S. Woodward, University of Nottingham

Organic Thermoelectrics

Are Sustainability and Performance Compatible ?

EPSRC Thermoelectric Network Workshop, National Physical Laboratory, 21.04.2016

Preliminary Results From The 'h2esot Consortium'

Simon Woodward, School of Chemistry, University of Nottingham

The University of Nottingham
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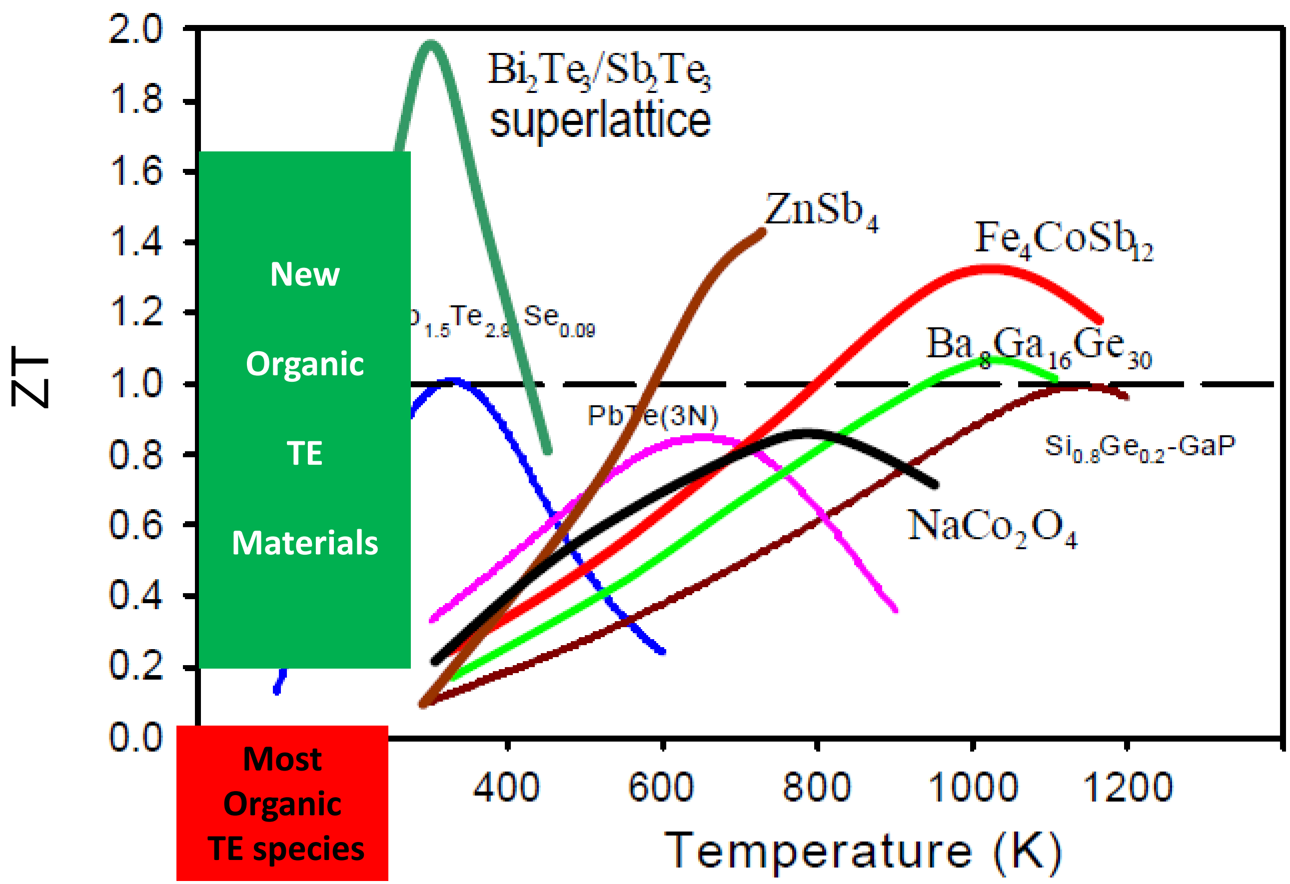
Home pages: www.nottingham.ac.uk/~pczsw/SWGroup/
www.h2esot.com

OTEM Orientation: 1



- **What types of organic materials ?**
- **Limitations ?**
- **Advantages ?**

$$Z = \frac{\sigma S^2}{\kappa}$$

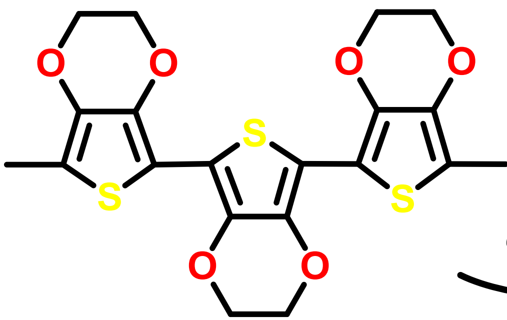
G. Min, University of Cardiff, personal communication.

OTEM Orientation: 2

Polymer/ Oligomer

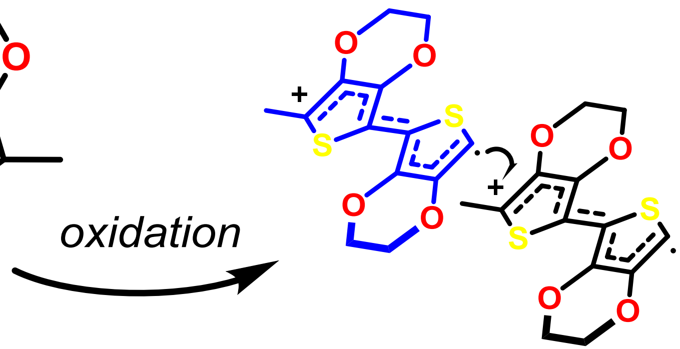
Organic Thermo Electric Material (OTEM)

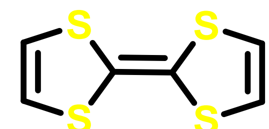
Discrete Small Molecule



poly(3,4-ethylenedioxythiophene)
(PEDOT)

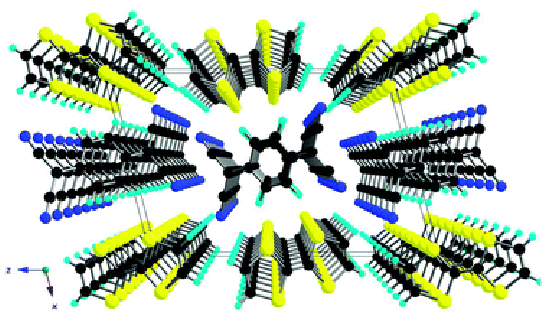
~£900 per gram
[687316 Sigma-Aldrich]



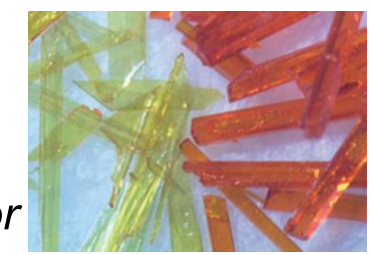


Tetrathiafulvalene (TTF)

£150 per gram
[183180 Sigma-Aldrich]

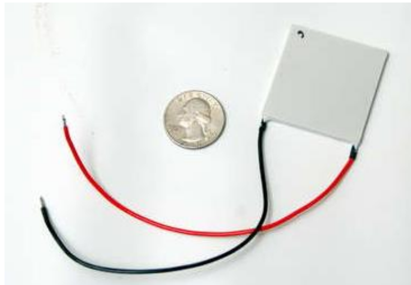


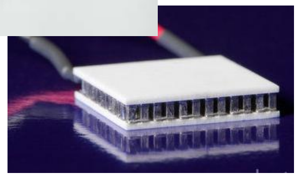
acceptor

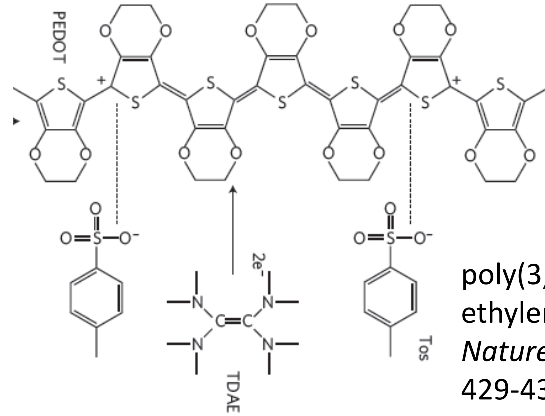


Good Overviews: *(a) P. J. Taroni, I. Hoces, N. Stingelin, M. Heeney, E. Bilotti, Israel J. Chem.* ***2014****, 54, 534-552. (b) Q. Zhang , Y. Sun , W. Xu , D. Zhu, Ad. Mat.* ***2014****, 26, 6829-6851. (c) N. Martín, Chem. Commun.* ***2013****, 49, 7024-7027.*

Current State-of-the-art & Problems







poly(3,4-ethylenedioxythiophene)
Nature Materials **2011**, *10*, 429-433.

Existing systems (and problems)

- Based on Bi_2Te_3-alloy (use is limited to <350 t yr^{-1} [Te is the 9^{th} rarest element (rarer than platinum), toxic and global resources expected to be depleted by 2030].
- Such generators currently use relatively large amount of Bi_2Te_3 and are assembled by jointing technology limiting size of units to *ca*. 25 cm^2.
- Relatively expensive (>£20 per W) and limited to niche markets.

Organic-based solutions to these problems.....?

- Mechanical flexibility - adaptation of the generator shape – bend it, wear it, *etc*.
- Potentially improved processing properties (ultimately standard production lines for printable organic electronics)
- Intrinsic low thermal conductivity (0.1–4 W K^{-1} m^{-1}).

What else is out there ?

Table 1. Overview of (thermo)electric properties of some organic charge transfer salts and inorganic materials (TTT—tetrathiotetracene, BEDT-TTF—bis(ethylen-dithiolo)tetrathiofulvalene, TMTSF—tetramethyl tetraselene fulvalene, Ni(mnt)—bis(maleodinitriledithiolato)nickelate(II)).

Material	S (μV K^{-1})	σ (10^4 S cm^{-1})	ρ (Ω cm)	κ (W m^{-1} K^{-1})	z (10^{-6} K^{-1})
Antimony (Sb)	35	2.6		24.3	131
Iron (Fe)	16	11.2		80.2	36
Nickel (Ni)	−19	14.6		90.7	58
Bismuth (Wi)	−70	0.9		7.84	563
TTT_2–I_3	35.8 [25]		1.0×10^{-5}		64
$(BEDT$–$TTF)_2I_3$	49 [21]		7.5×10^{-5}		16
TTF_2CuCl_2	35 [26]	1.4×10^{-3}			0.86
$TTF_{7/3}CuCl_2$	30 [27]	1.0×10^{-3}			0.45
TTT–I	80 [28]	1.4×10^{-4}			0.45
$(BEDT\text{-}TTF)_{7/5}CuBr_2$	55 [26]	1.7×10^{-4}			0.26
$TTF_{5/3}CuBr_2$	30 [26]	1.5×10^{-4}			0.07
$(TMTSF)_2NO_3$	24 [29]		1.3×10^{-2}		0.02
$TTT_{1.2}$–Ni(mnt)	1.5 [30]	3.0×10^{-4}			0.003
TTF–TCNQ	−28 [19, 20]		2×10^{-5} [31]	1 [23]	39
$(BEDT\text{-}TTF)Cu_2Br_4$	−850 [32]		1		0.36
TTF–Ni$(mnt)_2$	−655 [33]		6.31		0.03
TTT–Ni$(mnt)_2$	−170 [33]		3.24		0.004

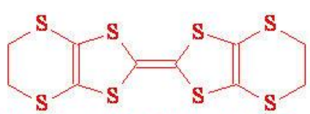
~0.1 to 4

σ is the electrical conductivity

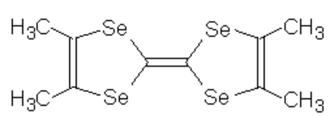
κ is the thermal conductivity

S is the Seebeck coefficient.

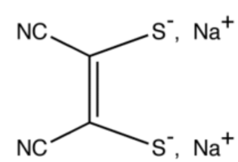
$$Z = \frac{\sigma S^2}{\kappa}$$

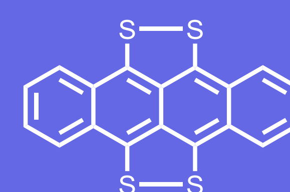


Bis(ethylenedithio)tetrathiafulvalene
BEDT-TTF (ET)



TMTSF





Tetrathiotetracenes
TTT

J. Wüsten and K. Potje-Kamloth, J. Phys. D: Appl. Phys. ***2008****, 41, 135113.*

Our EU ‘h2esot’ project

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PHYSIKALISCHES INSTITUT
epVI

TECHNICAL UNIVERSITY OF MOLDOVA

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1869

LATVIJAS UNIVERSITATE
ANNO 1919

European Thermodynamics Limited
Intelligent Thermal Management

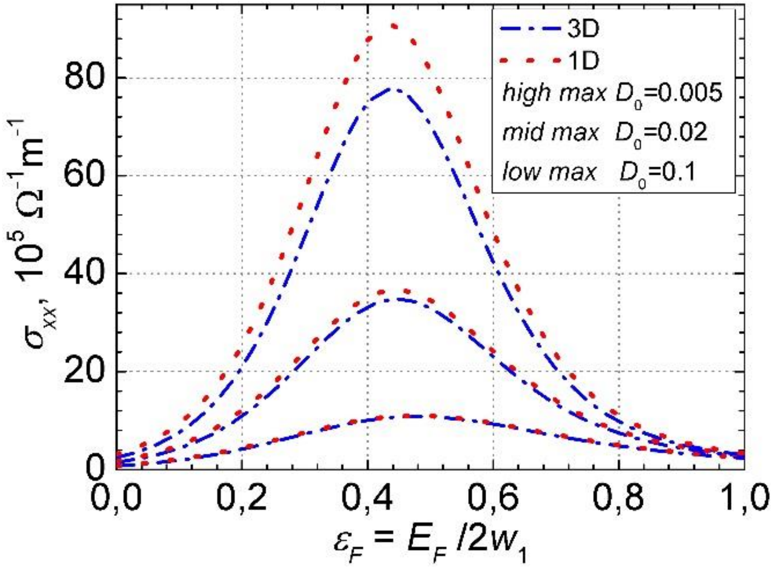
Disciplines required: CHEMISTRY · EXPERIMENTAL PHYSICS · MATERIALS SCIENCE · THEORETICAL PHYSICS · ELECTRONICS

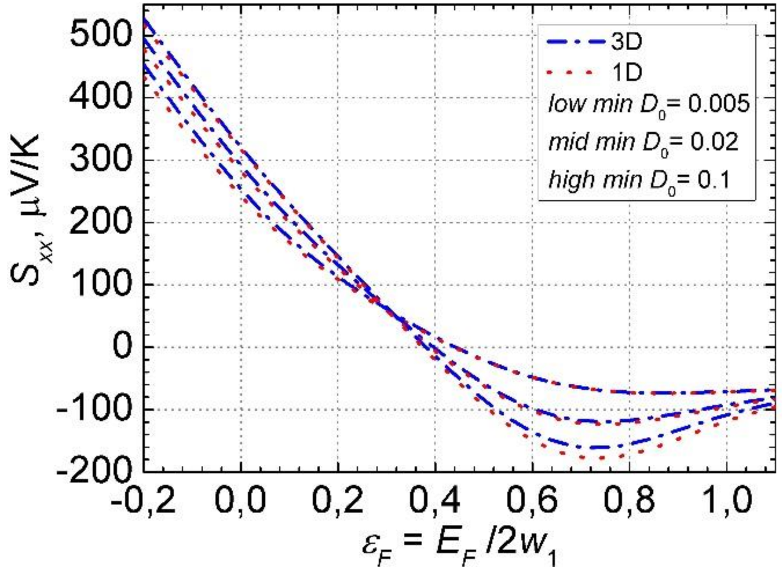
In theory TTT derivatives are ideal, but playing ‘Devil’s Avocate’.....

- **TTT** known since 1946, but existing syntheses plagued by multi steps and product insolubility (*ca*. 10^{-4} M).
- High ZT value **TTT** materials are quasi-1-D-crystals – often sensitive to substitution pattern changes.
- Very high purity crystalline materials (**TTT**$^{+}$X^{-}) needed for device manufacture.

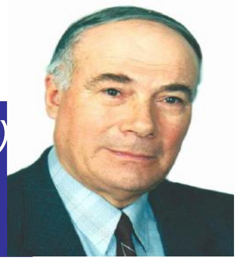
See: www.h2esot.com

Theoretical Predictions: 1



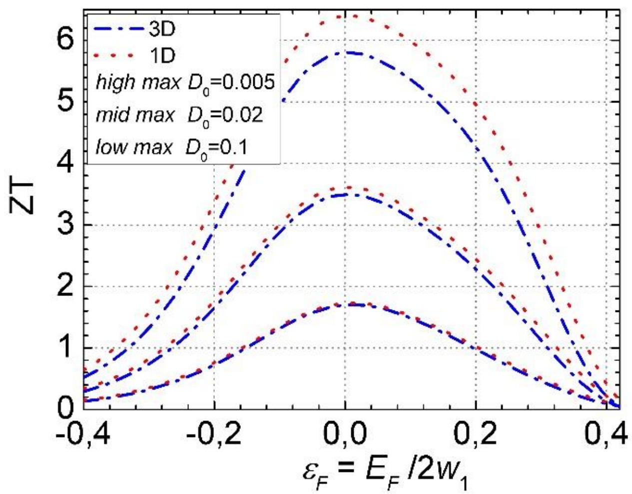


- w_1 the carrier transfer energy along the 1D axis (estimated to be 0.16 eV in **TTT_2I_3**).
- D_o introduced to model the reduction of (hole) carrier efficiency via scattering defects and 'non perfect' lattice/crystal defects.
- $\varepsilon_F = E_F/2w_1$, a dimensionless parameter where the **TTT_2I_3** Fermi energy is measured in units of twice the 1D carrier transfer energy – as it is useful in graphical visualisations, parameters outputted from the model such as ε_F are unit-less .

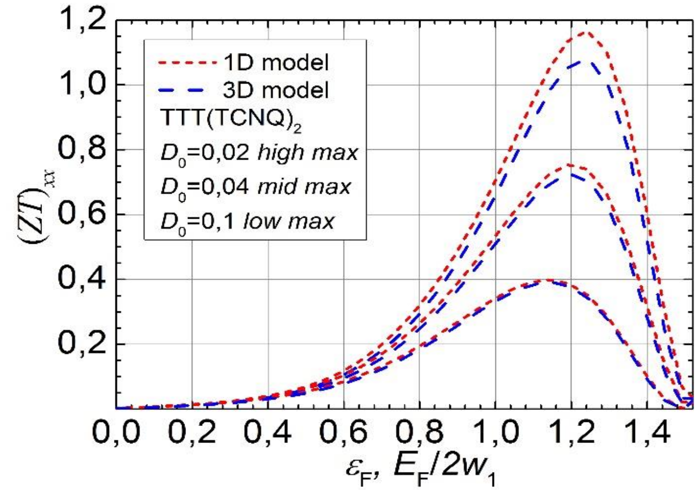


*(a) A. I. Casian, I. I. Sanduleac, J. Electronic Materials **2014**, 43, 3740-3745. (b) A. Casian, I. Sanduleac, Mat. Today Proc. **2015**, 2, 504-509 and references therein.*

Theoretical Predictions: 2

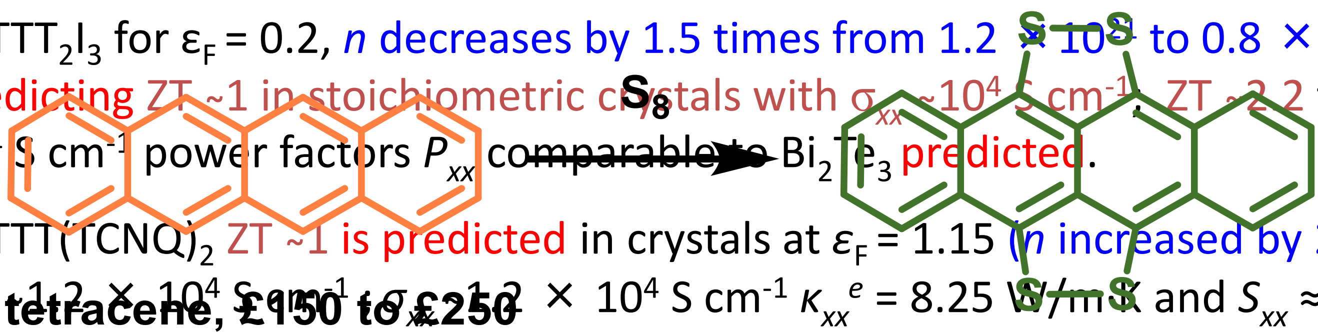


Thermoelectric figure of merit ZT in TTT_2I_3 as function of dimensionless Fermi energy ε_F.



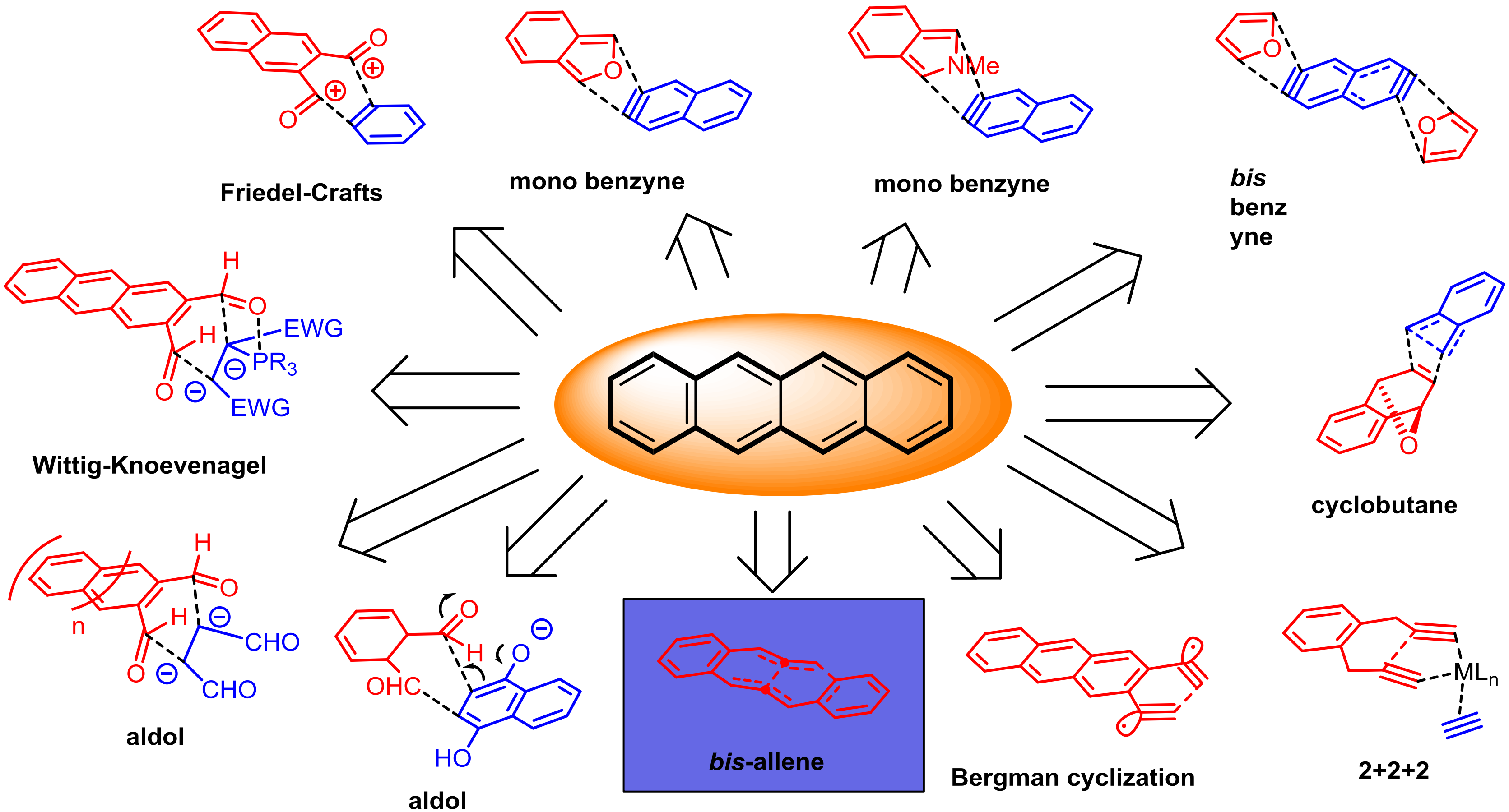
Thermoelectric figure of merit, ZT in $TTT(TCNQ)_2$ as function of ε_F.

- In TTT_2I_3 for $\varepsilon_F = 0.2$, *n* decreases by 1.5 times from 1.2×10^{21} to 0.8×10^{21} cm^{-3}, predicting ZT ~1 in stoichiometric crystals with σ_{xx} ~10^4 S cm^{-1}; ZT ~2.2 for σ_{xx} ~3×10^4 S cm^{-1} power factors P_{xx} comparable to Bi_2Te_3 predicted.
- In $TTT(TCNQ)_2$ ZT ~1 is predicted in crystals at $\varepsilon_F = 1.15$ (*n* increased by 2.3 times) with σ_{xx} ~1.2×10^4 S cm^{-1}; σ_{xx} ~1.2×10^4 S cm^{-1} $\kappa_{xx}^e = 8.25$ W/m·K and $S_{xx} \approx -150$ µV/K.



(a) A. I. Casian, I. I. Sanduleac, J. Electronic Materials **2014**, 43, 3740-3745. (b) A. Casian, I. Sanduleac, Mat. Today Proc. **2015**, 2, 504-509 and references therein.

Routes to Tetracenes

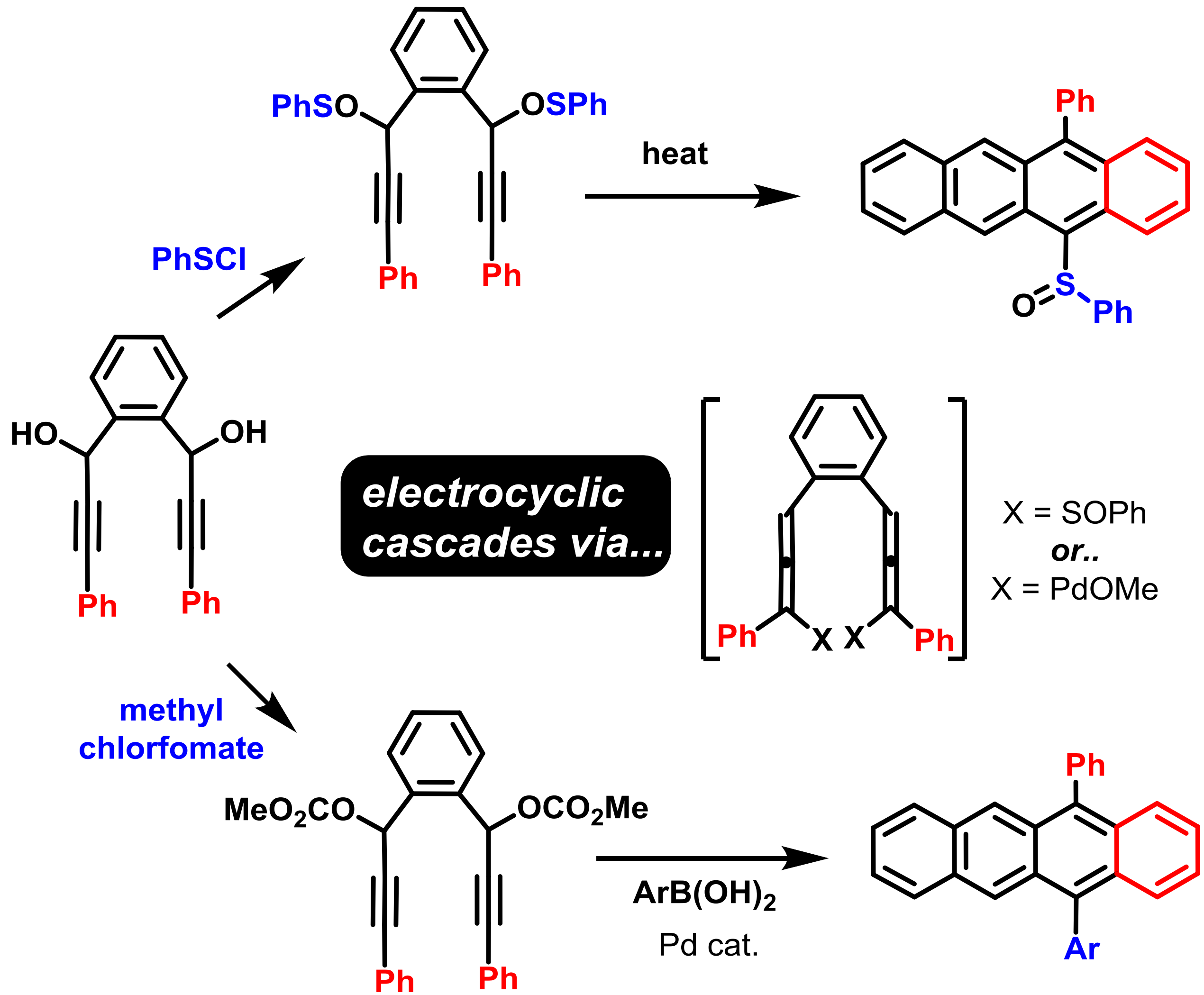


Comments.....

- Most multi-step, poor yield, time intensive....

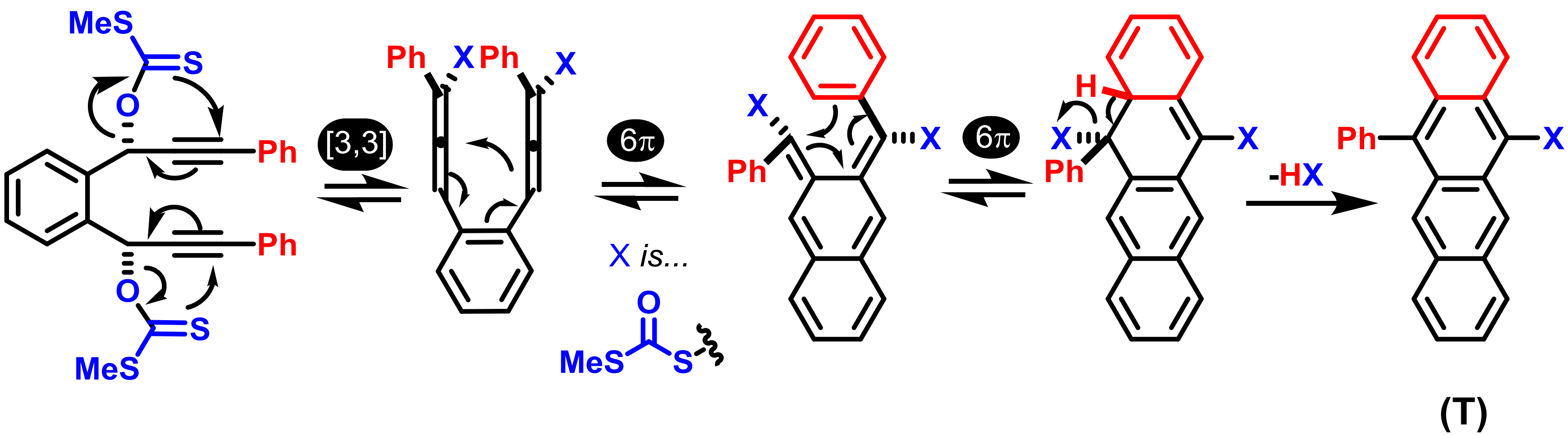
H. Qu, C. Chi. Current Organic Chemistry ***2010****, 14, 2070-2108.*

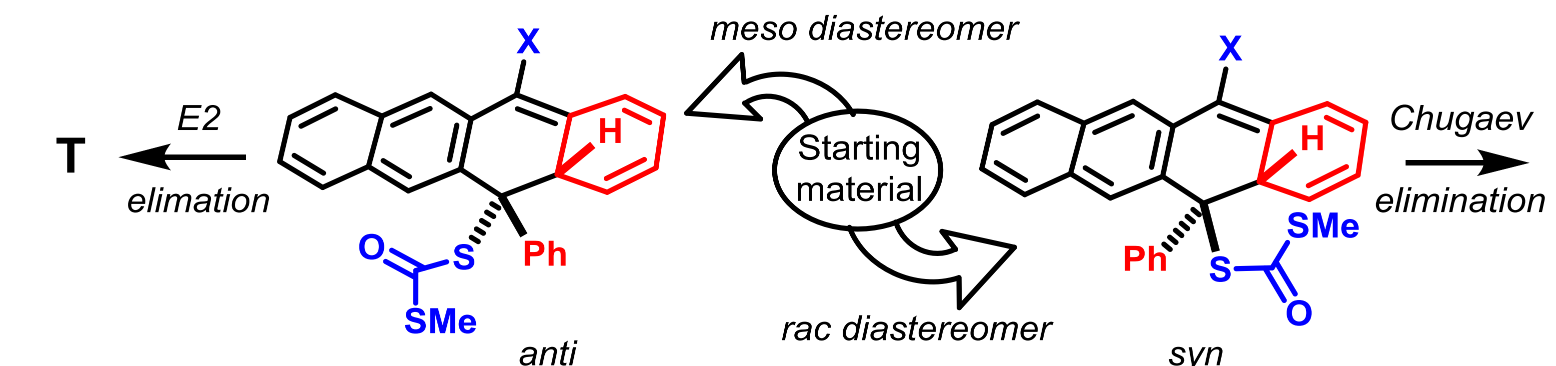
Literature Allene Cascades



(i) Lin, Y.-C.; Lin, C.-H. Org. Lett. ***2007****, 9, 2075–2078. (ii) Chen, M.; Chen, Y.; Liu, Y. Chem. Commun.* ***2012****, 48, 12189–121191.*

Our Initial Plan

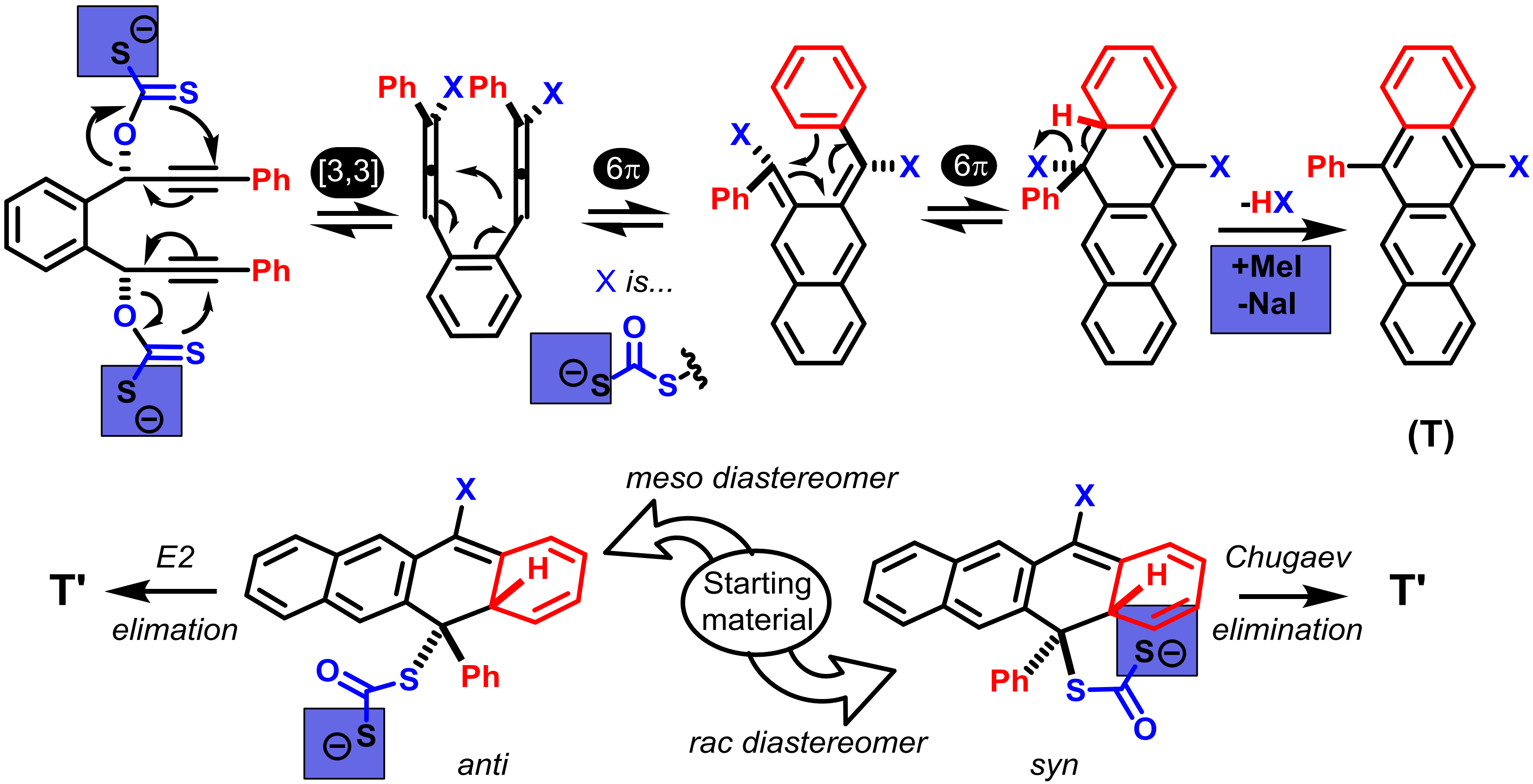





L. Burroughs

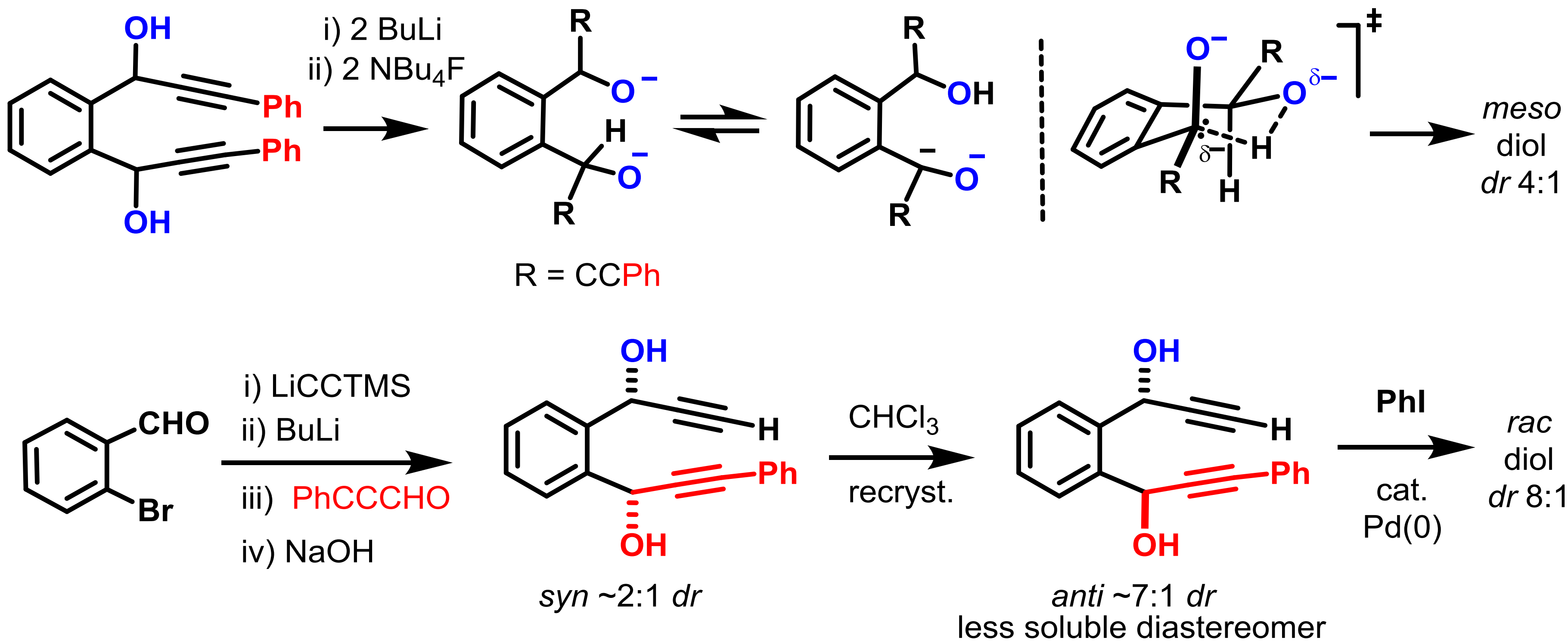
(i) Burroughs, L.; Ritchie, J. Ngwenya, M.; Khan, D.; Lewis, W.; Woodward, S. *Beilstein J. Org. Chem.* **2015**, 11, 273-279. (ii) Tomita, K.; Nagano, M. *Chem. Pharm. Bull.* **1968**, 16, 1911–1917.

...and its modification



(i) Burroughs, L.; Ritchie, J. Ngwenya, M.; Khan, D.; Lewis, W.; Woodward, S. Beilstein J. Org. Chem. ***2015****, 11, 273-279. (ii) Tomita, K.; Nagano, M. Chem. Pharm. Bull.* ***1968****, 16, 1911–1917.*

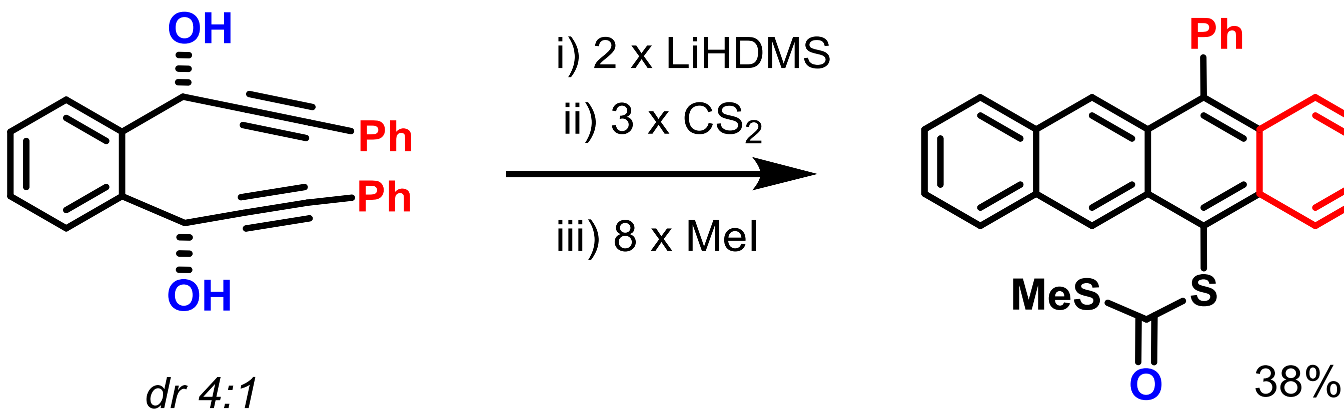
Synthesis of *Anti/Syn* Diols



Burroughs, L.; Ritchie, J. Ngwenya, M.; Khan, D.; Lewis, W.; Woodward, S. Beilstein J. Org. Chem. ***2015****, 11, 273-279.*

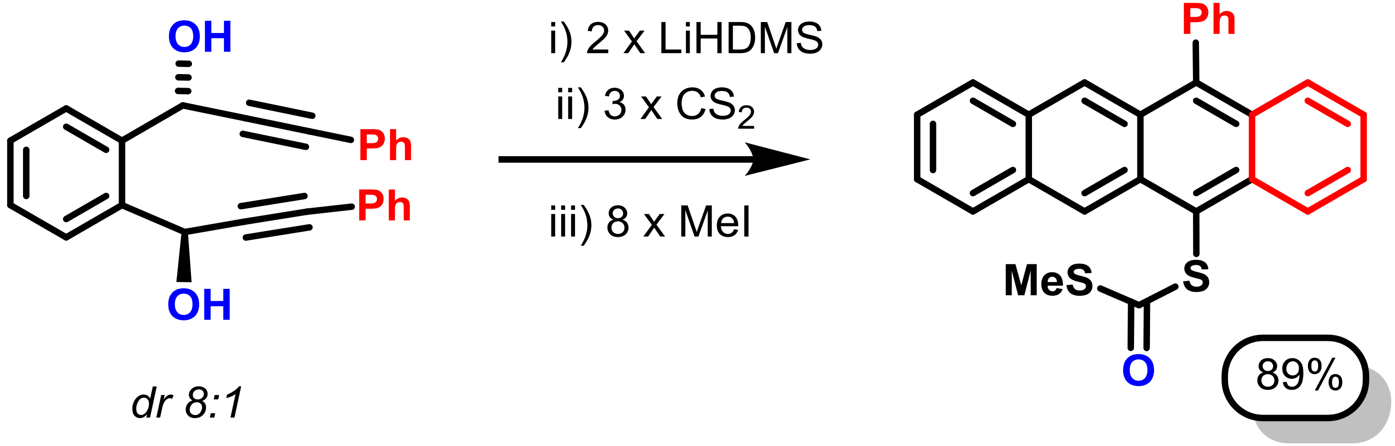
Confirmation of Stereocorrelation

meso...



dr 4:1

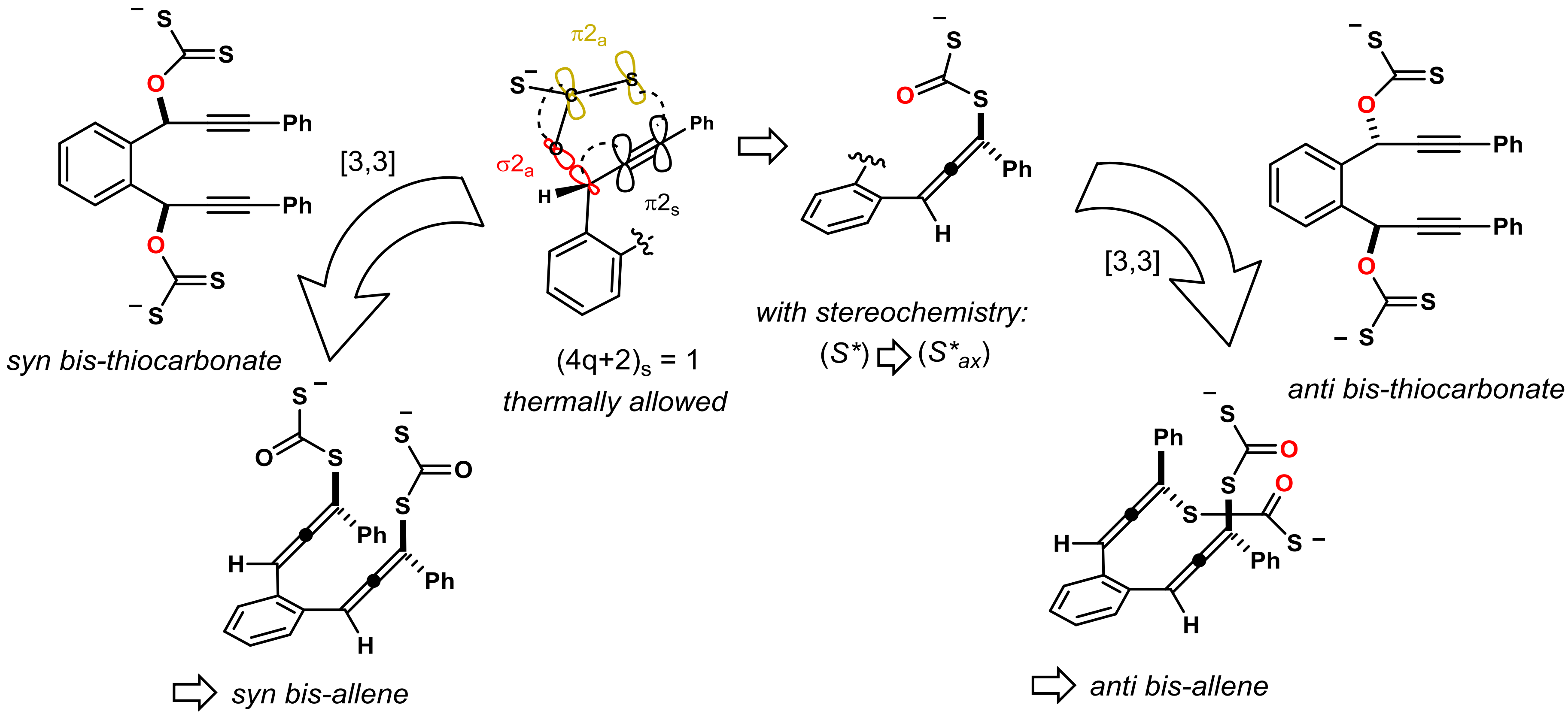
rac...



dr 8:1

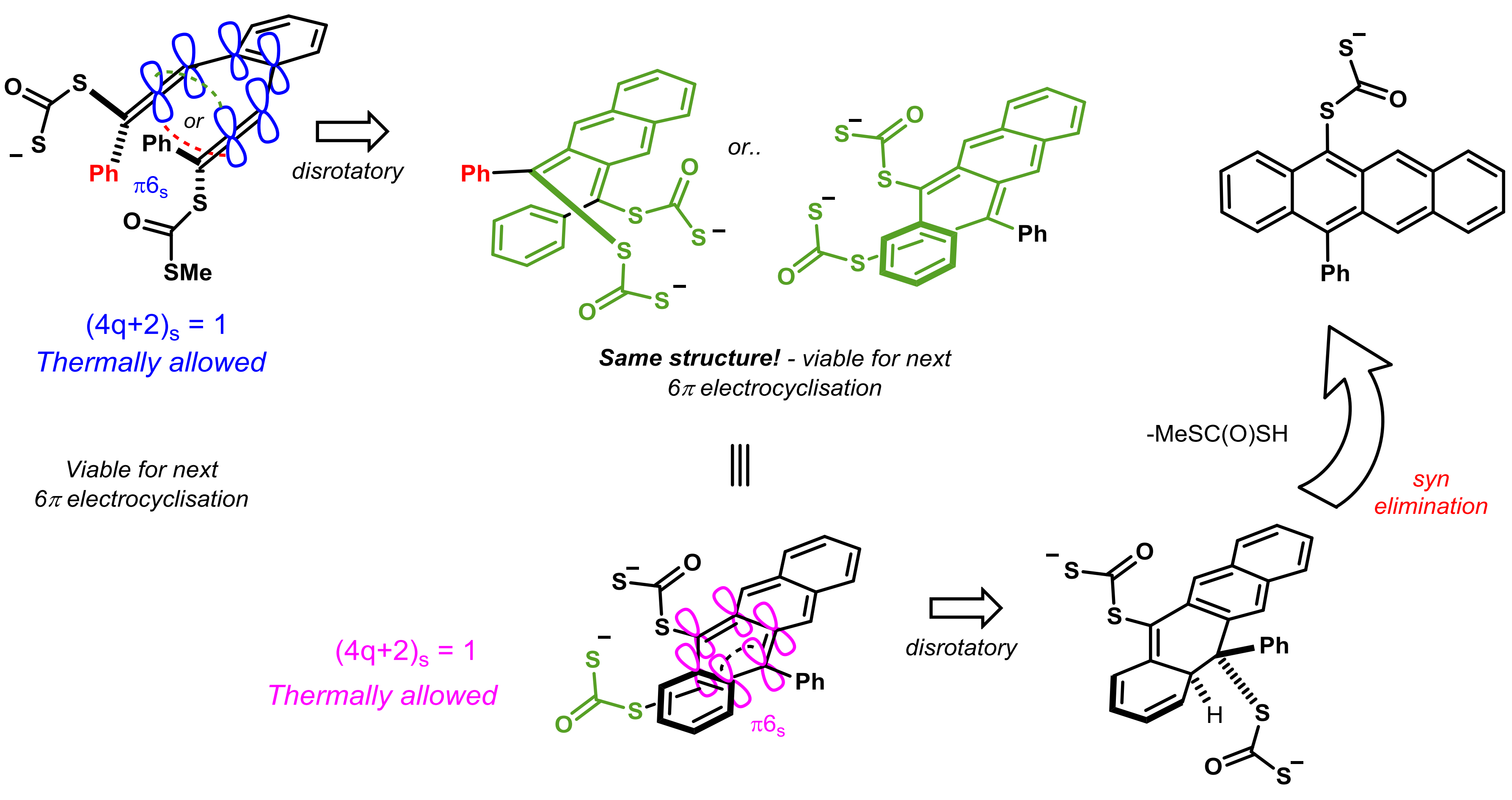
Burroughs, L.; Ritchie, J. Ngwenya, M.; Khan, W. Lewis, S. Woodward, Beilstein J. Org. Chem. ***2015****, 11, 273-279.*

Woodward-Hoffmann: 1



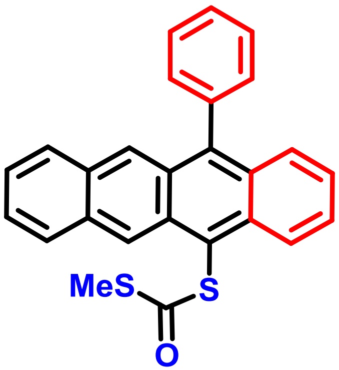
(a) L. Burroughs, J. Ritchie, M. Ngwenya, D. Khan, D.; Lewis, W.; Woodward, S. Beilstein J. Org. Chem. ***2015****, 11, 273-279. (b) (b) L. Burroughs, J. Ritchie, S. Woodward, Tetrahedron* ***2016****, 72, 1686-1689.*

Woodward-Hoffmann: 2

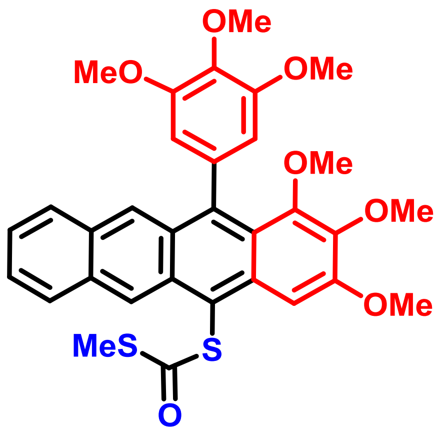


(a) L. Burroughs, J. Ritchie, M. Ngwenya, D. Khan, D.; Lewis, W.; Woodward, S. Beilstein J. Org. Chem. **2015**, 11, 273-279. (b) (b) L. Burroughs, J. Ritchie, S. Woodward, Tetrahedron **2016**, 72, 1686-1689.

Scope of Reaction



60-85%



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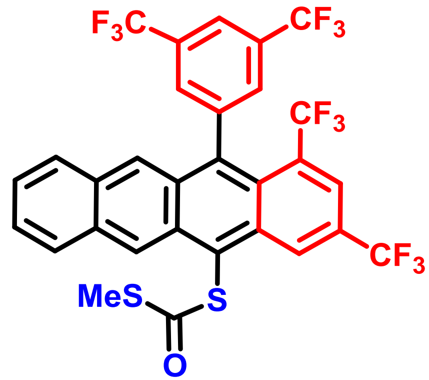

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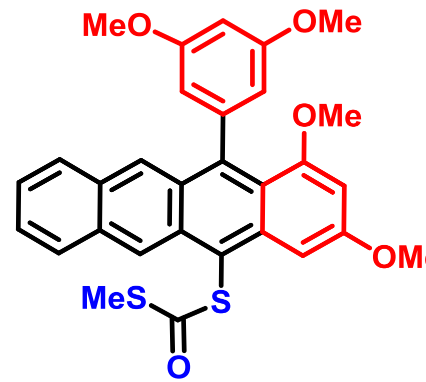

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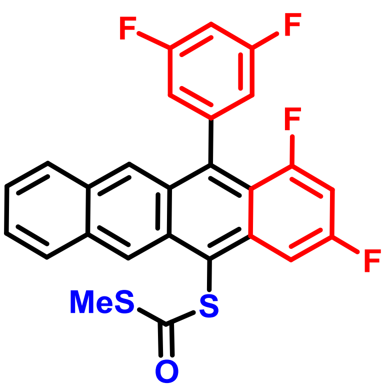

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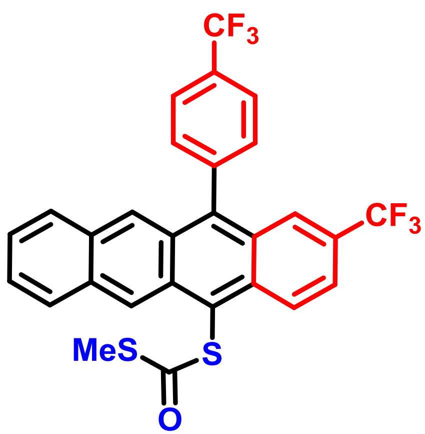

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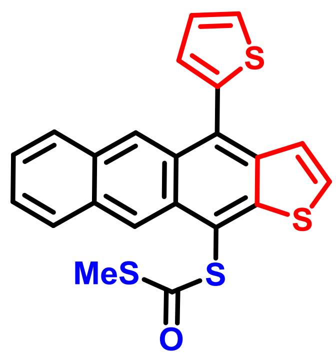

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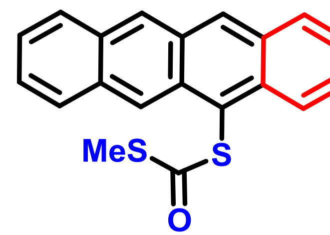

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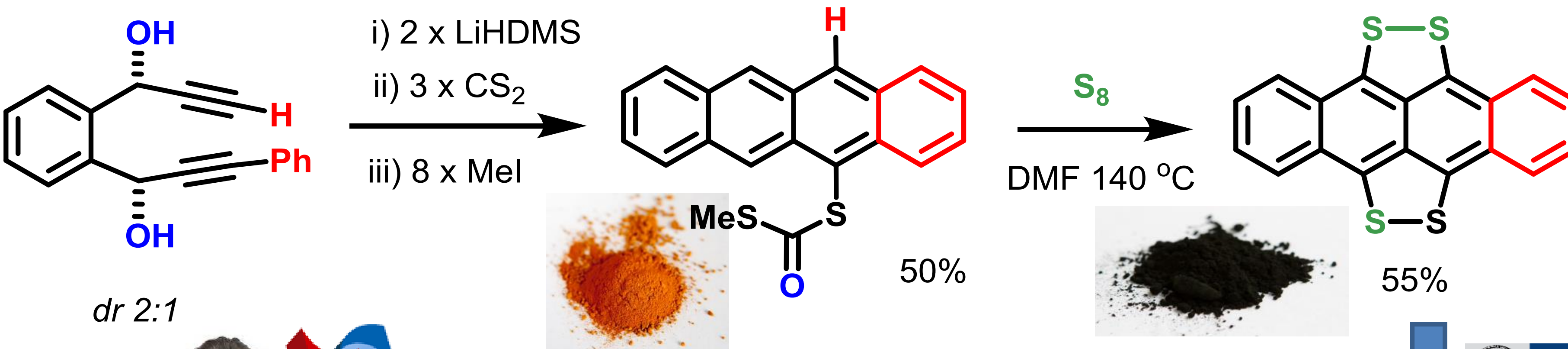
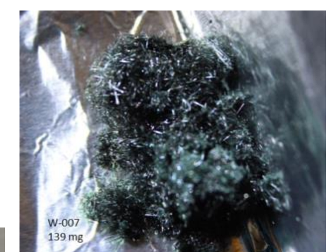
Burroughs, L.; Ritchie, J. Ngwenya, M.; Khan, D.; Lewis, W.; Woodward, S. Beilstein J. Org. Chem. ***2015****, 11, 273-279.*

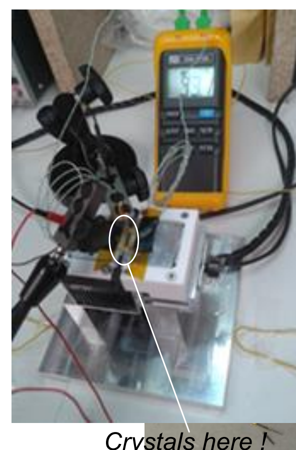
Onward towards Devices



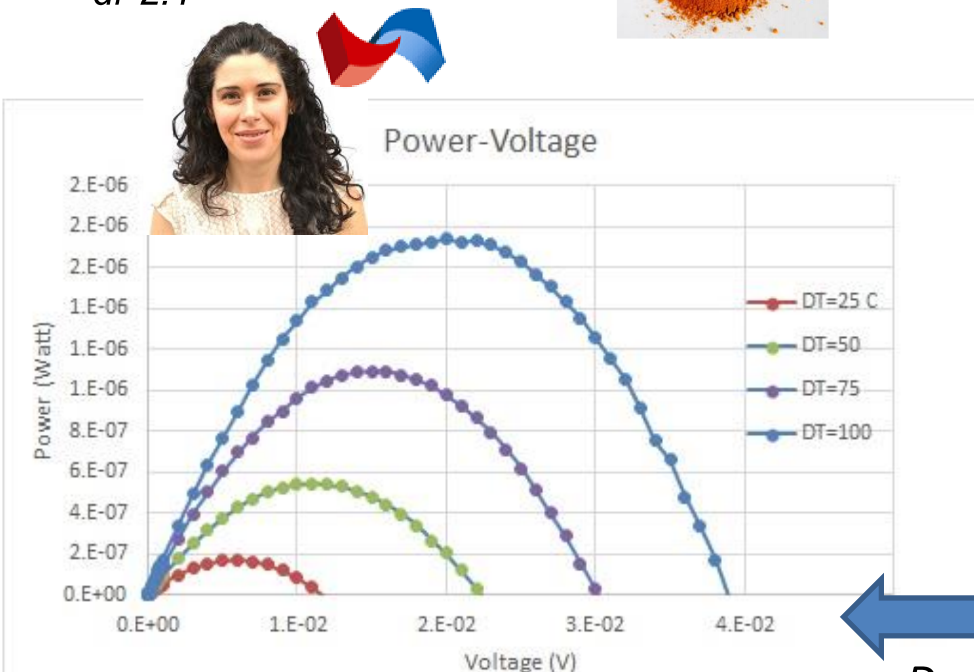
Sublimation



I_2 oxidation

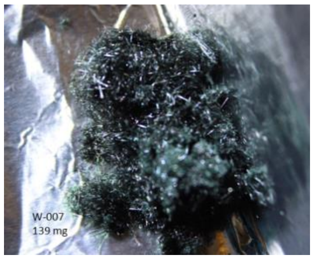


Device…

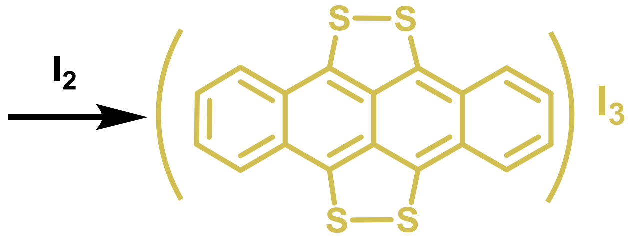


http://www.h2esot.com/videos.html

Characerisation of the materials

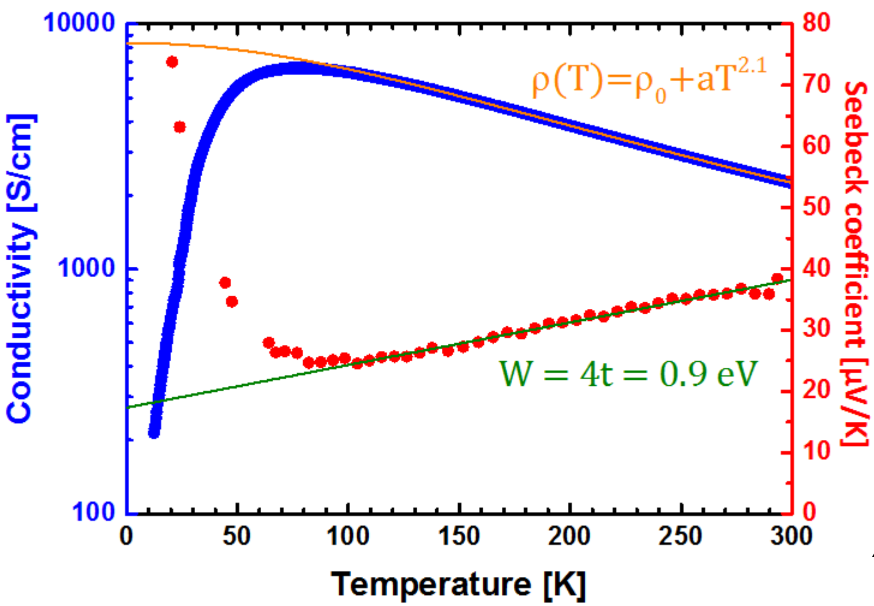


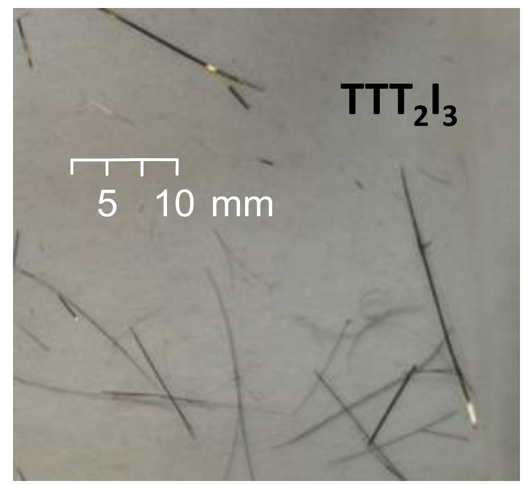
Conductivity < 10^{-7} S/cm



TTT_2I_3

J. Pflaum and A. Steeger





Alex Steeger results in line with literature…

I. F. Shchegolev, E. B. Yegubskii in Extended Linear Chain Compounds, Ed. J. S. Miller, Vol. 2, Plenum Press, New York, 1982, Chp. 9, pp. 385-435, especially p. 398.

Future Goals

- Finalise behaviour of device: currently at µW levels
- Power factor of the TTT_2I_3 material is comparable to 'mid-range' PDOT-PSS based devices.
- Performance on a weight-for-weight basis of our devices are ca. 10-20% of current commercial BiTe materials
- Theory indicates that carrier doping level is critical to exceptional performance but significant amounts of further work are necessary to define methods to control this experimentally.
- A better n-type material is needed.
- Better methods for device fabrication need to be developed.

H2esot Publications

- L. Burroughs, J. Ritchie, M. Ngwenya, D. Khan, W. Lewis, S. Woodward , *Beilstein J. Org. Chem*. **2015**, *11*, 273-279 (open access link).
- L. Burroughs, L. Eccleshare, J. Ritchie, O. Kulkarni, B. Lygo, S. Woodward, W. Lewis, *Angew. Chem. Int. Ed.* **2015**, *54*, 10648-10651 (open access link).
- L. Burroughs, J. Ritchie, S. Woodward, *Tetrahedron* **2016**, *72*, 1686-1689 (doi link).
- I. Sanduleac, A. Casian, J. Pflaum, *J. Nanoelectron. Optoelectron*. **2014**, *9*, 247-252 (open access link).
- A. I. Casian, J. Pflaum, I. I. Sanduleac, *J. of Thermoelectricity* **2015**, 16-26 (open access link).
- F. Huewe, A. Steeger, I. Bauer, S. Doerrich, P. Strohriegl, J. Pflaum, *Phys. Rev. B*. **2015**, *92*, 155107 (open access link doi).
- K. Pudzs, A. Vembris, J. Busenbergs, M. Rutkis, S. Woodward, *Thin Solid Films* **2016**, *598*, 214-218 (open access link available from Dec 2017 due to journal policy, doi).
- A. I. Casian, I. I. Sanduleac , *J. of Thermoelectricity* **2013**, 11-20 (open access link).
- I. Sanduleac, *J. of Thermoelectricity* **2014**, 50-56 (open access link).
- A. I. Casian, I. I. Sanduleac, *J. Electronic Materials* **2014**, *43*, 3740-3745 (open access link, doi).
- I. Sanduleac, A. Casian, *J. Elec. Materials* **2015**, *44*, 1-5 (open access link, doi).
- A. Casian, I. Sanduleac, *Mat. Today Proc*. **2015**, *2*, 504-509 (open access link, doi).

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