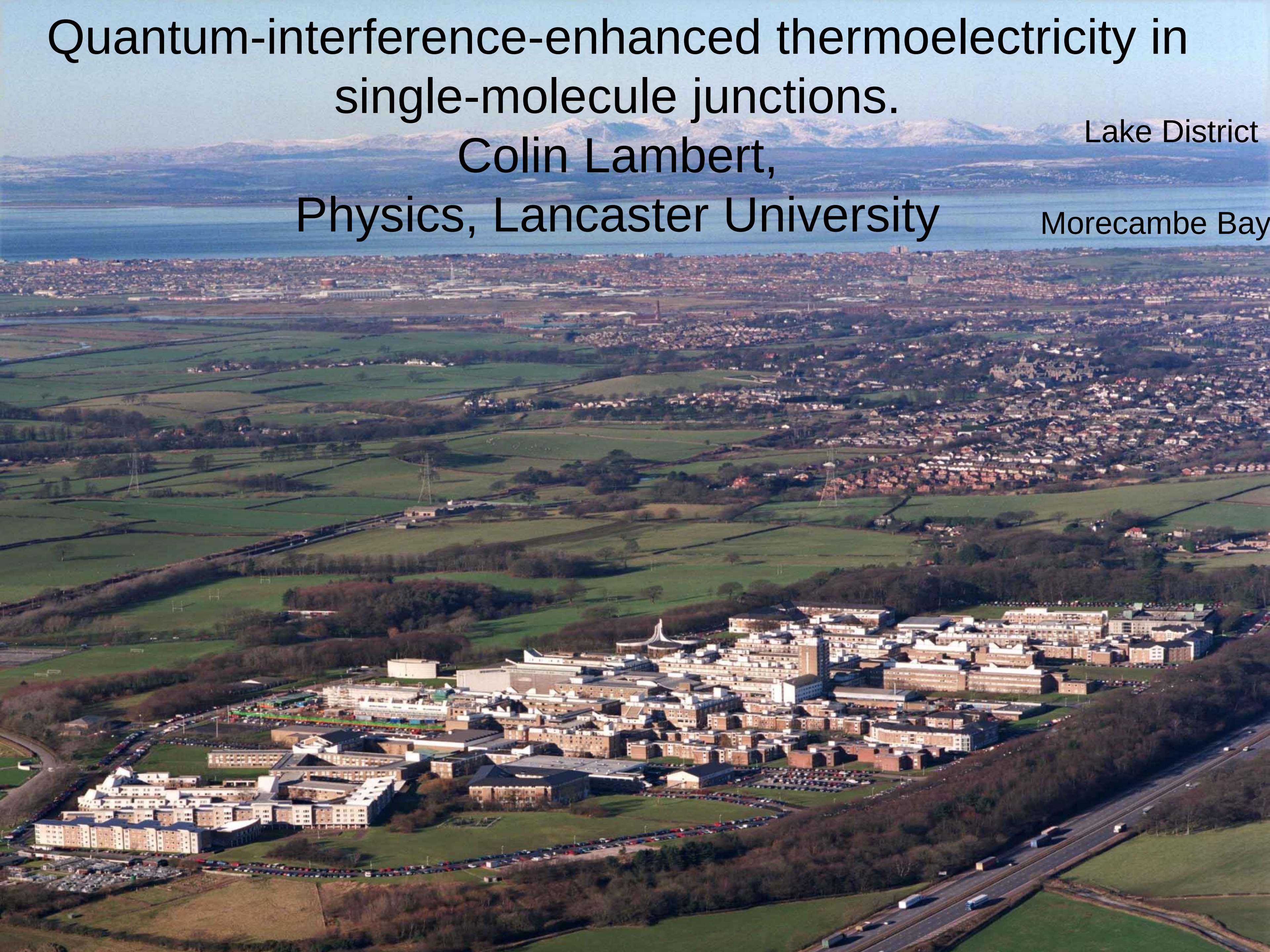
Quantum-interference-enhanced thermoelectricity in single-molecule junctions.

Colin Lambert,
Physics, Lancaster University



Collaborating experimentalists

M. Bryce,
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R. Nichols
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T. Wandlowski,
S. Decurtins,
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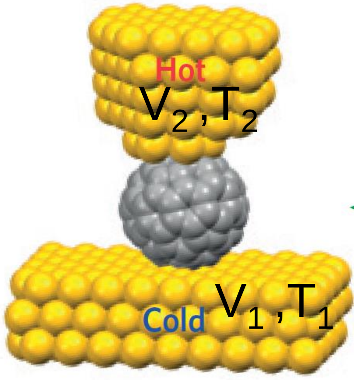
L. Cohen, Imperial

N. Agrait,
Madrid

P. Low,
Perth

Can quantum interference be exploited to enhance thermoelectric properties of single molecule devices and thin films?

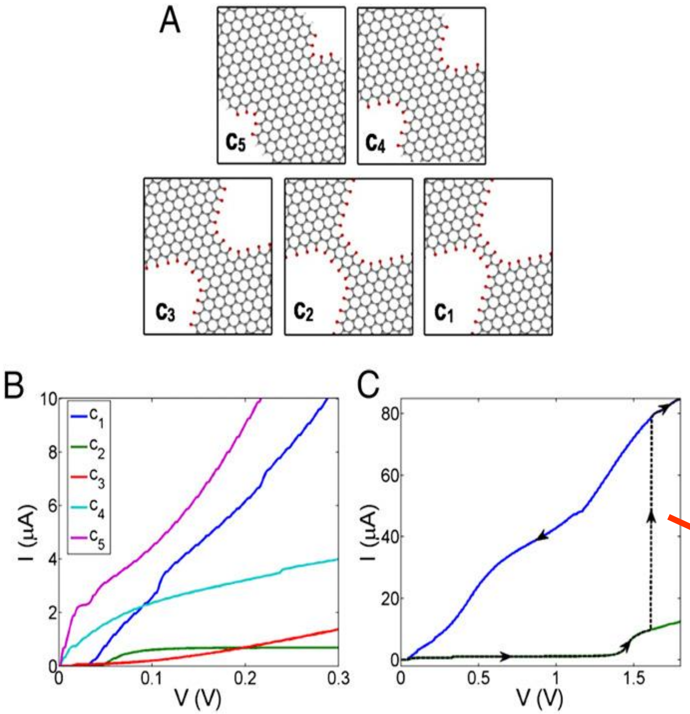


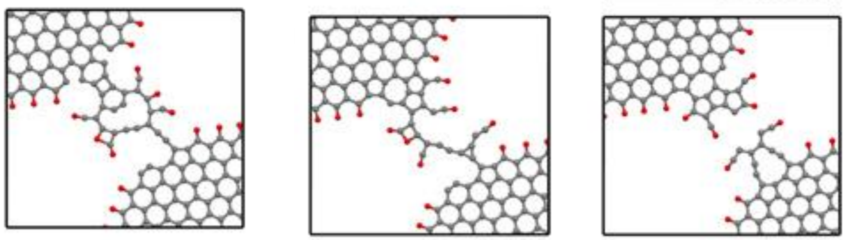
$$(V_2 - V_1) = -S(T_2 - T_1)$$

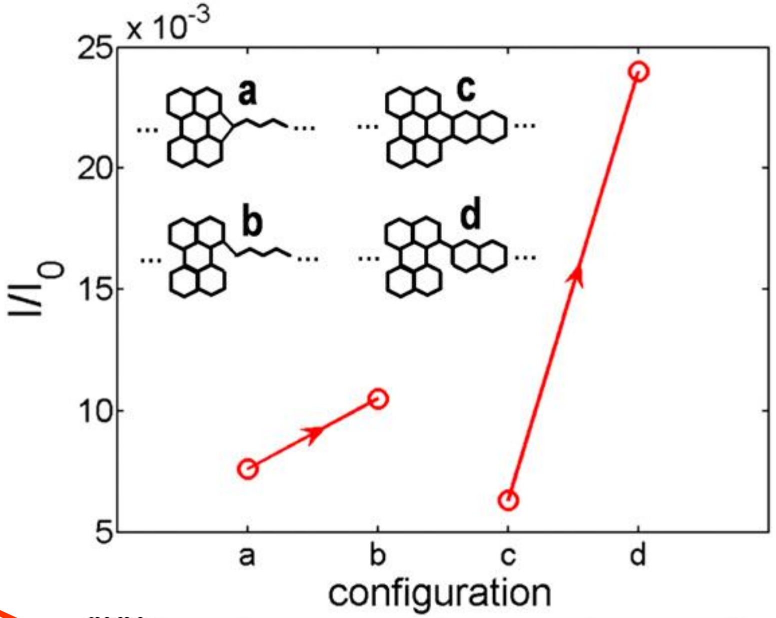
- Evidence of room-temperature quantum interference
- Three strategies for enhancing thermoelectric properties of single molecules
- One strategy for reducing thermal conductance

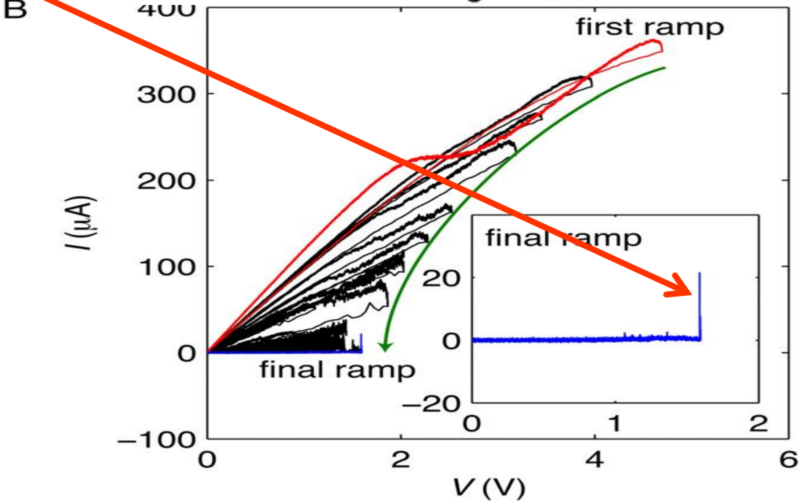
Evidence of QI in electroburnt junctions

Sadeghi et al., PNAS **2015**, *9*, 2658-2663

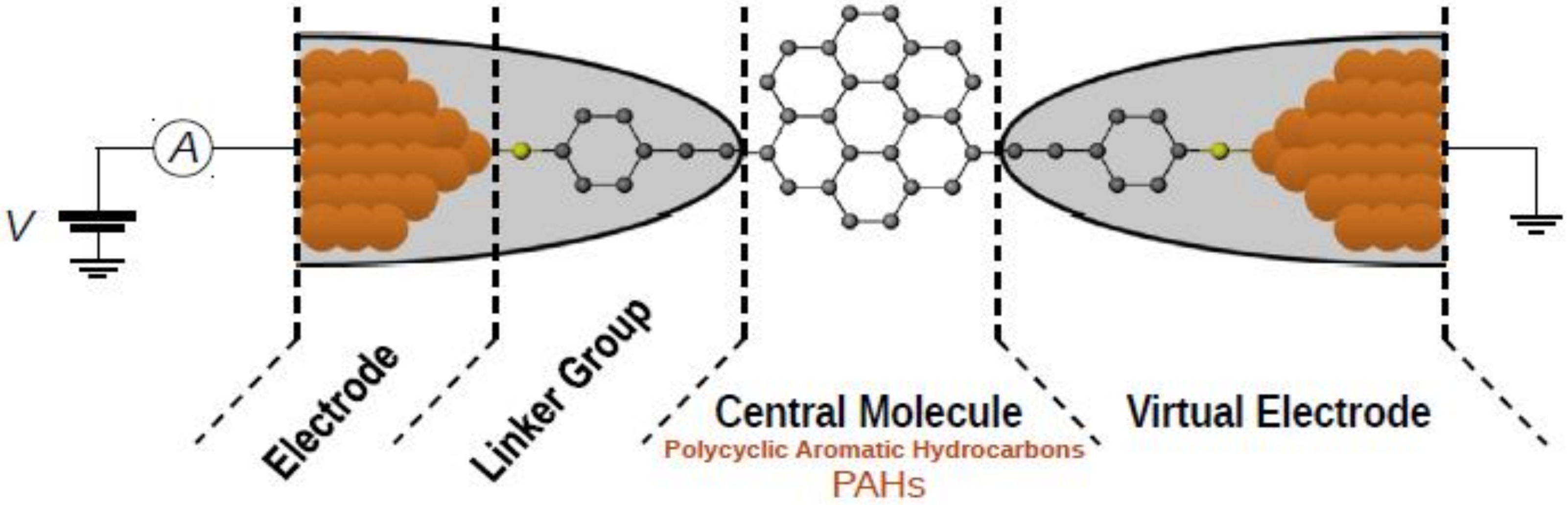


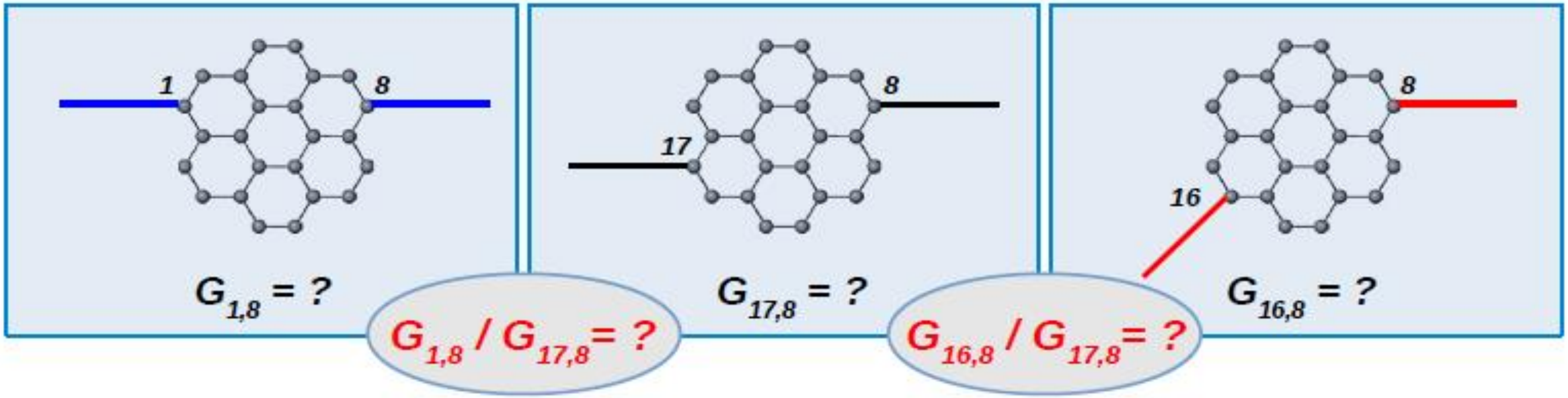






Molecules vs. Quantum dots





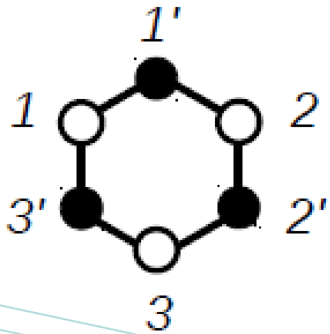
Answer provided by a magic number table.

Magic Ratio Rule (MRR) $G_{1,8}/G_{17,8}$ = ratio of the squares of their magic numbers

An example of constructing M-table

Benzene (Bipartite Lattice)

$G_{11'}/G_{12'} = 1^2/(-1)^2 = 1$



$M = dC^{-1}$

$d \sim \det C$

$$C = \begin{array}{c|cccccc} & 1 & 2 & 3 & 1' & 2' & 3' \\ \hline 1 & 0 & 0 & 0 & 1 & 0 & 1 \\ 2 & 0 & 0 & 0 & 1 & 1 & 0 \\ 3 & 0 & 0 & 0 & 0 & 1 & 1 \\ 1' & 1 & 1 & 0 & 0 & 0 & 0 \\ 2' & 0 & 1 & 1 & 0 & 0 & 0 \\ 3' & 1 & 0 & 1 & 0 & 0 & 0 \end{array}$$

$\bar{C}$

$\bar{C}^t$

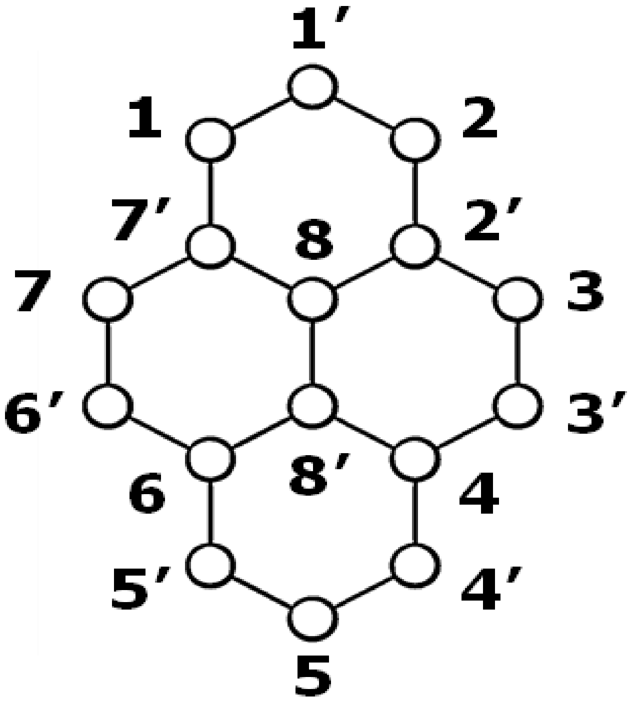
$$M = \begin{array}{c|cccccc} & 1 & 2 & 3 & 1' & 2' & 3' \\ \hline 1 & 0 & 0 & 0 & 1 & -1 & 1 \\ 2 & 0 & 0 & 0 & 1 & 1 & -1 \\ 3 & 0 & 0 & 0 & -1 & 1 & 1 \\ 1' & 1 & 1 & -1 & 0 & 0 & 0 \\ 2' & -1 & 1 & 1 & 0 & 0 & 0 \\ 3' & 1 & -1 & 1 & 0 & 0 & 0 \end{array}$$

$\bar{M}^t$

$\bar{M}$

Sangtarash, et. al, JACS, 2015, 137(35), 11425

Fun with magic numbers:the pyrene M-table



C=

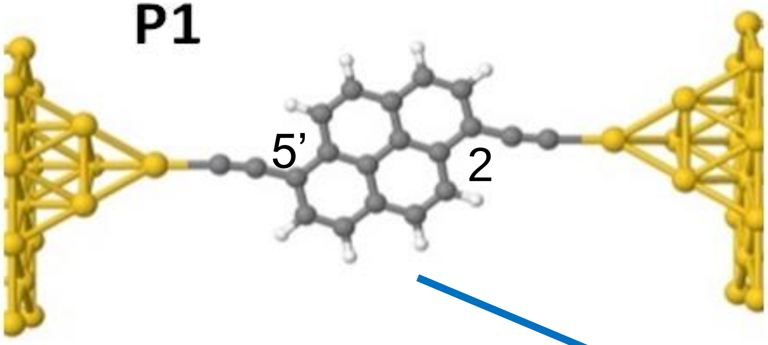
	1	2	3	4	5	6	7	8
1’	1	1	0	0	0	0	0	0
2’	0	1	1	0	0	0	0	1
3’	0	0	1	1	0	0	0	0
4’	0	0	0	1	1	0	0	0
5’	0	0	0	0	1	1	0	0
6’	0	0	0	0	0	1	1	0
7’	1	0	0	0	0	0	1	1
8’	0	0	0	1	0	1	0	1

M =

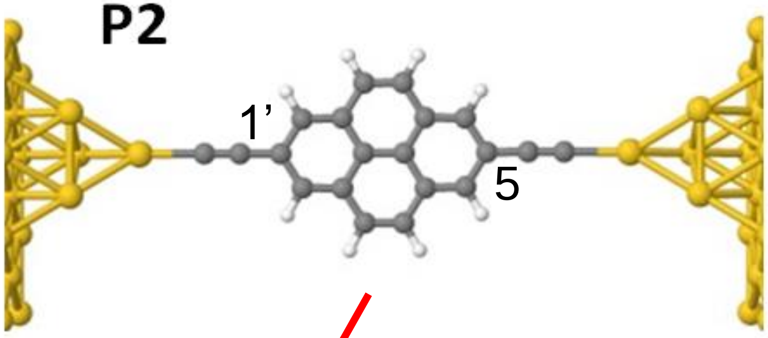
	1’	2’	3’	4’	5’	6’	7’	8’
1	3	-3	3	-3	3	-3	3	0
2	3	3	-3	3	-3	3	-3	0
3	-1	1	5	-3	3	-1	1	-2
4	1	-1	1	3	-3	1	-1	2
5	-1	1	-1	3	3	-1	1	-2
6	1	-1	1	-3	3	1	-1	2
7	-1	1	-1	3	-3	5	1	-2
8	-2	2	-2	0	0	-2	2	2

Comparison with experiment

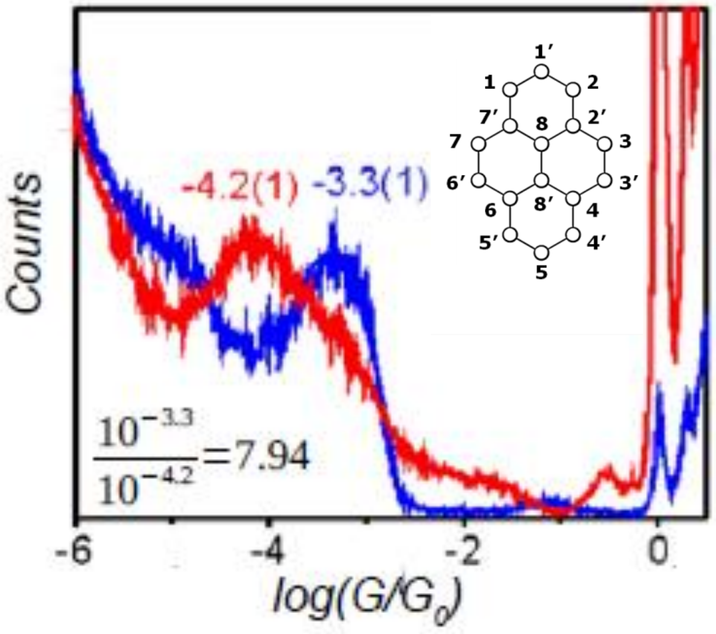
P1



P2



Experiment

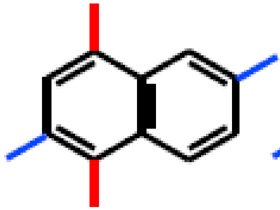


$$\frac{10^{-3.3}}{10^{-4.2}} = 7.94$$

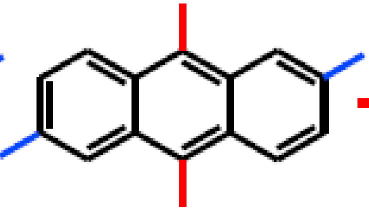
$$\overline{M} = \begin{array}{c|cccccccc} & 1' & 2' & 3' & 4' & 5' & 6' & 7' & 8' \\ \hline 1 & 3 & -3 & 3 & -3 & 3 & -3 & 3 & 0 \\ 2 & 3 & 3 & -3 & 3 & -3 & 3 & -3 & 0 \\ 3 & -1 & 1 & 5 & -3 & 3 & -1 & 1 & -2 \\ 4 & 1 & -1 & 1 & 3 & -3 & 1 & -1 & 2 \\ 5 & -1 & 1 & -1 & 3 & 3 & -1 & 1 & -2 \\ 6 & 1 & -1 & 1 & -3 & 3 & 1 & -1 & 2 \\ 7 & -1 & 1 & -1 & 3 & -3 & 5 & 1 & -2 \\ 8 & -2 & 2 & -2 & 0 & 0 & -2 & 2 & 2 \end{array}$$

MRR: $G_{25'}/G_{51'} = (-3)^2/(-1)^2 = 9/1 = 9$

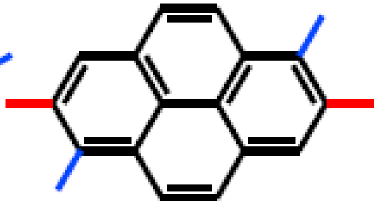
Mid-gap Ratio Rule MRR – A new rule



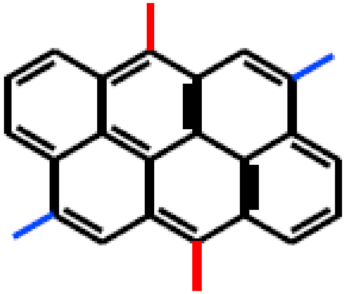
Naphthalene



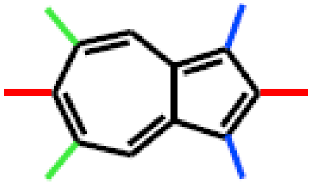
Anthracene



Pyrene



Anthanthrene



Azulene

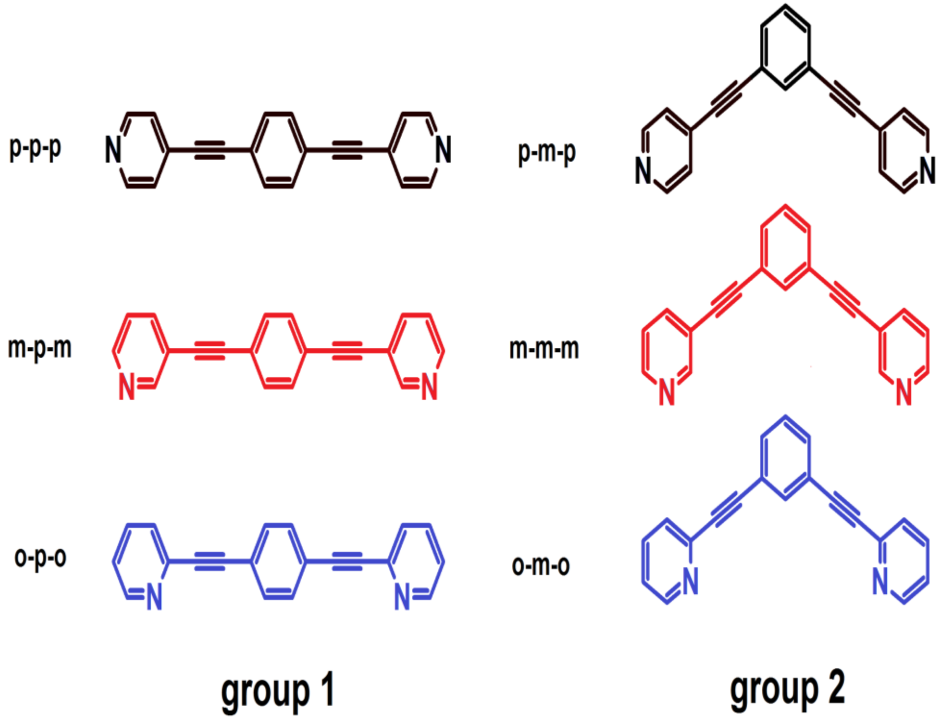
Molecular heart	Anchor group	Literature notation "Conductance Ratio of connectivity"	Mid-gap MRR	Experimental ratios	GW prediction	DFT Prediction
Naphthalene	thiol	Red / Blue (JACS, 2012)	4	5.1	NA	2
Anthracene	thiol	Red / Blue (JACS, 2012)	16	10.2	NA	13
Pyrene	carbon	Red / Blue (JACS, 2015)	9	8	NA	9
Anthanthrene	pyridyl	Red / Blue (JACS, 2015)	81	79	NA	81
Azulene	thiochroman	Red / Blue (Nano Lett., 2014)	0.72	1	0.32	0.93
Azulene	thiochroman	Green / Blue (Nano Lett., 2014)	0.003	0.06	0.1	0.05

Sangtarash, et. al, JACS, 2015, 137(35), 11425; Xia, et. Al, Nano Lett., 2014, 14 (5), 2941; Kaliginedi, et. al, JACS, 2012, 134 (11), 5262

More evidence of QI: A quantum circuit rule for room temperature conductance

Nat Comm **2015,** *6*, 6389

$$G_{ppp}G_{mmm} = G_{mpm}G_{pmp}$$



Experiment

Molecule	Log G/G_0
p-p-p	-4.5±0.4
m-p-m	-5.5±0.4
p-m-p	-6.0±0.5
m-m-m	-6.9±0.5

Experiment

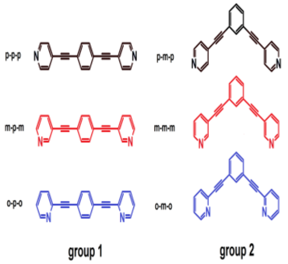
$$\log(G_{ppp}/G_0) + \log(G_{mmm}/G_0) = -4.5 - 6.9 = -11.4$$

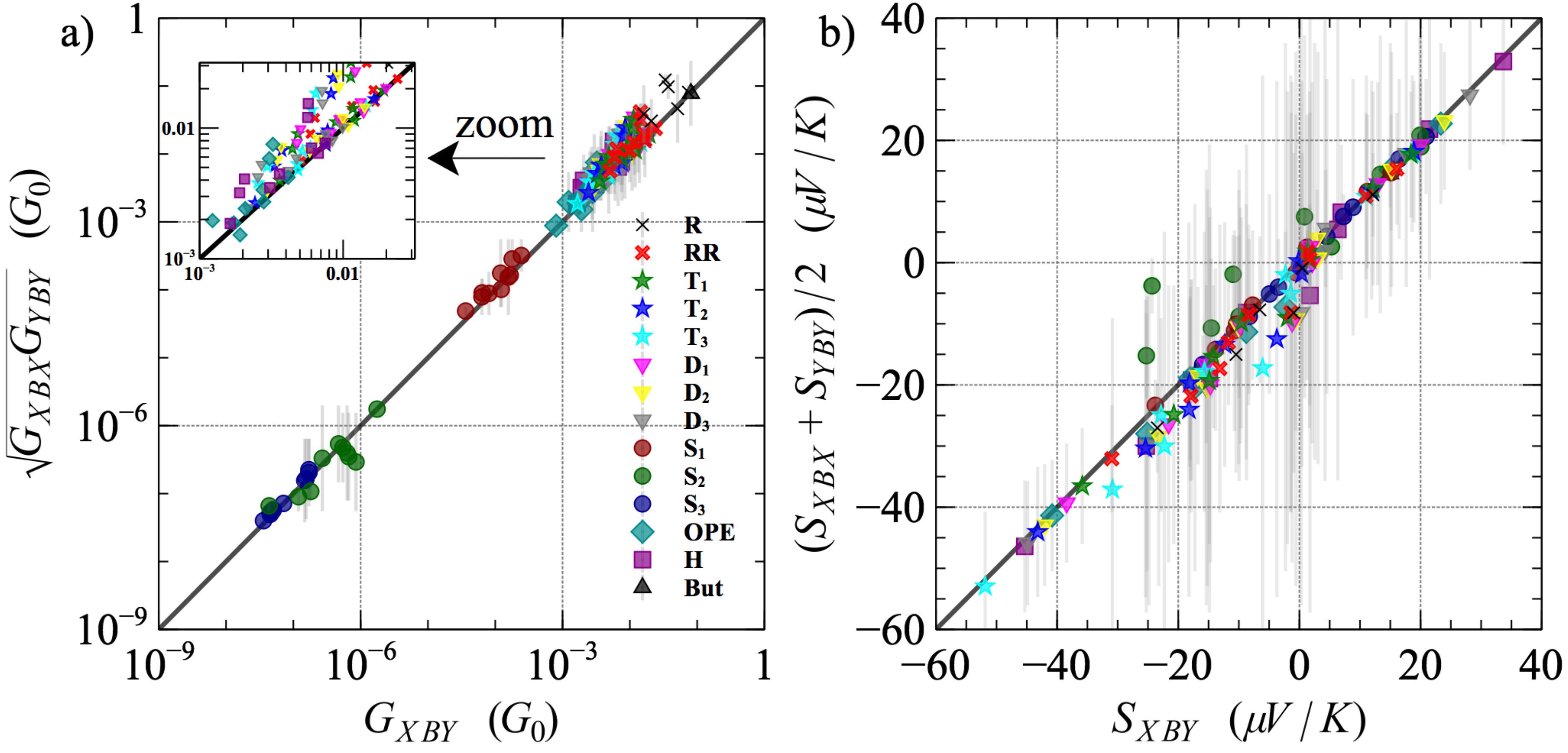
$$\log(G_{pmp}/G_0) + \log(G_{mpm}/G_0) = -5.5 - 6.0 = -11.5$$

A quantum circuit rule for room temperature conductance and thermopower:

$$S_{ppp} + S_{mmm} = S_{mpm} + S_{pmp}$$

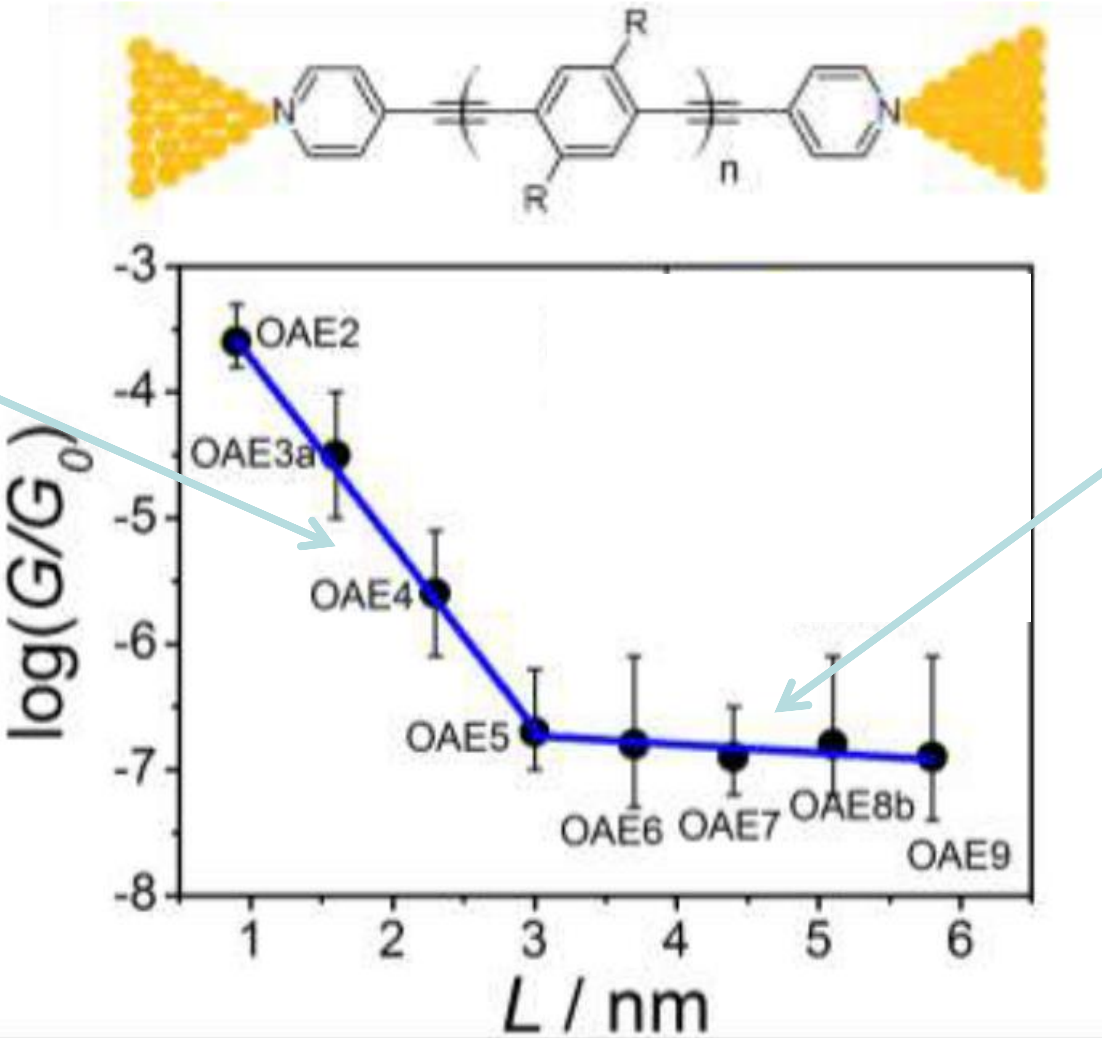
$$G_{ppp}G_{mmm} = G_{mpm}G_{pmp}$$





QI effects disappear when a molecule is too long.

Cross-over from phase-coherent tunneling to incoherent hopping in a family of olig(oaryleneethynylene) (OAE) derivatives



Phase-coherent tunneling for short molecules
G ~ exp –(βL)

Incoherent hopping for long molecules
G ~ 1/L

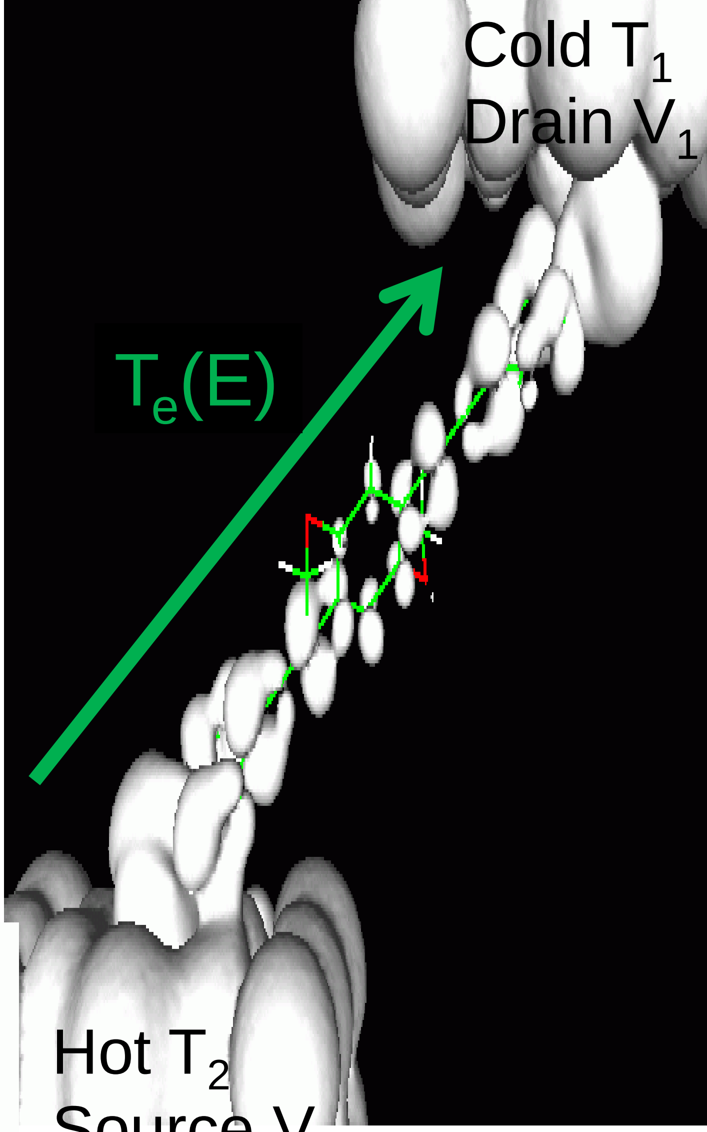
Zhao et al, Chemistry of Materials, 25 21 4340 (2013)

Why is quantum interference expected to be helpful?

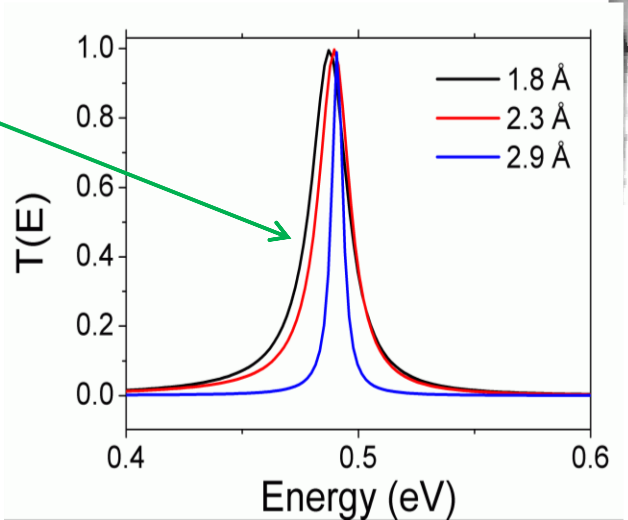
Mott formula:

$$S \sim -\, d[\log T_e(E_F)]/dE_F$$

$T_e(E)$ = transmission probability for electrons of energy E travelling from the source to the drain via the molecule.



High slope = large S,
provided the high slope coincides with the Fermi energy of the electrodes



Strategies for controlling thermoelectric properties of single molecules

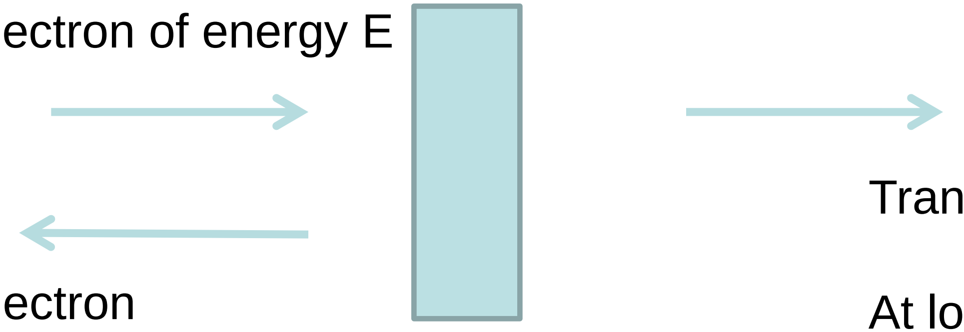
1. Creating quantum scatterers in series
2. Control of thermopower by mechanical gating
3. Electrostatic gating via charge transfer complexation
4. Suppression of phonon transport in ‘edge-over-edge’ porphyrins and molecular Christmas trees

<u>Note regarding a target value for S and κ_p</u>

Wiedemann-Franz: $\kappa_e = \alpha TG$, so if $\kappa_p << \kappa_e$, $ZT = S^2GT/\kappa_e = S^2/\alpha$

So to achieve $ZT > 1$ requires $S^2 > \alpha$ ie $S > 150\mu V/K$

Strategy 1. Quantum scatterers in series



Incident electron of energy E

transmitted electron

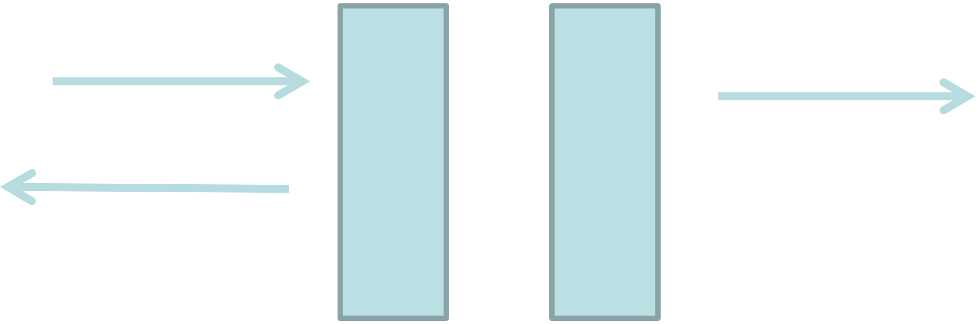
reflected electron

Scattering region

Transmission probability $T_e(E)$

At low temperature or for not-too-narrow resonances:

$S=-(\Pi^2 k_B^2 T/2e)\, d\ln T_e(E_F)/dE_F$



Two scatterers in series

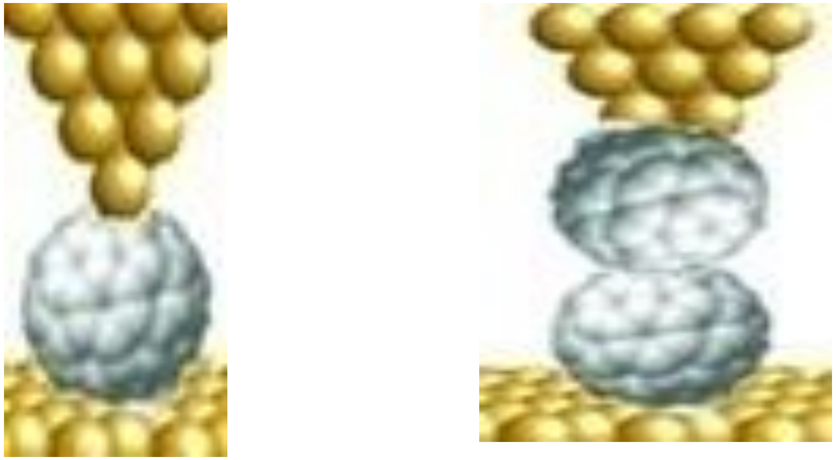
Transmission probability T_e^2

$\ln T^2_e = 2\ln T_e$

So Seebeck coefficient should double!

Does it work?
Application to C_{60} molecular junctions: a quantum ball game

Evangeli, et al, NanoLett (2013) 13 2141

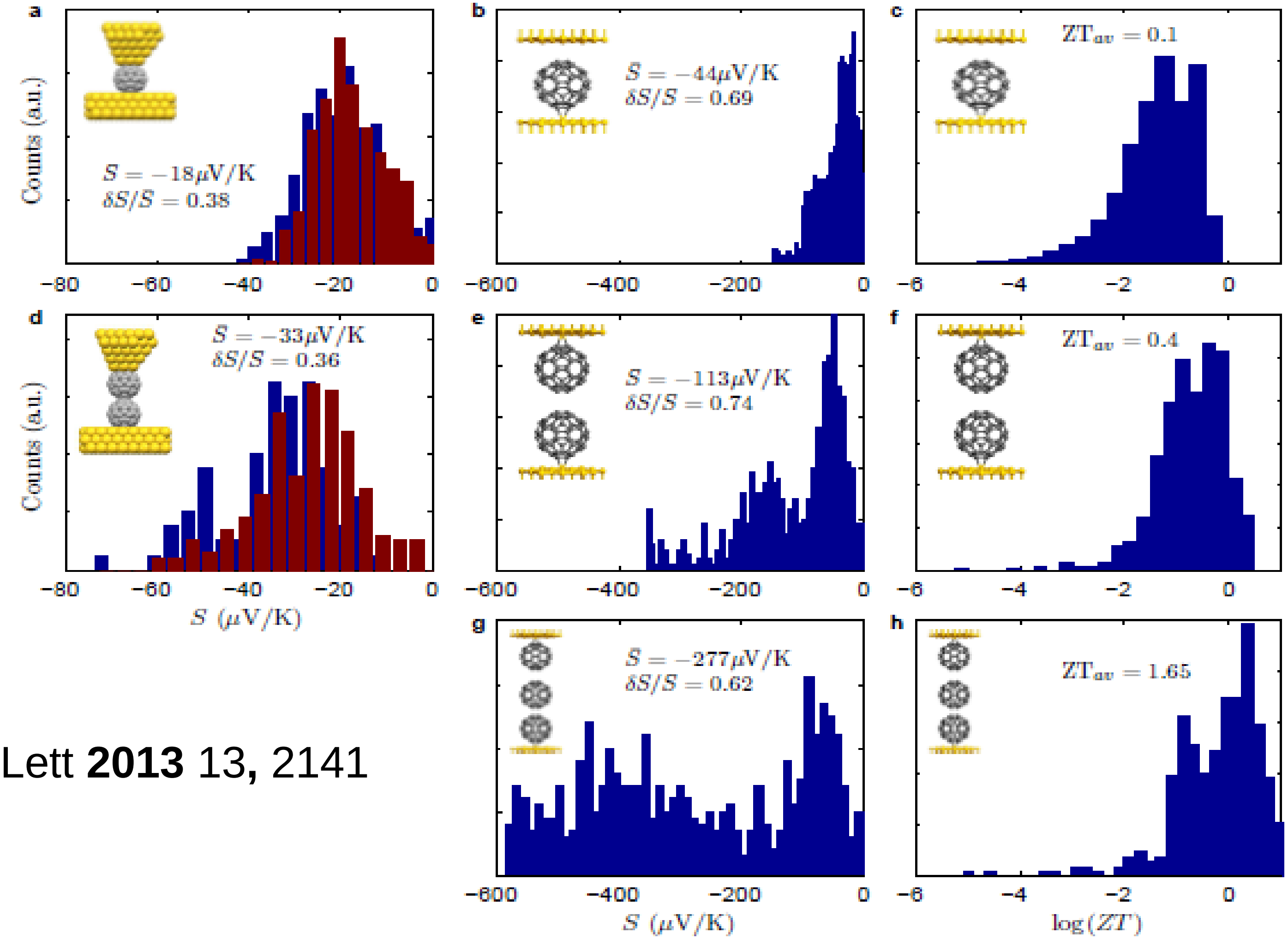


T_e → T_e^2

S → 2 S   ???

Comparison between theory and experiment

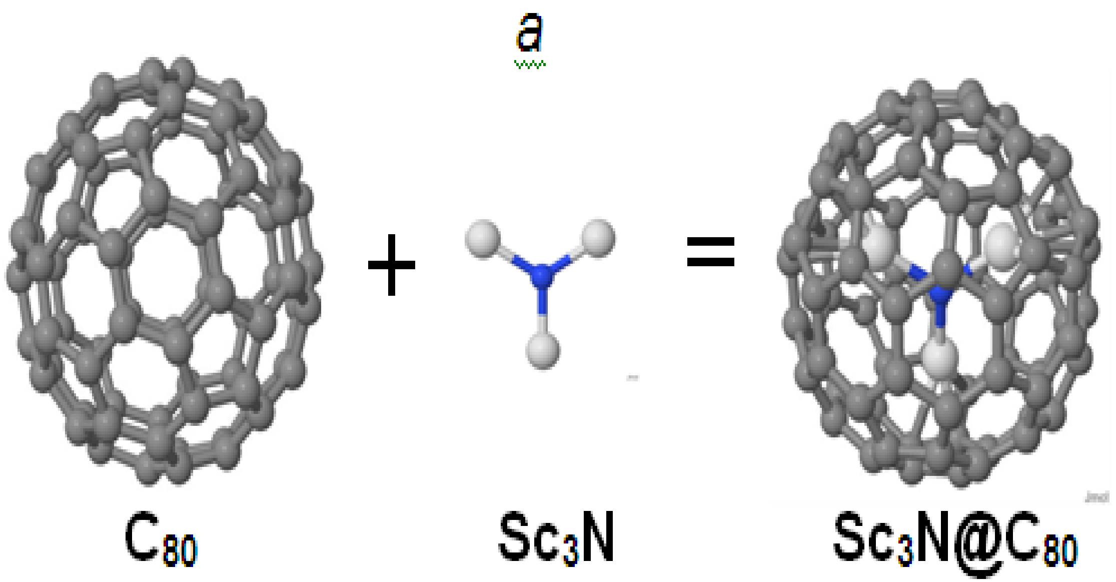
S (experiment) S (theory) ZT (theory)



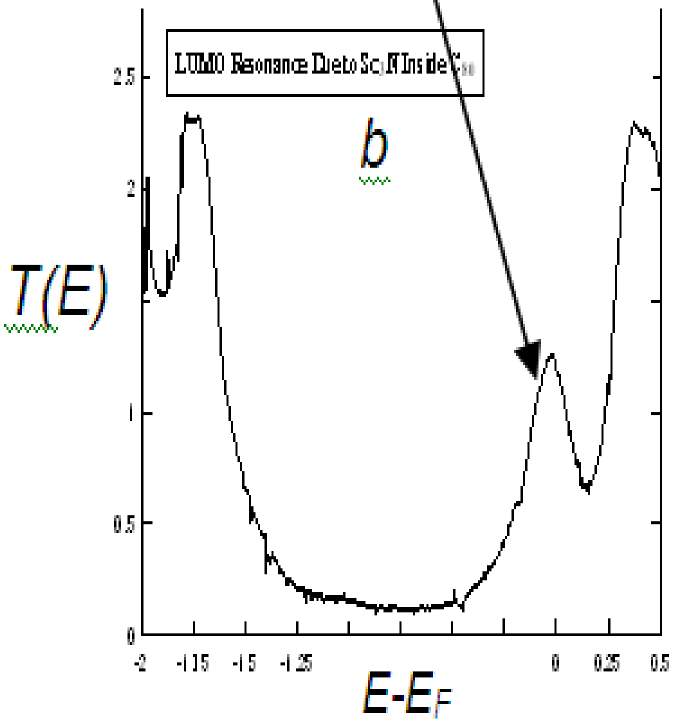
Nano Lett **2013** 13**,** 2141

Strategy 2: Control of thermopower by mechanical gating

L. Rincón-García, A. Ismael, et al. *Nature Materials*, **15**, 289–293 (2016)

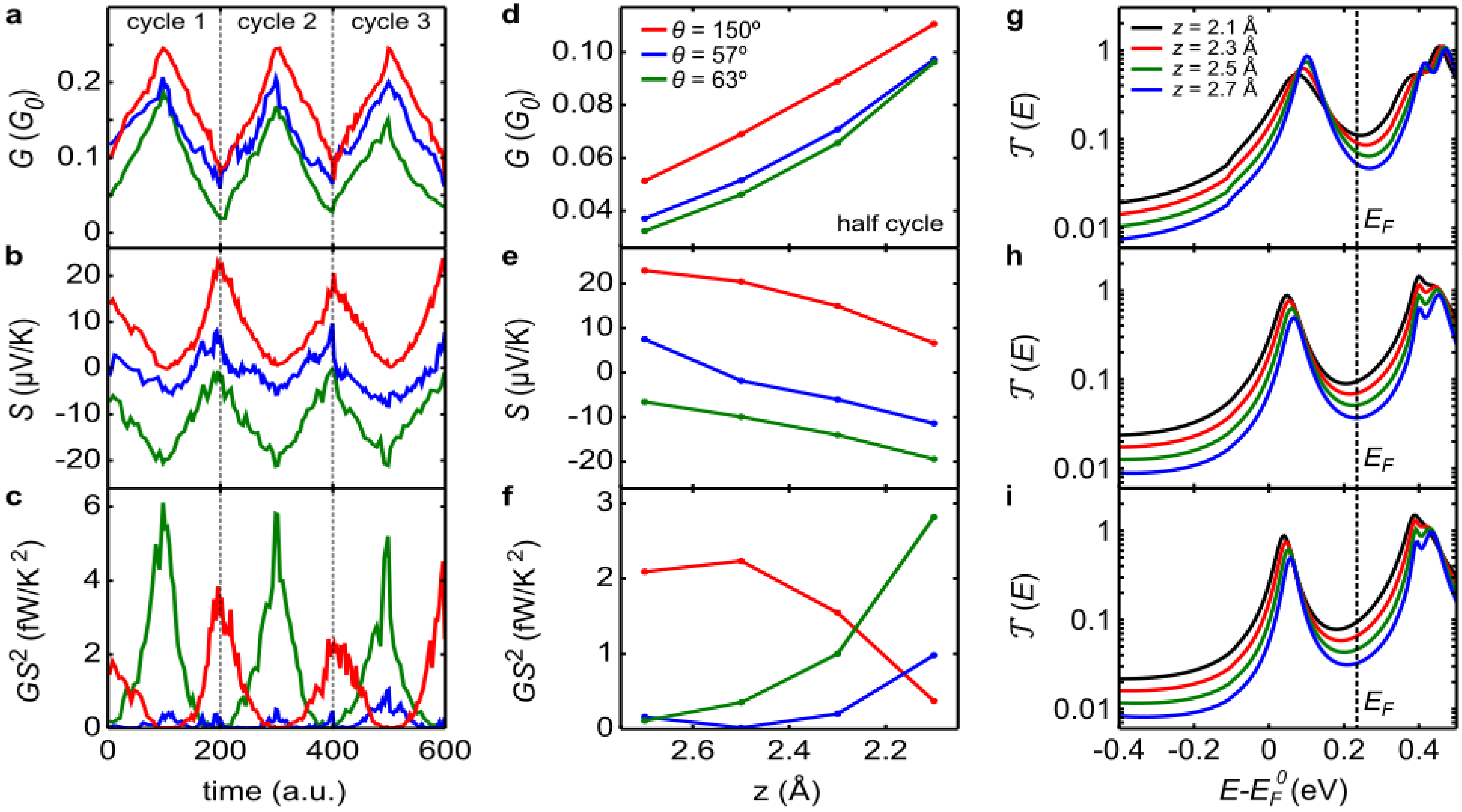


Breit Wigner resonance due to the presence of Sc_3N inside the C_{80}



Control of thermoelectricity via tip pressure

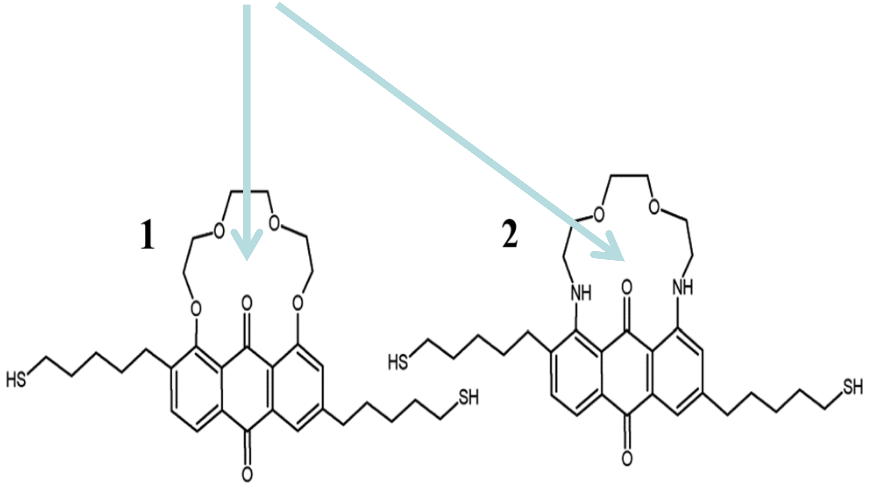
Nature Materials, **15**, 289–293 (2016)

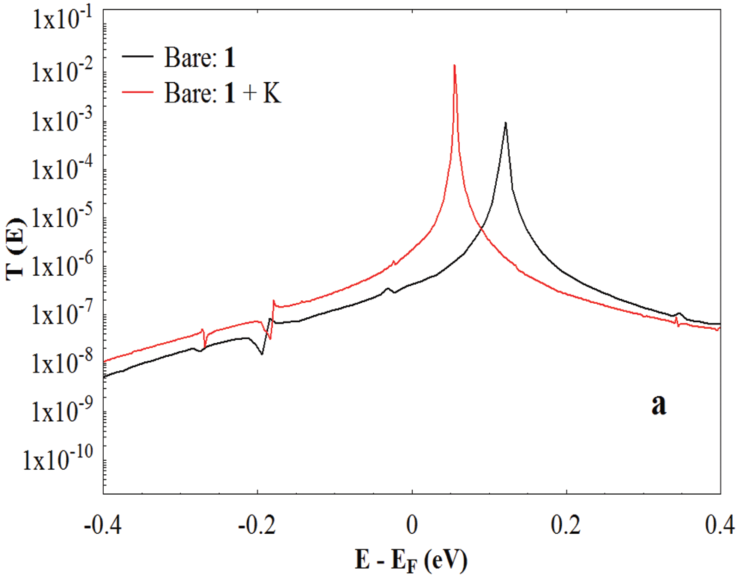


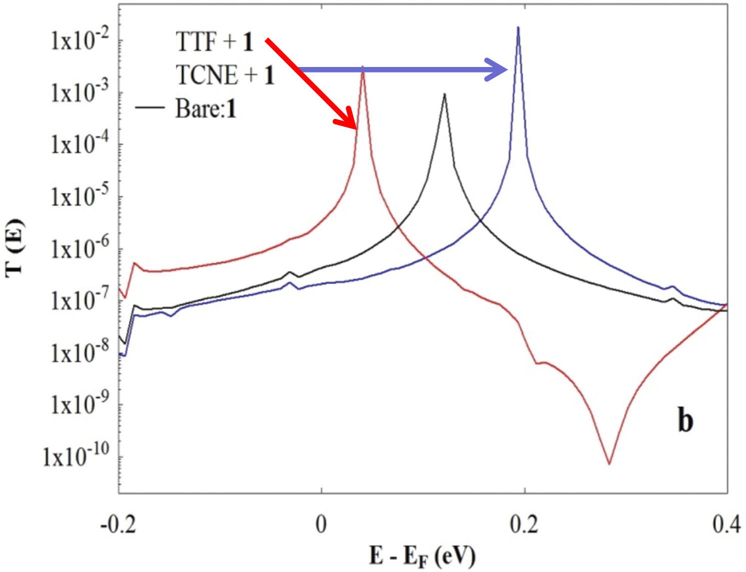
Strategy 3: Electrostatic gating via charge transfer complexation in "crown-ether anthraquinones"

AK Ismael, I Grace, CJL, *Nanoscale* 7 (41), 17338-17342 (2015)

Na^+, K^+, ...

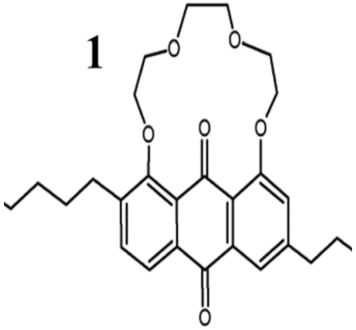




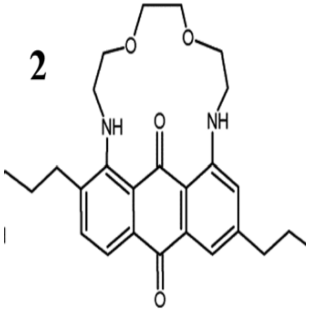


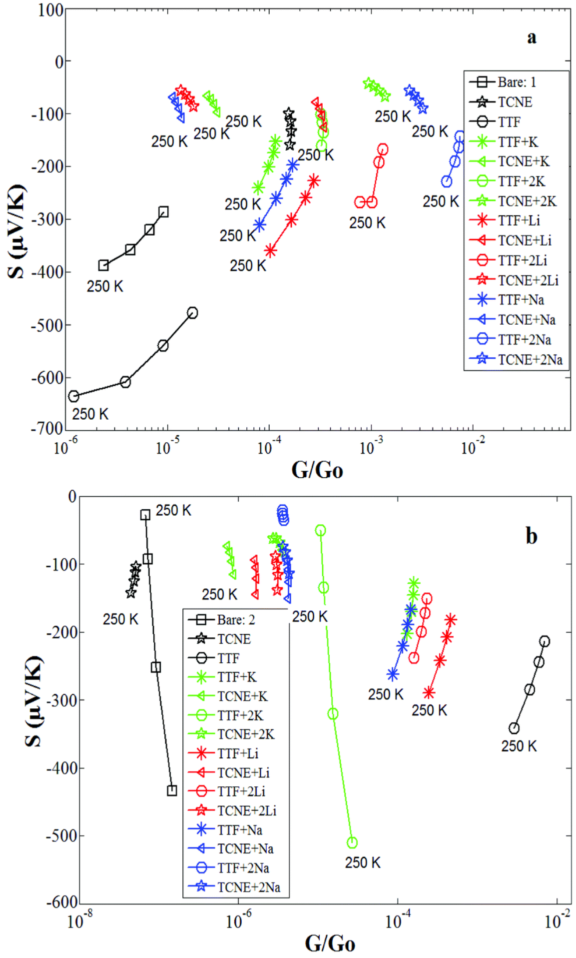
Seebeck coefficient S and power factor P

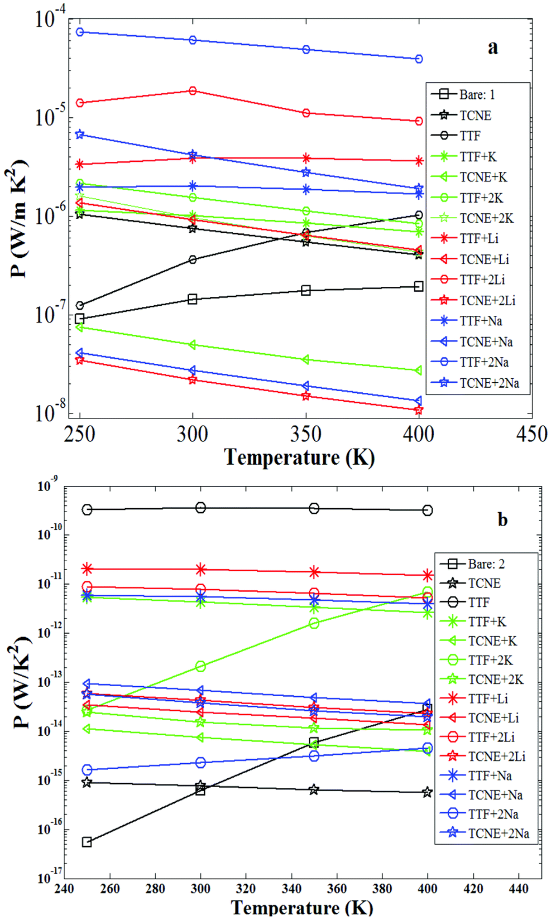
1



2

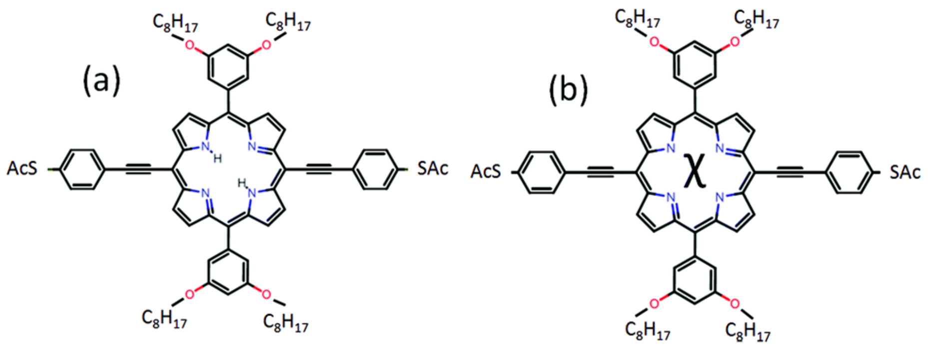


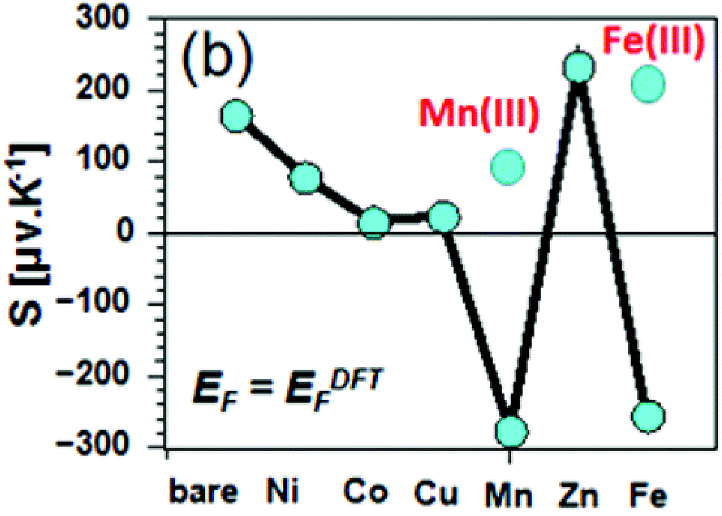


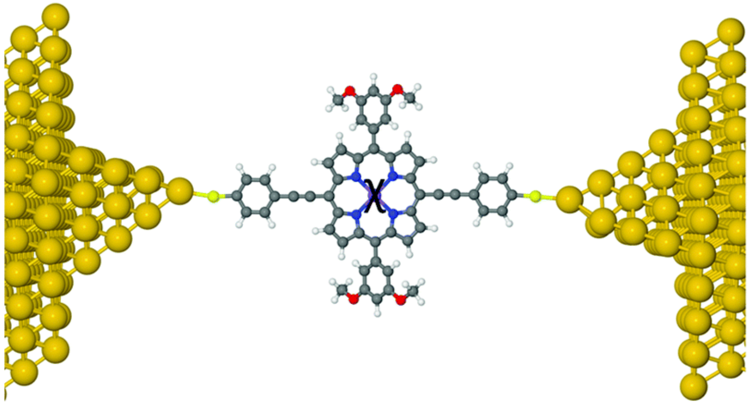


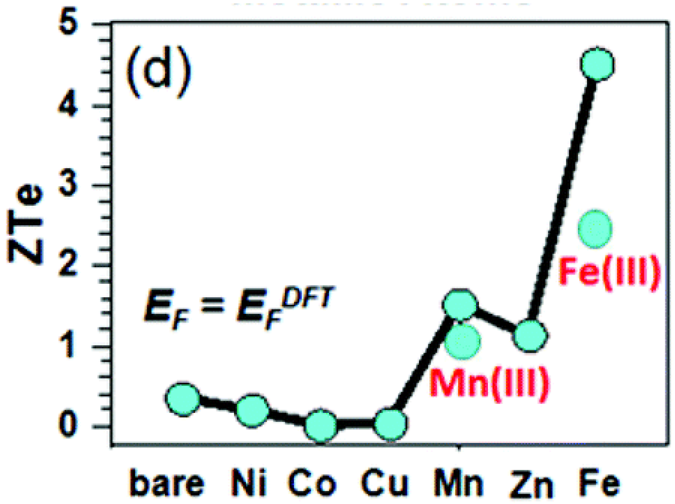
1 doped with TTF possesses S=−640 μV/K, which is higher than any single-molecule thermopower measured to date. At room temp. P= 73 μW $m^{-1}K^{-2}$ for **1** + TTF + 2Na and 90 μW $m^{-1}K^{-2}$ for **2** + TTF. These compare favourably with other organic materials. eg P = 0.016, 0.045 μW $m^{-1}K^{-2}$ and 12 μW $m^{-1}K^{-2}$ for Polyaniline , Polypyrole and PEDOT:PSS.

Thermoelectric properties of metallo-porphyrins



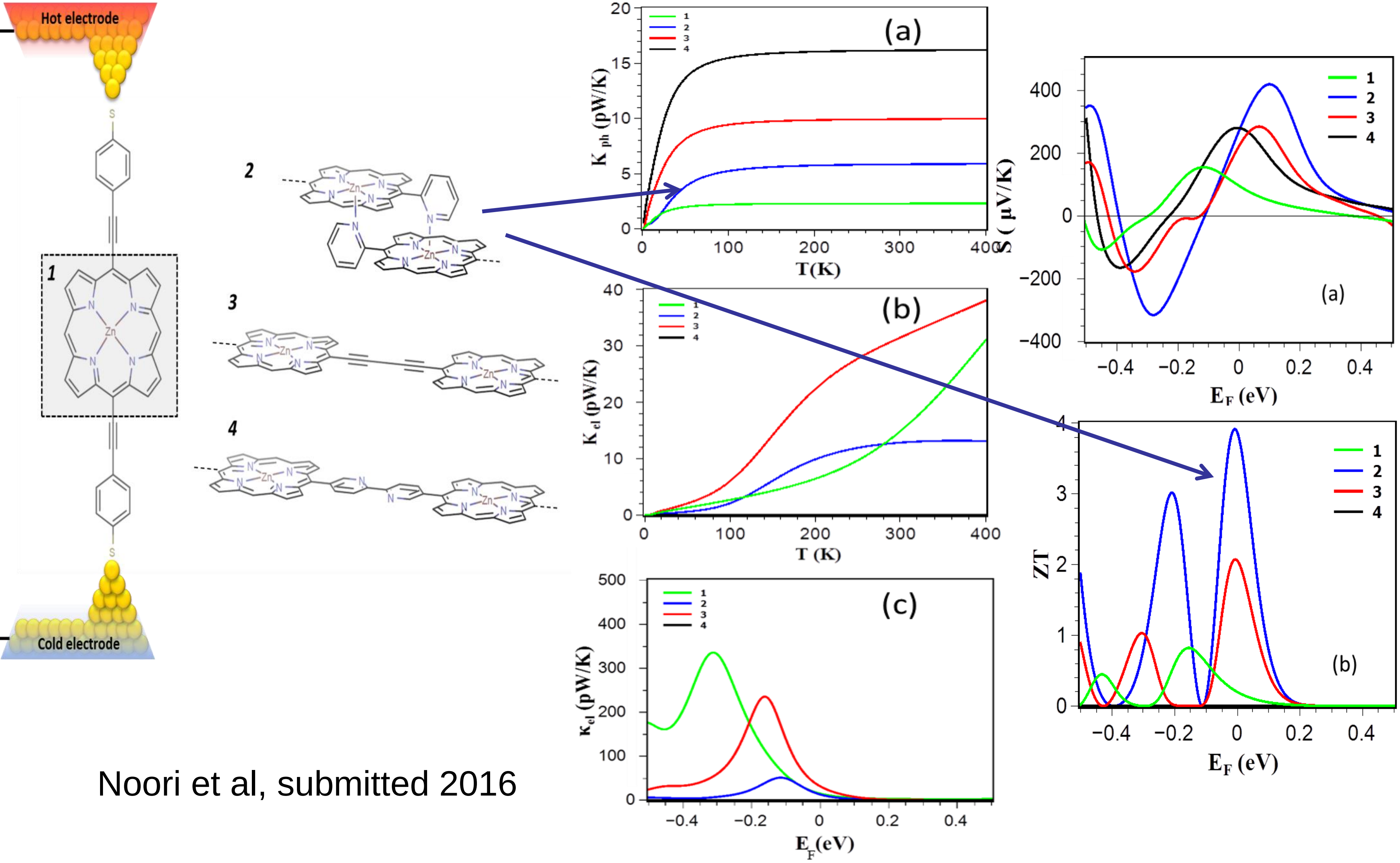






Al-Galiby et al., Nanoscale, 2016, 8, 2428

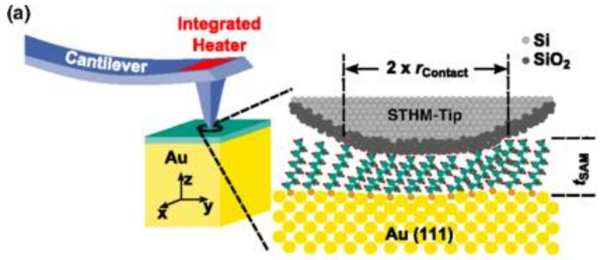
High-performance thermoelectricity in edge-over-edge zinc-porphyrin molecular wires.



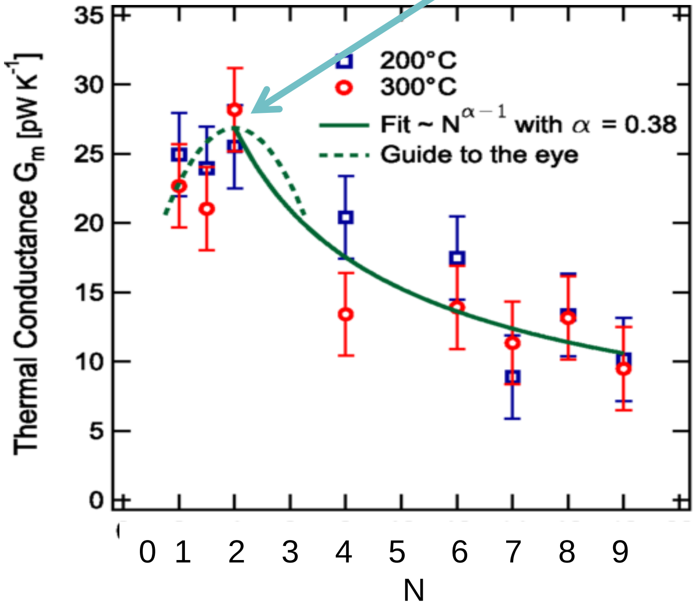
Noori et al, submitted 2016

Can phonon interference effects be exploited to reduce thermal conductance?

Length dependence of the thermal conductance of alkanes



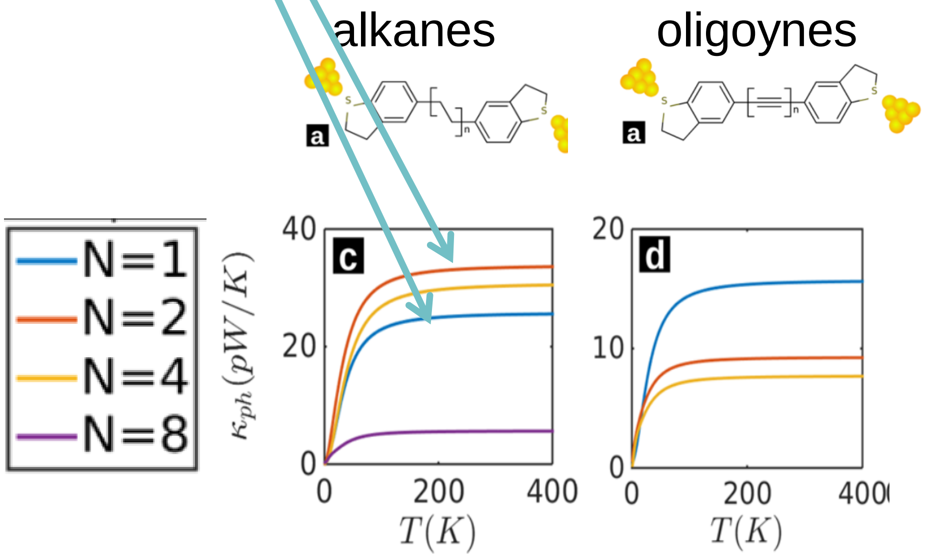
Surprise: κ_{ph} initially increases with length



Experiment: Meier et al., Phys. Rev. Lett. (2014) 113, 060801

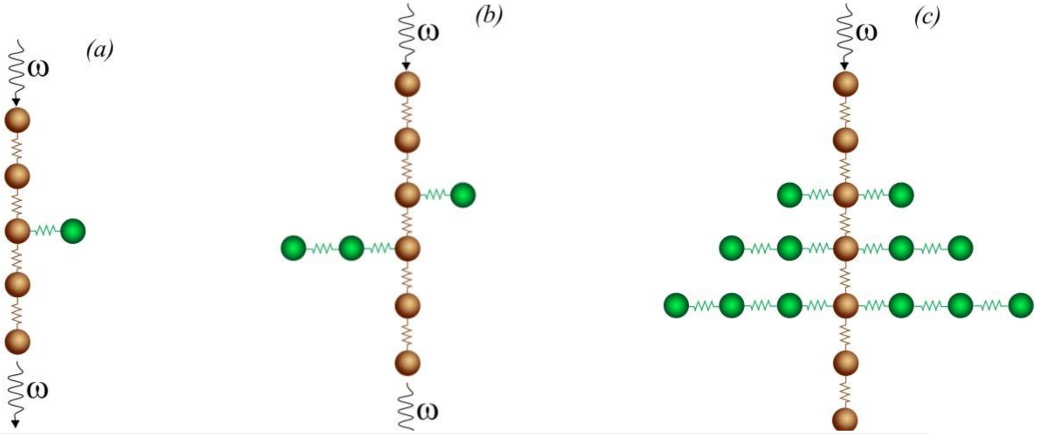
Theory reveals the origin of this effect

The effect is predicted to be absent for oligoynes



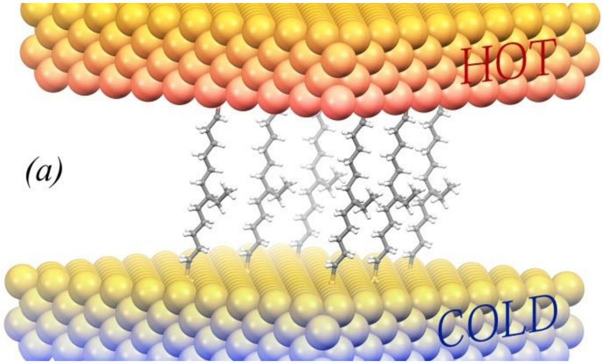
Theory: Sadeghi et al., Nano Lett. (2015) 15, 7467

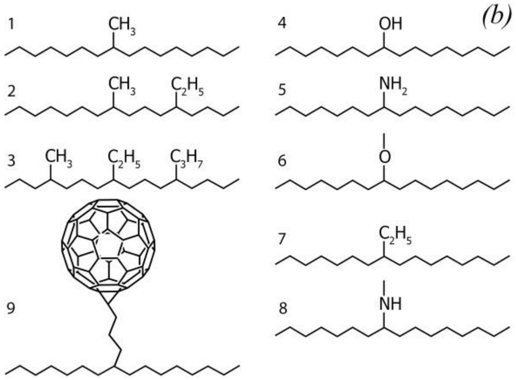
Suppression of thermal conductance through molecular christmas trees



$$\kappa_{ph}(T) = \frac{1}{2\pi}\int_0^\infty \hbar\omega T_{ph}(\omega)\frac{\partial f_{BE}(\omega,T)}{\partial T}\,d\omega$$

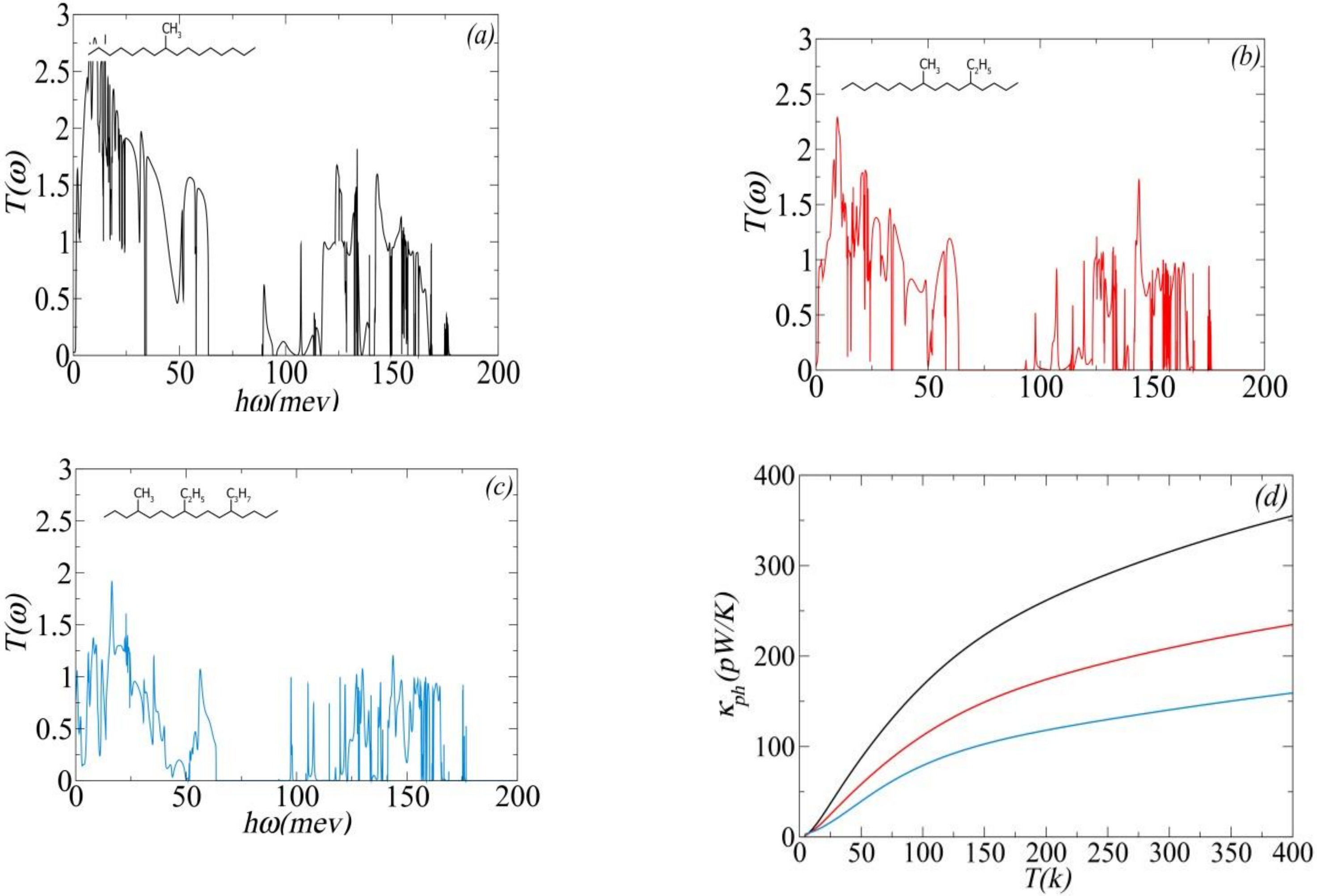
$$T(\omega) = 1/[1+x]$$





M. Famili, I. Grace, H. Safdeghi and CJL, submitted Nat. Comm. (2016)

Eg: Alkane trunk with alkyl branches



Marjan Famili, Iain Grace, Hatef Sadeghi and CJL, submitted

Summary

- Electroburnt graphene junctions Synthesis Anderson, measurements Briggs group (Oxford): *PNAS* **2015**, *9*, 2658; *Nano Letters* **2016** 16, 170
- Connectivity-driven electron transport Experiments by Bern group of Silvio Decurtins: *JACS* **2015** 137,11425; *JACS* **2015** 137, 4469
- Quantum circuit rule for single-molecule electrical junctions Synthesis by Durham group of Martin Bryce, + measurements by Bern group: *Nat. Comm.* **2015** 6 6389
- Fullerene-based thermoelectricity Synthesis by Porfyrakis – Oxford, measurements by Madrid group): Nature Mat.**2016** **15**, 289–293
- Thermoelectricity in crown-ether anthraquinones and metallo-porphyrins *Nanoscale* **2015** 7 (41), 17338; Nanoscale, **2016**, 8, 2428
- Suppression of phonon transport in molecular Christmas trees submitted Nano Lett.

Lancaster theory: S. Bailey, I. Grace, D. Manrique, H. Sadeghi, S. Sangtarash, Q. Al-Galiby, O. Al-Owaedi A. Ismael, M. Noori, M. Famili, E. Almutib, V. García-Suárez, N. Almutlaq, Z. Mijbil, Q. Wu.