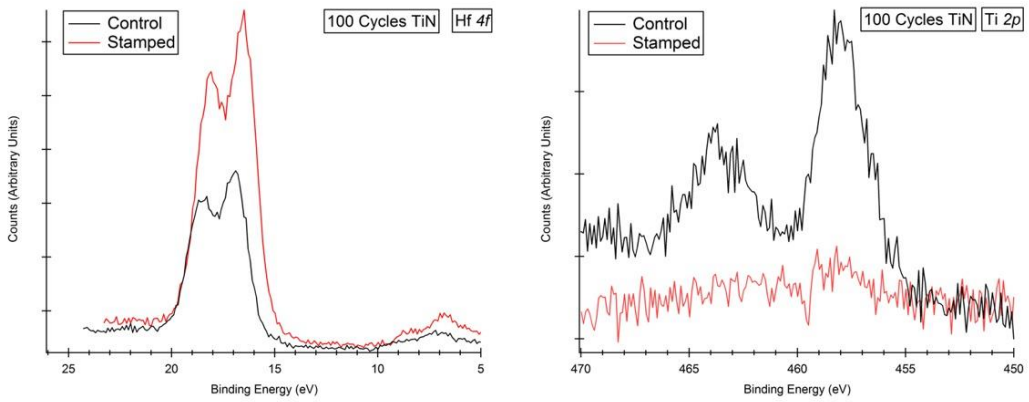
Conventional strategies for microelectronics fabrication rely on top-down approaches of planar deposition followed by photolithography and etch. In contrast, microcontact printing enabled area-selective atomic layer deposition (AS-ALD) is an additive patterning approach that simplifies process steps and reduces cost while retaining pattern fidelity. In atomic layer deposition, sequential, self-limiting surface reactions are used to grow conformal films with atom-level thickness control. Film nucleation depends heavily on the surface chemistry of the substrate. Through microcontact printing,

surface sites can be selectively modified to produce a pattern for preferential nucleation, thereby enabling selective deposition of thin films.
This work focuses on the selective deposition of titanium nitride for application in conductive word lines for memory structures. Poly(dimethyl siloxane) (PDMS) structured templates were wetted with octadecylchlorosilane (ODTS) before being stamped onto Si wafers coated with hafnia (HfO_2). In this system, surface hydroxyl sites serve as reactive sites for TiN deposition. Upon ink transfer, ODTS molecules react with surface hydroxyl sites and align to form self-assembled monolayers (SAMs) with hydrophobic methyl-terminated ends, thus passivating the stamped regions. Following passivation, several hundred cycles of titanium nitride were deposited via ALD and the composition of the resulting surface layers analyzed via X-ray photoelectron spectroscopy. We have observed complete passivation of planar surfaces and demonstrate pattern transfer and controlled growth over millimeter-scale patterned regions. We also explore the role of water in the SAM formation process and investigate improvements to the PDMS formulation and stamping process, which will enable patterning of micro-/nanoscale features. Further work will apply the patterning scheme to device-scale structures and cobalt oxide deposition for spin-transfer torque random access memory (STT-RAM).



After deposition, the passivated samples shows little titanium deposition and little attenuation of the substrate (hafnium) peak, indicating good blocking.

2015 Joint Southeastern/Southwest Regional Meeting 754

Chemical methylation of lysine residues can severely weaken gold nanoparticle-protein interactions

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Understanding the interactions of gold nanoparticles (AuNPs) with biological macromolecules is becoming increasingly important. This is in part due to the potential applications in drug delivery, biosensing, diagnostics, and imaging. Our long-term goal is to use protein functionalized AuNPs as a general tool for molecular sensing and drug delivery. The ability to use nanomaterials as biosensors and drug delivery vectors in cellular uptake is directly dependent on the amount of protein that is able to bind to the surface of any given nanoparticle. We hypothesize that electrostatic interactions play an important role in the protein-AuNP interaction, since citrate-stabilized AuNPs carry a net negative charge. Using an NMR-based approach developed by our group, we have

monitored apparent binding capacity of the 56-residue GB3 protein and two chemically modified variants with different charge. At physiological pH, the GB3 protein carries net positive charge because of its 7 lysine residues. We are exploring ways to modify the electrostatic interactions by chemically modifying these lysines. In this study, we have reductively methylated all of these residues. While this modification does not alter the net charge, it is expected to modify the local electrostatic potential of the lysine residues, primarily by increasing steric bulk. Complete methylation has been confirmed using LCMS. Furthermore, this modification does not appear to change the tertiary structure of GB3, as evidenced by NMR. Interestingly, we observe at least a 4-fold reduction in binding to AuNPs when GB3 is methylated, supporting hypothesis that electrostatic interactions are critical for binding.

2015 Joint Southeastern/Southwest Regional Meeting 755

Exploring composites of high work function 2D materials with semi-metal and semiconducting 2D materials

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Graphene is a 2-dimesnsional allotrope of carbon whose properties, including strength and electron-mobility, make it desirable for consumer electronics. However, graphene does not have high enough conductance to compete with current semiconducting technology. We look to increase the conductivity of graphene by driving charge transfer between graphene and another 2-dimensional material with a high workfunction. Due to its high workfunction, MoO_3 will transfer positive charge carriers to the graphene. By conducting this interaction between nanosheets of the two materials, we expect to avoid the traditional band bending that usually results from such interactions at the contact surface in semiconducting materials. The resulting composite material could then be made into a thin-film that would serve as an improved transparent conducting material. This material would be suitable to many unique applications, such as transparent photovoltaic cells. In this paper we establish the parameters for the synthesis of 2-dimensional graphene and MoO_3 nanosheets and the synthesis of thin films of these materials. Composite films have been synthesized and characterized with SEM and EDS to ensure proper mixing of the nanomaterials. Sheet resistance measurements on thin-films of graphene, MoO_3, and graphene-MoO_3 composite were 0.515 Ω/□, 1.073E-11 Ω/□, and 0.116 Ω/□ respectively. Further measurements are needed on film thickness in order to properly compare the conductivity of the materials.

2015 Joint Southeastern/Southwest Regional Meeting 756

Synthesis and characterization of organo-soluble $Au_{102}(SPh)_{44}$ nanomolecules

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Gold nanomolecules have attracted extensive interest because of their size-dependent properties and potential applications such as microelectronics, optoelectronics, catalysis, photocatalysis, etc. This work reports of the first synthesis and isolation of the organo-soluble $Au_{102}(SPh)_{44}$ nanomolecules facilitating composition determination using high resolution electrospray ionization mass spectrometry(ESI-MS) and first report of

electrochemical and temperature dependent optical behavior. Theoretical analysis on the titled nanomolecules validates the experimental data and shows π-π interactions among phenyl rings are attributed to the stability of the $Au_{102}(SPh)_{44}$ species.

Dextran-iron oxide nanoplates and nanoflowers showing excellent aqueous phase stability

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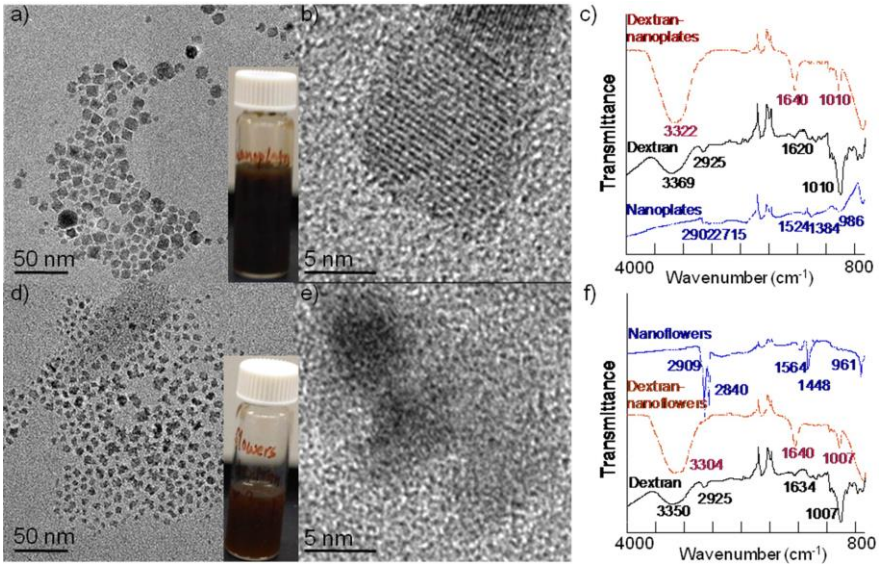
Superparamagnetic iron oxide nanoparticles (NPs) show tremendous potential in targeted imaging and drug delivery. Especially, dextran coated iron oxide NPs find clinical use as magnetic resonance imaging (MRI) contrast agents. However, wide size distributions and low crystallinity limit the biological stability and magnetic properties of these NPs prepared via co-precipitation. Recently, shape-controlled iron oxide NPs showed great potential in targeted MRI due to their enhanced circulation and high surface for bio-conjugation. In this study, a facile aqueous phase transfer technique for anisotropic NPs is demonstrated using iron oxide nanoplates and nanoflowers as model systems. Highly crystalline nanoplates and nanoflowers are first prepared by thermal decomposition of iron oleate complex. Subsequently, the organic nanoplates and nanoflowers are rendered hydrophilic via sonication in dextran/water mixture to form a second ligand layer of dextran on the NP surfaces. Figure 1. shows the stable aqueous dispersions of iron oxide nanoplates and nanoflowers. Transmission electron microscopy (TEM) and dynamic light scattering (DLS), are used to investigate the size and morphology of the water soluble NPs. The attachment of dextran on the nanoplate and nanoflower surfaces is confirmed via fourier transform infrared spectroscopy (FTIR). Dextran is found to sterically stabilize the nanoplate and nanoflower surfaces. The aqueous NP dispersions are most stable in pH 6-7 and phosphate buffer saline. This report will provide practical insights into the synthesis of anisotropic NPs for promising bio-applications.

Figure 1. Aqueous phase iron oxide nanoplates and nanoflowers. (a) TEM image of nanoplates, (inset) aqueous nanoplate dispersion, (b) HRTEM of nanoplates, (c) FTIR of nanoplates, (d) TEM image of nanoflowers, (inset) aqueous nanoflower dispersion, (e) HRTEM of nanoflowers, and (f) FTIR of nanoflowers.



2015 Joint Southeastern/Southwest Regional Meeting 758

Triblock copolymers for thermally triggered drug delivery

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Two different triblocks were synthesized with the purpose of preparing drug loaded micelles with a reduced burst effect. Polycaprolactone macromonomer (M_n ~ 8,200) was made by the tin-catalyzed ring-opening polymerization of caprolactone initiated by benzyl alcohol. The PCL was reacted with 1,6-hexane diisocyanate and the isocyanate end-capped macromonomer was reacted with poly(ethylene glycol), M_n ~ 5,000, to give the triblock, PEG-TPU-PCL. Polymer micelles were formed with the triblock and the critical micelle concentration for the PEG-TPU-PCL was 7 mg/L at 25 °C. Polycaprolactone diol, M_n ~ 14,000 was end capped with toluene diisocyanate and subsequently reacted with poly(ethylene glycol) M_n ~ 5,000, to give a PEG-PCL-PEG triblock. The critical micelle concentration for this triblock was 1mg/L. Doxorubicin was trapped in the semi-crystalline core of the micelles. Preliminary results of isothermal release of doxorubicin from both polymers will be presented.

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Colloidal self-assembly of multifluorescent silsesquioxane microparticles

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Nanoscale particles derived from silsesquioxane core structures are important nanomaterials that can be applied in electronic devices. As the surface silsesquioxane core structure can be easily functionalized with various semiconduting organic moleculaes, there has been a great effort to use them as emissive layers for

optoelectronic devices. However, There has been a significant challenge assembling nanoscale to microscale particles into a well ordered microstructures. Here we describe a novel method to assemble microparticles into three-dimensional micro-colloids using organic-inorganic hybrid particles through strong H-bonding interactions. To do that, a series of reactive group functionalized silsesquioxane microparticles were prepared by direct hydrolysis and co-condensation of their respective silane precursors. Particle sizes were controlled upon adjusting the molar ratios of organotrialkoxy silane to the base concentrations. These resulting microparticles with reactive amine groups and benzyl chlorides groups are found to be more advantageous for the self-assembly in a variety of polymer matrices due to the formation of strong H-bonding interaction of amine group with actice sites of the polymer substrate.

2015 Joint Southeastern/Southwest Regional Meeting 760

Hybrid nanoparticles: Progress towards photocatalytic water splitting

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The production of H_2 gas via the photocatalytic splitting of water to H_2 and O_2 presents a green, renewable method for energy production. Hybrid nanoparticles contain disparate materials on the same nanoparticle, and their synergistic properties can be tailored to improve photoinduced charge separation and drive photocatalytic reactions. Hybrid nanoparticles of a semiconductor domain and a metallic catalyst domain have been shown to reduce H_2O to H_2, but sacrificial reductants are required. Concomitant catalytic oxidation processes such as water oxidation have yet to be demonstrated. This work presents our efforts towards complete water splitting on CdSe/CdS rods with Pt tips by including a molecular chelated oxidation catalyst anchored to the nanoparticles surfaces. We present the synthetic development of an asymmetric bipyridine ligand with a conjugated dithiocarbamate ligand- a functional group known to expand the valence band wave function of CdSe and CdS quantum dots. TEM, absorbance and time-resolved fluorescence spectroscopies indicate the ligands coordinate particle surfaces while concomitantly chelating Cu ions. Computational models indicate good energetic alignment with previously used dithiocarbamate ligands, as well as formation of a mid-gap state between the valence and conduction bands of CdS, resulting in charge transfer. This interaction between the ligands and nanoparticle provides the framework for a system that can be used to perform complete water splitting under solar irradiation without the need for sacrificial reagents.

2015 Joint Southeastern/Southwest Regional Meeting 761

Bottom-up fabrication of porous gold with large surface area

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Porous gold materials are used in many applications that include catalysis, biosensing and fuel cells. Reported herein is a comparative study of bottom-up assembled porous gold fabricated by aggregating gold nanoparticles (AuNPs) with 15 different types of electrolytes including halides, sulfates, and nitrates. Using 2-mercaptobenzimidazole as

a model ligand, the specific surface area of AuNP aggregates was determined by quantitative ligand adsorption. $CuSO_4$ induced porous gold aggregates has the highest specific surface area of 16 m^2/g, which is higher than the mostly reported values for porous gold (2-12 m^2/g). A reaction pathway was proposed for fabricating highly porous gold with large surface area. Specific surface area of porous gold fabricated with F^-, sulfate, and nitrate critically depends on the counter cation, and the concentration of the electrolyte, and displayed a higher specific surface area compared to chloride, bromide, and iodide counter parts. In contrast, specific surface area for Cl^-, Br^-, and I^- induced AuNP aggregates displayed a significance dependence only on the electrolyte incubation time with AuNPs. The insight provide in this work is important to enhance the understanding the electrolyte-AuNP interaction, and porous gold with large surface area would be useful to extend their applications in real world.

2015 Joint Southeastern/Southwest Regional Meeting 762

The best of both worlds: Incorporating peer instruction with POGIL activities

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As student-centered learning strategies, both peer instruction and POGIL implementation have been shown to improve retention in chemistry and other science courses. POGIL activities have been the primary means of instruction in my general chemistry courses for 17 years. In the past few years, peer instructors (PIs) were incorporated to assist during class times as well as conducting their own evening, hour-long PI sessions. The PIs were chosen based on their successful performance in science courses and were junior and senior chemistry majors. Each PI received upper-level course credit for their work. The PIs also received weekly instruction and were provided structured tasks to complete during their PI sessions. Participation in the evening PI sessions by the general chemistry students was voluntary, but appropriate incentives were provided to encourage their attendance at the weekly sessions. Participation was high and overall student performance and retention in the course was improved.

2015 Joint Southeastern/Southwest Regional Meeting 763

Balancing chemical equation in middle school classrooms

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In middle school science classrooms across the globe, due to limited resources and time confinements, many students have difficulty understanding the terminology and new vocabularies used in today's science textbooks. Due to limited resources and time confinements, many middle science teachers utilize the science text book for the main delivery of science instruction, which may not be the most exciting or engaging method to middle school students. In fact, most nonfiction text or informational text reliability levels may be much higher than the instructional level of the students. Therefore, the

students may become unmotivated about the science content. As a alternative solution to this problem, many educators seek innovative methods and materials to actively engage middle school students. In this report, STEM experts, educational experts, and general science education majors collaborated to create a hands-on inquiry based module to teach students how to effectively balance chemical equations. Although the module focuses on science objectives, other subject areas such as reading, writing, music, and math are integrated into the module to increase the overall student achievement of the science objectives.

2015 Joint Southeastern/Southwest Regional Meeting 764

Chemical enrichment Fridays at San Jacinto College using ACS Webinars and other internet resources to motivate student engagement with science courses

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Lecture and tradition laboratory work are important ways to provide students with a strong factual foundation for advanced course work and research at a professional level. Unfortunately students in traditional professor-led courses often come away with the foundation along with the misconception that science is a body of facts, where the right answers have been found and all one needs to do is remember what you've been told for the exam. Students in such classes are left unaware that actually what scientists do is "push back the frontiers of ignorance" an idea expressed by Dr. Robert Dudley, UC Berkeley, and expanded by Dr. Stuart Firestein, Columbia U, in his book *Ignorance, How It Drives Science*. According to Dr. Beau Lotto, University College London, real science, that is, research in its many manifestations is a human activity of exploring the world which is in many ways very closely associated to play. When students realize that science can be fun and a way to answer questions about the world of interest to them they are much more likely to take on greater responsibility for their own learning. San Jacinto College is using what we call Chemistry Enrichment Fridays to provide at least a glimpse of the exploring and playful aspects of science. We have found that ACS Webinars and Presentation on Demand are excellent resources on which to build an hour long session where students interact with the science, one another and faculty to explore not what we know but how what we know is used to address the unknown. This presentation with discuss "Chemical Enrichment Fridays", what we have done, the student response and improvements planned for the 2015/2016 academic year.

2015 Joint Southeastern/Southwest Regional Meeting 765

Using Skype as a mentoring tool for chemistry majors: An online field trip

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Student retention is a very important issue especially for Historically Black Colleges and Universities. It is estimated that 50% of students who enroll will drop out of college[1]. A college education is a long term goal on which the millennial student may find difficult to focus. To improve retention the higher education process must be relevant and relational to reach the millennial student[2]. Therefore it is important that we as mentors provide constant reminders that the journey is worth the struggle. Social media can be used to keep students in touch with the career visions and aspirations which initially

brought them to college.
Undergraduate chemistry majors taking Instrumental Analysis, Skyped a recent graduate and her colleagues who were participating in a post-baccalaureate premedical program. They briefly discussed the purpose of the post-bac program and the significance of current undergraduate course content to professional school entrance examinations. An online survey conducted at the end of the session indicated that the chemistry majors involved found the activity useful and recommended that it be extended to other courses. The possibilities are limitless.
1. Swail, S.; Redd K.E.; and Perna, L.W.; Retaining Minority Students in Higher Education: A Framework for Success Watson, ASHE-ERIC Higher Education Report, **2011** 30, 2.
2. Price, C. , Why Don't My Students Think I'm Groovy? *The Teaching Professor,* **2009**, 23 (1), 7

2015 Joint Southeastern/Southwest Regional Meeting 766

Interdisciplinary application of thermodynamics for a mechanism of binding of ions to a cell membrane

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This paper elucidates a method to teach fundamental concepts in thermodynamics using a real world research data. A short paraphrased part of a journal paper involving the concepts of thermodynamics applied to a biological mechanism, is selected. In this paper, the biological mechanism involves binding of a large cation and anion across a cell membrane. A data table containing free energy, entropy and enthalpy is selected to teach a physical significance of the thermodynamic parameters and their signs to the binding properties of ions across a cell membrane. Besides, students analyze the free energy data of the cation and anion structure to make a connection between the ionic charge and the binding affinity. Further, a set of questions test the students reading comprehension skills. It is a multifaceted activity that can be introduced as a short case study, a group activity or a part of homework assignment. It can be used as discussion board assignment as well. Such student centered learning assignment conveys the importance of critical thinking and application of knowledge to a different discipline.

2015 Joint Southeastern/Southwest Regional Meeting 767

Cheminformatics OLCC: An evolving ontological framework based intercollegiate course management system

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Cheminformatics is changing the fundamental cognitive artifacts used to represent, manipulate and communicate chemical information. These represent interesting challenges and opportunities for chemical educators in the dawn of the social and semantic web. This presentation will provide information from the context of Microsoft Research's Fourth Paradigm of Science and the second level digital divide, providing the argument that experts who have automated the use of schema based on

established cognitive artifacts find it more difficult than novices to adapt and assimilate new artifacts into their workflow. This presentation will describe the Cheminformatics OLCC, an intercollegiate hybrid online/f2f course being hosted by the ACS CHED Committee on Computers in Chemical Education and piloted at 4 schools during the Fall of 2015. A novel course management system developed for the needs of intercollegiate curriculum development and delivery will be described, which can enable an evolving educational ontological framework based on an extensible nodal network of scaffolded and forked Teaching and Learning Objects. Although the course is currently ongoing, information will be presented on student interactions and issues in this hybrid classroom environment.

2015 Joint Southeastern/Southwest Regional Meeting 768

Science attitudes in an introductory chemistry course: Examining group differences and its relationship with achievement

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Decisions about instruction, research, or policy often require interpretation of student assessment scores. Increasingly, attitudinal variables are included in an assessment strategy, and it is important to ensure that interpretations of students' attitudinal status are based on instrument scores that apply similarly for diverse students. Too few studies of this phenomenon, also known as measurement invariance, exist for instruments that are relevant for college chemistry courses. In this study, a three-factor attitudinal instrument was used to examine students' attitude toward science within the first few weeks of an introductory college chemistry course. Results showed that that instrument scores had good overall internal consistency and acceptable evidence for factorial validity, with an overall slightly positive student response on each factor. This talk will discuss the results of an investigation into whether the instrument functioned similarly for different groups of students within the sample, including the relationship of the attitudinal scores with achievement in chemistry.

2015 Joint Southeastern/Southwest Regional Meeting 769

Developing and implementing an assessment technique to measure linked concepts

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The links students make among chemistry content is considered essential for a robust, enduring understanding in multiple learning theories. This presentation describes the development and implementation of an assessment technique, termed a Measure of Linked Concepts, designed to inform instructors on students' understanding of linking content throughout General Chemistry. Student performance on the assessment technique has provided unique insights relevant for instruction. For example a substantial proportion of students could not identify when a model was used beyond its intended limit or show proficiency in tasks that the course assumed was prior

knowledge. Student response process for the assessment provided by interview data and future work will also be discussed in the presentation.

2015 Joint Southeastern/Southwest Regional Meeting 770

Academic motivation scale-chemistry: A theory-based instrument to investigate student motivation toward chemistry

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The theory-based Academic Motivation Scale (AMS) is designed to probe students' motivational profile toward going to college. The AMS showed good reliability, reasonable data fit, and the ability to detect motivational differences by sex in college chemistry courses. Based on expert panel discussions and cognitive interviews with students, the Academic Motivation Scale toward Chemistry (AMS-Chemistry) was developed. Other evidence of validity (internal structure and relation to other variables) and internal consistency reliability were gathered in an organic chemistry class. The psychometric evidence suggests that the AMS-Chemistry can be used to investigate student motivation toward chemistry in college chemistry courses. The 28-item AMS-Chemistry is easy to administer and is capable of providing motivational information to faculty. This type of data can be used to better understand students' motivation status and how it might change across the curriculum. Faculty interested in promoting student intrinsic motivation may also use the AMS-Chemistry to evaluate the impact of their efforts.

2015 Joint Southeastern/Southwest Regional Meeting 771

Exploring the role of students' study habits in general chemistry

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Past work has shown that college students' study habits impact general academic performance, but relatively little has been done to explore the role of study habits in chemistry. This presentation employs a novel approach termed Experience Sampling Method to measuring study habits. In this method, participating students received repeated text messages to students throughout the semester inquiring "Have you studied for General Chemistry I in the past 48 hours? If so, how did you study?" Student responses were analyzed for frequency and type of study habits and patterns in study habits were related to student performance in the course. The results indicate that students who study comprise approximately one-third of the sample and this cohort out-performed their peers on a common cumulative final exam. Instructional implications through the use of experience sampling method and influencing study habits will also be discussed.

2015 Joint Southeastern/Southwest Regional Meeting 772

Examining student conceptual understanding using automated lexical analysis of open-ended responses

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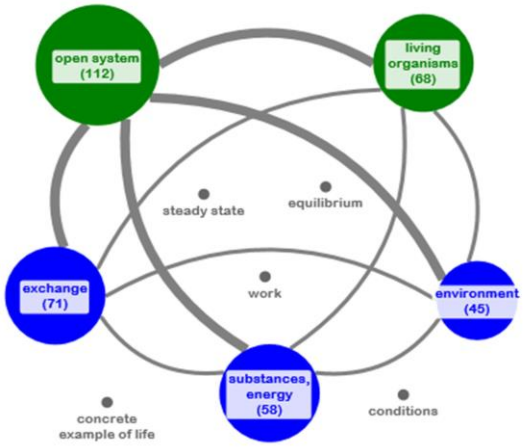
Conceptual assessment is pivotal to elicit student knowledge to inform instruction. Multiple-choice item format is easy to use but lacks the rich information of student thinking, while open-ended questions require too much time to code and to provide timely feedback targeted on student response in a typical large enrollment college classroom setting. This study investigated the real-time information in students' written responses to open-ended questions in a biochemistry classroom using automated lexical analysis. Items have been developed to assess a threshold concept related to cellular steady state. Questions probed student understanding of cellular thermodynamics, including the dynamic, non-equilibrium condition of living organisms. Web diagrams for students' responses in the most frequent categories were produced in SPSS to elicit the common patterns in the students' writing. A web graph, as below, demonstrated that students tended to write about "open system" and "living organisms" (repeated from the question prompt), along with terms related to ideas about exchange, substance and energy, and environment. These patterns are in alignment with the correct understanding that living organisms are open systems and need to exchange matter and energy with their surroundings. A report on student responses with a web graph can be helpful for instructors to make decisions regarding questions such as whether more time should be spent on particular aspects of course content, or whether the intended goal of instruction has been achieved.



Web diagram for student responses to question:
Are living organisms open or closed systems? How do you know?

Web diagram for student responses to the question:
Are living organisms open or closed systems? How do you know?

Characterizing postsecondary chemistry instructional practices: A pilot test of survey items and a stratified sampling strategy

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Characterizing instructional practices in postsecondary STEM instruction is of keen interest as national initiatives push for the adoption of evidence-based teaching practices. Accurate measures of instructional practices and the identification of influencers on instructional reforms are of utmost importance to these initiatives. We will describe work to develop a national survey instrument aimed to capture the teaching practices of postsecondary chemistry instructors. We will highlight survey items pilot tested, development of a stratified sampling strategy, and situate our work in a working model of teacher-centered educational reform.

Measurement of NADH production by lipid bodies in *Brassica napus*

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NADH production by lipid bodies isolated from Brassica napus in the presence of acyl-CoA's was measured using an NADH cycling assay. During germination the fats stored in the lipid bodies of seedlings is mobilized to support seedling growth. Triacylglycerols in the lipids bodies are degraded by lipases to form free fatty acids which are then converted to acyl CoA's and metabolized by beta oxidation in glyoxysomes. Acyl-CoA synthetase activity has been observed in isolated lipid bodies from germinating Brassica napus suggesting other enzymes necessary for metabolism of fatty acids may be present in lipid bodies. The rate of NADH production by isolated lipid bodies in the presence of different acyl-CoA's was measured by following the reductions of phenazine ethosulfate and thiazolyl blue tetrazolium bromide.

Ladybirds: Detection and determination of alkaloid compounds

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Predatory ladybird beetles (Coleoptera: Coccinellidae) are known as natural enemies for several agricultural pest insects. They contain various alkaloid compounds for their defense and aposematic coloration. In general, alkaloids are a large group of compounds that are divided into three basic categories: steroid, straight chain, and heterocyclic. A thorough analysis of the alkaloids can provide insight towards the nutrition levels and defensive status of the insects. Two sample groups of ladybird beetle eggs from *Coccinella septempunctata* were collected in different time periods and analyzed by UV-Vis, fluorimeter, HPLC, and GC-MS. During the course of the project, novel methods were developed to quantify three (3) different alkaloids of

cholesterol, octadecyl acetate, and estradiol. The results showed that the overall amount of the 3 different alkaloids was similar; however, the average concentration of each varied between the groups. Those variations might be explained by females' reproductive conditions including age and feeding habit.

2015 Joint Southeastern/Southwest Regional Meeting 776

Synthesis of chalcones that mimic resveratrol and curcumin and inhibit amyloid-beta (1-40) aggregation

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Amyloidogenisis in Alzheimer's disease is the association of amyloid-beta peptides (Aβ-peptides) into oligomeric structures ultimately leading to the formation of fibrils and plaques. Aβ-peptides are rapidly produced by enzymatic processing of the neuronal transmembrane amyloid precursor protein (APP). Aβ-peptides are found primarily outside the neuronal cells and are produced by two alternative pathways, a non-pathogenic or non-amyloidogenic pathway, and a pathogenic or amyloidogenic pathway. Aβ-peptides are typically produced in varying lengths and often possess amphipathic properties. The most widely studied of Aβ-peptides are the amylodogenic Aβ(1-40) peptide and the slightly longer and significantly more pathogenic Aβ(1-42) peptide.
Recent studies show that both Aβ(1-40) and Aβ(1-42) peptides form cytotoxic oligomers that penetrate neurons and disrupt normal neuronal functions. Further studies have shown that classes of small molecules (mostly polyphenolic in nature) act to inhibit the formation of oligomers. Two small molecules of particular interest to us are resveratrol, and curcumin—both have been shown to inhibit amyloidogenisis.
In an effort to gain understanding of the binding interactions of resveratrol and curcumin to Aβ-peptides, and to optimize inhibition of amyloidogenisis, we report the synthesis, purification, and Aβ(1-40) amyloidogenic inhibitory kinetics of three small molecules that are structurally related to resveratrol and curcumin. (2E)-1-(2,4-dihydroxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one, ((2E)-1-(2,5-dihydroxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one, and (2E)-1-(3,5-dihydroxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one were synthesized, purified by preparative thin-layer chromatography, and assayed for amyloidogenic inhibition using the Thioflavin-T assay.

2015 Joint Southeastern/Southwest Regional Meeting 777

The structural analysis of aspartame using a 60 MHz NMR

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Experiments using nuclear magnetic resonance (NMR) spectroscopy can be designed to teach students a basic understanding of structural analysis using NMR spectra. Teaching advanced NMR techniques such as Correlated Spectroscopy (COSY) and Nuclear Overhauser Effect Spectroscopy (NOSY) is relatively difficult in smaller institutions with only lower field NMR instruments, and most of the experiments in the literature are designed for either higher field instruments or are relatively uncomplicated. However, an understanding of advanced NMR structural techniques is important for all

students. An experiment is described here using a low-field (60 MHz) instrument for the analysis of a small peptide. Students prepare component amino acids and peptide samples in DMSO and D_2O. Proton peaks are initially assigned to certain atoms in the peptide using a simple ^1H NMR spectrum. Comparative analysis of individual amino acid spectra to the peptide spectrum confirms the original assignment of peaks to specific atoms. Water Eliminated Fourier Transform (WEFT) analysis is utilized to assist in detecting proton peaks masked by water. Students utilize (COSY) and solve for coupling constants from ^1H NMR spectra to finalize the relationship between tentatively assigned peaks and atoms. The experiment incorporates (NOESY) for the determination of intramolecular distances in solution. Lab instructors can include an optional computational chemistry exercise for students to compare experimental and computer-generated data. This experiment is appropriate for undergraduate organic or biochemistry lab using accessible and non-hazardous biomolecules.

2015 Joint Southeastern/Southwest Regional Meeting 778

Biosynthesis of the recently discovered peptide hormone preptin

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Preptin, a 34-amino-acid peptide, is the newest member of the insulin family of peptide hormones, and was isolated from the secretory granules of pancreatic β-cells in 2001. It has been found to participate in vital processes such as cellular differentiation, modulation of insulin sensitivity, and regulation of bone density. However, the hormone active site, and subsequently, its mode of action have yet to be determined due to the short life span of native peptide. Preptin is highly susceptible to enzymatic cleavage, and its short life span has hindered biochemical characterization. It was recently reported that preptin analogs chemically synthesized with mutations at position 21 are resistant to enzymatic cleavage. Solid phase peptide synthesis is prohibitively expensive for primarily undergraduate research labs. We report the successful synthesis of native rat preptin and a green fluorescent protein fusion with Ala^{21} preptin. It is believed that these are the first reported biosyntheses of preptin or preptin analogs.

2015 Joint Southeastern/Southwest Regional Meeting 779

Characterization and biochemical analysis of noncanonical coronavirus macrodomains

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Coronaviruses (CoVs) are complex, positive-sense RNA viruses that are responsible for mild to severe respiratory tract infections. Infecting both humans and animals, these viruses undergo complex infectious cycles including multiple RNA processing steps. These viruses produce a class of proteins classified as macrodomains which are a key poly(ADP-ribose) (PAR) binding module. They are involved in many cellular processes such as DNA damage repair and cell signaling. We are investigating the macrodomain proteins of bat coronaviruses (Bt-CoV) HKU4 and HKU9, which share sequence identity with human coronaviruses such as SARS (severe acute respiratory syndrome) and MERS (Middle East respiratory syndrome). Through homology modeling, solution NMR

analysis, and biochemical assays, the domain M of HKU4 has been shown to bind G-quadruplex DNA and RNA, similar to the SARS-CoV. With future studies and analysis, our goal is to fully understand the relationship between structure and biochemical functions of these coronavirus macrodomains.

2015 Joint Southeastern/Southwest Regional Meeting 780

Identification of factors stabilizing the 3D structure of the goodpasture autoantigen of glomerular basement membrane

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In Goodpasture disease, autoantibodies bind to α3 and α5 NC1 domains of collagen IV in glomerular basement membrane (GBM), leading to rapidly developing glomerulonephritis and renal failure. These domains exist in GBM as a hexameric complex, termed the Goodpasture autoantigen, which is composed of α3, α4 and α5 NC1 monomers. Significant amounts of these monomers are crosslinked with sulfilimine bonds, which might be the reason why the native α345 hexamers do not bind Goodpasture autoantibodies. Here, we investigated the factors that contribute to the hexamer stability and inertness toward binding of autoantibodies. For this study we have purified human recombinant α3, α4, and α5 NC1 monomers from mammalian cell culture media using FLAG affinity chromatography. Through FPLC size exclusion chromatography on Superdex S200 column, we demonstrated that α345 hexamer assembly requires the presence of physiological concentration of NaCl. Furthermore, we showed that sulfilimine bond introduced through the oxidation of methionine residues with hypobromous acid stabilizes hexamer and prevents dissociation into monomers in the chloride-free environment. We conclude that both Cl^- ions and sulfilimine crosslinks stabilize the α345 hexamer and that perturbation of either may induce pathological conformational changes initiating Goodpasture disease.

2015 Joint Southeastern/Southwest Regional Meeting 781

Loss of extracellular matrix Protein X causes altered function of sensory neurons in *Drosophila*

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Protein X, whose related proteins in humans may be involved in craniofacial and kidney disorders, was studied in the fruit fly *Drosophila* to determine if it is required in the function of ciliated cells as previously observed in zebrafish. In addition to chemosensory assays, sensory neurons were studied under confocal and electron microscopies. Loss of Protein X caused altered chemosensory function as well as shortened and disorganized cilia in organs responsible for hearing and proprioception. These studies have gotten one step closer in understanding Protein X's mechanism of action in order to better understand its role in human diseases.

2015 Joint Southeastern/Southwest Regional Meeting 782

Development of a neuronal viability assay using SH-SY5Y cells

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Alzheimer's disease affects more than 35 million people internationally and accounts for 50-70% of all dementia cases1,2. This is a compounding problem as the general population is aging and living longer. There are many potential causes of dementia, but one of the most striking is neuronal cell death. Viability assays are an important scientific tool that allows one to compare the toxicity of harmful substances of interest by a standard of cell death using precise conditions and measurement techniques. Here, a viability assay was created using the human neuroblastoma cell line, SH-SH5Y, and increasing concentrations of hydrogen peroxide (H2O2) were used to elicit cell stress and cytotoxicity. Neurotoxicity was measured using flow cytometry in combination with a proprietary live/dead dye. Previously, phosphorylated tau protein oligomers have been shown to be neurotoxic, and possibly be one of the steps that is responsible for eliciting dementia and potentially Alzheimer's3. Good et al. has shown that Aβ oligomers are neurotoxic to cultured SH-SY5Ys4. This work will provide assistance for future experiments in which a pure tau sample can be obtained and assayed for cytotoxicity.

Biogenesis of cytochrome oxidase: Mechanism of heme *a* synthase

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The synthesis of the heme A cofactor is an essential step in the biogenesis of cytochrome oxidase, which is Complex IV of the mitochondrial respiratory chain. The heme A cofactor is unique to cytochrome oxidase and related enzymes. It is synthesized in the cell from heme B precursor by the sequential action of the heme O and heme A synthase enzymes. However, the mechanism of heme A biosynthesis has not been established, and there is little structural information on the heme A synthase. In this study, we evaluated the roles of structural features of this enzyme by generating mutant forms of the enzyme in the eukaryotic model organism *Saccharomyces cerevisiae* and analyzing their ability to function and to form oligomeric structures. The goal of this project is to elucidate the enzymatic mechanism of heme A synthase and to define the role of active site residues in substrate binding and catalysis.

SdsA1 sulfohydrolase and homologous proteins

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SdsA1 is a member of the metallo-β-lactamase superfamily that allows the bacterium *Pseudomonas aeruginosa* to utilize the detergent sodium dodecyl sulfate (SDS) as its

sole source of carbon and/or sulfur. Homologous proteins have been identified in all kingdoms of life, and this widespread conservation raises questions about the true biological substrate(s) of the SdsA1 homologs. In the current study, we are recombinantly expressing and subsequently purifying selected homologs of SdsA1 proposed to have different substrates, with the goal of studying their activity towards an array of substrates to determine the possible function of each enzyme *in vivo*. Here we describe progress in protein expression and purification for SdsA1 and a eukaryotic homolog.

2015 Joint Southeastern/Southwest Regional Meeting 785

Synthesis and screening of antimicrobial peptoid combinatorial libraries against the fungi *Aspergillus*, *Candida*, and *Cryptococcus*

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Due to increasing rates of antibiotic resistant fungal infections, alternative treatment options must be explored. One option to combat this growing issue is the use of antimicrobial peptides (AMPs). However, AMPs are severely restricted as a therapeutic choice due to limited half-lives within the human body. To address this issue, peptide mimics called peptoids are employed to identify antimicrobial properties. This research consists of synthesizing a diverse combinatorial library of peptoids and screening this library against different fungi. The combinatorial library's design will allow for millions of unique compounds to be synthesized and screened for antimicrobial properties in a few days. The methods developed in this project will be an efficient way to determine other therapeutic options in dealing with antibiotic resistant infections, and design compounds that can be used universally with these species.

2015 Joint Southeastern/Southwest Regional Meeting 786

Kemp eliminase activity of ketosteroid isomerase: Kinetic behavior of active site mutants

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The Kemp elimination is a model for base-catalyzed proton transfer reactions. Aprotic solvents greatly accelerate its rate when negatively-charged bases are used, presumably because of desolvation of the base. We found that ketosteroid isomerase from *Comamonas testosteroni* (tKSI) significantly accelerates the Kemp elimination of 5-nitrobenzisoxazole, with rate constants approaching those obtained by computationally-designed enzymes. Surprisingly, tKSI is even more active when aspartate 38, which is the catalytic base in the normal reaction catalyzed by tKSI, is mutated to asparagine. Herein, we studied the pH-rate dependencies of other variants (D38G, D38L, and D38K) and found that all of these mutants are more active then wild type tKSI, suggesting that the negative charge on residue 38 is detrimental for the reaction. Mutation of a high pK_a aspartate residue present in the active site of tKSI, D99, brings

the reaction rate to the background level, suggesting that D99 is the catalytic base. Bronsted plots of D38 mutants suggest that the active site of KSI is more hydrophobic than water, and similar to those of the computationally-designed Kemp eliminases. In conjunction with data available in the literature, our results suggest that the Kemp elimination can be significantly accelerated by providing a hydrophobic environment with no specific interactions with the substrate.

2015 Joint Southeastern/Southwest Regional Meeting 787

Synthesis of resveratrol analog to block Aβ-peptide (1-40) aggregation

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A group of peptides called amyloid-beta peptides form fibrous aggregates in the brain when enzymatically cleaved from amyloid precursor protein. This aggregation is known to be a cause in the procession of Alzheimer's disease. The inhibition of this aggregation could lead to a possibility treatment for the disease. Currently, the only treatments for Alzheimer's disease consist of slowing the progression of the disease. It is believed that if the plaques are inhibited from forming, the symptoms will lessen. Current research shows that it is possibly the oligomers, the forms of the peptides before the aggregation, which are the toxic forms of the peptides. Polyphenols, compounds that have two or more hydroxyl groups on an aromatic ring, have been noted to have inhibitory effects toward the aggregation of the Aβ peptides.
This project is aimed to complete the following goals: the synthesis and purification of a polyphenolic chalcone ((2*E*)-3-(2,4-dihydroxyphenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one) that is related to the structure of resveratrol. This research is intended to have a positive impact on Alzheimer's disease treatment progression. The chalcone will be analyzed for its relative ability to inhibit *in-vitro* Aβ- peptide (1-40) aggregation. The synthetic chalcone polyphenol desired will be synthesized by way of an aldol condensation reaction. Reagents are inexpensive and readily available from several vendors. The advantages to using this reaction is that it is a clean reaction that typically provides highly yielded products and having few contaminants or by-products. One of the advantages of synthesizing chalcones as a compound is that they have many substitution capabilities, and there are many structural variations of hydroxyl group placements that are feasible. Several variations of resveratrol-like synthetic pholyphenolic chalcones will enable us to probe and ultimately determine the optimal hydroxyl placement for inhibition of amyloid-beta aggregation. The final goal of the project is to study the binding kinetics between the synthesized chalcone and the Aβ-peptide (1-40) by using a ThT fluorescence assay.

2015 Joint Southeastern/Southwest Regional Meeting 788

Computational modeling for understanding the activation of the receptor for advanced glycation end products

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The receptor for advanced glycation end products (RAGE) is a critical cell surface pattern recognition receptor that is involved in the inflammatory processes of the human body. A diverse array of ligands have been reported to activate RAGE including, advanced glycation end products, amphoterin, amyloid beta peptide, and several members of the S100 class of EF-hand calcium binding proteins. Misregulation of RAGE expression is connected to tumor outgrowths, diabetic complications, and neurodegenerative disorders, which are increasing worldwide concerns. Hence, RAGE is a potential target for the therapeutic intervention. Understanding the molecular mechanisms and interactions that induce the activation of RAGE will allow for the rational design of small molecule inhibitors with the potential to help treat and prevent such inflammatory disease. Here we present a model of the receptor-ligand complex of RAGE and S100A12 determined using a computational docking approach. We also describe a fluorescence binding assay that shows the dissociation constant for the RAGE-S100A12 complex is on the order of micromolar. Comparisons to other structures of RAGE complexes reveal that the high affinity ligand binding surface of RAGE is comprised of a conserved positively charged surface together with a hydrophobic surface.

Pegylation of bacterioferritin, a protein scaffold for delivery of toxic iron to cancer cells

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An iron storage protein scaffold (bacterioferritin, Bfr) has been adapted for a novel approach to cancer therapy. Tumor-targeting drugs can be conjugated to the 24 subunits of the protein shell, and photosensitizers (ZnPPIX) can substitute into the native heme binding sites. After binding to cancer cell receptors, photo-excitation would trigger release of ferrous iron to generate a flux of toxic hydroxyl radicals. In order to mask the Bfr from the immune system and make the diameter of the complex larger to aid in retention time, long chains of polyethylene glycol (PEG) can be conjugated to the protein shell on a cysteine substituted in place of an exterior exposed glutamate. In these experiments, the gene encoding the E81C-Bfr was synthesized and inserted into an E.coli expression plasmid. The E81C-Bfr was readily expressed and purified by standard anion exchange and size exclusion chromatography methods. The purity was assessed by 12% SDS-PAGE and then the purified E81C-Bfr was reacted with two types of PEG. First to bind any free surface exposed lysines, a 2kDa PEG using a N-hydroxysuccinimide ester linkage was used. Then a 5kDa PEG using a maleimide functional group to attach to the reduced cysteine on the protein shell. These two types were assayed for conjugation by a PEGylation ladder on a 10-20% gradient gel and stained with Coomassie Blue. Additionally the samples were run on an analytical size exclusion column and compared to standards to determine if the protein was still a 24 subunit shell. Further experiments are underway to test whether the attachment of PEG alters the photochemical abilities of Bfr and to characterize the diameter of the PEGylated protein shell.

A routine ESI-MS method to screen drug effectiveness in inhibition of amyloid-beta peptide aggregation rate

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Alzheimer's disease affects millions of individuals and their families. This disease worsens as Amyloid-Beta peptides form oligomers which ultimately form into amyloid plaques. Potential treatments involve drugs that will reduce the rate at which the oligomers and thus plaques develop. The next problem lies with finding a method that will test the rate of oligomer formation and effectiveness of potential drug candidates. Using a mass spectrometry-based assay will allow the development of a sensitive method to test the fibril formation along with the ability to distinguish between monomers, dimers, trimers, and other oligomers, based on unique mass-to-charge ratios (m/z).
The aim of our research was to find the optimum conditions for measuring Amyloid-Beta peptide aggregation rates by ESI-MS using a commercially available electrospray quadrupole ion-trap mass spectrometer. Presented will be the determination of proper solvents, flow rates, and peptide concentrations needed to perform these measurements. Dynorphin A (1-13), a small hydrophilic peptide that does not aggregate, was used as an internal standard to improve quantitation of Amyloid-Beta (1-40) peptide aggregation rate. We report the effectiveness of our optimized assay using a known Amyloid-Beta peptide aggregation inhibitor, resveratrol.

2015 Joint Southeastern/Southwest Regional Meeting 791

SdsA1: A bioinformatics and kinetic study

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SdsA1 is a dimeric enzyme proposed to be involved in the degradation of sodium dodecyl sulfate (SDS, a common component of soaps and detergents) by the opportunistic pathogenic bacterium *Pseudomonas aeruginosa*. SdsA1 is indeed capable of hydrolyzing SDS (as well as, other alkyl sulfates), but it is inhibited at moderate levels of SDS, suggesting that the biology function of this enzyme might not be SDS hydrolysis. Furthermore, protein BLAST of this enzyme reveals more than 500 proteins with 35% or more identity to SdsA1, including proteins from eukaryotes, such as the homolog from *Saccharomyces cerevisiae* Bds1. Bds1 has been implicated in the hydrolysis of alky- and aryl- sulfates, but it is highly unlikely that this organism would have evolved or acquired this protein under selective pressure to hydrolyze detergents. Furthermore, network modelling suggests a very close relationship between the two proteins, once again implying that SDS hydrolysis might not be the biological function of SdsA1. Thus, it is possible that these proteins perform some as yet unknown function or that the scaffold of SdsA1 can rapidly adapt to evolve new functions. We are currently investigating substrate preference of SdsA1, and we are expressing Bds1 to compare the substrate specificities of these two very closely related enzymes.

2015 Joint Southeastern/Southwest Regional Meeting 792

Role of gag domains in bovine leukemia virus RNA packaging

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The Gag polyprotein is involved in the formation of virus particles during retroviral replication. Retroviral Gag consists of three major domains: matrix (MA), capsid, (CA), and nucleocapsid (NC). In lentiviruses such as human immunodeficiency virus type 1 (HIV-1), MA attaches to the inner leaflet of the cell membrane while NC remains bound to the viral genomic RNA. In deltaretroviruses such as bovine leukemia virus (BLV), the process of assembly at the membrane is not clear. *In vitro* binding experiments have shown that MA binds to RNA as strongly as NC, suggesting a more important role for MA in genome packaging. In this study, nucleic acid binding and virus-like particle (VLP) assembly are studied *in vitro* under different conditions in order to clarify the contributions made by each domain to the assembly process. We observed that the presence of purified Gag and nucleic acid was sufficient for VLP formation. As shown previously for HIV-1, the presence of ribonuclease or high salt concentrations result in VLP disassembly; this is inhibited by inositol hexakisphosphate (IP6), a membrane phospholipid analogue. Results from binding studies performed with domain-deletion mutants and mutants that have been shown to poorly package RNA are also discussed.

2015 Joint Southeastern/Southwest Regional Meeting 793

Purification and RNA-binding properties of the West Nile virus core protein

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West Nile virus (WNV) is an arthropod-borne pathogen that is capable of causing fatal illness in humans. Like most viruses, its genomic RNA is enclosed in a protein coat that provides protection from nucleases. In WNV, many copies of the core protein (C) interact with the RNA genome to form the viral capsid. WNV-C also interacts with the lipid bilayer of the virus, which is formed from the ER membrane of the host cell. Two RNA-binding domains have been identified in WNV-C, but many questions remain unanswered with regards to the specific interactions between protein and RNA. To better understand the WNV assembly process, WNV-C was cloned and expressed in *E. coli* cell culture. This was accomplished by single-step reverse transcriptase polymerase chain reaction using WNV genomic RNA as a template. The resulting double-stranded DNA was inserted into an expression vector using directional cloning, and the protein was successfully over-expressed and purified in good yield. WNV-C was used in binding experiments with both non-specific and specific targets to elucidate the influence of electrostatic interactions on capsid assembly. A salt-titration binding assay was also performed to further study the binding of WNV-C to its RNA target. Finally, a key mutation to WNV-C was made to render the protein monomeric in order to determine the impact of dimerization upon its function. The data from these experiments collectively shed new light on WNV-C's role in viral replication.

2015 Joint Southeastern/Southwest Regional Meeting 794

Integrin subunits α3 and α6 mediate FGF10-dependent signaling events in collecting duct cells bound to LM511

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The collecting system of the kidney develops from the ureteric bud (UB), which undergoes branching morphogenesis, a process regulated by multiple factors, including cell–extracellular matrix (ECM) interactions. Integrins are the principal cell receptors for ECM and the laminin (LM)-binding integrins (Itg) α3β1, α6β1 and α6β4 are most important integrin's in this process. In addition growth factors, like fibroblast growth factors (FGFs) are involved in cell signaling pathways in this developmental process. The role of laminin-binding integrins, α3β1, α6β1 and α6β4, in FGF10-dependent signaling events that regulate renal branching morphogenesis has not been investigated. In this study, we used collecting duct cells (CD) which lack specific integrin subunits to identify these interactions. Itgα3$^{f/f}$α6$^{f/f}$ and Itgα3$^{-/-}$α6$^{-/-}$ CD cells were plated on LM-511, treated with FGF10 and after which they were assessed for spreading. In addition, CD cell lysates were immunoblotted to deteremine Akt activation. Itgα3$^{-/-}$α6$^{-/-}$ CD cells showed reduced spreading and Akt activity. Akt activity was also reduced in Itgα3$^{f/f}$α6$^{f/f}$ CD cells treated with Akt Inhibitor IV. These data suggest that that integrin α3β1 and α6 containing integrins interactions with LMs regulate FGF10-dependent activation of Akt signaling which mediates CD cell spreading .Thus, the interaction of FGF10 with LM binding integrins α3β1, α6β1 and α6β4 may play a role in UB branching morphogenesis.

2015 Joint Southeastern/Southwest Regional Meeting 795

Bioconversion of curcumin and its analog

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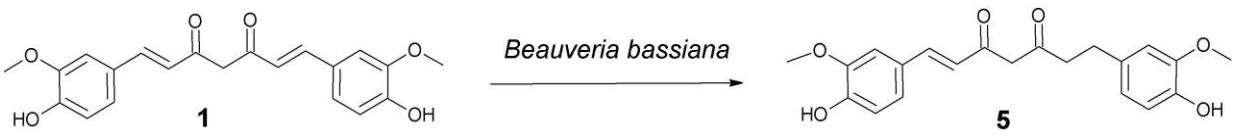
Reduction of curcumin (**1**), a chemopreventive agent from Turmeric (*Curcuma longa* L.), yielded five products. The three major compounds were identified as 1,7-bis(4-hydroxy-3-methoxyphenyl)heptane-3,5-dione (**2**), 5-hydroxy-1,7-bis(4-hydroxy-3-methoxyphenyl)heptan-3-one (**3**), and 1,7-bis(4-hydroxy-3-methoxyphenyl)heptane-3,5-diol (**4**). Incubation of compound (**2**) with *Beauveria bassiana* ATCC 7159 afforded the compound (**3**) as the sole metabolite. Bioconversion of curcumin (**1**) with *Rhizopus oryzae* ATCC 11145 yielded 1,7-bis(4-hydroxy-3-methoxyphenyl)hept-1-en-3,5-dione (**5**) and metabolites **3** and **4**. Metabolite **2** was not produced. No transformation of curcumin (**1**) was observed with *Aspergillus niger* ATCC 16888. The bioactivities and structural elucidation of these metabolites are reported herein.



2015 Joint Southeastern/Southwest Regional Meeting 796

Statistical analysis of tobacco for country of origin via ^{1}H-NMR and multivariate component analysis

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The chemical makeup of tobacco plants are known to vary according to weather, seed and soil variety, the treatments they are exposed to, and other contributing variables. Given the variables, the country where tobacco is grown influences the composition of tobaccos due to the effects of geographical location. The country affects the plant due to its geographical location, and the location's contributing factors, including soil composition, climate, farming environment, etc. This research focuses on comparing cigar extracts from the Dominican Republic, Nicaragua, and Honduras for statistical difference via ^{1}H-Nuclear Magnetic Resonance (^{1}H-NMR). The ability to determine the country of origin of a cigar via ^{1}H-NMR can aid the development of cigars by determining the chemical composition and possibly aiding the development of new flavors, creating environment-friendly treatments, and even reducing the health-risks of tobacco inhalation/chewing. Using Principle Component Analysis (PCA) of ^{1}H-NMR spectra, chemical differences between tobacco leaves can be determined which can lead to a ^{1}H-NMR-based method to detect the country of origin of tobacco products. Using spectroscopy, the composition of each cigar can be analyzed for variations within and between the tobacco samples from different countries by a statistical comparison of the spectra. We hypothesize that tobacco from different countries will group separately from each other on a PCA plot due to their individual statistical variation in ^{1}H-NMR spectra. The data gathered show that with this method, Nicaraguan tobacco can be statistically differentiated from the tobaccos of the Dominican Republic and Honduras, but the tobaccos from the Dominican Republic and Honduras cannot be differentiated from one another. Additionally, tobaccos from the Dominican Republic and Honduras had a statistically significant variation within themselves. Tobacco from Nicaragua has a noticeable statistical difference from the other two countries analyzed which may be due to its environmental factors, such as the richness of the soil and the weather of the country, which are not similar to those in the Dominican Republic nor Honduras.

2015 Joint Southeastern/Southwest Regional Meeting 797

Silver(I)-promoted regioselective oxidative aryl−aryl cross-coupling resulting in a direct C-H activation

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Aryl-aryl coupling or cross-coupling resulting in the formation of a new C-C bond through a direct C-H activation are of particular interest due to the prevalence of biaryl building blocks in several biologically active molecules, and in functional materials such as light-emitting diodes, electron transport devices, and liquid crystals. A silver(I)-promoted regioselective cross-coupling between phenols and aniline derivatives resulting in the formation of a new C-C bond through a direct C-H activation has been developed. The reaction involves the use of a large range of oxidizing agents, under mild conditions, resulting exclusive in the formation of a 2'-aminobiphenyl-2-ol derivatives in a quantitative yield. The optimization of the reaction conditions and the expansion of the scope of the reaction are discussed.

2015 Joint Southeastern/Southwest Regional Meeting 798

Model studies of the synthesis of the 2-(5*H*)-furanone moiety of myrtoidine

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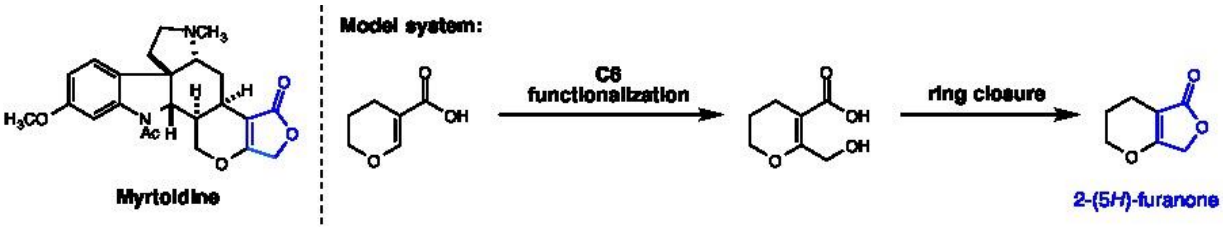
The Malagasy alkaloids extracted from *Strychnos myrtoides* have shown potential antimalarial activity. A total synthesis of the Malagasy alkaloid malagashinine has recently been completed in our lab, and we hypothesize that we would be able to potentially access the analogous alkaloid myrtoidine by a common synthetic intermediate. Synthesis of myrtoidine requires the development of a synthetic method that provides access to a crucial 2-(5*H*)-furanone moiety. Initially, we wished to explore a strategy involving vinylic C-H halogenation at the 6-position in a 3,4-dihydro-2*H*-pyran model. Using $[RhCp^*(MeCN)_3](SbF_6)_2$ as a catalyst, various iodination, bromination, and chlorination conditions were explored using carboxylic acids or carboxamides as directing groups; however, no desired products could be efficiently isolated due to undesired background reactivity of the halogenation reagents with our substrate. Currently we are exploring possible 6-lithiation of our 3,4-dihydro-2*H*-pyran-5-carboxylic acid model as a possible method for functionalization at this position.



2015 Joint Southeastern/Southwest Regional Meeting 799

Indolizine-squaraine NIR fluorescent materials

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Near-infrared (NIR) emissive organic materials are an emerging area of study with an array of applications for both military and civilian purposes including night vision technologies, secure communications, surveillance, homing, fluoresence imaging, secure displays as NIR OLED materials, heat-blocking coatings, *in vivo* fluoresence biological imagaing, and additional optoelectronics device applications.

We have developed a series of organic NIR emissive materials based on an indolizine donor and squaraine acceptor. The novel-to-squaraine donor, indolizine, exhibits a remarkable increase in absorption maximum wavelength when compared with benchmark indoline-based squaraine dyes (700 nm vs. 625 nm) with molar absorptivities ranging from 70,000-100,000 $M^{-1}cm^{-1}$. Emission is observed at 800 nm in chloroform, corresponding to a stokes shift of 100 nm, which is a substantial increase

when compared with the 5 nm stokes shift commonly observed for indoline-squaraine dyes. Our molecular design was evaluated by computational analysis which reveals clues about the origin of this stokes shift and the water solubility observed for these compounds without appending water solubilizing groups.

2015 Joint Southeastern/Southwest Regional Meeting 800

Divergent synthesis of novel 3-α- and 3-β-*C*-functionalized ribose derivatives

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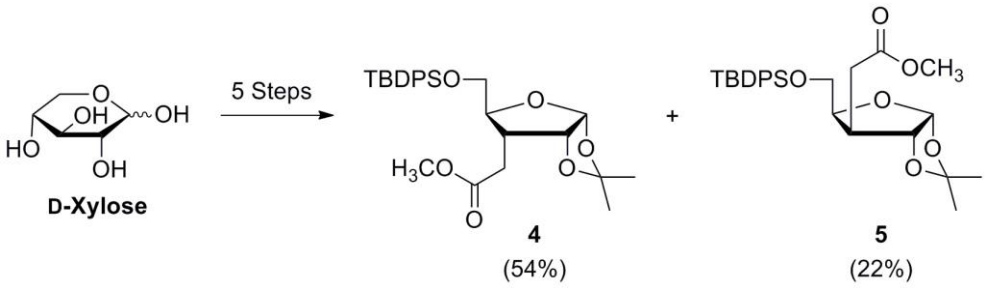
Carbohydrates are extensively used as templates for the stereoselective synthesis of chiral molecules. In order to simultaneously access both epimers of 3-*C*-functionalized 3-deoxyribose synthons, we devised a divergent synthesis of *tert*-butyl(diphenyl)silyl-protected 3-deoxy-3-α-methoxycarbonylmethyl-D-ribose **4** and 3'-β-methoxycarbonylmethyl-D-ribose **5**. The title compounds were stereoselectively synthesized from D-xylose in 5 steps and 54 and 22% overall yield, respectively. The key steps of our synthetic procedure were a regioselective Horner–Wadsworth–Emmons olefination followed by a face-specific, regioselective hydrogenation.



2015 Joint Southeastern/Southwest Regional Meeting 801

Lewis acid-catalyzed Minisci reactions

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Lewis acid and silver(I) catalysts were together employed in Minisci reactions between phenylboronic acid and various heterocycles. Different silver salts were examined determine if silver could function as both the Lewis acid and radical initiator. It was demonstrated that heterocycles containing electron-withdrawing groups provided the highest yields of the aryl-heterocycle coupled product.

2015 Joint Southeastern/Southwest Regional Meeting 802

Exploring amino acid-derived scaffolds to construct "smart" therapeutics

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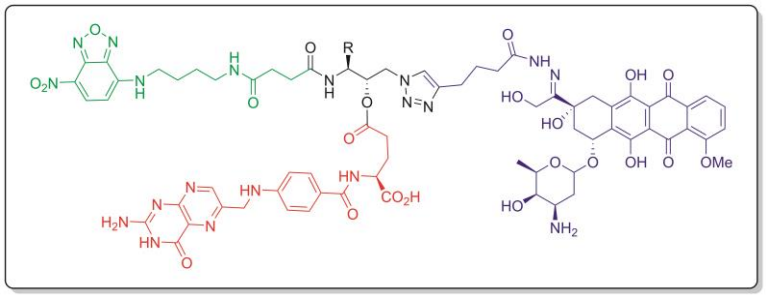
We are presently developing synthetic technology that allows for the rapid, efficient creation of “smart” therapeutics—a novel class of molecules that contain a targeting group, fluorescent tag, and drug all covalently linked to a central scaffold. Such agents would provide a flexible means to (a) localize desired tissue for treatment, (b) specifically deliver a drug to the intended site, reducing off-target side effects, and (c) monitor therapy in real time. We believe the linchpin in our synthetic endeavors is the development of an amino acid-derived central scaffold ideally suited in regard to structure (i.e., steric size of the “R” group), chirality, and orthogonal reactivity. As such, this poster will highlight the creation of multiple scaffold candidates and linker molecules, as well as a thorough assessment of their subsequent bioconjugation to the desired cargo units.



The initial "smart" therapeutic prototypes being developed against FR+ cancer cells contain an amino acid-derived central scaffold (black), and NBD flurophore (green), a folate targeting group (red), and doxorubicin (blue).

2015 Joint Southeastern/Southwest Regional Meeting 803

Advances in the development of druggable β-secretase inhibitor prodrugs

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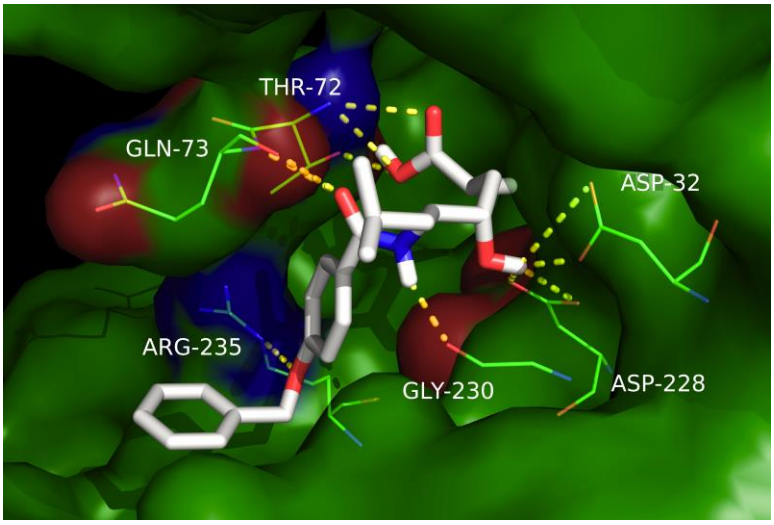
The continued development of a novel class of drug candidates to combat Alzheimer’s disease, central nervous system permeable β-secretase inhibitors, has been enabled by recent synthetic advances made in our laboratories. This poster will outline 1. key elements in the design of potent, druggable inhibitors of this enzyme, 2. our newly developed lactonization reaction and its impact on the overall yield and diastereoselectivity of our synthetic routes, 3. docking and structure/activity relationship data for this novel drug class obtained via in silico analysis, and 4. the results of *in vitro* metabolism studies (performed using human plasma and liver microsomes) to assess the bioavailability of our synthesized drug candidates.



2015 Joint Southeastern/Southwest Regional Meeting 804

Novel aromatic bridging ligands as nanoparticle colloid stabilizing agents

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Iron oxide nanoparticles are being studied for a variety of biomedical applications such as possible carriers for targeted drug delivery and as a contrasting agent for MRI imaging. The use of iron oxide nanoparticles will require several components to ensure effectiveness in the body. One component required is the binding of the iron oxide nanoparticles to a biological molecule by a linker ligand to improve interaction with the biological makeup. 2,5-dihydroxyisophthalic acid was chosen to be synthesized as a possible linker ligand because it possesses multiple coordination sites for the nanoparticles. 2,5-Dihydroxybenzoic acid was coupled with allyl bromide to produce 5-allyloxy salicylic acid with an average percent yield of 66.5%. This product was then formylated with hexamethylenetetramine to produce 3-formyl-5-prop-2-enoxysalicylic acid with an average percent yield of 62.3%. Oxidation of the product produced 5-alkoxy-2-hydroxyisophthalic acid with a percent yield of 68.7%. The alkoxy tail was then cleaved to produce 2,5-dihydroxyisophthalic acid. The acid was then recrystalized from water to improve purity. The structures of the products were confirmed by H1 NMR. Moving forward, the addition of various substituents at the 5-hydroxy position on the acid is being optimized for bioconjugation. The pka values of 2,5-dihydroxyisophthalic acid will be determined as they are not currently reported.

2015 Joint Southeastern/Southwest Regional Meeting 805

Design and synthesis of a cyclic citryl-ornithine analog as a novel inhibitor for Staphyloferrin A biosynthesis

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Staphylococcus aureus (*S. aureus*) is the bacteria responsible for Staph infection. While *S. aureus* has long been considered a public health concern, the emergence of methicillin-resistant strains coupled with the migration of the infections from hospitals to the community has demanded the development of new methods for the prevention and treatment of Staph infection. Iron is an essential element for *S. aureus* which uses two iron binding siderophores, Staphyloferrin A and Staphyloferrin B, to get the required iron. Literature suggests that Staphyloferrin A is more prevalent then Staphyloferrin B. Therefore, the aim of the present study is to synthesize citryl-ornithine analogs to serve as novel inhibitors for the biosynthesis of Staphyloferrin A. By mimicking an intermediate in the Staphyloferrin A biosynthetic pathway, the compounds could serve to hinder the production of Staphyloferrin A thus making it a potential treatment agent for Staph infection.

2015 Joint Southeastern/Southwest Regional Meeting 806

Multifunctional polyurethane hydrogels for biomedical applications

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Polyurethanes represent a broad class of polymers widely applied in everyday-life. Although polyurethanes are easy to produce and have a broad range of adjustable properties, only a few polyurethane-based nanomaterials have been realized so far. Here we designed a novel class of water-soluble polyurethanes that combine multiple functionalities relevant for biomedical nano-applications. They have the potential to change their chemical and mechanical properties, triggered by both changes in pH inside the body and intracellular redoxosomes. Crosslinking water-soluble polyurethanes leads to hydrogels, which are materials with soft mechanical properties useful for applications like drug delivery or tissue engineering. However, previously reported methods to create polyurethane-based hydrogels are limited for biomedical use, since they are based on toxic isocyanate-terminated prepolymers. Our novel gelation mechanism is based on physical interactions and does not require any free isocyanate groups, rendering our hydrogels non-toxic and applicable as drug delivery systems or injectable gels for in-situ tissue engineering.

2015 Joint Southeastern/Southwest Regional Meeting 807

One-pot sequential conversion of aldehydes to N-tert-butyl amides

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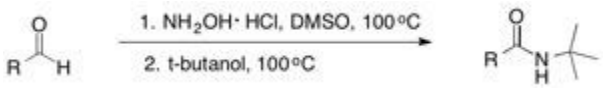
Building on our facile conversion of aldehydes to nitriles using hydroxylamine hydrochloride we have successfully coupled this reaction with the well-known Ritter reaction to prepare N-tert-butyl amides when using t-butanol as the solvent in the Ritter reaction. This one-pot sequential reaction yields hindered amides in moderate to good

yields and has proved more successful with aliphatic aldehydes. Work continues to optimize the conditions to convert aromatic aldehydes into hindered amides.



2015 Joint Southeastern/Southwest Regional Meeting 808

Identification and development of novel CDK inhibitors

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Cyclin-dependent kinases (CDKs) play important roles in cell cycle regulation and proliferation. Changes in CDK activity have been implicated in numerous debilitating diseases such as neurodegenerative disorders, renal diseases, and cancers. Inhibition of CDK activity can be achieved through a variety of approaches, including the prevention of ATP binding to CDK through the use of small molecule competitive inhibitors. Our recent work investigating indazole and phthalimide compounds as potential small molecule CDK inhibitors led us to the development of 2 novel indazoles and the identification of a phthalimide compound showing significant activity in CDK1 and CDK2. These compounds all showed sub-micromolar inhibition potency in CDK1 and CDK2 kinase inhibition assays in-vitro. The identification and synthesis of the inhibitors are presented.

2015 Joint Southeastern/Southwest Regional Meeting 809

An alkyne strategy for the stereoselective synthesis of piperidines

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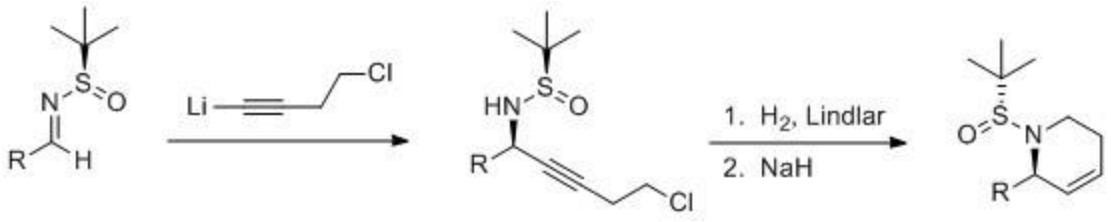
Chiral piperidine ring systems are present in a variety of natural products and biologically active molecules. In light of the prevalence of this scaffold, we have developed an alkyne-based strategy to stereoselectively access piperidines containing an endocyclic alkene suitable for further functionalization. We demonstrate the addition of 4-chloro-1-butyne to Ellman N-*tert*-butanesulfinyl imines with high stereoselectivity and in good yield. Reduction of the resulting propargylamines and cyclization under basic conditions affords the desired chiral piperidine ring.

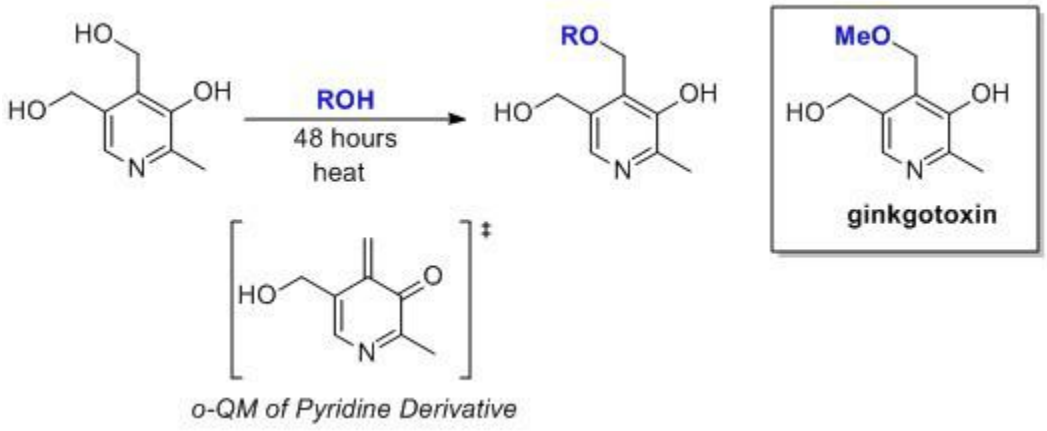


2015 Joint Southeastern/Southwest Regional Meeting 810

Synthesis of ginkgotoxin and related ether analogs

Jessica Yazarians, *jayazarians9560@eagle.fgcu.edu, Gregory R. Boyce. Chemistry and Physics, Florida Gulf Coast University, Estero, Florida, United States*

The synthesis of ginkgotoxin and related ether analogs from pyridoxine (vitamin B6), a cheap, readily available and nontoxic compound, is presented. Pyridoxine is demonstrated to undergo facile ortho-quinone methide (o-QM) formation under thermal conditions without the presence of an acid catalyst or the use of microwave irradiation to provide clean conversion to the desired ether products. A range of ether analogs is reported with high regioselectivity in good to excellent yields. The minor byproducts are also identified to account for the mass balance.



2015 Joint Southeastern/Southwest Regional Meeting 811

WITHDRAWN

2015 Joint Southeastern/Southwest Regional Meeting 812

Preliminary syntheses of tricyclic furan-bridged ring systems

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The aim of this project is to synthesize Sarcodictyin A and other biologically relevant furan-bridged ring systems via an altered [4+3] cycloaddition method followed by a Baeyer-Villiger oxidation and transesterification pathway. The alpha-monochlorination of cycloheptanone proceeded smoothly to yield the desired monochlorinated 2-chlorocycloheptanone product at an excellent yield with no byproducts. The [4 + 3] cycloaddition to yield tricyclic furan bridged rings, derived from 2-chlorocyclohexanone and 2-chlorocycloheptanone with various 2,5-disubstituted furans through the aminoallyl transient intermediates has been examined to assess its scope and potential limitations of the Schmid cycloaddition method. Effects of variations of the ring size and alternative furan substrates have been investigated. Through the Schmid cycloaddition method utilizing alpha-chloroenamines, a new tricyclic furan bridged nine carbon ring system was synthesized, 2,5-dimethyl-11-oxatricyclo[4.3.1.12,5]undec-3-en-10-one. The dimethyl furan structure provides protection against the acid-catalyzed decomposition pathway that was not afforded with the original furan based tricyclic adduct. Analysis of the molecule was complete using traditional direct detection methods as well as indirect 2D spectral analysis methods. The limitations of concentration, solvent, pulse sequences and coupling constants on 2D spectral analysis have been analyzed.

2015 Joint Southeastern/Southwest Regional Meeting 813

Design, synthesis, and antimicrobial evaluation of a novel 3'-*C*-acetohydrazide puromycin analog

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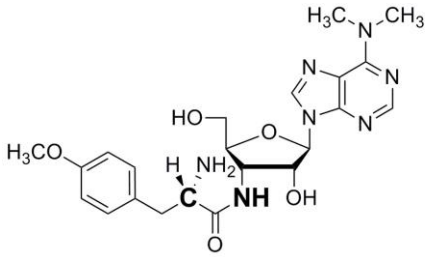
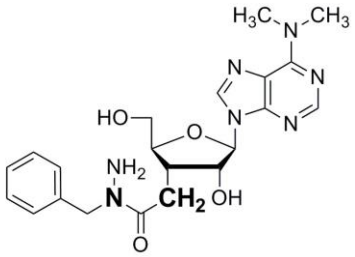
Puromycin is a peptidyl nucleoside endowed with significant antibiotic and anticancer properties, but also with an unfortunate nephrotoxic character that has hampered its use as a chemotherapeutic agent. Since hydrolysis of puromycin's amide is the first metabolic step leading to nephrotoxicity, we designed a 3'-*C*-hydrazide analog, where the nitrogen and carbon functionality around the amide carbonyl of puromycin are inverted. The title compound, synthesized in 11 steps from D-xylose, cannot be metabolized to the nephrotoxic aminonucleoside. Evaluation of the title compound on *Staphylococcus Epidermidis* and multi-drug resistance *Staphylococcus Aureus* cells did not show significant antimicrobial activity.



Puromycin



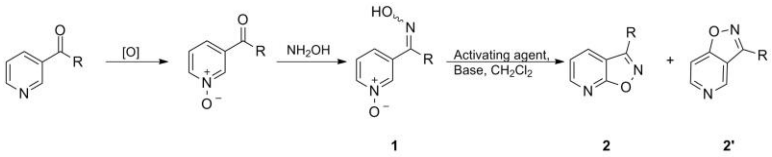
3'-*C*-Hydrazide analog

2015 Joint Southeastern/Southwest Regional Meeting 814

Synthesis of isoxazolopyridines via cyclization of 3-acylpyridine *N*-oxide oximes

***Brandon J. Hicks**, hicksb4@winthrop.edu, James M. Hanna. Chemistry, Physics, and Geology, Winthrop University, Rock Hill, South Carolina, United States*

Isoxazoles are associated with a wide spectrum of biological functions including antiviral, anthelmintic, anti-inflammatory, anticonvulsant and insecticidal activities. Derivatives of isoxazolopyridines are reported to have cholesterol lowering activities. Recently, our laboratory reported that tosylhydrazones formed using 3-acylpyridine *N*-oxides could be cyclized into pyrazolopyridines. Reaction of an *N*-oxide tosylhydrazone with a proper electrophile formed an activated intermediate that allowed nucleophilic attack at C2 or C4 on the pyridine *N*-oxide; in the presence of base an E2 elimination gave the desired cyclized product. We envisioned that this same method could be applied to form isoxazolopyridines from 3-acylpyridine *N*-oxide oximes (figure). Cyclization of 3-pivaloylpyridine *N*-oxide oxime (**1**, R=*t*-Bu) to the corresponding isoxazolopyridine was accomplished using various electrophile/base combinations, the most effective of which was triisopropylbenzenesulfonyl chloride and diisopropylethylamine in dichloromethane, giving an 86% yield of **2** and a 9% yield of **2′**. Cyclization of 3-acetylpyridine N-oxide oxime (**1**, R=Me) using the standard reaction conditions unfortunately proved to afford no detectable amounts of **2** or **2′** (R = Me). The difference is most likely due to the configuration of the oxime: ^{13}C-NMR confirmed the oxime hydroxyl to be *syn* to the pyridine ring in (**1**, R=*t*-Bu), but *anti* to the pyridine ring in (**1**, R=Me).

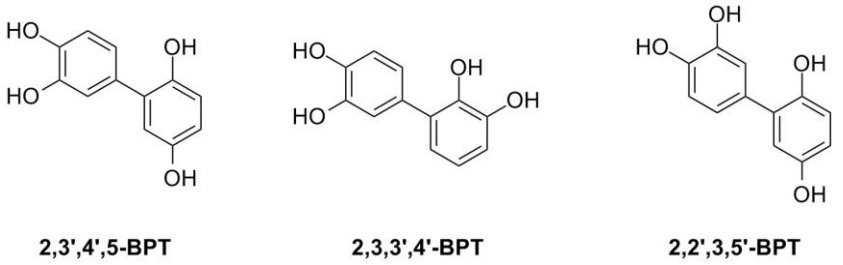


Synthesis and evaluation of unsymmetrical biphenyltetrols as aggregation inhibitors for Alzheimer's amyloid-β peptide

***Jake A. Roberts**, robertsj18@winthrop.edu, Andrea L. Taylor, Matthew J. Hurtt, Benjamin P. Hernandez, Sarah Wicks, James M. Hanna, Robin K. Lammi. Chemistry, Physics, and Geology, Winthrop University, Rock Hill, South Carolina, United States*

Amyloid-β peptide (Aβ) self-assembles into neurotoxic, β-structured aggregates, which are the primary component of the extracellular senile plaques characteristic of Alzheimer's disease. A variety of small molecules have been shown to inhibit the aggregation process; typically, these contain aromatic groups and one or more hydrogen-bond donors to enable binding to Aβ. We have previously identified biphenyltetrols (BPTs) as a class of molecules exhibiting promising inhibitory efficacy. 3,3′,4,4′-tetrahydroxybiphenyl (3,4-BPT) is the most promising, reducing equilibrium aggregation by 50% when present in stoichiometric concentrations (i.e., IC_{50} = 1X); 2,5- and 2,3-BPT also show significant inhibition. Based on these results, we hypothesized that "hybrid" unsymmetrical biphenyltetrols combining these arrangements of hydroxyl

groups may also be successful inhibitors. 2,3′,4′,5-BPT, 2,3,3′,4′-BPT, and 2,2′,3,5′-BPT (figure) were therefore synthesized and evaluated for inhibitory efficacy using the Congo red (CR) spectral-shift assay, which exploits CR's specific binding to β-structured aggregates to enable monitoring of Aβ aggregation as a function of time. Preliminary results indicate that neither 2,3,3′,4′-BPT nor 2,2′,3,5′-BPT were effective inhibitors; however 2,3′,4′,5-BPT appeared to be a promising inhibitor of Aβ aggregation (preliminary IC_{50} ~ 2X).



2,3',4',5-BPT 2,3,3',4'-BPT 2,2',3,5'-BPT

2015 Joint Southeastern/Southwest Regional Meeting 816

Palladium-catalyzed synthesis of ureas

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A palladium-catalyzed synthesis of ureas has been developed. An examination of phosphine ligands compatible with this reaction was performed. Various starting electrophiles and amines have been shown to provide the urea products in good yields.

2015 Joint Southeastern/Southwest Regional Meeting 817

Mosquitocidal and antibacterial activity of the essential oil of *Solidago gigantea* (Giant Goldenrod)

Caleb Ardizzone[1], *msu-cardizzone@student.mcneese.edu, Nick DeVito*[2], *Tatiana A. Estrada*[3], *Janet Woolman*[4], *Margaret Cochran*[5], *William Dees*[1], *Chris Struchtemeyer*[1], *Omar E. Christian*[3]. *(1) Biology and Health Sciences, McNeese State University, Lake Charles, Louisiana, United States (2) Biological Sciences, Vanderbilt University, Nashville, Tennessee, United States (3) Chemistry and Physics, McNeese State University, Lake Charles, Louisiana, United States (4) Louisiana Environmental Research Center, McNeese State University, Lake Charles, Louisiana, United States (5) Louisiana Scholars College, Northwestern State University, Natchitoches, Louisiana, United States*

Mosquito-borne diseases like chikungunya, dengue fever and yellow fever remain a significant threat to public health. *Aedes aegypti* and *Aedes albopictus* are the primary vectors of these diseases. New and more efficacious strategies to combat these mosquitoes at various stages in their life cycle are critical to controlling the spread of these diseases. Studies are underway in our laboratory that may lead to innovative personal protective measures against these pests. In this study, the essential oil of

Solidago gigantea was obtained by hydrodistillation using a Clevenger apparatus. The oil displayed concentration-dependent toxicity toward *Aedes aegypti* mosquitoes in a Petri dish contact assay. The essential oils also displayed moderate antibacterial activity against *Staphylococcus aureus*. This study describes the evaluation of the essential oil derived from *Solidago gigantea* for mosquitocidal and antibacterial activity.

2015 Joint Southeastern/Southwest Regional Meeting 818

Concentration-dependent antibacterial evaluation of the essential oil of *Pycnanthemum tenuifolium* against *Staphylococcus aureus*

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Health-care associated bacterial infections, especially infections from *Staphylococcus aureus*, remain a significant concern in U.S. hospitals. The ever-growing battalion of antibiotic resistant microbes requires the development of new and different antibacterial agents to combat these pathogens. Plant metabolites are an attractive source for new antimicrobial compounds. In previous studies, we demonstrated both antimicrobial and mosquitocidal activity of the essential oil from leaves and stems of Slender Mountain Mint, *Pycnanthemum tenuifolium*. The main component was identified as pulegone. Our current investigation describes the concentration-dependent antibacterial evaluation of the essential oil of *P. tenuifolium* against *S. aureus*.

2015 Joint Southeastern/Southwest Regional Meeting 819

Effect of botanical metabolites from 21 plant species on the yellow fever mosquito, *Aedes aegypti*

Caleb Ardizzone[1]*, msu-cardizzone@student.mcneese.edu,* ***William Dees***[1]*, w.dees.01@gmail.com, Omar E. Christian*[2]*, Janie Theriot*[1]*, Kathryn Leonards*[1]*, Allison Fusilier*[1]*, Cecilia Richmond*[3]*, Jill Hightower*[4]*, Adam D. Richard*[1]*, Jesse Dupre*[1]*, Margaret Cochran*[5]*, Joel Byrne*[1]*, Tatiana A. Estrada*[2]*, Andre Daugereaux*[6]*, Susan Mopper*[6]*, Janet Woolman*[3]*. (1) Biology and Health Sciences, McNeese State University, Lake Charles, Louisiana, United States (2) Chemistry and Physics, McNeese State University, Lake Charles, Louisiana, United States (3) Louisiana Environmental Research Center, McNeese State University, Lake Charles, Louisiana, United States (4) Calcasieu Parish Mosquito and Rodent Control , Calcasieu Parish Police Jury, Lake Charles, Louisiana, United States (5) Louisiana Scholars College, Northwestern State University, Natchitoches, Louisiana, United States (6) Center for Ecology and Environmental Technology, University of Louisiana-Lafayette, Lafayette, Louisiana, United States*

We are investigating if components and/or derivatives (e.g., essential oils) of plants native to Louisiana alter the behavior and development of medically important arthropods (e.g., mosquitoes and nuisance flies). Information obtained from these investigations may lead to innovative area-wide pest management methodologies as well as novel personal protective measures against biting arthropods. Current studies

focus on the effects of botanical components on mosquito mortality. We evaluated the effects of freshly-cut plant parts from eight plant families on female *Aedes aegypti* mosquitoes. Plant families included: Apiaceae, Apocynaceae, Asteraceae, Euphorbiaceae, Lamiaceae, Lythraceae, Malvaceae, and Verbenaceae. Standard plastic Petri dishes were used to hold mosquitoes and cut plant parts. We recorded percent mortality at 24 and 48 h. Mosquitoes exposed to fresh-cut flowers/petals, buds, leaves, stems, and seeds from Apiaceae, Asteraceae and Lamiaceae exhibited over 50% mortality when compared with the controls. Genera of interest include: *Chrysanthemum*, *Eryngium*, *Eupatorium*, *Rudbeckia*, *Monarda*, and *Pycnanthemum*. Mosquitoes exposed to different parts of a chrysanthemum plant (flowers, buds, leaves, stems and seeds) exhibited 100% mortality in 24 h. Mosquitoes exposed to cut buds of *Pycnanthemum muticum*, *P. tenuifolium*, and *Monarda fistulosa* as well as crushed seeds of *M. fistulosa* exhibited 100% mortality in 24 h.

2015 Joint Southeastern/Southwest Regional Meeting 820

Milestoning

***Ron Elber**, ron@ices.utexas.edu. University of Texas Austin, Austin, Texas, United States*

Milestoning is a theory and algorithm that exploits the use of short trajectories between interfaces in phase space (milestones) to compute equilibrium and long time behavior. Milestoning was introduced as a method of computing efficiently kinetics and thermodynamics along a one-dimensional reaction coordinate in complex molecular systems, provided that a de-correlation condition is met. I will discuss an extension of Milestoning to the simultaneous consideration of a significant number of coarse variables and the build up of kinetic networks. I will also discuss a recent and exact formulation of Milestoning, and the limiting cases that are frequently used in practical calculations. The use of kinetic networks to describe unfolding of a helical and coiled-coil system, and for water migration through membranes will be discussed.

2015 Joint Southeastern/Southwest Regional Meeting 821

Dynamic potential surfaces for sodium diffusion in type II silicon clathrates

*Jason G. Slingsby[1], Nicholas A. Rorrer[1], Lakshmi Krishna[4], Eric Toberer[3], Carolyn A. Koh[2], **Christopher M. Maupin**[1], cmmaupin@mines.edu. (1) Chemical and Biological Engineering, Colorado School of Mines, Golden, Colorado, United States (2) Colorado School of Mines, Golden, Colorado, United States (4) Physics, Colorado School of Mines, Golden, Colorado, United States*

Earth abundant semiconducting type II Si clathrates have attracted attention as photovoltaic materials due to their wide band gaps. To realize the semiconducting properties of these materials, guest species that arise during the synthesis process must be completely evacuated from the host cage structure post synthesis. A common guest species utilized in the synthesis of Si clathrates is Na, which templates the clathrate cage formation. Previous experimental investigations have identified that it is possible to evacuate Na from type II clathrates to an occupancy of less than 1 Na per unit cell. This work investigates the energetics, kinetics, and resulting mechanism of Na diffusion through type II Si clathrates by means of biased molecular dynamics and kinetic Monte Carlo simulations. Well-tempered metadynamics has been used to

determine the potential of mean force for Na moving between clathrate cages, from which the thermodynamic preferences and transition barrier heights have been obtained. Kinetic Monte Carlo simulations based on the metadynamics results have identified the mechanism of Na diffusion in type II Si clathrates. The overall mechanism consists of a coupled diffusive process linked *via* electrostatic guest-guest interactions. The large occupied hexakaidechedral cages initially empty their Na guests to adjacent empty large cages, thereby changing the local electrostatic environment around the occupied small pentagonal dodecahedral cages and increasing the probability of Na guests to leave the small cages. This coupled process continues through the cross-over point that is identified as the point where large and small cages are equally occupied by Na guests. Further Na removal results in the majority of guests residing in the large cages as opposed to the small cages, in agreement with experiment, and ultimately a Na free structure.

2015 Joint Southeastern/Southwest Regional Meeting 822

Mp2 solvation free energy of simple ions obtained through force matching to simple pairwise potentials

*Jicun Li, **Feng Wang**, fengwang@uark.edu. Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas, United States*

Simple non-polarizable potentials were developed for Li^+, Na^+, K^+, F^-, Cl^-, and Br^- using the adaptive force matching method with *ab initio* MP2 method as reference. Our MP2-AFM force field predicts the solvation free energies of the nine salts formed by the ions with an error of no more than 2%. Other properties, such as the ion-water radial distribution functions, first solvation shell water tilt angle distributions, ion diffusion constants, concentration dependent surface tension of the solutions were calculated with this potential. Very good agreement was achieved for these properties. In particular, the diffusion constants of the ions are within 6% of experimental measurements. Although the potential provides satisfactory prediction for the concentration dependent surface tension, the model predicts all the ions to be repelled from the top-most layer of the liquid-vapor interface, which may be a limitation of the implicit treatment of polarization effect.

2015 Joint Southeastern/Southwest Regional Meeting 823

Modeling of protein systems with complex landscapes

***Ulrich H.E. Hansmann**, uhansmann@ou.edu. Dept. of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma, United States*

A detailed knowledge of the processes by that proteins fold, self-assemble or aggregate is crucial for an understanding of disease pathways and the working of drugs at the level of cells. As these fundamental processes are difficult to trace in experiments, there is a need for reliable computational tools that complement experiments in studying folding and aggregation of proteins. In this talk, I will describe recent advancements in sampling techniques and simulations of protein folding and aggregation that these techniques enable.

2015 Joint Southeastern/Southwest Regional Meeting 824

Using simulations to link molecular design to macromolecular morphology and function in polymer composites

***Arthi Jayaraman**, arthij@udel.edu. Chemical and Biomolecular Engineering, University of Delaware, Newark, Newark, Delaware, United States*

Polymer nanocomposites (PNCs) are a class of materials that consist of a polymer matrix embedded with nanoscale fillers or additives that enhance the inherent properties of the polymer. Since the PNC morphology dictates its macroscopic behavior/properties, in order to tailor PNCs for specific applications with target macroscopic properties (e.g. photovoltaics, photonics, automobile parts) it is important to have design rules that relate molecular features to the morphology of the composite. We use a combination of theory and molecular simulations to link molecular design features of the polymer grafted nanoparticles on particle assembly/dispersion in a polymer matrix. I will present our recent work on a) on homopolymer grafted particles in chemically dissimilar homopolymer matrix to show how we can tune the thermodynamic driving forces for particle dispersion and aggregation in a homopolymer matrix, and b) copolymer grafted nanoparticles in homopolymer blend matrices to show how the copolymer graft sequence and composition tunes compatibilization of blend interfaces.

2015 Joint Southeastern/Southwest Regional Meeting 825

Density functional model for nondynamic and strong correlation

***Jing Kong**, jingkong@gmail.com, Emil Proynov. Chemistry, Middle Tennessee State University, Murfreesboro, Tennessee, United States*

Proper treatment of nondynamic and strong correlation is considered the last frontier of density functional theory (DFT). A single-term density functional model for nondynamic and strong correlation is presented, based on single-determinant Kohn-Sham density functional theory. It is derived from modeling the adiabatic connection and contains only a few nonlinear empirical parameters. Preliminary tests show that the model, based on full Hartree-Fock reference, recovers majority of nondynamic correlation during a molecular dissociation and at the same time performs reasonably for atomization energies. It demonstrates the feasibility of developing DFT functionals for nondynamic and strong correlation within the single-determinant KS scheme

2015 Joint Southeastern/Southwest Regional Meeting 826

Newly developed methods for describing excited states

***Rod Bartlett**, bartlett@qtp.ufl.edu. Quantum Theory Project, University of Florida, Gainesville, Florida, United States*

We will discuss several new methods for excited states, including TDDFT, EOM-CC, and STEOM-CC One focus with be on core-excitation spectra and another will focus on tetrakis.

2015 Joint Southeastern/Southwest Regional Meeting 827

Large-scale variational 2-RDM-driven CASSCF methods

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Complete active-space self-consistent-field (CASSCF) methods are enormously important in electronic structure theory, as they allow for the description of the electronic states that are dominated by more than one electronic configuration. Unfortunately, most implementations of CASSCF are configuration-interaction (CI)-based, and the exponential scaling of CI severely limits the size of the active space that can practically be employed. The application of CASSCF to large active spaces requires that one abandon CI in favor of polynomial-scaling approaches such as the density-matrix renormalization group (DMRG) or variational two-electron reduced-density matrix (2-RDM) methods. Using a combination of state-of-the-art semidefinite programming techniques and density-fitting approximations, we have developed a computer implementation of a variational 2-RDM-driven CASSCF procedure. Quantitative agreement with CI-based methods can be achieved through the application of partial three-particle N-representability conditions, while qualitative accuracy requires only the application of two-particle conditions. We use the approach to evaluate singlet-triplet gaps in a series of dinitrene biradicals and the linear acene series. Our largest computations consider active spaces with 50 electrons in 50 orbitals, while simultaneously optimizing more than 1800 orbitals.

2015 Joint Southeastern/Southwest Regional Meeting 828

Methodologies and development towards quantitative accuracy for the heavy elements: Structural, energetic, and spectroscopic properties

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While significant effort has been invested in accurate computational methodologies for main group species, there has been much less focus upon f-block chemistry. Here, DFT and *ab initio* single reference and multireference methodologies have been considered in conjunction with a variety of basis sets for the prediction of structural, energetic, and spectroscopic properties of several classes of lanthanide species in the common 3+ oxidation state, as well as in lower oxidation states. Routes to address relativistic effects have been considered, and possible composite strategies are addressed. The role of orbitals in bonding and the impact of the correlation of the subvalence upon thermochemical and photophysical properties are considered.

2015 Joint Southeastern/Southwest Regional Meeting 829

Getting down to the fundamentals of hydrogen bonding

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This presentation summarizes our ongoing efforts to generate benchmark harmonic and anharmonic vibrational frequencies for hydrogen bonded clusters that are converged to the complete basis set (CBS) limit with correlated electronic structure methods, specifically the MP2 and CCSD(T) methods. This work systematically examines the basis set convergence of MP2 and CCSD(T) harmonic vibrational frequencies of small

clusters composed of H_2O, HF and/or HCl. In general, basis sets of quadruple-zeta quality are required to get reasonably close to the estimated CBS limit frequencies for all modes of small homo- and heterogeneous clusters composed of H_2O, HF and/or HCl. Second-order vibrational perturbation theory (VPT2) anharmonic corrections yield CCSD(T) vibrational frequencies in excellent agreement with experimental spectra, differing by no more than a few cm^{-1} for the intramonomer fundamental vibrations, including the challenging donor stretch. D_0 values predicted by CCSD(T) VPT2 computations with a quadruple-ζ basis set closely match the experimental values for $(H_2O)_2$, $(HF)_2$, $(HCl)_2$ and HCl/H_2O. The deviation between experiment and theory is much larger, however, for HF/H_2O. The analytic Hessians recently developed by our research group for the N-body:Many-body integrated QM:QM method provide a means to overcome the unfavorable scaling of canonical CCSD(T) Hessian computations and extend the calculation of benchmark harmonic and anharmonic vibrational frequency calculations to larger clusters.

2015 Joint Southeastern/Southwest Regional Meeting 830

Advances and challenges in the calculations of intermolecular potentials with spectroscopic accuracy

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Theoretical determination of highly accurate potential energy surfaces has been indispensable for interpreting experimental data and guiding future measurements. However, spectroscopic (1 cm^{-1}) accuracy is very hard to attain in interaction energy calculations: it requires both a precise estimate of the coupled-cluster with singles, doubles, and perturbative triples [CCSD(T)] complete basis set (CBS) limit and a reasonable account of corrections beyond the frozen-core CCSD(T) level, that is, the correlation of core electrons, coupled-cluster excitations beyond CCSD(T), relativistic effects, and the post-Born-Oppenheimer corrections. In the former term, the most accurate CCSD(T)/CBS limit values can typically be computed with a combination of midbond functions and explicitly correlated (F12) approaches, although the residual approximations in, say, the CCSD(T)-F12b method may become critical at this level of accuracy. For the post-CCSD(T) corrections, basis sets of at least aug-cc-pVDZ quality are needed to obtain any reliable estimate. The presented examples range from the He-H_2 and He-C_3 complexes, where accurate potential energy surfaces were computed and used to obtain spectral, transport, and scattering data, to complexes with triple bonds such as CO-CO and N_2-N_2 that exhibit a particularly slow convergence of high-order coupled-cluster excitations.

2015 Joint Southeastern/Southwest Regional Meeting 831

Rovibronic quantum chemistry

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The computation of rovibrational properties of small molecules via highly-accurate quartic force fields (QFFs) has recently began to produce *ab initio* vibrational

frequencies to within spectroscopic accuracy on a regular basis. Additionally, spectroscopic constants provided by such techniques have, in a couple of cases, superseded the related experimental work. However, all of these advances are limited to ground electronic state computations. Accurate quantum chemical prediction for the rovibrational structure of electronically excited states has proven to be difficult for anything beyond the harmonic approximation. However, we are developing new approaches to describe accurate QFFs that can be applied to electronically excited states. Hence, quantum chemical rovibronic spectral data is being generated for new molecules. We computed the HOC radical's ground ^{1}A' and first-excited ^{1}A'' states' rovibrational properties utilizing a combination of the established QFF procedures, equation-of-motion coupled cluster theory, and subsequent systematic corrections. Additionally, we have produced vibrational frequencies and spectroscopic constants for the A $^2\Pi$ state of C_2H, a common hydrocarbon radical. Most notably, the ν_1 C-H stretch appears to lie more than 250 cm^{-1} below previous estimates. Finally, the application of this method to treat dipole-bound excited states of anions is currently being developed. Preliminary results with the BO^- diatomic anion show that vibrational frequencies and rotational constants of its candidate dipole-bound excited state can be computed effectively. This type of approach opens the promise for the rovibronic spectra of difficult molecular systems, such as anions and radicals, to be determined to a high level of confidence.

2015 Joint Southeastern/Southwest Regional Meeting 832

Amino derivatives of 6-methylpentacene and 6-methylene-6,13-dihydropentacene

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In 1949, Clar and Wright reported that 6-methylpentacene exists as 6-methylene-6,13-dihydropentacene at room temperature due to a [1,5]-sigmatropic hydrogen shift. This shift causes the side rings to bend one way and the methylene to bend in the opposite direction destroying the planarity of the overall compound. Amino derivatives of the two parent isomers are investigated to determine which substitution positions can stabilize the methyl isomer in which the overall planarity of the rings is maintained. The result is important because synthesis of derivatives of alkyl-substituted pentacenes is rare. Optimum equilibrium geometries, harmonic vibrational frequencies, and the corresponding zero-point vibrational energies are computed for each set of isomers using density functional theory. The functionals employed are Becke's three-parameter hybrid functional using the LYP correlation functional and the M06-2X high nonlocality hybrid functional from Thular and Zhao. The basis sets employed are Dunning and coworkers' correlation consistent basis sets: cc-pVDZ and cc-pVTZ. We gratefully acknowledge support from the NSF (EPS-0903787) and the W.M. Keck Foundation.

2015 Joint Southeastern/Southwest Regional Meeting 833

Applying kinematics models to obtain insights into surface structure from gas/surface collisions

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Gas-liquid scattering dynamics have been extensively studied for atomic and molecular species in collisions with liquid surfaces by directing a supersonic molecular beam at continuously refreshed surfaces of these liquids and collecting time-of-flight and angular distributions of the inelastically scattered projectiles, with the use of a rotatable mass spectrometer detector. The scattered products generally are known to be divisible into two components, impulsive scattering (IS) and thermal desorption (TD). TD molecules exit the surface with a Maxwell-Boltzmann distribution of velocities given by the surface temperature. IS molecules scatter from the surface mainly in the specular direction while maintaining a large fraction of their initial translational energy and, depending on the system, can only sometimes be fit by a Maxwell-Boltzmann temperature. However, the average fractional energy transfer of the IS molecules can be fit well by an impulsive model that allows determination of the effective mass of the localized region of the surface that interacts with the incident molecules. In light of the observed dynamics for the various projectiles scattering on qualitatively different surfaces, we have employed a surface analog of the gas-phase kinematic analysis, known as the Newton diagram, which might in principle be used to obtain effective surface masses for collisions of gas-phase species with surfaces and thereby allow insight into the surface structure. This model has been applied with consistent success to both molecular beam scattering data and molecular dynamics simulations of atoms and molecules colliding with liquids and self-assembled monolayer surfaces.

Alexander et al., ***Faraday Discuss.***, 2012,**157**, 355-374, **DOI:** 10.1039/C2FD20034A

2015 Joint Southeastern/Southwest Regional Meeting 834

Determination of fluoride levels in name and generic brand mouthwashes

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The benefits of supplemental forms of fluoride from various sources has been investigated for years. An optimal concentration of fluoride in human systems is necessary to avoid both dental caries and fluorosis. The Department of Health and Human Services recommends a range of 0.7 to 1.2 milligrams per liter. This range minimizes the chance for dental fluorosis. Samples from name and generic brands of mouthwashes were analyzed using ion chromatography. Mouthwash samples showed levels of fluoride consistent with those listed on the bottle by the manufacturer.

2015 Joint Southeastern/Southwest Regional Meeting 835

Application of Cr(III) as a protonating enhancement agent in MALDI/TOF mass spectrometry: Studies of small peptides

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Matrix assisted laser desorption ionization (MALDI) is a common soft ionization mass spectrometry technique utilized in the analysis of biomolecules and polymers. Ionization by MALDI most commonly involves the production of singly charged protonated molecular ions, $[M+H]^+$. In this study, addition of chromium(III) nitrate, $Cr(NO_3)_3$, to peptide solutions was found to increase the intensity of $[M+H]^+$ produced by MALDI/time-of-flight (TOF) mass spectrometry. This work involved the basic peptides

bradykinin and substance P, as well as the acidic peptides hirudin (54-65) and human fibrinopeptide b. Addition of Cr(III) increased the intensity of $[M+H]^+$ by several orders of magnitude when using the common MALDI matrix 2, 5-dihydroxybenzoic acid (DHB). Surprisingly, production of adduct ions of peptide and Cr(III) did not occur, but instead a very clean spectral background was observed. In contrast, the use of Cr(III) in conjunction with the matrix 1, 5-Diaminoaphthalene (DAN), which has no carboxylic acid groups, resulted in a poor protonated peptide signal by MALDI. Instrument parameters such as, laser intensity, deflection, scan number, and calibration methods were also optimized.

2015 Joint Southeastern/Southwest Regional Meeting 836

Transformation of $Au_{144}(SCH_2CH_2Ph)_{60}$ to $Au_{133}(SPh\text{-}tBu)_{52}$ nanomolecules: X-ray crystallography, optical, electrochemical, experimental, and theoretical analysis

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X-ray crystallographic structure has been successfully solved for the largest reported thiolated gold nanomolecule as $Au_{133}(SPh\text{-}tBu)_{52,}$ which has been also verified by high resolution electro-spray mass spectrometry (ESI-MS). The structure of Au_{133} is organized with four shells: first shell consist of Au_{12} icosahedral shell surrounding the central Au atom, second shell with Au_{42} icosahedral shell, third shell with 60-atom rhombiicosidodecahedron and finally, the outmost 26 atoms that are part of the 26 [−SR−Au−SR−] units. Core size conversion and compositional changes of ultra-stable nanomolecules $Au_{144}(SCH_2CH_2Ph)_{60}$ was studied by etching with excess tert-butylbenzenethiol to form an entire new nanomolecule with the core of $Au_{133}(SPh\text{-}tBu)_{52}$. Experimental analysis was performed using high resolution ESI-MS, which shows that the core size conversion is initiated after 22 ligand exchanges, suggesting a relatively high stability of the $Au_{144}(SCH_2CH_2Ph)_{38}(SPh\text{-}tBu)_{22}$ intermediate. The core size conversion of Au_{144} to Au_{133} using tert-butylbenzenethiol is different from the case of reported Au_{144} to Au_{99} using thiophenol. Moreover, successful formation of crystals is mainly due to the presence of rigid and bulky ligand group as indicated by the theoretical analysis.

2015 Joint Southeastern/Southwest Regional Meeting 837

Monitoring surface water of Lake Sinclair in Georgia

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Pollution through sewage water contamination, industrial fertilizer, and coal burning power plants can lead to degradation of water quality. Eutrophication, the ecosystem response as a result of the addition of excess nutrients, will further degrade water quality by depleting the oxygen in water. Nutrient levels are measured using HACH

surface water kits and YSI probes to access eutrophic conditions. Purge-n-Trap coupled with GC/MS is used to test for potential gasoline additives and byproducts found in the surface water around well-populated, high traffic areas of Lake Sinclair. Liquid chromatography (HPLC) is used to search for commonly used pesticides and fertilizers. This presentation highlights the EPA protocol for water quality in recreational areas, method development and experimental design for the analysis, as well as the results of the project.
Livingston, Robert J. Eutrophication Processes In Coastal Systems. New York: CRC, 2001. Print.1

2015 Joint Southeastern/Southwest Regional Meeting 838

Qualitative identification of volatile organic compounds present in electronic-cigarette vapor via GC/MS detection

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The rising popularity of electronic cigarettes and the congruent lack of regulations is cause for concern. Electronic cigarettes contain a heating mechanism which vaporizes a mixture of propylene glycol with flavoring compounds and nicotine.[1] Electronic cigarette vapor is known to contain some of the same harmful compounds as traditional cigarettes, including volatile organic compounds such as acrolein.[2] Environmental Tobacco Smoke (ETS) encompasses second-hand, side-stream, and third-hand smoke, which is when harmful chemicals from smoke are absorbed into cloth. Volatile organic compounds found in ETS are identified by analyzing the headspace of cloth samples exposed to electronic cigarette vapor via gas chromatography/mass spectrometry (GC/MS). This presentation summarizes the experimental design and qualitative results.

[1] McCoy, M. The Nicotine Fix For E-Cigarettes. *Chemical & Engineering News Archive.* **2014** 92 (14), 24-25
DOI: 10.1021/cen-09214-bus2 [accessed 2015 Aug 6]
[2] Lockwood, D. Controversy Clouds E-Cigarettes. *Chemical & Engineering News Archive* **2014** *92* (10), 32-33
DOI: 10.1021/cen-09210-scitech1 [accessed 2015 Aug 6]

2015 Joint Southeastern/Southwest Regional Meeting 839

Determination of protein binding constants of epigallocatechin-3-gallate (EGCG) with rapid equilibrium dialysis and LC/MS/MS analysis

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Tea is the second most consumed beverage in the world behind water. Catechins are polyphenols with antioxidant properties found in high amounts in tea, especially green tea. Green tea beverages and dietary supplements containing green tea extracts are often marketed for health benefits. The most abundant catechin in tea is epigallocatechin-3-gallate (EGCG). While EGCG has a high amount of antioxidant activity compared to other catechins in tea, it is also believed to have the least

bioavailability due to protein binding. We sought to measure protein binding using an *in vitro* rapid equilibrium dialysis method. Post dialysis, EGCG concentrations were measured with a reverse phase gradient elution liquid chromatography-tandem mass spectrometry (LC/MS/MS) method with a 4 minute cycle time. EGCG binding constants will be measured by dialysis of human blank-pooled serum, human serum albumin (HSA), and human α1-acid glycoprotein (AAG).

2015 Joint Southeastern/Southwest Regional Meeting 840

Method development and optimization for detection of cyanide antidote sulfur donor X (SDX) by use of gas chromatography-mass spectrometry

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Cyanide (CN) is a toxic agent and it can be found in many foods (cherries, apples, almonds, etc.) and people can be exposed to CN during a fire. The human body has a natural defense for CN intoxication through the enzyme rhodanese, which converts CN into a less toxic anion, thiocyanate by using sulfur donors. However, the sulfur donor will be depleted when high exposure to CN is involved. While antidotes are available, there are limitations to their efficacy. Through Dr. Petrikovics lab, a new antidote, sulfur donor X (SDX) was found and an intramuscular formulation was developed to treat CN intoxication. Our aim was to develop a detection method for the SDX from mice brains by using gas chromatography-mass spectrometry (GC-MS). SDX was detected from the head space above a brain sample using solid phase microextraction onto a polydimethylsiloxane (PDMS) fiber. Sample preparation and the MS detection were optimized. The mice brains were homogenized in water, 15% Polysorbate 80, and ethanol. Ethanol proved to be the best solvent for SDX detection. Stirring during the incubation of PDMS fiber in the head space improved analyte recovery times, but sodium chloride addition did not. Ten suitable ions were selected for mass spectrometric detection. A calibration curve was prepared in 0-60 µg/ml concentration range for SDX recovered from brain homogenate. The goodness-of-fit (R^2) was 0.9986, and the limit of detection was 0.28µg/ml. This detection method is suitable for future *in vivo* studies.
The study was funded by the Robert A. Welch Foundation at Sam Houston State University (x-0011) and the USAMRICD (Contract No.W911NF-11-D-0001).

2015 Joint Southeastern/Southwest Regional Meeting 841

The surveillance of anions in natural water determined by ion chromatography

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Natural waters have been shown to contain trace amounts of anions which vary depending on geographic region. These anions can be indicative of the health of the region; for example, perchlorate, a substance possibly toxic to humans, has been found in water sources in some western states due to runoff from rocket propellants. We are interested in surveying the southern Appalachian regions to probe the health of the environment surrounding local rivers, creeks, and lakes by monitoring the type and the amount of anions with ion chromatography (IC).

For this project, we venture to local water sources and collect samples which are subsequently analyzed on the IC system. We have determined the detection limits and retention times and formed calibration curves for several anions to form a library. As we have monitored the anions over time, we noticed an increase in the sulfate concentrations in local waters that coincided with leaf fall last autumn. We hypothesized that the leaves were the source of the sulfate. To test our hypothesis, we soaked some leaves harvested from the ground in ultrapure water over a span of two months and periodically analyzed the supernatant. We found an initial increase and eventual plateau in concentration of sulfate relative to the other anions in the supernatant. These results suggest that the sulfate was originating from the leaves, and a fixed amount was entering the water and remaining in solution. In natural waters, these results suggest that a fixed amount of sulfate should enter the water during the autumn months and remain until it washes downstream. Additional experiments were conducted after the initial observation to further explore the source and pervasiveness of the sulfate from the leaves. For example, we compared ultrapure water and river water to digest the leaves, we compared leaves that were living on the tree to leaves that had fallen, and compared the differences in location of leaf harvesting. Results from our studies on the leaves will be presented as well as other data from the water systems of the southern Appalachian region.

Automated spectrophotometric titrations: Seeing the unseen

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Titrations and Beer's law determinations are two of the most routine and powerful tools for quantitation. Contemporary technology makes the titration mixing and spectrophotometric measuring a real-time process. Major off-the-shelf components used to provide this capability were an Ocean Optics UV/vis spectrometer, an f100 Chemyx syringe pump, and Reactlab Equilibria software from J-Plus. To test this system 2mL mixtures of Co^{2+}, and Zn^{2+} were titrated with EDTA while collecting spectra every second. Formation of the cobalt complex produces an absorbance change but the zinc complex is only evident by its indirect effect on the timeline for the formation of the cobalt complex. Nevertheless, the matrix algebra treatment of the time, wavelength and absorbance data produced using Reactlab Equilibria resulted in excellent reaction profiles and quantitation of both reactants. These results show that titrations lasting a mere 100 seconds are capable of providing a complete chemical accounting even when some species are experimentally cloaked.

Analysis of aspartame in Diet Coke using solid phase extraction and HPLC

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A method to extract and quantitatively analyze aspartame in diet soda samples was developed by a summer undergraduate research student. This method will later be utilized by students enrolled in an upper level Instrumental Analysis course. Solid phase extraction using reversed-phase C-18 packing was used to extract aspartame from an aqueous sample. Both acetonitrile/pH 3 buffer and methanol/pH 3 buffer eluents were evaluated for their elution efficiency. The eluate containing aspartame was then analyzed and quantified by reversed-phase HPLC. Initial results using aqueous standards indicated a 95-99% recovery. Results from diet soda samples will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 844

Investigation of novel hydrogen bond donors and halogens in deep eutectic solvents

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Deep eutectic solvents (DES), formed by mixing a choline salt with a hydrogen bond donor, such as water, show unexpected physical properties such as extremely low melting points and endothermic reaction states. These solvents are currently used in the purification of biofuels and as an environmentally friendly alternative to solvents used in organic chemistry. The most commonly studied composition of eutectics has been glycerol, urea, and water as hydrogen bond donors and choline chloride as the halogen/choline atom. This research focused on finding alternative hydrogen bond donors, namely alcohols, as well as alternative choline halides: choline bromide and choline iodide. Mixtures of water, ethanol, and methanol as hydrogen bond donors with choline bromide, choline iodide, and choline chloride were analyzed with constant-pressure calorimetry and differential scanning calorimetry (DSC). The melting points were observed by bringing the solvents to freezing and monitoring the temperature in a series of trials. The formation of all the potential DES in the experiment was an endothermic process, with the exception of the choline iodide/ethanol combination. The heat of formation was largest in the samples in which water was the hydrogen bond donor, and smallest in the samples in with ethanol. There was an interaction observed in all of the samples, indicating the possibility of a eutectic formation. There was a significant depression in the expected melting point in all of the samples where water was used as a hydrogen bond donor, indicating a unique interaction in these samples but not necessarily in samples with other hydrogen bond donors.

2015 Joint Southeastern/Southwest Regional Meeting 845

Uptake and release studies of the biocides polyhexamethylene biguanide and alexidine on contact lenses utilizing ultra performance liquid chromatography and mass spectrometry

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Biocides have become increasingly popular antimicrobial agents over the past few years due to both the increasing resistance of bacteria to traditional antibiotics and the broad range of applicability that biocides exhibit. Therefore, it has become necessary to characterize the activity of these biocides to fully understand their underlying properties. Two of these substances, the polycationic biocides polyhexamethylene biguanide (PHMB) and alexidine dihydrochloride, are among the most commonly observed in the market today, particularly in commercial multipurpose solutions (MPS) for contact lens care. Alexidine exhibits a single cationic structure while PHMB is actually a complex, polydispersed mixture. Using ultra-performance liquid chromatography (UPLC) and Mass Spectrometry (MS), analytical techniques have been developed for the analysis and quantitation of both alexidine and PHMB. Furthermore, we have conducted uptake and release studies for both PHMB and alexidine in an effort to elucidate the mechanisms of interaction with various contact lens materials.

2015 Joint Southeastern/Southwest Regional Meeting 846

Determination of Appalachian stream health in the Maryville College woods

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There is a 140 acre plot of land on the Maryville College campus that is known as the college woods. The creeks that run through the college woods are Duncan's Branch and Brown's Creek, and these streams combine near one edge of the end of the woods. The stream health of the Maryville College woods was studied in 2014; it was concluded that more sensitive macroinvertebrates were able to survive downstream of the creek than upstream. Therefore, it was hypothesized that the stream was becoming less polluted as it ran through the college woods. Sampling sites were marked along these three sections: along Duncan's Branch, along Brown's Creek, and along the combined stream. Collection of samples occurred as often as was permitted; ideally, samples were collected on a weekly basis. The pH, conductivity, dissolved oxygen, and temperature readings were recorded at each sampling site with a YSI-Pro Plus probe during each sample collection. Water and soil samples were collected from each site. The water samples were tested for ammonium, nitrate, calcium, and pH using Vernier probes and LoggerPro software; the water samples were also tested using ion chromatography. The soil samples were tested for calcium, barium, cadmium, and lead using flame atomic absorbance spectroscopy.

2015 Joint Southeastern/Southwest Regional Meeting 847

Size characterization and alternative synthesis of monolayer-protected quantum dots

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Water-soluble, monolayer-protected quantum dots (QDs) were synthesized using several water-soluble thiols and alternative metal salts (e.g., cadmium acetate, zinc sulfate). QDs were synthesized at temperatures as low as -47 °C in attempts to control the growth of the nanoparticles. The optical properties of QD solutions were characterized using UV-visible and fluorescence spectroscopies. The hydrodynamic radius of the QDs was determined using 2D NMR techniques. From the NMR experiments, the diffusion coefficient of the nanoparticles, in concert with a small reference molecule (ferrocene), was determined. Subsequently, the size of the nanoparticles was calculated using a modified version of the Stokes-Einstein equation. This work is funded, in part, by the National Science Foundation (CHE-1126231).

2015 Joint Southeastern/Southwest Regional Meeting 848

Correlation between different extraction methods and the ratio of neral to geranial in the essential oils of lemongrass

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Citral is a compound that is found in the essential oils of the lemongrass plant. Citral contains two different isomers, neral(Z) and geranial(E). The purpose of these experiments is to investigate the effects that different extraction methods, and dilutions have on the citral in a sample of lemongrass. The extracts were diluted in organic solvent to different concentrations, and the first two samples were steam distilled multiple times. Diluting a sample results in a larger ratio of E/Z. The three different extraction types analyzed were steam distillation, solvent soak with exposure to the sun, and solvent soak in a cool, dark, well ventilated place. The results from the GC-MS provide data that supports the fact that as the energy in the extraction increases, the more geranial is converted to neral. More energy in the extraction causes the keto-enol form allowing the isomers to interconvert. This is represented by in increase in ratio of Z/E as the energy in the extraction increases. Different extraction methods should be used depending on weather more neral or geranial is desired.

2015 Joint Southeastern/Southwest Regional Meeting 849

Evaluating the use of dicationic pairing reagents for detecting alkylsulfonates by paired-ion electrospray ionization mass spectrometry

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Research in this group has recently focused on examining the requirements necessary for using electrospray ionization ion trap mass spectrometry (ESI-IT-MS) as a *quantitative* tool to study the composition of mixed alkanethiol self-assembled monolayers (SAMs). Given the low numbers of analyte species that are typically produced upon oxidative desorption into the effluent, the relatively high detection limits of many standard benchtop IT mass spectrometers have generally limited their use in such studies. In the work presented here, ion pairing between the oxidation products of these SAMs (alkylsulfonic acids) and a dicationic ion pairing agent (1,9-nonanediyl-bis(3-methylimidazolium cation)) was examined to determine if adduct formation occurred and whether the resulting adducts could be detected at concentrations

commensurate with those expected from SAM desorption. Data will be presented demonstrating the utility of this approach.

2015 Joint Southeastern/Southwest Regional Meeting 850

Validation of separated hemoglobin variants A, F, S, C

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Dynamic IEF is a new method related to capillary isoelectric focusing that can provide good resolution and separation capabilities by controlling the shape of the electric field using additional high voltage power supplies. Both the location and width of the focused protein bands can be controlled by manipulation of the electric field. Current research focuses on demonstrating and improving the performance characteristics of the system. Hemoglobin variants A, F, S, C have been separated using dynamic IEF to illustrate that this method has the same separation capabilities as capillary IEF. In order to establish what variant has been separated, the four variant standards have been digested and analyzed using gel electrophoresis and ESI-MS.

2015 Joint Southeastern/Southwest Regional Meeting 851

Automation of dynamic isoelectric focusing

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The complex nature of the proteome requires separation methods capable of separating a large number of proteins in order to permit comprehensive analyses. Dynamic IEF is a new method related to capillary isoelectric focusing that can provide excellent resolution and separation capabilities by controlling the shape of the electric field using additional high voltage power supplies. Both the location and width of the focused protein bands can be controlled by manipulation of the electric field.
Current research utilizing dynamic IEF focuses on automating the system using an integrated switching valve to remove the focused protein bands. The use of an injector allows dynamic IEF to be coupled to a second dimension with minimal effort while maintaining resolution. Dynamic IEF allows for a focused protein band to be isolated, removed, and analyzed by a second dimension, such as LC-MS, while the rest of the system is concurrently focusing another protein fraction.

2015 Joint Southeastern/Southwest Regional Meeting 852

Synthesis and characterization of 3,4-dialkoxybenzyl substituted bis-urea organogelators

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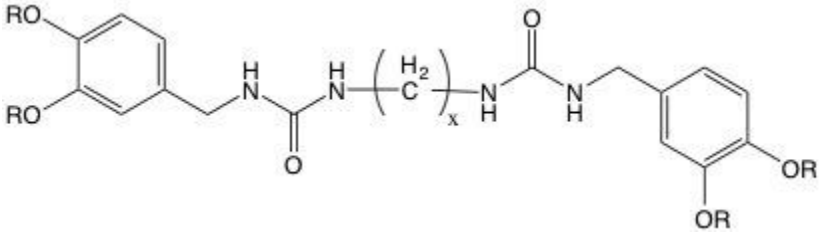
The goal of the research was to synthesize a series of branched bis-urea molecules using 3,4-dihydroxybenzaldehyde (3,4-DHB) as the starting material for an organogelation structure function study. By starting with 3,4-DHB it is possible to vary

the length of the alkyl tails (R=C_{10} toC_{22}) attached to the phenols at the 3 and 4 positions through a standard Sn2 reaction. The alkylated benzaldehyde can then be converted to an oxime in situ then reduced to the benzylic amine either by nickel/sodium borohydride under basic conditions or using zinc and acetic acid. The overall conversion to amine typical occurs in high yield. The benzylic amine is then reacted with a diisocyanate ($OCN(CH_2)_xNCO$, x= 6 or 12) to generate the desired bis-urea. Preliminary synthetic yields of the intermediate aldehydes, amines and final bis-ureas will be presented. Initial critical concentration studies of the bis-ureas in common organic solvents (toluene, octane, acetone, ethanol, oil) will be presented along with our interpretation of the molecular interactions responsible for the gelators behavior. Of particular note, several bisurea compounds form transparent solid gels well below 1 wt/wt% in toluene placing these compounds in the class of supergelators.



General structure of bis-urea organogelators

2015 Joint Southeastern/Southwest Regional Meeting 853

Examining the effects of cis double bond incorporation in the alkyl tail region of bis-urea organogelators

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Bis-urea organogelators have been studied for over two decades, however in this time frame only straight chain alkyl tails have been incorporated into the structure. In general it is believed that the ureas are the primary functional groups to initiate monomer aggregation. The aggregation continues to grow until you have a thread, which interacts with other threads to create fibers. Once the fibers associate a complex matrix is set and a solid gel is produced. It is the role of the alkyl tails to interact/entangle that ultimately has bearing on the strength of the organogel. The more the threads and fibers entangle the stronger the gel should be. It is believed that by creating more disorder in the alkyl tails more entanglement can be generated and stronger gels may be created. It is the goal of this research to synthesize a variety of bis-urea molecules that incorporate cis double bonds between the 9,10 carbons of an octadodecyl tail to create more disorder in the alkyl tais of these organogelators and test this hypothesis. Bis-urea molecules that contain a cis double bond will then be evaluated for their organogelation capability and compared to the strait chain derivatives. The synthesis of double bond containing gelators as well as the straight chain derivatives will be presented as well as their respective critical concentration for gelation.

2015 Joint Southeastern/Southwest Regional Meeting 854

Analysis of the terpene and sesquiterpene hydrocarbons of lemon and lime oils

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The research is centered on performing different methods on lemons and limes in order to find there terpenes and sesquiterpene hydrocarbons. Terpenes are aromatic hydrocarbons and sesquiterpenes are a group of terpenes that have three isoprene units. During the first method simple distillation of the peels of lemons and limes was used to obtain the essential oils. Each essential oil was then used in column chromatography to isolate the desired components from the mixture. Then the fractions collected during column chromatography were analyzed using gas chromatography and mass spectrum. The results were analyzed and compared between the lemon and lime oil.

2015 Joint Southeastern/Southwest Regional Meeting 855

Elucidating the exciton transport in tetracarboalkoxyphenyl porphyrin thin films for enhanced organic optoelectronics

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Porphyrin light-harvesting systems have recently shown promise in solar energy conversion applications because of their ability to absorb a broad portion of the solar spectrum and to be easily tuned with peripheral substituents. Four tetracarboalkoxyphenyl porphyrins, 5,10,15,20-Tetrakis(4-carbobutoxyphenyl) porphyrin (TCB_4PP), 5,10,15,20-Tetrakis(4-carbohexoxyphenyl)porphyrin (TCH_4PP), 5,10,15,20-Tetrakis(4-carbooctoxyphenyl)porphyrin (TCO_4PP), and 5,10,15,20-Tetrakis(4-carbo-2-ethylhexoxyphenyl)porphyrin ($TCEH_4PP$) were synthesized and analyzed as solution-cast thin films. The spectroscopic and excited-state energy transfer dynamics of these materials were examined using time-resolved photoluminescent studies. The photoluminescence (PL) decay of pristine films and those blended with a fullerene quencher (PCBM)were used to evaluate the efficiency of the exciton transport. Exciton diffusion lengths (L_D) were obtained by fitting the (PL) decay of pristine porphyrin films and films containing small amounts PCBM to a 3D Monte Carlo exciton hopping model. The effects of heat treatment on diffusion length and steady state fluorescence emission were studied to develop a deeper understanding of composition and morphologies of porphyrins in thin films.

2015 Joint Southeastern/Southwest Regional Meeting 856

Development of lipid probe for labeling and discovering lipid-binding proteins

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Lipids are important biomolecules due to their involvement in many key biological pathways. By binding proteins on the surfaces of cell membranes, lipids localize and

alter the function of those proteins. One such biologically significant lipid is diacylglycerol (DAG), which binds in this way to certain members of the protein kinase C (PKC) family, a group of related proteins that regulate cell growth and are directly linked to tumor formation, as well as to diabetes. Synthetic DAG analogues, or probes, are tools that allow for the elucidation of protein-DAG binding. The aim of our present study is to synthesize a novel DAG activity probe that contains a photoaffinity tag for covalent labeling of bound proteins as well as two azide tags, which can be conveniently modified after labeling *via* "click chemistry" to introduce chemical handles that allow us to visualize and identify DAG-bound proteins. This probe will be incorporated into liposome studies leading to the identification of DAG-binding proteins in complex biological samples. Additionally, the nature of this DAG probe will allow for future synthetic steps toward probes corresponding to more structurally complex lipids, such as phosphatidic acid (PA), phosphatidylserine (PS) and the phosphoinositides (PIP_ns).

2015 Joint Southeastern/Southwest Regional Meeting 857

Synthesis of polycyclic compounds using NHC-borenium ions

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The purpose of this research is the biomimetic cyclization of polycyclic compounds from acyclic carbon chains, using NHC-borenium ions. NHCs have been shown to be good ligands for borenium ions that create a very strong Lewis acid due to the combination of a positive charge with electrophilic boron's empty p-orbital. Current polycyclic compound cyclization methods can be successful with a range of polyene chains, but have known limitations. It is hypothesized that NHC-borenium ions may enable a new method for the synthesis of polycyclic compounds. This work presents the initial results of substrate synthesis towards the investigation of polyene cyclization.

2015 Joint Southeastern/Southwest Regional Meeting 858

Synthesis of *N*-acetyl oligopeptides and their methyl ester derivatives

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The main goal of the project is to examine how the kinetics of proteolysis under acidic conditions (non-enzymatically and enzymatically by HIV-1 protease) depend on substrate length. To investigate this, we have been synthesizing a series of homologous oligopeptides of varying lengths. HIV-1 protease is specific for hydrophobic residues and thus the target compounds have a –Phe-OMe or –Leu-OMe terminus that mimics the sites where HIV-1 protease cleaves its natural substrate, the HIV-polyprotein. The synthetic approach includes a combination of methods like acetylation, Fischer esterification, and peptide bond formation using conventional coupling agents. For example, acetylation of leucine and two dipeptides was performed to give the intermediates Ac-Gly-Gly-OH, Ac-Gly-Leu-OH, and Ac-Leu-OH. Fischer esterification was then used to synthesize Ac-Gly-Leu-OMe and Ac-Leu-OMe. The results thus far show that varying the acid concentration has effects on the rate of esterification. Conventional peptide bond-forming reactions to synthesize targets like Ac-Gly-Gly-Phe-OMe will also be performed. After synthesis of the products, ^{1}H NMR spectroscopy is

used to characterize the reactivity of products. The analyses will provide information that can be used to better understand reaction mechanisms of protein strands.

2015 Joint Southeastern/Southwest Regional Meeting 859

Synthesis of oligopeptides to be subjected to HIV-1 protease cleavage

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HIV-1 protease tends to cleave its substrate at positions next to larger hydrophobic side chains. By the use of eight synthetic oligopeptides esters varying in length and containing such side chains, we can test whether HIV-1 protease tends to cleave longer chains faster than smaller ones and how it does so. Our synthetic methods include acetylation and Fischer esterification of specific amino acids and oligopeptides. The desired oligopeptides include: Ac-$(Gly)_n$-Leu-OMe and Ac-$(Gly)_n$-Phe-OMe, where n = 0-3. Long-term goals of this research are to subject these esters to cleavage by HIV-1 protease to determine the enzyme's selectivity in reference to substrate length and to investigate the enthalpy and entropy of activation for the enzymatic and non-enzymatic cleavage of oligopeptides. The immediate goal is the successful synthesis of all of the targeted esters. Preliminary results shows that we can successfully acetylate di- and tripeptides. Fischer esterifications of acetylated oligopeptides have posed some complications requiring further experiments.

2015 Joint Southeastern/Southwest Regional Meeting 860

The multi-step synthesis of the tripeptides Ac-Sar-Sar-Sar-OEt and Ac-Sar-Sar-Pro-OEt

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This poster begins with a review of a conformational analysis of serine proteases and some of the kinetics data obtained by our group for a non-enzymatic solvolysis of oligopeptides. We also present progress toward a short-term goal of synthesizing two tripeptides, Ac-Sar-Sar-Sar-OEt and Ac-Sar-Sar-Pro-OEt. Solvolytic studies of several such oligopeptides should help us to understand observed effects of long-range structure on relative reactivity. The results may also help to explain the influence of structural factors in corresponding enzymatic studies.

2015 Joint Southeastern/Southwest Regional Meeting 861

Kinetics of tripeptide ester methanolysis

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This project is investigating the substrate length dependence of solvolysis kinetics for a series of tripeptide esters. Progress has been made towards completing the syntheses

and collecting kinetics data for the fifteen tripeptide esters we have selected. For proteases in general, the phenomenon of hydrolysis rates increasing with substrate lengths has often been observed. We have reported that a similar rate enhancement phenomenon is observed in the absence of the enzymes and also that there are extensive alignments of atomic orbitals in crystal structures of serine proteases. It seems that these effects are inherent to the fundamental structure of proteins. Our tripeptide study will better characterize this property of proteins and give us more insight into both its mechanism and the roles it may play in enzymatic catalysis.

2015 Joint Southeastern/Southwest Regional Meeting 862

Synthesis and activation of N-heterocyclic carbene boranes

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Boron is an important element in organic chemistry because it is prevalent in many organic reactions, such as hydroboration-oxidation reactions and Suzuki cross-coupling reactions. The goal of this work is to show that borylation of a carbon-hydrogen bond into a carbon-boron bond is possible through the use of the borenium ion. The formation of the desired diamido NHC-borane proved quite difficult to accomplish. However, the use of a commercially available NHC, without electron withdrawing groups or large steric groups proved to be successful for the synthesis of an NHC-borane . Further investigations must be performed to synthesize the NHC-borane with various NHC backbones in order to determine steric and electronic effects of various backbones on the molecules.

2015 Joint Southeastern/Southwest Regional Meeting 863

Synthesis, design, and computational analysis of a novel multifunctional porphyrin-thiazolothiazole framework

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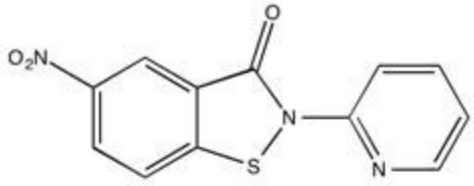
Organic photovoltaics are at the forefront of renewable energy conversion because of cheap cost, nontoxicity, scalability, and rising efficiencies. Porphyrin light-harvesting systems have recently shown promse in solar energy conversion because of their abilities to absorb a broad portion of the solar spectrum and to be easily tuned with peripheral substituents. However, porphyrins are plagued with low hole mobilities. The thiazolothiazole molecule possesses one of the highest reported hole mobilities in small molecules. By coupling electron deficient thiazolothiazole and electric rich porphyrins, two new novel electron donor-acceptor-donor (DAD) and acceptor-donor-acceptor (ADA) motifs are created. Excitons quickly transfer to the electron deficient portion of the molecule, enabling better charge separation and improved charge mobility. Absorption and fluorescence spectra, fluorescence quantum yields, density functional theory calculations, time dependent density functional calculations, and exciton diffusion length measurements lead to conclusions that donor-acceptor motifs extend the lifetime of excitons and additionally may serve purposeful in organic optoelectronics.

2015 Joint Southeastern/Southwest Regional Meeting 864

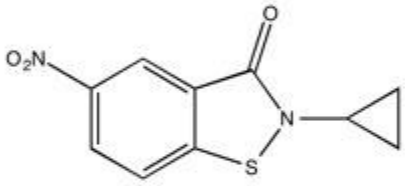
Synthesis of novel benzoisothiazolone organocatalysts for dehydrative condensation reactions

***Mariko Morimoto**, mariko.morimoto94@emory.edu, Lanny S. Liebeskind, Pavan Gangireddy Reddy. Chemistry, Emory University, Atlanta, Georgia, United States*

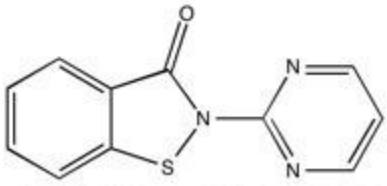
In oxidation-reduction condensation reactions, loss of water can be driven stoichiometrically through the use of an organic reductant—most typically triphenylphosphine—and an organic oxidant. These traditional dehydration methods, however, are largely wasteful processes that are additionally accompanied by the use of hazardous oxidants and inseparable products. The objective of this project is to streamline redox dehydration reactions by optimizing a catalytic approach that involves the coupling of an organocatalytic benzoisothiazolone (BIT) as the oxidant and O_2 in the air as the terminal oxidant with triethylphosphite as the reductant (instead of triphenylphosphine), thus eliminating chemical waste and enhancing energy efficiency. Catalytic efficacy can be improved by manipulating the electronic and substituent effects that come from the different functional groups and substitutents on the basic BIT framework. In this study, three novel BIT compounds were synthesized, of which the 5-nitro-2-(pyridin-2-yl)benzo[*d*]isothiazol-3(2*H*)-one is expected to have the most advanced catalytic properties based on previous results obtained by the Liebeskind group. Relevant compounds were characterized using ^{13}CNMR, HNMR, IR, and mass spectroscopy as well as X-ray crystallography. Several synthesis pathways, particularly for the synthesis of nitro-substituted BITs with electron withdrawing group functionalization, were identified and optimized, elucidating the path for further BIT synthesis and thus a Greener catalytic cycle.



5-nitro-2-(pyridin-2-yl)benzo[*d*]isothiazol-3(2*H*)-one



2-cyclopropyl-5-nitrobenzo[*d*]isothiazol-3(2*H*)-one



2-(pyrimidin-2-yl)benzo[*d*]isothiazol-3(2*H*)-one

2015 Joint Southeastern/Southwest Regional Meeting 865

Novel deoxygenation dimerization of benzoisothiazolones

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The Liebeskind Laboratory is exploring the use of benzoisothiazolones (BITs) as organic oxidants for various synthetic organic applications. As part of that study we are investigating the redox reaction of benzoisothiazolones with P(III) reducing agents, such as triethylphosphite. Reacting these two substrates in solution produces an unexpected and interesting product resulting from a deoxygenation and dimerization process of the BIT.[1] My study focuses on the scope of this dimerization reaction with the intent to explore its generality and optimize the reaction conditions for production of the deoxygenation-dimer. Running these reactions at varying temperatures, in various solvents, and with various BIT molecules will provide a deeper understanding of the processes and help deliver a general and efficient reaction. Reactants, reaction progression, and products were analyzed and characterized using thin layer chromatography, ^{1}H, ^{31}P, and ^{13}C Nuclear Magnetic Resonance spectroscopy. Further analysis was done using infrared spectroscopy, mass spectrometry, and X-Ray crystallography. Additional study will help understand differences in yields and extraction difficulties and arrive at a general and informative library of BIT-deoxygenation dimers. Having a comprehensive library will then allow for the study of these C-2 symmetric BIT deoxygenation-dimers as C-2 symmetric ligands in metal complexes for possible asymmetric enantiocontrolled metal catalyzed reactions.

References

[1.] Unpublished results of Dr. PavanKumar R. Gangireddy, Liebeskind Laboratory.

2015 Joint Southeastern/Southwest Regional Meeting 866

Optimization of direct arylation of 1,2,3-triazoles

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Heterocyclic compounds are of great importance in organic and medicinal chemistry. The triazole motif is of particular interest due to its presence in diverse therapeutic compounds. The triazole moiety can act as an isostere for the pyrimidine group and displays versatile biological activities. 1,5-Disubstituted-1,2,3-triazoles have classically been synthesized *via* the azide-alkyne Husigen cycloaddition reaction. The drawback of this method is that it often produces mixtures of the 1,4- and 1,5-disubstituted regioisomers. Further, cycloaddition does not facilitate substitution of diverse functionalities. Therefore, we seek to develop a method for the preparation of 1,5-disubstituted 1,2,3-triazoles *via* a C-H activation strategy. A simple $Pd(OAc)_2$-catalyzed oxidative coupling of 1,3,4-oxadiazoles with various aryl groups has recently been described; we seek to extend this methodology to the synthesis of disubstituted

triazoles. Such a procedure could subsequently be applied to the synthesis of medicinally important triazoles.

2015 Joint Southeastern/Southwest Regional Meeting 867

Selective mono-reduction of conjugated ester functional groups using lithium borohydride

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Regioselectivity in organic functional group transformations is an essential component to the efficient production of interesting and useful molecules. In our research we are able to selectively reduce one ester functional group in the presence of a chemically identical ester within a variety of aromatic diesters using *in-situ* generated Lithium Borohydride. Having the diesters located in a conjugated system is essential and we hypothesize that one ester group functions as an electron withdrawing group to activate the other ester allowing reduction using this mild reducing agent. Once one ester is reduced to an alcohol, further reduction of the system is stymied. Sodium Borohydride is too weak of a reducing agent and results in no reduction, whereas Lithium Aluminum Hydride is too strong of a reducing agent and results in complete reduction of both esters. Lithium Borohydride, however, is “just right” and performs well in this selective reduction.

In particular, we found that both meta and para diesters are selectively reduced in high yields using Lithium Borohydride. Likewise, aromatic triesters and tetraesters are also selectively reduced, but in lower yields. Ester groups located ortho to one another are unreactive. Purification of the products is minimal as column chromatography is only necessary for triesters and tetraesters. Characterization of the reduction products is performed using ^{1}H and ^{13}C NMR, IR, and GC/MS. Work currently underway includes examining the role that both conjugation and electron donation play in selective mono-reduction of an ester.

Lithium borohydride effectively, cleanly and selectively reduces aromatic diesters. Additionally the reduction is performed in only one step with no need for protecting groups. This method has the potential to be an easy and effective means for selectively reducing esters into alcohols.

2015 Joint Southeastern/Southwest Regional Meeting 868

Functionalized nanoporous polysulfone membranes via silane chemistry

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Nanoporous materials are attractive because of their potential and established utility as separation media, ion exchange membranes, catalysts, and scaffolds for the growth of nanoscopic materials. Controlling pore size and property is essential in creating effective nanoporous materials. We have prepared nanoporous polysulfone (PSU)

membranes and selectively modified their pores via silane coupling chemistry. First, polysulfones with partially substituted propenyl side groups were synthesized to give propenyl polysulfone (PPSU). PPSU then underwent ring opening polymerization of D,L-lactide to yield polylactide-polysulfone-polylactide triblock copolymers (PLA-PPSU-PLA). The self-assembled membranes were prepared by solvent-cast and annealing to promote nanoscale phase separation, followed by complete degradation of PLA block to expose a hydroxyl functional group lining in the nanopores. The nanopore surface was further modified using a variety of silane coupling reagents to explore their effects on membrane properties. An array of pore-surface structures were successfully prepared using silane coupling agents on the nanoporous membrane template. The modified membranes exhibit distinct differences on water uptake and dye affinity.

2015 Joint Southeastern/Southwest Regional Meeting 869

Synthesis of novel 1,2,3-triazoles using click chemistry

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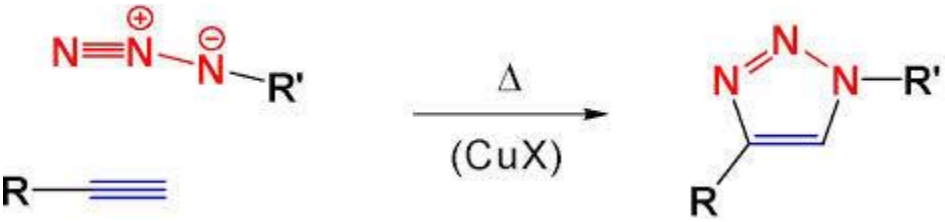
The use of Click Chemistry to perform cycloaddition reaction of alkynes and azides to form a variety of novel organic compounds which can lead to further studies of the products in Organic Synthesis, Bioconjugation and finally Drug discovery .
The synthetic method known as click reactions, which assembles molecules with high efficiency, selectivity and yield by Barry Sharpless , et al, in 2001 has helped chemists and even undergraduate students to construct compounds which can be used in variety of fields like drug discovery, chemical biology, medicinal chemistry, material science, polymer chemistry to name a few.
These reactions require a set of criteria as follows:
The reactions are modular, wide in scope, high yielding, create no offensive by-product, are stereospecific, simple to perform and performed in benign solvents which make them ideal research projects for undergraduate students even in a small university setting.
We are concentrating and have already synthesized few azide and phenyl triazole derivatives using the click reaction, which can lead to further investigations.



Triazole Formation via Copper 9I) - Catalyzed Azide-Alkyne cycloaddition

2015 Joint Southeastern/Southwest Regional Meeting 870

One-pot Suzuki coupling synthesis of substituted isoxazoles under green, microwave conditions

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Heterocyclic compounds that contain the 3,5-diarylisoxazole moiety have been shown to possess strong anti-cancer properties. Unfortunately, previous methods of synthesizing these compounds have resulted in poor reaction rate, poor yield, and unfavorable environmental effects. The goal of this research is to overcome these issues by optimizing microwave-assisted Suzuki coupling with a green solvent and reusable catalyst. Microwave heating will greatly increase the reaction rate while Suzuki cross-coupling should produce few side products, thereby increasing the yield of our desired isoxazole product. Finally, using the green solvent mixture alongside a reusable catalyst will greatly minimize the chemical waste resulting from this reaction. To test and optimize this reaction method, the synthesis of two isoxazole compounds, 3-phenylisoxazole and 3-(4-methoxyphenyl)-5-phenylisoxazole, were studied. Further optimization of the procedure used to synthesize these two isoxazoles will hopefully lead to the ideal conditions under which potential anti-cancer compounds containing the 3,5-diarylisoxazole moiety can be synthesized.

2015 Joint Southeastern/Southwest Regional Meeting 871

Synthesis and catalytic activity of (R)-3-methylpyrrolidine-3-carboxylic acid

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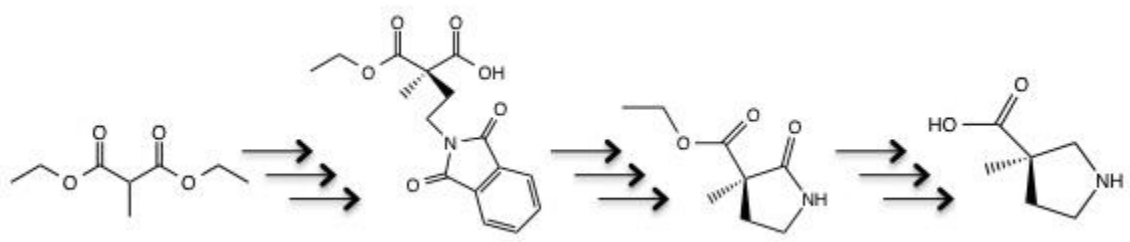
L-Proline is an organocatalyst widely used in pharmaceutical research. It is used in a variety of chemical reactions, especially the Aldol, Mannich, and Michael reactions. Organocatalysts have contributed to advancements in green chemistry. The absence of transitions metals in organocatalysts prevents the production of hazardous waste and allows “cleaner” synthetic reactions. Another advantage is the chiral centers that allow stereoselective reactions to occur. This research will focus on the production of a unique proline analogue and the potential reactions to be used to explore its reactivity and compare to known proline analogues. The steps provided display the known synthesis that will be utilized to produce the proline analogue.
There are many reactions that utilize organocatalysts. This includes the Aldol reaction. One issue with organocatalysts is low solubility in organic systems. Using the Aldol reaction, the difference in reactivity of reported proline analogues can be compared to the analogue produced in this research.



2015 Joint Southeastern/Southwest Regional Meeting 872

Design and synthesis of small molecule HDAC inhibitors for selective targeting of breast cancer

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The purpose of this research project is to design and synthesize multiple organic molecules that will help answer the question of what part of a previously made molecule is responsible for the high potency in killing breast cancer cells. The previously made molecule is a tam-histone deacetylase inhibitor; its job is to target breast cancer cell (tamoxifen portion) and destroy them (HDACi portion). When this molecule was synthesized, it was tested on cancer cells with and without estrogen receptors and the results collected showed that a significant amount of both cancer cell lines were killed. The purpose of my research was to synthesize four molecules that were truncated version of the tam-HDACi. Once these molecules were synthesized, they were tested on cancer cells with and without estrogen receptors and also healthy cells. This research could lead to a better targeted and effective treatment for breast cancer.

2015 Joint Southeastern/Southwest Regional Meeting 873

Sugar-coated PDA liposomes for pathogen detection

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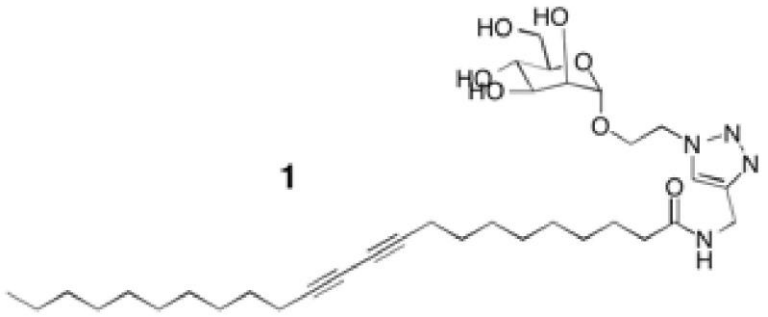
Polydiacetylene-containing liposomes have shown promise as sensors for the detection of toxins, viruses and harmful bacteria. These species undergo a blue to red color change when exposed to various stressors, while decoration of their surfaces with appropriate moieties can impart selectivity. Towards these ends, 10-12-pentacosadiynoic acid was converted into N-(2-propynyl)pentacosa-10,12-dynamide. This, in turn, was treated with an acetyl-protected azidoethylglucopyranose, resulting in a copper-catalyzed click reaction. Subsequent deprotection of the glucose alcohols through Zemplen deacetylation afforded the monomer **1** in good yield. An isopropyl alcohol solution of the monomer was dispersed as picoliter-sized drops into water using an inkjet printer to form pathogen sensors.



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Solution ATRP reaction of oligo(ethylene glycol) methacrylate and sulfobetaine methacrylate for the preparation of antifouling surfaces

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The monomers oligo(ethylene glycol) methacrylate (OEGMA, mw=500) and sulfobetaine methacrylate (SBMA) were polymerized in water or methanol in an atom transfer radical polymerization process. The reaction was initiated on a symmetrical disulfide that featured two initiation sites and was catalyzed with a copper bromide derivative. The resulting polymers had very low polydispersity, as shown by dynamic light scattering, and the molecular weight could be adjusted by varying the initiator/monomer ratio. After purification, the resulting polymers were cleaved with Tris(2-carboxyethyl)phosphine to give thiols. These are then used to modify surfaces to reduce biofouling.

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Temperature-responsive polymersomes for controlled delivery of anticancer drugs

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We report on a novel type of triblock copolymer polymersomes with temperature-controlled permeability within the physiological temperature range from 37 to 42 °C for sustained delivery of anticancer drugs. These polymersomes combine characteristics of liposomes such as biocompatibility, biodegradability, monodespersity, and stability at room temperature with tunable size and thermal responsiveness provided by amphiphilic triblock copolymers. The temperature-sensitive poly(-N-vinylcaprolactam)$_n$-poly(dimethylsiloxane)$_{65}$-poly(-N-vinylcaprolactam)$_n$ (PVCL$_n$-PDMS$_{65}$-PVCL$_n$) copolymers with n=10, 15, 19, 29, 50 and polydispersity indexes less than 1.17 are synthesized by controlled RAFT polymerization. The copolymers are assembled into stable vesicles at room temperature, with diameter decreasing from 530 to 40 nm with increase in PVCL length from 10 to 19 monomer units. Importantly, the permeability of polymersomes loaded with anticancer drug, doxorubicin, can be precisely controlled by PVCL length in the temperature range from 37 to 42 °C. Increase in temperature above LCST of PVCL results in either gradual vesicle shrinkage (n=10 and n=15) or reversible formation of the bead-like aggregates with no size change (n=19), both leading to sustained drug release. All temperature-triggered morphological changes are reversible and do not compromise structural stability of the vesicles. Finally, concentration- and time-dependent cytotoxicity of drug-loaded polymersomes to human alveolar adenocarcinoma cells is demonstrated. Considering high loading capacity (~40%) and temperature responsiveness in the physiological range, these polymer vesicles present a considerable potential as novel types of stimuli-responsive drug nano-carriers.

2015 Joint Southeastern/Southwest Regional Meeting 876

Live tissue as a drug-delivery vehicle - surface modification of pancreatic islets

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Much work has gone into the development of drug-delivery strategies focused on spatially and/or temporally controlling the release of active compounds. Antibody-drug conjugates (ADCs) present one popular example of an attempt to spatially control drug delivery. Numerous additional examples are found in biomaterials research, where drug-coated and drug-eluting stents provide commercially important examples of spatial and spatial/temporal control. Our lab is interested in utilizing chemical tools developed in these disparate areas in order to modify *ex vivo* the surfaces of viable human pancreatic islets. These covalent tissue modifications are designed to be either stable *in vivo* or to afford the controlled release of active compounds, and are expected to provide a protective environment for the islets subsequent to their transplant into type 1 diabetic patients. This talk will describe the synthesis of active compounds, functionalized for bioconjugation, that are expected to protect transplanted islets by a variety of mechanisms. Additionally, various bioconjugation approaches for the biocompatible modification of live islet surfaces with these agents (small molecules as well as peptides, proteins, and polymers) will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 877

Electrospun chitosan nanofiber membranes for guided bone regeneration

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This study compared two novel chitosan nanofiber membranes to a collagen membrane for guided tissue regeneration in a critical size rat calvarial model. Chitosan nanofibrous membranes, prepared by electrospinning (5.5% wt/vol chitosan (71% DDA) in 70% trifluoroacetic acid(TFA)-30% methylene chloride, 25 kV), were treated by two methods to remove TFA salts and stabilize nanofiber structure; 1] surface acylation reactions using 50-50 (v/v)% butyric anhydride-pyridine, 2] washing in 10(v/v)% triethylamine (TEA) then surface reacted with 2.5g/ml tert-butyl dicarbonate (tboc). Chitosan discs (15 mm diameter) were punched and ethylene oxide gas sterilized. Collagen discs (15 mm diameter, Biomend Extend, Zimmer, Inc.) were purchased and sterile punched. Specimen (n=1/animal) were implanted to cover 8 mm diameter critical sized defects in male Sprague Dawley rats (250-280g) following University approved IACUC protocol. At 3 and 12 weeks, 5 animals/ implant group were euthanized, x-rayed and tissues analyzed histologically. Blinded sections were scored for inflammation (0-3) by a pathologist. Defects were still visible in x-rays at 3 weeks in all groups. At 12 weeks, x-rays showed evidence of bone bridging in all groups. Qualitatively, increased radio-

opacity was observed in animals treated with chitosan membranes as compared to collagen membranes, though no difference between chitosan membranes was observed. Histologically, bone forming at edges of defects for all groups was observed at 3 weeks, and evidence of new bone bridging defects was observed at 12 weeks for chitosan membranes. Median scores for inflammation at 3 weeks were 1 for both chitosan membranes and 2 for collagen and scores were not statistically different (Chi Sq, $p>0.05$). Membranes were not penetrated by soft tissues. The results thus far suggest that both chitosan membranes are biocompatible and that they support healing of a critical sized defect similar to a commercial collagen membrane

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Tetracycline loaded chitosan microspheres utilized for local drug delivery

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Musculoskeletal injuries account for 60 to 67% of all injuries annually. Preventing infection is a major issue in treating musculoskeletal injuries as it could lead to delayed healing and possible surgical intervention. Systemic administration of antibiotics is typically used for 4-6 months after surgery to prevent infection. However, local antibiotic delivery is advantageous as it avoids challenges presented by systemic administration. These challenges include difficulty in reaching sites with damaged vasculature and potential toxicity issues due to the high dose needed to treat systemically. We have developed a procedure for making chitosan beads loaded with tetracycline as a model drug. We hypothesize that chitosan beads our lab have produced will display adequate characteristics to be an effective local drug delivery device. Our process involves making the beads using a water-in-oil emulsion technique and crosslinking with glyoxal. Studies have shown that glyoxal is an effective crosslinker that is less toxic than glutaraldehyde, a common crosslinking agent. Glyoxal crosslinks through a Schiff reaction creating an imine bond with the free amines of chitosan polymer and the aldehyde groups of glyoxal. Characterization of the beads was analyzed using scanning electron microscopy (SEM), fourier transform infrared spectrophotometry (FTIR) and ninhydrin assay to measure degree of crosslinking. *In vitro* cytocompatibility experiments using RAW264.7 mouse macrophages and NIH3T3 fibroblasts were performed to test toxicity of the beads. The loaded chitosan beads were compared to unloaded beads as control. Fibroblast growth was not inhibited by the loaded chitosan beads, exhibiting equal or greater fibroblast growth after five days. Macrophages were not activated by the loaded chitosan beads. A slight reduction in crosslinking degree was exhibited by the loaded beads. This experiment will be repeated to account for the weight of tetracycline loaded. SEM imaging portrayed uniform shaped and spherical beads with no visible difference in morphology as compared to unloaded beads. Zone of inhibition tests on Staphlycoccus aureus using the eluates from the elution study were performed to ensure tetracycline was still active after the bead making process.

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Development of injectable *in situ* forming depot systems for long-acting contraception

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Birth control is still a major concern worldwide. The currently commercially available injectable contraceptives are only effective for 1–3 months and require patients to return to their provider 4–12 times per year. The frequent clinic visits could result in discontinuation due to users' difficulty in complying with the multiple injection schedules. The purpose of this study is to develop injectable polymeric *in situ* forming depot system containing levonorgestrel (LNG) for contraceptive effect for six months or longer after single shot that help to reduce unintended pregnancies with high patient compliance and low cost. *In situ* forming depot formulations were prepared using a blend of polymers containing poly (lactide-co-glycolide) and polylactic acid, and a mixture of solvents containing N-methyl-2-pyrrolidone and benzyl benzoate or triethyl citrate. Manual injectability test showed that the formulations can go through 21-23G needle. Injection force measurements were proportional to the viscosity of the formulations. Formulations with viscosity around 0.6 P.s have shown to pass easily through 23G needle while those with 1.7 P.s pass through 21G needle. The depots formed *in vitro* remained intact for up to 3-7 months depending on the composition of the formulation. *In vitro* release kinetics fitted to the Korsmeyer-Peppas model show that the drug release from the depot followed anomalous transport, both diffusion and erosion. Depending on the intrinsic viscosity of the polymer used, the formulations were able to release LNG *in vivo* that can achieve plasma LNG levels within a range of 0.5-4 ng/mL till seven months. In the rats treated with LNG containing formulations, body weight increased with time compared to that of control. Vaginal cytology study results showed that all of these cells are either from early diestrus, diestrus or proestrus stages in all the formulations and none of them show estrus stage. After the end of the treatment, rapid and predictable return of fertility was observed in rats. The prototype formulations can pass through thin size needle and showed promising LNG release *in vivo* to achieve target plasma LNG levels for six months or longer and showed contraceptive effect in rats. The data showed that the prototype formulations have a great potential for developing future robust long-acting contraceptive products.

Tuning cell/surface interactions on microporous materials for neuronal scaffolds using organic surface coating strategies: Surface properties of emerging aerogel biomaterials and planar substrates

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Limitations with existing methods and materials used for nerve repair necessitate the design and characterization of novel materials that can support electrical circuitry and promote controlled precise adhesion, growth, and directionality of neurons on artificial "smart" substrates and scaffolds. The overlapping long-term goal of the Alexander and Sabri groups is the development of designer biomaterials necessary for creation of

“smart” neuronal scaffolds. Currently, growth and adhesion-promoting coatings such as collagen, matrigel, and laminin are physically deposited (with a pipette) directly onto conductive gold-coated aerogel substrates without any bonding between the gold layer and the protein mixture necessary for neuron attachment and proliferation.This crude technique leads to uneven distribution of the coating, inconsistencies in the deposited layer thickness as well as possibilities of void regions. The coating thickness is heavily influenced by the morphology, roughness, and surface chemistry of the surface to be coated which will lead to local variations and inconsistencies in the attachment, growth, and extension of neurites by the neurons. It is therefore necessary to develop a reliable and reproducible mechanism that can covalently attach the peptides of interest directly to the gold layer. There exist decades of research study on functionalized alkanethiolate attachment/self-assembly to gold surfaces to form self-assembled monolayers (SAMs), which provides a robust and proven chemistry to achieve our coating goals. But can our extensive knowledge of planar SAM surface properties be transferred to microporous substrates such as microporous aerogels, which have shown promise as new biomaterials? This talk will focus on experimental and computational efforts to answer this question. Surface spectroscopy, material characterization, and molecular dynamics methods are employed to compare gold-coated aerogel surface properties to that of planar gold surfaces. These surface properties will be discussed within the context of tuning the surface to control overall cell/surface interactions.

2015 Joint Southeastern/Southwest Regional Meeting 881

High protein loading efficiency by kinetic doping for biosensor applications

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Easy to use and easy to produce biosensors would have a huge range of applications. To reach this goal many see the incorporation of a protein into a sol-gel network as one of the most viable options. The current most prevalent technique of pre-doping presents inherent limits on the concentration possible for the resulting thin film. Here we demonstrate a new process utilizing the newly discovered kinetic doping method to load silica sol-gel thin films with Horseradish Peroxidase (HRP) and Cytochrome C (CytC) via spin-coating. Both proteins are shown to successfully load and have a concentration increase over their original loading solution by factors of 2600x and 1350x, respectively. Importantly, each protein once loaded retained the ability to act as a catalyst for the detection of hydrogen peroxide. Ultimately the thin films were found to have concentrations of 6.0±0.4 mM and 11±1 mM, a considerable step up from the concentrations reported with the pre-doping method. Furthermore, we extend this process to dip coating, a process capable of coating surfaces of all shapes and sizes.

2015 Joint Southeastern/Southwest Regional Meeting 882

Poly octylthiophene-based solid contact electrodes with improved potential reproducibility

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Analysis of small volumes of clinical samples (e.g. blood samples of newborns or tear fluid of individuals with dry eye syndrome) proves difficult for conventional ion-selective electrodes (ISEs). Solid contact (SC) ISEs are attractive for analyzing these small volumes of samples because of the possibility of sensor miniaturization. In solid contact sensors, a conductive polymer (CP) film serves as an ion-to-electron transducer between an electron-conducting metal substrate and the ion-conducting ion-selective membrane. However, SC ISEs often have poor potential stability and irreproducible standard potentials. Good potential stability is crucial in monitoring experiments and reproducible standard potentials are important for single-use sensors. The irreproducible standard potentials and the poor potential stability of SC ISEs are thought to be due to gradual oxidation of the conductive polymer (CP), i.e., to changes in the CP redox potential over time. In this study, we have implemented a redox couple (7,7,8,8-tetracyanoquinodimethane, (TCNQ)) into the CP layer (poly(3-octylthiophene), (POT)) at high concentrations. The ratio of the oxidized and reduced forms of TCNQ in the POT film was set to 1:1 electrochemically. TCNQ has a standard redox potential below that of POT so its reduced form is more easily oxidized than POT. A high concentration of TCNQ in the POT film with a 1:1 ratio of its oxidized and reduced forms is expected to stabilize its overall potential and thus improve the potential stability of the SC ISE. Preliminary results of SC potassium-selective electrodes with TCNQ in the POT layer showed improved potential reproducibility upon initial contact with a calibration solution compared to SC ISEs without TCNQ in its POT-based solid contact. The potential stability of SC ISEs with TCNQ in the POT film was comparable to those prepared without TCNQ over 24 hours. Future work will focus on further improving the potential reproducibility, which will be important for single-use sensors, as well as improving the long-term stability, which is necessary for extended use of SC ISEs. To work towards this goal, TCNQ will be implemented into both the CP as well as the potassium-selective membrane.

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Sugar sensing using boronic acid-modified poly(amidoamine) dendrimers

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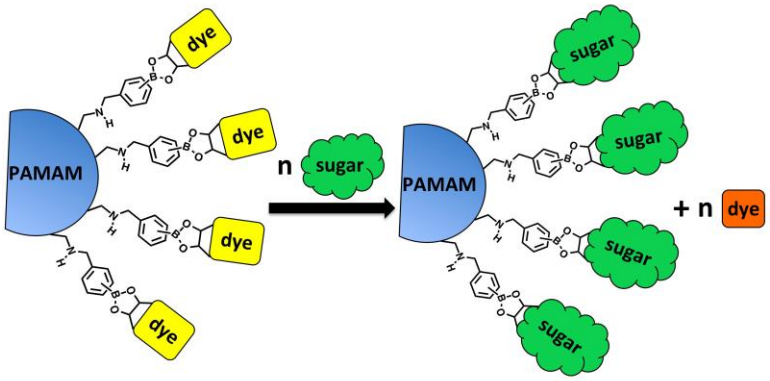
Boronic acids can be used as receptors in chemical sensors for sugars. However, their binding affinity and solubility are usually poor in H_2O. We improved these parameters by covalently connecting boronic acid moieties to the surface of third-generation poly(amido)amine (PAMAM) dendrimers, to form a PAMAM-boronic acid receptor (**PAMAMba**). We first monitored the interaction of this modified boronic acid receptor with sugar-like structures by absorbance and fluorescence spectroscopy using dyes such as 4-methylesculetin and alizarin Red S that contain diol moieties. We then studied the interaction of the PAMAMba receptor with sugars by setting up an indicator displacement assay based on these results. Addition of sugars (e.g. fructose, glucose, galactose, ribose, and selected disaccharides) to the [**PAMAMba●**$(dye)_n$] complexes allowed us to study their complexation to **PAMAMba** by following the displacement of the bound dyes. Promising results obtained with these [**PAMAMba●**$(dye)_n$] self-assembled sensors will support the construction of a multivariate array sensing platform for the discrimination of simple sugars in H_2O.



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Intracellular degradable hydrogel cubes and spheres for anti-cancer drug delivery

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Shape and responsiveness of nano-engineered delivery carriers are crucial characteristics for rapid and efficient delivery of therapeutics. We report on a novel type of micrometer-sized hydrogel particles of controlled shape with dual pH- and redox-sensitivity for intracellular delivery of anticancer drugs. The cubical and spherical poly(methacrylic acid) (PMAA) networks with disulfide links are obtained by cross-linking PMAA with cystamine within hydrogen-bonded multilayers of (PMAA/polyvinylpyrrolidone) (PMAA/PVPON) on sacrificial mesoporous templates. The pH-triggered hydrogel swelling/shrinkage not only affords effective doxorubicin entrapment but also efficient endosomal/lysosomal escape, and redox-triggered degradation provides drug release into the cytosolic space. The hydrogels degrade rapidly to low molecular weight chains in the presence of the typical intracellular concentration of glutathione, which should ensure a rapid renal clearance in-vivo. Particle shape is found to affect internalization at the initial step of cell-particle interactions. Drug-loaded spherical particles are found to be 12% more cytotoxic than the corresponding cubes within the first 10 hours of cell incubation suggesting more rapid internalization of spheres. Both doxorubicin-loaded hydrogel cubes and spheres demonstrate 50%- and 90%-cytotoxicity when incubate with HeLa cancer cells for 24 and 48 hours, respectively. The presented approach integrates the advantages of pH-sensitivity, enzymatic degradation, and shape-regulated internalization for novel types of ‘intelligent’ 3D networks with programmable behavior for use in controlled delivery of therapeutics.

2015 Joint Southeastern/Southwest Regional Meeting 885

Developing a copper responsive MRI contrast agent

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Copper is the third most abundant trace metal in the body. Normally bound to important biomolecules, copper is an essential redox cofactor in several enzymatic reactions. Disruption of copper homeostasis is associated with a number of diseases including Alzheimer's, Parkinson's, Menkes, and Wilson's disease.[1] Local concentrations of copper can vary from a few micromolar to several millimolar in these diseases.[2] Early versions of copper responsive MRI agents demonstrated that Zn^{2+} interferes with the Cu^{2+}/Cu^{+} response, limiting its use in MR diagnostic applications.[3] Here, we report the synthesis and MR properties of a new copper responsive contrast agent for magnetic resonance imaging (MRI). This MR sensor consists of a DO3A gadolinium-based contrast agent where a bis(benzoic-acid)methyl)amine copper-selective recognition motif (L_1), was introduced. The sensor shows high selectivity to copper ions. Also exhibits high relaxivity (r_1) with a 42% increase in relaxivity upon binding to 1 equivalent of Cu^{2+} and Cu^{+}. Interestingly, only when fully bound to both Cu^{2+} and Cu^{+}, the sensor presents a 610% increase in r_1 (~35$mM^{-1}.s^{-1}$) in the presence of physiologic concentrations of human serum albumin (HSA), as uniquely reported for high affinity zinc sensors (Figure 1).[4] These results demonstrate that it is possible to design a functional MRI contrast agent responsive and selective to copper at low concentrations, paving the way for the possible translation to pre-clinical imaging.

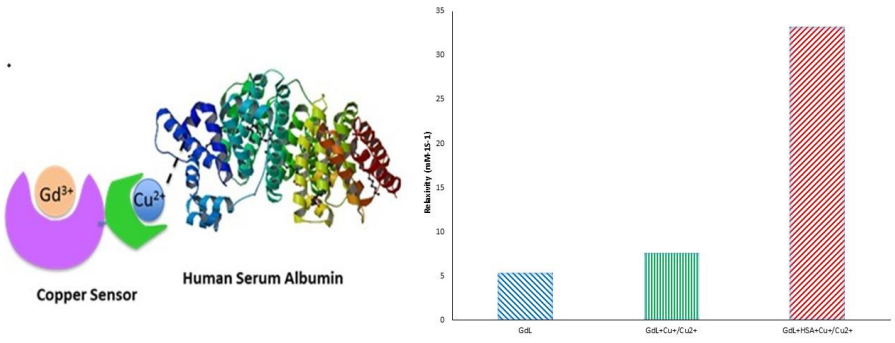

Figure 1. Longitudinal relaxivity (r_1) of the copper sensor in the presence of Cu^{2+}/Cu^{+} and Human Serum Albumin (HSA) at 0.6mM, 310K, pH=7.0 in MOPS buffer

2015 Joint Southeastern/Southwest Regional Meeting 886

CDD Vault, CDD Vision, and CDD Models for drug discovery collaborations

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(1) Independent, Montreal, Quebec, Canada (2) Collaborative Drug Discovery, Inc, Burlingame, California, United States (3) Collaborations in Chemistry, Fuquay Varina, North Carolina, United States

CDD has over 11 years developed and marketed a robust commercial software platform that enables scientists to archive, mine and (optionally) share research data. CDD hosts the software and customers' data vaults on its secure servers. Users access their data through a web browser. CDD's software incorporates mining, analysis, calculation and visualization tools. The CDD platform and processes have passed comprehensive security audits required to host data for 4 major pharmaceutical companies, the Bill and Melinda Gates Foundation (BMGF) and the NIH (FISMA Compliant and Accredited for the Neuroscience Blueprint). CDD software platform demonstrates CDD's best-in-class skills in designing clear and intuitive user interfaces to organize and present vast amounts of data without clutter while enabling users to easily perform a wide range of actions, including secure selective sharing of data with collaborators. The CDD platform includes a public database that hosts over 100 significant public data sets that can serve as the nucleus for generating community-based models, including extensive neglected infectious disease SAR datasets (malaria, tuberculosis, Chagas Disease, etc.), and datasets that are broadly applicable to many projects (vendor libraries). CDD is the repository for over 300 million data points and growing rapidly. CDD Vision for data visualization and CDD Models for machine learning will also be described in the context of use for drug discovery collaborations.
image

2015 Joint Southeastern/Southwest Regional Meeting 887

Discovery of ClpP allosteric activators using ^{19}F fragment screening

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ATP-dependent Clp proteases are primarily responsible for the degradation of mis-folded proteins in stressed cells, and are regulated by AAA+ molecular chaperones. This group of proteases are considered antibiotic targets and the protein-protein interaction site found to activate the proteolysis has been characterized. Fragment based hit generation has seen increasing application in medicinal chemistry programs as an early stage tool to jump start drug discovery. The flexibility and sensitivity of ^{19}F-NMR allows routine measurement of lower affinity fragments to be expanded into competition experiments, screening significant numbers of fragments relative to approaches using ^{1}H-NMR. Our library of fluorinated and non-fluorinated fragments has been screened for binding to the activation site of ClpP. Fragments identified by this process will provide key insight into scaffolds to be either expanded or linked to obtain hits for further development.

2015 Joint Southeastern/Southwest Regional Meeting 888

Investigation of possible suicide inhibition of cytochrome P450BM-3 by *N*-fatty acyl amino acids with terminal carbon-carbon triple bonds in their acyl chain

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Cytochrome P450 enzymes are responsible for detoxification of foreign chemicals and for the metabolism of drugs. Enzyme activities can be affected by substances and result in enzyme inhibition or enzyme induction. Previous studies have shown that the enzymatic reaction of P450BM-3 with fatty acids possess terminal *carbon-carbon triple bonds in acyl chain* can lead to making covalent bond between enzyme and product and as a result, losing enzyme activity and resulting in death of the fatty acid hydroxylase enzyme. Drugs can be designed according to this basic inhibition mechanism and can inhibit enzyme activity. Previous studies in our lab have proven that long chain N-fatty acyl amino acids are more potent substrates for P450BM-3 than fatty acids. Three *N-fatty acyl amino acids with carbon-carbon triple bond in their acyl chain, (N-(10-undecynoyl)glycine, N-(10-undecynoyl)-L-methionine, and N-(17-octadecynoyl)glycine), were synthesized in order to investigate their possible suicide inhibitory effect. P450BM-3 proteins were expressed in E. coli DH5aF'IQ harboring pProEX-1 and purified using* immobilized metal affinity chromatography (IMAC). Inhibitor binding to enzymes were investigated by measuring the UV spectra Soret band shifts from 418 nm to 392 nm and enzyme kinetics were characterized.

A directed high-throughput screening approach for the identification of a novel small molecule inhibitor of Constitutive Androstane Receptor (CAR)

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Current targeted drug discovery processes heavily rely on high-throughput screening (HTS) technology for identifying potential modifiers of the selected target. We will provide an overview of current HTS technologies, especially those employed by the HTS Center at St Jude. As an example, we will describe the phases in the identification of CINPA1 as a specific small molecule inhibitor of the xenobiotic receptor CAR (constitutive androstane receptor).

CAR and PXR (pregnane x receptor) are xenobiotic sensors that respond to drugs and endobiotics by modulating the expression of metabolic genes for detoxification and elimination. Elevated levels of drug metabolizing enzymes and efflux transporters can promote the elimination of chemotherapeutic agents leading to reduced therapeutic effectiveness. Multidrug resistance in tumors after chemotherapy can be associated with errant CAR activity, as in the case of neuroblastoma. CAR inhibitors used in combination with existing chemotherapeutics could be utilized to attenuate multidrug resistance and resensitize chemo-resistant cancer cells. All previously reported CAR inhibitors are also activators of PXR, thus rendering them mechanistically counterproductive since CAR and PXR have overlapping functions. We used a *directed* screening approach to identify new CAR inhibitors from a subset of small molecules shortlisted as PXR inhibitors in a high-throughput screen of 320,000 chemicals. We reasoned that this would allow us to eliminate the possibility of finding CAR inhibitors that activate PXR.

The directed HTS helped identify 27compounds belonging to 5 distinct structural groups. Further evaluation using a range of secondary validation assays resulted in the identification of CINPA1, a potent small molecule capable of reducing CAR-mediated transcription with an IC_{50} of ~70 nM, without activating PXR. The mechanisms by which CINPA1 inhibits CAR function were also extensively examined and elucidated. Ongoing structure activity relationship studies have revealed some key features of our lead compound. *In vitro* pharmacokinetic assays facilitated the identification of the cytochrome P450 enzymes responsible for metabolism of CINPA1 in human liver microsomes.

Through a directed HTS method and subsequent validation and lead development, we have identified a potent inhibitor of CAR which could be utilized as a novel pharmacological tool for understanding CAR function and for resensitizing chemo-resistant cancer cells.

2015 Joint Southeastern/Southwest Regional Meeting 890

Streptococcus mutans **glucosyl transferase inhibitors for the prevention of dental caries**

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Dental caries is considered to be a major health concern in the United States. Accordingly, developing drugs to prevent and control dental caries is now the ‘mantra’ in American Dentistry. Fluoride has been used in community water supplies and toothpastes to control dental caries over the years. Though these preventive measures are successful to some extent, it does not prevent caries formation completely. Current marketed mouthwashes kill pathogenic as well as commensal bacterial species. Thus, new innovative approaches are necessary to combat dental caries. Although a large number of oral bacteria have been associated with dental caries, *Streptococcus mutans* has been implicated as the major etiological agent in the initiation and development of dental caries. We target *S. mutans* GTFs to discover agents that will selectively inhibit bacterial biofilm formation without disturbing the bacterial growth. Unlike traditional antibiotics, *S. mutans* GTF inhibitors are designed to selectively inhibit cariogenic biofilms without affecting commensal oral bacterial flora. With the help of *in-silico* screening and SAR studies, we have identified low micromolar inhibitors of *S. mutans* GTFs and biofilm without affecting the growth of *S. mutans*, and other commensal streptococci. Structurally similar analogs of our lead compounds that were inactive against GTFs were also found to be inactive against biofilm, indicating that these effects are directly related. We are continuing to optimize the potency of the lead compounds to identify more potent and selective anti-biofilm agents. The results on the design, synthesis and evaluation of the lead compounds will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 891

Photoligation mechanism of DNA bases to the cis bis-aqua Ru(II)bis(2,2'-bipyridine) complex

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The *cis* diammine dichloroplatinum (II) (cisplatin), FDA approved for treatment of testicular cancer in 1978, represents the current paradigm in transition metal based chemotherapy agents. Cisplatin and various analogs have now emerged as significant antineoplastic chemotherapy agents towards a wide range of solid tumors cancers. The $(NH_3)_2(H_2O)_2$ Pt(II) complex binds to the major groove of gDNA targeting the N7 atoms of guanine bases resulting in primarily 1,2 intra-strand crosslinks. Despite the success of cisplatin type drugs in treating many forms of cancer, the drug suffers from the propensity of cancer cells to relapse after the initial exposure. In addition, cisplatin type complexes also exhibit general cellular toxicity and are not specific to cancer cells. Ruthenium based metal complexes may offer an alternative to Pt based chemotherapy agents. Octahedral Ru(II)tris(2,2'-bipyridine) (RuBpy) complexes containing bidentate ligands exhibit a rich photochemistry that has been exploited in applications ranging from solar cells to drug development. Of specific interest is the excitation of Ru(II)bis(2,2'-bipyridine)$(L)_2$ ($RuBpy_2L_2$) type complexes where L = sterically hindered bpy, primary amine, nitrile, etc which leads to the photoexchange of L with solvent molecules. Photolysis of $RuBpy(L)_2$ complexes in aqueous solutions and in the presence of DNA results in the formation of an $RuBpy_2$-DNA adduct providing for a potential photo-active cisPlatin analog. However, little is known on the exact mechanism through which $RuBpy_2$ binds to DNA bases. Here we have examined the binding of nucleobases, nucleosides and nucleotides to the $RuBpy_2(H_2O)_2$ complex using optical spectroscopy and computational chemistry methods. Our results demonstrate a strong affinity of the $RuBpy_2$ toward guanine with binding taking place at the N7 position, similar to cisPlatin.

2015 Joint Southeastern/Southwest Regional Meeting 892

Use of ferrocenylated N-heterocyclic carbenes to alter the metabolism of reactive oxygen species in human cancer cells

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Normal cellular metabolism generates intracellular by-products identified as reactive oxygen species (ROS). While ROS levels are safely maintained by the antioxidant pathway, the rapid metabolism of cancer cells causes unusually high levels of ROS. These cells survive due to the continued function of antioxidants, but the equilibrium between ROS generation and ROS reduction is significantly closer to lethal ROS levels than that of healthy cells. To capitalize on this difference, we have synthesized and mechanistically studied gold N-heterocyclic carbenes that incorporate additional redox-active moieties capable of influencing ROS levels in cancer cells. These efforts have led to the development of complexes capable of inducing enhanced ROS formation and persistence by targeting antioxidant pathways via multiple mechanisms.

2015 Joint Southeastern/Southwest Regional Meeting 893

Dynamic injection surface plasmon resonance enables one pass fragment kinetics and affinity in addition to aggregation assessment through determination of diffusion coefficients

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Gradient dynamic injection techniques in surface plasmon resonance technology have revolutionzied the label-free field by providing the capability to capture complete kinetic and affnity metrics in one pass across a sensor surface with no intra-assay regeneration. Coupled with recently developed "active" algorithims for the data anaysis software, it is now possible to screen a fragment based library and determine high probability drug targets without the need for a secondary characterization proces, dramatically increasing efficieny and quality in fragment based lead discovery. The gradient injection method with its natural difussion phenomena will be presented as a means to capture diffusion coefficients to better assess aggregation, a key parameter in therapeutic drug discovery.

2015 Joint Southeastern/Southwest Regional Meeting 894

Nucleic acid detection and multivalent display on synthetic PNA backbones

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We are developing two classes of chemically-modified peptide nucleic acids and their associated translation to nucleic acid detection and multivalent display platforms. Peptide nucleic acids (PNAs) are synthetic oligomers in which nucleobases are attached to a peptidic backbone consisting of alternating glycine and ethylene diamine units. PNAs bind to complementary nucleic acid sequences following Watson-Crick hydrogen bond pairing rules. We have developed a basic strategy to predictably improve the binding of PNA to complementary nucleic acids by introducing cyclopentane rings into the PNA backbone. This chemical modification routinely increases the thermal stability of PNA binding to nucleic acids by about 5 degrees Celsius per cyclopentane ring. We have used this strategy to develop an effective detection system for nucleic acids associated with HIV. Another PNA modification we have developed is the introduction of a gamma-lysine sidechain into a position of the PNA backbone that will not interfere with DNA binding and which also serves as an attachment point for the multivalent display of ligands. A lysine sidechain is one of the most versatile attachment points for covalent modification in peptides and proteins. By attaching protein binding ligands onto the gamma-lysine sidechains of a PNA, we can use an array of oligonucleotide sequences to probe for multivalent effects in protein receptor binding.

2015 Joint Southeastern/Southwest Regional Meeting 895

Sequence-targeted invasion of DNA and RNA G quadruplexes by peptide nucleic acid

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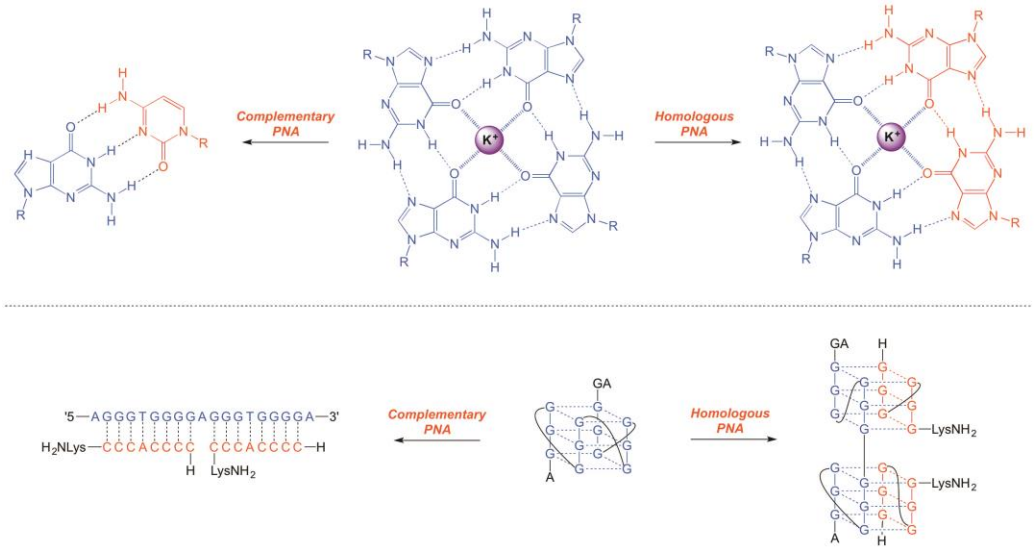
G quadruplexes are secondary structures formed by guanine-rich DNA and RNA sequence motifs. Growing evidence implicates G quadruplexes in a wide variety of cellular processes, most notably in regulation of gene expression at numerous stages (e.g. transcription, splicing and translation). Given the biological importance of G quadruplexes, considerable effort is currently directed toward development of synthetic molecules that can bind and perturb the function of these structures. In contrast to the more common strategy of developing small molecule ligands that recognize quadruplexes based on shape, we are pursuing a sequence-targeted approach involving peptide nucleic acid oligomers. In one format, the PNA is complementary to the target. Upon invasion of the quadruplex structure, a PNA-DNA or PNA-RNA heteroduplex is formed. In a second format, the PNA is itself G-rich and invades quadruplex DNA or RNA to form heteroquadruplex structures. Biophysical and biochemical experiments will be presented showing low nanomolar K_D and IC_{50} values for quadruplex-targeted PNAs. The benefits of using a second-generation PNA analogue, gammaPNA, will also be presented.



2015 Joint Southeastern/Southwest Regional Meeting 896

Gamma peptide nucleic acids: As orthogonal nucleic acid recognition codes for organizing molecular self-assembly

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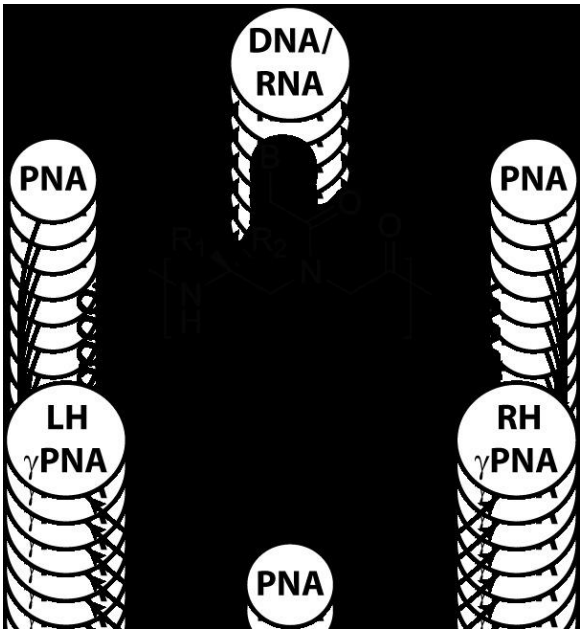
Nucleic acids are an attractive platform for organizing molecular self-assembly because of their specific nucleobase interactions and defined length scale. Routinely employed in the organization and assembly of materials *in vitro*, however, they have rarely been exploited *in vivo*, due to the concerns for enzymatic degradation and cross-hybridization with the host's genetic materials. The presentation will highlight our recent development of a tight-binding, orthogonal, synthetically versatile and informationally-interfaced nucleic acid platform for programming molecular interactions, with implications for *in vivo* molecular assembly and computing. The system consists of three molecular entities: the right-handed and left-handed conformers and a non-helical domain. The

first two are orthogonal to each other in recognition, while the third is capable of binding to both, providing a means for interfacing the two conformers as well as the natural nucleic acid biopolymers (*i.e.,* DNA and RNA). The three molecular entities are prepared from the same monomeric chemical scaffold, with the exception of the stereochemistry or lack thereof at the γ-backbone that determines if the corresponding oligo adopts a right-handed or left-handed helix, or a non-helical motif. These conformers hybridize to each other with exquisite affinity, sequence selectivity, and level of orthogonality. Recognition modules as short as 5 nucleotides in length are capable of organizing molecular assembly.



2015 Joint Southeastern/Southwest Regional Meeting 897

Micro-RNA-21 responsive DNA nanostructures for sensing and therapeutics

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A common challenge in the early discovery and subsequent treatment of cancer lies in the ability to discriminate the aberrant cells from similar healthy tissues. Recently, interest in micro-RNAs (miRs) has led to the discovery of oncogenic miRs that play a role in early cancer development that are highly expressed in cancerous cells relative to healthy tissue. miR21, specifically, is widely overexpressed in a range of cancers. As compared to other biomarkers, the easy and specific recognition of nucleic acids by base pairing to a cognate sequence simplifies the design of biosensors and responsive therapeutics relative to similar protein or small molecule targeted systems. A quadruplex-based molecular beacon was prepared with functionally separate structural and recognition domains to facilitate facile exchange of targets without loss of function. This system is capable of cyclical opening and closing in response to sequential addition of guide (GS) and target (TS) strands, as followed by state-dependent fluorescence quenching. Additionally, a duplex-based DNA-small molecule chimera was synthesized with miR21 responsive inhibition of human carbonic anhydrase II (hCAII)

with an activated K_i of 3.12 μM. This work was supported by the NIH (R01GM097571) and an NSF Graduate Fellowship.

2015 Joint Southeastern/Southwest Regional Meeting 898

Nucleic acids: The target or the ligand

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An emerging area in molecular diagnostics is the characterization of cell-free DNA because of its ability to detect and monitor a variety of diseases as well as treatment efficacies associated with those diseases. In addition to base sequence analyses of circulating DNA fragments, consideration must be given to the structural features and/or stabilities that allow these DNA fragments to survive nuclease digestion under cell-free conditions. Of particular interest to our laboratory are the DNA fragments generated by the telomeric region of chromosomes upon cellular apoptosis. These DNA fragments readily fold into nuclease resistant three-dimensional structures called G-quadruplexes (G4). Our laboratory has demonstrated that cell-free telomeric DNA fragments are preferentially released from cancer cells in response to chemotherapy-induced cell death. Circulating levels of telomeric G4 DNA are readily detectable in the serum of cancer patients. *In vivo* studies from our laboratory have demonstrated G4 telomeric DNA fragments to be highly effective in the induction of a TLR9-mediated cancer cell invasion. The data presented here reveal insights into the versatile role of nucleic acids as biological response modifiers.

2015 Joint Southeastern/Southwest Regional Meeting 899

Effects of 5-hydroxymethylcytosine epigenetic modifications within the VEGF promoter region on G-quadraplex and i-motif DNA structure and stability

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Epigenetic modifications to DNA base sequences may regulate gene expression. CpG islands can contain methylated (5mC) or hydroxymethylated (5hmC) cytosine. Most CpG islands are found primarily in promoter regions that may also contain a high number of repeated cytosines and/or guanines. G-quadraplexes (G4) and i-motifs (iM) are two unique DNA secondary structures that can form in repeating sequences of either guanine or cytosine, respectively. Both G4 and iM sequences may contain CpG sequences that can be methylated or hydroxymethylated. The effects of CpG islands on DNA secondary structures were determined by incorporating a single 5hmC at varying positions in the VEGF G4 and iM sequences. An Olis DSM-20 spectropolarimeter and a Cary 100 UV-visible spectrometer were used to monitor the effects of 5hmC on G4 and iM thermal stability. Two of the three 5hmC-containing loops showed a notable decrease in stability for G4s and increased intermolecular structure formation. Contrastingly, the iM stability increased when 5hmC was incorporated into its sequence.

Additionally, there was little change in the iM pK_a. In summary, our results suggest the 5hmC has little effect on iM structure, but can destabilize the G4's.

2015 Joint Southeastern/Southwest Regional Meeting 900

DNA in tight spaces: Linking structure, stability, and protection in packaged DNA

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Packaged DNA is ubiquitous in nature and the laboratory with examples ranging from chromatin, viruses, sperm cells, bacterial nucleoids, artificial viruses and gene therapy constructs. Sperm nuclei are one of the best examples of *in vivo* maximum DNA compaction and therefore an ideal model system to study biophysically. Despite intense research, the physical mechanisms underlying tight packaging of DNA remain poorly understood especially at the molecular level. Spermiogenesis is a unique multi-step process resulting ultimately in the replacement of histones by protamines in sperm nuclei to a final volume roughly 1/20th that of a somatic nucleus. The near crystalline organization of DNA in mature sperm is thought crucial for both DNA delivery and the protection of genetic information due to the absence of DNA repair. In this talk, I will first discuss our past studies on understanding how cations modulate DNA-DNA forces in the condensed phase and the interrelationships between cation chemistry, packaging densities and compaction. The last half of my talk will discuss recent experiments aimed at understanding the various biological implications for both protamine-DNA packaging and correlations to infertility and oxidative stress in sperm chromatin.

2015 Joint Southeastern/Southwest Regional Meeting 901

Effective Riemannian diffusion model for conformational dynamics of membrane transporters

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Molecular dynamics (MD) simulation technique offers a dynamic picture of molecular processes with an unparalleled spatiotemporal resolution. However, functionally relevant conformational changes of proteins often occur on timescales far beyond those currently accessible to conventional MD. For instance, membrane transporters undergo large-scale conformational changes between inward- and outward-facing structures to transport molecules across the membrane, a process which takes tens of milliseconds to seconds per cycle. These conformational changes are almost entirely unknown due to the limitations associated with both computational and experimental techniques. Employing a novel computational approach based on ideas from nonequilibrium statistical mechanics and Riemannian geometry and taking advantage of petascale computing, we have reconstructed the entire transport process of a transporter at an atomic level within a multiscale framework. The underlying assumption is the existence of a low-dimensional manifold on which lie most of the relevant conformations visited during the functionally relevant structural transitions. The effective dynamics of the system in this low-dimensional space is modeled as Riemannian diffusion. This study provides a detailed description of the transport mechanism in a membrane transporter and, more generally, introduces a robust framework for the study of structure-function relationships in proteins.

2015 Joint Southeastern/Southwest Regional Meeting 902

Membrane-protein interactions: Analysis using particle and continuum models

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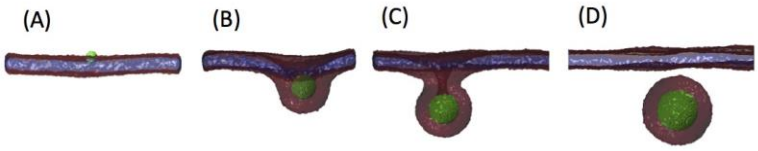
I'll discuss our recent analysis of protein-membrane interactions using both particle and continuum models. The work has been motivated by experimental observation of protein localization in bacteria regulated by specific lipids such as cardiolipin. By integrating implicit membrane and explicit membrane simulations, we are able to systematically analyze the contributions from electrostatic interactions, hydrophobic insertion and lipid packing defects to the binding strength and orientation of proteins to lipid membrane. As a step towards larger scale analysis of cellular protein localization aided by membrane, I'll also discuss the value and limitation of continuum mechanics models for the analysis of protein-membrane interactions.

2015 Joint Southeastern/Southwest Regional Meeting 903

Wrapping, aggregation and spontaneous endocytosis of nanoparticles by tensionless lipid membranes

***Mohamed Laradji**, mlaradji@memphis.edu. Physics and Materials Science, University of Memphis, Memphis, Tennessee, United States*

Significant advances in nanoscience and nanotechnology led to an increasing use of nanomaterials in a wide range of applications. Meanwhile, there exist an environmental concern due to the increased production of nanomaterials in research laboratories and industry. Since the plasma membrane constitutes the point of entry for living cells, a fundamental understanding of how nanoparticles interact with biomembranes is urgently warranted. In this talk, I will present results based on systematic simulations of the interaction of spherical nanoparticles with tensionless lipid membranes using a coarse-grained molecular model. I will show that single nanospheres can be unbound, partially wrapped, fully wrapped or endocytosed by the lipid membrane. The existence of the partially wrapped states of the nanoparticles by the lipid bilayer is surprising, since existing mean field theories predict that a nanoparticle is either unbound from or completely wrapped by a tensionless lipid bilayer. We are able to explain the existence of the partially wrapped state by a generalized elastic theory that accounts for the fact that the interaction between the nanoparticle and the bilayer extends beyond the contact region. I will also show that the interplay between adhesion of the nanoparticles and the curvature elasticity of the lipid membrane lead to either lateral linear aggregates or tubular aggregates of the nanoparticles.



2015 Joint Southeastern/Southwest Regional Meeting 904

Transformer proteins: Friends and foes

***Bernard Gerstman**, gerstman@fiu.edu. Physics, Florida International University, Miami, Florida, United States*

Proteins are the molecular machines that are responsible for actively maintaining self-organization in living cells, which is a fundamental condition for life. Proteins perform a myriad of tasks such as molecular transportation, enzymatic activities, energy transfer, and signaling. In order to perform their physiological functions, most proteins fold to their native state structure, which are highly specific three-dimensional conformations. Recently, a new class of multifunctional proteins has been identified that are called transformer proteins. Transformer proteins show a remarkable ability to rearrange their structure to significantly different stable conformations that perform completely different functions. A developing field of research involves identifying the interaction mechanisms and pathways of various protein transformational changes, and determining if there are mechanisms for controlling the transformations that are common for multiple proteins. I will discuss our work using the concept of transfer entropy on a helpful transformer protein, RfaH, and a lethal transformer protein, VP40 of the Ebola virus.

2015 Joint Southeastern/Southwest Regional Meeting 905

Multiscale modeling of peptide folding and self-assembly

***Jianing Li**, jianing.li@uvm.edu. Chemistry, University of Vermont, Burlington, Vermont, United States*

Peptides play a wide variety of structural and functional roles in complex macromolecular systems. Their activities are often dependent on their conformational as well as aggregation states. It is an important but highly challenging task to access the biologically relevant temporal and spatial scales for peptide folding and self-assembly. To meet this challenge, we are developing multiscale methods and models for peptides. Starting from the all-atom (AA) resolution, we have studied how typical antimicrobial peptides (AMPs) fold and aggregate in solutions and membranes. With our newly developed mixed-resolution model (AACG), we could simulate the folding and self-assembly dynamics of peptides in a coarse-grained environment. A significant speedup in tandem with high accuracy has been shown in our tests. Further, to capture the supermolecular nature of a bacterial peptide assembly, we have developed an ultra coarse-grained (CG) model, in good agreement with experimental observations. Generally, multiscale modeling of peptides provides a full spectrum of models to understand the multiscale nature of peptide folding and self-assembly.

2015 Joint Southeastern/Southwest Regional Meeting 906

The role of the mucus layer in the human tear film

***Ashwin Vaidya**, vaidyaa@mail.montclair.edu. Mathematical Sciences, Montclair State University, Montclair, New Jersey, United States*

We discuss a multiscale problem inspired by the dynamics of the occular tear film. While a considerable amount of attention has been paid to understanding various

complex physical mechanisms of the eye, some fundamental questions remain open. One of these questions includes the role of mucus which lines the cornea in the eye and is assumed to provide lubrication and protection to the eye. The literature remains vague about the meaning of the term ‘protection’ in general. In the context of the eye, it is attributed to the fluidity and high viscosity of mucus. However, we hypothesize that the answer is more complex than currently suggested and in fact, could well depend upon the non-Newtonian, viscoelastic aspects of the liquid. The objective of this talk is to elucidate the complex biomechanics of lubrication and protection in a non-Newtonian medium as a multiscale problem by examining the motion of the tear film coupled with that of embedded mucin proteins and potential foreign particles in the fluid. It has recently been argued that transmembrane mucins could break off, stick to foreign particles, and help them be transported out of the tear film. Our mathematical analysis, based on this hypothesis reveals that the shearing motion of a wall does indeed aid in transporting away any embedded foreing particle towards the moving boundary under the right conditions. Our computations suggests a possible mechanism by which the human eye could clear out any debris beneath the eyelid, under responsive blinking and also has consequences on our understanding of pathologies of the eye.

2015 Joint Southeastern/Southwest Regional Meeting 907

In situ spectroscopic characterization of an organic dye at the surface of TiO_2 and ZnO nanoparticles dispersed in a liquid medium

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Adsorption of organic dyes to semiconducting nanoparticles (NPs) is an important process that plays a role in various applications such as environmental remediation, photo-catalysis, and nanotechnology. Specifically, understanding the binding affinity and surface properties of dyes on NPs is essential for the development of efficient dye sensitized solar cells (DSSCs). However, traditional spectroscopic methods such as UV-Vis, photoluminescence, and IR, do not provide the surface selectivity to probe dye-NP interactions *in situ*. We have used second harmonic generation (SHG), a special case of second order nonlinear spectroscopy, to study the adsorption of a coumarin dye from acetonitrile solution onto the surfaces of ZnO (diam. 18 nm) and TiO_2 (diam. 100 nm) NPs. By collecting SHG polarization anisotropy data, we demonstrated the surface sensitivity of SHG in probing molecular binding onto the surface of crystalline ZnO NPs. For TiO_2 NPs, SHG isotherms were collected and a Gibbs free energy of -35.2 ±0.4 kJ/mol was determined. In addition to equilibrium properties, kinetics of adsorption and spectral properties of the coumarine dye at the solid NP-liquid interface will be presented. The significance of SHG as a surface probe for NPs and the implication of binding constants for DSSC development will be highlighted.

2015 Joint Southeastern/Southwest Regional Meeting 908

Functionalization of single wall carbon nanotubes with group 6 metals

***Kourtney D. Wright**[2], wrigkour@isu.edu, Andrew R. Barron[1]. (1) Rice Univ, Houston, Texas, United States (2) Chemistry, Rice University, Houston, Texas, United States*

Single wall carbon nanotubes (SWNTs) have been shown to have high ampacity and long mean-free path lengths, making them attractive for electronic devices. Before nanotubes can be utilized in devices, multiple obstacles need to be overcome. As produced, SWNTs are a mixture of semiconducting and metallic types, which form Schottky barriers where the dissimilar tubes cross. This decreases the conductivity of SWNT fabrics and films. Attempts at separating SWNTs has proved to be challenging and results in contamination, damage, and low yields. This work is focused on functionalizing SWNTs with Cr^0, Mo^0, and W^0 in order to bridge the resistive SWNT-SWNT and SWNT-contact junctions, thus, eliminating the need for SWNT separation. The effectiveness of this approach is tested by measuring the resistance of functionalized SWNT thin films on Si wafers using the four point probe method. These materials were characterized using infrared (IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and energy dispersive X-ray spectroscopy (EDS).

2015 Joint Southeastern/Southwest Regional Meeting 909

One pot synthesis of hierarchically porous carbon/Ni nanoparticle monolithic composites by nanocasting and their catalytic activity for 4-Nitrophenol reduction

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Carbon/Ni nanoparticle monolithic composites, with varying Ni loading were synthesized by a nanocasting pathway as a one-pot synthesis. Transmission electron microscopic (TEM) images of the composites show mono-dispersed nanoparticles in the carbon matrix where small nanoparticles are located within the mesopores while larger nanoparticles are located outside the mesopores. Scanning electron microscopic (SEM) images show that the larger Ni nanoparticles are located within the macropores and they are unevenly distributed within the monoliths. The Brunauer-Emmett-Teller (BET) surface area and the mesopore volume of the carbon decreased with increasing metal loading. X-ray diffraction (XRD) suggests the nanoparticles are metals at zero oxidation state but X-ray photoelectron spectroscopy (XPS) results show that both the zero and 2+ oxidation states are present. Raman spectra show that the degree of graphitization increases with increasing metal loading. The prepared catalysts were used to reduce 4-nitrophenol to 4-aminophenol. Some adsorption of dye to the carbon and nickel/carbon composites was observed, and both carbon and the nickel/carbon composite showed catalytic activity.

2015 Joint Southeastern/Southwest Regional Meeting 910

Designed emergent behavior in molecular magnets

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Molecular magnetism is a highly interdisciplinary research niche, and the synthesis and characterization of single-molecule magnets (SMMs) has played a key role in the field's development. Our efforts have been to extend the molecules into polymeric aggregates and by design induce certain qualities of the materials. This emergent behavior can have practical applications in sensing, in environmental technologies, as well as in quantum computing and spintronics devices. This presentation will thus include several

new materials we have recently synthesized, including their interdisciplinary study by x-ray crystallography, magnetochemistry, as well as high-field EPR spectroscopy.

2015 Joint Southeastern/Southwest Regional Meeting 911

Study on the effect of ligand incorporated metal on the graphitization and electrical conductivity of hierarchically porous monolithic carbon

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We describe the synthesis of metal doped hierarchical polymeric monolithic carbon formed by resol-formaldehyde polymerization and pyrolysis.Metal salen complexes were synthesized and used as metal precursors.Salens were synthesized using ethylene diamine and 1,6 diamino hexane and their reaction with dihydroxybenzaldehyde and denoted as E-salen and D-salen.Their respective metal salen complexes are denoted as M-Esal/C and M-Dsal/C, where M= Ni/Cr/Mn.The overall synthesis involves-a)Synthesis of metal salen complexes b)preparation of M-sal/C polymeric monoliths by a co-gelation technique involving simultaneous co-polymerization of resorcinol,M-salen and DAH with formaldehyde to form a poly(benzoxazine-co-resol-co-M-salen),c)carbonization of the resulting polymer at 500 °C/800 °C,respectively.Metal nanoparticles form within the carbon matrix during carbonization and are anticipated to impact the graphitization of the hierarchically porous amorphous carbon.All M-sal/C pyrolyzed at 500°C/800°C were characterized using BET-SA,XRD,Raman spectroscopy and SEM This provides insight into the textural and structural properties of monoliths pyrolyzed at two different temperatures.The textural characterization showed the presence of macro and mesopores with a specific surface area ranging from 250-500m^2/g for all the samples pyrolyzed at 500°C.The surface area and porosity of the samples was lost when pyrolyzed at 800°C.In all the cases, the extent of graphitization was observed to increase from the samples pyrolyzed at 500°C to 800°C evaluated by the I_D/I_G ratio obtained from analysis of the Raman spectra.The electrical conductivities of the monolithic carbons increased along with pyrolysis temperature and also increased with decreasing I_D/I_G ratio and FWHM of the XRD peak of amorphous carbon consistent with increasing graphitization giving higher electrical conductivity.The conductivity trend was Ni>Mn>Cr and M-Esal/C conductivities were significantly lower than their D-salen counterparts.

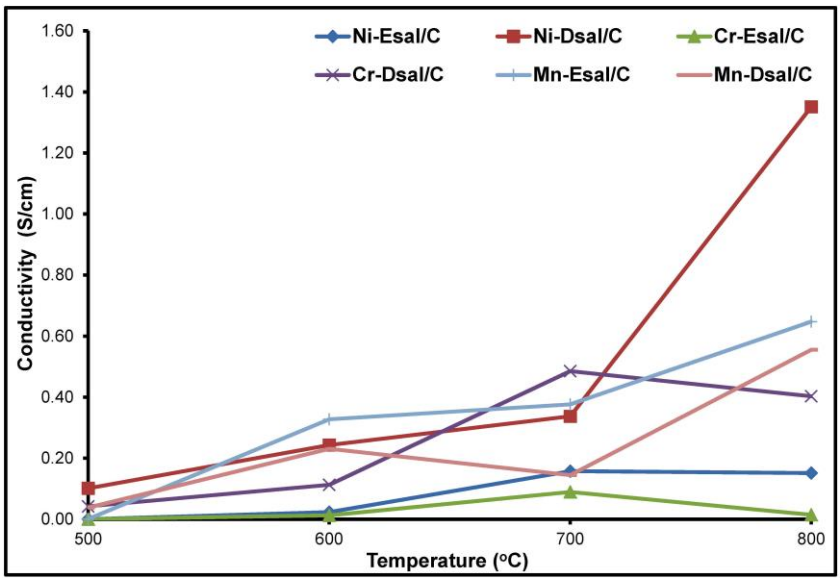

Fig. 1. Electrical conductivities of M-sal/C materials pyrolyzed at different temperatures.

2015 Joint Southeastern/Southwest Regional Meeting 912

Investigation of the stability of silver bromide films on the atomic scale

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In previous research completed by Iski et al., it was found that through specific electrochemical methods, a silver (Ag) monolayer could be formed on an Au(111) surface in an electrochemical environment in both a chloride-free and chloride-rich solution. The previous study showed that, in a chloride-free environment, the Ag monolayer could be formed and atomically resolved; however, once removed from the cell, it could be completely removed via hydrogen flame annealing. Interestingly, in the presence of chloride, the same Ag monolayer was formed and was found to be extremely thermally stable after removal from the cell and was resistive to temperatures as high as 1,000 K. The atomic structure of these films can be studied with electrochemical scanning tunneling microscopy (EC-STM), which not only allows for atomic scale imaging of the surface layer within an electrochemical environment, but also facilitates the taking of cyclic voltammograms (CVs), which can be used to examine the redox behavior of the systems. Since it is known that the stability of bulk metal halide structures decreases as the halogen ion increases in size, an investigative study was performed following the same procedure, substituting chloride with bromide. As with the AgCl system, once AgBr was used to form the Ag monolayer, a new surface structure formed which was also thermally resistive to a hydrogen flame. Further studies into this new Ag monolayer formed under a bromide environment are being conducted in an attempt to better understand the properties of this surface and how they compare to the chloride layer formed previously. Furthermore, density functional theory (DFT) will also be used to look at the equilibrium coverage and the diffusion barrier of the bromide on the Ag monolayer. Using EC-STM and DFT, we plan to study the ways in which this remarkable stability is imparted to the single crystal surface under ambient conditions.

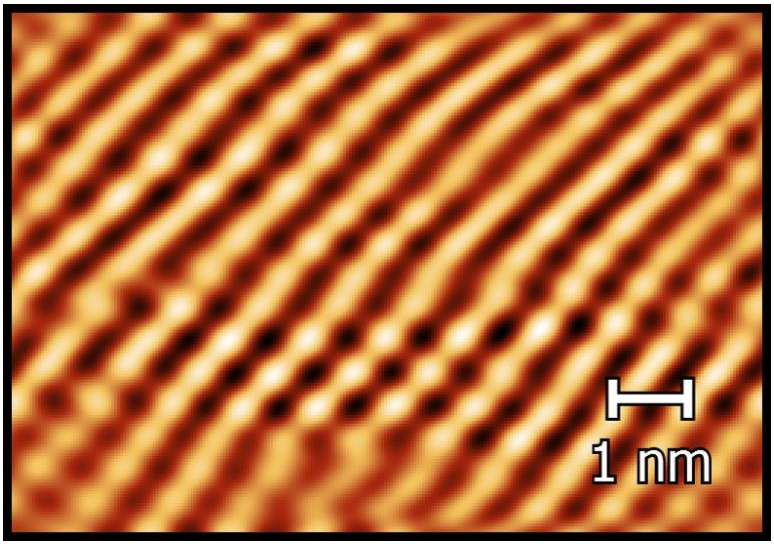

Figure 1. Atomically resolved Ag layer formed from a AgBr solution. The film persists after flame annealing at 1000K.

2015 Joint Southeastern/Southwest Regional Meeting 913

Modulation of the electron transfer rate of gold nanoparticles by changes in pH and ligand composition

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In order to effectively incorporate gold nanoparticles into biological and electronic applications, research must first be conducted to determine the kinetics of varying types of particles. To this end, we determined the forward heterogeneous electron transfer rate constant (k_f) of monolayer protected gold nanoparticles (AuNPs). Using SECM approach curves, we were able to determine k_f for both water-soluble and organic-soluble nanoparticles. By altering the monolayer composition through place exchange as well as changing the ligand charge by adjusting solution pH, we demonstrate effective means of modulating electron transfer rates.

Our results show that the electron transfer rate is largely dependent on the composition and charge of the protecting monolayer. By adding a relatively small amount of highly conductive molecular wire to the non-conductive alkane ligand shell, we can increase k_f in organic-soluble nanoparticles. Additionally, changing the ligand charge on water-soluble tiopronin protected AuNPs through increasing the solution pH results in a decreased electron transfer rate. Because increasing pH increases the overall charge of the shell, charges on ligands must inhibit the tunneling of the electron through the protecting monolayer and lowers k_f.

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Photoelectrochemical studies of TiO_2 and Fe_2O_3 nanoparticulate surface-modified films

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Both TiO_2 and Fe_2O_3 nanoparticulate semiconductors have been used for photoelectrochemical cells because of their relative low cost. In general, TiO_2 films have a higher efficiency of photocurrent production than Fe_2O_3 films, but Fe_2O_3 has the advantage of absorbing photons in the visible range and thus may enhance TiO_2 efficiency when used together. The surface of the semiconductor particles can be further modified with enediol ligands such as 3,4-dihydroxyphenylacetic acid (DOPAC) to enhance the charge-separation and thus the efficiency.

Coupling and plasmonic enhancement of chromophores with hybrid gold nanoparticles

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Renewable energy has become an increasingly relevant field in recent years due to elevated demands for energy and finite levels of fossil fuels. Quantum dots are very attractive due to their simple synthesis, tunability, bright fluorescence and absorption across the visible spectrum.[1] Porphyins are another attractive material which have the ability to convert solar radiation into electric current as a consequence of their high exciton diffusion rates.[2] Noble metal nanoparticles also show utility in this field due to their high molar absorptivites and ability to concentrate incident radiation in the form of a localized surface plasmon resonance. In quantum dots, proximal surface plasmon resonances have been shown to enhance radiative emission rates, absorption rates and multi-exciton emission rates, resulting in an increase in efficiency and performance in devices.[3] Utilizing the strong plasmonic absorption of gold nanoparticles can also help boost the maximum available photocurrent of devices which use porphyins as the active material.[4] Gold nanoparticles can be coated with semiconductor shells that can act as a dielectric spacer between the metal surface and exterior of the nanoparticle.[5] In this work, gold nanoparticles will be coated with either CdS or ZnS shells. Quantum dots or porphyins will be bound to the surface of the semiconductor shell in order to monitor the optical response of the coupled and uncoupled species. Transmission Electron Microscopy will allow for confirmation of shell thicknesses and determination of coupling distances between the gold particle and outer chromophore.

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2015 Joint Southeastern/Southwest Regional Meeting 916

Defect luminescence from wurtzite $CuInS_2$ nanocrystals

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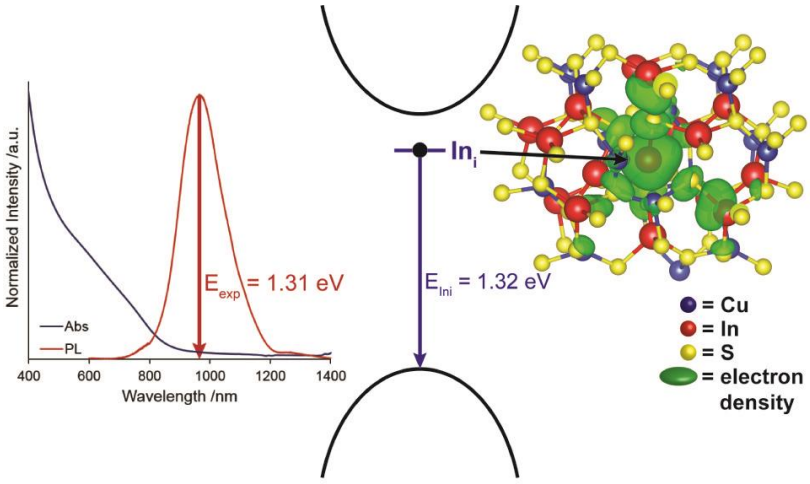
$CuInS_2$ nanocrystals with the wurtzite structure show promise for applications requiring efficient energy transport due to their anisotropic crystal structure. We investigate the source of photoluminescence in the near-infrared spectral region recently observed from these nanocrystals. Spectroscopic studies of both wurtzite $CuInS_2$ itself and samples alloyed with Cd or Zn allow the assignment of this emission to a radiative crystalline defect within the nanocrystal structure. Further, by varying the organic passivation layer on the material, we are able to determine that the atomic species responsible for non-radiative decay paths on the nanocrystal surface are Cu- or S-based. Density functional theory calculations of defect states within the material allow identification of the likely radiative species. Understanding both the electronic structure and optical properties of wurtzite $CuInS_2$ nanocrystals is crucial for their efficient integration into potential biological, photovoltaic and photocatalytic applications.



2015 Joint Southeastern/Southwest Regional Meeting 917

Synthesis and characterization of bulky-thiolated nanomolecules

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Ultra-small gold nanomolecules have been extensively studied for their utilization in drug delivery, medical devices, and catalysis. Thiolate capped gold nanomolecules are especially intriguing due to their size dependence on the type of capping thiol used. Aromatic, aliphatic, and bulky thiolated ligands are each known to produce a unique set of molecular series. Until now $Au_{30}(SR)_{18}$ as reported by Crasto, et al. was the largest nanomolecule known with tert-butylthiol. Here we report the first characterization of a larger size species of bulky thiolate gold nanomolecules. This report details the synthesis of these new species of nanomolecules and their characterization using various analytical techniques to study their electrochemical, mass spectra, and optical properties.

2015 Joint Southeastern/Southwest Regional Meeting 918

Contradictory dual effects: Organothiols can induce both silver nanoparticle disintegration and formation under ambient conditions

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Using propanethiol (PrT), 2-mercaptoethanol (ME), glutathione (GSH), and cysteine (Cys) as model thiols, we demonstrated herein that organothiols can induce both silver nanoparticle (AgNP) disintegration and formation under ambient conditions by simply mixing organothiols with AgNPs and $AgNO_3$, respectively. Mechanistically, organothiols induce AgNP disintegration by chelating silver ions produced by ambient oxygen oxidizing the AgNPs, while AgNP formation in $AgNO_3$/ organothiol mixtures is the result of organothiols serving as the reducing agent. Furthermore, surface-plasmon-active and fluorescent-active AgNPs can be interconverted by adding excess Ag^+ or ME into the AgNP-containing solutions. Organothiols can also reduce gold ion in $HAuCl_4$/organothiol solutions into fluorescence- and surface-plasmon-active gold nanoparticles (AuNPs), but no AuNP disintegration occurs in the AuNP/organothiol solutions. This work highlights the extraordinary complexity of organothiol interactions with gold and silver nanoparticles. The insights from this work will be important for AgNP and AuNP synthesis and applications.

2015 Joint Southeastern/Southwest Regional Meeting 919

Molecular inhibition of oligomer formation and Aβ peptide (1-40) aggregation in Alzheimer's disease

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One of the characteristics of Alzheimer’s development is the amyloidogenesis. This is the process by which amyloid-beta peptides (Aβ-peptides) form oligomers which turn into toxic fibrils and plaques in the brain. These fibrils and plaques are what aggregate in the nervous tissue and result in the deterioration of neural function. The two specific peptides found to be most involved in the aggregation process are Aβ-40 and Aβ-42. Along with these peptides, metal ions such as copper (II) and zinc have been found to have a connection with the appearance of these toxic aggregates in the brain. With this

in mind, much of the research today has focused on inhibiting this aggregation in the hopes of slowing progression of the disease. It has been found that molecules with polyphenol rings, such as those found in stilbenoids and chalcones, are effective in aggregation inhibition.
An aldol synthesis will be used to condense the reactants 8-hydroxyquinoline-2-carboxaldehyde with 3,5-dihydroxyacetophenone in an attempt to produce (2E)-3-(3,5-dihydroxyphenyl)-1-(8-hydroxyquinolin-2-yl)prop-2-en-1-one. Structure of the synthesized molecule will be confirmed through IR, HNMR, and TLC; melting point and percent yield will also be recorded. The product will be purified with preparative TLC and tested for amyloidogenic inhibition via Thioflavin-T spectroscopic assay.
The aim of this project is two-fold. The product being synthesized will be developed with the aim of inhibiting aggregation of Aβ fibrils and plaques in the brain, and also with the aim of preventing oligomer formation to begin with by tampering with the metal ions present. The product should interact with fibrils and plaques due to its phenolic ring structure to decrease Aβ aggregation while the placement of the 8-hydroxyquinoline group will allow the molecule to act as a ligand and disrupt the function of any zinc or copper (II) ions present.

2015 Joint Southeastern/Southwest Regional Meeting 920

Cellular uptake of polyphenols in a bacterial protein expression system

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The biosynthesis of single chain insulin (SCI) analogs is prohibitively inefficient due to their propensity to form non-specific aggregates and ordered fibrils. It is well recognized that certain polyphenol compounds are inhibitors of fibril formation *in vitro* and in eukaryotic cells. However, there has been no systematic exploration of their effect in bacterial expression systems. We propose to quantify the cellular uptake of polyphenol compounds in bacteria to determine if intracellular concentrations equivalent to published IC_{50} values can be attained. The baseline absorbance spectrums of two polyphenols, phenol red and congo red, in Luria Broth was established and were found to be stable for over at by absorbance spectroscopy. BL21(DE3) *E. coli* cultures were incubated in LB media spiked with polyphenol and dye concentration was monitored by UV-Vis spectroscopy. A time dependent reduction in extracellular dye concentration was observed, and polyphenol effects on protein expression levels are being determined.

2015 Joint Southeastern/Southwest Regional Meeting 921

The fight against Alzheimer's disease: Combatting Aβ aggregates synthesized on latex beads

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Alzheimer’s disease (AD) is a neurodegenerative disease that causes dementia, memory loss, and cognitive dysfunction and does not yet have a cure. Aggregation of amyloid beta (Aβ) peptides have been found to play a central role in the development of Alzheimer’s disease, and often AD is diagnosed by the presence of insoluble Aβ fibril

plaques in the brain. While the fibril plaques of Aβ are indicators of AD, soluble oligomers of Aβ have been shown to cause the serious cognitive dysfunction. This research uses a novel method to aggregate Aβ peptides covalently on aliphatic amine latex beads and in solution to assess the effects of small phenolic compounds, which are potential AD drug candidates, in the aggregation and disaggregation of Aβ oligomers. Three different methods were used to assess the disaggregation of the peptide oligomers after adding each phenolic compound: UV-Vis spectroscopy, ELISA, and a thioflavin T fluorescence assay. Overall, the UV-Vis, ELISA, and thioflavin T assay results demonstrate that phenolic compounds interfere with the aggregation and facilitate the disaggregation process of Aβ. Gallic acid appeared to be the most effective of the phenolic compounds tested. The findings will lead to further understanding of how these phenolic compounds interact with Aβ aggregates and thus can provide information to find more effective treatment options for Alzheimer's disease.

2015 Joint Southeastern/Southwest Regional Meeting 922

Introduction of fluoroaromatics in proteins via S_NAr

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The electronic environment within proteins is highly idiosyncratic. IR and NMR are useful tools to garner information about local properties. By taking advantage of the nucleophilicity of cysteine, we introduced fluorine atoms and nitrile groups as probes using nucleophilic aromatic substitution (SNAr). We found that the N- and O-protected cysteine reacts with a variety of fluoroaromatics, including 3,4,5-trifluorobenzonitrile (TFBN). FT-IR analyses showed that the nitrile stretching frequency of the cysteine-fluorobenzonitrile is dependent on the solvent electronic properties. We have used this reaction to modify a small peptide, glutathione, as well as proteins including BSA, bovine hemoglobin, and porcine hemoglobin. Analysis of the TFBN-treated proteins through Ellman's procedure and mass spectrometry strongly suggests that solvent-exposed cysteine residues of these proteins were modified by TFBN.

2015 Joint Southeastern/Southwest Regional Meeting 923

Effects of dextran on the stabilization of i-motif DNA

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Cells are tightly compacted units consisting of intracellular fluids, DNA, RNA, and proteins that regulate the processes of life. The DNA promoter regions of several proto-oncogenes contain sequences that enable the formation of unusual structures known as i-Motifs, which are four stranded DNA structures stabilized by cytosine-cytosine hydrogen bonding. These DNA structures have the potential to be used for drug targeting that could regulate gene expression. This in turn might form the basis of innovative cancer therapeutics. Recent studies show that high molecular weight polymers such as polyethylene glycol (PEG) that are used to mimic molecular crowding within cells increases the stability of i-Motif DNA structures under physiologically relevant conditions. For comparison with PEG, our study examines the effects of

Dextran of various molecular weights and concentrations on the stabilization of i-Motif DNA. Circular dichroism was used to obtain thermal melting profiles for i-Motifs in solution at pH 5.4, at which the typical i-Motif is formed. A range of 20 % to 40 % Dextran (1,000-6,000 g/mol) was examined. Our results indicate that high concentrations of Dextran thermally stabilize i-Motif DNA similarly to PEG.

2015 Joint Southeastern/Southwest Regional Meeting 924

Development of a sensing system for the measurement of the hydrolysis of β-lactam antibiotics

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Bacterial resistance to antibiotics is a problem that has developed over the last 75 years due to over-prescribing of and improper usage of these drugs. Through these processes, bacteria have developed and spread the gene for a protein known as β-lactamase, which catalyzes the hydrolysis of the β-lactam ring in many penicillins, rendering them ineffective. Accordingly, the purpose of this research is to create a sensing system to measure the hydrolysis of β-lactam antibiotics using the enzyme β-lactamase. To accomplish this, the gene for β-lactamase can be fused with the gene for a fluorescent protein known as enhanced green fluorescent protein (EGFP), which will decrease in fluorescence upon the local pH change generated by the catalysis of a β-lactam ring. While previous research in this area has been successful in the development of an *in vitro* fusion of the genes encoding for β-lactamase and EGFP, present research is focused on separately incorporating the individual genes for EGFP and β-lactamase into pFLAG-MAC expression vectors to verify the local pH theory and to redesign this process to create an *in vivo* protein, thus creating a whole cell sensing system.

2015 Joint Southeastern/Southwest Regional Meeting 925

Biosynthesis of mitochondrial derived peptide MOTS-c for biological characterization

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There is growing epidemiological evidence linking type II diabetes with increased cancer risks. While the underlying factors are not clear, hyper activation of one-carbon metabolic cycles, such as the methionine and folate cycles, has been shown to be a driving factor of oncogenesis. A newly discovered mitochondrial derived peptide, MOTS-c, has been shown to target these cycles as well as decrease insulin resistance similar to the type II diabetes treatment Metformin. Our cohort aims to determine the effect of MOTS-c and Metformin treatments on MDA-MB-468 breast cancer cells and MCF-12F normal breast cells. To support this biological characterization, a synthetic gene was designed to express a green fluorescent protein/MOTS-c fusion protein. The custom gene was cloned using IN-Fusion® protocol and expressed in BL21(DE3) E. coli. The proteins were purified by nickel affinity chromatography and GFP cleaved to produce native MOTS-c.

2015 Joint Southeastern/Southwest Regional Meeting 926

Oxidation of endocrine disrupting chemicals by *Trametes versicolor* laccase

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Endocrine disrupting chemicals (EDCs), including 17 b-estradiol (E2), 17 a-ethynylestradiol,(EE2) and bis-phenol A (BPA), are pollutants with estrogenic activity. Unfortunately, these contaminants are not properly removed by current wastewater facility treatments. Laccase from white-rot fungi is a multi-copper oxidase with broad substrate specificity. The enzyme is capable of catalyzing EDC oxidation. Therefore, use of a high-potential, fungal laccase (*e.g. Trametes versicolor* laccase (*Tv*L)) in decontamination applications is of interest. While removal of EDC estrogenic activity in the presence of laccase has been demonstrated, a thorough kinetic study for this reaction has not been reported. In addition, the metabolites of the oxidation reaction have not been adequately characterized. Herein, a unique assay for monitoring the rate of oxygen depletion was developed, and reproducible results for the rate of EE2 oxidation were obtained. In addition, the metabolic products of laccase-catalyzed oxidation were identified using mass spectrometry. Previously unreported, high-order polymers were noted for each EDC, providing additional insight into the laccase-catalyzed mechanism. The results of this study confirms *Tv*L as an optimal choice for EDC remediation applications.

Synthesis of MTSL-labeled elastin-like proteins for paramagnetic NMR

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Elastin-Like Proteins (ELPs) have been proposed as a novel drug delivery vector for treating cancer. These proteins aggregate reversibly above a specific temperature, allowing ELPs to be thermally targeted to cancerous tumors. Though proven successful in mouse models, without a molecular understanding of how ELPS aggregate, it remains extremely difficult to optimize these molecules for drug delivery in humans. Our long-term goal is to test the hypothesis that ELP aggregation is non-specific and does not originate at a specific nucleation point. In this project, we have completed the initial characterization of these proteins and begun paramagnetic labeling in preparation for critical NMR experiments. We successfully purified and expressed seven ELPs according to established methods with purity of ELP40 higher than 99% at a yield of 150mg/L. Using dynamic light scattering and one-dimensional proton NMR we have begun characterization of the temperature-dependent transition in our ELPs. In addition, we have labeled our protein using MTSL, a paramagnetic NMR probe that will help us to monitor protein association. Here, a series of chromatography methods are applied to achieve the MTSL-labeled ELP. Future work will utilize this MTSL-labeled ELP to monitor the extent to which protein interactions occur below the transition temperature.

GPR31 modeling and pharmacophore-guided antagonist discovery

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GPR31 is a G protein-coupled receptor implicated in aiding the growth and motility of cancer upon activation by an agonist. This effect can be suppressed by an antagonist. This study describes the construction of a model that displays strong intermolecular interactions with the known agonist, 12-S-HETE, and the known antagonist 13-S-HODE. Docking validates that this model makes poor interactions with eicosanoids that fail to displace 12-S-HETE, including 15-S-HETE, 5-S-HETE, LTB4, PGA1, PGE2, and PGF2α. Because this GPR31 model is consistent with the known pharmacological trends, it has been used to construct a pharmacophore consisting of features specific to the binding pose of antagonist 13-S-HODE. After searching approved drugs from the DrugBank database for potential antagonists of GPR31, we propose four candidate drug molecules to be screened experimentally. This study yields information concerning the specific interactions between GPR31and its agonist and antagonist that can aid in the development of novel drugs targeting GPR31.

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Modeling GPR6: A potential therapeutic target in the treatment of Parkinson's disease

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For years, G protein-coupled receptors (GPCRs), the largest group of transmembrane receptors in humans, have been prominent therapeutic targets in the pharmaceutical industry, targeted by 30% of drugs currently on the market. The pharmacological importance of GPCRs has made these receptors of particular interest. One such GPCR, GPR6, has proven to be associated with symptoms of Parkinson's Disease, making this receptor of interest as a potential therapeutic target. Using computational homology modeling and loop modeling techniques, a model of GPR6 was built that showed favorable interactions with an endogenous phospholipid agonist, and rationalized binding of five patented GPR6 antagonists while exhibiting only modest consistency with potency trends. Validation of this model can be done in lab by mutating Arg153 which formed a strong ion pair with the phospholipid agonist and the most potent antagonist, as well as His237 and Tyr245, which form key contacts with all except the least potent antagonist. The model of GPR6 can then be used to search for candidate drug-like antagonists, which could lead to novel treatments of Parkinson's Disease.

2015 Joint Southeastern/Southwest Regional Meeting 930

LKE as a potential therapeutic for neurodegeneration in a mouse model of neuronal ceroid-lipofuscinosis

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Neuron damage by injury or disease can lead to axon degeneration and to the eventual death of the neuron. This problem can be approached in multiple ways, one of which is stabilizing the axon during the “therapeutic window” between degeneration and cell death to prevent the cell from dying. As a model for this phenomenon, we studied neuronal ceroid-lipofuscinosis (NCL), a pediatric neurodegenerative disorder characterized by seizures, blindness, loss of motor coordination, and early death. We used a representative mouse model in this study (*Cln6*^{nclf}) to assess the therapeutic potential of lanthionine ketamine ester (LKE), a compound known to promote neurite outgrowth and potentially stabilize the axon during degeneration. Weanling and *Cln6* mice were given LKE in their chow for 12 months and sacrificed. Throughout various timepoints, visual acuity was tested by visual cliff, and motor coordination was tested using rotarod and pole climb. Immunohistochemistry was used to assess accumulation of NCL-characteristic autofluorescent storage material (ASM), microglial and astrocytic activation as a measure of immune response, and cortical thickness as a measure of neuron proliferation and outgrowth. Pathologically, LKE reduced ASM accumulation, rescued cortical thickness deficits, and increased microglial activation in *Cln6*^{nclf} mice. Behaviorally, LKE improved survival but did not prevent early death in *Cln6*^{nclf}. LKE also improved visual acuity but failed to improve motor deficits in *Cln6*^{nclf} mice. In conclusion, LKE may have a therapeutic effect in the *Cln6*^{nclf} variant of NCL. These findings provide understanding of therapeutics for neurodegenerative diseases and NCL in particular, and may potentially lead to the design of combinatorial therapeutics in the future.

2015 Joint Southeastern/Southwest Regional Meeting 931

Heat shock response in lung fibroblasts to changes in environmental calcium

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Pulmonary fibrosis is a terminal disease caused by progressive scarring of the lungs. Fibrosis results when specialized cells called myofibroblasts are recruited to repair damage, but do not die or migrate away once the repair is complete. Myofibroblast apoptosis, or programmed cell death, is crucial to prevention of the onset of fibrosis. Unfortunately, these cells appear resistant to apoptosis and the mechanisms that govern them are poorly understood. For this study, fibrosis progression was modeled using cultured human fetal lung fibroblasts. The “wound healing” response to changes in extracellular calcium concentrations, with and without additional extracellular insulin was performed. Given the roles of HSP 70 and HSP 47 in fibrosis and wound healing, the presence and relative expression of these proteins under varying extracellular calcium and insulin concentrations were observed via immunoblotting. Through scratch assay experiments, we have also measured calcium-dependent changes in cell migration.

2015 Joint Southeastern/Southwest Regional Meeting 932

Characterization of transcription factors from the extremophile *Thermus thermophilus*

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The power of modern genetic sequencing has yielded a wealth of knowledge in the past decades, with the genomes for thousands of organisms now fully sequenced. However, the function of many genes and the biological roles of their encoded products are still not well characterized. Given the sequence-specific DNA-binding properties of transcription factor (TF) proteins, it is possible to purify them, identify the responsible polypeptide(s), determine their consensus binding sequences, and identify their genomic binding sites. Thus, one can go from cellular extract to proposed biological regulatory roles in relatively short order. Our goal is to identify and characterize previously unknown TFs in the extremophile *T. thermophilus* using the novel combinatorial technique, Restriction Endonuclease Protection Selection Amplification (REPSA). REPSA does not require any prior knowledge of a ligand in order to determine its preferred binding site on duplex DNA and has been previously utilized successfully to identify binding specificity for a variety of ligands. SbtR is a transcriptional regulator in *T. thermophilus* that has been implicated in regulation of transporters and metabolism. A binding profile for SbtR has been previously determined, however a combinatorial technique like REPSA has not been utilized. Thus, SbtR provides a proof-of-concept by which to optimize REPSA and a roadmap for the study of other orphan TFs. This research is expected to lead to a greater understanding of bacterial biology at a molecular level and ultimately advance public health by characterizing orphan regulatory proteins that can be critical players in many different microbial diseases.

Characterization of a potential allosteric site in tetrahydrodipicilonate-N-succinyltransferase (DapD) using the effector molecule 2-aminoterephthalic acid

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Multi-drug resistance is a growing problem in the treatment of life-threatening bacterial infections. The identification of new molecular targets is crucial in order to continue the use of pharmacological therapy on drug-resistant pathogens. Tetrahydrodipicilonate-N-succinyltransferase (DapD) is an enzyme responsible for the committed step in lysine and meso-diaminopimelate (a component of the peptidoglycan) biosynthesis for gram-negative bacteria. Preliminary data suggest the existence of a previously unidentified, allosteric site on this known antibiotic target. Characterization of this site will enable design of novel, species-specific therapeutics that target a less conserved region of the enzyme.

Docking studies suggest the presence of an N-terminal allosteric site (Site 1) distal to the known catalytic site of DapD (Site 2) that preferentially binds the natural substrate, tetrahydrodipicolinate (THDP). The THDP mimic, 2-aminoteraphthalic acid (2-ATPA), docked favorably to sites 1 and 2. The generation of conformational changes associated with ATPA binding were analyzed by fluorescence measurements. 2-ATPA effectively quenches intrinsic enzyme fluorescence ($appK_D$ = 0.5 mM; Stern-Volmer constant, K = 4.46). In support of the allosteric model, pre-incubation with substrates, both of which occupy Site 2, results in an increased affinity for 2-ATPA and more effective quenching ($appK_D$ = 0.2 mM; Stern-Volmer constant, K = 7.85). Preliminary kinetic data suggest an increase in DapD activity in the presence of 2-ATPA. All of the data collected are

consistent with the existence of a targetable allosteric site for an enzyme that produces two essential metabolites in pathogenic, multi-drug resistant bacteria.

2015 Joint Southeastern/Southwest Regional Meeting 934

Cloning, expression, and purification of two pyridoxal 5'phosphate-dependent enzymes to be used in the development of novel activity-based probes

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Activity-based probes have addressed the need for new tools to facilitate assignment of protein function *in vivo*. While probes have been developed for several enzyme families, to our knowledge, no probe exists for a pyridoxal 5' phosphate (PLP)-dependent enzyme. Human cystathionine gamma lyase (CSE) catalyzes the conversion of cysteine to hydrogen sulfide, an important cell signaling molecule. *O*-acetylserine sulfhydrylase-A (OASS-A) from *Haemophilus influenzae*, another PLP-dependent enzyme, shares a similar active site architecture to CSE. OASS-A catalyzes the last step of cysteine biosynthesis in bacteria and plants. Herein, CSE was subcloned into a suitable expression vector to allow over-expression and purification in *E. Coli*. OASS-A was over-expressed and purified for parallel use in small molecule inhibitor screens and probe development studies. Potential ligand warheads identified using computational chemistry were screened using activity assays. Preliminary studies are consistent with gabaculine as a previously unidentified effector of OASS-A. The mode of action for this effector is currently under investigation.

2015 Joint Southeastern/Southwest Regional Meeting 935

Synthesis and characterization of modified poly (xylitol sebacate) (PXS) copolymers for improved nanoparticle formation

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To date polymeric drug delivery for chemotherapeutic drug has been extensively studied, with very few advances. The most widely used delivery vehicle for chemotherapeutic drug is poly (L-lactic-co-glycolic acid) (PLGA), an amphiphilic biodegradable polymer, with a good *in vivo* halftime life. Our alternative to PLGA, poly-xylitol sebacate, on the macroscale, has been researched and proven to be more biocompatible than PLGA. The only drawback is that the hydrophilic nature of PXS makes it difficult for nanoparticle formation. Therefore the goal of this research is to synthesize hydrophobic monomers to be incorporated along the backbone of PXS, to increase its hydrophobic character. The PXS molecule will become more amphiphilic by conjugating the polymer with hydrophobic block monomers. So far, successful synthesis of hydrophobic monomers, such as stearic xylitol has been accomplished. ^{1}HNMR confirmed the formation of stearic xylitol by the visible esters peaks of stearic xylitol at 2.3 and 4.3ppm.

2015 Joint Southeastern/Southwest Regional Meeting 936

Functional analysis of NMDAR *GRIN1* mutations associated with infantile-onset epilepsy and encephalopathy

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N-methyl-D-aspartate receptors (NMDAR) are ionotropic ligand-gated glutamate receptors which are permeable to cations such as calcium and are expressed in the brain. This study focuses on three *de novo* GluN1 subunit missense mutations (1-D552E, 1-G815R, and 1-M641I) identified in patients with early-onset epileptic encephalopathy. The functional change in the mutant receptors compared with the WT receptors as measured by agonist potency and sensitivity to negative modulators was determined and rescue pharmacology was attempted.
Site-directed mutagenesis via the Quick-Change protocol was used to create the mutant receptors. Transcription of cRNA and expression in *X. laevis* oocytes followed. Two electrode voltage clamp analysis was conducted and it was determined that the 1-D552E mutation resulted in a decrease in NMDAR function as determined by decreased glutamate (17 ± 2.7 µM vs. 4.3 ± 0.5 µM for the WT) and glycine (3.6 ± 0.4 µM vs. 1.4 ± 0.7 µM for the WT) potency, and increased proton and magnesium inhibition compared with the WT receptors. The 1-M641I mutant receptors displayed an increase in receptor function as determined by increased glycine potency and decreased magnesium sensitivity compared with the WT receptors. The 1-G815R mutant receptors displayed varied effects, showing a decrease in glutamate and glycine potency, but also a decreased magnesium sensitivity compared with the WT receptors.
Application of the neurosteroid pregnenolone sulfate caused potentiation in 1-D552E and 1-G815R mutant receptors. Memantine application successfully inhibited the 1-M641I mutants. The results raise the possibility that an NMDAR antagonist or potentiator might be useful in correcting NMDAR dysfunction, whether hyperfunction or hypofunction. This in turn could decrease seizure burden in these patients.

Geochemistry before biochemistry: Plausible prebiotic reaction spaces involving mineral surfaces

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In the search for systems from which the complexities of life may have emerged, mineral surfaces possess attributes which make them enticing candidates for inclusion in an abiotic reaction scheme. Chiral selection by mineral surfaces may have led to the single-handedness seen in amino acids, for example. Extending the general concept of these surfaces having useful activity to specific experimental testing requires a selection of appropriate minerals and reaction conditions such as pH. We present possible combinations of mineral surfaces, reactants, and reaction conditions likely to be most amenable to experimental probes based on affinities developed by differing points of zero charge, isoelectric points, and pH gradients.

Engineering a mutation in the heparin binding pocket of the human fibroblast growth factor

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Fibroblast growth factors (FGF) are proteins that are found in mammals and play a significant role in mitogenesis, angiogenesis, differentiation, organogenesis, and tissue repair. In summary, their main functionality is involved in cell division and proliferation. Because FGF plays such a vital role in cell proliferation, it is involved in wound healing and injuries. FGF is known to bind to heparin with strong affinity to show its biological activity.
FGF has many implications to it since it is heavily involved in wound healing, however, FGF does not remain active for very long when it is not bound to heparin. With this in mind, this research project focuses on increasing the half-life of FGF while also maintaining its stability.
Residue R136 of FGF has been shown to be of great interest because making a single point mutation around this residue can allow for an increase in stability of FGF. R136 is part of a specific amino acid sequence, LVPRGS, which is recognized by thrombin as a cleavage site. A secondary amino acid sequence, RGPRTH, is also used to compare with the amino acid sequence recognized by thrombin because both of these sequences have similar peptide bonds. In the secondary amino acid sequence of FGF, the arginine and threonine bond displays great sensitivity. Due to this reason, the specific mutation conducted in this experiment will be done on residue T137E. Threonine will be mutated to glutamic acid, which is negatively charged, and this single point mutation can allow further detailed biophysical analysis of the stability and function of FGF.

Synthesis, characterization, and activity of graphene oxide (GO) modified bismuth niobium oxide (BNO)

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Due to increasing global energy demand and environmental issues, a clean and sustainable energy source is required. Because of their potential for solving current energy and environmental problems, semiconductor based photocatalysis has received tremendous attention in the last few decades. A significant number of studies have been reported recently on the development of new photocatalytic materials, modification of existing materials to enhance the light harvesting, and increase the number of active sites in order to buttress the photocatalytic activity. At the same time, high recombination of photo excited charge carriers and limited efficiency under visible light are the two limiting factors in the development of efficient semiconductor-based photocatalysts. The composite formation by using two or more semiconductor catalysts is the promising approach to achieve enhanced visible light induced photocatalysis by reducing the photogenerated electron hole pair recombination. The project includes synthesis, complete structural, chemical and physical characterization, and investigation of the catalytic performance of a composite made of Graphene Oxide (GO) and Bismuth Niobium Oxide-BNO (Bi_3NbO_7).

2015 Joint Southeastern/Southwest Regional Meeting 940

Synthesis, characterization, and catalytic oxidation studies of first-row copper and cobalt complexes supported by redox-active ligands

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The ability to selectively oxidize organic substrates represents a major goal of current chemical research, from transforming petrochemical feedstock into industrially utile chemicals to functionalizing molecules for pharmaceutical pursuits. Although great strides have been made in this field with the use of second and third-row transition metal catalysts, these metals are environmentally scarce and economically costly. In biology, metalloenzymes with active sites incorporating first-row transition metals, such as galactose oxidase often catalyze selective oxidation reactions using environmentally abundant dioxygen as a terminal oxidant. Inspired by model enzyme systems and green chemistry, this project reports on the preparation and characterization of cobalt and copper complexes supported by redox-active ligands. The project further explores the reactivity profiles of the complexes with dioxygen and a variety of organic substrates. Through the success of this project, the selective oxidation of organic substrates could be greatly reduced in price while becoming an environmentally friendly alternative to previous reactions.

2015 Joint Southeastern/Southwest Regional Meeting 941

Synthesis of $Cu_2(Zn_{1-x}Co_x)SnS_4$ solid solutions and kinetics of methylene blue adsorption

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In recent years, transition metal sulfides (e.g. Cu_2ZnSnS_4, $Cu_2ZnSnSe_4$) prepared from earth-abundant and non-toxic elements have received significant attention as promising materials for thin film solar cells. However, other environmental applications of these materials have not been studied widely. This work quantifies the kinetics of adsorption of methylene blue dye, a toxic industrial waste, onto Cu_2ZnSnS_4-Cu_2CoSnS_4 solid solutions. $Cu(Zn_{1-x}Co_x)SnS_4$, with rationally controlled composition were successfully synthesized in pure wurtzite phase using microwave reaction starting from metal salts in ethylene glycol, and thiourea as sulfur source. X-Ray Diffraction (XRD), Raman Spectroscopy, BET N_2 isotherms and Transmission Electron Microscopy were employed to understand how changes in Zn:Co ratio influenced particle size, phase purity, vibrational modes, surface area and morphology of the synthesized materials. Different kinetic models were fitted to study the decolorization process.

2015 Joint Southeastern/Southwest Regional Meeting 942

Synthesis of isoquinoline derived pentadentate ligands

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To modify the redox potentials of Co complexes, we replaced pyridyl groups in N,N-bis(2-pyridinylmethyl)-2,2'-bipyridine-6-methanamine (DPA-Bpy) with isoquinoline derivatives. This study validates the methods applicable in synthesizing these compounds with moderate yields.

2015 Joint Southeastern/Southwest Regional Meeting 943

Photocatalytic TiO_2 coatings for reduction of ammonia and methane livestock emission concentration

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TiO_2 colloidal suspensions are applied as an air-purifier onto a range of natural materials. Loading concentrations, application methods, and adhesive properties are examined to investigating the abilities of the TiO_2 coatings to reduce the concentration of ammonia and methane gas emission.

2015 Joint Southeastern/Southwest Regional Meeting 944

Toward the synthesis of small silver clusters

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Small silver clusters are a useful platform for studying interesting organosilver catalyzed reactions. Efforts to synthesize the $(Ag)_3^+$ cation (known in the gas phase but not in molecular form) have centered around two approaches: reduction of a silver carbonate (in analogy to a known synthesis of cationic gold clusters) or removal of the capping ligand from an oxo- or sulfide- multiply bridged complex. While the synthesis of the carbonate has been straightforward, reduction to a cationic metal complex has proven challenging, as have the syntheses of bridging complexes. Current directions focus on a route to the bridging sulfide complex via the carbonate. Preliminary data suggests that the bridging gold sulfde complex is easily accessible, and future directions with silver clusters will follow accordingly.

2015 Joint Southeastern/Southwest Regional Meeting 945

Development of new iminophosphorane-based catalysts for the ring-opening polymerization of renewable lactones

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Polylactic acid is one of the highest consumed biodegradable bioplastics in the world. One of the most common industrial routes to usable bioplastic is by ring-opening polymerization of lactide using a metal catalyst, like tin octoate. We describe our attempts to form polylactic acid by the construction of titanium and zirconium catalysts for polymerization using phosphosalen ligands as support.

2015 Joint Southeastern/Southwest Regional Meeting 946

Effect of particle size on the magnetic induction heating efficiency for magnetite nanoparticles

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Single crystal magnetite nanoparticles were prepared either by the thermal decomposition of iron(III) acetylacetonate or iron(III) oleate in high boiling solvents in the presence of capping ligands. X-ray diffraction and high resolution X-ray photoelectron spectra confirmed the particles were magnetite. Measuring the temperature rise during magnetic induction heating of dispersions containing the particles gave values of the specific absorption ratio (SAR). The values of SAR depended on the frequency and the amplitude of the applied radio frequency magnetic field. For constant values of frequency (194 kHz) and amplitude (47.7 kA/m) the values of SAR increased from 22 to 55 W/g as the particle diameter increase from 8 to 18 nm.

2015 Joint Southeastern/Southwest Regional Meeting 947

Initial investigation on structural mimicking of the photosynthetic catalysts

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The relevance of Mn carboxylate clusters as an active site mimic for various metalloproteins and enzymes is profound. For example synthetic chemists are trying to mimic the active site of the oxygen-evolving complex (OEC) of photosystem II, available in green plants and cyanobacteria for decades. The OEC in photosystem II is known to catalyze the light-driven oxidation of water to dioxygen. The structure of the OEC has not been completely comprehended; however, the assumption is that it comprises of a high-valent, cubane subunit, Mn_4Ca complex surrounded by a network of H-bonds, responsible for the multi-electron transfer process. In this regard inorganic Mn/Ca complexes can act as synthetic models of the OEC as they can help to understand the magnetic and spectroscopic properties of the native site and the mechanism of its function for water oxidation. Nature has been efficiently carrying out the conversion of water to dioxygen for approximately 2.7 billion years. Hence, one of the many practical applications of mimicking this photosynthetic catalyst would be a more efficient and cost reduced way to produce molecular oxygen. A potential side benefit of this would also be a possible fuel source since H_2 gas would be a byproduct of the oxidation of water. Herein, the strategic synthesis of combining various manganese and calcium carboxylates with a multi-dentate, aromatic, ligand precursor has been explored for the first time in the field of bioinorganic chemistry. The ligand in use is Vitamin-B6

(Pyridoxine), an essential vitamin which displays several coordination modes with different charges and hard/soft behavior. The initial reactivity of the potentially tetradentate, alcohol based chelate (N,O,O,O), 2-methyl-3-hydroxy-4,5-bis(hydroxymethyl)pyridine, commonly known as pyridoxine as an essential ingredient of vitaminB6 has been investigated in Mn/Ca carboxylate chemistry. The synthesis, elemental composition, spectroscopic characterizations like IR, UV-Vis, ^{1}H NMR studies are currently being performed for the manganese-calcium-pyridoxine complex.

2015 Joint Southeastern/Southwest Regional Meeting 948

Spectroscopic investigation of amyloid beta(1-28) in the absence and presence of Cu(II): Comparing and contrasting human, R5G, H13R, and rat peptides

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Alzheimer's disease (AD) is a neurodegenerative disease which causes decreased cognitive function and memory loss. It is the sixth leading cause of death in the United States, affecting 35 million people around the world. Hallmarks of AD in the human brain includes neurofibrillary tangles, which are caused by hyper-phosphorylation of the tau protein, and amyloid plaques, which are caused by aggregation of the amyloid beta (Aβ) peptide at their hydrophobic residues. Aβ peptides found in rats do not aggregate at an appreciable rate. Rat Aβ differs from the human peptide by only three amino acid substitutions (R5G, Y10F, and H13R). Metal ions have been shown to effect peptide aggregation and both human and rat Aβ peptides form complexes with ions such as Cu(II).
Previous studies from the Spuches lab utilizing truncated peptides indicate that the rat Aβ(1-28) peptide may form more structured complexes with buried hydrophobic residues upon Cu(II) complexation than the human Aβ(1-28). Furthermore, our studies and results from other groups indicate the R5G and H13R substitutions in the human peptide play important roles in Cu(II) binding and complex formation. The goal of this study was to test this hypothesis by obtaining structural information on the free and Cu(II) bound forms of the human(1-28), rat(1-28), R5G mutant, and H13R mutant peptides by circular dichroism (CD) and fluorescence spectroscopy. Interesting results obtained shed light on the effect Cu(II) binding has on the overall structure of these peptides and what role it may play in subsequent aggregation pathways.

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2015 Joint Southeastern/Southwest Regional Meeting 949

Solid-state anticancer drug synthesis using Merrifield resin

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Bortezomib is a proteasome inhibitor consisting of a modified peptide with the C-terminus replaced by a boronic acid. Bortezomib has been used as an anticancer drug because the inhibition of proteasomes leads to cell death, but current methods for producing it is time and labor intensive. We describe work towards simplifying the synthesis of bortezomib using a solid-state Merrifield resin.

2015 Joint Southeastern/Southwest Regional Meeting 950

Developing iron triazene and formamidine catalysts

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Bulky chiral amines were used to synthesize triazenes and formamidines. These novel ligands were used with iron precursors to form iron complexes. The iron formamidine complexes were investigated for use as catalysts in hydrophosphination reactions.

2015 Joint Southeastern/Southwest Regional Meeting 951

New catalysts for ethanol conversion to biofuels

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Ruthenium complexes have been used to undergo Guerbet Reactions to form a higher energy biofuel, iso-butanol, from methanol and ethanol. Due to ruthenium's rarity and price, it is an unsustainable option, so we decided to test iron as catalyst to biofuels. We describe our attempts at catalyzing these reactions with inexpensive iron complexes and comparing our results to similar ruthenium catalysts.

2015 Joint Southeastern/Southwest Regional Meeting 952

A stimuli-responsive, site-specific nano-drug delivery ideal for oral administration

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There is an increasing gap between the ever-growing demand for effective and patient-friendly drug delivery technologies and the longstanding drawbacks of conventional drug-delivery methods. Oral administration of drugs, the most economic and user-friendly method, for instance, has been suffered by (i) drugs' digestive decomposition in the low-pH environment in stomach and (ii) polymeric microcapsules with drug-inclusion voids disconnected by polymer-matrix. Therefore, increasing hope and in turn grand challenges have been put on the smart engineering of new nano- and micro-structured materials, devices and even systems.
Here we report for the first time a hollow-microcapsule with (i) a tunable void-volume for maximally loading drugs and (ii) a smart wall for time-programmable release of the drugs in response to the external stimuli such as pH-changes. In experiment, the low-cost microcapsule was walled by self-assembled bionanofibers, and then surface-coated by a pH-sensitive biodegradable biopolymer with widely tunable layer-thicknesses and nanopore-closure down to sub-nm scale. In this preliminary work, methylene blue dye was loaded through diffusion as a model drug. For the first time, the in-vitro release profiles reached (i) a ~99% drug loading efficiency and (ii) sustained and programmable releases over a 48-hour time period in simulated body fluid at 37 ^{o}C. This work proves a new scalable and highly translational technology in biomedical engineering and nanomedicine.

Titanium-mediated reduction of imine substrates

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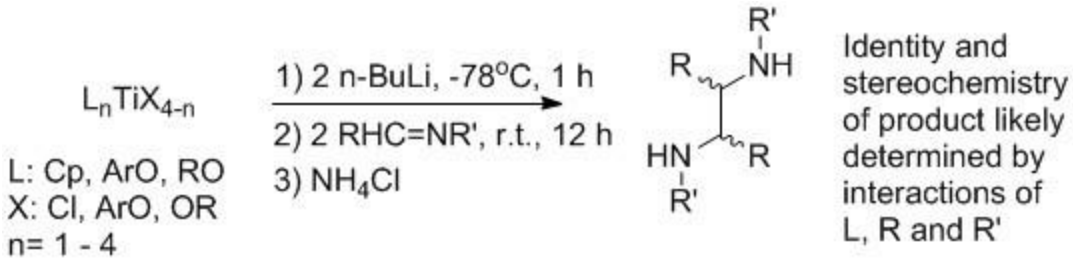
Reactions that form new carbon-carbon bonds are central to the synthesis of complex organic molecules. Titanium complexes can initiate certain reactions – such as reductive coupling of deactivated, unsaturated substrates – that would not otherwise occur. Titanium is appealing as a catalyst due to abundance, cost, and non-toxicity. However, a limited scope of ligands – almost exclusively isopropoxide and the cyclopentadiene anion – have been investigated with Ti thus far. We have initiated a series of studies on titanium-mediated coupling of imines to form vicinal diamines, which are a common motif in many biologically active molecules. A series of substituted phenoxides (e.g., 2,6-dimethylphenoxide, 2,6-diphenylphenoxide, 2,6-di-*t*-butylphenoxide), cyclopentadienide, and alkoxide groups have been selected as potential ligands to probe the effect of variation of ligand electron donor capabilities on coupling efficiency and product distribution. Additionally, we seek to specifically interrogate the role of ligand sterics on the rates and stereoselectivity of the coupling reaction. A range of imine substituents with varied steric bulk is being investigated to elucidate the entire spectrum of steric interactions between ligand and substrate.



2015 Joint Southeastern/Southwest Regional Meeting 954

Towards multinuclear spin crossover Fe(II) complexes in {N4S2} coordination environments

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A number of 3d transition-metal complexes exhibit spin crossover (SCO) between high- and low-spin electronic states, which differ in the orbital distribution of metal?s 3d electrons. Most SCO complexes are based on Fe(II) ions in an {N6} coordination, but recently an {N2S2}-donor ligand, S,S'-bis(2-pyridylmethyl)-1,2-thioethane (BPTE), was shown to result in SCO in mononuclear Fe(II) complexes.[1] In this work, we report the synthesis of a cyanide-bridged multinuclear Fe(II) SCO complexes by connecting the $[Fe(BPTE)]^{2+}$ building blocks via $[Au(CN)2]^{-}$ metalloligands. The neutral complex that was crystallized features a hexanuclear cation composed of two BPTE-capped Fe(II) ions held together by two bridging $[Au2(CN)4]^{2-}$ units. Similar architectures formed with a different capping ligand were shown to exhibit thermally-induced SCO behavior.[2]

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2. Hietsoi, O.; Dunk, P. W.; Stout, H. D.; Arroyave, A.; Kovnir, K.; Irons, R. E.; Kassenova, N.; Erkasov, R.; Achim, C.; Shatruk, M. *Inorg. Chem.* **2014**, *53*, 13070-13077.

2015 Joint Southeastern/Southwest Regional Meeting 955

Synthesis of iron(II) chloride alkyl and aryl complexes

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The arylation and alkylation of transition metals is a standard way of forming organometallic compounds. Utilizing two major ligands, the napthyl group and the mesityl group we were able to investigate synthesis of organoiron complexes of high molecular complexity. Our research focused on synthesizing and characterizing organoiron complexes in Fe(II) and Fe(IV) oxidation states.

2015 Joint Southeastern/Southwest Regional Meeting 956

Ligand photorelease from Ru(II)bis(2,2'-bipyridine)L_2 complexes encapsulated within a Zn(II)-trimesic acid based metal organic framework

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The development of new photodynamic therapy agents has remained an active area of research with regards to targeted therapeutics. The Ru(II) bis(2,2'-bipyridine)L_2 type metal clusters (where L = ligand containing primary or secondary amine, thiol, etc) are becoming an important class of photo-active drug delivery system as L can be released on ns time scales and with relative high quantum yields (~0.5 to ~5%). Biologically active ligands containing primary or secondary amine groups have been previously examined with regards to photo-release from the Ru(II) bis(2,2'-bipyridine)L_2 complex including tyramine, tryptamine, and g aminobutyric acid (GABA). As an extension to this work, the present study probes the feasibility of selectively photo-releasing bioactive molecules from porous metal organic framework materials that could be developed as implants for photodynamic therapy. Two complexes have been examined here containing ligands of different steric bulk: acetonitrile and 6,6'- dimethyl - 2,2' – bipyridine. The data indicates the successful encapsulation of the Ru complexes within the polyhedral MOF USF2. In addition, the data reveals that illumination of the Ru(II) bis(2,2'-bipyridine)(acetonitrile)$_2$@USF2 results in ligand ejection and diffusion of the ligand from the internal pores of the MOF while illumination of the bulkier Ru(II) bis(2,2'-bipyridine)(6,6'-dimethyl-2,2'-bipyridine)@USF2 leaves the Ru cluster intact. These results demonstrate the possibility of using MOFs coupled with Ru-Ligand complexes to develop new materials for photo-dynamic therapy.

2015 Joint Southeastern/Southwest Regional Meeting 957

Importance of phosphine ligand design in the elucidation of homogeneous gold (I) mechanisms

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Homogenous gold (I) catalysts are growing in popularity due to their broad applicability, excellent selectivity, high atom-economy, good functional group tolerance, as well as being able to selectively coordinate to a variety of carbon-carbon π-systems. While gold (I) complexes are known to catalyze a vast range of reactions, less is understood about exactly how the underlying reaction works. As part of efforts to design and synthesize new functional ligands which will assist in the elucidation of these mechanisms, we have prepared a series of phosphine ligands and their corresponding gold (I) chloride precatalyst complexes. The complexes targeted incorporate two bulky biphenyl substituents and have been characterized in solution using NMR spectroscopy and in solid state using X-ray crystallography. Our design originated from the concept of steric stability. With large supporting substituents, it is proposed that these groups will provide added durability to the gold catalyst during the reaction. In future studies we will use these new catalysts to obtain information concerning the kinetics of intermolecular

alkene exchange via observation of dynamic NMR processes. This fundamental information will in turn be correlated with overall catalyst and reaction efficiency.

2015 Joint Southeastern/Southwest Regional Meeting 958

Serotonin gold nanocorals for trace level detection of nitroexplosives

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Serotonin is a neurotransmitter and a derivative of tryptophan. It is known to complex with nitroexplosives like picric acid. In the present work, we have used Serotonin as a reducing agent and stabilizer to synthesize gold nanocorals (AuNCs). The as synthesized nanocorals were found to have excellent optical and spectroscopic properties. The synthesized nanocorals were characterized using TEM microscopy, UV-Vis and FT-IR spectroscopy. Our preliminary studies indicate the serotonin AuNCs have excellent binding with picric acid in water samples at a pH of 10. The work is ongoing to further study the selectivity and sensitivity of the AuNCs nanoprobe for ultrasensitive and selective detection of picric acid in the presence of other similar structural analogues. We were able to detect picric acid concentrations as low as 750uM.

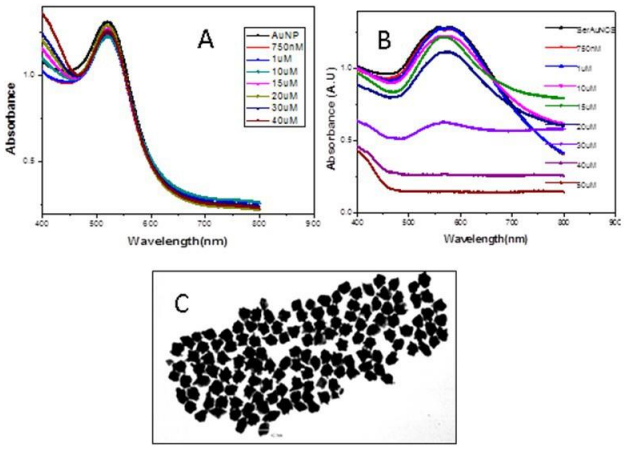

Figure: UV-Vis spectra of (A) AuNPs and (B) Serotonin AuNCs at pH 10 and (C) TEM image of synthesized AuNCs

2015 Joint Southeastern/Southwest Regional Meeting 959

Synthesis of nitrogen-rich ligands and cobalt complexes for hydrogen production

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In order to understand electronic and steric effects for hydrogen production by Co catalyst, various forms of a Co complex with the ligand scaffold, 1-([2,2'-bipyridin]-6-yl)-N,N-bis(pyrazin-2-ylmethyl)methanamine (D4-PZA-Bpy) were explored. The catalytic properties of the hydrogen production were observed. This study showed that the efficiency of the catalyst can be dramatically different at most pH levels with more N-rich ligand.

2015 Joint Southeastern/Southwest Regional Meeting 960

A pedagogic green chemistry demonstration using dye-sensitized solar cells

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A solar cell kit was obtained from Beyond Benign which utilizes titanium dioxide and indium tin oxide plates with iodide/iodine electrolyte.with blackberry juice as sensitizer. This dye sensitized solar cell has three major steps: the anthocyanin from the blackberry juice is adsorbed into the titanium dioxide, which is a semiconductor that interacts with the visible light and excites electrons, the dye is diffusedbetween two layers, titanium dioxide and indium tin oxide; and when the multi-meter is connected, it forms an outside circuit, the dye returns to its normal state. The graphite used in the demonstration enhances the interaction with electrolytic solution. This demonstration has been used in conjunction with NCW program, at schools, civic clubs etc to highlight the green chemistry principles by UTM Student Members of the American Chemical Society Also under study are other natural chemicals such as indigo as sensitizers.

2015 Joint Southeastern/Southwest Regional Meeting 961

Benchtop NMR spectroscopy for at-line and on-line reaction monitoring

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The science of organic chemistry looks to build carbon-carbon bonds in a straightforward and repeatable manner. This requires a toolbox of reliable reactions that chemists can use to build a specific molecule. However, these reactions must be tailored to different substrates and different starting materials. This can require a great deal of reaction monitoring and optimization. Typical reaction monitoring mechanisms include quenching an aliquot and monitoring reaction progress with thin layer chromatography (TLC), and/or gas chromatography-mass spectrometry (MS). Nuclear Magnetic Resonance Spectroscopy (NMR), however, can be beneficial as it provides more information about the specification and relative quantity of the reaction components. Herein we describe the use of benchtop NMR Spectroscopy to monitor a variety of reactions, from simple small molecule to polymerizations. This monitoring can be done through traditional sampling techniques paired with the at-line or flow-through the online NMR spectroscopy.

2015 Joint Southeastern/Southwest Regional Meeting 962

Exploring the potential and limits of two-channel benchtop NMR with indirect detection capabilities for undergraduate research

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Benchtop Nuclear Magnetic Resonance (NMR) plays a crucial part in undergraduate organic chemistry education. The limits of such systems are mainly the poor resolution of 1H resonances. This requires the molecules studied to have unique and well-defined chemical shift regimes in order to avoid signal overlap, which convolutes the spectrum and complicates it's interpretation. Additionally, the need for high concentrations of sample for 13C acquisition and enough time to run the samples also presents limitations. These limitations can be easily overcome by simply designing laboratory experiments in order to teach pertinent concepts to the students. The real limit of these instruments lies in the area of undergraduate research, where such well-defined outcomes are harder to control. Additionally, sample concentrations are often low to the point of making 13C acquisition impractical or impossible. Here we explore the use of the Spinsolve 2-channel benchtop NMR system as it pertains primarily to undergraduate research due to its ability to run the indirect-dection protocols HSQC, HMQC, HMBC and DEPT. As the indirect experiments detect neighboring 13C nuclei through spin-couping to 1H, the need for high concentrations is greatly reduced. Three highly different compounds (an aromatic heterocycle, a linear alkynylthioester, and a rigid bicyclic ketoether) were synthesized in the research laboratory and characterized to different extents using these protocols. As specific 13C-1H coupling constants must be accounted for during detection, one system never showed a correlation to 13C nuclei via indirect detection that was clearly visible in the higher field or higher concentration direct detection experiment. Therein lies the major limitation of this system. However, through deduction and an understanding of the Karplus equation, this NMR system significantly reduced the number of visits to the nearby high-field instrument, thus opening research opportunities in our laboratory that would be slowed to a nearly impractical pace due to the amount of instrument time at an off-site, high-field instrument.

Small-molecule models of poly(amidoamine) dendrimers

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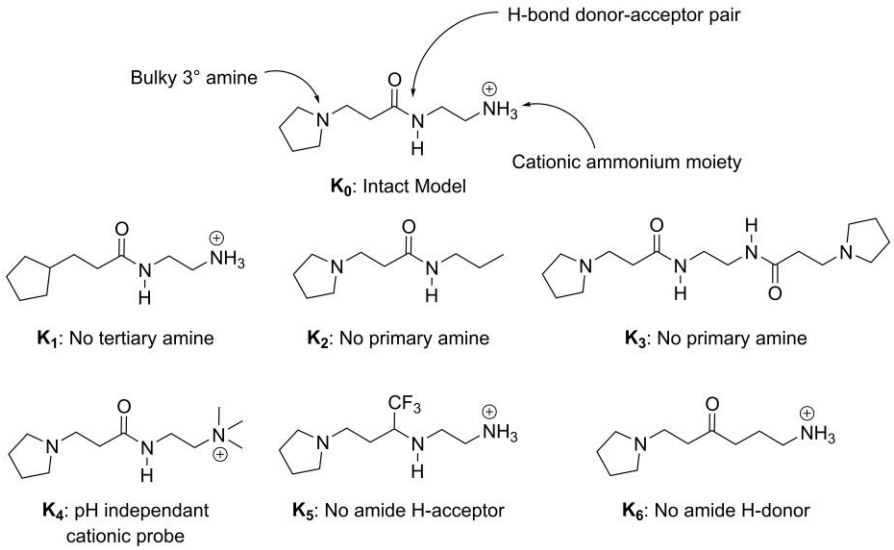
Amine-terminated poly(amidoamine) dendrimers (PAMAM) are hyperbranched polyelectrolytes which can bind to small anionic molecules through non-covalent interactions. To determine the individual contribution, cooperativity, and multivalency of these interactions in water, we are in the process of preparing a series of model molecules. The intact model $\mathbf{K_0}$ contains all key functional groups present in PAMAM dendrimers. Additional compounds are being synthesized as well; these “knockouts” **($\mathbf{K_n}$)** are missing moieties that may be involved in the binding process. $\mathbf{K_1}$ omits the tertiary amine while $\mathbf{K_2}$ and $\mathbf{K_3}$ omit the primary amine. The $\mathbf{K_1}$-$\mathbf{K_3}$ series will provide insight into electrostatic effects and afford a comparison of the relative importance of protonation of the primary and tertiary amines. $\mathbf{K_4}$ is a pH-independent protonation probe that will allow us to study the effect of changing pH without affecting the charge

state of the probe. $\mathbf{K_5}$ and $\mathbf{K_6}$ will provide insight into the individual contribution of H-bond acceptor and H-bond donor locations, while retaining structural rigidity. Comparison of the binding properties of these model compounds with those of the intact model, and of the full dendrimers, will allow us to explore the effects of each target interaction, as well as of cooperativity among these interactions.



2015 Joint Southeastern/Southwest Regional Meeting 964

Routes toward greener, polymer-supported catalysts and polymer functionalization

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This talk will describe our current efforts geared toward the use of polypropylene-based oligomers as catalyst supports as well as the use of metal-free click-type reactions for polymer modification toward functional polymeric materials.

2015 Joint Southeastern/Southwest Regional Meeting 965

Synthesis of a 3-diazonium-4-(trifluorovinyloxy) - perfluorobutanesulfonylfluoride zwitterionic monomer for polymer electrolyte membrane fuel cell

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3-Diazonium- 4-(trifluorovinyloxy) - perfluorobutanesulfonyl fluoride zwitterionic monomer (**I**) is proposed to be polymerized and further act as a new electrolyte for Polymer exchange membrane fuel cell(PEMFCs). One reason is aromatic trifluorovinyl aryl ether (TFVE) can easily be homopolymerized to aromatic perfluorocyclobutane (PFCB) polymer. Furthermore, the diazonium moiety in the monomer is expected to covalently attach the electrolyte to the carbon electrodes support to maximize the efficiency of utilization of the catalyst. A seven steps synthetic scheme is designed to

obtain such monomer from polytetrafluoroethylene. After successfully synthesizing 4-(2-bromotetrafluoroethoxy)-3-nitro-benzensulfonyl amide, the next stage of the work is to couple it with the nonafluorobutanesulfonyl fluuoride group $C_4F_9SO_2F$. All the intermediates were characterized by ^{1}H and ^{19}F NMR and FTIR spectroscopy.

Figure 1 3-Diazonium- 4-(trifluorovinyloxy) - perfluorobutanesulfonyl fluoride zwitterion **I**

2015 Joint Southeastern/Southwest Regional Meeting 966

Artificial membrane fusion driven by click chemistry

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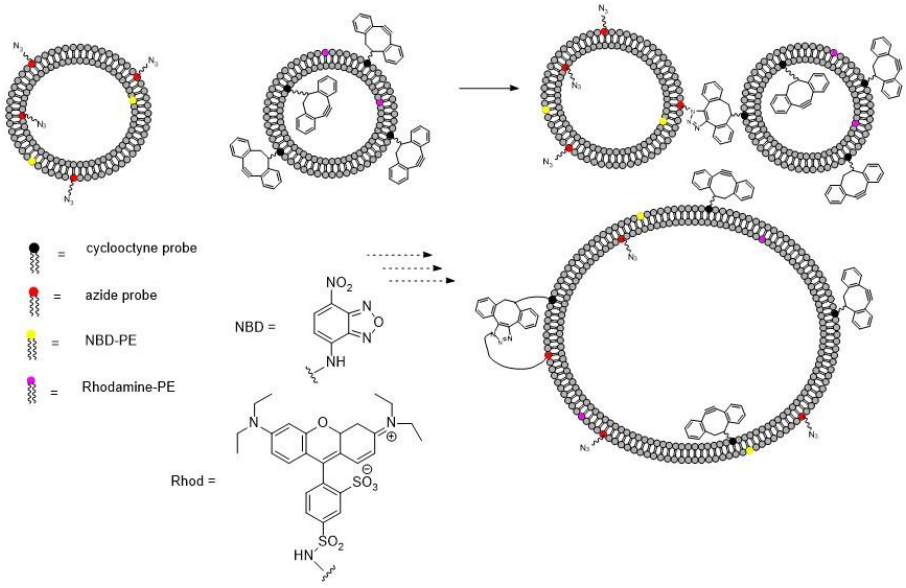
Membrane Fusion is a complex process that controls critical pathways in biological systems. Artificial membrane fusion using synthetic lipid analogs has been studied as a means to control this process for medicinal applications such as targeted drug delivery. Multiple avenues have been used to take advantage of this process by synthesizing complementary lipids that react or assemble, thereby bringing separate membranes into proximity and promoting fusion. Here, we describe efforts to exploit the copper-free ‘click’ reaction (1,3-dipolar Huisgen cycloaddition reaction) to trigger membrane fusion in liposomal samples. Towards this end, synthetic lipids bearing either cyclooctyne or azide analogs have been synthesized and incorporated into separate liposome samples to drive the opposing bilayers together and promote fusion. Fusion has been tracked using FRET mixing and demixing assays and dynamic light scattering (DLS) experiments.



Artificial membrane fusion strategy via click chemistry

2015 Joint Southeastern/Southwest Regional Meeting 967

A dehydrative aromatization protocol for the synthesis of highly distorted para-phenylenes: A new tool for the synthesis of carbon nanostructures

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The synthesis of bent benzene rings that comprise biaryl systems of natural products and hydrocarbon materials represents a significant challenge for synthetic chemistry. In essence, the use of cross-coupling reactions that simultaneously involve biaryl bond formation and arene bending is a weak synthetic method. Recently, we reported the use of macrocyclic 1,4-diketones as surrogates to 1,4-arene-bridged macrocycles that contain nonplanar benzene and *p*-terphenyl ring systems. This strategy has enabled the synthesis of a homologous series cyclophanes that contain some of the most distorted benzene rings to be isolated and characterized by X-ray crystallography. This has been achieved by using mild dehydrative aromatization reaction that features the Burgess reagent.

2015 Joint Southeastern/Southwest Regional Meeting 968

Azulene-modified polysiloxane for use as a gas chromatography stationary phase

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Azulene is a highly colored aromatic molecule consisting of a five-membered ring fused to a seven-membered ring. It is isoelectronic with naphthalene. However, while naphthalene is nonpolar, azulene has a dipole moment of 1.08 D – approximately equal to that of HCl. The properties of azulene might be of advantage in certain chromatography applications. In unpublished work we have observed that azulenes are much more strongly retained on gas chromatography stationary phases relative to other aromatics with the same number of carbons. We postulate that azulene-modified stationary phases would demonstrate a unique mode of retention: polarity without heteroatoms. This paper describes the synthesis of a new polysiloxane material containing trimethylazulene- and trifluoroacetylazulene-based side chains. These materials were synthesized by the hydrosilylation of alkene-functionalized trimethylazulene or trifluoroacetylazulene onto poly(hydromethyl/dimethyl)siloxane. These polymers were coated onto capillary columns and an evaluation of their separation properties was performed. Results show that these stationary phases form good films on the interior of the capillary, and give sharp peaks and good separation. Analysis of the retention properties of the columns indicate the material is relatively nonpolar. We are also investigating other azulene-containing stationary phases and their separation properties.

2015 Joint Southeastern/Southwest Regional Meeting 969

Synthesis, supramolecular chemistry and solid-state reactivity of 2,3-substituted dienes: 3,4-Bis(methylene)hexanedioic acid and fulgenic acid

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A number of solid-state polymerization of terminally substituted dienes have been well documented in the literature. Less well known is the solid state reactivity of internally substituted dienes. We report the first example of a topochemical polymerization of 3,4-bis(methylene)hexanedioic acid, an internally substituted diene. We also report on the solid state behavior of fulgenic acid and the supramolecular chemistry of co-crystals containing either fulgenic acid or 3,4-bis(methylene)hexanedioic acid. Crystallographic analysis of these compounds and their co-crystals show different modes of packing and reactivity for these structurally similar compounds.

2015 Joint Southeastern/Southwest Regional Meeting 970

Functionalized polyanilines as novel curing agents for epoxy resins

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Electrically conducting polyaniline was functionalized by covalent attachment of aliphatic polyamines by a concurrent addition/reduction reaction. These functional polymers were then applied as curing agents for DGEBA resin. Successful modification of the polymer backbone was confirmed by FTIR with the appearance of aliphatic C-H stretching from 2990 to 2800 cm^{-1} as well as N-H stretching bands from 3500-3300 cm^{-1}. UV-visible spectroscopy was used to monitor the change in the π-π* transition peak at λ_{max} 650 nm which indicates the oxidation state of the PAn backbone. DSC and TGA were used to measure the curing characteristics and thermal stability of the resin-filler system. Poly(aniline) derivatives were found to possess sufficient curing ability to produce a rigid freestanding composite, with the curing temperature decreasing as a function of primary amine groups.

2015 Joint Southeastern/Southwest Regional Meeting 971

Student-centered learning in the chemistry laboratory: The POGIL approach

Frank J. Creegan*, fcreegan2@washcoll.edu. Chemistry, Washington College, Chestertown, Maryland, United States*

The POGIL laboratory is one in which students, in advance of any classroom work on underlying principles, conduct experiments rather than exercises that verify previously taught principles. In a pre-experiment session the instructor poses a Question of the Day and students propose a set of tentative answers. To test these hypotheses, students run reactions and/or collect data, which are pooled and then analyzed with the aid of in-laboratory and post-experiment or post-laboratory guided inquiry questions. The format for the laboratory is similar to that of the POGIL classroom in that students work in self-managed groups with members having well defined roles. The experiments follow a three-stage learning cycle composed of an exploration phase (E), concept invention phase (I)l and application phase (A). This presentation will illustrate the use of this student-centered approach in a year-long course in organic chemistry

2015 Joint Southeastern/Southwest Regional Meeting 972

Incorporating gas chromatography-mass spectrometry into one-year general chemistry courses

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First-year general chemistry students are rarely exposed to or much less allowed to perform their own measurements on modern chemical instrumentation. The acquisition of a gas chromatograph-mass spectrometer (GC-MS) instrument through a National Science Foundation grant, however, has allowed us to change this approach at Grand Rapids Community College (GRCC). The instrument was integrated into our general chemistry sequence to help students clarify the differences between an element and its isotopes, to introduce the science of chromatographic separation and mass spectrometry identification, and to provide students with hands-on experience in its use. With the goal of improving students' knowledge of GC-MS and providing a kinesthetic learning experience, experiments were developed and adapted to include the use of the instrument. This presentation will discuss the methods and outcomes of this work including curriculum development, student feedback, and assessment of student achievement.

2015 Joint Southeastern/Southwest Regional Meeting 973

Teaching nucleophilic substitution reactions of alkyl/aryl halides using inquisitive approach

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In this experiment, students receive three compounds of each primary, secondary, and tertiary alkyl/aryl halides along with two solvents: aprotic and protic to study S_N2 and S_N1 mechanisms. Overall they perform two sets of reactions for all the given compounds at two different temperatures, for each solvent. Before they start the experiment, they draw the structures of all compounds. For inquisitive approach, students choose any three or four compounds (e.g. if they select 1-Chlorobutane, 2-chlorobutane etc.). They focus on the same chosen compounds for investigation in protic and/or aprotic solvent. Based on the structures, they design a question; write hypothesis and prediction. Some students prefer to perform a comparative study of reactivity of the selected compounds in both the solvents or they compare the rates of reactions at two different temperatures for one of the solvent. Some students evaluate the reactivity of aryl versus alkyl halides at a particular temperature, in one or both the solvents. Thus the inquisitive approach allows students to come up with creative ideas to study the same experiment from various perspectives. Finally in the discussion section, they are required to make a connection between the structure and reactivity to indicate whether their hypothesis is confirmed or not confirmed.

2015 Joint Southeastern/Southwest Regional Meeting 974

Revisiting course design to address higher level learning outcomes in a general chemistry laboratory

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The typical 100 level laboratory course at a large university usually contains the following common components: offering a lab handout, explaining the lab handout in a lab lecture, requiring a pre-lab in a notebook, having students use the notebook *and* handout in the lab, grading lab reports and finally, evaluating students using paper exams. This design often times results in students reading and copying information from the handouts to be "prepared" for lab without any cognition about the procedure or chemistry they will be performing. If our intent is to reach higher levels of Bloom's Taxonomy such as creating, analyzing and evaluating in preparing science majors, the design of a lab should provide students the freedom to think creatively and solve experimental problems. With this strategy in mind and in consultation with an undergraduate biochemistry major from Virginia Tech and a teaching assistant from Virginia Commonwealth University, a course design was implemented for a summer second-half general chemistry lab lecture with three sections of associated labs. This summer course was used as a test case for the viability of a course design that better addresses performance aspects and higher level learning outcomes. The major changes implemented included: the recording of *general* laboratory procedures and the elimination of laboratory handouts, the implementation of a performance grade and two open-inquiry type practical exams. Rubrics were designed and shared with the students for the lab reports and the lab practical exams to assist in consistency and ease of grading for the teaching assistants. A survey after the course with an 88% response rate indicated the following: (1) 100% of the students believed the practical exams were more appropriate than the paper exams to test the learning outcomes expected from a laboratory (2) 84% felt that not reading a handout during lab increased their ability to focus on what was going on in lab experimentally and (3) 96% reported feeling more confident about performing under pressure because of their lab experience. With the overwhelmingly positive feedback from the survey one may expect that the students found the format easier than their previous experiences. Contrary to that assumption, 91% reported being challenged to a higher level than they had been in their previous lab courses. This design may provide a template for larger scale implementation of a more appropriate 100 level experience.

Spatial reasoning for the 21st century student: Computer vs. handheld models

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Chemistry involves a plethora of 3-D topics including chirality and conformational changes that require students to understand molecular spatial relationships and perspective. Though we often try to show students molecular models, today's learners often see computer based models rather than physical models. Given the everyday exposure of our students to hand-held technology and the wide-spread use of 3-D images in technology, many educators wish to use this technology in their classrooms to either enhance or replace the use of traditional physical models. This study investigates the 21st century student to see if computer based models or traditional

hand-held models are best for assisting students in their development of 3-D spatial reasoning skills.

2015 Joint Southeastern/Southwest Regional Meeting 976

Increasing student engagement using cross-disciplinary course-based research experiences

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Pedagogical studies suggest that course-based undergraduate research experiences (CUREs) can increase student knowledge of and interest in related subject matter, improve student retention, and influence academic and career paths. Here we describe the development of cross-disciplinary CUREs that are integrated into upper and lower-level chemistry and biology courses. Students in impacted labs develop their own hypotheses and apply a variety of biological and chemical approaches to make novel discoveries about the anticancer ruthenium complex indazolium *trans*-[tetrachlorobis(1*H*-indazole)ruthenate (III)], also known as KP1019. To promote cross-disciplinary thinking and collaboration, students upload their findings to a CURE-associated wiki and consult the wiki during experimental design and data analysis. Students reported that these CUREs significantly increased their degree of experience with integrating disciplines and working on problems with no known outcome. These results were consistent with analysis of student wiki postings and laboratory reports, as well as findings from an external evaluator, who also noted that students who participated in more than one of these CUREs reported significantly greater gains in many areas. With respect to their ability to interpret results, to analyze data, and to write scientifically, students reported gains comparable to those obtained during intensive summer research programs. In addition to validating the pedagogical value of integrating research and teaching, this work suggests that cross-disciplinary CUREs provide a powerful mechanism for helping students integrate their knowledge of different disciplines. Moreover, virtual collaboration tools, such as wikis, can be used to successfully illustrate the interdisciplinary nature of modern research.

2015 Joint Southeastern/Southwest Regional Meeting 977

The first-year research experience (FYRE) program: Introducing research to first year students at the University of Oklahoma

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The First-Year Research Experience (FYRE) program promotes STEM undergraduate research at the University of Oklahoma (OU) through allowing first-year students to conduct semester-long, mentored primary research internships. Started as a program for students in the Department of Chemistry and Biochemistry in 2011, FYRE has evolved into a campus-wide STEM- research development vehicle allowing first-year students from many different majors, including non-science majors, to gain valuable experience and insight in laboratory research. In addition to the hands-on research experience, the FYRE program is a conduit to building a campus-wide undergraduate research community; students participate in biweekly joint meetings allowing them to form a peer group as well as to meet STEM-research professionals and gain

perspective of research-oriented career paths. During the last three years, 129 student have participated in FYRE, with 67 in the 2015 program. The 2016 program is projected to accommodate ~90 FYRE students working in research groups throughout the university, include engineering disciplines, psychology mathematics and physics. Beyond developing research interested STEM students, FYRE is also been a gateway to laboratory research for non-science majors, through the “Molecular Gastronomy of Coffee” FYRE project. This project emphasizes the application of molecular techniques to elucidate the chemical composition of coffee flavor, and this project is ideal in introducing freshmen students to inquiry-driven, bench-centered research. This project allows the students to design and conduct research, using mass spectrometry and other analytical techniques, to test individual hypotheses related to the study of coffee flavor. This project demonstrates a scalable program to engage students in meaningful research that can readily incorporate independent inquiry.

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Student engagement strategies and small-scale research in a community college setting

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In a rural-setting community college with a sparse local area population distribution, a typical chemistry class is small (sometimes fewer than 10) with a manageable work load including number of papers to grade and number of sets of experiments per class. Even though the number is small, it is interesting to find that the student body is actually very diverse in terms of family background, chemistry/science background knowledge, needs and expectations of individual student, in-class student involvement, and time spent by a student outside of class. Addressing each student’s need and fulfilling the course objectives at the same time sometimes becomes very challenging, if not properly handled. This talk will focus on strategies of teaching and small-scale research in chemistry and other physical sciences in such environment with ultimate goal of increasing student enrollment and retention in chemistry in particular, and in STEM field as a whole.

2015 Joint Southeastern/Southwest Regional Meeting 979

How we teach; what students learn

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Research can be a great teaching tool, but is often relegated to only upper-level courses or small groups of students. By using research with a large class, an array of conditions and procedures may be examined allowing the students to use the results to form conclusions. This allows students to use the scientific method, use statistics, form conclusions based on data, and develop communication skills. Students learning in this environment see the purpose behind the skills developed and become aware of why these skills need to be practiced and improved.

Using this methodology, the synthesis of Lidocaine was improved from 50% yields to nearly 90% yields. The presentation will demonstrate how the use of research arrays

can be used in sophomore organic labs to more effectively teach students.

2015 Joint Southeastern/Southwest Regional Meeting 980

Examining the effects of urbanization on Boone Creek

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Boone Creek is a mountain headwater stream that drains an urbanized area in western North Carolina. Total metals, anions, and total suspended solids (TSS) were monitored monthly at six sites to determine if the stream was impacted by urbanization. ICP emission spectroscopy was used to measure the concentrations of Ca, Na, Al, and several transition metals. Four months of data indicate that the As, Cd, Cr, Cu, Ni, Pb, and Se concentrations were below the detection limit at all sites. The Al, Fe, Mn, and Zn concentrations increased at the downstream sites, which are more urbanized than upstream, but all concentrations were less than 0.588 ppm (n=3, SD=0.007) except in the case of a rain event when the highest concentration reached 3.07 ppm (n=3, SD=0.02). Anion concentrations (Cl^-, NO_3^-, SO_4^{2-}) also increased at the downstream sites, but were diluted below the confluence of a tributary. Nitrate and sulfate concentrations ranged from 2-9 ppm for all sites. Chloride concentrations depended on weather conditions due to road salt with the high being 331.4 ppm (n=3, SD=3.4) in January, 2015. A direct correlation between the concentrations of Cl^- and Na was observed for all six sites (R^2 = 0.972). TSS results were relatively low throughout all six sites (< 3 mg/L).

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Sulfide induced dispacement of gold nanoparticle ligands

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Today gold nanoparticles are finding many applications in fields such as drug delivery, catalysis, and surface-enhanced Raman spectroscopy (SERS) substrates. Most of these applications come from functionalizing the gold nanoparticles with thiols and other sulfur based ligands. Therefore the need to understand sulfide's interaction with gold nanoparticles is important. In this work, sulfide's ability to replace aromatic thiols, dithiols, monothiols, and adenine on the surface of the gold nanoparticle is shown. UV-vis spectroscopy and SERS are used to study the kinetics of this reaction and its dependence on the concentration of sulfide. In addition, the sulfide's ability to stabilize gold nanoparticle solutions and induce the redispersion of gold nanoparticle aggregates is explored. This work is important for understanding the fundamental aspects of gold nanoparticle interaction with sulfur compounds.

2015 Joint Southeastern/Southwest Regional Meeting 982

Acute toxicity of FA-GLU, surfactin, and surfactin isomers, microbial based biosurfactants, on larval gulf killifish *Fundulus grandis*

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The Gulf killifish, *Fundulus grandis*, is an abundant estuarine fish found throughout the northern Gulf of Mexico. Surfactants are chemical dispersants and were used widely following the Deepwater Horizon oil spill in April of 2010 for cleanup and remediation within open waters. Dispersants break up surface oil droplets and can cause oil compounds to enter the water column increasing bioavailability and thus have the potential to increase the toxicity of oil to aquatic organisms.

The objectives of this study were to assess the toxicity of FA-Glu and surfactin as potential alternative biosurfactants, which are produced by *Bacillus subtillis* bacterium. We conducted acute toxicity bioassays on recently hatched larvae that were exposed to FA-Glu or Surfactin to create dose-response curves for these compounds. Median lethal concentration (LC_{50}) curves were created in order to determine the maximum concentration these fish could live in from 96-hour acute exposures. Acute toxicity of FA-Glu was conducted at treatment salinities of 4, 12, and 24 g/L. Three distinct isomers of surfactin were isolated from microbe cultures and thus we were able to determine the comparative acute toxicity of these isolates at an environmental salinity of 12 g/L. Water quality parameters were monitored throughout the study to ensure that conditions were within the acceptable range for this species.

Acute toxicity of FA-Glu was influenced by salinity, with increased salinity (24 g/L) resulting in lower LC50 values for these 96-hour bioassays. These results are consistent with previous examinations of industrially produced surfactants such as dioctyl sodium sulfosuccinate which alter ion regulation at the gill epithelium. Surfactin and its isomers have higher toxicity than FA-Glu, however the surfactin isomers are individually less toxic than non-fractionated surfactin (Table 1). These results represent some of the first toxicological information on estuarine aquatic organisms for these biologically produced surfactant compounds.

Type	Salinity (‰)	LC_{50} (mg/L)	Lower-Upper Confidence Interval (mg/L)
FA-Glu	4	126	106.0 -138.7
FA-Glu	12	110.1	96.2-126.9
FA-Glu	24	68.2	64.0-72.5
Non-fractionated Surfactin	12	3.3	2.35-4.92
Surfactin Isomer 1	12	7.1	4.6-10.5
Surfactin Isomer 2	12	17.1	11.3-35.4
Surfactin Isomer 3	12	9.9	8.7-11.3

Table 1

WITHDRAWN

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Extraction and analysis of xylitol in sugar free gum: A “green” laboratory experiment for chemistry students

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Xylitol is a popular sweetener in many sugar-free products such as chewing gum, mints, oral-care products, and baked goods. Xylitol is generally considered safe for human consumption. Unfortunately, this polyol has been discovered to be toxic for canines. Recently, our research group has developed a method to extract and analyze xylitol in sugar-free gum sticks. We developed this extraction method with several modifications in order to incorporate it as an experiment procedure in a teaching laboratory for chemistry students that can be performed within a three hour time frame. The amount of xylitol in a gum extraction was determined by gas chromatography with a mass detector (GC/MS) by direct aqueous injection. Several groups of students were exposed to the new experiment and each group was successfully able to perform the experiment within the three hour time frame.

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Quantitative HPLC analysis of n-(n-butyl) thiophosphoric triamide (NBPT) using UV detection

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Urea is commonly used nitrogen fertilizer, but it is notorious for Potential for high volatile nitrogen losses. Significant losses of nitrogen to the atmosphere occur in the form of ammonia as urea is converted to ammonia gas by action of soil bacteria. In order to solve this problem, NBPT has gained the popularity as urease inhibitor to enhance the efficiency of nitrogen utilization. NBPT treated urea fertilizers contains the nitrogen needed to fertilize plants, and it is designed to reduce the amount of nitrogen loss, eliminating the need for the fertilizer to be applied multiple times. In order to put NBPT on the market, an effective method must be developed to determine the precise amount of NBPT in solutions used to treat urea fertilizers. The purpose of this research project was to develop a simple and routine analytical method to quantify the amount of NBPT in any given solution using a high performance liquid chromatograph (HPLC). Previous studies have demonstrated the problems associated with quantifying NBPT in the UV range when the concentration is about 0.01 mM. Also, it is not feasible to quantify NBPT by GC analysis because it is thermally unstable. In the scheme developed, several samples of NBPT solution were analyzed using the standard addition method. A known amount of NBPT solution was added to each sample to determine the amount of NBPT in each sample. The method targets accurate determination of the amount of NBPT sold on the consumer market. The analytical and instrumental methods developed as well as results of the research project will be discussed in this presentation.

2015 Joint Southeastern/Southwest Regional Meeting 986

Determination of mVOCs for distinguishing virulent from hypo-virulent *Cryphonectria parasitica* via headspace-SPME-GC-MS

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In the early 1900s, the fungus *Cryphonectria parasitica* was accidentally introduced into the eastern United States and virtually eliminated the American chestnut (*Castanea dentata*) by 1940 throughout the specie's entire range. Natural control occurred in Europe on the European chestnut (*Castanea sativa*) when debilitated virus-infected strains of pathogen, hypovirulent (HV) isolates, were found which convert the lethal virulent (V) forms into HV's. However, determination of HV strains requires intensive laboratory screening and must be confirmed by field studies. The main objective of this study is to utilize a cost/time effective method of identifying the key chemical emissions that distinguish V from HV fungal isolates. Recently, microbial volatile organic compounds (mVOCs) were collected via headspace solid phase extraction (HS-SPME) with an 85 µm carboxen/polydimethylsiloxane (CAR/PDMS) fiber coupled with gas chromatography-mass spectrometry (GC-MS). Additional studies have been conducted exploring how varying temperature and growth media alters the MVOC profile. Data pattern recognition was achieved by utilizing chemometrics.

Development and validation of HPLC-MS methods for the quantification of eumelanin and pheomelanin pigments in tissue samples

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Quantitative melanin analysis is an important tool for scientific studies ranging from the examination of skin pigment abnormalities to the identification of pigmentation in ancient feathers. Two forms of melanin are present in animals – eumelanin and pheomelanin. Current techniques to quantify melanin entail chemical degradation of the pigment into markers specific to each natural form. These chemical markers are then separated and quantified by high performance liquid chromatography with ultraviolet detection (HPLC-UV). While this characterization has proved useful, in biological matrices there are interferences that complicate UV identification of the critical markers. To overcome these limitations, we have developed a new method for identifying the markers of eumelanin and pheomelanin that is compatible with UV and mass spectrometric detection. The non-volatile buffer conditions that prevented the use of mass spectrometric detection and decreased the lifetime of expensive columns have been replaced with a compatible volatile solvent system. Due to the interferences present in biological matrices, mass spectrometric detection is vital for confident peak identification. This new method allows for sensitive and accurate identification of melanin markers, which may benefit future diagnostic methods and the examination of historical pigmentation patterns.

Characterizing structure-function relationships in bisurea organogelators using infrared spectroscopy

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Transmission infrared spectroscopy was introduced for characterizing the structure-function relationships in bisurea organogelators. Organogelators were classified into 2 major categories: those with a core based on vanillin and had varying lengths of carbon tails and those with C18 tails containing a cis double bond and without it. Organogels were prepared by dissolving the gelators in benzene using heat and stirring. The lowest concentration that led to the formation of a rigid gel was defined as the critical concentration and was determined by inverting the vial after the samples were given time to cool. A demountable liquid cell with sodium chloride windows was used to acquire transmission IR spectra. The degree of hydrogen bonding can be determined by examining the amide II band and the relative number of conformational defects in the tail groups can be determined by examining the methylene bending region. While strong hydrogen bonding is required for gelation, it is not sufficient on its own. The entanglement of the tails of the molecules is also necessary to form the strong junction zones between fibers that give the organogel rigidity. The organogelators with the vanillin core do this through forming conformational defects in their alkyl tails. The organogelator with a cis double also helps with the entanglement of the tail groups, leading to lower critical concentrations.

2015 Joint Southeastern/Southwest Regional Meeting 989

Deviations of the glass transition temperature (T_g) of polystyrene nanospheres under hard and soft confinement

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The effect of confinement on the glass transition temperature (T_g) has been studied in various systems such as thin films, nanocomposites, and nanoparticles. While deviations from bulk T_g has been observed in all of these systems, the exact nature of each deviation is surprisingly inconsistent. For the case of nanospheres, researchers have reported increases in T_g, decreases in T_g, no deviations in T_g, and size dependency of T_g.

Here temperature-varied fluorescence spectroscopy was used to study the T_g of polystyrene nanospheres under various surfactant concentrations (and thus varying types of confinement). T_g was found to be size independent, but have a novel dependency on the type of confinement.

2015 Joint Southeastern/Southwest Regional Meeting 990

Spectroscopic and theoretical investigation of solvent and temperature effects on optical activity of (*R*)-3-methylcyclohexanone dominant conformers

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(*R*)-3-methylcyclohexanone is an important chiral ketone that is found in living cells and many biological systems and can exist in five possible conformers. In this talk, experimental and computational investigation of solvent and temperature effects on the circular dichroism (CD) and optical rotation (OR) of (*R*)-3-methylcyclohexanone (*R*3MCH) conformers will be discussed. OR measurements of *R*3MCH gaseous sample and in ten common solvents of wide polarity range were recorded. Also, temperature dependent CD and OR spectra over 100 ^{0}C range will also be shown. Density functional theoretical calculations were performed using Gaussian09 at B3LYP/aug-cc-pVDZ level of theory. *R*3MCH will be shown to exist in five possible conformers at room temperature, with the chair equatorial and chair axial conformers being predominant. OR spectra for the optimized geometries of *R*3MCH dominant conformers were computed over the ultraviolet and visible region in the gas phase as well as in ten solvents of varying polarity range, and under the umbrella of the polarizable continuum model (PCM). Upon comparison between theoretical and experimental results, the enthalpy difference between the equatorial and axial conformers in solvation will be estimated and compared to theoretical value.

2015 Joint Southeastern/Southwest Regional Meeting 991

Synthesis of metal-impregnated xero- and aero-gel catalysts for carbon dioxide reduction

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For long-term space travel and inhabitation, carbon dioxide reduction technology is necessary to reclaim oxygen from metabolic carbon dioxide and is vital to reduce the delivery mass of metabolic oxygen. Traditional processes for carbon dioxide reduction result in the deposition of solid carbon onto a steel wool catalyst and resulting inhibition of the catalyst. Because of this, a large mass and volume of additional catalyst would be required to support a Martian surface-like, crewed mission. Therefore, aerogels are being investigated as catalytic supports due to their high surface area and porosity, which allows them to achieve the same performance with significantly less mass and volume. Gels composed of silica, alumina, and carbon were impregnated with various metal-containing compounds, tested for bulk kinetic activity in the carbon-depositing step of the Bosch CO_2 reduction process, and analyzed using scanning electron microscopy before and after catalytic testing. The results of this study suggest that aerogels are a viable candidate to decrease cost and waste material generated by catalyzed carbon dioxide reduction, increasing the possibility of long-term space travel.

2015 Joint Southeastern/Southwest Regional Meeting 992

Longitudinal alignment and optical characterization of gold nanostars in electrospun polymer fibers

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The objective of this study is to align branched nanoparticles in polymer fibers on the macroscale by electrospinning and to learn how alignment affects their optical properties. Branched gold nanoparticles, or “nanostars” (GNSs) were synthesized and suspended in a poly(ethylene oxide) (PEO) solution, which was then electrospun to produce a GNS-embedded polymer fiber nanocomposite. The PEO fibers and embedded GNSs were imaged by electron microscopy to assess the orientation of the GNSs and to measure the fiber diameters. The GNSs aligned along their longest axis parallel to the axis of the fiber due to shearing during electrospinning. The fibers were then aligned on the macroscale by deposition on a rotating mandrel, orienting all of the fibers in the same direction and thus aligning the GNSs on the macroscale. Aligned fiber mats exhibit polarization-dependent optical absorption, where the absorbance is redshifted and blueshifted for light polarized parallel and perpendicular to the fiber axis, respectively. This result is consistent with the observed alignment of the long axes of GNSs parallel to the fibers.

2015 Joint Southeastern/Southwest Regional Meeting 993

Thermal, mechanical, and optical characterization of luminescence-doped PDMS thin film sensors

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Thermographic phosphors offer a non-invasive and remote temperature sensing mechanism with a very high degree of thermal sensitivity. La_2O_2S:Eu is one of the most sensitive thermographic phosphors currently available with a demonstrated sensitivity of 0.05 C. However, the fine powder form of these materials severely restricts the range of applications. In this study, thermographic phosphors were embedded within an inert polymeric encapsulant at various concentrations and the effect of the encapsulating medium on the thermal, optical, and mechanical behavior of the phosphor powder was investigated and fully characterized. Using the spin-coating technique, thin polymer films with 10% to 50% phosphor concentrations were created and fully characterized. Results demonstrate the feasibility of a flexible “peel-and stick” thermal sensor where the sensitivity of the sensor strongly depends on the concentration of the powder embedded in the polymer, and, the cluster sizes formed during the synthesis stage.

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Why does the acetaldehyde enolate favor reaction at the O atom during gas-phase nucleophilic substitution? Contributions by resonance and inductive effects

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Enolate anions are bidentate nucleophiles that can undergo reaction at the O atom or the alpha C atom. In solution, the C atom is usually the preferred reaction site, but in the gas phase, the O atom is. To better understand this preference in the gas phase, we carried out density functional theory calculations at the MPWPW91/6-311++G(3df,3pd) level of theory to determine the contributions by resonance and inductive effects toward the enhanced reactivity at O over C for the SN2 reaction between the formate anion and

CH3F. To separate the contribution by resonance from that by inductive effects, we applied the vinylogue extrapolation method. Our results suggest that the dominant factor is the loss of resonance from the enolate nucleophile upon going to the transition state. That loss of resonance serves to disfavor both C attack and O attack, but C attack is disfavored significantly more than O attack.

2015 Joint Southeastern/Southwest Regional Meeting 995

Assigning acetol: Simulated IR spectra using high-level ab initio methods

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CFOUR is a program that utilizes coupled-cluster techniques to perform computations in quantum chemistry on a wide range of atoms and molecules. The molecule of interest in this study involves acetol (C3H6O2), a largely reactive organic compound, which contains a carbonyl and hydroxl functional group. The purpose of this research is to assign a highly accurate IR simulation to acetol using ab initio calculations that are performed in CFOUR, compared to excellent quantitative IR spectra from the NWIR database. Acetol was geometrically optimized to an energy minimum that included no symmetry about the molecule. The methyl rotor was investigated with a series single-point energy calculations: no symmetrical conformer was found. The optimization computed was further employed to assign fundamental vibrational modes, harmonic frequencies and IR intensities, and anharmonic frequencies and intensities using the second-order Møller-Plesset perturbation theory (MP2) with the TZP basis set. The observed simulated IR spectra of this data indicated CFOUR was successful in computing accurate fundamentals in addition to combination bands and overtones for the C-H and O-H stretching bands in acetol.

2015 Joint Southeastern/Southwest Regional Meeting 996

Characterization of P3HT/graphene composites synthesized via *in-situ* GRIM methods

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Poly(3-hexylthiophene)/Graphene (P3HT/G) composites are synthesized via in-situ Grignard metathesis and characterized with an array of techniques including ^{1}H NMR, WAXS, FTIR and Raman spectroscopies and AFM. Broadening of FTIR features corresponding to the P3HT thiophene backbone and an increase in the band intensity of other vibrational modes suggest significant ground-state interactions between the P3HT and graphene moieties. An increase in the intensity of the (220) Bragg peak observed in WAXS data is indicative of enhanced interchain ordering of P3HT/G composites. AFM images of P3HT/G films provide additional evidence that the presence of graphene during polymerization has a significant effect on the organization of P3HT chains.

2015 Joint Southeastern/Southwest Regional Meeting 997

Adsorption of immunoglobulin on cellulose and chitin films using surface plasmon resonance

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Chitin and cellulose are useful as biomaterials because of their mechanical properties, abundance in nature, and biocompatibility with humans. Potential applications of chitin and cellulose include wound healing agents and drug delivery. In order to achieve and enhance these applications, it is important to understand how proteins will interact with chitin and cellulose. The goal of this study was to compare the degree to which the antibody Immunoglobulin G (IgG) adsorbs onto cellulose and chitin using surface plasmon resonance (SPR). In order to accomplish this objective, thin polysaccharide films were generated by spincoating solutions of trimethylsilyl (TMS) derivatives of the polymers. The TMS groups were then cleaved by placing the sensors over a 10% HCl solution. Changes in the resonant angle due to IgG adsorption onto these films as a function of time was tracked by SPR. Typical SPR spectra consisted of a baseline established using a phosphate buffer solution (PBS) (pH=7.4), an increase in the resonant angle arising from IgG adsorption, and finally another baseline established using PBS to remove all protein that had reversibly adsorbed. The change in the resonant angle due to adsorption was then converted to surface concentration (Γ) as a function of IgG solution concentration. Freundlich adsorption isotherms were then used to model the data for these surfaces. These isotherms suggest greater IgG adsorption onto chitin than cellulose which could be due to stronger van der Waals interactions between IgG and the acetyl groups of chitin.

Green synthesis: Characterization of saccharide coated gold nanoparticles for catalytic applications

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Gold nanoparticles (AuNPs) have gained an immense interest due to their wide applications in the fields of biomedical and pharmaceutical, which is due to their unique physico-chemical properties when they are reduced to their nanoscale size range. Here, we present a novel single step bio-friendly process for synthesis of fructose (monosaccharide), sucrose (disaccharide) and raffinose (trisaccharide) capped AuNPs, wherein saccharides are directly capped onto gold without the use of any secondary capping/stabilizing agent. Our study is mainly focused on the effect of various lengths of the saccharides in the formation and catalytic reduction activity of saccharide capped AuNPs. Characterization of synthesized AuNPs was accomplished using various analytical characterization techniques such as TEM, SEM-EDS, FTIR, and UV-Vis spectroscopy. A 4-nitrophenol reduction assay was utilized to evaluate the catalytic reduction activity of various saccharide capped AuNPs at different temperatures using UV-Vis spectroscopy. Using the spectroscopic data, rate constant for three saccharide capped AuNPs were determined followed by its activation energy and exponential factor using different equations. Utilizing the exponential factor data we were also able to calculate the kinetics of the change in entropy of the catalysis. From the kinetic data, the

catalytic reduction activity for three saccharides was, in the descending order: fructose, sucrose and raffinose AuNPs respectively. This difference in the catalytic activity is believed to be due to the size of ligand on gold surface which greatly influences the surface/volume ratio.

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Selected *f*-element coordination polymers incorporating glutarate and terephthalate derivatives

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We were able to demonstrate that the combination of the terephthalate (TP) ligand with the glutarate (Glut) entity leads to an Nd-coordination network of formula $Nd_2(Glut)_2(TP)(H_2O)_4 \bullet 17H_2O$ with little strain on the crystal lattice and quite spacious pores of ~140 $Å^3$. We learned that this compound can be recreated incorporating the 2-aminoterephthalate derivative ($TPNH_2$) resulting in a mixture of TP and $TPNH_2$, introducing a functional group into the lattice, without altering the structural properties of this coordination polymer whatsoever ($Nd_2(Glut)_2(TP)_x(TPNH_2)_y(H_2O)_4 \bullet 17H_2O$, with y= 1-x). Moreover, it turned out feasible to synthesize the pure $Nd_2(Glut)_2(TPNH_2)(H_2O)_4 \bullet 17H_2O$ analog.
While we synthesized extended series of lanthanide coordination polymers in a hydrothermal setting at 170˚C before, such as the lanthanide 2-niroterephthalates, $Ln_2(TPNO_2)_3(H_2O)_2 \bullet 2H_2O$ (Ln = Pr - Lu, except Pm), any attempt to create one of the above described compounds under such conditions with any different lanthanide element failed.
We attempted the creation of an extended series at room temperature by obtaining crystalline materials through slow diffusion. This approach enabled us to extend these coordination polymers onto the lanthanide elements Pr, Ce, Sm, and La in their trivalent states, resulting in identical structures.
Moreover, we were able to synthesize and structurally characterize uranyl-compounds that incorporate one of these ligands at a time, using the same slow diffusion room temperature approach. While the lanthanide structures form three-dimensional (3D) coordination polymers, the uranyl compounds assemble either as one-dimensional intermeshed chains ($[UO_2](TP)(H_2O)_2 \bullet 2THF$), two dimensional intermeshed sheets ($[UO_2](TPNH_2)(H_2O)_2 \bullet 2H_2O$), or 3D-lattices $Na_2[UO_2]_2(Glut)_3 \bullet 8H_2O$.

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Structural and magnetic characterization of Mn/Ln (Ln = Gd, Tb, Dy, Ho) single-molecule magnet clusters from the use of 2-(hydroxymethyl)pyridine and its bulkier derivatives

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Polynuclear clusters can behave as single-molecule magnets (SMMs) if they possess a combination of a relatively large ground state spin (S) and Ising (easy-axis-type)

magnetoanisotropy, i.e., negative zero-field splitting (D). In the last ten years, 3d-4f heterometallic complexes have been one of the fastest growing sources of SMMs due to the often large number of unpaired electrons and high anisotropy of lanthanide (Ln) ions, and often ferromagnetic coupling with transition metals. In the present study, we have explored and successfully achieved a triad of Mn/Ln cluster types from the use of 2-(hydroxymethyl)pyridine anion (hmp^-), which had proven to be a versatile chelating and bridging ligand in previous work, and its two bulkier derivatives dimethyl-hmpH (dmhmpH) and diphenyl-hmpH (dphmpH). These three Mn/Ln families have been prepared under exactly the same conditions but differing in the size and electronic effects of the two substituents. This has allowed a systematic investigation of how targeted modification of chelates can affect the structural identities and magnetochemical properties of the obtained Mn/Ln complexes.

2015 Joint Southeastern/Southwest Regional Meeting 1001

Predicted properties of LnF_4 and LnF_4^- complexes: The role of the Ln oxidation state

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The reactions of lanthanide metals and fluorine gas in a rare gas matrix are being studied by IR spectroscopy by the Reidel group in Germany. Density functional theory (DFT) was used to predict the structures and vibrations of lanthanide fluorides LnF_x to help interpret the experimental data with a focus on LnF_4 and LnF_4^- complexes. Both types of complexes were studied as the lanthanides exist in the +3 and, in some cases, the +4 oxidation state. The LnF_4^- are formed by adding F^- to $Ln(III)F_3$. The geometries were optimized using DFT with the B3LYP exchange-correlation functional, the DZVP2 basis set on F and the Stuttgart basis set and effective core potentials for the Ln. The vibrational frequencies, spin densities, electron affinities, and fluoride affinities were calculated. The results provide additional insights into various properties of the LnF_4 complexes and the oxidation state of the lanthanides.

2015 Joint Southeastern/Southwest Regional Meeting 1002

Synthesis of red, green, and blue phosphors for solid state lighting

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The synthesis of red, green, and blue phosphors was accomplished by doping Eu^{3+}, Tb^{3+}, and Eu^{2+} respectively into earth abundant nanospinel hosts passivated by β-diketonate ligands. The ligands as well as the small size of the host (3-4 nm) allows for efficient energy transfer, reducing the amount of lanthanide ions required for high quantum efficiencies. By adding β-diketonate ligands to the surface of the nanospinels, they act as a photosensitizer capable of harvesting UV and blue light. In addition to having a favorable energy overlap with the lanthanides, the ligands also possess a

much larger absorption cross section leading to highly efficient energy transfer resulting in highly luminescent phosphors. The ligands on the surface of the particles also help to solubilize the nanophosphors, making it viable for them to be integrated into LED epoxy lens. The ligands on the surface of the particles also help to solubilize the nanophosphors, making it feasible for them to be integrated into LED cladding material. By choosing Eu^{3+}, Tb^{3+}, and Eu^{2+}, the whole visible spectrum can be accessed making them viable options as RGB phosphor for white light.

2015 Joint Southeastern/Southwest Regional Meeting 1003

Computational study of metallo-bis(dithiolene) complexes. Effect of d-electron count on the central twist angle between two MS_2 planes; a surprising discovery for d^9 systems

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Late transition metals with d-electron counts ranging from six to ten coordinated by two bidentate ligands have received considerable attention because of their interesting electrochemical, magnetic, and structural properties. Metallo-bis(dithiolene) complexes, $[M(mnt)_2]^{n-}$ (M = Ni, Pd, and Pt with n = 0, 1, 2, 3; M = Cu with n = 2), are perhaps the most studied members of this class of compounds and are the focus of our current work. Electronic structure calculations coupled with existing crystal structure data reveals a wide diversity of molecular geometries for these compounds. Specifically, the twist angle between the two MS_2 planes was found to be a function of the d-electron count on the metal, spanning from 0^o (planar d^6, d^7, and d^8), to 42^o (d^9), to 90^o (pseudo-tetrahedral d^{10}). The range of geometric structures can be explained in terms of varying electronic and nuclear repulsion energies and through analysis of the molecular orbitals. Structures of the d^9 members of this series are of particular interest because of the unusual twist angle and because there have been very few solid state structures reported. In addition, we report on the structural and thermochemical aspects of the ion-pairing between one member of this series (M = Ni and n = 3) and two equivalents of $K(diglyme)^+$.

2015 Joint Southeastern/Southwest Regional Meeting 1004

New annulated N-heterocyclic carbenes and their transition metal complexes

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In the last few decades N-heterocyclic carbenes (NHCs) have emerged as a powerful class of carbon-based ligands. Owing to their unique electronic and steric properties, they have been incorporated in a large variety of catalytically active metal complexes. One of the strategies that have been used to modify the ligand properties of NHCs is annulation with different carbo- and heterocyclic groups. It has been shown that annulation in 4-5 position of the imidazole ring significantly influences the stability and the σ-donor/π-acceptor properties of the carbene species, and this may be used as a versatile tool for the fine-tuning of their electronic properties. Herein, the synthesis and structural characterization of a new class of fused N-heterocyclic carbene ligands with a

rigid bidentate architecture will be reported. Complexes of type [M(COD)Cl] and [M(CO)2Cl] (M=Rh and Ir) were prepared and characterized using spectroscopic and crystallographic methods.
The results of our preliminary catalytic studies using these new complexes will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 1005

Synthetic analogs of the nickel superoxide dismutase catalytic site

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Reactive oxygen species (ROS), such as superoxide ($O_2^{\bullet-}$), hydrogen peroxide, and hydroxyl radicals, are formed as byproducts of the metabolism of oxygen in aerobic organisms. Buildup of ROS can lead to oxidative stress and cell damage, thus aerobic organisms have developed mechanisms for eliminating these harmful species. Superoxide Dismutase (SOD) are a family of metalloenzymes that regulate $O_2^{\bullet-}$ levels in aerobic organisms by facilitating the disproportionation of $O_2^{\bullet-}$ to atmospheric oxygen and hydrogen peroxide. Nickel Superoxide Dismutase (NiSOD) is a recently discovered member of the SOD family of enzymes. The reduced form of NiSOD has the nickel(II) metal center being coordinated by one primary amine nitrogen, one carboxamido nitrogen, and two thiolato sulfur donors to form a square-planar coordination motif. In the oxidized form, the metal center gets oxidized to nickel(III), and undergoes a geometry change to square-pyramidal through axial ligation by a neighboring histidine. In this presentation, I will discuss the synthesis and characterization of low molecular weight, nitrogen-rich analogs of the active site of NiSOD. They have been designed to mimic both the square-planar and square-pyramidal geometric forms of NiSOD. Tuning of the metal center to better catalyze the disproportionation of $O_2^{\bullet-}$ is attempted through various pyridine and quinoline substitutions of the ligand's nitrogen donors. These modifications will provide a better understanding of the affect of the steric bulk on the Ni(II)/Ni(III) couple. These biomimetic studies utilize functional mimics of native NiSOD to better understand the mechanism of catalytic disproportionation of $O_2^{\bullet-}$.

2015 Joint Southeastern/Southwest Regional Meeting 1006

Biomimetic models of ni-superoxide dismutase: Exploring the impact of N rich primary coordination sphere

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Superoxide anion radicals ($O_2^{\bullet-}$) are cytotoxic byproduct of aerobic respiration, which if unregulated leads to a variety of diseases such as cancer, neurodegenerative disorders, diabetes etc. The aerobic organisms develop Superoxide dismutase (SOD) as a unique enzymatic defense system against these anionic radicals. Superoxide dismutases are metalloenzymes that quench $O_2^{\bullet-}$ via alternate oxidation and reduction into dioxygen and H_2O_2, respectively. This catalytic mechanism utilizes electron transfer characteristic (changing different oxidation states) of first row transition metals. NiSOD is the recent entry in the SOD family. The primary coordination sphere of NiSOD involves unique ligand set consists of amino terminus, peptide nitrogen and cysteinate sulfur atoms. The NiSOD possess several different structural features than other SODs,

for example additional histidyl N coordination in its oxidized state, presence of reactive Ni-S coordination etc. Hence for better understanding of these special features of NiSOD ligation, this work will focus on modeling the structure and mechanism of NiSOD by molecular complexes. In this work, we present synthesis and characterization of three different tetradentate and one pentadentate ligand framework containing pyridyl/quinoline/amine variants. Various substitutions in the pyridine ring were also used in parent ligand framework that will help us to understand the effect of various electron withdrawing and electron donating group towards $O_2^{\bullet-}$ dismutation mechanism. Synthesis, Characterization and preliminary results of reactivity studies of these metal complexes will be discussed in this presentation.

2015 Joint Southeastern/Southwest Regional Meeting 1007

Pincer-type N-heterocyclic carbene complexes of late transition metals: Synthesis, characterization, and reactivity studies

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N-heterocyclic carbenes (NHCs) have opened up a new class of spectator ligands in organometallic catalysis since the first isolation of a stable NHC[1] and first application of their complexes as catalysts.[2] Despite the extensive application of TM-NHC complexes in reduction catalysis and cross-coupling reactions, the oxidation chemistry of them have stayed far less developed.

Pincer-type bis-NHCs are the most abundant class of carbene ligands due to a facile synthesis by a variety of linkers between NHC units. An important linker that can act as a donor group in the structure of TM-NHC complexes is pyridyl group. Contrary to the strong electron donating properties of carbene and pyridine, the structurally characterized homoleptic complexes of these ligand with less bulky groups on imidazole are restricted only to a Ru[3] and a Ni[4] complex. The main drawback of developing new complexes has been attributed to the low solubility of the imidazolium units and the corresponding complexes.

Herein we report the one step synthesis of homoleptic dinuclear Cu(I) complexes of IMe^{CNC} and IEt^{CNC} ligands using the corresponding imidazolium salts and a Cu(I) precursor. The single crystal X-ray analysis confirms the ligation of each Cu(I) center by two carbon donors from two different NHC molecules. The Cu – Cu distance (2.804 Å) represents a single bond between to copper centers. The closest nitrogen to each Cu(I) lies at 2.463 Å which is longer than the distance expected for a single bond between two elements. The electrochemical DPV studies confirm the presence of two oxidation peaks due to the generation of a mixed-valence Cu(II)Cu(I) and a dinuclear Cu(II) species. The presence of pyridine groups as hard-atom donors in structure can play a role in stabilizing a higher oxidation state of copper which are of relevance in oxidation chemistry.

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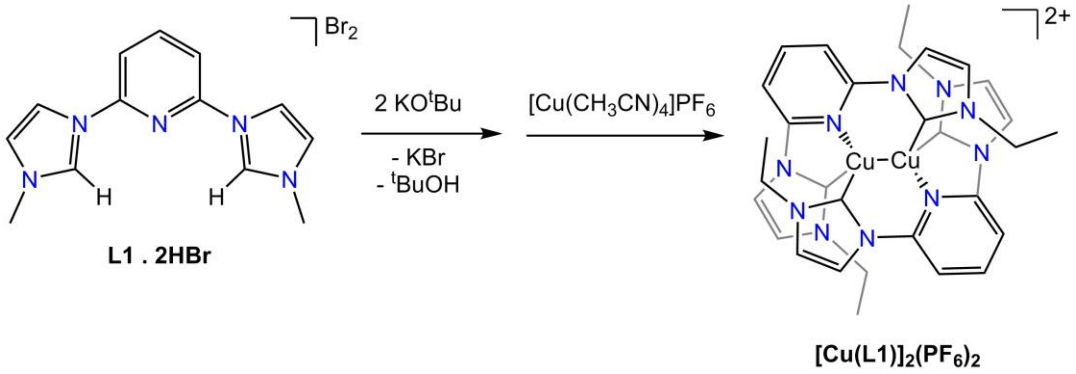

2015 Joint Southeastern/Southwest Regional Meeting 1008

Development of a turkey DNA allele frequency database

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Data for a forensic DNA database for eastern turkey (*Meleagris gallopavo*) in Tennessee is examined. PCR reactions involving 13 loci were used to analyze samples from 179 turkey collected from across Tennessee. Results indicate the tests and database are appropriate for forensic applications in Tennessee. This database is also applicable for forensic applications in adjacent states which do not have a database for eastern turkey.

2015 Joint Southeastern/Southwest Regional Meeting 1009

Analysis of e-liquids

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With the increasing research on the dangers of cigarettes, people are looking for a safer alternative to smoking. Electronic Cigarettes were introduced in the early 2000's to serve this purpose. The e-cigarette works by heating a coil that vaporizes a vegetable glycerin and propylene glycol based liquid, which can contain nicotine or flavor additives. The vapor is then released through a mouthpiece to be inhaled by the user. Many e-cigarette companies claim that the use of e-cigarettes is completely harmless because of combustion of the organic liquids would cause the inhalation of only water vapor and carbon dioxide along with the flavors and nicotine. Companies also advertise their products to help smokers quit smoking. Recently, "vaping" has grown increasingly popular especially with minors since several states still allow the sale of e-cigarettes to minors. Studies have shown that more teenagers are vaping, and that it may lead to the use of real cigarettes. A Simultaneous Thermal Analyzer is used to simulate the reaction that occurs inside the e-cigarette. The resultant vapors are transferred to an infrared spectrometer for analysis. Early results indicate that the vapors released are not simply carbon dioxide and water, so the liquids do not undergo combustion as claimed. Further analysis must be done in order to determine exactly what is being released by these e-cigarettes, and their potentially harmful effects on the human body.

2015 Joint Southeastern/Southwest Regional Meeting 1010

Analysis of flathead catfish for mercury content in Lake Columbia, AR

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The consumption of fish is recommended because it is a good source of omega-3 fatty acids, which have been associated with health benefits due to its cardio-protective effects. All fish contain traces of mercury. However, some fish contain higher levels of mercury that may harm an unborn baby or young child's developing nervous system. Mercury occurs naturally in the environment and can also be released into the air through industrial pollution. Mercury falls from the air and can accumulate in streams and is turned into methylmercury in the water. Methylmercury can be harmful to an unborn child and young children. Fish absorb methylmercury as they feed and accumulate it in their bodies.
Lake Columbia is a 3,000-acre impoundment stretching for six miles along Beech Creek about six miles northwest of Magnolia in south central Arkansas. It was constructed in 1986 by the Arkansas Game and Fish Commission, and is an excellent fishing spot for the locals. Currently Lake Columbia is placed under fish consumption notice issued by Arkansas Game and Fish Commission and Arkansas Department of Environmental Quality, which was established in early nineties.
Nine flathead catfish were collected from Lake Columbia, AR. The fish were digested and analyzed for mercury using Buck Scientific mercury analyzer.

2015 Joint Southeastern/Southwest Regional Meeting 1011

Carbon 13NMR studies of saturated fatty acids bound to bovine serum albumin

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This research investigates the effect of varying the length of fatty acids bound to Bovine Serum Albumin (BSA) in relation to binding sites. The binding properties of BSA have been well studied but further investigation and information can be gained by understanding the binding sites involved between varying fatty acids and BSA. Currently, octanoic and palmitic acid have been analyzed using carbon 13NMR to determine and understand BSA binding sites. Eventually, this research seeks to investigate the realtionship between fatty acids and different breeds of cattle.

2015 Joint Southeastern/Southwest Regional Meeting 1012

Determination of effect of chewing rate on releasing xylitol from gum sticks

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Xylitol is a naturally occurring sweetener that is often used as a substitute to glucose in sugar-free gum. In humans, xylitol consumption has beneficial properties such as fighting certain harmful bacteria in the body and boosting salvia production in order to fight plaque build-up. However, xylitol is dangerous to dogs because it causes them to exhibit gastrointestinal problems and acute liver failure. Sugar free gum samples

containing xylitol were chewed at rates of 60 times per minute, 30 times per minute, and 120 times per minute for a certain period of time. A novel xylitol extraction method was used to collect remaining amount of xylitol in chewed gum samples and it was analyzed by GC/MS with direct aqueous injection.

2015 Joint Southeastern/Southwest Regional Meeting 1013

Purification and clean-up of glycans

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According to the American Academy of Allergy, Asthma, and Immunology, millions of people in the U.S. are affected with seasonal allergies, with grass pollens contributing the most. Glycoproteins, or proteins with attached carbohydrates, are thought to play an important role in the immunogenic response. There are currently 13 groups of grass allergens, and groups 1,4, and 11 have been found to contain N-linked glycans. Since plant N-glycans are somewhat conserved between species, precise characterization of proteins/glycans is needed in order to better understand the immunogenic response. Characterizing the pollen proteins and glycans could result in more precise therapeutics for seasonal allergies.

2015 Joint Southeastern/Southwest Regional Meeting 1014

Stability-indicating UPLC-MS/MS assay for 1960's Eli Lilly and Company pharmaceuticals in dosage forms

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Four 1960's pharmaceuticals, each approximately 50 years old, were analyzed in dosage form via ultra performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) in order to assess the respective stability of each pharmaceutical sample. More specifically, the active ingredients of each pharmaceutical sample were quantified and compared to the expected mass of active ingredient reported; this allowed for an assessment of drug expiration and lifetime. Expiration date validation was assessed in relation to the definition of expiration date, noting that valid pharmaceuticals must have >90% of the active ingredient remaining. The pharmaceuticals analyzed (along with the respective active ingredients) are as follows: Ilosone (erythromycin), Darvon (propoxyphene), Darvon-65 (propoxyphene, aspirin, caffeine, phenacetin), and V-Cillin K (penicillin-V). Individual dosage forms of each pharmaceutical were massed, transferred to designated volumetric glassware, and dissolved; upon complete dissolution of the dosage form, the solution was then 0.2µm filtered, diluted gravimetrically, and analyzed using the developed UPLC-MS/MS assay. In some cases, it appears that significant percentages of an original drug dose can persist in stoppered vials in a dark environment for up to a 50 year time period.

2015 Joint Southeastern/Southwest Regional Meeting 1015

Analysis of urine organic acids via GC/MS-based metabolomics to determine the effect of diet on urine composition

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How does diet influence our health? As it is well-known, a college student's diet is notorious for being unbalanced. Researchers are contemplating the relationship of diet and health through the use of GC/MS-based metabolomics which is commonly used to diagnose metabolic disorders. Gas chromatography/mass spectrometry (GC/MS) is utilized to study the composition of urine due to its high sensitivity towards multiple factors that affect the urine's composition- i.e. diet, age and gender.[1]
The multi-step undergraduate research project (1) focuses on how the organic acid profile of urine changes based on diet via the use of GC/MS coupled with a purge-n-trap autosampler, (2) determines the significance of the suspected alterations, and (3) correlates findings with the diagnosis of common metabolic disorders. This presentation summarizes the method development and preliminary results.
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2015 Joint Southeastern/Southwest Regional Meeting 1016

Discrimination of carbohydrate isomers as transition metal adducts using ion mobility spectrometry and tandem mass spectrometry

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Carbohydrates are responsible for many functions in living organisms, including their purpose as an energy source, influence of protein structure and stability, as well as a factor in metabolism and cell signaling. In order to comprehend the functionality of carbohydrates, oligosaccharide structures must be fully deduced. Mass spectrometry (MS) has been applied to the study of carbohydrates for many years. However, the complete characterization of these molecules is complicated by the presence of varying isomers. Unlike traditional methods, such as nuclear magnetic resonance spectroscopy, high performance liquid chromatography, and capillary electrophoresis, MS separations require much less time and sample. Here, we explore the effects of five Period 4 transition metal ions (Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) and their corresponding electron transfer (ET) products ($Fe^{+\bullet}$, $Co^{+\bullet}$, $Ni^{+\bullet}$, $Cu^{+\bullet}$ and $Zn^{+\bullet}$) as charge carriers for carbohydrate isomer discrimination by ion mobility spectrometry (IMS) and tandem mass spectrometry (MS/MS). These metals were chosen because they have been found to display interesting fragmentation patterns. Four pentasaccharide isomers (lacto-N-fucopentaose I, lacto-N-fucopentaose II, lacto-N-fucopentaose III, and lacto-N-fucopentaose V) were studied that have proven difficult to distinguish by both IMS and MS/MS. In total, 40 carbohydrate/metal adduct species were obtained. Experiments were performed using a quadrupole time-of-flight hybrid mass spectrometer (Q-TOF-MS) coupled with a traveling wave ion mobility spectrometer and equipped to carry out gas-phase ion-ion ET reactions.

2015 Joint Southeastern/Southwest Regional Meeting 1017

Analysis of electrolyte changes in athletes using ICP

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Electrolytes are charged minerals in the body that maintain blood chemistry, hydration, blood acidity, and aid in muscle action. They aid in hydration and prevent muscle cramping, especially in athletes. Common electrolytes are calcium, chloride, magnesium, phosphorus, potassium, and sodium. In this study calcium, potassium, and sodium were the target electrolytes studied. The objective of this experiment was to determine electrolyte changes in elite Division II football athletes during regular preseason practices. Sweat samples were collected from athletes during warm-ups, at the mid-point of practice, and at the conclusion of practice at each regular preseason practice over the course of fourteen practices. The samples were analyzed using the Inductively Coupled Plasma (ICP) Optical Emission Spectrometer utilizing the *Standard Methods for the Examination of Water and Wastewater 22nd Edition's* 3120 B. Inductively Coupled Plasma (ICP) Method.
During warm-ups, calcium ranged from 0.000179mg–0.0532mg, potassium from 0.00101mg-0.0677mg, and sodium from 0.00137mg-0.205mg. At the mid-point of practice calcium ranged from 0.00126mg-0.111mg, potassium from 0.00106-0.0901mg, and 0.0107mg-0.314mg. At the conclusion of practice calcium ranged from 0.00135mg-0.0697mg, potassium from 0.00167mg-0.103mg, and sodium from 0.0104mg-0.332mg. These data will be used to create electrolyte replacement strategies for athletes. Further studies include expanding sample size, looking at different sports, determining the impact of time on electrolyte loss, and comparing electrolyte loss in male and female athletes.

Analysis of pen inks using a portable Raman spectrometer

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Forensic examinations of questioned documents often involve chemical and physical analysis of pen inks. Raman Spectroscopy has been often used for ink analysis because of the rapid results given with no destruction of the evidence. The objective of this work is to assess whether Raman Spectroscopy is appropriate to differentiate different types of commercial ballpoint blue pens. Because inks are complex mixtures consists of unknown components, identifying specific ink components using Raman Spectroscopy can be a difficult task. Instead, spectral fingerprinting comparison is preferably used to differentiate ink in forensic contexts. This involves examining the overall pattern of the spectra, band intensities, and differences in the position of the band. Raman spectra using 785 nm laser wavelength showed the differences in the vibrational frequencies of each blue pen. The shapes of the spectrums varied, as did the number of peaks. At the 785 nm wavelength, the blue pen inks absorbed at about 1,000 cm^{-1}. Although the 532 nm laser gave individual bond vibrations, differences in the pen inks were poorly distinguished. Laser wavelengths of 785 and 532 nm are compared in terms of the effect of paper and the laser power on the band shape and spectral intensity.

2015 Joint Southeastern/Southwest Regional Meeting 1019

Plant uptake of commonly prescribed pharmaceuticals and Splenda® in reclaimed water by water lettuce (*Pistia stratiotes*)

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Pharmaceuticals, personal care products, and artificial sweeteners have become prevalent in wastewater systems because of the high consumption rates of the population and the limitations of traditional water treatment. The persistence of these organic contaminants through the wastewater treatment system has been a continuous area of research, including how to modify the treatment process to effectively remove emergent contaminants. Constructed wetlands are a secondary or tertiary treatment option that uses the biological degradation process of plants, sunlight, and other veritable substrates as the treatment process. Using Water Lettuce (Pistia stratiotes) as a single variable, plants were exposed to reclaimed water under monitored conditions to test the capability of a plants uptake of a list of target compounds, including commonly prescribed drugs and Splenda. A SPE-HPLC-MS with a HESI-II ionization source was used to analyze both water samples and plant extracts after three weeks of continued exposure in the test habitats. The resulting plant extractions exposed to the reclaimed water showed detectable amounts for five of the six target compounds.

2015 Joint Southeastern/Southwest Regional Meeting 1020

Spectrophotometric determination of concentration of phosphates and nitration in vegetables, soils, fertilizer, and water samples by molybdenum blue method

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A simple and sensitive spectrophotometric method has been developed for the determination of concentration of phosphates and nitrates in various vegetables, soils, water, and fertilizers. The results will be compared to determine whether a higher soil or fertilizer content results in higher phosphate or nitrate content in the plant and to see how they correlate. The increased concentration of phosphate is the key factor for richness of nutrients in a lake or other body of water which causes an abundant growth of plant life and death of animal life from lack of oxygen. Thus the importance of determination in water in this experiment. Nitrate serves as an essential plant nutrient helping with tissue development and building immune systems, and seed production. The amount of phosphates and nitrate is determined by molybdenum blue phosphorous method and UV- visible spectrophotometer. This method is based on the formation of phosphomolybdate complex added with the added molybdate followed by the reduction of the complex with hydrazine sulfate in aqueous sulfuric acid medium. This method was observed at 800-900 nm in the concentration range 0.1- 11 ppm. The effect of time on the formation of phosphomolybenum blue complex and addition of the order of the reagents was also studied.

2015 Joint Southeastern/Southwest Regional Meeting 1021

Monitoring click reactions on titanium dioxide using ATR infrared spectroscopy

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Because many of the resources used to currently meet our energy needs cause climate change, it is important to increase the efficiency of cleaner, renewable energy sources such as dye-sensitized solar cells. The goal of this project is to increase the efficiency of this conversion process by controlling the orientation and surface concentration of the dye molecules on the surface of the titanium dioxide to favor electron injection to the conducting band of the titanium dioxide. Dye molecules are covalently bound to the surface of the titanium dioxide by a click reaction between a surface-bound azide and a alkyne tagged dye complex. Silane chemistry is used to prepare an azide terminated monolayer, followed by derivatization by the click reaction. These reactions are monitored *in situ* by preparing a film of titanium dioxide particles on a zinc selenide internal reflection element contained in a flow cell and acquiring attenuated total reflectance infrared spectra as a function of time. The presence of the monolayer is detected by the azide stretch at 2100 cm^{-1}. A solution of the target alkyne and a copper(I) catalyst are allowed to stir at room temperate for 16 hours and then is introduced through the flow cell to react the alkyne tagged target to the surface-bound azide. Upon reaction, a decrease in azide stretch is observed as the reaction proceeds. These reactions both proceed by first order kinetics than can be measured by integrating the area under the azide stretch. Several factors have been investigated to help increase the reproducibility of the click reaction.

2015 Joint Southeastern/Southwest Regional Meeting 1022

Mineralized springs of Lampasas, Texas

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Nine springs in and around Lampasas, Texas were sampled over the course of a year and profiles of each spring were constructed. When in proximity to the springs, a strong smell of ‘rotten egg’ is evident and permeates the area. As the springs are generally located in karst environments, the source of the smell is puzzling. Based on the geology of the area, there are no sulfur bearing minerals, indicating the origins of the waters is far removed from Lampasas. Specifically, the waters were analyzed for iron, lead, zinc and copper using Inductively Coupled Plasma-Mass Spectrometry to aid in the determination of the origin of the sulfur. Additional analyses done include; pH, sulfate, carbonate, and hardness. The complete characterization of these springs will assist in the delineation of the source of mineralization in the area and help in the determination of what controls the distribution of the highly mineralized ground water occurrences versus normal karst springs.

2015 Joint Southeastern/Southwest Regional Meeting 1023

Detection of microbial volatile organic compounds from *Cryphonectria parasitica* species by gas chromatography, mass spectrometry, and pattern recognition

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Microbial volatile organic compounds (MVOCs) are either intermediate or end products of organism metabolic pathways, and have been involved in different biological processes such as serve as biomarkers of a disease. Recently, MVOCs produced by virulent and hypo-virulent *C. parasitica* isolates have been studied by Headspace Solid Phase Microextraction (HS-SPME) with an 85 µm Carboxen/Polydimethylsiloxane (CAR/PDMS) fiber coupled with Gas Chromatography-Mass Spectrometry (GC-MS). Herein, we report further studies on facts that can alter the MVOCs profile such as temperature and growth media. Moreover, the MVOCs profiles associated with fungi life circle were also detected. And finally, data pattern recognition was achieved by chemometrics.

2015 Joint Southeastern/Southwest Regional Meeting 1024

The relation of synthesis time and calcination temperature to resultant size of TiO_2 nanoparticles

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With the increased presence of organic contaminants in drinking water, it has become increasingly necessary to find affordable and viable alternatives for water purification applications. Nanoparticles (NPs) with their size and resultant large surface area offer new pathways to achieve successful filtration. Titanium oxide (TiO_2), as a widely available, non-toxic material, is optimal for use as a filtration medium. In this study, TiO_2 NPs were prepared by sol-gel method. Synthesis time and calcination temperatures were varied, and change in size of NPs was analyzed by X-Ray Diffraction Spectroscopy. The direct relationship between calcination temperature and particles size was observed: low calcination temperatures lead to presence of smaller NPs, while higher temperatures produced larger NPs.

2015 Joint Southeastern/Southwest Regional Meeting 1025

Improving NOE methods in obtaining inter-proton distances for 3-methylpiperidine

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NOE (the Nuclear Overhauser Effect) is a method that determines inter-proton distances by utilizing the magnetic effects of two proton nuclei. While current methods of converting PANIC intensities on a Noesy spectra to distances works well for rigid molecules, small molecules (such as 3-methylpiperidine) end up producing large errors. This is due to low intensities and anti-phasing peaks on the spectra as a result of the molecule tumbling too fast in solution. We describe our attempts at improving these and

minimizing percentage errors by using temperature and viscosity manipulation of the solvent containing 3-methylpiperidine.

2015 Joint Southeastern/Southwest Regional Meeting 1026

The effects of vegetated mats on nutrient levels of storm water retention ponds

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Storm water retention ponds (SWRP) are used to enhance water quality by allowing sediments, nutrients and other pollutants to settle and/or be absorbed by surrounding vegetation. It has been shown that increased vegetation surrounding SWRP increases the efficiency of the pond[1]. By deploying floating vegetation mats within the pond, it was hypothesized that the rate of efficiency would increase with the addition of vegetation. To test this hypothesis, samples of runoff and pond input / outputs were collected from four campus stormwater ponds before and after the deployment of floating vegetation mats. In addition, a small scale experiment was conducted comparing the performance of vegetation mats versus surface coverage using eighteen 440-gallon pond simulation tanks. Samples from tanks were collected biweekly and analyzed using ion chromatography to determine the concentrations of phosphate and nitrate as indicators of nutrient concentration. General water quality parameters such as pH, turbidity, temperature and TDS were also monitored. This presentation will specifically address the results of the small-scale experiment. Further studies investigating vegetative impact on artificially increased metals and nutrient loads are anticipated.

1. Davis, *et al*. *Water Environ. Res*., **2003**, *75*, 73-82.

2015 Joint Southeastern/Southwest Regional Meeting 1027

Photoacoustic spectroscopy with SF_6, an optically thick greenhouse gas

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Photoacoustic spectroscopy was used to test the photoacoustic properties of sulfur hexafluoride, an optically thick and potent greenhouse gas. Detection of trace amounts of the gas was also implemented. The conditions in which the gas was tested, gas cell length, temperature, concentration, and power of the laser, were varied in order to determine their effect on the photoacoustic signal, and an ideal condition to detect trace gas amounts. A detection limit of 2.86 ppb was determined for SF_6.

2015 Joint Southeastern/Southwest Regional Meeting 1028

A kinetic study of the dependence of ascorbic acid concentration on temperature and time

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Vitamin C, containing ascorbic acid ($C_6H_8O_6$), is a water-soluble vitamin and an immensely vital nutrient for the human body. Research shows that different processing techniques, including traditional and flash pasteurization, cold pressing, and fresh squeezing (raw), affect the degradation rate of ascorbic acid in juice. In this study, a series of iodometric titrations and back titrations were performed to determine how much ascorbic acid remains in flash pasteurized orange juice after being stored at 8°C, 23°C, and 40°C over 24-hour periods. At each temperature, the concentration of ascorbic acid was calculated at 1, 2, 4, 6, 16, 18, 20, 22, and 24-hour increments. The results showed that ascorbic acid degradation followed zero kinetics for the back titration method at 23°C, as well as for the traditional titration method at 40°C, which corresponds to results obtained by other similar research studies. Complications with the iodometric titration techniques led to conflicting results in the determination of the kinetic order of the reaction at several of the temperature and time points. Future work includes studying the effectiveness of lowering the concentration of iodine tincture utilized in the traditional titration method, completing the data set for the iodometric back titration at 8°C, and modifying the back titration method from a redox reaction to an acid-base reaction. Once the best titration technique has been determined, the kinetics of the degradation of ascorbic acid in orange juice processed by other methods will be explored.

2015 Joint Southeastern/Southwest Regional Meeting 1029

Wettability of mercaptoundecanoic acid and dodecanethiol on gold

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In solutions of ethanol, akanethiols adsorb onto the surface of gold in an organized monolayer. This study evaluated the composition and organization of 11-mercaptoundecanoic acid (MUA) and dodecanethiol (DDT) mixed self-assembled monolayers (SAMs). Gold slides were cleaned with ethanol, acetone, and ozone. One set of gold slides were immersed in a solution of MUA for eight hours. After rinsing with ethanol and air drying, they were placed in a solution of DDT for eight hours. This process was repeated in reverse order, where the sample was initially immersed in DDT and then in MUA. A third approach was used to grow mixed monolayers, where gold slides were immersed in solutions containing both MUA and DDTwith varied concentrations.
For all samples, surface wettability was measured using an optical tensiometer. Cassie's equation was applied to these values to determine the percentage of MUA & DDT in each film. The samples were also investigated by an open-air polarization-modulation infrared reflection/absorption spectrometer (PM-IRRAS). With this data, the packing of monolayers and the presence of alkyl and methyl groups could be determined.
MUA forms a disorganized layer on its own. In the presence of DDT, the MUA film order and composition were not reproducible. There were no detectable patterns in adsorption. The percentages of MUA and DDT found in the films were erratic, often changing drastically on slides immersed in the same solutions and in the same manner.

2015 Joint Southeastern/Southwest Regional Meeting 1030

Convex solubility parameters for polymers

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Solubility parameters are certain measurable quantities that are observed to influence the ability of a solvent to fully dissolve a polymer. Current theory partitions the intermolecular forces between dispersion, polar, and hydrogen bonding interactions, thereby generating a three-dimensional solubility parameter space. The Hansen solubility parameters of a polymer are taken to be the center of a sphere obtained from the best fit of the coordinates of good solvents in the parameter space. Investigations of several polymers (lignin, polyethersulfone, and bitumen) show that the convex hull of all known good solvents in the three-dimensional parameter space also gives a meaningful interpretation of the solubility region. Several methods for computing the convex solubility parameters of a polymer from the convex solubility region are described

2015 Joint Southeastern/Southwest Regional Meeting 1031

Experimental and theoretical gas-phase studies of $Fe(NO_3)_4^-$ and $Co(NO_3)_3^-$ anion clusters

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Metal nitrates are common precursors used in the synthesis of metal oxides for catalysts, thin films, and nano-materials. We studied the formation of metal oxide anions from dissociation of gaseous $Fe(NO_3)_4^-$ and $Co(NO_3)_3^-$ using electrospray ionization (ESI), and collision-induced dissociation (CID) in a tandem quadrupole mass spectrometer. Energy-resolved mass spectrometry (ERMS) was employed to measure dissociation energies for the formation of specific fragment ions. Both $Fe(NO_3)_4^-$ and $Co(NO_3)_3^-$ showed sequential loss of $NO_2^\bullet$ to yield metal-oxide nitrate anion complex fragments. $Fe(NO_3)_4^-$ also showed loss of $NO_3^\bullet$ via electron transfer from a nitrate ligand to the metal, but reduction was not observed for $Co(NO_3)_3^-$. The $Fe(NO_3)_3^-$ fragment did not undergo further reduction, but showed sequential elimination of $NO_2^\bullet$.

2015 Joint Southeastern/Southwest Regional Meeting 1032

Convergent quantum chemistry for challenging dispersion-dominated non-covalent dimers

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Five homogeneous dispersion-dominated dimers, composed of acetylene (HCCH), diacetylene (HCCCCH), cyanogen (NCCN), diphosphorous (P_2), and 1,4-diphosphabutadiyne (PCCP), were used to study the basis set convergence of the interaction energy (E_{int}) and the higher-order correlation corrections to E_{int}. Each dimer was composed of two identical monomers at their experimental geometries, with the exception of the 1,4-diphosphabutadiyne monomer, for which the geometry was optimized using a density functional method. Each dimer was examined in three different configurations – cross (X), t-shaped (T), and parallel-displaced (PD) – and the

distance between the two monomers in each dimer was allowed to take on three different values roughly corresponding to the potential energy minima at the MP2, CCSD, and CCSD(T) levels of theory. Single-point energy computations were performed on each monomer and each dimer, using MP2, CCSD, and CCSD(T), in conjunction with a series of Dunning's correlation-consistent basis sets augmented with diffuse functions on all non-hydrogen atoms (cc-pV*X*Z for H and aug-cc-pV*X*Z for C, N, and P, where *X*=5,6; denoted ha*X*Z). The interaction energy, both counterpoise- and non counterpoise-corrected, was computed for each system and extrapolated to the CBS limit, using a variety of extrapolation schemes. This estimate was compared to previous estimates of the CBS limit extrapolated from values calculated with the aTZ and aQZ basis sets. Additionally, higher-order correlation effects were assessed using CCSD(T) with the same series of ha*X*Z basis sets. The current estimate of E_{int} at the CBS limit varied from the previous estimates of the CBS limit by as much as 0.1 kcal/mol at both the CCSD(T) and CCSD levels and 0.09 kcal/mol at the MP2 level, while the higher-order correlation values varied less between extrapolation schemes, with the CCSD(T)/MP2 term varying by a maximum of 0.07 kcal/mol and the CCSD(T)/CCSD term varying by a maximum of 0.01 kcal/mol.

2015 Joint Southeastern/Southwest Regional Meeting 1033

Practical methodologies towards analytical analysis of iron nickel phosphides

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Before the surface chemistry of a mineral can be studied, it must be prepared in such a way that it presents an optimized surface to the analytical instrument used. In the case of reflection-absorption infrared spectroscopy, the surface of the sample must be polished to a surface defect size of less than 1 micron and vacuum systems, liquid-solid cells and purge lines must be utilized to eliminate undesirable background signals and allow for *in situ* measurements. To get to this state, a variety of methods must be used in conjunction with knowledge of properties such as the phase diagram of the mineral. The meteoric mineral schreibersite ($(Fe,Ni)_3P$) was studied as a source of prebiotic phosphorous, but natural samples are expensive and difficult to process, so creating a synthetic sample was desirable. The metallurgical properties of the mineral were studied, samples were pressed from meshed powder, sintered in a tube furnace, and polished. These processed samples then had mounts designed that allowed for a variety of measurement conditions. The preparation of schreibersite samples as well as the design and manufacture of the sample mounts will be discussed at length.

2015 Joint Southeastern/Southwest Regional Meeting 1034

Reactivity of aqueous thorium(IV) and plutonium(IV) clusters

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An understanding of the behavior of metal ions in solution is important to controlling the formation of complexes and for improving chemical separations. Actinides including plutonium and thorium are of particular concern because they are by-products of

nuclear fission in nuclear reactors. Polynuclear thorium (IV) complexes have previously been synthesized and studied computationally and a good agreement between experiment and the calculations was observed for neutral close ion pairs. We are studying the monomers which form the known polymers via condensation reactions. The +1 and +2 monomers of thorium (IV) and plutonium (IV) in water are $M(OH)_2(H_2O)_6^{2+}$, $M(OH)_2(H_2O)_7^{2+}$, and $M(OH)_3(H_2O)_5^{+}$. After initial hydrolysis, the hydroxides are substituted by the selenates $HSeO_4^-$ and SeO_4^{2-}. The calculations were performed at the level of density functional theory (DFT) with the B3LYP exchange-correlation functional and the cc-pvdz-PP for Th, Stuttgart for Pu, DZVP2 for O and H, and DZVP for Se basis sets. The COSMO self-consistent reaction field intrinsic solvation model was used to predict free energies in aqueous solution including pK_a's.

2015 Joint Southeastern/Southwest Regional Meeting 1035

Molecular dynamic simulations to study the self assembly of fullerene molecules on graphene

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Graphene and other carbon nanomaterials, such as fullerenes and carbon nanotubes, have a wide range of application within the medical and electronics fields due to their extraordinary electrical, mechanical, and thermal properties. The addition of fullerenes can change the electronic and mechanical properties of graphene. The strong structure of these nanomaterials allows for use within the body as stints or other structural aids in blood vessels, etc. In order to manufacture materials to be useful in this wide range of applications, the interfacial properties and morphology of carbon nanocomposites need to be better understood. Minor changes in processing conditions, chemistry and composition of nanomaterials have led to unpredictable morphology formation. Molecular dynamic (MD) simulations were run using AMBER software and a general Amber force field (GAFF), which is parameterized for organic molecules. MD simulations were used to study the self-assembly of C_{60} molecules on a single layer of graphene in different solvent environments. The solvent effects on the organization of the fullerene molecules were examined based on the solubility of the carbon allotropes within each solvent system. Fullerene-graphene systems were study *in vacuo* as well as in explicit solvents of chloroform, water, and carbon disulfide.

2015 Joint Southeastern/Southwest Regional Meeting 1036

A microcalorimetry study of cations adsorption at the goethite solution interface: Effect of valence and hydration energy

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The behavior of the electric double layer that develops between metal oxide surfaces and the bulk solution influences all interfacial processes, including mineral dissolution

and precipitation, crystal growth, colloidal transport and flocculation, catalysis as well as adsorption of ions from solutions. It has been proposed that the hydration energies of cations have a significant influence on their partitioning between inner-sphere and outer-sphere species, whereby cations with increasing hydration enthalpies adsorbing mostly as outer-sphere species. Using flow microcalorimetry to measure the enthalpies of adsorption in situ, this study will look at the effect of hydration energies across different valence cations to determine whether the trend will be reflected in adsorption enthalpies. Goethite was chosen as it is a well understood surface and representative of metal oxides, one of the most important geochemical componentscontrolling solubility and mobility of anthropogenic pollutants in the environment. The cations chosen for this study are Li+, Na+, K+, Cs+, Mg2+, Ca2+, Ba2+, and Y3+ listed here in an increasing order of valence and then decreasing order of hydration energy.

The heats of exchange will be obtained using 50 mM solutions of the chloride salts adjusted to pH 10.0 using a carbonate-bicarbonate buffer.

The heats of exchange (in kJ) will be normalized to mole of charge and compared for all cations. It is expected that cations adsorbing mostly through inner-sphere will not only have a larger molar enthalpy of adsorption but also exhibit a larger extent of irreversibility in their exchange as marked in differences in the relative shape and size of the evolution of their respective heat of exchange.

2015 Joint Southeastern/Southwest Regional Meeting 1037

Infrared, Raman, NMR, and conformational stability of 1,1,3,3,5,5-hexafluoro-1,3,5-trisilacyclohexane

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The Infrared, Raman, and Nuclear Magnetic resonance spectra of 1,1,3,3,5,5-hexafluoro-1,3,5-trisilacyclohexane (c-$C_3H_6Si_3F_6$) as a solid powder have been recorded. The vibrational spectra reveal that the crystalline compound exists as a chair conformer with C_{3v} symmetry at ambient temperature. Additional conformers such as twist or boat were not detected although quantum chemical calculations indicated a negligible energy difference between the chair and twist forms. The wavenumbers of the IR and Raman bands were measured and the assignments were initially supported by quantum chemical B3LYP/cc-pVTZ calculations in the harmonic approximation. An average relative deviation of ca. 2.9% between the observed and the scaled harmonic calculations was found. Additional force field calculations were carried out, in which the symmetry was reduced to C_s symmetry by a slight distortion of the hexagonal ring. Employing these calculations, a favorable agreement between the observed and calculated wavenumbers was obtained. Further calculations, involving a twist conformer, were not consistent with the spectral results. Neither the modes nor the wavenumbers agreed with the spectral results.

2015 Joint Southeastern/Southwest Regional Meeting 1038

DNA-conjugated silver clusters with near-infrared spectra

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Silver clusters with ≲30 atoms are molecules with diverse electronic spectra and wide-ranging emission intensities. Specific cluster chromophores develop within DNA strands, and we consider the DNA scaffold for one such chromophore with near-infrared spectra. The 16-nucleotide strand has the sequence $C_3AC_3AC_3TC_3A$. This sequence exclusively yield clusters with near-infrared absorption at ~730 nm and emission at ~800 nm results. These clusters develop when Ag^+ associates with the single-stranded oligonucleotide and are reduced by borohydride. Our studies how the reaction conditions influence the spectrum of the cluster.

2015 Joint Southeastern/Southwest Regional Meeting 1039

Circular dichroism studies of Ag+-DNA complexes

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Silver clusters with ~10 atoms develop with oligonucleotides. These clusters develop when Ag^+ associates with the single-stranded oligonucleotide and are reduced by borohydride. We studied the complexes that form between silver ions and single-stranded DNA using circular dichroism. We used continuous variation analysis to determine the stoichiometries of Ag^+ with a range of oligonucleotides. We particularly focused on the effect of DNA length of sequence on the number of bound Ag^+.

2015 Joint Southeastern/Southwest Regional Meeting 1040

Electronic spectroscopy and mass spectrometry studies of DNA-conjugated silver clusters

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Silver clusters associate with DNA strands and form distinct chromophores. Silver nanoclusters consisting of ~10 atoms coordinate with DNA, and the DNA ligand tunes the cluster spectra. In this work, we discuss different DNA templates based on repeated sequences. We use absorption and circular dichroism spectroscopies to measure the cluster spectra and mass spectrometry to measure the cluster stoichiometry. Our studies concentrate on the effect of DNA sequence on the cluster environment.

2015 Joint Southeastern/Southwest Regional Meeting 1041

Conventional strain energies and relative stabilities of the isomers of dimethylcyclobutadiene

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The conventional strain energies for 1,2-dimethylcyclobutadiene, 1,3-dimethyl-cyclobutadiene, and 1,4-dimethylcyclobutadiene are determined within the isodesmic, homodesmotic, and hyperhomodesmotic models to see if reduction of strain might correlate with the stabilizing effect these different dimethyl substitutions have on

cyclobutadiene. Optimum equilibrium geometries, harmonic vibrational frequencies, and corresponding electronic energies are computed for all pertinent molecular systems using SCF theory, second-order perturbation theory (MP2), and density functional theory (DFT). The DFT functionals employed are Becke's three-parameter hybrid functional using the LYP correlation functional and the M06-2X high nonlocality hybrid functional from Thular and Zhao. In addition, single point CCSD(T) calculations employing the cc-pVQZ basis sets are computed using the MP2/cc-pVQZ optimized geometries to ascertain the contribution of higher-order correlation. The basis sets employed are Dunning and coworkers' correlation consistent basis sets: cc-pVDZ, cc-pVTZ, and cc-pVQZ. Finally, computed bond angles are also examined for correlation with the relative stability and the relative strain energies of the different isomers. We gratefully acknowledge support from the NSF (EPS-0903787).

2015 Joint Southeastern/Southwest Regional Meeting 1042

Relative stabilities of derivatives of 9-methylanthracene and 9-methylene-9,10-dihydroanthracene

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In 1949, Clar and Wright reported that 6-methypentacene exists as 6-methylene-6,13-dihydropentacene at room temperature due to a [1,5]-sigmatropic hydrogen shift (Nature 1949, 163, 921). Thus, the aromaticity of the central ring and the planarity of the overall compound is destroyed by this shift. The same does not occur in anthracene. While the 9-methylene derivative of anthracene is a local minimum, the planar methyl derivative is the more stable. In the current study we investigate if certain derivatives of these systems stabilize the methylene system relative to the methyl.

Derivatives of the two parent isomers are investigated to determine if certain substituents can stabilize the methylene isomer. Specifically, nitro and trifluoromethyl derivatives are investigated. Optimum equilibrium geometries, harmonic vibrational frequencies, and the corresponding zero-point vibrational energies are computed for each set of isomers using density functional theory. The DFT functionals employed are Becke's three-parameter hybrid functional using the LYP correlation functional and the M06-2X high nonlocality hybrid functional from Thular and Zhao. The basis sets employed are Dunning and coworkers' correlation consistent basis sets cc-pVDZ and cc-pVTZ. We gratefully acknowledge support from the NSF (EPS-0903787).

2015 Joint Southeastern/Southwest Regional Meeting 1043

Conventional strain energies of the oxaphosphetanes and the oxadiphosphetanes

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The conventional strain energies of 1,2-oxaphosphetane, 1,3-oxaphosphetane, 1,2,3-oxadiphosphetane, and 1,2,4-oxadiphosphetane are determined within the isodesmic, homodesmotic, and hyperhomodesmotic models. Optimum equilibrium geometries, harmonic vibrational frequencies, and corresponding electronic energies and zero-point vibrational energies are computed for all pertinent molecular systems using SCF theory,

second-order perturbation theory, and density functional theory (DFT). The DFT functionals employed are Becke's three-parameter hybrid functional using the LYP correlation functional and the M06-2X high nonlocality hybrid functional from Thular and Zhao. The basis sets employed are Dunning and coworkers' correlation consistent basis sets: cc-pVDZ, cc-pVTZ, and cc-pVQZ. In addition, cc-pV(D+d)Z, cc-pV(T+d)Z, and cc-pV(Q+d)Z basis sets are also investigated to determine the effect of the extra d function for phosphorus on the overall results. The computed conventional strain energies are compared to those of small cyclic hydrocarbons and to other heterocyclic systems. We gratefully acknowledge support from the NSF (EPS-0903787).

2015 Joint Southeastern/Southwest Regional Meeting 1044

Enthalpies of formation of cyano and methyl derivatives of furan and pyrrole by homodesmotic reactions

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Furan is a heterocyclic aromatic compound that is highly volatile. Due to its aromaticity its chemistry is quite different from most heterocyclic ethers. Several derivatives have gained interest lately. 2,5-dimethylfuran has been proposed as a possible biofuel, and 3-chlorofuran has been investigated for its effect in furan Diels-Alder reactions. In addition, pyrrole and its derivatives have gained interest due to the large number of pyrrolic compounds in pharmaceuticals and natural products. In the current study, we focus on the computation of the standard enthalpy of formation of methyl and cyano derivatives of furan and pyrrole by homodesmotic reactions. In homodesmotic reactions the number and types of bonds and the bonding environment of each atom are conserved.

The enthalpy of all of the reactants and products in each homodesmotic equation is computed using SCF theory, second-order perturbation theory (MP2), and density functional theory. The DFT functionals employed are Becke's three-parameter hybrid functional using the LYP correlation functional, the M06-2X high nonlocality hybrid functional from Thular and Zhao, and the ωB97XD functional from Head-Gordan and coworkers which includes empirical dispersion. The basis sets employed are Dunning and coworkers' correlation consistent basis sets, cc-pVDZ, cc-pVTZ, and cc-pVQZ. From the resulting enthalpy of reaction, the desired enthalpy of formation is determined by use of reference values for all other systems in the reaction. We gratefully acknowledge support from the NSF (EPS-0903787).

2015 Joint Southeastern/Southwest Regional Meeting 1045

Characterization of historical lime mortar using single-sided nuclear magnetic resonance

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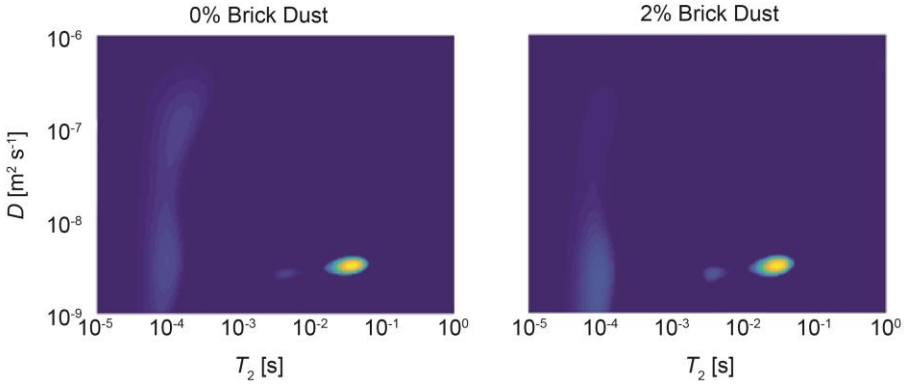
Lime mortar, a mix of binder, aggregate, and other additives, was extensively used in historical construction, such as that in Colonial Williamsburg. For effective preservation, physical properties of repair mortar, including porosity, capillary action, and physical strength, should be matched to that of the historical material. Due to the diversity of

additives used, as well as the length of time necessary for curing, the study of lime mortar remains difficult. Through the use of Nuclear Magnetic Resonance with a single-sided magnet, the porosity of mortar and both the self-diffusion (*D*) and spin-spin relaxation time (T_2) of water within mortar can be noninvasively measured. Additionally, T_2-*D* measurements can be performed, allowing for a better understanding about the interconnectedness of the pores through the motion of water within them. These measurements allow us to quantify the effects of additives within the mortar, such as clay, brick dust, and ash. A better understanding of the effects of individual additives on the physical properties produced in mortar allows us to assist conservators in tailoring the mixture of mortar used on buildings.



T_2-*D* maps for lime based mortar without brick dust (left) and 2% brick dust (right) by mass. It can be seen that the sample with brick dust is very similarn to that without, but has fewer faster diffusing pores at the lower T_2 time, which is indicative of a sample with fewer small pores.

2015 Joint Southeastern/Southwest Regional Meeting 1046

Ultrafast two-dimensional relaxometry with single-sided NMR

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Single-sided NMR is a low cost, non-invasive method of studying the properties of materials. T_1 and T_2 are two values that are particularly important in the field of single-sided NMR. The number of T_1 and T_2 components may correspond to the number of distinct components in a sample, and changes over time in the values of T_1 and T_2 can be used to determine changes in the properties of a sample.[1] Two-dimensional experiments can measure T_1 and T_2 simultaneously, providing more information than studies of either component alone and an increased signal-to-noise ratio. However, typical T_1-T_2 experiments are time consuming, with low SNR also becoming a problem.[2] Ultrafast two-dimensional NMR methods have been developed to greatly reduce the runtimes of multidimensional experiments in high-field.[3] Here we extended ultrafast inversion recovery-CPMG (IR-CPMG) methods to single-sided NMR experiments to measure T_1-T_2 relaxation spectra.[4] Results with similar accuracy and experiment time speedups of up to 20 times were observed for ultrafast experiments versus the typical IR-CPMG experiment with the same parameters.

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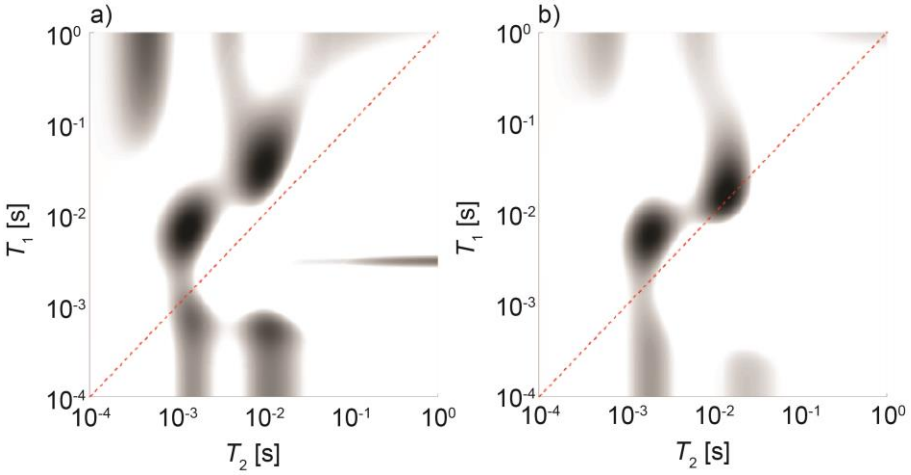

Two-dimensional IR-CPMG maps giving T_1-T_2 distribution information. The sample represented in this figure consisted of two vials, one containing glycerol and the other containing H_2O with $GdCl_3$, placed side-by-side in the sampling range. a) An ultrafast IR-CPMG experiment map with a runtime of 20 minutes. b) A conventional two-dimensional IR-CPMG experiment with a runtime of 91 minutes.

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Rovibrational analysis of third row atom hydroxides and isomers

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Molecules such as $HSiO^+$, $SiOH^+$, HPO, HOS^+, HSO^+ and other third row atoms may be interesting with regards to the chemistry of the interstellar medium (ISM). HPO and HOP are believed to form from a DC-glow discharge of PH_3, CO_2, and H_2 (D_2) gas mixture. HPO is an intermediate in the oxidation of phosphine (PH_3) which may allow for the formation of phosphoric acid (H_3PO_4) in planetary atmospheres. Additionally, $HSiO^+$ and $SiOH^+$, may serve an important role in the Earth's ionosphere allowing radio communication to distant locations due to the transference of signal through electronically charged atoms and molecules. Hence, $SiOH^+$ and its other isomeric partner, $HSiO^+$, are likely among the molecular species responsible for such radio proliferation. Studies have been made to elucidate the existence of these molecules in the gas phase by the use of neutralization-reionization mass spectrometry (NRMS). It has been proposed that Si^+ reacts with H_2O to create $SiOH^+$. It also suggested that HOS^+/HSO^+ are formed from an abstraction (a more common reaction) with an oxygen atom and the addition method (least common reaction) with H_2SO. Our computations of these species make use of quartic force fields and high-level coupled-cluster theory to derive spectroscopic constants and anharmonic vibrational frequencies in order to

examine the possibility that $HSiO^+$, $SiOH^+$, HOP, and HPO may exist on our planet or even in the larger ISM. It has been shown that HOP is not suitable for rovibrational analysis due to its instability in its analyzed first singlet state. Astronomical observations and laboratory experiments of these and other molecules may further advance our understanding of the ISM and ionosphere but only if reference data is available. This work serves to provide this data for comparison.

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WITHDRAWN

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The predicted ensemble of 3D structures for OR1A1-4

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Human olfactory receptors (hORs) are members of Class A G protein-coupled receptors (GPCRs), which is the largest class of GPCRs; molecules binding to hORs, known as odorants, give us our sense of smell. However, the 3D structure and binding details of most hORs are not known. The energetically-best 3D conformations were predicted for OR1A1-4 using Monte Carlo methods to sample ~200,000 structures from ~40 trillion possible conformations. The top 25 structures for OR1A1-4 were ranked according to energy, and three structures were selected for ligand docking using criteria including structural diversity, hydrogen bond energy, and conserved 1-2-7 and 3-6 interactions. OR1A1-4 was then docked with two structurally similar odorants, one (nonanal) that had been previously determined to activate OR1A1-4 and one (hexanal) that did not activate OR1A1-4. Both odorants docked to a previously identified amino acid (Q100) that was a putative residue for activation. Five cycles of quench annealing were then run to lower the energy. After comparing the final nonbonding energies, the activating odorant showed stronger binding to OR1A1-4 than the non-activating odorant. These results suggest key activation characteristics in OR1A1-4 and the top binding residue for nonanal and hexanal.

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Ketosteroid isomerase catalyzed Kemp elimination

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Ketosteroid isomerase (KSI) catalyzes the isomerization of ketosteroids by using a catalytic aspartate in its active site (Asp 38 in KSI from *Comamonas testosteroni*). The Kemp elimination is a reaction promoted by abstraction of a proton from the relatively acidic C3 of benzisoxazoles. Because of the similarities between these two reactions, we investigated whether KSI could catalyze the Kemp elimination. We found that KSI catalyzes the Kemp elimination of 5-nitrobenzisoxazole as well as other substituted benzisoxazole substrates. Surprisingly, mutation of Asp 38 does not slow down the

reaction, suggesting that it is not involved in proton abstraction. The two mutants tested, D38G and D38N, are both more active than the wild-type enzyme. Mutation of a different aspartate (Asp 99) located within the active site resulted in ~200-fold decrease in catalytic efficiency, indicating that this residue could be the catalytic base. 4-chlorophenol and equilenin, two competitive inhibitors of native KSI activity, also inhibit the KSI-catalyzed Kemp elimination, suggesting that this reaction takes place at the active site. Remarkably, D38N KSI catalyzes the Kemp elimination with a second-order rate constant greater than those measured for several computationally-designed Kemp eliminases, suggesting that the designed Kemp eliminases do not provide transition state stabilization beyond the one arising from non-specific effects.

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The effects of mercury (II) ion on secondary DNA structures formed by T-rich DNA

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T-rich DNA, in the presence of mercury (II) ion, is capable of forming secondary structures similar to that of i-motifs, by forming T-Hg^{2+}-T bonds and folding back on itself. A variety of techniques, such as UV-visible spectroscopy, circular dichroism (CD) spectroscopy, and size-exclusion chromatography using an HPLC column, were used to detect changes in the structure of the TiM DNA (sequence: 5'-$(TTTC)_3$TTT-3') in the presence of mercury (II) ion, as well as in the presence of potassium chloride. UV-visible spectroscopy shows that increasing concentration of mercury (II) ion in solution with TiM decreases the absorbance at 260 nm. CD spectroscopy shows a redshifting in the peak of the spectrum, confirming that there was a conformational change in the T-rich DNA. This conformational change can be reversed by the addition of potassium chloride, which was confirmed by both UV-visible and CD spectroscopy. Size exclusion chromatography, used to determine whether the structure is intra- or intermolecular, indicates that the structure is intra-molecular, as evidenced by higher retention times of TiM in the presence of mercury (II) ion compared to retention times of TiM without the addition of mercury (II) ion. It is also found that the TiM secondary structure that is formed in the presence of mercury (II) ion is very thermodynamically stable; attempts to determine a T_m of the T-rich DNA in that structure by taking CD spectra at 5 °C increments from 10 °C to 90 °C failed, as the signal did not change significantly at higher temperatures.

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Single-cell mass spectrometry: A tool for rapid biochemical analysis

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Lipids are a major component of cellular biology and regulate many biochemical processes, but analyzing the concentrations of these molecules in real time currently presents a technological challenge. Although lysates can be prepared to selectively extract lipids from a population of cells, lysate preparation inherently homogenizes these extracts, thus obscuring important stochastic differences among individual cells.

Moreover, these experimental methods may even degrade or remove important cellular components during lysate preparation, resulting in an incomplete picture of cellular phenomena. One innovative way to address this problem is through single-cell mass spectrometry (SCMS), which allows for cellular biochemical analysis at an unparalleled level of precision. SCMS is a cutting-edge, rapid analytical tool that pushes bioanalysis beyond the limits of current methods, which require sampling large populations of heterogeneous cells. During SCMS, cells remain intact and are exposed to very few analytical reagents, thus protecting the cells' structural integrity and minimizing their exposure to harsh conditions. Conversely, cell lysate preparations destroy cell viability and homogenize thousands or even millions of cells, while exposing the sample to extreme changes in temperature, denaturing solvents, and other potentially damaging conditions. In the report herein, we use SCMS to immediately analyze the lipid profiles of single cancer cells. Then, we compare these data to cells treated with the natural product anticancer compound, OSW-1 (a small molecule that affects lipid processing) to observe unique patterns in the mass spectra. Finally, we compare these SCMS profiles to cell lysates that were ionized using liquid-chromatography mass spectrometry (LC-MS). In sum, we present this method of SCMS as a new and powerful tool to analyze stochastic cellular profiles in real time, demonstrating the potential of this technology to rapidly detect transient biochemical changes that might be obscured by the harsh conditions used in cell lysate preparations.

Developing a PiggyBac gene delivery system to generate autonomously bioluminescent stem cells

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Animal models are frequently utilized in toxicity screening to evaluate the safety of compounds used in medicines, agricultural products, industry and cosmetics. This methodology requires many animals, is extremely costly, labor-intensive, and time-consuming. Stem cell-based toxicity assays present a cost-effective and time-efficient alternative to conventional animal toxicity studies, and allow for assessment of the toxicity of compounds in undifferentiated cell lines. In recent years, the inhibition of light emitted via a bioluminescent pathway has been the basis for several toxicity bioassays, which correlate the degree of light inhibition with the toxicity of the compound of interest. Our laboratory has developed a "humanized" bacterial luciferase (*lux*) gene cassette that allows for human cells expressing these genes to constitutively luminesce throughout their lifetime. This study sought to develop a *PiggyBac* transposon gene delivery system to generate constitutively bioluminescent stem cells for use in toxicity bioassays. Due to stem cells' difficult-to-transfect nature, four commercially available transfection reagents (Lipofectamine, Viafect, FuGENE, and EndoFectin) were evaluated for their effectiveness to co-deliver a *PiggyBac* transposon containing the humanized *lux* cassette under the control of a CMV promoter and a vector coding for the *PiggyBac* transposase to human embryo kidney (HEK293) and pancreatic cancer (AsPC-1) cells. The Viafect transfection agent consistently demonstrated the highest transfection efficiency in both cell lines, producing at least a 2-fold increase in bioluminescence in transfected cells compared to those transfected with other agents. It

was also demonstrated that although the CMV promoter-driven *lux* cassette produced a higher bioluminescence in many immortalized cell lines, human elongation factor 1-α (EF1-α) promoter was able to drive higher level of bioluminescence in equine mesenchymal stem cells. As a result, a novel *PiggyBac* transposon harboring the EF1-α-driven *lux* cassette was developed in this study and is currently being evaluated in stem cells using the Viafect transfection agent.

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Carbapenem functionalized gold nanoparticle synthesis, characterization and antibacterial susceptibility testing

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With soaring increase in the cases of multi-drug resistant (MDR) bacteria all over the world, we are on the verge of entering post-antibiotic era if no immediate action is taken against this global crisis. As an alternative route to modify current commercial antibiotics, we made an attempt to design an array of effective antibacterial agents involving gold nanoparticles (AuNPs) conjugated to an antibiotic, like those of the carbapenem drug class. Carbapenems, a sub-class of β-lactams, are considered to be among those drugs of last resort with regards to bacterial infections. Due to recent emergence of infections due to both Gram-positive and Gram-negative bacterial strains with advanced patterns of antimicrobial resistance bactericidal agents such as these are being view as a prime candidates for further development and augmentation. Unlike conventional methods, a unique self-patented green process was used for AuNPs synthesis wherein the antibiotic assists in both reducing and stabilizing the AuNPs resulting in antibiotic conjugated gold nanoparticles (Car-AuNPs) which were morphologically characterized using transmission electron microscope (TEM), UV-Vis spectroscopy, scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM-EDS), and dynamic light scattering (DLS). The presence of ligand (antibiotic) onto AuNPs was confirmed using TGA analysis. Antibacterial efficiency was evaluated on Gram-positive and Gram-negative bacterial strains using turbidmetric and spread plate assay. AuNPs activity was further confirmed with propidium iodide assay. Super-thin cross-sections of bacteria treated with Car-AuNPs observed under TEM showed bactericidal activity by causing perforations and disturbing the cellular environment leading to cell lysis and apoptosis. The minimum inhibitory concentrations (MIC) of Car-AuNPs was significantly less when compared to pure antibiotic drugs which proves the synergistic activity of Car-AuNPs.

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"Click" approach to HMGA disruption

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Commonly found in healthy human embryos to facilitate transcription and cell differentiation, the high mobility group A family of proteins (HMGA) has been linked to metastatic cancer when over-expressed in adults. Through cooperative binding of A/T

hooks motifs, HMGA binds A/T rich regions of minor groove DNA. As HMGA activity is directly related to the protein's ability to bind DNA, means of inhibiting this binding are of vast interest in the development of novel chemotherapeutics. Presently, studies seek to architecturally modify the DNA binding site by means of "click"- enabled bioconjugation with the goal of characterizing the selective inhibition of cooperative binding by HMGA.

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Metalloregulation by Nur from *Streptomyces coelicolor*

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Streptomyces coelicolor is a soil-dwelling actinomycete of medical importance as a result of its ability to produce several antibiotics. Nickel accumulation within this organism has been shown prevents the production of the antibiotic undecylprodigiosin. The transcriptional repressor protein important in regulation of nickel uptake is the homodimeric Nur, a member of the Fur family. In addition to maintaining nickel homeostasis within the cell, Nur regulates the response to oxidative stress. Nur contains two metal-binding sites per monomer. Our research seeks to determine the role of each of the metal-binding sites, the key residues at each of the binding sites, and the affinity of Nur for metal and DNA through metal titrations, spectroscopic assays, and fluorescence anisotropy. We have developed a new model for the action of Nur based upon metal binding at each binding site. Further biophysical characterization of Nur will allow us to confirm our model and will contribute to a better understanding of nickel regulation and conditions influencing antibiotic production within S. coelicolor.

2015 Joint Southeastern/Southwest Regional Meeting 1057

Utilization of biologically derived polyester polyols in surfactants for polyurethane foams

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Polyurethane foams have become a multimillion dollar industry as increased use of the plastics has grown. The increasing production of polyurethane foams has driven a movement to integrate more biologically friendly compounds into the synthesis of the foams. Natural triglycerides from soy are used as starting materials for the surfactant, as well as a contributing polyol in the polyurethane foam synthesis. Foams were synthesized using traditional polyether surfactants and a variety of bio-based surfactants and compared to one another to determine differences between the densities, rise height, and rise times.

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Solid-phase peptide synthesis and antimicrobial assessment of a plant-derived cyclic peptide

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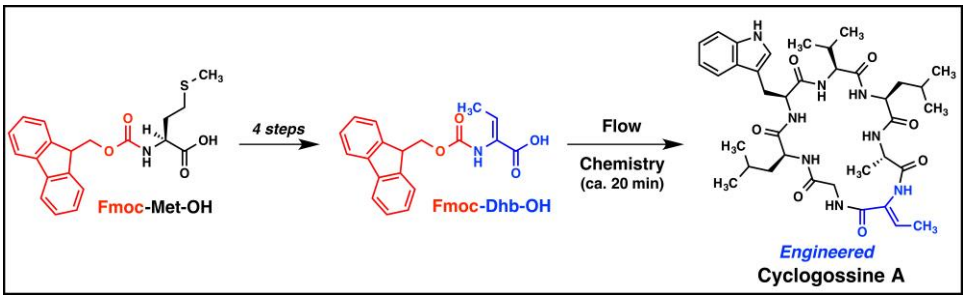
Jatropha, a genus of woody trees and shrubs ubiquitous in the dry tropics, is prevalent in Latin American, Asian, and African ethnopharmacology. Peptides isolated from *Jatropha* species exhibit diverse biological activity, including purgative, wound-healing, antimalarial, and antifungal effects. Cyclogossine A, a cyclic heptapeptide with the primary structure VLATWLG, is isolated from *J. gossypiifolia*. Although the medicinal use of the plant is well documented, the biological activity of Cyclogossine A remains unreported. Due to its rigid structure and hydrophobic side chains, Cyclogossine A possesses therapeutic potential. Expedient access to Cyclogossine A was enabled by flow chemistry methods, which were engineered for Fmoc-based solid-phase peptide synthesis. HPLC purification and Q-TOF mass spectrometry were utilized to confirm the synthesis and purity of the primary structure. After optimizing the cyclization reaction, which formed an amide bond between the C-terminus and N-terminus of the linear peptide, the naturally occurring ring structure was created. Using the cyclic peptide as a scaffold, the incorporation of the alkene-containing amino acid dehydrobutyrine, which is found in lantibiotics, was successful. 2-D NMR spectroscopy data further support the desired synthesis and cyclization of both the natural and engineered peptides. Studies are underway to explore the antimicrobial effects of Cyclogossine A against a library of bacteria, parasites, and fungi. Following confirmation of activity, cytotoxicity assays, fluorescence spectroscopy, and electron microscopy may be employed to further investigate the biological mechanisms of Cyclogossine A.



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Encapsulation of calcein within polymerizable diacetylene vesicles

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Amphiphile-based vesicles have found use as drug delivery vehicles. Incorporation of the diacetylene moiety in the amphiphile tail permits polymerization upon UV exposure, allowing for dramatic alteration of drug release profiles. Vesicles in the 120 nm range were prepared from 10,12-pentacosadiynoic acid in the presence of the fluorophore calcein with the goal of measuring encapsulate release rates. The resulting structures where characterized by dynamic light scattering. However, these failed to assemble appropriately for polymerization at pH level basic enough to solubilize calcein to self-quenching concentrations. Acidification after vesicle formation permitted maintenance of satisfactory calcein concentration within the vesicle, but also failed to produce a

polymerizable capsule. In order to address this problem, the alternatives to the carboxylic acid head group have been developed.

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Using rational drug design to identify novel flavonoid derivatives as acetylcholinesterase inhibitors for the treatment of Alzheimer's disease

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Research has shown that the neurotransmitter acetylcholine (Ach) is less expressed in the brain of Alzheimer's patients when compared to normal patient's levels. It is proposed that this decrease stems from the hydrolysis of Ach by the enzyme acetylcholinesterase. As a result, acetylcholinesterase inhibitors have been identified as a viable option for the treatment of various symptoms associated with cognitive function in patients with Alzheimer's disease. Flavonoids, natural products that exhibit acetylcholinesterase inhibitory activity, can potentially serve as promising leads for the treatment of Alzheimer's disease. Through the use of rational drug design, this research project will investigate the design and synthesis of novel flavonoid derivatives that incorporate nitrogen-containing fused heterocyclic rings, which were identified through SAR as crucial structural elements, and test the biological activity of the various derivatives in an effort to propose an effective treatment of Alzheimer's disease.

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Time-resolving unimer exchange in block copolymer micelles

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Full comprehension of micelle dynamics is required if polymeric micelles are to be used as targeted drug delivery vehicles. Contrast-matching Time-Resolved Small Angle Neutron Scattering (TR-SANS) has proven useful in understanding unimer (polymer chain) exchange rates, however, it is a time and resource exhaustive technique. In this work, we explore the utility of NMR spectroscopy techniques, such as spin-lattice relaxation time and pulsed-field-gradient diffusometry, as an alternative to TR-SANS. We use ^{1}H- and ^{2}H-based poly(ethylene oxide)-polycaprolactone diblock copolymers that self-assemble into spherical micelles at 1% w/v. Analogous to the contrast-matching TR-SANS experiment, mixing of ^{1}H- and ^{2}H-based micelles shows an increase in spin-lattice relaxation time with time due to mixing of the unimers. We further evaluate the mechanism of unimer exchange through NMR diffusometry to show two-component diffusion coefficients, suggestive of both free unimer and micelles existing in solution. The combined data is suggestive of free unimer exchange as the dominate exchanging mechanism. As an alternative to traditional characterization techniques, NMR is a much more easily accessible and cost effective method of analysis. We

believe that NMR spectroscopy and diffusometry will prove to be promising techniques for more general characterization of micelle dynamics.

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Optimization of the transfer-to approach for bottlebrush polymer synthesis

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Ring-opening metathesis polymerization (ROMP) and reversible addition–fragmentation chain transfer (RAFT) polymerization were employed sequentially to prepare bottlebrush polymers using the transfer-to approach. RAFT transfer-to is a unique strategy for synthesizing bottlebrush polymers wherein a polymeric chain transfer agent (PCTA) is synthesized using ROMP with the Z-group attached to the polymer backbone. In the RAFT step, side chains detach from the bottlebrush backbone, propagate freely in solution, and then return to a new reactive site on the bottlebrush backbone. This study focused on optimizing the RAFT transfer-to step for preparing bottlebrush polymers by varying PCTA concentration, radical initiator concentration, and temperature. Size exclusion chromatography (SEC) was used to determine molecular weight and dispersity of the bottlebrush polymers, and aminolysis was conducted to cleave off the side chains to evaluate grafting density as well as the molecular weight and dispersity of the polymeric side chains. Based on SEC, it was concluded that CTA concentration gave control of the molecular weight of bottlebrush polymers as well as the side chains. Lower CTA concentration yielded high molecular weight bottlebrushes (1,600 kDa) of narrow dispersity (1.02). Radical initiator concentration also had an effect on the dispersities of the polymers, with higher radical initiator concentrations leading to a broadening of the bottlebrush molecular weight distribution. Finally, high temperatures (> 75 °C) degraded the PCTA, reducing control over the polymerization. These conclusions will enable the preparation of ultra-high MW bottlebrush polymers with high grafting densities and well-defined side chains.

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Synthesis of heteroditopic AB monomer for host-guest supramolecular polymer system

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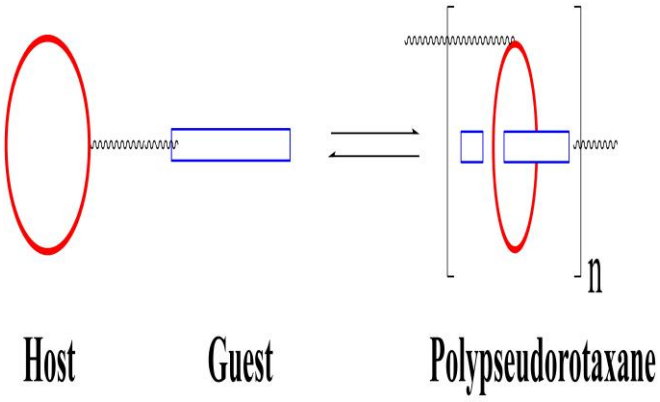
Supramolecular polymers are composed of monomeric units held together by noncovalent, reversible interactions, including hydrogen bonding, van der Waals forces, and π-π stacking. Host-guest systems consist of hosts and guest molecules that form complexes through non-covalent interactions. Host-guest systems can be used to effect self-assembly of supramolecular polymers. A monomer may be end-functionalized with two host moieties or two guest moieties (AA-BB, homoditopic system). A monomer may also be end functionalized with both the host and the guest units (AB, or heteroditopic system). To create a self-assembling system capable of yielding high degrees of polymerization (DP), a high association constant (K_a) must exist between the host-

guest. Pyridyl cryptands (macrobicyclic, pre-organized crown ethers) are good hosts for paraquat derivative guests as they exhibit high K_a values. The resulting threaded complex is called a pseudorotaxane. Supramolecular polymers can be formed via pseudorotaxane repeat units. The focus of this investigation was to synthesize a heteroditopic AB monomer to yield a self-assembling supramolecular polymer; a polypseudorotaxane. Such supramolecular polymers are expected to exhibit smart properties, such as responding to external stimuli, e.g., pH, temperature, and solvent, as well as self-healing features. In addition to synthesizing the heteroditopic AB monomer in high yields, the mechanical properties of the supramolecular polymer will be studied, contributing to an area that has not received much attention yet.



Monomer complexation for formation of supramolecular polymer.

2015 Joint Southeastern/Southwest Regional Meeting 1064

Development, synthesis, and degradation studies of drug-infused biologically compatible polymers

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Modified polyurethanes are being developed for use as drug delivery platforms. For this study we have formed a series of prepolymers containing the active drug prodrug species and an aliphatic diisocyanate to ensure that the drugs and biologically based polyols are fully dispersed in the polymer, and minimal unreacted drug remains in the polymer matrix. The pre-polymers are then reacted with a difunctional alcohol derived from edible soybean oil derivatives. The diol pre-polymer is produced from the reaction between the carboxylic acid moiety of a drug and a ketal species derived from glycerin. The alcohols allows for the pre-polymer to be incorporated into the polyurethane backbone, while the esters are easily hydrolyzed under physiological conditions to release the drug over time. For the initial trials, ibuprofen has been the target molecule, but this technology is applicable to other drugs. A successful drug delivery material was made from nalidixic acid, a simple antibiotic compound as well as 3,4,5 trimethoxycinnamic acid (TMCA) and alpha-methyl cinnamic acid (AMCA), two potent chemotherapeutic agents. In addition, trials will be initiated investigating alternative synthetic approaches to form a diol pre-polymer as well as the overall copolymer. Upon exposing these drug delivery materials to physiological media, significant drug release was observed in as little as 20 hours. This year we are exploring new synthetic approaches to these polymeric materials to yield products with varying applications

including type of drugs being released, rate of drug release, and overall composition of the material. In addition, long-term degradation studies of these materials are being performed to confirm their safety in biological environments, and the results are being monitored by LC-MS.

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Expedient access to 1,2-oxazadecalin core and studies towards 1,2-oxazadecalin secondary metabolites

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Trichodermamide A, B, and C are a unique set of natural products which are isolated as secondary metabolites from marine fungus trichoderma virens. They contain a rare 1,2-oxazine moiety fused to a densely functionalized cyclohexene scaffold with four contiguous stereocenters. With the exception of trichodermamide A, both B and C show significant antiproliferative activity against HCT 116 with IC_{50} values of 0.32 and 0.68 mg/mL respectively. Aspergillazines A-E, which are structurally related to trichodermamides, are also known to have cytotoxic properties. The isolation of trace amounts of these secondary metabolites from ecologically fragile entities is an obstacle to further studies of these compounds as therapeutic agents. The goal of this project is to develop an expedient route to the synthesis of 1,2-oxazadecalin secondary metabolites. Salient features include its overall conciseness, limited chromatography, and employment of protecting group-free strategies.

2015 Joint Southeastern/Southwest Regional Meeting 1066

Zinc triflate catalyzed Minisci reactions

***Savannah Jones**[1], savannahlj930@gmail.com, Joyce L. Biaco[2], Timothy J. Barker[2]. (1) Chemistry and Biochemistry, College of Charleston, Charleston, South Carolina, United States (2) College of Charleston, Charleston, South Carolina, United States*

We report a zinc triflate-catalyzed coupling between heterocyles and arylboronic acids. The substrate scope with respect to the arylboronic acid has been examined. Control experiments revealed that the zinc triflate is functioning as a Lewis acid in an aqueous solvent mixture.

2015 Joint Southeastern/Southwest Regional Meeting 1067

Synthesis of new gold carbene complexes with potential catalytic ability

***Alyssa Romano**, aromano2@elon.edu. Chemistry Department, Elon University, Emmaus, Pennsylvania, United States*

In recent decades, nitrogen acyclic carbene (NAC) gold complexes have become an increasingly important research topic in organometallic chemistry- particularly as potential catalysts. In this research, an amine compound and seven total gold carbenes were synthesized. The NAC gold complexes are new compounds that have never have been reported in the literature thus far. The amine was used in five syntheses. A

previously synthesized, different amine was used for the remaining two syntheses. NMR studies, mass spectroscopy and infrared spectroscopy were used to confirm crystal structures of the NAC gold complexes. Although this research focused on the synthesis of new NAC gold complexes, three of these complexes were selected for supplemental catalytic testing as well.

2015 Joint Southeastern/Southwest Regional Meeting 1068

Total synthesis of the natural products hibiscone C and hibiscone B

Hayden Rudd[1]*, hayden.rudd@furman.edu, Brian C. Goess*[2]*. (1) Furman University, Pinehurst, North Carolina, United States (2) Dept of Chemistry, Furman University, Greenville, South Carolina, United States*

Hibiscone C is a furanosteroid containing a furan ring with adjacent conjugated carbonyls; this notable structure makes hibiscone C an inhibitor of the enzyme Phosphoinositide 3-kinase (PI3K). PI3K is an enzyme critical in cell growth and differentiation pathways and has been found to have increased levels of activity in cancerous cells. Therefore, the inhibition of PI3K is commonly targeted in chemotherapeutic research. Members of Dr. Brian Goess's organic synthesis lab have developed a 12 step synthesis of hibiscone C, which is now being used as a starting point for the synthesis of other hibiscone family members. The ultimate goal of synthesizing these natural products is to allow for the biological evaluation of their ability to inhibit PI3K. The basic structure of the molecules suggest their potential to inhibit PI3K, while their differences in electron density could lead to differences in selectivity for PI3K inhibition. This summer, our lab developed the first known synthesis of hibiscone B by building off the hibiscone C synthesis. The synthesis is performed through a selective reduction of a hibiscone C carbonyl, followed by a Mitsunobu reaction to achieve the appropriate stereochemistry for hibiscone B. The comparison of the biological evaluations of hibiscone C and B will provide insight into which specific structures are optimal for the inhibition of PI3K.

2015 Joint Southeastern/Southwest Regional Meeting 1069

Synthesis, substitution, and attempted metalation of a rigid, fused bis-indenyl "batwing" ligand

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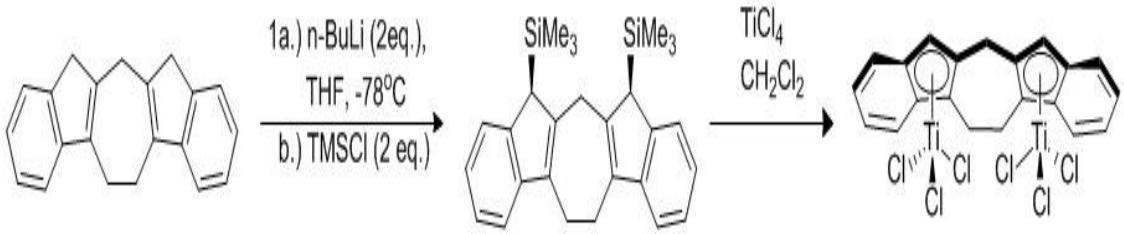
A novel, fused bis-indenyl "batwing" molecule has been designed and synthesized as a ligand for a dinuclear titanium polymerization catalyst. New generation dinuclear complexes—which incorporate two metal atoms per catalyst—have recently demonstrated polymerization capabilities that vary from those of their mononuclear counterparts: higher activity, greater molecular weight and uniformity of tacticity, as well as enhanced comonomer incorporation into the polymer product. That last property is potentially advantageous for producing various block polymers, which are desirable as materials with new properties. To date, many dinuclear catalysts have employed flexible ligands capable of free rotation. The fused bis-indenyl ligand we have pursued provides an extraordinarily rigid scaffold for a dinuclear titanium polymerization catalyst (see figure). This molecule will be discussed in terms of its synthesis, stability, reactivity, and

ability to be complexed to metal centers; additionally, studies intended to determine the effect of the ligand's rigidity on polymerization and copolymer formation will be introduced.



2015 Joint Southeastern/Southwest Regional Meeting 1070

Synthesis and isolation of 5,6,7-trimethoxy indoles for the creation of novel combretastatin derivatives linked at the 3-position

***Teresa Rocha**, trocha@unca.edu, Herman Holt. UNC Asheville, Asheville, North Carolina, United States*

Indoles are common molecules found throughout nature that show to have highly active and diverse pharmacophoric properties. Here we propose the melding of CA4 with an indole by replacing the benzene ring that CA4's trimethoxy moiety typically resides on with an indole ring, by positioning the indole with the alkene bridge bound at its 3-position (a commonly occurring position in nature). Due to the high cost of 5,6,7-trimethoxy indole, one has been synthesized. Synthesis of the trimethoxy indole was done by utilizing Hemetsberger-Knittel indole methodology to make an indole ester. A saponification reaction was then performed converting the ester into a carboxylic acid and subsequent decarboxylation was attempted in two ways (refluxing in copper and quinoline and thermolysis) with the greatest yield being obtained of through thermolysis. Bromination at the indole's 3-position will allow for the coupling between the indole and other aromatic ring systems that will correspond to that of CA4's. Tuning of the resulting alkyne to an alkene or other heterocycles will provide CA4 derivatives worthy of bioactivity exploration.

2015 Joint Southeastern/Southwest Regional Meeting 1071

Scope expansion of the Winstein-Masamune reaction: Tsuji-Trost variant

***Lorenzo Spencer**, Lorenzo.spencer@eagles.usm.edu, Matthew Donahue. Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, Mississippi, United States*

In this talk we will discuss our ongoing efforts to expand the scope of the Tsuji-Trost variant of the Winstein-Masamune reaction. The intramolecular para-alkylation of a phenol derivative is a convenient method to synthesize a spiro[4.5]deca-6,9-dien-8-one. The incorporation of an allylic carbonate as the electrophile in the alkylation affords a spirocycle with a pendant alkene. Recent efforts by the Hamada and You groups have employed palladium and iridium with enantiopure ligands to render the reaction

asymmetric. We have become interested in this reaction en route to the Lycopodium alkaloid magellanine. Toward this aim, we have begun to screen bifunctional organocatalysts of with different chiral motifs in effort to avoid using a transition metal. We will present our findings employing the effect priveleged

2015 Joint Southeastern/Southwest Regional Meeting 1072

Cationic gemini surfactants used for enhanced oil recovery

Adam X. Woods[1]*, adam.woods@pop.belmont.edu, Kimberlee A. Daus*[2]*. (1) Chemistry, Belmont University, Nashville, Tennessee, United States (2) Dept of Chemistry Physics, Belmont University, Nashville, Tennessee, United States*

Surfactants used for enhanced oil recovery (EOR) have been applied commercially for many years dating back to the 1970s and 1980s[1]. Surfactants or surface-active agents are compounds that reduce surface tension between two liquids or a liquid and a solid. In the field of EOR, surfactants are used to reduce the surface tension between rock and oil by water flooding. This process releases trapped oil in presumed depleted oil reservoirs.New gemini (double head) surfactants posses the capability to reduce the surface tension to lower values than previously reported single head surfactants[2]. This factor garners attention to gemini surfactants as prime candidates for enhanced oil recovery.
We aim to synthesize quaternary ammonium salts, a class of gemini surfactants, previously used as fabric softeners[3]. The two surfactants differ by the total number of tails on each compound. Bis(2-hydroxy-3 (dodecyldimethylammonio)propyl)methylamine dichloride (2a) contain two tails while bis(2-hydroxy-3 (dodecyldimethylammonio)propyl)dodecylamine dichloride (2b) contain three tails. See figures 1 and 2 below. The presentation will describe the synthesis and characterization of the two surfactants. We hypothesize that compound 2b will show superior ability to disperse oil in an enhanced oil recovery systems based on the trimeric gemini abilities.

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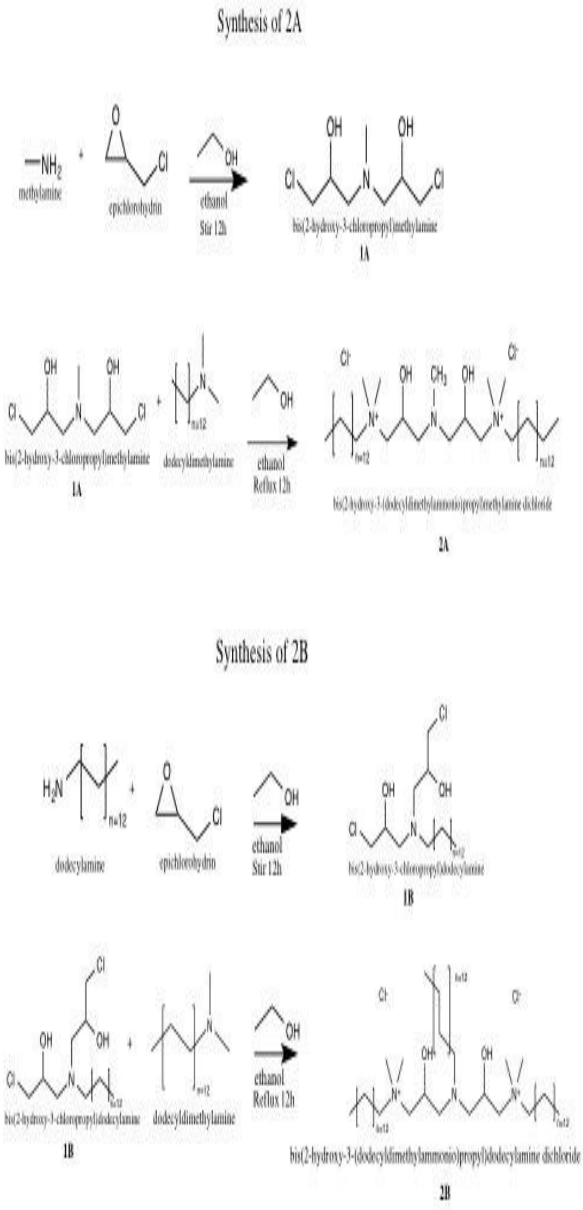

2015 Joint Southeastern/Southwest Regional Meeting 1073

Synthesis of 1,3-*S*,*O*-esters from α-oxoketene dithioacetals

***James Law**, jlaw9@students.kennesaw.edu, David Kercher, Christopher W. Alexander. Dept of Chemistry, Kennesaw State University, Kennesaw, Georgia, United States*

1,3-*S*,*O*-esters are molecular building blocks used in the synthesis of heterocycles, natural products, and other ester derivatives. We have developed a a convenient method to synthesize functionalized 1,3-*S*,*O*-esters by the acid hydrolysis of α-oxoketene dithioacetals using Amberlyst-15. We will report the scope and limitations of our method. Additionally, we will present our preliminary results for the synthesis of 1,3-dicarbonyl compounds from the 1,3-*S*,*O*-esters that we have prepared.

2015 Joint Southeastern/Southwest Regional Meeting 1074

Asymmetric reduction of single geometric isomers of diaryl oxime ethers

Binit Sharma Poudel[1]*, binit.poudel@selu.edu, Ignatius Bonck*[1]*, Suraj K. Ayer*[1]*, Connor Dugan*[2]*, Zhexi Li*[2]*, Timothy S. Snowden*[2]*, Debra D. Dolliver*[1]*. (1) Chemistry & Physics, Southeastern Louisiana University, Hammond, Louisiana, United States (2) Chemistry, University of Alabama, Tuscaloosa, Alabama, United States*

The enantioselective borane reduction of single geometric isomers of diaryl oxime ethers [$Ar^1C(Ar^2)$=NOR] using a chiral spiroborate catalyst is described. These reductions result in pharmaceutically-useful asymmetric diarylmethanamines. The effect of the alkyl group (R = Me, *i*-Pr, Bn) attached to oxygen on the enantioselectivity will be discussed. Temperature and solvent effects on the stereoselectivity will also be examined. Reaction optimization, product isolation, and determination of enantiomeric ratios will be presented. There will also be a discussion of the effect of substituents on Ar^1 and Ar^2 on the stereoselectivity of the reaction.

2015 Joint Southeastern/Southwest Regional Meeting 1075

Synthesis of single geometric isomers of *N*-benzyloxydiarylimines

Ignatius Bonck[1]*, ignatius.bonck@selu.edu, Binit Sharma Poudel*[1]*, Suraj K. Ayer*[1]*, Connor Dugan*[2]*, Zhexi Li*[2]*, Timothy S. Snowden*[2]*, Debra D. Dolliver*[1]*. (1) Chemistry & Physics, Southeastern Louisiana University, Hammond, Louisiana, United States (2) Chemistry, University of Alabama, Tuscaloosa, Alabama, United States*

The synthesis of a series of *N*-benzyloxydiarylimines with various electron-withdrawing or electron-donating substituents is reported. The route involves benzylation of the hydroxamate salt to form the *O*-benzylhydroxamate, tosylation of the hydroxamate to produce an *O*-benzylbenzimidoyl tosylate with subsequent iodination to yield an *O*-benzylbenzimidoyl iodide. Suzuki coupling of the iodide with boronic acid produces a single geometric isomer of the desired *N*-benzyloxydiarylimine. These *N*-benzyloxydiarylimines will be used as starting materials in investigations of the stereoselectivity of asymmetric, spiroborate-catalyzed borane reductions to synthesize single enantiomers of diarylmethanamines.

2015 Joint Southeastern/Southwest Regional Meeting 1076

Fluorescent amphiphile exchange in polydiacetylene liposomes

Ian Miller[2]*, ian.miller2@furman.edu, Michael Evans*[1]*, Timothy W. Hanks*[2]*. (1) Furman Univ, Greenville, South Carolina, United States (2) Furman University, Greenville, South Carolina, United States*

Long-chain amphiphiles containing the diacetylene moiety midway along the chain can be assembled into ~100 nm sized bilayer vesicles that readily polymerize in the presence of UV light. Such structures undergo a dramatic color change when the conjugated backbone in perturbed. If a hydrophobic fluorophore is incorporated into the bilayer, the fluorescence is also modulated by the backbone state. This behavior is complicated by the exchange of fluorophores between vesicles under certain conditions. In addition, treatment with lipopolysaccharides (LPS) and certain surfactants unexpectedly, and very rapidly, modulates the fluorescence without the concomitant color change. Liposomes were prepared using a picoliter scale solvent dispersion

method and fluorescent intensity was measured over a two-hour period. The data indicate that the colorimetric and fluorescence behaviors are a function of both the amphiphile head group and tail length.

2015 Joint Southeastern/Southwest Regional Meeting 1077

Zwitterion polymer brush growth in a quartz crystal microbalance

***Elizabeth Bundy**, esbundy@gmail.com, Timothy W. Hanks. Furman Univ, Greenville, South Carolina, United States*

Gold-coated quartz crystal microbalance (QCM) resonators were derivatized by treating the active surface with a solution w-mercaptoundecylbromoisobutyrate in ethanol. These were then placed in a QCM flow cell. An “incomplete reaction mixture” was prepared from ascorbic acid, copper (II) chloride, and bipyridine in degassed Milli-Q water. A “complete reaction mixture” was prepared in the same way, but also included the monomer sulfobetaine methacrylate. The incomplete reaction mixture was run through the QCM at the 0.5 µl/min until the resonator’s oscillation stabilized. The flow was then increased to 10 µl/min until stabilization was again achieved. At this point, the solution was switched to the complete reaction mixture for a period of about 2 hours at the same flow rate. The growth of the polymer brush was monitored by the change in the frequency of the resonator and the viscoelastic properties by the change in the dissipation of the resonance.

2015 Joint Southeastern/Southwest Regional Meeting 1078

Synthesis of polypyrrole-alginate ionomeric composites

***Melissa Kuester**, mkuester01@gmail.com, Timothy W. Hanks. Furman Univ, Greenville, South Carolina, United States*

Alginic acid sodium salt solutions of 2% w/v and pyrrole of various concentrations were mixed with sodium persulfate and sodium bicarbonate on ice for six hours, allowing for the polymerization of the pyrrole. Following 48 hours dialysis, excess water was removed under vacuum to return the situation to original volume, after which solutions were stored at 4 C. Solutions were then crosslinked with various concentrations of calcium carbonate and GDL, and samples were characterized spectroscopically, then analyzed by thermal gravimetric analysis, and capillary rheometry to observe changes in viscosity and thermal decomposition at various ratios of alginate to pyrrole and at different crosslinking percentages.

2015 Joint Southeastern/Southwest Regional Meeting 1079

Synthesis and kinetic studies of a manganese(V)-oxo corrole

***Haleh Jeddi**, haleh.jeddi231@topper.wku.edu, Weilong Luo, Rui Zhang. Chemistry, Western Kentucky University, Bowling Green, Kentucky, United States*

Free base corrole ligands are unsaturated analogues of corrin, found in vitamin B12, and are 19-carbon analogues of well-studied porphyrins. In this study, 5,10,15-tripentafluorophenyl corrole [H_3TPFC] and its manganese complex [Mn^{III}(TPFC)·OEt_2] were successfully synthesized according to literature-reported methods. A

manganese(V)-oxo species [Mn^{V}(TPFC)O] was generated by oxidation of the corresponding manganese(III) precursor with different oxygen sources. The kinetics of its epoxidation, hydroxylation and sulfoxidation reactions were investigated under pseudo-first-order conditions. Typical rate constants for hydroxylation of ethylbenzene, sulfoxidation of thioanisole and epoxidation of *cis*-cyclooctene include 2.68 x 10^{-4} $M^{-1}s^{-1}$, 0.530 $M^{-1}s^{-1}$ and 1.06 x 10^{-2} $M^{-1}s^{-1}$, respectively. The kinetic data indicates that Mn^{V}(TPFC)O reacts via a disproportionation pathway to generate a putative manganese(VI)-oxo species as the true oxidant.

2015 Joint Southeastern/Southwest Regional Meeting 1080

Synthesis, characterization, and luminescent properties of lanthanide dipyridophenazine functionalized complexes for potential bio-imaging applications

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Lanthanide complexes are used for their luminescent properties in bioimaging; however, their application is limited do to their high toxicity. The purpose of this research is to synthesize phenanthroline based ligands that can coordinate with lanthanides and allow the complexes formed to be occluded into a silica matrix. These complexes will also contain Thenoyltrifluoroacetone (TTA) ligands complexed to the lanthanide. TTA ligands are known to act as antenna ligands which efficently absorbs and transfers energy directly to the lanthanide. We have synthesized a family of dipyrdio[3,2-a:2',3'-c]phenazine (DPPZ) based ligands and measured their quantum yields. We are working toward incorporating silyl ether functional groups so that these complexes can be easily coated in glass. In doing so, the toxicity of the molecule will be reduced and rendered safe for biomedical imaging. The results we will report for are various ways to synthesize these molecules and measure the fluorescence of each variation.

2015 Joint Southeastern/Southwest Regional Meeting 1081

5-isopropyl 1,3-cyclohexanedione synthesis

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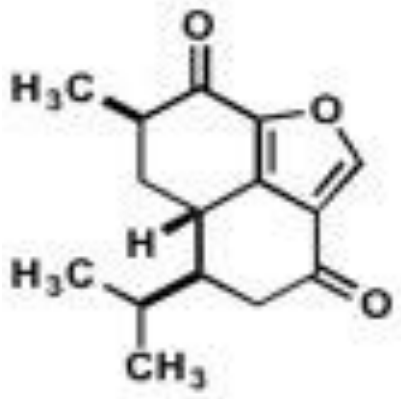
5-isopropyl 1,3-cyclohexanedione is the starting material used in the synthesis of hibiscone C. Hibiscone C is a furanosteriod, analogous to viridin and wortmannin. The furanosteriod family is of interest to the scientific community due to their possible usage as a chemotherapeutic. At various points in the synthesis there are chances to modify the molecule in different ways such as cyclopropanation. Further study of hibiscone C and its derivatives is needed to fully understand its biological activity and progress towards these goals will be discussed.



2015 Joint Southeastern/Southwest Regional Meeting 1082

Abstract of synthesis and characterization of Co complex with isoquinoline group for H_2 production

***Kandria Driskill**, kandria.driskill@smail.astate.edu. Arkansas State University, Little Rock, Arkansas, United States*

The long term goals for our study is to eventually replace all fossil fuels with renewable sources of energy such as water and sunlight. To achieve this goal, out lab is working to develop a better understanding of the fundamentals of water splitting for hydrogen production along with the mechanism of metal complexes in this process and with that understanding be able to discover new catalysts for the production of hydrogen.
There has already been one catalyst for water splitting be made, known as DPA-BPY or just DPA, but it is not very efficient, so my purpose was to synthesize and analyze the reactivity a new catalyst from an Isoquinoline structure through the means of photolysis and gas chromatography. This new catalyst is referred to as Iso-DPA-$CoCl_2$.
Photolysis is the simply explained as shining a light of a certain wavelength at your catalyst and by taking a sample via syringe and analyzing it with a gas chromatography machine, you can analyze how much hydrogen was produced from the light energy splitting the water.
Through running numerous photolysis tests at pH levels ranging from 3.89-7, my Isoquinoline catalyst showed to be significantly less efficient at producing hydrogen than the original DPA catalyst; this is thought to be caused by the reaction between the second ring on the isoquinoline interacting with the close-by pyridine ring and thus shifting both rings out of their plain. The solution to this was designed by one of my mentors, Dr. Ramana Reddy, who created the Isoquinoline catalyst with the second ring is shifted over one carbon allowing it to react free of the pyridine. This catalyst has been tested at only two of the pH levels, pH 5.01 and 3.89; at pH 5.01 it had almost reached to amount of hydrogen produced as the DPA catalyst, and at pH 3.89 the new isoquinoline catalyst's hydrogen production actually exceeded that of the DPA. This new Isoquinoline catalyst seems to be a promising replacement for DPA, but further research has to be done before any conclusions can be made.

2015 Joint Southeastern/Southwest Regional Meeting 1083

A process for the production of a stain-resistant polymer application

***Joe Holland**, Jsholl1683@ung.edu, Avery Shupert. Chemistry, University of North Georgia, Thomasville, Georgia, United States*

This project comprises a stain-resistant configuration for copolymer chains of styrene maleic anhydride (SMA), as well as the process involved in the creation and application of the stain-resisting compound. The stain-blocking agent is bonded to nylon 6,6, a common component of nylon carpeting. A sample portion of nylon was created as a component for this experiment; the synthesised nylon is representative of nylon carpet fiber. As a control, we apply 0.05 molar red food dye to a portion of the nylon sample. Under controlled conditions, the food dye bonds with the polymer chains of the nylon, ultimately staining the sample. Furthermore, we will synthesize a SMA copolymer to create a stain-blocking compound that will be applied to the polymer chains of nylon. Once the stain-blocker is applied to a portion of the nylon sample, food dye will be used to test the effectiveness of the stain-blocking composition. The control group will then be compared with the experimental group. The results should show that the stain-blocker prevents the food dye from staining the nylon sample, and result in the synthesis of a successful stain-blocking agent for nylon, 6,6 carpet fibers.

2015 Joint Southeastern/Southwest Regional Meeting 1084

Determining the mechanism of oxidation of β-estradiol by lactoperoxidase

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Estrogenic hormones, when oxidized, are known to present carcinogenic risk for humans. Free radical derivatives of estrogenic hormones, created through enzymatic oxidation reactions, may cause mutations of DNA. β-Estradiol, in particular, is susceptible to oxidative changes by the enzyme lactoperoxidase (LPO). LPO is produced in the mammary glands, suggesting that this oxidation could be implicated in breast cancer. Therefore, this research looks to understand the mechanism by which β-estradiol is oxidized, to help understand how such oxidation could be prevented. Model studies of oxidation were performed with the hormone β-estradiol and known oxidizing agents, either hydrogen peroxide (H2O2), copper (II) salts, or a mixture of the two. Each oxidation reaction was monitored spectroscopically in order to quantify the oxidative change. The estradiol product from each model system was analyzed through NMR in order to identify the molecular structure of each. With these model studies complete, the reaction between β-estradiol and lactoperoxidase (LPO) was run. The oxidized product was analyzed the same way, comparing the results to each model system. Similarities in product structure from LPO-oxidation suggest similarities in reaction mechanisms.

2015 Joint Southeastern/Southwest Regional Meeting 1085

Modification of fabric surfaces to prevent biofouling

*Timothy W. Hanks[1], **Shaquana Douglas**[2], quanad13@gmail.com, Godfrey Mbah[2]. (1) Furman Univ, Greenville, South Carolina, United States (2) Chemistry, Johnson C. Smith University, Charlotte, North Carolina, United States*

Polyester, cotton, nylon, and Lycra fabrics were coated with polypyrrole (PPy) and then treated with a thiol-terminated polyethylene glycol (PEG). The fabrics were characterized by surface resistivity, FTIR-ATR, thermogravimetric analysis, and contact

angle measurements. Each fabric type was then exposed to E-coli BL21(DE3) modified to express green fluorescent protein (GFP). After incubation, they were washed gently to remove non-adhered cells. The relative amount of e-coli adsorbed on the uncoated fabric, fabric-PPy, and fabric-PPy-PEG were determined using fluoremetry. For the polyester, nylon, and lycra fabrics, GFP evaluation showed that there were significantly less e-coli adsorbed on the fabric-PPy-PEG as compared to the fabric-PPy and the uncoated fabrics. For the cotton fabric, the GFP evaluation suggested that there were less e-coli on the fabric-PPy-PEG but the evidence was not as conclusive.

2015 Joint Southeastern/Southwest Regional Meeting 1086

Biological activity of hibiscone C

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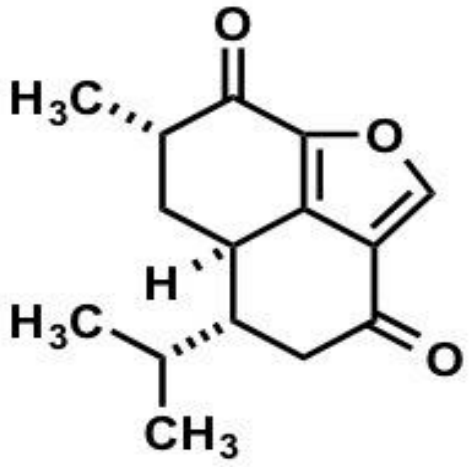
The sesquiterpene furanosteroid family includes molecules such as hibiscone C and wortmannin. Wortmannin, a natural product in this family, is of interest because of its ability to inhibit PI3-K, an enzyme important to cell growth and differentiation. The natural product is very unstable because of its reactivity towards water in aqueous solutions, making it unideal as a practical inhibitor *in vivo*. Understanding the inhibition of PI3-K is important when considering cancerous cell proliferation and survival. Biological activity of hibiscone C has shown to inhibit the PI3-K.



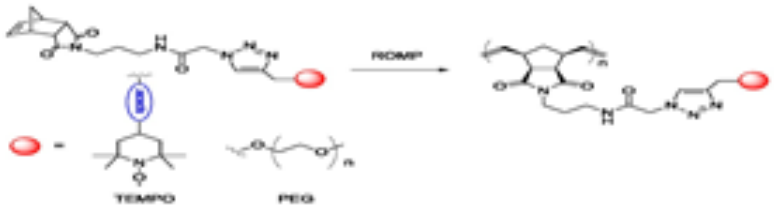
Hibiscone C

2015 Joint Southeastern/Southwest Regional Meeting 1087

(7-oxa)norborene derivatives containing TEMPO and PEG for the production of copolymeric materials via ROMP with potential vasodilating properties

Carl A. Jones*, cj03223@georgiasouthern.edu, Helen Saenz, Hans J. Schanz. Chemistry, Georgia Southern University, Statesboro, Georgia, United States*

The reducing properties of the 2,2,6,6-tetramethylpiperidine-1-oxidyl (TEMPO) group have been used to regulate the concentration of reactive oxygen species (ROS) in mammalian and human tissue. Excessive concentrations of ROS cause inflammation and hence, vasoconstriction. TEMPO derivatives have been demonstrated to offset this effect. Polyethylene glycol is a biocompatible, water-soluble polymer which reduces the response of the immune system to body foreign entities. Our project focuses on the efficient production of copolymers which contain both functionalities, PEG and TEMPO, and investigate those for potential medical applications. For this purpose we designed a template synthesis of (7-oxa)norbornene derivatives where we are able to attach PEG and TEMPO via click reaction in the final step. These derivatives can be polymerized to give new copolymers via ring opening metathesis polymerization (ROMP) using a 3rd generation Grubbs-type olefin metathesis catalyst. We anticipate that these materials are metabolized slowly and hence may be able to maintain their vasodilating properties significantly longer than low-molecular weight TEMPO compounds.



ROMP of TEMPO and PEG containing (oxa)norbornene derivatives

2015 Joint Southeastern/Southwest Regional Meeting 1088

Functionalizing (7-oxa)norbornene derivatives with TEMPO and PEG via click reaction

***Caleb Bohannon**, cb06635@georgiasouthern.edu, Sarah E. Roessler, Hans J. Schanz. Chemistry, Georgia Southern University, Statesboro, Georgia, United States*

In our search for a stable, extracellular form of hemoglobin that can be used as an efficient and storable substitute for red blood cells which is compatible with any blood type, we are developing new polymers containing 2,2,6,6-tetramethylpiperdinoxidyl (TEMPO) groups and polyethylene glycol (PEG) to a polymer. We anticipate that hemoglobin can be modified with these copolymers to offset the toxic side effects of cell-free hemoglobin. Key to the template synthesis of monomers which can be polymerized via ring opening metathesis polymerization is the 1,3 Huisgen cycloaddition, aka click reaction, which can bind these functionalities to a modified norbornene derivative using the click-reaction. We have investigated two major pathways by using (oxa)norbornene azides and alkyne-modified TEMPO and PEG as well as the reverse, with (oxa)norbornene alkynes and TEMPO and PEG azides. We will present findings of the efficiency of the coupling reactions and polymerization of the functional monomers.

2015 Joint Southeastern/Southwest Regional Meeting 1089

Design and synthesis of tetrahydro-β-carbolines

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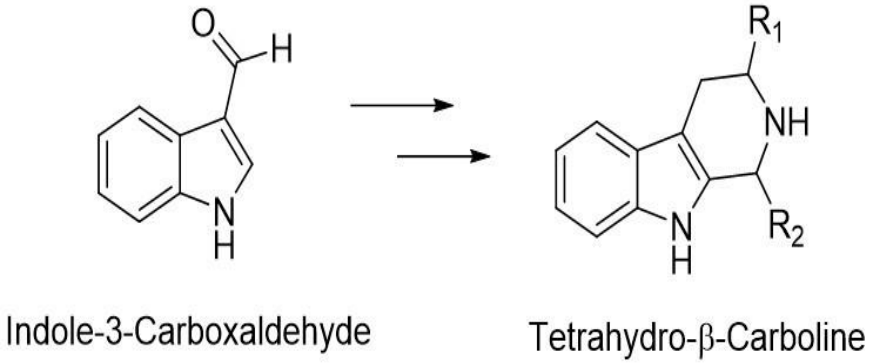
Tetrahydro-β-carbolines (Tryptolines) are a part of the indole alkaloid family and are found in many plants and animals. They possess a wide range of biological activities including: antimalarial, antibacterial, and antifungal. Many tryptolines are also known to be competitive selective monoamine oxidase inhibitors (MAOIs) used for the treatment of depression and anxiety. Herein we report the synthesis of a small library of 1-substituted tryptoline compounds via the Pictet-Spengler reaction.

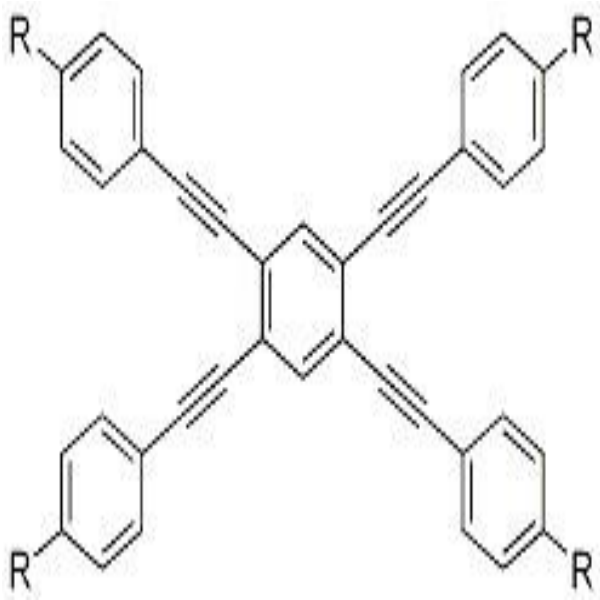


2015 Joint Southeastern/Southwest Regional Meeting 1090

Synthesis of polyphenylethynylarenes as antitumor agents

***Christopher Fisher**, ccfisher@mc.edu, Trent D. Selby. Chemistry & Biochemistry, Mississippi College, Clinton, Mississippi, United States*

The syntheses of a variety of polyphenylethynylarenes are reported here. Starting with 1,2,4,5-tetraiodobenzene and reacting with various arylacetylenes under Sonogashira coupling conditions, [$Pd(PPh)_3Cl_2$], afforded the 1,2,4,5-tetrakis(2-arylethynyl)benzene derivatives in high yields. 1,2,4,5-Tetraiodobenzene was prepared from the reaction of benzene with periodic acid / potassium iodide in concentrated sulfuric acid and isolated in a 60% purified yield. The polyphenylethynylarene molecules are potential antitumor agents.



2015 Joint Southeastern/Southwest Regional Meeting 1091

Characterization of halogen bond interactions in thiophene-based building blocks

Jamey L. Wilson*, jlwilso5@go.olemiss.edu, Chesney Petkovsek, Peyton L. Reves, Jon Williams, Jonah W. Jurss, Nathan Hammer, Gregory S. Tschumper, Davita L. Watkins. Chemistry and Biochemistry, University of Mississippi, Oxford, Mississippi, United States*

Organic semiconducting devices such as organic light emitting diodes (OLEDs) and organic photovoltaics (OPV) offer an alternative to inorganic electronics as they consist of low cost, flexible, and eco-friendly materials. However, the efficiency of these devices depends significantly on the supramolecular structure formed by the organic molecules. Non-covalent interactions—such as halogen bonding (XB)—have shown to act as powerful tools for programming nanoscale architectures. Halogen bonds, analogous to hydrogen bonds, are interactions between Lewis acidic halogen atoms and electron-pair donating heteroatoms. Reported is the analysis of supramolecular structures formed by thiophene-based building blocks equipped with self-assembling halogen bonding (XB) domains. Solution phase studies of XB complexations between nitrogen containing heterocycles and aryl-halides were conducted using nuclear magnetic resonance (NMR) and Raman spectroscopy. Among the XB assemblies, 1:1 complexation of pyridine derivatives and iodopentafluorobenzene exhibited the strongest interaction. Along with computational methods, pyridyl thiophene derivatives were designed and

synthesized via Stille coupling. X-ray crystallography was used to investigate the natural solid state packing abilities of the single components and their XB assembly. Thermal analysis using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) revealed that co-crystals containing iodopentafluorobenzene exhibit higher decomposition temperatures. The results of the study speak to the use of halogen bonding molecules in organic electronic device application.

2015 Joint Southeastern/Southwest Regional Meeting 1092

Design and synthesis of hybrid furan-based oligomers for application in optoelectronic devices

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In the field of organic electronics, there is a need for new semiconducting materials possessing properties that afford high efficiency devices. It is well established that thiophene containing molecules are the most commonly used organic materials because of their superior electronic properties. However, oligothiophenes tend to suffer from low solubility and inefficient luminescence. Recently, studies have emerged focusing on their close analogues, oligofurans. Replacement of the sulfur atom with oxygen yields electron-rich oligomers having a greater dipole resulting in both higher solubility and fluorescence as well as rigidity. However, furans possess relatively high-lying HOMOs making them more susceptible to decomposition. Reported is the synthesis and characterization of novel hybrid furan-based building blocks for semiconducting materials. To provide better comparison, the synthesis of the hybrid systems via Stille coupling was completed in parallel with fully-thiophene congeners and characterized by nuclear magnetic resonance (NMR) spectroscopy. These hybrid oligomers—as opposed to the corresponding oligothiophene congeners—are highly solution-processable and display ~10 ^{o}C difference in stability evident from thermal decomposition temperatures. In addition, the hybrid materials feature absorbance onset values within the 600 nm range—in good agreement with most efficient semiconducting molecules. The results indicate that furan-based hybrid oligomers can yield stable organic electronic devices possessing optical and charge carrier mobilities that are comparable to—even surpass—those of the commonly used oligothiophene.

2015 Joint Southeastern/Southwest Regional Meeting 1093

Synthesis of flat dendrimers

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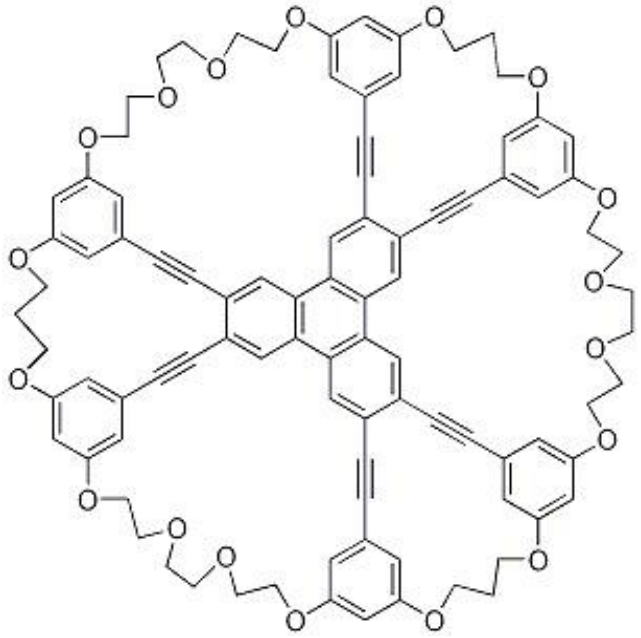
Organic structures that are highly-conjugated (π-resonance) are useful materials for advanced electronic and photonic applications. We report here the preparation of highly-conjugated, flat, ethynyl dendrimers with ether linkages between the dendritic arms. Dendritic architectures, by definition, are spherical, three-dimensional structures that branch outward in a symmetrical fashion. Typical ethynyl dendrimers have poor conjugation due to rotation/twisting about the bonds. We seek to redefine the term dendrimer by constructing two-dimensional structures. Tying the arms of the dendrimer together by cylclization will avoid any twisting or rotation about the bonds and should promote better conjugation throughout the structure.



2015 Joint Southeastern/Southwest Regional Meeting 1094

Synthesis of 2-dimensional aminopolyphenylethynylarenes

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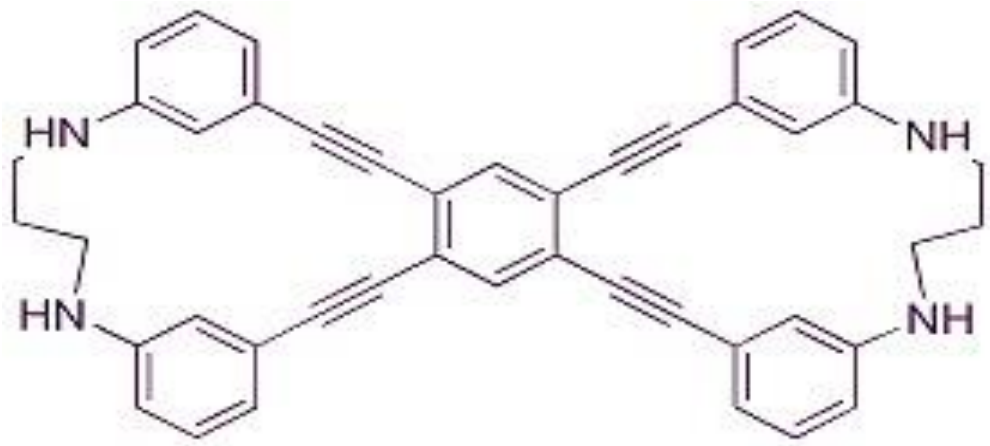
Molecules containing high degrees of π-conjugation are ideal materials for advanced electronic and photonic applications. Conjugation should be promoted by constructing flat 2-dimensional architectures. We report here, the synthesis of highly-conjugated 2-dimensional aminopolyphenylethynylarenes. The synthesis begins with alkynylation of 3-nitro-1-bromobenzene with trimethylsilylacetylene under Sonogashira coupling conditions. The resulting alkyne is deprotected under mild conditions using potassium carbonate and methanol to give 1-ethynyl-3-nitrobenzene in high yield. This key intermediate, 1-ethynyl-3-nitrobenzene, can be used to synthesize a large variety of flat 2-dimensional structures. Additionally, these nitrogen containing molecules can easily be oxidized to radical cations giving rise to some unique electronic properties.

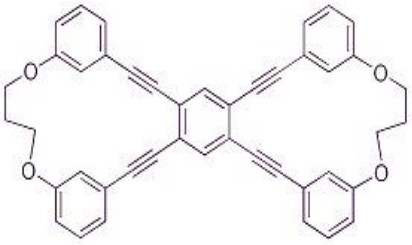


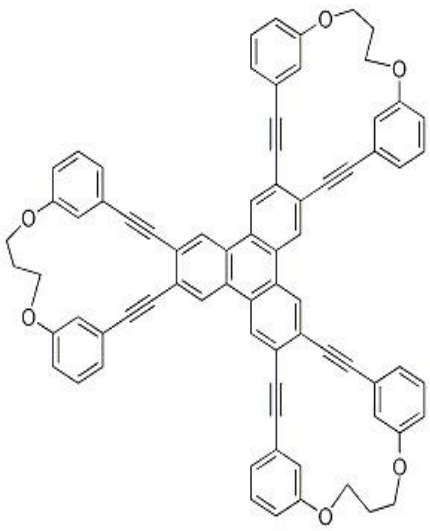
2015 Joint Southeastern/Southwest Regional Meeting 1095

Synthesis of conjugated macrocyclic polyphenylethynylarenes

Lauren Bicker*, albicker@mc.edu, Trent D. Selby. Chemistry & Biochemistry, Mississippi College, Raymond, Mississippi, United States*

A series of “flat” two-dimensional macrocyclic polyphenylethynylarenes were prepared in good yields. The syntheses involved Sonogashira coupling of phenylethynylarenes with the appropriate aryl halides followed by cyclization with ether linkages. Cyclization reduces twisting and promotes electron conjugation throughout the structures. These “flat” molecules are expected to show directed energy and electron transfer within a highly conjugated system and may potentially be effective in the preparation of photoreactive materials such as electronic sensors or light harvesting materials.





2015 Joint Southeastern/Southwest Regional Meeting 1096

The Wittig reaction: Analysis of product yield, purity, and greenness

***Jenny Whitmire**, jwhitmire0611@lions.piedmont.edu, Elaine L. Bailey. Natural Science, Piedmont College, Dahlonega, Georgia, United States*

There has been a major push in organic chemistry to improve upon some of the more useful chemical reactions by making them more environmentally friendly, this movement is known as green chemistry. The Wittig reaction is one such reaction. It has been used for many years as a general method of making alkenes from aldehydes or ketones. Although the reaction is extremely versatile, the Wittig reaction is not very green. Since most undergraduate organic chemistry students perform the Wittig reaction, being able to make this reaction more green would be beneficial to the environment. The purpose of this research was to investigate three alternative Wittig procedures and determine their effects on product yield and purity. Analysis of the reactions green character was also investigated. Reaction 1 was done using the standard Wittig procedure. Reaction 2 was done by replacing the solvent with a more environmentally friendly one. Reaction 3 was done using a solvent free procedure. Analysis of the percent yield of each reaction proved to be non-normal, so a nonparametric Kruskal Wallis test was applied. A p value of 0.004 revealed a significant difference between the average percent yield of the three reactions, so a Mann-Whitney U test was used to locate the difference. A p value of 0.056 indicated a non-significant difference between the percent yields of reaction 1 and 2. However, a significant difference was found when comparing the percent yield of reaction 1 with 3, and 2 with 3. These conclusions were derived from p values of 0.008 and 0.009. Melting point analysis determined the product purity from each reaction. Results show that the product from Reaction 1 contained many impurities, while Reaction 3 was the most pure. Anastas and Warner's 12 Principles of Green Chemistry were used to investigate each reactions green character. Conclusions about the overall "best" reaction is dependent on if the desired product is one of high percent yield, purity, greenness, or energy efficiency.

2015 Joint Southeastern/Southwest Regional Meeting 1097

Vapor liquid coexistence properties of hydrofluoromethanes using first principles Monte Carlo simulations

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For the past 40 years chlorofluorocarbons (CFCs) have been banned in the United States as a result of their negative impact on the environment and the damage caused to the ozone layer. As a result, hydrofluorocarbons (HFCs) have been introduced as replacement for CFCs in the role of propellants, refrigerants, metered dose inhalers and various other uses. Understanding their structural and thermodynamic properties is critical to process design and development. To understand the saturation properties of fluoromethane, difluoromethane, and trifluoromethane, we've employed First Principle Monte Carlo (FPMC) simulations via the CP2K software suite. In order to accurately predict vapor liquid behavior of these compounds, it is important to account for the dispersion interactions. These dispersion forces arise due to the induced dipole-induced dipole interactions, and are critical in understanding the thermodynamic properties of HFCs. The traditional and widely used local and semilocal Kohn-Sham Density Functional Theory (KS DFT) does not accurately account for van der Waals forces.

Here, we have examined the efficacy of different dispersion-corrected and nonlocal density functionals (PBE-D3, BLYP-D3, and rVV10), which are designed to capture dispersion interactions. Our simulations indicate that the PBE-D3 functional performs better than rVV10 for the saturated liquid densities. Additionally, all of the models drastically under predict the vapor density of the HFCs in our simulations, to the detriment of boiling point, critical pressure, and critical temperature predictions. Our simulations suggest that further refinements in the density functionals are necessary to accurately predict vapor liquid equilibria of hydrofluoromethanes.

2015 Joint Southeastern/Southwest Regional Meeting 1098

Preparation and characterization of a palladium catalyst on ceria support

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Metal catalysts are most commonly used in catalytic converters to remove air pollutants. Recent efforts on the development of more efficient catalysts for carbon monoxide oxidation have been reported. The objective of this project is to develop a better catalyst for low temperature catalytic oxidation of carbon monoxide in the temperature range 25-100 ^{0}C. A palladium catalyst on ceria support is prepared by slurry method technique, dried overnight and then calcined at 450 ^{0}C. The catalyst is characterized by a Pulse Chemisorb equipment (Micrometrics) with oxygen gas as the adsorbate. Pulse chemisorption data is used to calculate total surface area, percent dispersion, and average crystallite size. The results of this undergraduate research will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 1099

Construction of p-type heterojunction CuO|CuBi2O4 nanowires for photochemical reduction of aqueous protons as sustainable source of energy

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For over a decade, copper oxides (CuO and Cu2O) have been utilized as p-type semi-conductor oxides for solar water splitting. Very recently, an FTO CuO|CuBi2O4|Pt electrode was produced, which yielded a significantly improved photocurrent compared to the FTO CuO|Pt or FTO CuBi2O4|Pt electrodes alone. While the original photoelectrode was formed on FTO slides using the dropcast method, the parameters of this research also included application by spin-coating and on ITO slides. Moreover, concentrations and layers on slides were varied to observe differences in morphology and photocurrent efficiency. Ultimately, ITO and FTO electrodes showed similar efficiency, with photocurrency decreasing with additional layering.

2015 Joint Southeastern/Southwest Regional Meeting 1100

Molecular electronics: Using computational chemistry to design devices

***Sam King**, sam.king@live.longwood.edu, Benjamin Topham. Chemistry and Physics, Longwood University, Farmville, Virginia, United States*

The field of molecular electronics has received much attention in recent years. This has led to much progress in the fabrication of molecular devices, but the viable production of efficient devices has not yet been established and a complete theoretical understanding is still being pursued. We have undertaken a computational study of molecular devices to better understand how key chemical properties govern device function. We have used a Landauer-based scattering approach with self-consistent non-equilibrium Green's function formalism to calculate electron transmission through single molecule devices. We have studied the effects of molecule length, linking groups, and geometry using representative molecules in an effort to determine how to optimally design efficient molecular devices and control device function through chemical modification.

2015 Joint Southeastern/Southwest Regional Meeting 1101

Molecular rotors: An investigation of planar boron clusters as Wankel motors

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Molecular machines have become a very intriguing area of research in chemistry and material science. In the past few years, our group and others have become interested in understanding the mechanical and thermodynamic properties of boron clusters. The planar geometry is preferred for small to medium sized boron clusters (B_n) and it has been shown that the clusters tend to form concentric rings. For certain n values the inner ring rotates with extremely low rotational barriers relative to the outer ring. It has been proposed that the use of electric fields may allow for the controlled unidirectional rotation of one of the rings relative to the other. We investigate in this work the thermodynamics of the rotation of the rings relative to each other in B_{19}^-. We have been especially interested in understanding how the rotational patterns depend on temperature, and in developing a detailed understanding of the dynamics of the bonding as the rings rotate relative to each other. The lessons learned from this system are to be applied to other novel proposals for molecular Wankel motors based on the bonding motif observed for boron clusters.

2015 Joint Southeastern/Southwest Regional Meeting 1102

Conventional strain energies of thiaziridine and the thiazetidines

Joshua Gramm, Shelley A. Smith, ***David H. Magers****, magers@mc.edu. Chemistry Biochemistry, Mississippi Colg, Clinton, Mississippi, United States*

The conventional strain energies for thiaziridine, 1,2-thiazetidine, and 1,3-thiazetidine are determined within the isodesmic, homodesmotic, and hyperhomodesmotic models to investigate the effect of third-row elements on the strain energies of three- and four-membered rings. Optimum equilibrium geometries, harmonic vibrational frequencies, and corresponding electronic energies are computed for all pertinent molecular systems using self-consistent field (SCF) theory, second-order perturbation theory (MP2), and density functional theory (DFT). The DFT functionals employed are Becke's three-parameter hybrid functional using the LYP correlation functional and the M06-2X high nonlocality hybrid functional from Thular and Zhao. The basis sets employed are Dunning and coworkers' correlation consistent basis sets: cc-pVDZ, cc-pVTZ, and cc-pVQZ. In addition, cc-pV(D+d)Z, cc-pV(T+d)Z, and cc-pV(Q+d)Z basis sets are also investigated to determine the effect of the extra d function for sulfur on the overall

results. Results are compared to the conventional strain energies of small cyclic hydrocarbons and to other heterocyclic systems. We gratefully acknowledge support from the NSF (EPS-0903787) and from the Mississippi College Catalysts, the alumni support group of the Department of Chemistry & Biochemistry.

2015 Joint Southeastern/Southwest Regional Meeting 1103

The influence of organic substituents on the stability of dative bonding

***Ezana Befekadu**, ezana.befekadu@richmond.edu, Kelling J. Donald. Chemistry, University of Richmond, Richmond, Virginia, United States*

The stability of bonding interactions between MFH_3 molecules and borylene species (R--B), where M = Ge, Si, and C, is investigated. If these interactions are stable enough, proton transfer will not occur. Borylene is by no means a particularly stable species, we noticed, however, that under some conditions depending on the identity of the R substituent the H transfer does not occur and a dative bond (or weak sigma hole interaction) between the monovalent B—R and the M center. The energy barrier going from the monovalent to the trivalent B substituent is examined and discussed for a range of electron withdrawing and donating R substituents. For M group elements such as Silicon, proton transfer occurred more often, which may be explained by the low electronegativity of Silicon and the weakness of the Si---H bond. The reverse appears to be the case for Carbon.

2015 Joint Southeastern/Southwest Regional Meeting 1104

Conventional strain energy in ketene acetals and ketene aminals

*Sarah G. Travis, Shelley A. Smith, **David H. Magers**, magers@mc.edu. Chemistry Biochemistry, Mississippi Colg, Clinton, Mississippi, United States*

Cyclic ketene acetals and ketene aminals belong to a class of organic molecules characterized by a nucleophilic exo-methylene carbon attached to a carbon with two adjacent highly electronegative atoms. In the case of ketene acetals these two atoms are oxygen, and in ketene aminals these are nitrogen. Such systems have been shown to react with a large number of mono- and dielectrophiles to yield a rich variety of organic reactions including tandem cyclizations, arylvinyl ester formation, new heterocyclic ring and fused ring formation, ring-retained polymerizations, and stereoselective radical cyclizations. Since the stability of the ring of these ketene acetals and aminals are important in these reactions, the conventional strain energies for representative systems are determined within the isodesmic, homodesmotic, and hyperhomodesmotic models to investigate the role the external double bond plays in the ring strain of these heterocyclic systems. Specifically, the conventional strain energies of 2-methylene-[1,3]dioxetane, 2-methylene-[1,3]diazetidine, 2-methylene-[1,3]dioxolane, and 2-methylene-imidazolidine are compared to those of [1,3]dioxetane, [1,3]diazetidine, [1,3]dioxolane, and imidazolidine . Optimum equilibrium geometries, harmonic vibrational frequencies, and corresponding electronic energies are computed for all pertinent molecular systems using SCF theory, second-order perturbation theory (MP2), and density functional theory (DFT). The DFT functionals employed are Becke's three-parameter hybrid functional using the LYP correlation functional and the M06-2X high nonlocality hybrid functional from Thular and Zhao. The basis sets employed are Dunning and coworkers' correlation consistent basis sets: cc-pVDZ, cc-pVTZ, and cc-

pVQZ. We gratefully acknowledge support from the NSF (EPS-0903787) and from the Mississippi College Catalysts, the alumni support group of the Department of Chemistry & Biochemistry.

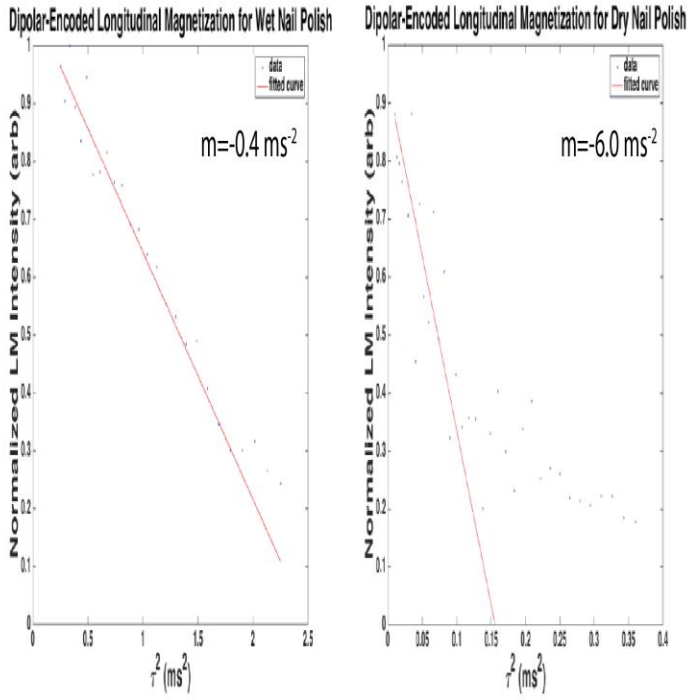
2015 Joint Southeastern/Southwest Regional Meeting 1105

Monitoring the development of intermolecular networks during the curing of coatings using single-sided NMR

***Frankie Morin**, fjmorin@email.wm.edu, Tyler K. Meldrum. Chemistry Department, College of William and Mary, Williamsburg, Virginia, United States*

We are using NMR in an inhomogeneous field in order to track local orientation or order in molecular networks in industrial and fine art coatings. Coatings show a change in cross-linking as the curing process occurs. We use a single-sided magnet to explore how molecular interactions affect nuclear relaxation times as spins realign with the magnetic field and the curing effect on residual dipolar couplings. Residual dipolar couplings are a measure of the interaction between two nuclei and their orientation with respect to the applied magnetic field; these couplings are indicative of intermolecular networks[i].
By taking the relaxation and residual dipolar coupling measurements at the beginning of the curing, and then regularly repeated at time intervals throughout the curing process we track the changes in the intermolecular network. These measurements help determine degree of order of the local orientation in the intermolecular network to establish how depth, thickness of coating, and paint and coating age alter the molecular interactions in the coating. This data compared to information known about both the kinetics of the curing reactions of coatings and the properties of the cured coatings gives a more cohesive picture of the intermolecular networks in coatings.

[i] Wiesmath, A., Filip, C., Demco, D. E., & Blümich, B. (2002). NMR of multipolar spin states excited in strongly inhomogeneous magnetic fields. *Journal of Magnetic Resonance (San Diego, Calif. : 1997)*, *154*(1), 60–72. doi:10.1006/jmre.2001.2458



Comparison of dipolar-encoded longitudinal magnetization between wet and dry nail polish to show residual dipolar couplings and cross-linking density difference.

2015 Joint Southeastern/Southwest Regional Meeting 1106

Polarizing substituents dictate the relative energies of weak (halogen-bonding) interactions

***Janak Jaini**, janak.jaini@gmail.com, Kelling J. Donald. University of Richmond, Mechanicsville, Virginia, United States*

Halogen bonds (R3MX---Y) are sensitive to changes in the chemical environments of the Lewis acid. Some of these factors have been formerly studied by our group and others, including the identity of the M center to which X is bonded. So we know, for example, that sigma holes can be tuned. But, the effect of different covalently bonded polarizing substituents (R), such as halides or sigma donors such as methyl groups on the interatomic separations and the interaction energies of bonds by a given halogen atom (X) to a nearby base (Y) is still not completely understood. In this study, the M062X density function method has been utilized to determine the interaction energies and halogen bond distances for pairs of species in which the H substituents are systematically replaced by the far more polarizing F atom. The systems of interest are $MH_{3-n}F_nI\text{-}NH_3$, where M = C, Ge, Pb, Sn and Si. The influence of the fluorine substituents on the sigma hole of iodine is assessed.

2015 Joint Southeastern/Southwest Regional Meeting 1107

Mixed self-assembled monolayers of alkanethiols and their formation on gold substrates

***Stuart Graham**, stuart.graham2831@furman.edu, Marion R. Martin. Furman University, Greenville, South Carolina, United States*

Alkanethiols self-assemble into a one-molecule-thick film on Au substrates called self-assembled monolayers (SAMs). Mixed SAMs, monolayers containing two or more compounds, are formed when multiple alkanethiols are dissolved in a single solution. Mixed SAMs could be immensely helpful in molecular recognition or nanofabrication where certain areas of the monolayer must be unique from the rest. Mixed SAMs of octadecanethiol (ODT) and 16-mercaptohexadecanoic acid (MHA) were formed on gold slides. Monolayer ordering and surface wettability were investigated using a polarization modulation-infrared reflection-absorption spectrometer (PM-IRRAS) and an optical tensiometer respectively. Mixed monolayers of ODT and MHA were formed from single solutions containing concentrations of the two in the ratios 1:3, 1:1, and 3:1. Pure SAMs of ODT and MHA were grown as references. The chemical composition of the monolayers was calculated using Cassie's equation applied to water droplet contact angles. Ordering of the monolayer was determined using the peak locations in the C-H stretching region of the PM-IRRAS spectra. The monolayers higher in ODT concentration produced more ordered and hydrophobic films than their MHA-dominant counterparts. Some work was done to make well-ordered pure MHA monolayers but was largely unsuccessful. Mixed monolayers of ODT and 11-ferrocenyl-undecanethiol were also briefly explored using the same instrumentation. In the future, the lab plans to characterize these monolayers using cyclic voltammetry.

2015 Joint Southeastern/Southwest Regional Meeting 1108

Characterizing mixed self-assembled monolayers of dodecanethiol and 11-mercapto-undecanol

***Alexis Glover**, alexis.glover2@furman.edu, Marion R. Martin. Furman University, Greenville, South Carolina, United States*

Self-assembled monolayers (SAMs) are the arrangements of molecules or atoms adsorbed onto solid surfaces. SAMs are composed of three groups: the head group binds covalently to the gold substrate, the alkane-chain stabilizes the monolayer, and the tail group determines the SAM chemistry. The particular goal of this study was to characterize mixed SAMs by two methods: varying the concentrations in a single solution and varying the deposition time in two separate solutions. Cassie's Equation was used to determine the composition of the film. Both 11-mercapto-1-undecanol (11-MUD) and dodecanethiol (DDT) were used to coat the gold slide. Solutions of varying concentrations were made with the following ratios: 3:1, 1:1, 1:3. Films were also grown with pure 11-MUD and DDT as references. In the second growth method, deposition time and order were tested in 1mM of 11-MUD and DDT with five ratios of time: 3:1 MUD: DDT, 1:3 MUD: DDT, 2:2 MUD: DDT, 3:1 DDT: MUD, and 1:3 DDT: MUD. The SAMs were analyzed using polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS.) PM-IRRAS evaluations focused on the peak intensities and the positions of the aliphatic C-H asymmetric and symmetric stretching vibrations. Surface wettability was studied using an optical tensiometer, indicating whether the film was hydrophobic or hydrophilic. Results show that, when decreasing the concentrations of DDT, the methyl symmetric peak intensities also decreased, which corresponds with the contact angle data, where the contact angle also decreased. Also, results show that the solution that the Au substrate is placed in first will be more prevalent in the monolayer, showing that varying the deposition time and order is not the most effective way to form a mixed monolayer. Furthermore, mixed SAMs of 11-MUD and DDT can be grown reproducibly.

2015 Joint Southeastern/Southwest Regional Meeting 1109

Computational studies of the binding of quinoline-based ligands to plasmepsin IV

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The malaria parasite, Plasmodium, is known to harbor aspartic acid proteases known as plasmepsins which are responsible for the degradation of hemoglobin in human red blood cells. These parasites, the most virulent of which is the falciparum species, derive nutrients from the human host through this degradation process. In this study, molecular docking and molecular dynamics simulations were used to investigate the binding of quinoline-based antimalarial drugs (chloroquine, amodiaquine, mefloquine, and quinine) to plasmepsin IV, as a way of gaining insight into whether the inhibition of hemoglobin degradation is a potential mechanism for antimalarial activity. Docking identified two predominant binding sites for the ligands on plasmepsin IV. The more favorable binding site was located in a pocket at the interphase between the two subunits of the plasmepsin dimer. The ligands bound to this site with average binding energies ranging from –6.45 kcal/mol to -4.77 kcal/mol. The second site, located in a groove on one of the subunits had average binding energies ranging from -5.96 kcal/mol to -4.52 kcal/mol. The most favorable binding modes for each ligand in the identified binding sites were also determined.

2015 Joint Southeastern/Southwest Regional Meeting 1110

The impact of soot morphology and mixing state on particle optical properties

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Soot particles are complicated both chemically and morphologically. Fresh soot from incomplete combustion has variable amounts of elemental carbon (EC) and organic carbon (OC) depending on the combustion conditions; and the particles can be spherical or fractal depending on the relative EC/OC ratios. Once generated from the source, the change in mixing state of soot can have significant impacts on soot properties. This study is exploring the relationship between the mixing state, morphology, and optical properties of atmospheric soot. Models based on Mie theory and Discrete-Dipole Approximation are used to simulate the light scattering property of soot particles with variable mixing states and morphological characteristics. The outcome of our study will contribute to the reconciliation between computational results and experimentally measured optical properties, and facilitate our understanding on the direct radiative forcing by soot aerosol in the atmosphere.

2015 Joint Southeastern/Southwest Regional Meeting 1111

Quenching of cyanoaromatics fluorescence and aromatic carbonyl triplets by model sulfur compounds

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Sulfur-bearing moieties play significant roles in various processes of interest to biology, agriculture, industry, and environmental pollution. The multifarious functions of S are made possible by the numerous oxidation sates in which the element can exist, including some that are capable of facile redox interconversions. We have investigated several model organosulfur compounds for their charge-transfer interactions as donors with photoexcited singlet states of three cyanoaromatics, namely, 1,2,4,5-tetracyanbenzene (TCB), 1,4-dicyanonaphthalene (DCN), and 9,10-dicyanoanthracene (DCA) and with triplet excited states of aromatic ketones (e.g., benzophenone). This paper will present and examine kinetic data on the quenching of steady-state fluorescence of cyanoaromatics by several thiols, sulfides and disulfides and on the quenching of ketone triplets by several thiols (studied by nanosecond laser flash photolysis). In addition, the data on the efficiency of hydrogen transfer from thiols to ketone triplets will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 1112

Effect of pretreatment procedure on Cu-Pd/Al_2O_3 catalysts for selective hydrogenation of acetylene

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The selective hydrogenation of acetyleneto ethylene is investigated over bimetallic single atom alloy (SAA) catalysts in this study. Cu-PdSAA catalysts with different palladium loadings were tested. Among the lower metal loading catalysts tested, the one with 200 ppm Pd loading reached the highest selectivity, and the one with 2% Pd loading had the best conversion. The 500 ppm Pd catalyst had the best conversion when reduced for one hour at 100°C in the feed. It had the best selectivity at low temperatures when reduced in plasma for an hour, and the best selectivity at higher temperatures when both reduced in plasma and in hydrogen. The highest yields for this catalyst were reached by all the samples at the reaction temperature 125°C with the exception of the sample reduced at 100°C for three hours in hydrogen which peaked in yield at 100°C. The catalyst of 500 ppm Pd is studied extensively using various reduction procedures, including changingreduction temperature, using plasma reduction procedure and adjusting reaction feed gas. The results, or the conversions, selectivities, and yields reached in the selective hydrogenation process, will be discussed and related to the pretreatment procedures.

2015 Joint Southeastern/Southwest Regional Meeting 1113

Bonding in group 12 dihalides and limitations on accuracy in optimizations with certain counterpoise correction strategies

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The reliability of relativistic and non-relativistic methods in determining the minimum energy geometry of group 12 dihalides is examined. The influence of counterpoise correction on structures predicted at these levels of theory is studied as well for these dimers, which have relatively high symmetry in the case of the ZnX_2 and CdX_2 dimers. There are different strategies for assessing the counterpoise corrections for basis set superposition energies. We investigate the effects of computing the corrections on the fly during the optimization process on the symmetry of the structure and the nature of the predicted geometries. We find that although the counterpoise corrections can have a beneficial effect – improving the accuracy of the predicted geometries – it may led to misleading geometrical data for high symmetry systems depending on the way in which the fragments are defined during the calculations of the counterpoise corrections. Possible ways of improving this situation, and what it tells us about the current standard implementations of the counterpoise correct, are discussed.

2015 Joint Southeastern/Southwest Regional Meeting 1114

Computational investigation of O-H bond cleavage reactions of primary alcohols and water on stepped rhodium (211) and planar rhodium (111) surfaces using density functional theory

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With current advancements in technology comes an increased dependence on electricity. Combustion of limited fossil fuel resources is the main global source of energy, as well as environmental pollution, leading scientists to search for alternative ways to generate electricity. Fuel cells are a means to efficiently generate energy from hydrogen gas and can produce more sustainable energy if the hydrogen is generated from sustainable hydrogen-containing biomolecules, such as alcohols. Metal heterogeneous catalysts, such as rhodium, are used to facilitate the C-H and O-H bond cleavage of alcohols in hydrogen generation. Density functional theory (DFT) methods were used to investigate O-H bond cleavage at planar (111) and stepped (211) metal surface catalysts. Lowest energy conformations, binding energies and reaction energies of alcohols from 1-5 carbon chain lengths and water as a model adsorbate are calculated by DFT to determine reactivity as a function of chain length at different catalytic adsorption sites.

2015 Joint Southeastern/Southwest Regional Meeting 1115

Computational investigations of molecular electronic properties and hyperpolarizability of organic molecules

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This project has extended previous research from our group investigating the structural and electronic features that contribute to the hyperpolarizability of organic molecules. The previous work found no good correlation between level of theory, basis set, substituents, solvation, total charge, etc. and the accuracy of calculated molecular hyperpolarizability (with respect to experimentally determined values). This project has examined additional molecular electronic properties to determine the correlations

between calculated dipole moment, HOMO-LUMO gap, electron density, electrostatic potential, etc. and calculated hyperpolarizability, for thepourpose of understanding and accurately predicting hyperpolarizability. Comparisons have been made for reference organic molecules [4-nitroaniline, 4'-nitro-4-(N,N-dimethlyamino)azobenzene, etc.], substituted saccharins, and transition metal saccharin complexes.

2015 Joint Southeastern/Southwest Regional Meeting 1116

Gas-phase decomposition studies of Ni^+-aldehyde systems

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Aldehydes are the precursor to many large-scale, industrial reactions. Their low energy and selective transformations impact this industry. This poster presents recent gas-phase decomposition studies of aldehydes mediated by the Ni+ cation. Gas-phase systems are not influenced by solvent and counter-ion effects creating ideal conditions for studying the most basic of reactions. This is conducted by generating electrostatically-bound binary clusters in a supersonic expansion. Energy is supplied to the isolated systems via laser photon absorption and the photon-excited species decompose into charged fragments on the microsecond time-scale. The dissociation event is monitored in a custom time-of-flight mass spectrometer and the kinetics are sampled in real-time.

2015 Joint Southeastern/Southwest Regional Meeting 1117

Why doesn't thermal analysis give consistent Arrhenius parameters for simple systems?

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In thermal analysis, a simple system is one that thermally decomposes in one step through the loss of one or more gaseous compounds to produce one new solid compound. [1,2] Several different approaches have been developed to measure the dynamics of these decompositions, but in general, these different approaches give different values for the Arrhenius parameters. Evidence will be presented that many of these differences result from the breakdown of the assumption that the reaction is following a simple mechanism. Several examples showing how reactions with the carrier gas or with the evolved gases can affect the measured reaction dynamics will be presented. Changing the experimental conditions by changing the cell configuration, the sample size, or the heating rate are easy ways to determine if these secondary processes are occurring.

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[1] Sergy Vyazovkin et al, Thermochim Acta 520 (2011) 1- 19.
[2] Sergy Vyazovkin et al, Thermochim Acta 590 (2014) 1- 23.

2015 Joint Southeastern/Southwest Regional Meeting 1118

Method for determining the enthalpy of reaction for metal oxalates using DSC

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An accurate set of chemical reactions must be determined to accurately determine the enthalpy of reaction. The thermal decomposition of metal oxalates is complicated by the possibility that secondary reactions such as the reaction between the primary products (metal oxide and CO) can occur complicating the analysis or the metal oxide catalyzed disproportionation of CO to produce CO_2 and C makes the determination of a precise set of chemical reactions actually occurring difficult to determine in minimal reactive environments. Evidence is presented that accurate enthalpies of reaction can be determined using slow scans in an oxidizing atmospheres if a flameless combustion catalyst (CuO was used here) is added to the DSC pan. Results obtained for the oxalates of Mn, Fe, Co, Ni, Cu, and Zn agree within a few percent of the better values reported previously.

2015 Joint Southeastern/Southwest Regional Meeting 1119

Reaction paths and path profiles: A new perspective for understanding reaction mechanism

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Chemical reaction paths, otherwise, called reaction mechanisms, provide a detailed atomistic description of a reaction from reactants to products. However, the calculation of such paths presents a formidable task despite the existence of several theoretical methods. Recently we have proposed a classical action-wave based formulation for calculating the reaction paths, where we have adapted a fast marching algorithm to solve the Hamilton-Jacobi equation. This method has the advantage that (i) *a priori* knowledge of a transition state is not required, (ii) the gradient or hessian of the potential are not required and (iii) one-single run with the knowledge of only the reactant state calculates the entire path of the reactions including that of a multi-step reaction. This advantageous feature of the method has allowed us to further explore this method and calculate the paths of a few complex reactions, such as the conformational change of Alanine Dipeptide and the bifurcation reaction of Methoxy Radical. We have computed the path profiles, especially, the reaction path energy (RPE) and reaction path force (RPF) of these reactions to understand the traditional energy-based formulation of reaction dynamics versus the force-based formulation of reaction dynamics. We will discuss our findings on the force-based formulation of reaction dynamics and see what new knowledge can be gained.

2015 Joint Southeastern/Southwest Regional Meeting 1120

Reactions of solvated electrons initiated by sodium atom collisions at the vacuum-liquid interface: Insights into solvation and ionization

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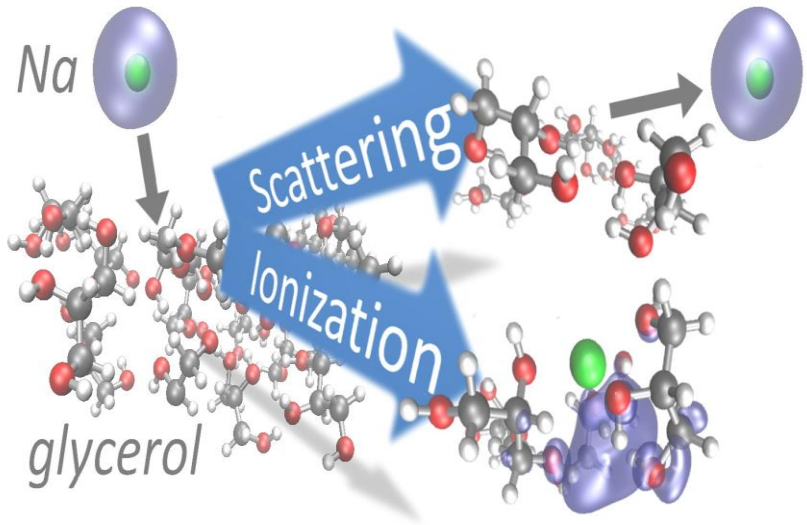
The reactive uptake and ionization of sodium atoms in glycerol were investigated by gas–liquid scattering experiments and ab initio molecular dynamics (AIMD) simulations. A beam of Na atoms was collided with liquid glycerol in vacuum, and the scattered Na atoms' velocity and angular distributions imply that any and all impinging atoms that thermally equilibrate on the surface remain behind to create solvated electrons and Na^+. Solvated electrons are powerful reagents in the liquid phase that break chemical bonds and thereby create additional reactive species, including hydrogen atoms. We explored the distinct chemistry that ensues when electrons are liberated near the liquid surface (using the relatively soft Na atom collisions as initiators) rather than within the bulk.[1] The surface-generated electrons reacted with deuterated glycerol, $C_3D_5(OD)_3$, to produce D atoms, D_2, D_2O, and glycerol fragments. A surprisingly large fraction of the D atoms traversed the interfacial region and desorbed into vacuum before attacking C-D bonds to produce D_2. Complementary AIMD simulations of Na striking a glycerol cluster show glycerol hydroxyl groups reorientation around the Na atom as it makes contact with the cluster and begins to ionize.[2] Distinct correlations among the extent of ionization, separation between Na^+ and e^-, solvent coordination, and binding energies of the Na atom and electron were observed. If time allows, I will also highlight some new insights into modelling the solvated electron in water and glycerol using implicit solvation methods.

(1) Alexander et al., ***Science***, 2012, **335**, 1072-1075; **DOI:** 10.1126/science.1215956
(2) Weins et al., ***J. Am. Chem. Soc***., 2014, **136**, 3065–3074; **DOI:** 10.1021/ja4106144



2015 Joint Southeastern/Southwest Regional Meeting 1121

Photochemical reduction of $CHCl_3$ in SPEEK/HCO_2- aqueous medium via a free radical mechanism

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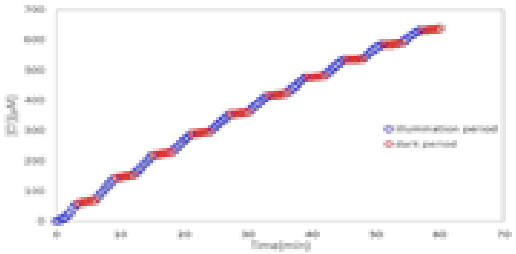
Illumination of aqueous systems containing sulfonated poly(ether etherketone), SPEEK, together with sodium formate have been found to effectively reduce chloroform to

dichloromethane in the absence of air. The polyketone acted as a sensitizer whereas HCO_2^- served as H-tom donor; the photoreduction process involves polymeric a–hydroxyl (SPEEK•) and CO_2^- radicals. Formation of Cl^- proceeded via a zero-order rate law for extended times after an initial short induction period. Reaction rates, $r(Cl^-)$, similar to those of systems free of O_2 were obtained via photolysis of solutions containing air, which exhibited much longer induction periods. For air-free solutions $r(Cl^-)$ increased slightly with light intensity (I_0) whereas the quantum yields of Cl^- generation, $f(Cl^-)$, decreased with increasing I_0. Irradiation with solutions containing chloroform concentrations below the solubility limit in water yielded a first-order dependence of $r(Cl^-)$ on $[CHCl_3]$. At the solubility limit and for solutions containing excess $CHCl_3$ a higher and constant rate was determined. Experiments in which irradiation was periodically interrupted showed that post-irradiation formation of Cl^- took place. GC-MS analysis performed on illuminated solutions confirmed that CH_2Cl_2 was the main organic product but traces of $C_2H_2Cl_4$ were also detected. These results together with the resulting empirical rate law of $r(Cl^-) = k_{obs}\,[CHCl_3]\,I_0^{0.5}$ indicate that the SPEEK-sensitized photoreduction of $CHCl_3$ took place via a chain process involving radical-radical termination steps. Highest values of $f(Cl^-)$ were determined at $6 \le pH \le 8$, coinciding with the range where SPEEK• is most efficiently photogenerated. However, a sharp maximum of $f(Cl^-)$ was determined at a pH of 7.3; DSC results suggest that aggregation of the polyelectrolyte under such conditions may influence the photoreaction.



2015 Joint Southeastern/Southwest Regional Meeting 1122

Developing spectroscopy techniques to study interaction of anticancer drugs with DNA

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Optical spectroscopy such as Raman scattering offers useful tools to study physical and chemical changes in cells and tissues, thereby providing a unique opportunity in diagnostics and therapeutics. When the Raman scattering is dramatically enhanced by the adsorption of molecules onto the surface of metal nanoparticles, it is known as Surface-Enhanced Raman scattering (SERS). SERS is an effective analytical technique due to its high sensitivity and selectivity. Our research utilizes the SERS technique to investigate how anticancer drugs modify DNA to further understand the nature of the

modifications at the molecular level. In this presentation, we will discuss the SERS spectra of anticancer drugs such as cisplatin, carboplatin and oxaliplatin and SERS spectra of the DNA bases. Further studies examining modifications in the spectra of drugs and bases under various sample preparation conditions such as temperature, pH, and concentration are in progress and will be discussed in this presentation. These spectra will serve as a baseline for future studies involving drug-modified DNA under various sample preparation conditions.

2015 Joint Southeastern/Southwest Regional Meeting 1123

Hydrodeoxygenation (HDO) of guaiacol and furfural using a Cu based water gas shift and Mo/Ni/K catalyst system

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Development of alternative sources of renewable energy is an important focus in labs around the world. Due to the depletion of fuel reserves, alternative fuel sources are needed. Bio-oil has been recognized as an alternative source for this problem. Bio-oils contain a complex mixture of oxygenated compounds, which lead to low fuel quality. Upgrading bio-oil using Hydrodeoxygenation (HDO) is one solution to overcome this problem. In this study, guaiacol and furfural have been used as the model compounds. These oxygenated compounds are present in significant quantities in bio-oil**.** A study of the upgrading of bio oil using the HDO process with a Cu based water gas shift and Mo/Ni/K catalyst system has been completed. Reactions were carried out in a batch reactor using two syngas mixtures: 50/50 syngas and bio-syngas. The reactions were kept at temperatures of 250 and 300 °C for 4 hours. Gas and liquid products were analyzed using GC/MS and catalyst characterizations were determined using AAS, BET, & SEM. Results show that temperature and catalyst both exert significant effects on conversion and product selectivity.

2015 Joint Southeastern/Southwest Regional Meeting 1124

Direct aminoglycoside coated gold nanoparticles synthesis, characterization, and antibacterial susceptibility testing

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With soaring increase in the cases of multi-drug resistant (MDR) bacteria all over the world, we are on the verge of entering post-antibiotic era if no immediate action is taken against this global crisis. As an alternative route to modify current commercial antibiotics, we made an attempt to design an effective antibacterial agent involving gold nanoparticles (AuNPs) capped with an antibiotic, like those of the aminoglycoside drug family. The aminoglycoside family is characterized as the traditional Gram-negative antibacterial therapeutic agents that inhibit protein synthesis and contain as a portion of the molecule an amino-modified glycoside. Due to recent emergence of infections due to Gram-negative bacterial strains with advanced patterns of antimicrobial resistance bactericidal agents such as these are being view as a prime candidate for further

development and augmentation. Unlike conventional methods, unique self-patented green process was used for AuNPs synthesis wherein the aminoglycoside assists in both reducing and stabilizing the AuNPs resulting in aminoglycoside conjugated gold nanoparticles (Amg-AuNPs) which were morphologically characterized using transmission electron microscope (TEM), UV-Vis spectroscopy, scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM-EDS), and dynamic light scattering (DLS). The presence of ligand (gentamicin) onto AuNPs was confirmed using TGA analysis. Antibacterial efficiency was evaluated on Gram-positive and Gram-negative bacterial strains using bacterial growth and spread plate assay. AuNPs activity was further confirmed with propidium iodide assay. Super-thin sections of bacteria treated with Amg-AuNPs observed under TEM showed bactericidal activity by causing perforations and disturbing the cellular environment leading to cell lysis and cell death. The minimum inhibitory concentrations (MIC) of Amg-AuNPs was significantly less when compared to pure aminogylcosidic drugs which proves the synergistic activity of Amg-AuNPs.

2015 Joint Southeastern/Southwest Regional Meeting 1125

Optimizing the ionization suppression effects of Cs on accurate ICP-OES determination of Li

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Periodic trends of the alkali earth metals reveal that they are generally easy to ionize. The trend also shows that as one goes down the group, the ease of ionization increases. The overall ease of ionization among the alkali earth metals made it relatively difficult to adequately quantify them using inductively coupled plasma (ICP). This ionization occurs when the atom goes beyond the excitation point as energy is added, releasing the furthest electron in the s-block configuration. Inductively coupled plasma depending on configuration may produce enough energy to cause ionization. This makes it difficult to accurately quantify most alkali earth metals of interest (Li, Na, and K) using ICP-OES due to their ease of ionization. In this study Cs is explored as ionization suppressant, to prevent the analytes of interest from ionizing. Different concentrations of the suppressants ranging from 1.0 - 7.0 ppm were added to standard concentrations of Li, Na, and K. The results for Li and preliminary results for Na and K will be presented. Li being technologically important element among the first three alkali earth metals, the primary aim of the study is to determine an optimized scheme for accurately quantifying it. The presence of Cs reduces the energy of the plasma available, but enough to cause excitation of Li. Consequently, the amount of Li in the sample is not lost to ionization and is therefore more accurately determined.
To demonstrate the effectiveness of Cs as the appropriate ionization suppressant for Li, Na, and K, the results for the use of Sc and Y as ionization suppressants will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 1126

Heavy metal removal from wastewater using magnetic rinsed ultra biochar

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Lead, cadmium, arsenic, and chromium are toxic heavy metals that find their way into the environment through industrial and mining waste and from energy production. Unfortunately, these metals have a tendency to bioaccumulate in the environment and are a serious concern because they can have detrimental effects on wildlife and humans at low concentrations. Therefore, it is imperative that they be removed from water. A novel method of heavy metal removal from wastewater is through the use of magnetic bio-char, which is a cheap, environmentally-friendly alternative to the traditional methods of membrane filtration, selective ion exchange, and precipitation. Magnetic bio-char was prepared by iron oxide precipitation onto the surface of commercially available Rinsed Ultra bio-char using an aqueous Fe^{3+}/Fe^{2+} solution followed by NaOH treatment. The surface chemistry and composition of magnetic bio-char were examined by SEM, SEM-EDX, TGA, PZC, elemental analysis, and surface area measurements. For both magnetic and non-magnetic bio-char, batch sorption studies were performed at 25- 35°C, pH 2-8 and different solid to liquid ratios. Concentration of the heavy metals was determined using AAS and ICP-MS. Results show that temperature and pH exert significant effects on the ability of bio-char and magnetized bio-char to adsorb heavy metals. Additionally, the magnetic bio-char removed the heavy metals and remediated the solutions more effectively than the non-magnetic bio-char.

2015 Joint Southeastern/Southwest Regional Meeting 1127

Investigating the antioxidant activity of sulfur/selenium compounds utilizing mass spectrometry, gel electrophoresis, and polymerase chain reaction

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DNA damage caused by reactive oxygen species (ROS) is a known precursor to the development of cancer and other degenerative diseases. Many sulfur and selenium compounds have been found to have antioxidant properties; however, their mechanisms of action are not fully understood. In order to further elucidate the operative mechanisms in this behavior, two compounds, *N,N'*-dimethylimidazole thione and selone (dmit and dmise) have been prepared and analyzed for their antioxidant properties. Mass spectrometry studies have been performed on $Fe(dmit)_2Cl_2$ and $Fe(dmise)_2Cl_2$ to analyze how these metal-coordinating compounds interact with intracellular, labile and radical-generating Fe(II) to inhibit DNA damage. Mass spectra show possible evidence for a sacrificial oxidation mechanism. In preparation for additional studies of the DNA antioxidant protection offered by S and Se-containing compounds, gel electrophoresis and PCR have been used with in conjunction with the natural S-containing antioxidant glutathione. Preliminary data indicates that glutathione partially protects DNA from damage by ROS and ensures that DNA is still replicated by PCR following oxidizer exposure.

2015 Joint Southeastern/Southwest Regional Meeting 1128

Preventing nosocomial infections: Antimicrobial photodynamic textiles

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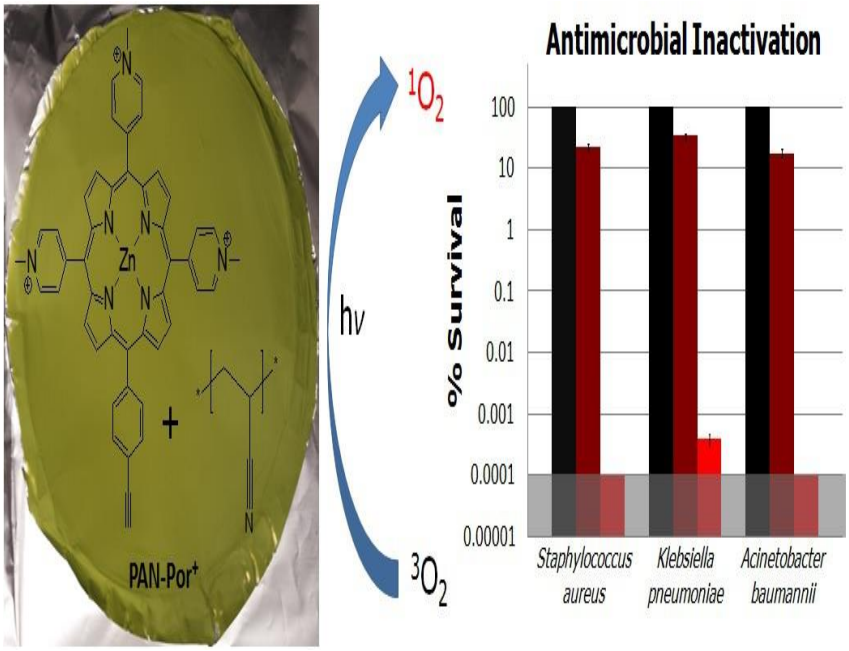
According to the CDC, 5-10% of all patients admitted into a hospital will acquire a new infection from exposure to local pathogens, resulting in approximately 1.7 million healthcare-associated infections in the United States each year. Such infections are the sixth leading cause of death in America, as well as a $30-45 billion burden on the healthcare system. In order to reduce the incidence rates of such nosocomial infections, we have envisioned employing textile products with antimicrobial properties to prevent pathogens from transmitting to immunocompromised patients in hospitals and in other high-risk environments. As our chosen method of sterilization, we have focused on antimicrobial photodynamic inactivation (aPDI), which employs a non-toxic photosensitizer, visible light, and ambient molecular oxygen to inactivate microbial pathogens. Upon illumination, the photosensitizer generates singlet oxygen ($^1O_2$), a highly reactive species that has been shown to cause non-specific cell damage, which is thought to prevent the evolution of drug resistance. In addition, singlet oxygen rapidly decays back to its triplet ground state if unreacted, so it is thought to be environmentally benign.

Via electrospinning, we have embedded a tricationic photosensitizer (Por^+) into polyacrylonitrile (PAN) to produce PAN-Por^+, a photodynamically-active nonwoven textile material. After washing to remove any photosensitizer remaining on the surface, the textile exhibited a broad spectrum of antimicrobial efficacy. Under reasonable illumination conditions (400-700 nm, 30 min), PAN-Por^+ demonstrates ~6 log units (99.9999+%) of inactivation with *Escherichia coli*, *Acinetobacter baumannii*, vancomycin resistant *Enterococcus faecium* (VRE) and *Staphylococcus aureus* , and ~5 log units (99.999+%) of inactivation with *Klebsiella pneumoniae*. Initial results against vesicular stomatitis virus also demonstrate an impressive 7+ log units of viral inactivation. The results of these and other investigations, including our control experiments and efforts to increase the durability of the material by increasing the fiber diameter or altering the thickness of the textile, will be discussed.



2015 Joint Southeastern/Southwest Regional Meeting 1129

Metal-organic frameworks with embedded basic sites for heavy metal capture from aquatic environments

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The pollution of water sources with heavy metals is an ongoing problem. Heavy metals, such as mercury, lead, and cadmium, that are present in contaminated water sources present a significant threat to humans and wildlife alike. The development of new materials to efficiently remove targeted heavy metal toxins from aquatic environments is essential to securing the future of our already stressed potable water supplies. Previous efforts in the development of materials for heterogeneous water purification and remediation have relied upon highly porous (such as activated charcoal) or functionalized materials (such as layered double hydroxides). In this work, we aimed to design and synthesize highly porous and water-stable metal-organic frameworks (MOFs) with embedded basic sites using hard-soft acid-base theory. A series of five UiO-66-based MOFs were synthesized, characterized, and analyzed for water stability and heavy metal uptake capabilities in order to probe the role of thio and thioether functionalities within a porous MOF toward heavy metal capture and selectivity. Preliminary results indicate capture performance that rivals that of current technologies.

2015 Joint Southeastern/Southwest Regional Meeting 1130

Characterization of mixed diacetylene self-assembled monolayers

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Diacetylene self-assembled monolayers (SAMs) have the ability to intercalate and immobilize other compounds. Immobilization requires conjugated diacetylene units which can crosslink when irradiated. Because of these characteristics, polydiacetylene (PDA) SAMs have a wide variety of potential uses in applications such as biological sensors, microelectronics, or adhesives. Herein we report the synthesis and characterization of PDA self-assembled mono- and multilayers on high grade ultraflat mica using ethanol as a solvent. Optimal conditions for the formation of SAMs of 10,12-octadecadiynoic acid (DA) were found to be a soak time of 45 seconds in 0.5 mM solutions. Bis(2,2'-bipyridyl)(10,12-octadecadiynamide-N-1,10-phenanthrolin-5-yl)ruthenium(II) hexafluorophosphate (RuDAphen) was synthesized. Mixed SAMs were prepared by combining solutions of the DA and the RuDAphen then simultaneously depositing them on mica. The mixed SAM was then photopolymerized and characterized via atomic force microscopy, fluorescent microscopy, and contact angle studies. Further fluorescence studies were conducted which differentiated Ru emission from background PDA emission.

2015 Joint Southeastern/Southwest Regional Meeting 1131

Designing a unique therapeutic agent involving gold nanoparticles conjugated with cephalosporins for potent antibacterial applications

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Antibiotic resistance, a global concern is now challenging the current antibiotic therapy to treat bacterial infections. Hence, there is a desperate need for making new antibiotics in response to the soaring increase in cases of multi-drug resistant (MDR) bacteria which are prevalently known as “superbugs”. In this research, we have attempted to design an effective antibacterial agent involving gold nanoparticles (AuNPs) conjugated with an antibiotic (belonging to the cephalosporin class). Cephalosporins, a sub-class of β-lactam antibiotics, disrupt the synthesis of the peptidoglycan layer forming the bacterial cell wall. In the medical field they are considered to be “a class of highly potent antibiotics that are among medicine's last defenses against several serious human infections” by the World Health Organization. By keeping twelve principles of ‘green chemistry’ in mind, an unique, single step process, unlike conventional methods was fabricated for making AuNPs using the combine reducing and capping ability of cephalosporins to yield an array of cephalosporin conjugated gold nanoparticles (Cep-AuNPs) which were then characterized using various analytical techniques such as transmission electron microscope (TEM), TGA, ICP-OES, scanning electron microscope (SEM) and UV-Vis spectroscopy to determine its morphology. Efficiency of Cep-AuNPs was assessed using several antibacterial assays such as turbidimetry, spread plate method and XTT assay. A variety of bacterial strains involving both Gram-positive and Gram-negative were used for above assays. The minimum inhibition concentration (MIC) of Cep-AuNPs, obtained from the assays was compared with the MIC of pure drug form of the cephalosporins in order to evaluate the superiority of Cep-AuNPs over pure cephalosporins.

2015 Joint Southeastern/Southwest Regional Meeting 1132

Solid surface free energy determination via contact angle measurement: An inexpensive undergraduate physical chemistry laboratory experiment

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Contact angles provide data for a number of thermodynamic values involving the interface between solid, liquid, and vapor phases. The goniometer, an instrument used to measure contact angles, is relatively expensive and uncommon in undergraduate physical chemistry labs. Using the sessile drop method, a mobile electronic device equipped with a macrolens and supported by a tripod photographs the contact angle which is then measured with a protractor. Based on the Young-Dupré equation and a Zisman plot, the solid surface free energy and the interfacial surface free energy can be determined by measuring the contact angle (θ) of multiple liquids using the aforementioned ubiquitous, inexpensive equipment. The surface free energy (i.e., surface tension) of the liquids can be plotted versus the cosine of the respective contact angles on a Zisman plot to determine the interfacial surface free energy. The surface free energy of the solid may then be extrapolated from the Zisman plot where $\cos \theta = 1$. The results demonstrate a method to calculate the surface free energy of a solid substrate via contact angle measurements and can be corroborated by published surface free energy values of several substrates.

2015 Joint Southeastern/Southwest Regional Meeting 1133

Binding of novel earth abundant metal coordination complexes as molecular spacers to single-walled carbon nanotubes

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We will report on the binding to and aggregation of carbon nanotubes by novel metal coordination complexes acting as molecular spacers. These complexes act to enhance available Electrical Double Layer Capacitance and add a significant pseudocapacitance increasing the specific capacitance, specific energy, and power. We will present results using compounds like 4-(tert-butyl)-2,6-bis((2-(phthalazin-1-yl)hydrazono)methyl)phenol (m_2-methoxo) dizinc(II) which use earth abundant metals and therefore enable a sustainable solution to a diffiecult societal problem. Kinetics of binding show zeroth order behavior supporting an indepemdemt binding model. Onset of aggregation and conductivity studies support an ion-pair binding model that differes significantly from previous studies in this area. Adsorption isotherm data are fit my the three parameter BET model which is statistically significant when compared to Langmuir and Freundlich models. Membrane resistance measurment suggest that the tub-tube distances are separated due to the intercalation of these molcular spacers. Molecular modeling of the ion-accessible surface area around the SWCNTs will be presented in the context of the enhanced capacitance found on these thin films materials.

2015 Joint Southeastern/Southwest Regional Meeting 1134

Liquid structure of hydrofluoromethanes using first principles Monte Carlo simulations

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In order to minimize environmental impacts, hydrofluorocarbons (HFCs) have virtually replaced chlorofluorocarbons (CFCs) that were commonly used as refrigerants and known to cause ozone layer depletion. HFCs also find numerous applications as propellants in metered dose inhalers and cleaning solutions. Given their widespread use, it is important to understand their structural and thermodynamic properties. Here, we employ First Principles Monte Carlo (FPMC) simulations to study the liquid structure of specific HFCs: fluoromethane, difluoromethane, and trifluoromethane. As the widely used local and semilocal density functional theory (DFT) inaccurately models induced dipole-dipole interactions, we use dispersion-corrected and nonlocal density functionals (rVV10, DFT-D3). These functionals are designed to capture dispersion interactions and are expected to provide accurate liquid state properties. In order to understand the molecular arrangement in the first solvation shell, we present spatial distribution functions (SDFs) as well as angular radial distribution functions (ARDFs). We find that fluoromethane and trifluoromethane show preference for a parallel orientation, whereas difluoromethane's orientation tends to maximize hydrogen bonding, sometimes at the expense of a parallel orientation. Additionally, we include radial distribution functions

(RDFs) of each HFC, which expounds upon the work of Lisal and Vacek's study of fluoromethane and trifluoromethane.

2015 Joint Southeastern/Southwest Regional Meeting 1135

Surface energy: A combinatorial experimental design for novel UV-curable coatings

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This paper presents a novel formulation screening methodology (FoSM) to predict surface properties of coatings. The van Oss-Chaudhury-Good (OCG) thermodynamic approach determines the surface free energy, based in part on the contact angle. Cassie's Equation relates the contact angle to the composition of the surface. By combining the data obtained via the OCG approach and Cassie's Equation, coatings scientists now have a predictive high-throughput experimental design methodology for new product development.

2015 Joint Southeastern/Southwest Regional Meeting 1136

Determination of the surface energy for UV-curable easy release coatings

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This presentation introduces an experimental design improving developmental efficiency of formulations that produce UV-curable coatings with easy release properties. The surface free energy of a coating is shown to be predictive of its release behavior. Analysis of basic contact angle data using the van Oss-Chaudhury-Good (OCG) approach is applied to determine the surface free energy of coating components; Cassie's equation is used to harness this information into a predictive process based on the coating composition. Coatings scientists now have a powerful tool minimizing time and material consumption to design release coatings.

2015 Joint Southeastern/Southwest Regional Meeting 1137

A physical approach for the determination of nanoparticle toxicity

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Nanotechnology is a growing field that represents a large financial market with many industrial and consumer applications. Nanoparticles are widely known to be toxic when inhaled, regardless of chemical composition. This is in contradiction with currently held theory which ascribes a chemical cause to the toxicity of nanoparticles. We propose that nanoparticle toxicity is caused by the presence of trapped electrons (electron donating) or holes (electron accepting) in defects on the surface of a particle through a physical mechanism of action in which electrons are transferred inducing biological damage. Phthalocyanine, a widely used nanomaterial, was acquired and characterized using infrared spectroscopy, optical microscopy, SEM, and X-ray diffraction. Samples of

phthalocyanine were fumigated in oxygen or ethanol vapor in order to withdraw or inject electrons at point defects respectively in order to alter their electronic properties. *In vitro t*oxicity of both fumigated and untreated material will be analyzed in lots of three in collaboration with the University of Montana. These measurements will be compared to determine the electronic nature of defect sites in the material and their role in toxicity. The purpose of this research is to create a framework for developing a physical set of criteria useful in determining the toxicity of nanomaterials that may be analyzed without the use of expensive, time-consuming biological methods.

2015 Joint Southeastern/Southwest Regional Meeting 1138

Supraparamagnetic Fe_3O_4 nanoparticles for magnetic isolation of anion exchange resin during water purification

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Dissolved organic matter in public water sources is difficult to remove and is a potential health hazard after chlorination. Carcinogenic Disinfection Byproducts (DBPs), result from reactions with chlorinated water. Research into new technologies for the detection and removal of minute amounts of pollutants from drinking water supplies is driven by the limitations of current technologies. Investigation of supraparticle assemblies suggests that the surface of the Single-Walled Carbon Nanotubes (SWCNTs) may be useful in adsorbing and removing toxins from the water; the attachment of nanotubes to magnetic nanoparticles provides a way to extract these supraparticles from water efficiently and thoroughly. Supraparamagnetic Fe_3O_4 nanoparticles, which are attracted to an external magnetic field, were successfully synthesized and characterized. These particles were coated with a gold shell and stabilized with citrate. SEM, DLS, zeta potential, magnetic, and spectroscopic studies of these particles will be presented. Capabilities of a nanoscale anion exchange resin have been determined and removal of surrogate contaminants will be reported as well as the progress toward full magnetic isolation of these supraparticle assemblies from solution. These particles have been found to be recylible and are therefore a sustainable technology.

2015 Joint Southeastern/Southwest Regional Meeting 1139

WITHDRAWN

2015 Joint Southeastern/Southwest Regional Meeting 1140

Gate-free electrical breakdown of metallic pathways in single-walled carbon nanotube crossbar networks

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Aligned single-walled carbon nanotubes (SWNTs) synthesized by the chemical vapor deposition (CVD) method have exceptional potential for next-generation nanoelectronics. However, the co-existence of semiconducting (s-) and metallic (m-) SWNTs remains a considerable challenge since the latter causes significant

degradation in device performance. Here we demonstrate a facile and effective approach to selectively break all m-SWNTs by stacking two layers of horizontally aligned SWNTs to form crossbars and applying a voltage to the crossed SWNT arrays. The introduction of SWNT junctions amplifies the disparity in resistance between s- and m-pathways, leading to a complete deactivation of m-SWNTs while minimizing the degradation of the semiconducting counterparts. Unlike previous approaches that required an electrostatic gate to achieve selectivity in electrical breakdown, this junction process is gate-free and opens the way for straightforward integration of thin-film s-SWNT devices. Comparison to electrical breakdown in junction-less SWNT devices without gating shows that this junction-based breakdown method yields more than twice the average on-state current retention in the resultant s-SWNT arrays. It is also found that this approach is comparable to the state-of-the-art technique (junction-less breakdown with gating) in terms of on/off ratio and current retention. Systematic studies show that the on/off ratio can reach as high as 1.4×10^6 with a correspondingly high retention of on-state current compared to the initial current value before breakdown. Overall, this method provides important insight into transport at SWNT junctions and a simple route for obtaining pure s-SWNT thin film devices for broad applications.

2015 Joint Southeastern/Southwest Regional Meeting 1141

Dual-mode organic-inorganic passivation of quantum dots

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“Dual-mode” passivation refers to a new paradigm in of control over the surface chemistry of quantum dots. We present a simple synthetic methodology that allows for passivation of surface anion and cation sites by alkyl chains and inorganic small molecules, respectively. What is unique about the dual-mode passivation it the ability to control the solubility and electronic properties of the quantum dots through the surface chemistry independently, which to date has not been possible. Using a combination of wet experiments, spectroscopy and DTF calculations, we show the organic capping ligand can be tailored to provide solubility in either polar or non-polar solvents, while having little effect on the quantum dot exciton. In contrast, the small molecule passivation of the surface cation sites were shown experimentally and computationally to change optical and electronic properties of the Q dots, and is less crucial to colloidal stability in various solvent than the organic component. We demonstrate a general example of the advanced functionality dual-mode passivated quantum dots by their use in a model photocatalytic reaction and show they are 2x more effective than quantum dots with a traditional single-mode capping. We will also describe our prediction of how this advanced contol of physical and electronic properties will touch broadly the photovoltaic, photocatalytic and biological applications of quantum dots.

2015 Joint Southeastern/Southwest Regional Meeting 1142

The preparation of biofouling-resistant films of surface-modified polyaniline nanofibers

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Electrochemically grown PAni thin films have been shown to react very efficiently with thiols, permitting ready modification of film surface properties while leaving the bulk electronic properties largely unaffected. Water dispersible PAni nanofibers were prepared in aqueous sulfuric acid using an optimized version of methods used by others. These colloidal dispersions were deposited onto silicon dioxide-coated quartz crystal microbalance (QCM) resonators by spray coating, followed by drying to produce rough, electrically conducting films. The nanofiber films were modified with low and high molecular weight PEG-thiols by simple immersion in aqueous solutions. After thoroughly washing, the reaction efficacy was investigated by thermogravimetric analysis. The resistance of the modified PEG-PAni nanofibers against adsorption by bovine serum albumin (BSA) was examined in a QCM flow cell. The PEG-thiol was observed to dramatically reduce biofouling by the protein.

2015 Joint Southeastern/Southwest Regional Meeting 1143

Silver cluster encapsulated by DNA strands

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Single-stranded DNA encapsulates silver clusters, and we consider silver cluster chromophores whose spectra are directed by DNA structural changes. We show how these changes are used to detect oligonucleotides. The DNA template has two components: the 3' sequence hybridizes with target oligonucleotides and the 5' sequence forms specific silver clusters. These composite strands exclusively harbor an ~10 silver atom cluster that absorbs at 400 nm with limited emission. When a target hybridizes with these single-stranded conjugates, cluster absorption shifts and strong emission develops. Fluorescence anisotropy, fluorescence correlation spectroscopy, size exclusion chromatography, elemental analysis, and temperature-dependent spectral measurements identify two structural and thermodynamic changes accompanying hybridization. First, the violet cluster folds its single-stranded host and inhibits DNA hybridization. Second, the violet cluster dimerizes its DNA host and forms a near-infrared cluster. Our key conclusion is that silver clusters are both chromophoric reporters and ligands that modulate analyte-sensor interactions.

2015 Joint Southeastern/Southwest Regional Meeting 1144

In-situ synthesis of vanadium pentoxide nanofibre/exfoliated graphene nanohybrid and its supercapacitor applications

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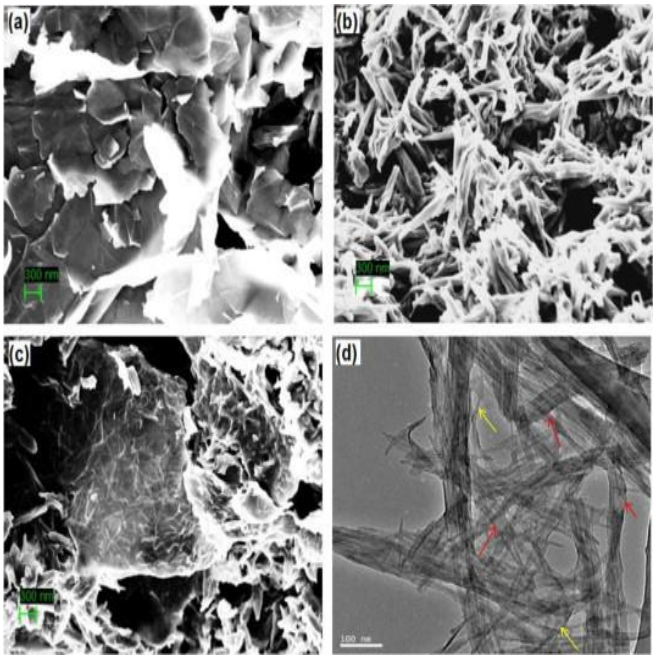
A novel nanohybrid material composed of vanadium pentoxide nanofibres (VNFs) and exfoliated graphene were prepared by in-situ growth of VNFs onto graphene nanosheets, and explicated as electrode material for supercapacitor applications. The existence of non-covalent interactions between VNFs and graphene surfaces was confirmed by Raman and Fourier transform infrared (FTIR) spectroscopes. Morphological analysis of the nanohybrid revealed that the VNF layer uniformly grown on the graphene surfaces, producing high specific surface area and good electronic or ionic conducing path. High crystalline structure with small d-spacing of the VNFs on graphene was observed in X-ray diffraction (XRD) analysis. Compared to pristine VNF, the VNF/graphene nanohybrid exhibited higher specific capacitance of 218 F g^{-1} at current density of 1 A g^{-1}, higher energy density of 22 Wh kg^{-1} and power density of 3594 W kg^{-1}. Asymmetric supercapacitor devices were prepared using the Spectracarb 2225 activated carbon cloth and VNF/graphene nanohybrid as positive and negative electrode, respectively. The asymmetric device exhibited capacitance of 279 F g^{-1} at 1 A g^{-1}, energy density of 37.2 Wh kg^{-1} and power density of 3743 W kg^{-1}, which are comparable and or superior to reported asymmetric devices consisting of carbon material and metal oxide as electrode components.



2015 Joint Southeastern/Southwest Regional Meeting 1145

Thermally activated release from polymer micelles

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Polymer micelles were made using either poly(ethylene glycol-b-caprolactone) diblocks or a poly(ethylene glycol-b-caprolactone-b-lactic acid) triblock. The micelles had a semi-crystalline core with melting endotherms for the crystalline polycaprolactone phase in the range of 40 to 55 °C. Dibucaine or doxorubicin was trapped in the core of the micelles with loadings in the range of 5 to 20%. Isothermal release curves, plots of percent dibucaine release as a function of time, were measured at 27, 37, 57 and 67 °C. The curves were fit to Crank's model for the late time release of small molecules from spheres, giving values of diffusion coefficient divided by the radius squared (D/r^2). The release rate (as measured by D/r^2) increased dramatically when release was measured at temperatures above the melting point of the core (i.e. 57 and 67 °C). The increase was attributed to the increased ability for the drugs to diffuse from the melted core.

2015 Joint Southeastern/Southwest Regional Meeting 1146

Subconjunctivally injectable nanogels for enhancing drug permeability across ocular barriers

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The efficacy of therapeutics for treating ocular diseases is limited by the therapeutics' short residence time and low permeability across ocular barriers. Nanoparticles show great promise for transporting drugs across biological barriers, reducing drug clearance, and improving the bioavailability of drugs at targets. In order to enhance the therapeutics' efficacy, we have developed and evaluated a polymeric nanogel system composed of N-isopropylacrylamide and hydrolytically degradable 2-hydroxyethylmethacrylate-lactate-dextran that has potential to enhance the permeability of therapeutics across ocular barriers and sustain the release of therapeutics. A series of the nanogels with different crosslinking density, hydrophobicity, and charge type are synthesized in aqueous solution at 45°C by UV photopolymerization. Small molecule drugs such as brimonidine and topotecan, and growth factors such as insulin are loaded as model drugs into the nanogels during the synthesis. The chemical structure and size of the nanogels are characterized using FTIR and DLS, respectively. Human fetal retinal pigment epithelial (hfRPE) are used to evaluate cytotoxicity of the nanogels by MTT assay. Permeability of the nanogels with or without drugs was evaluated across hfRPE cell monolayers, an *in vitro* RPE model; the sclera and the cornea of preterm and adult pigs, ex vivo models of sclera and cornea, respectively; and the sclera and other ocular barriers after subconjunctival injection in rats. Results FTIR and HPLC results confirm the successes of the nanogel synthesis and drug loading. The nanogels are not toxic to the hfRPE. Permeability studies show that the nanogels are significantly more permeable than 70kDa dextran across hfRPE cell monolayers, and the sclera and the cornea of preterm and adult pigs. *In vivo* data show that the nanogels can cross the sclera and accumulate in the retina and vitreous humor, and accumulate in the cornea and aqueous humor one day later after subconjunctival injection in rats. The *in vitro*, *ex vivo*, and *in vivo* studies show that the developed nontoxic nanogels have great potential to enhance drug permeability across ocular barriers including the RPE, sclera and cornea for treating diseases in both posterior and anterior segments of the eye. As the nanogels are also hydrolytically degradable, they have potential to sustain drug release for long term treatments of ocular diseases.

2015 Joint Southeastern/Southwest Regional Meeting 1147

Synthesis and characterization of anion exchange resin nanotubes for water purification

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Dissolved organic carbon (DOC) in natural waters is a source of a potential health hazard, and is difficult to remove. Modern water treatment methods use chlorine as a disinfectant to remove bacteria. However, certain DOCs (humic and fulvic acids) react with chlorine to form chlorinated disinfectant byproducts (DBPs), which are known carcinogens. The EPA lists the maximum contaminant level for DBPs in the range of 0.01-1.0 mg/L. At such low concentrations, it is very difficult to remove these DOCs before the chlorination process. We have synthesized supraparticle assemblies of a poly(vinylbenzyl trimethylammonium chloride - Single-Walled Carbon Nanotubes (SWCNTs) system, which acts as an anion exchange resin, for removal of these contaminants. The polymerization was grown via the Activators Regenerated by Electron Transfer (ARGET) Atom Transfer Radical Polymerization (ATRP) method, and attached to the SWCNTs using the same catalyst in one pot . Functionalized SWCNTs were then characterized using Raman Spectroscopy, IR, and SEM. Raman data showed a significant increase in D:G band ratio over pristine SWCNTs indicating covalent bonding to the nanotubes. SEM images showed conformal coating of the polymer around the nanotubes. Dissolved organic carbon can be extracted from water sources by adsorption to these polymer chains on the functionalized SWCNTs. These nano-resins are stable in water, and can be recycled and then reused upon rinsing in aqueous NaCl. This is a sustainable solution to a difficult environmental problem. Work has also been completed to optimize the polymer chain length for enhanced DOC adsorption. We have characterized the use of these functionalized SWCNTs through the adsorption of a surrogate dye from water and from marine samples in local aquifers using UV-Vis and TOC analysis. Significant decreases in contaminant concentration were observed, even at very low concentrations. Adsorption studies show that our functionalized SWCNTs are more efficient than currently available removal technologies and are capable of removing DOCs below the limits set by the EPA. Langmuir adsorption studies will be presented to quantify the adsorbate removal capabilities of our novel systems.

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Antimicrobial properties of gallium against *Bacillus subtilis*

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A major challenge in health care is the effective treatment of microbial infections. This presents a serious problem since hospital-acquired infections are often caused by bacterial strains resistant to currently available antibiotics. Therefore, there is an urgent need to identify new targets suitable for the development of the next generation of antibiotics. One strategy is to uncover biochemical processes essential to the life and virulence of pathogenic bacteria. Iron (Fe) and Fe-S metabolism might offer an excellent target for metabolic intervention because they are both essential and vulnerable to

stresses faced by the bacterium during infection. While free Fe levels are intrinsically low *in vivo* for most organisms, Fe is required for growth, enzyme function, and plays a critical role in oxidative stress defense. Interestingly, gallium (Ga) has been proposed as a promising antimicrobial agent due to its similarities in atomic structure with iron. However, the mechanisms by which Ga interferes with Fe metabolism have not yet been fully understood. We hypothesized that Ga causes growth inhibition by disrupting Fe-S clusters and thiol-redox homeostasis in bacteria. In this study, the possible mechanisms of gallium's antimicrobial efficiency were investigated through standard growth curves, Fe-S enzyme activity assays, WCAES and ICP-OES analysis, and by a redox sensitive bioprobe roGPF in *Bacillus subtilis*. Growth inhibition was caused by low micromolar concentrations of Ga and suppressed upon addition of Fe to the medium. Supporting our hypothesis, Ga challenge led to lower activity levels of the Fe-S enzymes aconitase and glutamate synthase, but did not affect the activity of non-Fe-S enzymes fumarase and malate dehydrogenase. Furthermore, *B. subtilis* strains lacking the low molecular weight thiol bacillithiol are more sensitive to Ga. Preliminary analysis using roGFP suggests that lack of bacillithiol does not affect the thiol redox homeostasis, but it impairs the activity of Fe-S enzymes, potentially through its participation on Fe mobilization to the biogenesis and/or repair of Fe-S clusters. WCAES and ICP-OES analysis has thus far shown that addition of sub-lethal concentrations of Ga causes uneven cellular localization, and Ga challenge alters the content and distribution of Fe and other metals.

2015 Joint Southeastern/Southwest Regional Meeting 1149

Understanding the role of glycine134 in heparin binding of FGF-1

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Human acidic fibroblast growth factor 1 (FGF-1) is a potent modulator of cell survival and is seemingly universal in various physiological processes. Though potent, FGF-1 unbound to heparin is known to exhibit a poor thermal stability and a relatively short *in vivo* half-life. Much is known about the structure and relation of FGF-1 with heparin yet there is still unknown information regarding the exact role of heparin in stabilizing FGF-1. Thus, my aim is to mutate wild type FGF-1's 134^{th} amino acid, glycine, into glutamic acid to understand the overall interaction between heparin and mutant form of FGF-1. A mutation of an amino acid in this important region could redefine the stability of FGF-1 bound to heparin; yet maintaining FGFs inherent mitogenic activity. FGF-1G134E mutant protein would be subjected to detailed biophysical characterization. Results of the mutant characterization will be discussed in greater detail.

2015 Joint Southeastern/Southwest Regional Meeting 1150

Modulating the mitogenic activity of the fibroblast growth factor

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Human acidic fibroblast growth factor (FGF-1) is one of the broadest known mitogens, with the ability to activate the entire range of fibroblast growth factor receptors (FGFR).

Through this interaction, FGF-1 is involved in initiating various processes such as organogenesis, angiogenesis, tissue repair, and differentiation. It has been shown that FGF-1 is an inherently unstable molecule, with a relatively short half-life and poor thermal stability. FGF-1 is stabilized *in vivo* by interacting with heparin; this interaction enhances the interaction of FGF-1 with its receptor, shields the protein from proteolytic degradation, and thermally stabilizes the molecule. The 84th position in the wild-type FGF-1 molecule contains an aspartic acid residue. It has been shown that upon interaction with heparin, this residue shifts from ~10 to ~7 angstroms from heparin. Inducing an aspartic acid to arginine mutation at the 84th position in the primary structure of FGF-1 via site-directed mutagenesis and studying the effects of this mutation on the structure, stability, and function retention of this mutant versus the wild-type form, including its interaction with heparin, to yield information regarding the role of this position and the structure to function relationship of the molecule as a whole is the fundamental intention of this study. Our study employs limited trypsin digestion, differential scanning calorimetry, far UV-circular dichroism spectroscopy, 8-anilinonaphthalene-1-sulfonic acid binding assay, and multidimensional NMR spectroscopy techniques on the D84R mutant.

2015 Joint Southeastern/Southwest Regional Meeting 1151

Post-translational modifications of FUN30 and its role in chromatin remodeling

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Post-translational modifications regulate the activity of many molecular pathways that occur in the cell. Conserved from yeast to human, Fun30, an ATP-dependent chromatin-remodeling enzyme, has been previously implicated in DNA repair, DNA replication, heterochromatin silencing and transcription. Powered by ATP hydrolysis, Fun 30 acts by “remodeling” the position of the nucleosome in cis or trans configuration; however, the regulation for this activity is unknown. Evidence suggests that post-translational modifications, such as sumoylation, aid in the regulation of Fun30 and other similar proteins. SUMO (small ubiquitin-related modifier) proteins are often conjugated to proteins that are involved in transcription, chromosome segregation, and DNA repair. SUMO conjugation and ligation involve a complex pathway that includes “helper” proteins that bind SUMO to its substrate. These post-translational modifications, like sumoylation, regulate the chromatin remodeling function of Fun30, thus contributing to the mechanism in which Fun 30 slides nucleosomes rendering DNA for transcriptional repression. Post-translation modifications regulate molecular activities and pathways used to carry out cellular functions essential for their vitality.

2015 Joint Southeastern/Southwest Regional Meeting 1152

Synthesis of dendrimer-encapsulated mono- and bimetallic Cu and Ni nanoparticles and investigation of their antimicrobial activity

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Nanoparticles are increasingly used in a wide variety of applications in biomedical, optical, and electronic fields. However, the behavior of nanoparticles toward biological systems is not well understood and possibly poses a serious health problem for our communities and environment. Our research for summer undergraduate students project explored the synthesis, characterization, and extraction of monometallic (Cu, Ni) and bimetallic (CuNi) nanoparticles and investigated their toxicity towards gram-negative and gram-positive bacteria. In short, metallic nanoparticles were formed through chemical reduction with sodium borohydride in the presence of a generation four polyamidoamine (PAMAM) dendrimer. Using x-ray diffraction and transmission electron microscopy, it was determined that the dendrimer-formed Cu, Ni, and CuNi nanoparticles exhibit a face-centered cubic crystal structure with an average particle diameter that is < 10nm. Paper disk diffusion assay test revealed that both Cu and Ni nanoparticles show toxicity towards both gram-negative and gram-positive bacteria. However, no antimicrobial activity “toxicity” is observed for the CuNi bimetallic counterpart when tested against both gram-negative and gram-positive bacteria. This phenomenon is potentially attributed to the observation of a polymeric “dendrimer” corona around the CuNi particle surface during the growth process.

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The importance of Ile716 in BF polymerase toward the mutagenic potential of 8-Oxo-2’-deoxyguaosine

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8-oxo-2’-deoxyguanosine (OdG) is a promutagic DNA lesion that arises from exposure of 2’- deoxyguanosine (dG) to reactive oxygen species (ROS) like peroxides, hydroxy radicals, and superoxides. ROS are produced by environmental carcinogens, exposure to radiation, and even during cellular respiration. OdG lesions are very common in mammalian cells and can base pair to both 2’-deoxycytidine (dC) and 2’-deoxyadenosine (dA), the latter of which can result in dG → thymidine transversions. These mutations are believed to be responsible for the link between OdG and aging, and diseases like cancer, lupus, and arthritis. To gain insight into the preference for dCTP or dATP incorporation opposite OdG, and thereby the mutagenic potential of OdG, the large fragment of the A-family polymerase I from the bacterium *Bacillus Stearothermophilus* (BF) was studied. Previous studies have suggested that clashing between the active site Ile716 and either the C8-position of OdG during dCTP incorporation, or the C2-position of OdG during dATP incorporation can heavily influence the mutagenic potential of OdG. To further test the importance of these clashing interactions, the activity of dCTP and dATP incorporation opposite OdG and seven of its analogues were compared between wild type BF, I716M BF, and I716A BF.

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Production of phenolic compounds by *Brettanomyces*

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Brettanomyces is a genus of yeast that is a common contaminant in commercial fermentation processes, such as brewing and winemaking. Brettanomyces produces the phenolic compounds 4-ethylphenol and 4-ethylguaiacol, which produce off-flavors, such as a medicinal taste, smoky flavors, and the taste of barnyards. In this experiment, broths containing four different types of sugar, including glucose, maltose, lactose, and sucrose, were inoculated with Brettanomyces and allowed to ferment. As a control, the common yeast used in fermentation, Saccharomyces cerevisiae, was subjected to fermentation in broths with the same four sugars. The purpose of this experiment was to determine if there was a difference in 4-ethylphenol and 4-ethylguaiacol production, based on the sugar used by Brettanomyces for fermentation, compared to that of normal fermentation using Sacchoramyces cerevisiae, as well as to determine at which point during fermentation the phenolic compounds were produced. The results of the experiment were gathered by high pressure liquid chromatography, and a measurement of the amount of 4-ethylphenol and 4-ethylguaiacol was taken in order to determine which type of sugar Brettanomyces would use during fermentation in order to produce the phenolic compounds. The data was also collected over time, which was used to determine at which point in fermentation the phenolic compounds were produced.

2015 Joint Southeastern/Southwest Regional Meeting 1155

DLS characterization of netropsin aggregates

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Small molecules have been developed to regulate a variety of biological processes. Many of these small molecules aggregate in aqueous solutions and a substantial fraction act as aggregate-based inhibitors. Therefore, aggregation studies are an important step in the evaluation of small molecules. The focus of this study is to optimize preparation protocol and data collection regarding Dynamic Light Scattering measurements of small molecules that were developed to target DNA. Initially, DLS has been utilized to assess the behavior of Netropsin, a polyamide, that binds AT-rich DNA.

2015 Joint Southeastern/Southwest Regional Meeting 1156

Interaction of a novel mitochondrial protein, 4-nitrophenylphosphatase domain and non-neuronal SNAP25-like protein homolog 1 (NIPSNAP1) with NAD and NADH

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The mitochondrial protein NIPSNAP1 (4-nitrophenylphosphatase domain and non-neuronal SNAP25-like protein homolog 1) is a member of a highly conserved family of proteins with unknown functions. Previous studies in our group have shown that NIPSNAP1 expression is highly correlated with several mitochondrial NAD-dependent dehydrogenases. Using blue native polyacrylamide gel electrophoresis of purified brain mitochondria, we found that NIPSNAP1 exists in large protein complexes. Using a

structure based ligand screening tool called FINDSITE, we found that the C-terminal region of NIPSNAP1 may bind to NADH and NADPH. In biochemical pull-down experiments using immobilized NADH beads, we found that purified NIPSNAP1 protein directly binds to NADH. In the present study, circular dichroism (CD) spectroscopy was used to verify the interaction between purified NIPSNAP1 and NAD+. We found a significant alteration of the near-UV CD spectrum of NIPSNAP1 in the presence of NAD+. Taken together, our results suggest that NIPSNAP1 may directly bind to NAD+ and possibly function as a subunit of different mitochondrial dehydrogenase complexes.

2015 Joint Southeastern/Southwest Regional Meeting 1157

Antimicrobial properties of extracts from *Hedera helix*

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Antibiotic resistance is becoming a significant problem within the health field. With more microbes developing resistance to many of the first-line antibiotics, there is a need to find novel compounds that can be used against these microbes. Plants are a viable source of possible antimicrobials. *Hedera helix*, also known as English ivy, is an invasive species that has reported medicinal uses, including antimicrobial activity. The purpose of this study was to test the antimicrobial properties of extracts from *Hedera helix* against common strains of pathogenic microbes. A crude extract was obtained from freshly picked ivy by stirring in 80% methanol for 24 hours, filtering out the solids, and evaporating off the methanol. The crude extract was then dissolved into one of four different solvents to create fractionated extracts. The fractions were centrifuged to remove any undissolved particulate. The fractionated extracts were then tested for antimicrobial properties against various microbes.

2015 Joint Southeastern/Southwest Regional Meeting 1158

Thermodynamic contributions of the inhibition of AT hooks by netropsin

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High Mobility Group A proteins influence cellular growth through activating gene transcription factors in early human development and activation of these proteins in adults is linked to cancer metastasis. One way to prevent continued activation of these genes is to target the DNA with small molecules that inhibit HMGA binding. Netropsin is being used as a model compound to understand the interplay between the DNA binding motifs (AT hooks) of HMGA and small molecules for DNA binding. The thermodynamic contributions of the binding of netropsin and an AT hook containing peptide to AT rich DNA is being studied by isothermal titration calorimetry and differential scanning calorimetry.

2015 Joint Southeastern/Southwest Regional Meeting 1159

Development of a PCR-based system to study HMGA disruption

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High mobility group A proteins are a family of proteins that help facilitate transcription of a broad array of genes and cause metastasis when over expressed in adults. The proteins have two to three AT hook motifs that bind to AT rich sections in the minor groove of DNA. The binding affinity of each successive hook increases affinity of the entire protein. Therefore, sterically hindering the binding of the first hook may prevent the whole protein from binding. To further understand the cooperative binding of HMGA through the AT hooks, DNA containing modified adenine nucleotides were synthesized by PCR and reacted with groups. By selectively and sterically hindering the AT hook the binding of HMGA to the successive AT hooks can be further studied.

2015 Joint Southeastern/Southwest Regional Meeting 1160

Probing the stability and ligand binding of heme proteins 'mineralized' within the ZIF-8 metal organic framework

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The ability to encapsulate proteins in solid state materials while retaining physiological function has been a long standing goal in biotechnology. Numerous porous materials have been explored including sol gels, Nafion membranes, hydrogels, etc. More recently, metal organic frameworks (MOFs) have been explored as platforms for the encapsulation/embedding of bioactive molecules. Recent studies in this area have demonstrated the ‘mineralization’ of heme proteins in the zeolite like MOF, ZIF-8 that may have applications in bio-inspired protein delivery systems. Here the effects of mineralization on the conformation and ligand binding associated with two heme proteins: Cytochrome C (Cc) and Myoglobin (Mb) have been examined using optical spectroscopy. In the case of mineralized Cc, the Soret maximum is observed at 409nm for the oxidized protein and shifts to 416nm similar to solution (406 nm and 415nm, respectively). However, the absorption spectrum of the ferrous protein lacks the 550 nm band characteristic of the six coordinate met80 bound heme. In addition, in the presence of CO the Soret max shifts to 414 nm and two bands appear in the visible region indicates destabilization of the heme-methionine bond in the mineralized protein. Horse heart Mb has also been mineralized in ZIF8 exhibiting a Soret maximum at 398nm (met Mb) which shifts to 404nm upon reduction. These values are significantly different than solution (408 nm for metMb and 430 nm for deoxy Mb). After CO is introduced to the mineralized protein the Soret peak narrows and red shifts to 422nm.

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Can native enzyme conformation act as a template for refolding of RNase A

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Protein aggregation is a very important biological process that is observed in several neurological diseases. Misfolded proteins potentially clump together and become extremely toxic to the cell. This misfolding is a cause of many degenerative diseases, such as Parkinson's disease, Alzheimer's disease, and Huntington's disease. In this study, we are hypothesizing that the presence of native folding protein might assist the misfolded proteins to gain structure similar to native state. Ribonuclease A (RNase A), an enzyme that catalyzes the hydrolysis of RNA by breaking a P-O bond, was used as a model protein. Using various *in vitro* biophysical experiments, we examine the effect of native template on the refolding denatured and reduced RNase A. Results of this study will be described in greater detail.

2015 Joint Southeastern/Southwest Regional Meeting 1162

The partial purification of a polyphenol oxidase from *Scorzonera hispanica*

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Polyphenol oxidase is a copper-binding enzyme that is responsible for catalyzing the oxidation of monophenols to ortho-diphenols and ortho-dihydroxyphenols to ortho-quinones. This enzyme was partially purified from *scorzonera hispanica*, known commonly as black salsify, using primarily two types of column chromatography. After initial extraction the activity of the enzyme was protected by ascorbic acid until the enzyme was isolated from its substrates. An ammonium sulfate fractionation, a size exclusion column, and a copper affinity column were used to separate the enzyme from other plant proteins.
After each step in the isolation process, a spectrophotometric enzyme activity assay and a protein concentration determination were run to verify which fractions contained the protein. Additionally, an SDS-polyacrylamide gel was run in order to estimate the purity of the enzyme. The enzyme activity of the copper column fractions was higher than the size exclusion column fractions, which indicates the process has further purified the protein. Further studies on the enzyme and its purification are ongoing.

2015 Joint Southeastern/Southwest Regional Meeting 1163

Electrochemical investigations of FAD-binding RNA aptamers

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Flavin adenine dinucleotide (FAD) is capable of carrying out a wide range of biological redox reactions due to its relatively high oxidation potential compared to other biological cofactors and its ability to participate in one-or two-electron transfer reactions. In cellular environments, FAD is found in the active site of flavoproteins, which catalyze a large number of metabolic reactions that require a strong oxidizing agent. We are interested in understanding how other biomolecules, including nucleic acids, can interact with cofactors and what effect binding has on their activity. The Burke group has previously identified RNA sequences known as aptamers that are able to bind specifically to FAD, but do not bind to $FADH_2$. Using electrochemical approaches, we are investigating the redox activity of FAD when bound to these RNA aptamers and the ability of these

complexes to mimic the characteristics of flavoproteins. Many flavoproteins modulate the redox potential of FAD when bound. This shift in potential can translate into various possible reactions that can be catalyzed by such protein-FAD complexes. The ability of the RNA aptamers to mimic such redox-modulating flavoproteins could open up opportunities for the RNA-FAD complexes to participate in a wide range of possible new redox reactions. We are currently using cyclic voltammetry to study the electrochemical behavior of FAD, including any possible shifts in the reduction potential, when bound to the RNA aptamers and our results will be discussed.

2015 Joint Southeastern/Southwest Regional Meeting 1164

PtSIT1: Protein function in silicic acid transport for biomimetic silica synthesis

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Diatoms are eukaryotic algae that mineralize an external cell wall composed of hydrated silica. This process requires diatoms to uptake soluble silicon (silicic acid) from the surrounding environment by specific silicic acid transport proteins (SITs). This family of proteins is relatively uncharacterized. The goal of this project was to 1) express and purify SIT1 from the diatom *Phaeodactylum tricornutum* (*Pt*SIT1), 2) reconstitute the protein into a synthetic lipid vesicle and to 3) determine whether SIT1 can behave as a silicic acid transporter *in vivo* for eventual applications in nanotechnology.
*Pt*SIT1 was overexpressed in yeast and purified in the solubilizing detergent Fos-choline 12. The purified protein was successfully reconstituted into synthetic liposomes and silicic acid uptake was assessed using a fluorescent assay which used zinc silicate fluorescence. This method also was used to determine that silicic acid transported by *Pt*SIT1 displayed Michaelis-Menten kinetics with a K*m* of 1.8 µM. Preliminary electron microscopy suggested that the silicic acid silicic acid transported into the liposome condense to form silica nanoparticles in the presence of tetraethylenepentamine, a condensing agent. This work confirms that *Pt*SIT1 can be utilized in further exploration of biomineralization of silica *in vivo* in an effort to explore ‘green’ syntheses of silica nanoparticles.

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Natural product isolation and activity-based fractionation of bioactive compounds found in English ivy, *Hedera helix*

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English Ivy, *Hedera. helix,* is an invasive climbing vine that originates from Northern Africa. The plant grows abundantly in the Maryville College woods. Although eradication of *H. helix* has proven difficult, evidence suggests that the plant harbors important biological activities; specifically the inhibition of tyrosinase, a key enzyme in the biosynthesis of melanin. *H. helix* is rich in saponins and flavonoids, which have shown

promise in the ability to inhibit tyrosinase. Fresh samples of *H. helix* were collected from the Maryville College woods and subjected to Soxhlet extraction. Samples of crude extract were then fractionated through the use of different chemical solvents. The fractionated components of the extract were screened for inhibition of tyrosinase-catalyzed oxidation of 3,4-dihydroxyphenylalanine using a colorimetric assay. Activity-guided fractionation, based on this assay, is being used to further isolate and identify compounds with promising tyrosinase-inhibitory activity.

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Novel labeling strategy of nucleic acids: Less is more

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NMR spectroscopy has proven highly useful for structural characterization of macromolecules. The sheer number of resonances in large molecules however creates complications in that resonances overlap to an extent that important information can no longer be extracted. This drove the development of multdimensional NMR experiments to alleviate peak overlap. Subsequently, the introduction of isotopes further simplified spectral appearance and also enabled the implementation of more sophisticated NMR experiment in proteins. Isotopic labeling (^{13}C and ^{15}N) of proteins is readily accomplished, labeling of RNA requires labeled triphosphates which are expensive. While labeling DNA using solid phase synthesis allows the specific incorporation of labeled residues ubiquitously or at specific locations, the costs are prohibitive.
We have developed a procedure to provide a cost effective and simple option to simplify DNA NMR spectroscopy and simultaneously introduce new isotopic labels. This method is based on the exchange GH8's and AH8's hydrogens with ^{2}H. Therefore, this procedure is particularly useful for sequences rich in guanosines and adenines. For example, ligand binding studies with DNA quadruplexes benefit greatly from a less cluttered aromatic resonance region and provides a clearer picture the involvement of loops and flanking sequences in binding, structure, and dynamics. We will demonstrate the application of this method on a regular DNA 10-mer duplex in presence and absence of a sequence specific ligand and a DNA quadruplex (PU22).

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PCBP2 knockdown leads to iron overload in mouse liver tissue

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Iron is an essential co-factor for many proteins involved in central cellular processes and is toxic at high concentrations. Therefore, iron storage, uptake and utilization are tightly regulated. Ferritin, the ubiquitous iron storage protein, Hepcidin a liver hormone that controls cellular iron release, Iron Regulatory Protein 2 (IRP2) and the Transferrin receptor, a protein and transmembrane iron importer respond to fluctuations in iron concentration and function to bring iron to stable levels.
Poly (rC)–binding proteins 1 and 2 (PCBP1 and PCBP2) are multifunctional adaptor proteins that bind cytosolic iron for delivery to target apoproteins. We studied the

regulation of iron related proteins in a mouse model of PCBP2 knockdown mice. We hypothesized that PCBP2 knockdown leads to iron overload in liver tissue. We used western blots to measure protein expression in response to PCBP2 is knocked down, Real-Time PCR to quantify the gene expression levels of iron related proteins. Compared to the wild type Heterozygous PCBP2 Knockdown mice showed significant elevation in liver Hepcidin levels along with decreased transferrin, and IRP2 levels. PCBP1 remained constant and PCBP2 expression was reduced by half. This shows that PCBP2 has a role in cellular iron regulation.

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The role of histone acetyltransferase 1 in DNA double-strand break repair

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Histone acetyltransferases are enzymes that catalytically transfer an acetyl group from acetyl-CoA to a lysine residue to form ε-*N*-acetyllysine. Histone acetylation not only loosens the coiling of the chromatin, but also is necessary for organismal development. Histone acetyltransferase 1 (Hat1) is a type B histone acetyltransferase that acetylates lysine residues 5 and 12 on histone H4. Hat1 exists in the cytoplasm and acetylates newly-synthesized histone H4 before its incorporation into chromatin. At the molecular level, Hat1$^{-/-}$ cells have unstable genomes; they have a higher basal number of DNA double-strand breaks (DSBs) and a higher number of DSB foci after treatment with a DNA-damaging agent compared to their wild-type counterparts. This research investigates the role of Hat1 on DNA DSB repair. Preliminary results suggest that Hat1 is involved in DNA DSB repair, but the mechanism of this involvement is unclear. This presentation implicates a more important role of Hat1 in DNA DSB repair.

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Characterization of the pattern and properties of fluorescence in Opiliones (harvestmen) captured in Cusuco National Park, Honduras

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It has been reported that many species of arachnids (spiders and scorpions) are fluorescent, however little is known about the evolutionary significance or the chemical nature of fluorescent compounds. Specimens of another fluorescing member of the arachnid class belonging to the order Opiliones (harvestmen) and classified as Eucynorta sp, were captured upon detection with black light in Cusuco National Park, Honduras. The opilionids glowed most intensely under long-wave ultraviolet light. The fluorescence was localized to a specific pattern on the dorsal carapace, abdominal tergites, and palps. Diffuse fluorescence was also detected on legs, trochanters and chelicerae. Carapace and leg samples from specimens were homogenized in either phosphate-buffered saline (PBS) or 95% ethanol, and the extracts were monitored for fluorescence using a fluorescence plate reader (lex=360 nm). Both ethanol and PBS extracts from the legs and the carapace had emission peaks near 450 nm, suggesting that the fluorescent compounds are polar. Studies are ongoing to separate and

characterize the fluorophores using thin layer chromatography and high-performance liquid chromatography. The results will be compared with profiles of fluorophores identified in other arachnids.

2015 Joint Southeastern/Southwest Regional Meeting 1170

An attempt to enhance the cell proliferation activity of the human fibroblast growth factor

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Human Fibroblast Growth Factor-1 (hFGF-1) is a 16kDa heparin-binding protein that is involved with many biological processes. FGF-1 is specifically related to processes involving cell differentiation, proliferation, angiogenesis, and wound healing. This heparin-binding protein interacts with the surface of a cell at its fibroblast growth factor receptors (FGFRs) and this interaction causes a sequence of events that lead the protein to carry out its specific task. The region of the protein that is responsible for binding to FGFR has a proline amino acid at position 135 (P135). The goal of this research is to understand how this proline contributes to the overall structure, stability, and functionality of the FGF-1 protein. Using site directed mutagenesis, the proline is replaced with a different amino acid, glutamic acid, at base pair 135 and the effects on the protein are measured using a variety of biophysical assays, some of them including DSC, multi-dimensional NMR spectroscopy, CD spectroscopy, IT calorimetry, and fluorescence. Information acquired from this study is expected offer great insight on the stability of the protein, and specifically how the protein can be stabilized to enhance cell proliferation.

2015 Joint Southeastern/Southwest Regional Meeting 1171

The optimization of catalytic loading in benzoxaborole synthesis

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Substituted benzoxaborole compounds have been used as medicinally active compounds since their discovery in the 1950’s. We describe our attempts to reduce catalytic loading, achieve enantioselectivity, and perfect purification methods in a novel synthesis of a benzoxaborole-based compound while maintaining high yields, minimal reaction times, and easily achievable reaction conditions.

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Synthesis of a fluorescent universal DNA nucleoside

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Fluorescence is a highly desirable property for a synthetic DNA base because it allows for the study of the structure of DNA and the ability to monitor its interaction with other compounds. In addition, a base that is universal can be integrated into a strand of DNA and have minimal effects on the strand's stability. The goal of our project is to synthesize a fluorescent universal DNA nucleoside containing dimethylaminonaphthylimide (DANI). Our progress of this synthesis will be reported. After the incorporation into DNA, DANI will then be used in various protein binding studies.

2015 Joint Southeastern/Southwest Regional Meeting 1173

Synthesis of a sulfate binding ligand

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In the pursuit of searching for viable sources of alternative energy, nuclear fission stands as a strong potential candidate; the large amount of energy yields that are returned from relatively small amounts of fuel – combined with increasingly efficient reactor technology – makes nuclear fission an appealing method to generate energy compared to conventional methods. This method is not without drawbacks, however, and the effective and safe storage of nuclear waste remains an issue. Species of sulfate anions that are commonly found within both high and low level nuclear waste destabilize vitrified waste products, and pose a serious risk to the environment should a containment vessel be breached in the thousands of years it takes for the radioactive waste to decay to safe levels of radioactivity. In this experiment, synthesis of a predetermined ligand that would have the ability to extract sulfate anions from water was explored. Each ligand synthesized comprised of the same basic features of a guanidine backbone disubstituted with phenylureas, but were varied in functional groups to alter secondary characteristics such as solubility and melting point. These basic features of each ligand theoretically allow two ligands to encapsulate a single sulfate anion through donation of 12 total hydrogen bonds as well as complementary charge and structure.

2015 Joint Southeastern/Southwest Regional Meeting 1174

Investigation of the shape of atropisomers using dipolar couplings

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This project encompasses the synthesis of an atropisomer and the determination of the shape of each conformer of the molecule using dipolar couplings measured by NMR spectroscopy. This research hopes to give us a means to address fundamental problems in determining the shapes of simple flexible molecules, thus making progress towards looking at more complicated flexible systems.

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Decarboxylative protein functionalization via photoredox catalysis

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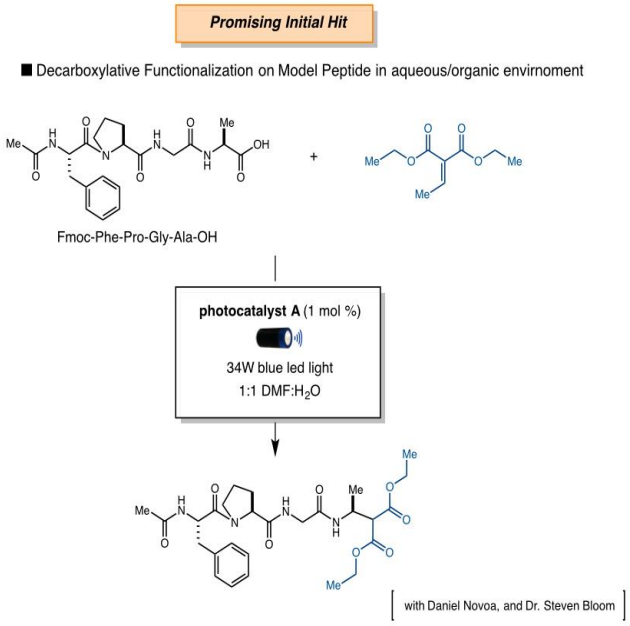
Current cancer therapies lack tumor selectivity. Antibody Drug Conjugates make use of antibodies with specific affinity to antigens over expressed on tumor cells, thus conferring improved target specificity. However, controlling the Drug to Antibody Ratio (DAR) and achieving Site-Specific Conjugation continue to be challenges in this field. This research is focused on employing photoredox catalysis to address this problem. Decarboxylative functionalization of small peptides with michael acceptors has been accomplished in aqueous/organic environments via visible light-mediated photoredox catalysis.



2015 Joint Southeastern/Southwest Regional Meeting 1176

Synthesis of a BIPY-urea ligand for the extraction of sulfate anions from a competitive aqueous environment

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The sulfate anions within nuclear waste cause many complications including: damaging machinery used in the vitrification process, decreasing the durability of the vitrified product, and leaving voids in the vitrified waste exposing radioactive molecules to the environment. Producing a product that has the ability to remove these anions is the overall goal of this research which consists of a multi step organic synthesis to obtain a BIPY-urea ligand. This ligand has the capability to donate twelve hydrogen bonds, and is hypothesized to bind and encapsulate sulfate ions to be separated from competitive

environments. The point of interest for this research is this ligand has the potential to improve the vitrification process and long term storage of nuclear waste. This will be accomplished through the binding of the sulfate anions contained in the waste followed by removal of the final structure.

2015 Joint Southeastern/Southwest Regional Meeting 1177

The metal-free hydration of terminal alkynes

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Most instances where terminal alkynes are hydrated, a heavy metal mercury compound such as mercuric oxide is used. Our group has found a method that gives the same product but uses no heavy metal. Through employment of a microwave reactor good yields were obtained of the Markovnikov carbonyl ketone.

2015 Joint Southeastern/Southwest Regional Meeting 1178

Synthesis of organic compounds with biological properties

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Alzheimer's Disease is a neurological disease growing steadfast in our aging population. Research has determined that Cathepsin B, enzymatic proteins are linked to the lysosomal activity in clearing tau protein accumulation.
Exploration of the PADK molecule will lead to a conclusion of the biological properties linked to linear structure of the molecule, connected nitrogen atoms, or polarity of the compound. PADK and its derivatives were researched using classical organic chemistry methods to determine which of those components were responsible for the effective biological properties

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Synthesis of the disaccharide moiety of the natural product OSW-1

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The natural product molecule OSW-1 has been shown to exhibit potent anti-cancer properties through a novel mechanism of action. The structure of OSW-1 contains two main components: a disaccharide and a sterol. My project has been to assist in the laboratory synthesis of the OSW-1 disaccharide and its analog compounds. The new OSW-1 analog compounds created will be tested for anti-cancer activity. The purpose of these tests will be to determine the active component of the molecule as well as what modifications can be made to it to improve its anti-cancer properties. These experiments will produce an optimized version of the OSW-1 for further preclinical drug

development. Our efforts to synthesize the OSW-1 disaccharide generated many unexpected and unidentified side products. To identify the structure of these various products, I used chromatography, including high-performance liquid chromatography (HPLC), to purify the disaccharide analogs. I then analyzed the purified compounds with NMR and mass spectroscopy to determine the identity of the compounds. My identification of the new side product disaccharide compounds could be used to prepare new OSW-1 for evaluation and testing.

2015 Joint Southeastern/Southwest Regional Meeting 1180

Novel N-benzylbenzamide- ased tyrosinase inhibitors

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The tyrosinase enzyme is a copper-containing enzyme which is a key component in the production of melanin. Inhibition of tyrosinase, could have many positive impacts, ranging from cosmetic applications, such as removal of freckles, to pesticides directly targeting insect development, as well as treatments for skin cancer. To date, quite a few types of tyrosinase inhibitors and their derivatives have been discovered and explored. However, a more recent class of inhibitors, the N-benzylbenzamide derivatives, have only been discovered and researched within the last decade. Although this class of inhibitors shows promise, only a few papers have been published exploring this class' potential as tyrosinase inhibitors, and current research focuses only on modification of the benzene rings of N-benzylbenzamide. A potential area of research for N-benzylbenzamide derivate inhibitors is to attach functional groups to both the nitrogen and the secondary carbon attached to the nitrogen. Synthetic progress will be presented towards attaching different functional groups to increasing the size of the pi systems as well as incorporating electron withdrawing and donating groups.

2015 Joint Southeastern/Southwest Regional Meeting 1181

Selective reduction of carbonyl and nitro groups by fruits and vegetables

***Jacqkis Davis**, jxd5345@louisiana.edu, August A. Gallo. Dept of Chemistry, Univ of Louisiana Lafayette, Lafayette, Louisiana, United States*

A variety of 15 fruits and 16 vegetables have been evaluated as biocatalysts for the reduction of several different functional groups. Several researchers have reported the use of plant cultures for the reduction of carbonyl groups including prochiral ketones to chiral alcohols in high yield. Our work focused on some fruits and vegetables not previously reported and their biocatalytic effect on di- and multifunctional molecules. The vegetables that looked most promising in reducing carbonyl groups are okra, parsley, parsnips, and sunchokes whereas plantain, cantaloupe, avocado and apricots were the active fruits. Okra when heated was able to reduce both aldehyde and ketone carbonyl groups in addition to the nitro group. Yields ranged from low to moderate. Acetates, diketones, and nitro groups were reduced with several other vegetables. Representative substrates include benzaldehyde, acetophenone, cyclopentanone, 2-heptanone, 4-nitrophenyl acetate, benzyl benzoate, 1-iodo-2-nitrobenzene, 4-nitrobenzonitile, and 1,4-naphthoquinone. Two general procedures were followed. The reactions were done in groups consisting of five simultaneous reactions per biocatalyst. The amount (50 microliters, µL) of a different given substrate was added to a 250-mL

Erlenmeyer flask. To each flask a standard was added (e.g. dodecane, 25 µL) followed by 20 grams of the biocatalyst, and finally 80 mL of deionized water (DI H_2O). The five flasks were place on an orbital shaker for 7days after which time they were extracted and analyzed by GC. Each biocatalyst was washed and cut into small-standardized pieces. Alternatively, the fruits and vegetables were disinfected and the reactions carried out in a phosphate buffer solution at pH= 6.8. The results of all biocatalytic reductions and their stereoselctivity will be presented.

2015 Joint Southeastern/Southwest Regional Meeting 1182

Progress toward the total synthesis of lauroside B

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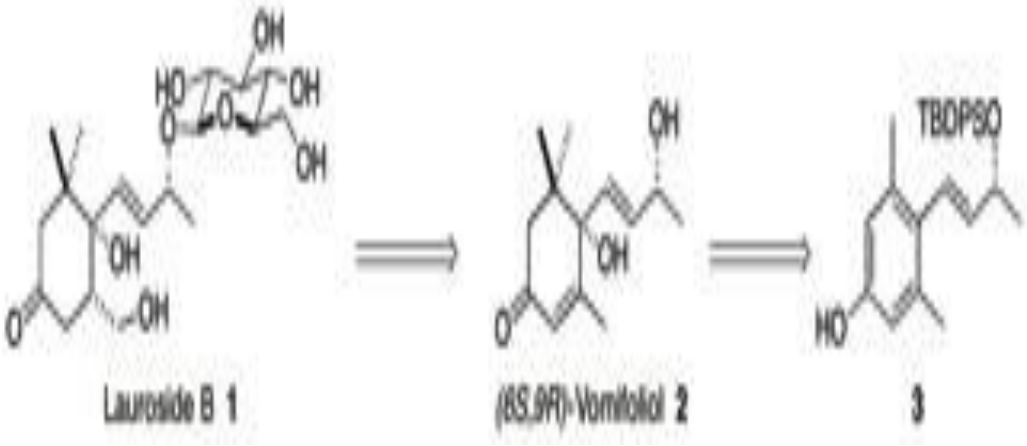
Lauroside B (**1**) has demonstrated potent biological activity against malignant skin cancer cells. Our research proposes synthetic access to **1** via **2** (itself also a natural product), which would arise from a phenolic oxidation of compound **3**. Efforts to access **3** via the Suzuki coupling of an aryl bromide and vinyl boronate ester will be discussed.

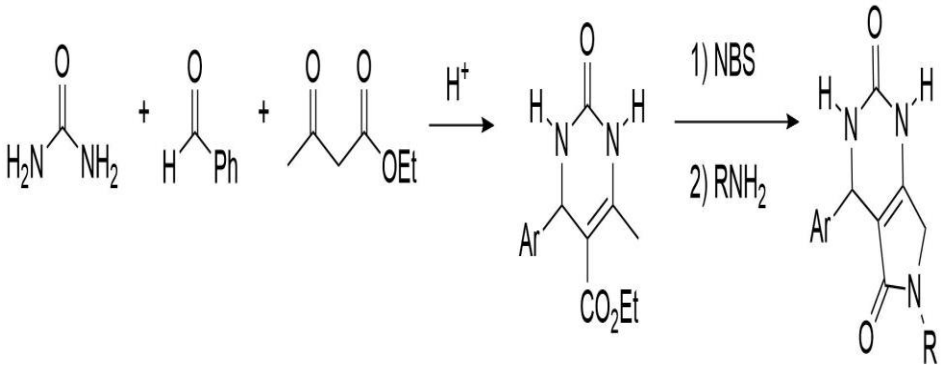


2015 Joint Southeastern/Southwest Regional Meeting 1183

Synthesis of new dihydropyrimidinone scaffolds

***John Hershberger**, jhershberger@astate.edu, Santiago Gonzalez. Chemistry and Physics, Arkansas State University, Jonesboro, Arkansas, United States*

The venerable Biginelli reaction has been known for over 100 years and is known to give biologically active dihydropyrimidinones as products. Phenethylamine derivatives are also known to be biologically active. However, there are few known scaffolds that contain both moieties. We report a three-step sequence to generate new dihydropyrimidinone-phenethylamine combination products.



2015 Joint Southeastern/Southwest Regional Meeting 1184

Using microwaves for organic syntheses in undergraduate organic labs

***Alex Rivas**, alex.rivas@cameron.edu, Elizabeth A. Nalley. Chemistry, Physics and Engineering, Cameron University, Lawton, Oklahoma, United States*

Allowing many chemical reactions to be completed within minutes, microwave heating has revolutionized preparative chemistry. As a result, this technology has been widely adopted in both academic and industrial laboratories. Integrating microwave-assisted chemistry into undergraduate laboratory courses enables students to perform a broader range of reactions in the allotted lab period. As a result, they can be introduced to chemistry that would otherwise have been inaccessible due to time constraints (for example, the need for an overnight reflux). A number of the chemical transformations use water as a solvent in lieu of classical organic solvents. This contributes to greener, more sustainable teaching strategies for faculty and students, while maintaining high reaction yields. The advantages inherent in microwave use make it ideal for the undergraduate laboratory. Although students are exposed to many different reactions in the classroom, many important organic reactions described in undergraduate textbooks are presently not included in the laboratory course owing to long reaction times, high temperatures, or sensitive reagents that present a potential danger to the students. In this poster, five syntheses using microwave heating will be described.

2015 Joint Southeastern/Southwest Regional Meeting 1185

Formation of asymmetric rhodamine derivatives for chiral sensing

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Xanthene dyes such as rhodamine can function as an off/on sensor and can therefore form extremely sensitive molecular sensors. Asymmetric derivatives of rhodamine are chiral and in the open (on) form this asymmetry provides axial chirality that makes the entire dye a chiral environment, thus, potentially forming a highly sensitive chiral fluorescent sensor. Herein, we present the synthesis and resolution of asymmetric rhodamine derivatives. These dyes will be used to examine the potential of

atropisomeric xanthenes dyes to function as chiral sensors. Rhodamine derivatives have been used in a wide range on sensing applications. The asymmetric modification, resolution methods, and preliminary testing presented here will demonstrate the utility of chiral rhodamine-based sensors.

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Microwave synthesis of phenyl salicylate and phenyl salicylate derivatives

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Allowing many chemical reactions to be completed within minutes, microwave heating has revolutionized preparative chemistry. As a result, this technology has been widely adopted in both academic and industrial laboratories. Integrating microwave-assisted chemistry into undergraduate laboratory courses enables students to perform a broader range of reactions in the allotted lab period. As a result, they can be introduced to chemistry that would otherwise have been inaccessible due to time constraints (for example, the need for an overnight reflux). A number of the chemical transformations use water as a solvent in lieu of classical organic solvents. This contributes to greener, more sustainable teaching strategies for faculty and students, while maintaining high reaction yields. Phenyl Salicylate can be synthesized from Salicylic Acid and Phenol using a conventional microwave oven. This synthesis and other synthesis of other derivatives phenyl salicylate will be discussed and the use of these products as starting materials for other reaction including Xanthone will also be described

2015 Joint Southeastern/Southwest Regional Meeting 1187

Microwave synthesis of tetraphenylporphyrins and tetraphenylporphyrin derivatives

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Allowing many chemical reactions to be completed within minutes, microwave heating has revolutionized preparative chemistry. As a result, this technology has been widely adopted in both academic and industrial laboratories. Integrating microwave-assisted chemistry into undergraduate laboratory courses enables students to perform a broader range of reactions in the allotted lab period. As a result, they can be introduced to chemistry that would otherwise have been inaccessible due to time constraints (for example, the need for an overnight reflux). A number of the chemical transformations use water as a solvent in lieu of classical organic solvents. This contributes to greener, more sustainable teaching strategies for faculty and students, while maintaining high reaction yields. Triphenylporphyrins can be synthesized from pyrrole and benzaldehyde using a conventional microwave oven. This synthesis and other synthesis of other derivatives of triphenylporphyrins will be described.

2015 Joint Southeastern/Southwest Regional Meeting 1188

Incorporation of dyes in polymers as a means of producing faux stained glass windows

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In an effort to make fun nanoparticle projects for students in a summer science academy in nanotechnology, we followed the procedure from the University of Wisconsin <http://mrsec.wisc.edu/Edetc/nanolab/silver> for making gold and silver nanoparticles. These were immobilized in PVA to produce a dye solution which could be applied to glass or Plexiglas that looked like stained glass windows. Incorporation of nanoparticles in glass to make stained glass is a procedure that has been utilized since the Middle Ages. The dye solutions produced by following this procedure were unpredictable, dull and unsuitable for use as stained glass. We then tried using organic dyes in place of the metallic dyes, and found that they gave the intense color that we had been seeking. Although the art form product resulting from this research were not colored in the same manner as traditional stained glass windows, the colors produced by nanoparticles were very vivid and allowed the light to pass through because of their very small size. Although the dyes prepared using PVA were beautiful in color and often were easy to apply. They were moisture and heat sensitive. For some time we have been investigating different methods to correct this. The addition of Polyvinyl Pyrrolidine has produced a stable dye which does not foam and adheres well to glass and Plexiglas.

2015 Joint Southeastern/Southwest Regional Meeting 1189

Studies on the synthesis and biological activity of hibiscone C

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I worked in the Goess Lab during Summer 2015. As a new member in the group, my main task is go through the 11 step organic synthesis and synthesize Hibiscone C molecules. I eventually finished the 10th step and get an incredibly low yield that cannot effectively proceed to the final step but I did gain a lot of experience through the process. I also studied some elementary computational chemistry techniques and run some calculations on the energies of several stereoisomer of Hibiscone C and its oxidization form; this is trying to provide a background proof that the oxidization the lab is trying to accomplish is theoretically accomplishable.

2015 Joint Southeastern/Southwest Regional Meeting 1190

Diels-Alder reactions of 2-cycloalkenylthiophenes and 2-cycloalkenylbenzo[*b*]thiophenes

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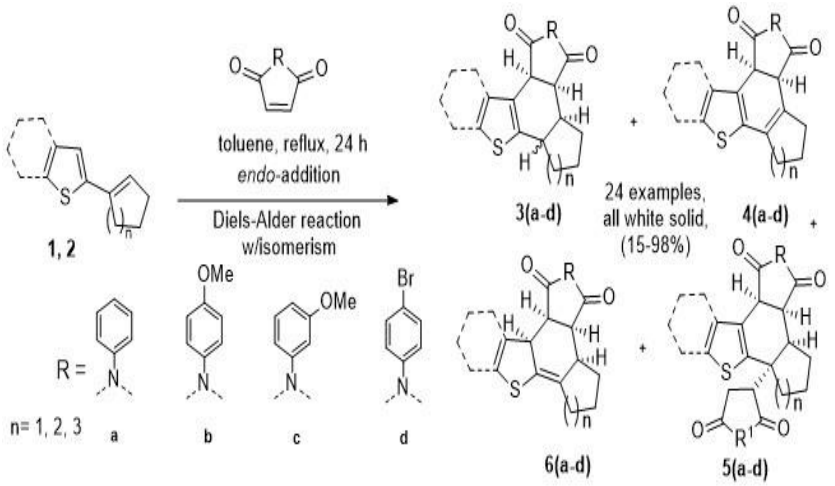
The heteroaromatic dienes 2-vinylthiophene **1** and 2-vinylbenzo[*b*]thiophene **2**, with the vinyl groups fused to five-, six-, and seven-membered cycloalkane rings, underwent normal-electron demand [4+2] cycloaddition reactions with *p*-benzoquinone, maleic anhydride, and variously substituted *N*-phenyl maleimides, giving the expected

isomerized *endo*-addition Diels-Alder adducts **6a-d** (36-98%). Also isolated as lesser components were the fully aromatized Diels-Alder adducts **4a-d** (15-25%), as well the product of a highly diastereospecific (≥ 98% de) Michael-addition between an unrearranged adduct and another molecule of dienophile **5a-d** (25-55%). This route to annulated thiophenes and benzo[*b*]thiophenes is versatile, and the starting materials are easily prepared. The newly synthesized compounds will be offered to the National Institute of Health (NIH) to explore their anti-tumor, anti-bacterial, or other biological activities.



2015 Joint Southeastern/Southwest Regional Meeting 1191

Efforts towards the direct γ-functionalization of cyclopentenones

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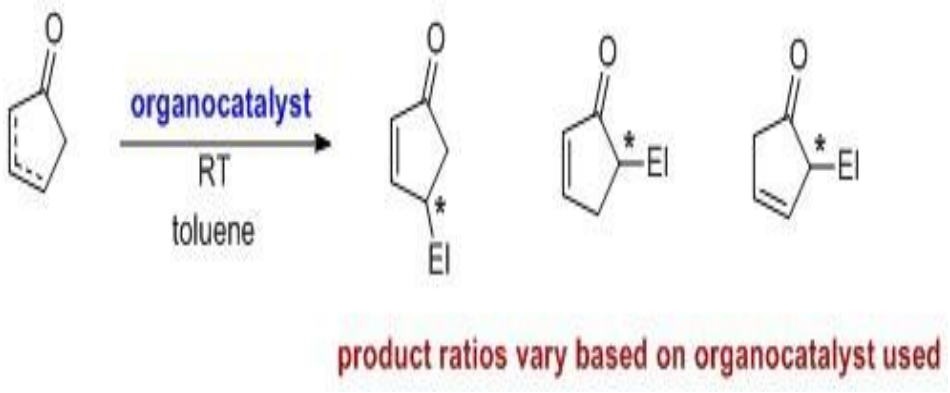
The direct γ-functionalized of cyclopentenones would be a useful method due to the prevalence these structures in medicinal targets including several prostaglandins, latanoprost, and phorbol. Despite the importance of this structural motif, no direct γ-functionalization protocol exists for their synthesis. Current syntheses typically require step-intensive functional group interconversion to obtain the moiety. Herein, our efforts towards the vinylogous aldol and Michael reactions with 2-cyclopentenone and 3-cyclopentenone are described. A rationale for the product ratios based on catalyst structure is also disclosed.



2015 Joint Southeastern/Southwest Regional Meeting 1192

Overcoming aromaticity: Progress towards the cyclization of cyclopropenones

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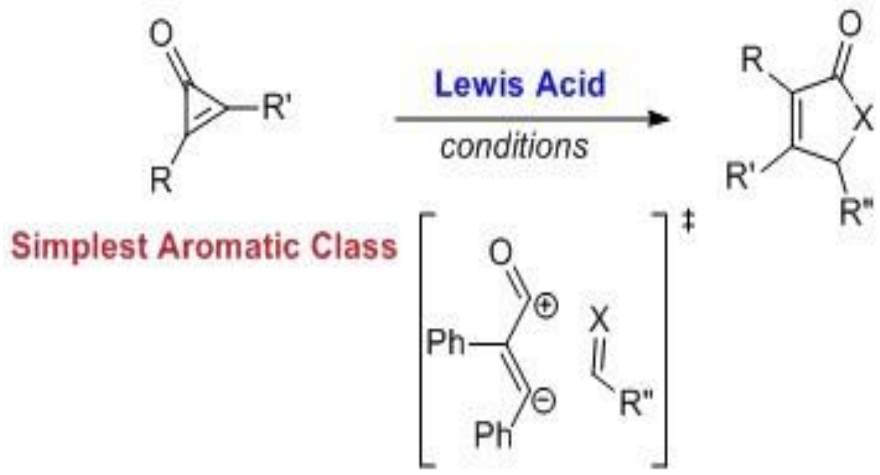
Despite possessing a high degree of ring strain and a highly functionalized core structure, the utility of cyclopropenones in cycloaddition chemistry has remained limited. This is likely due to the stabilizing aromatic character of cyclopropenones operating as a counterbalance to the destabilizing effect of ring strain that leads to ring opening. The presented research describes efforts to enable the cycloaddition of cyclopropenones and their non-ketal based derivatives with π-system coupling partners both under thermal and Lewis acid catalyzed conditions.



2015 Joint Southeastern/Southwest Regional Meeting 1193

Halogen effects on the enantiomeric excess (EE) of an S_N1 reaction

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Unimolecular Nucleophilic Substitution reactions, S_N1, are known for their production of racemic mixtures or optically inactive products. The mechanism for these types of reactions indicates that there is an equal chance of obtaining either enantiomer. In a study done by Mosher it was found that a reaction of L-lactic acid and hydrobromic acid resulted in a product that was not racemic. This is contrary to what is known about the mechanism of an S_N1 reaction. Further analysis revealed that this reaction proceeds through a mechanism that has 62% S_N1 character and 38% S_N2 character. The following experiment was done in an attempt to understand this reaction and the role of the halogen on the enantiomeric excess of the product. Hydrobromic and hydrochloric acids were reacted with L-lactic acid and the products were tested for enantiomeric purity. A Perkin Elmer Model 343 Polarimeter was utilized to determine the solutions optical rotation in degrees. From the observed optical rotation, optical purity and percent of each enantiomer were calculated. A nonparametric Mann-Whitney test was performed on the results from the 20 trials and yielded a P-Value of 0.0002. The results showed a significant difference between the bromide and chloride effects on enantiomeric excess. The data indicated that the bromide had a significantly greater effect on the percentage of *left handed* enantiomer produced from the reaction.