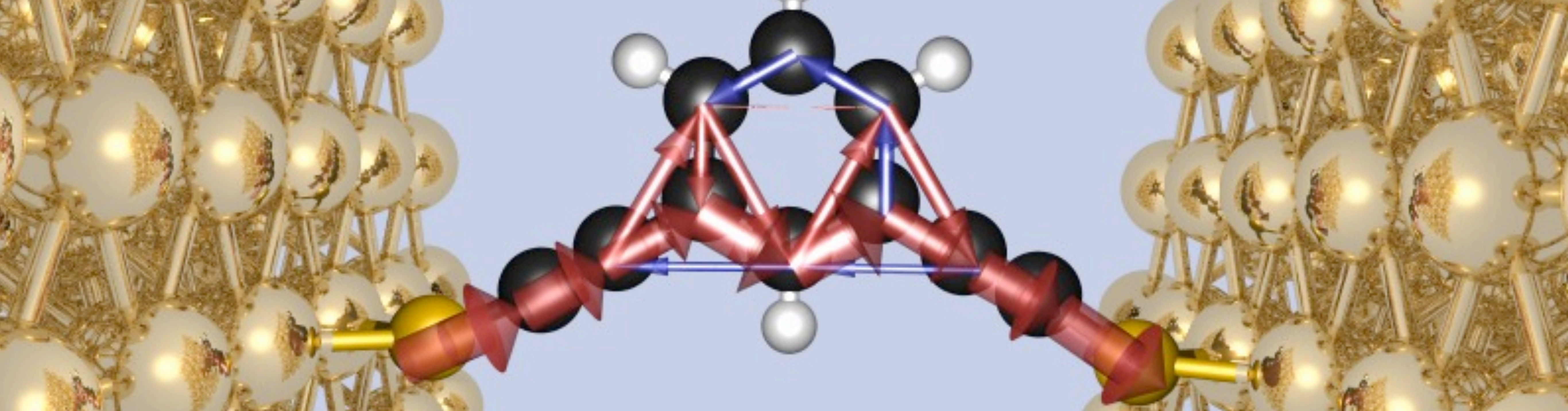
Molecular Electronics:

Exploiting the diversity that chemical space has on offer



Gemma C. Solomon
Nano Science Centre and Department of Chemistry
University of Copenhagen

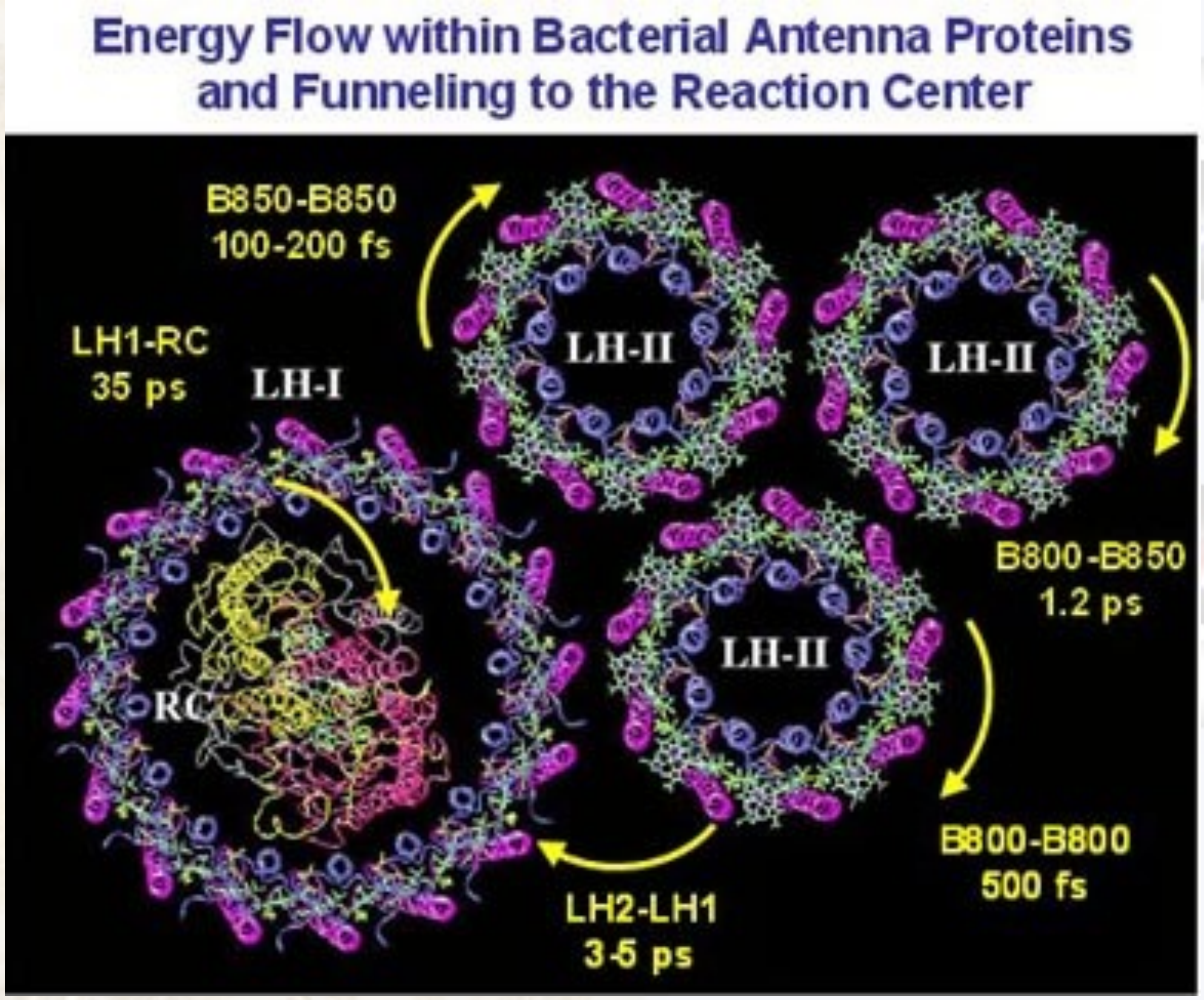
Outline

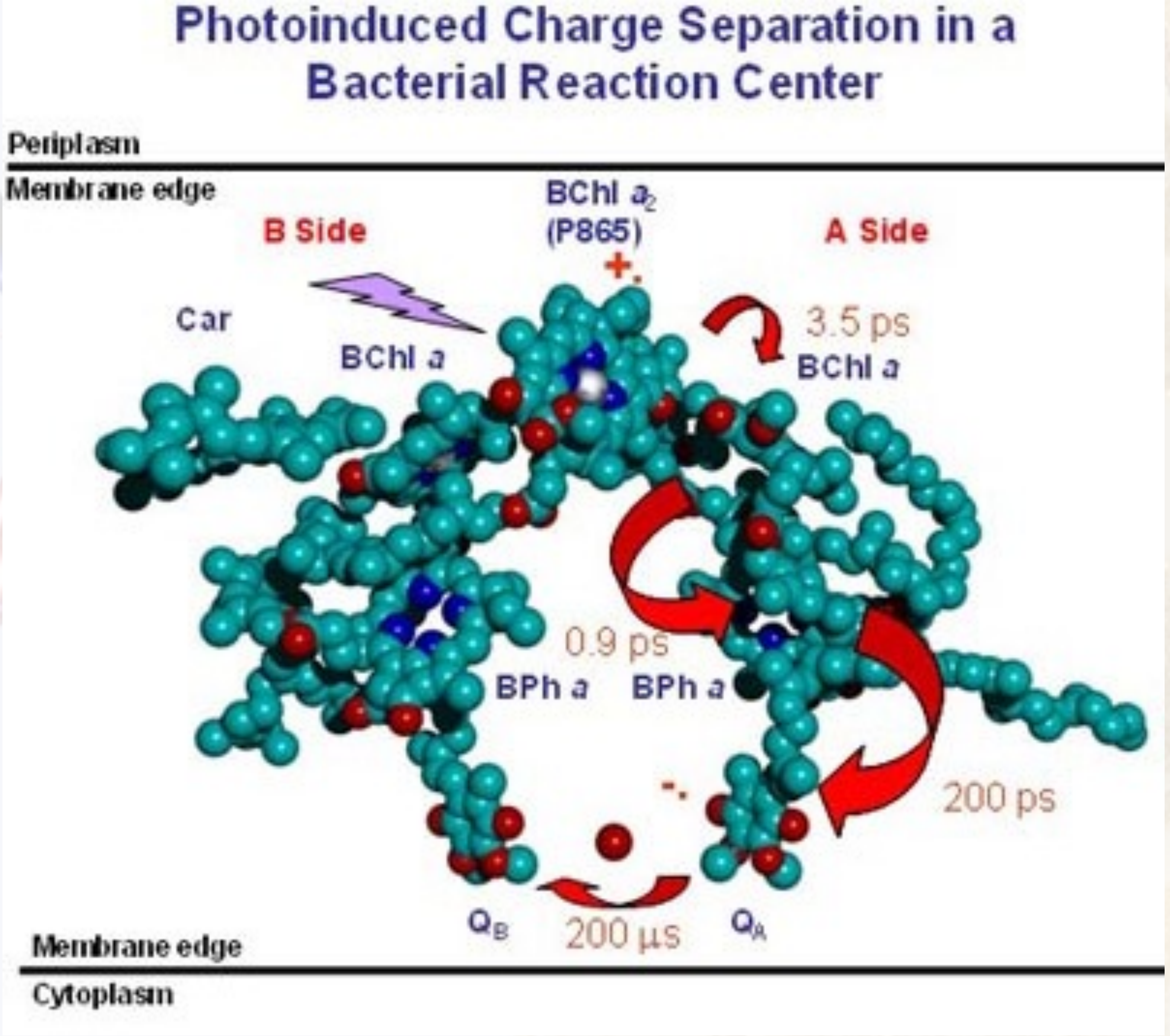
1. Making more than wires:
   Understanding and tuning quantum interference in cross-conjugated molecules

2. Going beyond bonds:
   Mapping through-space contributions to transport

3. Putting it all together:
   Understanding the transport through a bistable, fluctuating molecular system.

Nature’s ingenuity

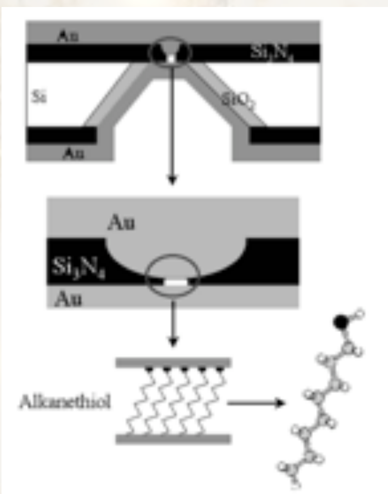




http://chemgroups.northwestern.edu/wasielewski/res/ap.htm

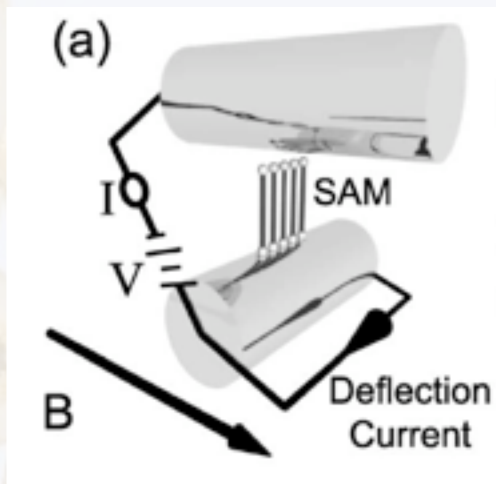
A range of experimental approaches...
... and experimental uncertainty

Nanopore



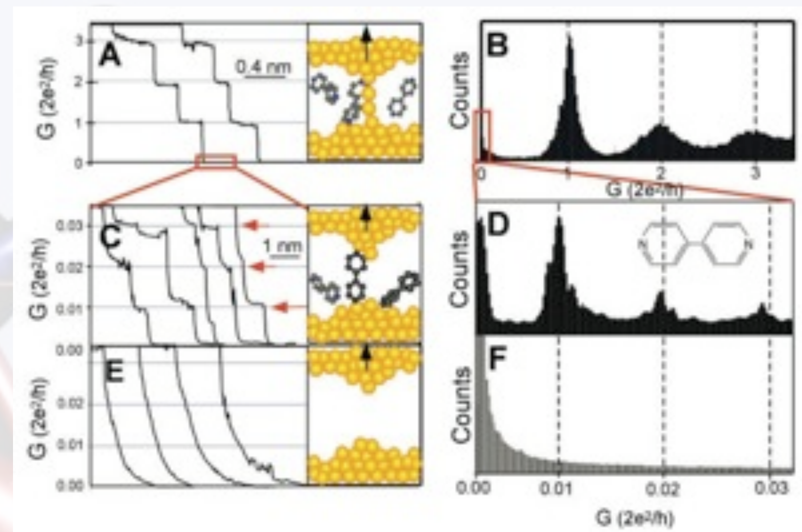
Wang et al.
PRB 68 (2003) 035416

Cross-wire



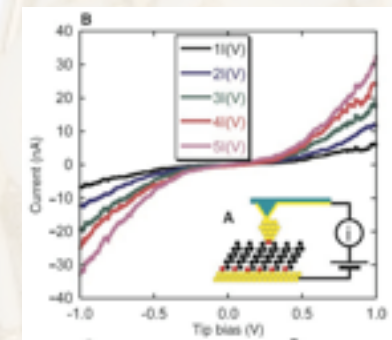
Kushmerick et al. PRL 89 (2002) 086802

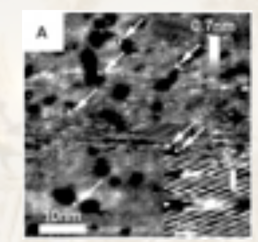
STM Break Junction



B. Xu & N. J. Tao Science (2003) 301, 1221

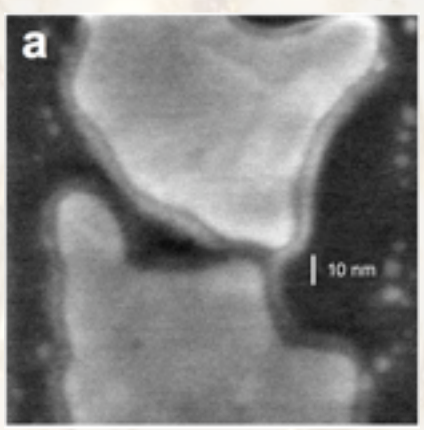
Scanning Probe

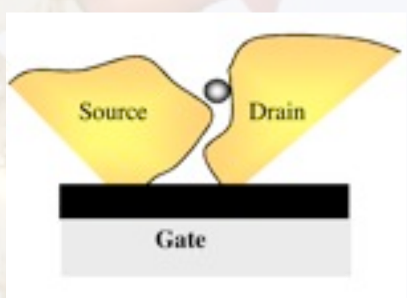




Cui et al.
Science 294
(2001) 571

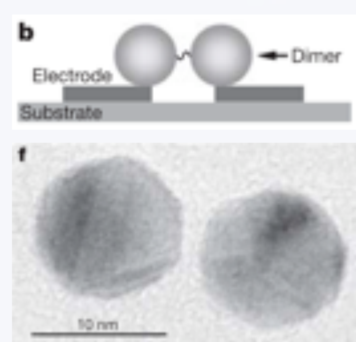
Electromigration





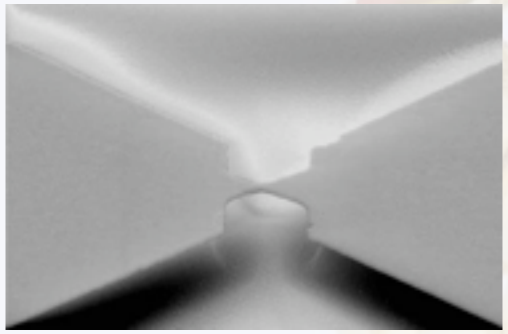
H. S. J. van der Zant et al.
Faraday Discuss. (2006)
131, 347

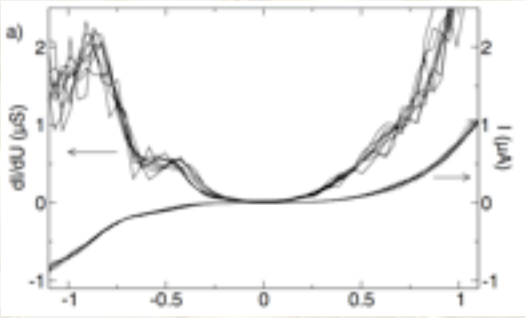
Nanocluster



Dadosh et al. Nature
436 (2005) 677

Mechanical Break Junction

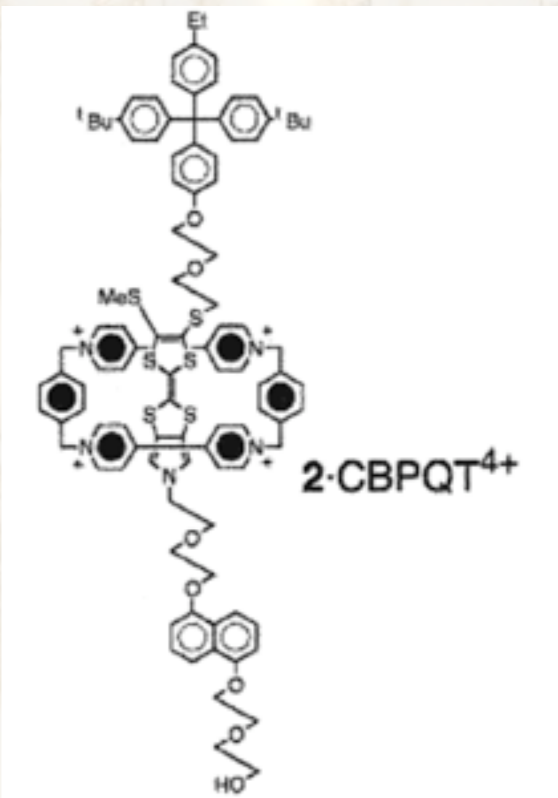


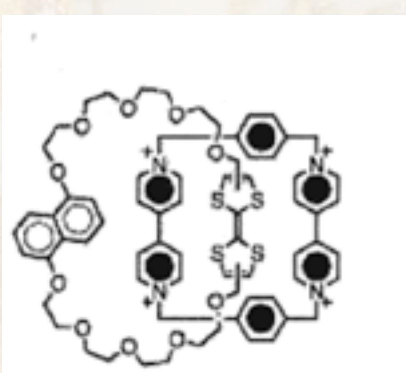


Reichert et al. PRL 88 176804

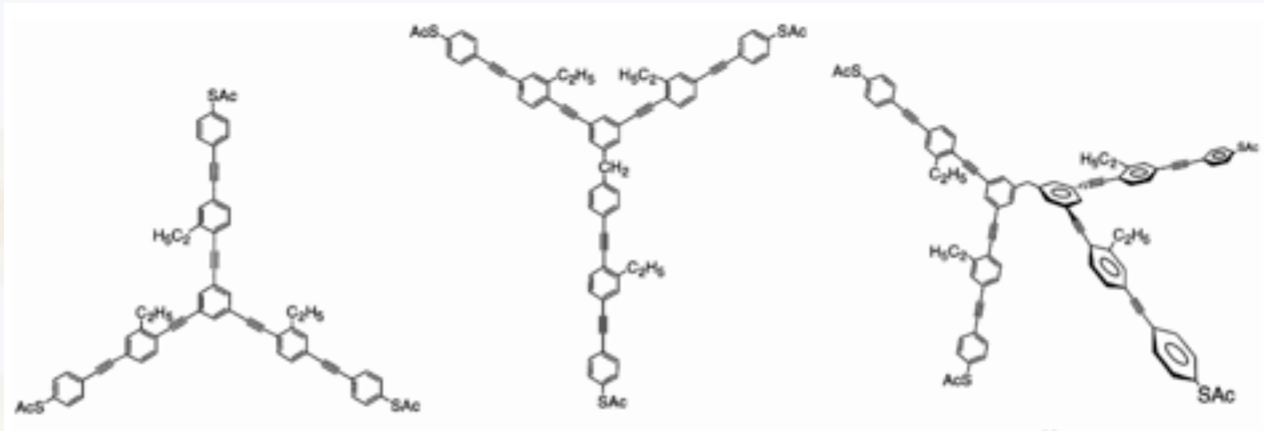
Chemical diversity ....

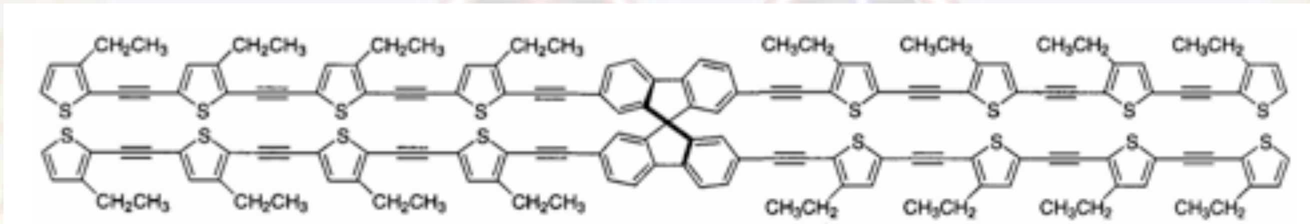
C. Collier et al.
JACS (2001) **123**, 12632



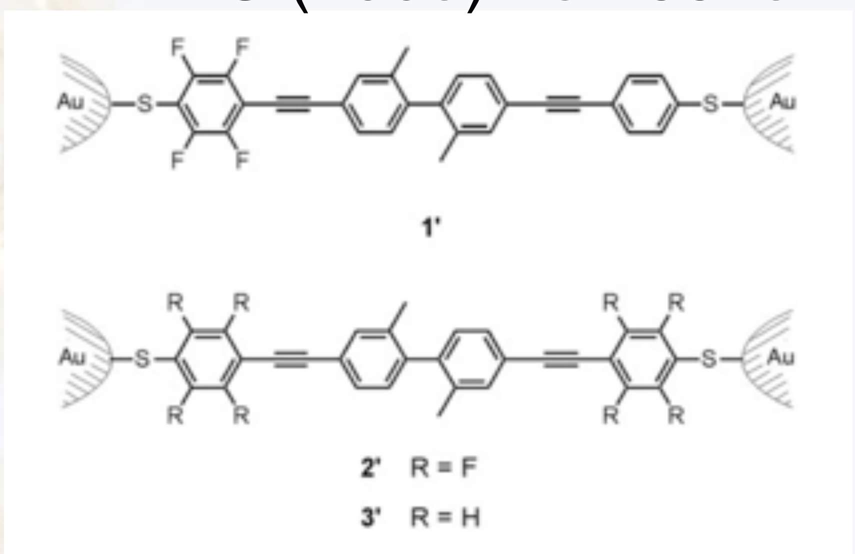


J.M. Tour
Acc Chem Res (2000) **33**,791

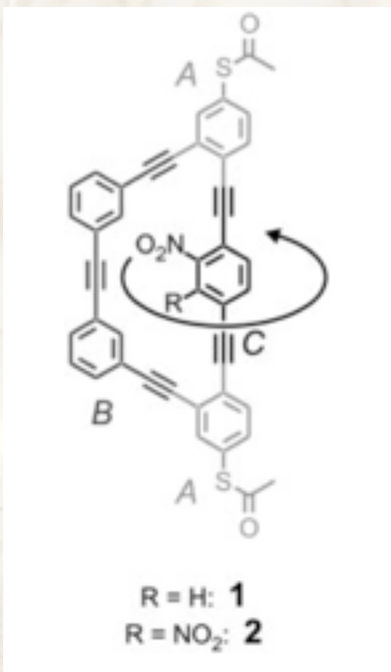




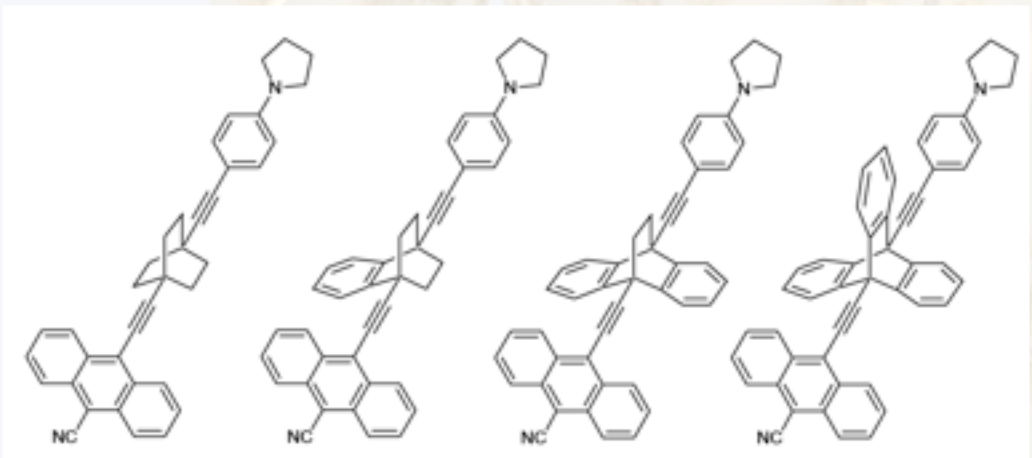
M. Elbing et al.
PNAS (2005) **102** 8815



A Błaszczyk et al.
Eur. J. Org. Chem. (2006) 3809



R. Goldsmith et al.



... reduced to barrier tunneling

C. Grave et al. Adv. Funct. Mater. **17,** 3816 (2007)

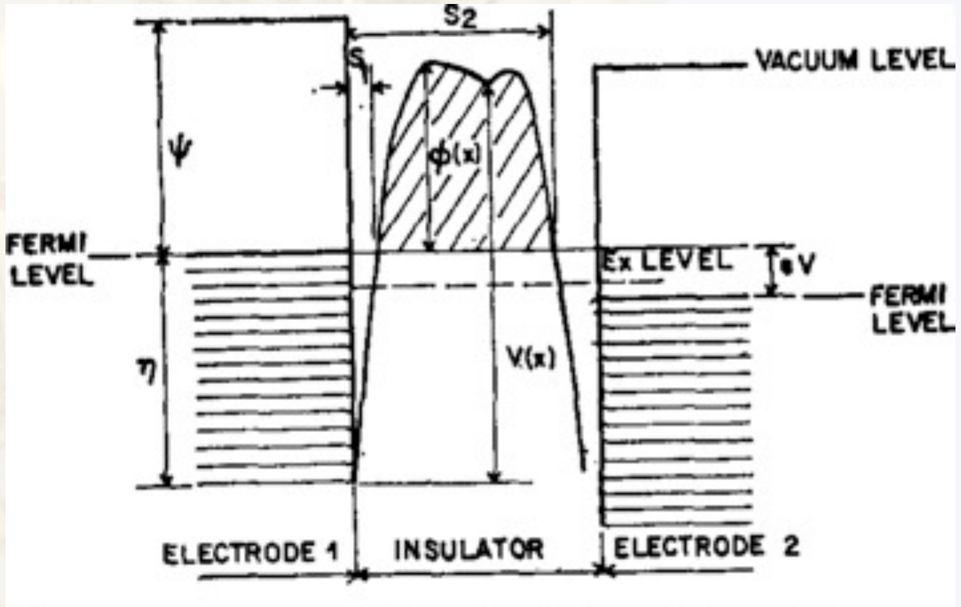
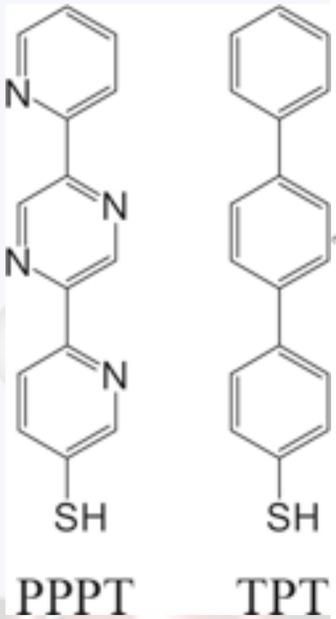
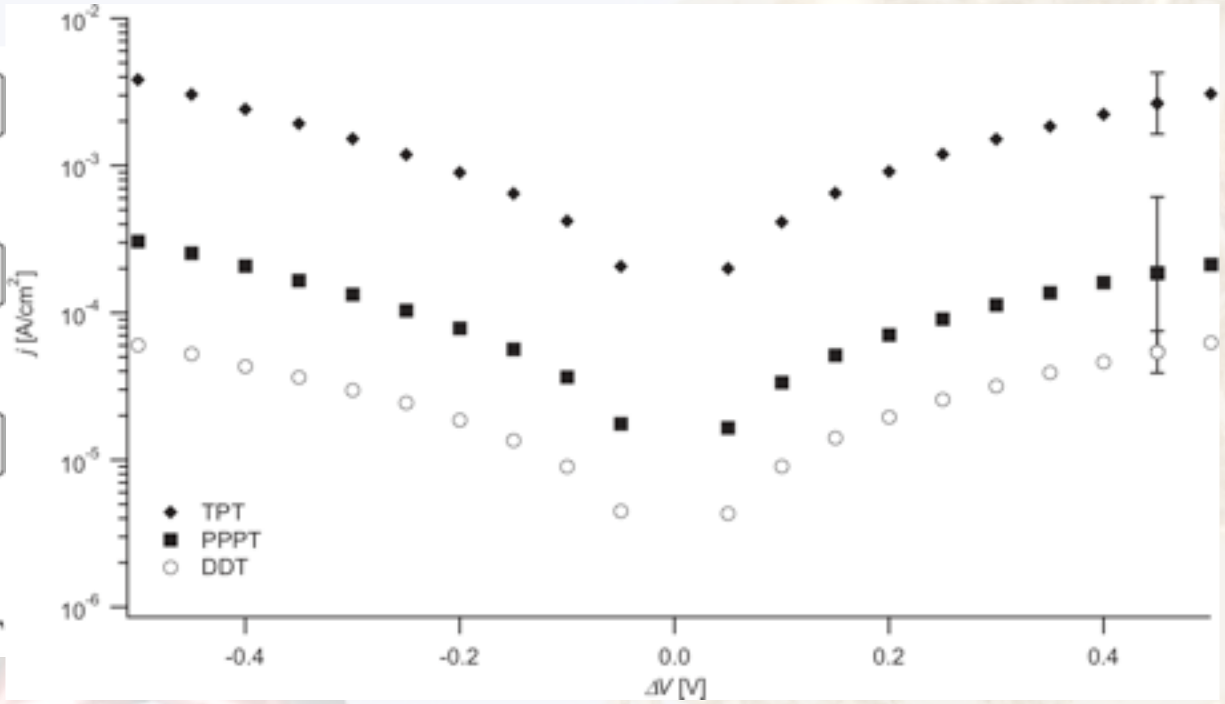
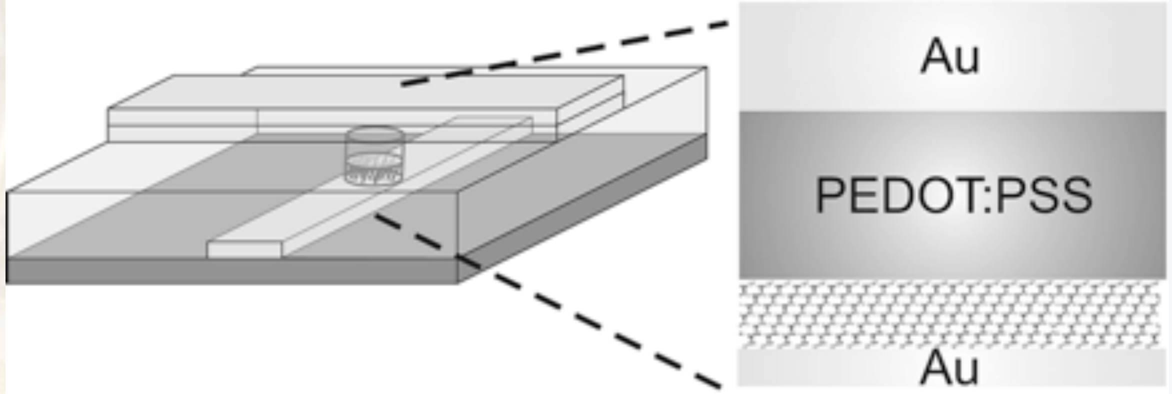


FIG. 1. General barrier in insulating film between two metal electrodes.

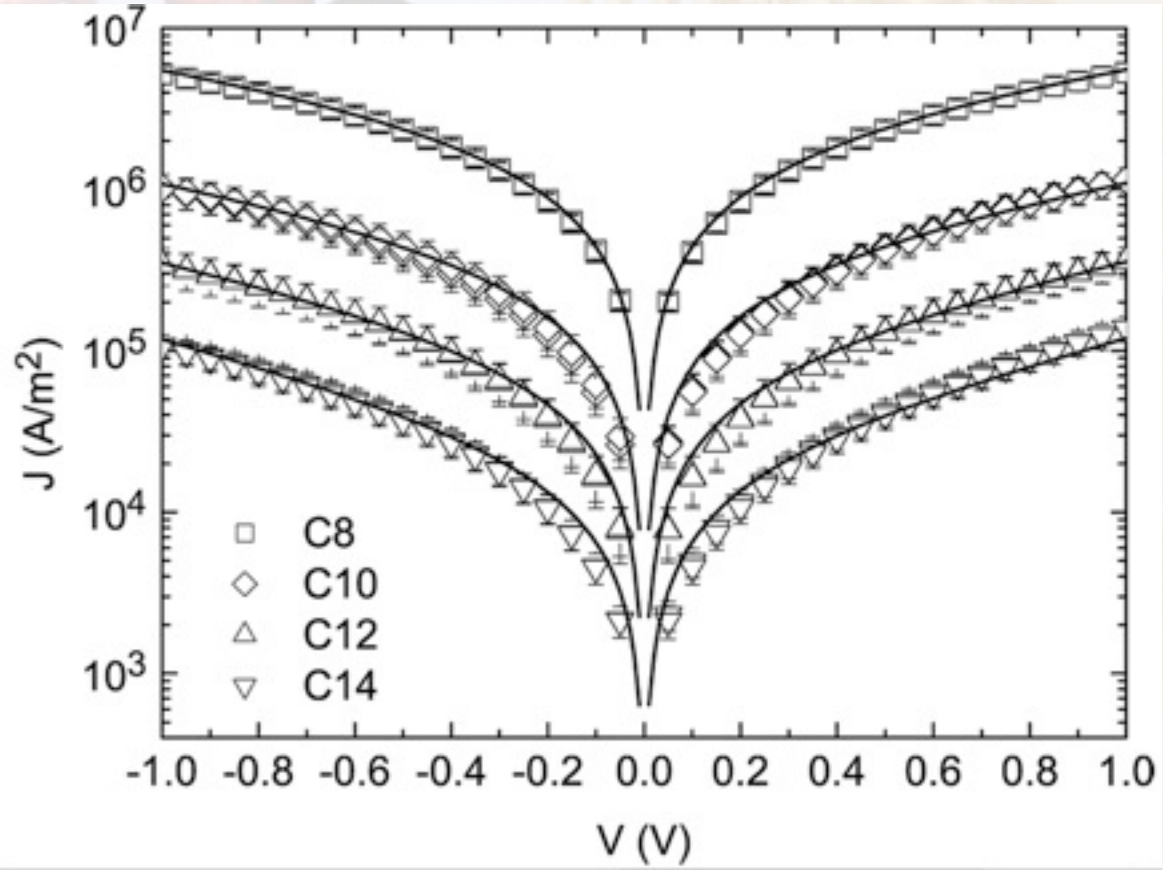
J. G. Simmons
J. Appl. Phys. **34,** 1793 (1963)



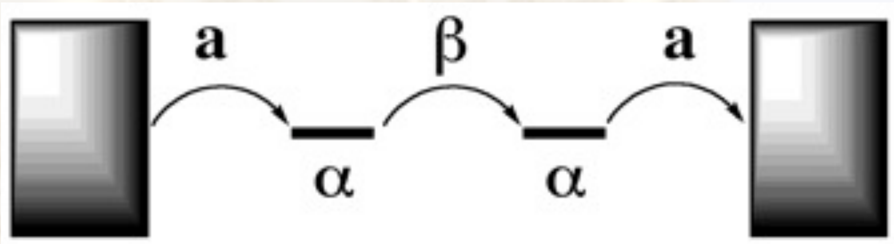




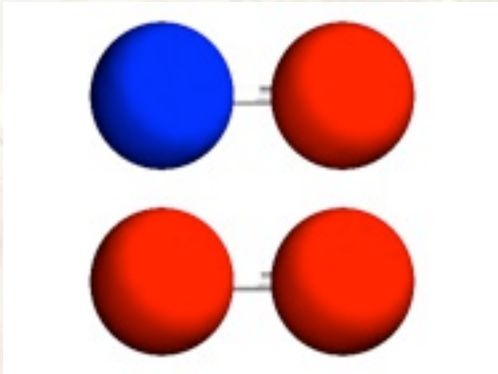
H. B. Akkerman et al.
PNAS **104,** 11161 (2007)



Calculating conductance



$$H = \begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix} \qquad \begin{aligned} E &= \alpha - \beta \\ E &= \alpha + \beta \end{aligned}$$

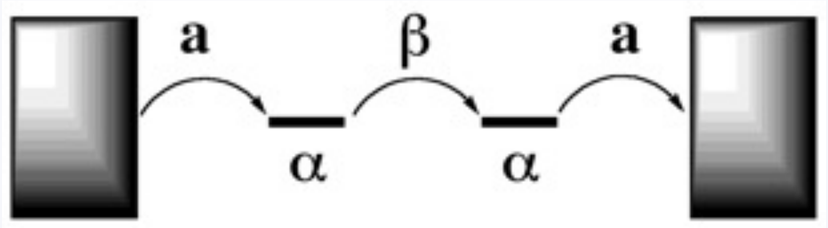


$$\Gamma_L = \begin{bmatrix} 2a & 0 \\ 0 & 0 \end{bmatrix} \qquad \Gamma_R = \begin{bmatrix} 0 & 0 \\ 0 & 2a \end{bmatrix} \qquad \Sigma = \frac{i(\Gamma_L + \Gamma_R)}{2}$$

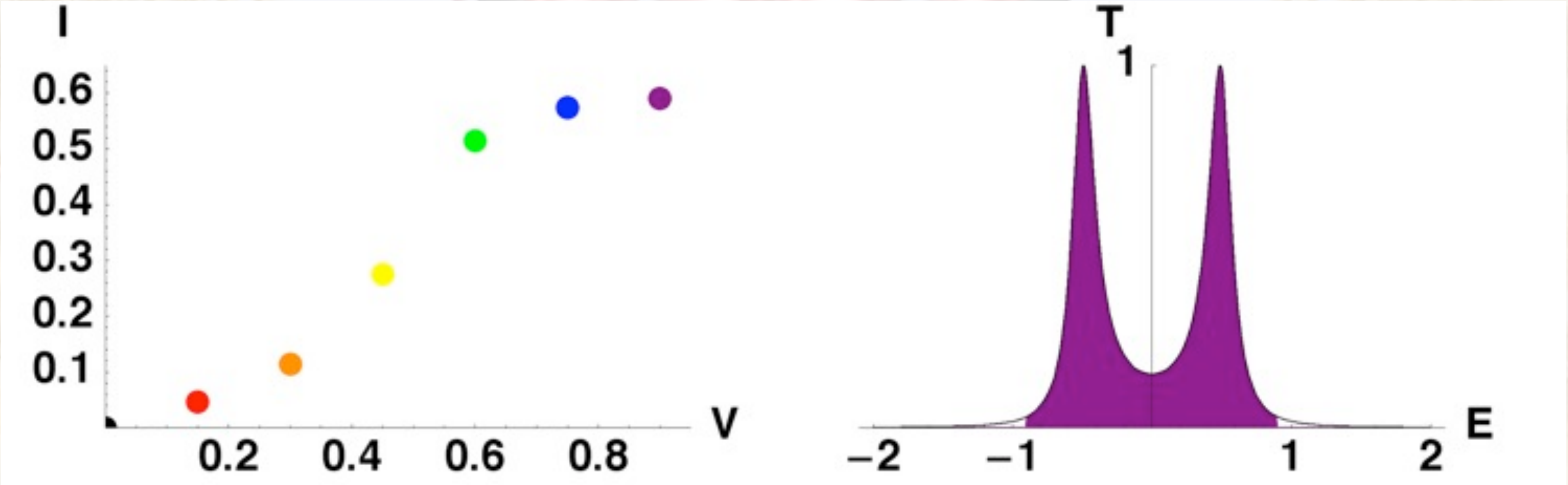
$$\begin{aligned} H' &= H - \Sigma \\ &= \begin{bmatrix} \alpha - ia & \beta \\ \beta & \alpha - ia \end{bmatrix} \end{aligned} \qquad G^r = \frac{1}{ES - H'} \qquad G^a = G^{r\dagger}$$

$$T = \mathrm{Tr}[\Gamma_L G^r \Gamma_R G^a]$$

Calculating current from transmission

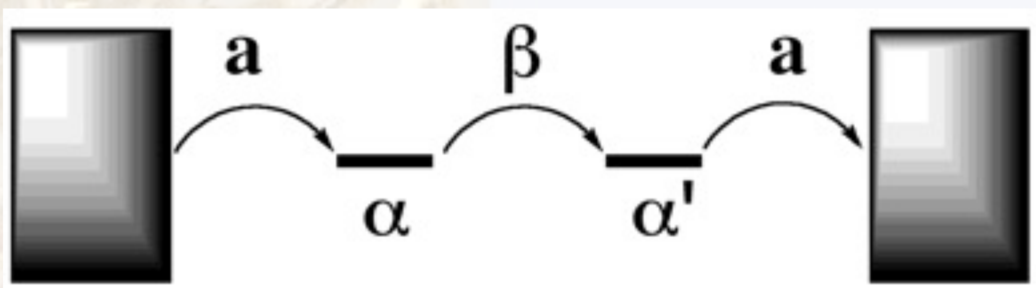


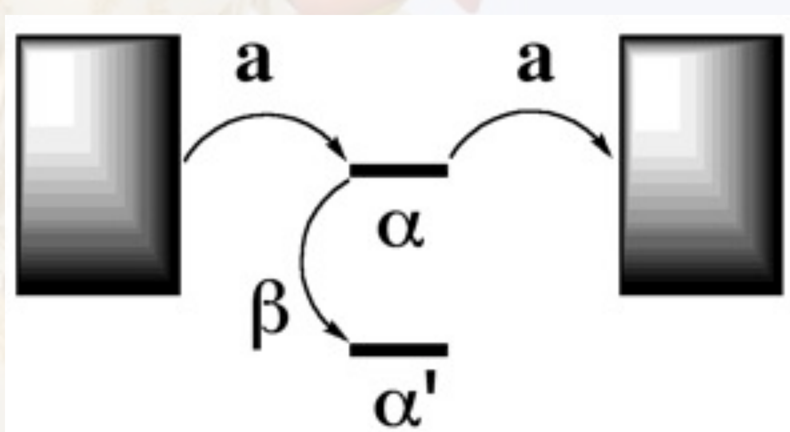
$$I(V) = \frac{2e}{h}\int_{-\infty}^{\infty} dE\,\mathrm{Tr}[\Gamma_L G^r \Gamma_R G^a](f_L - f_R)$$



A hint at something different

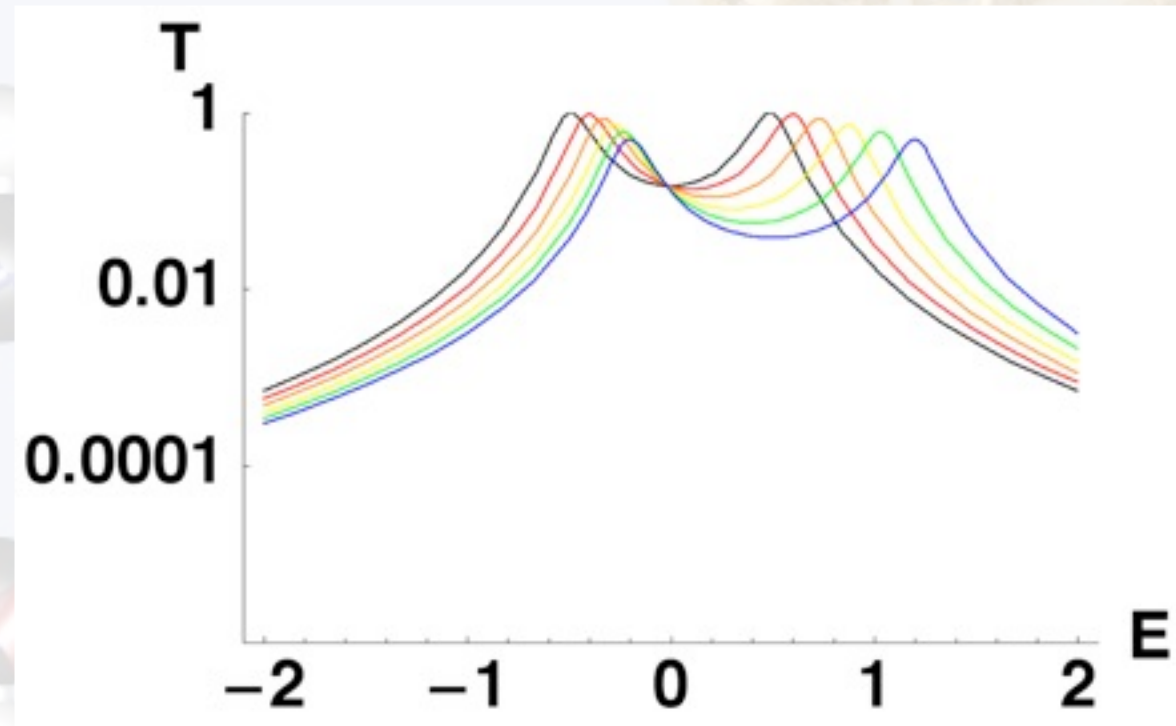
$$H = \begin{bmatrix} \alpha & \beta \\ \beta & \alpha' \end{bmatrix}$$

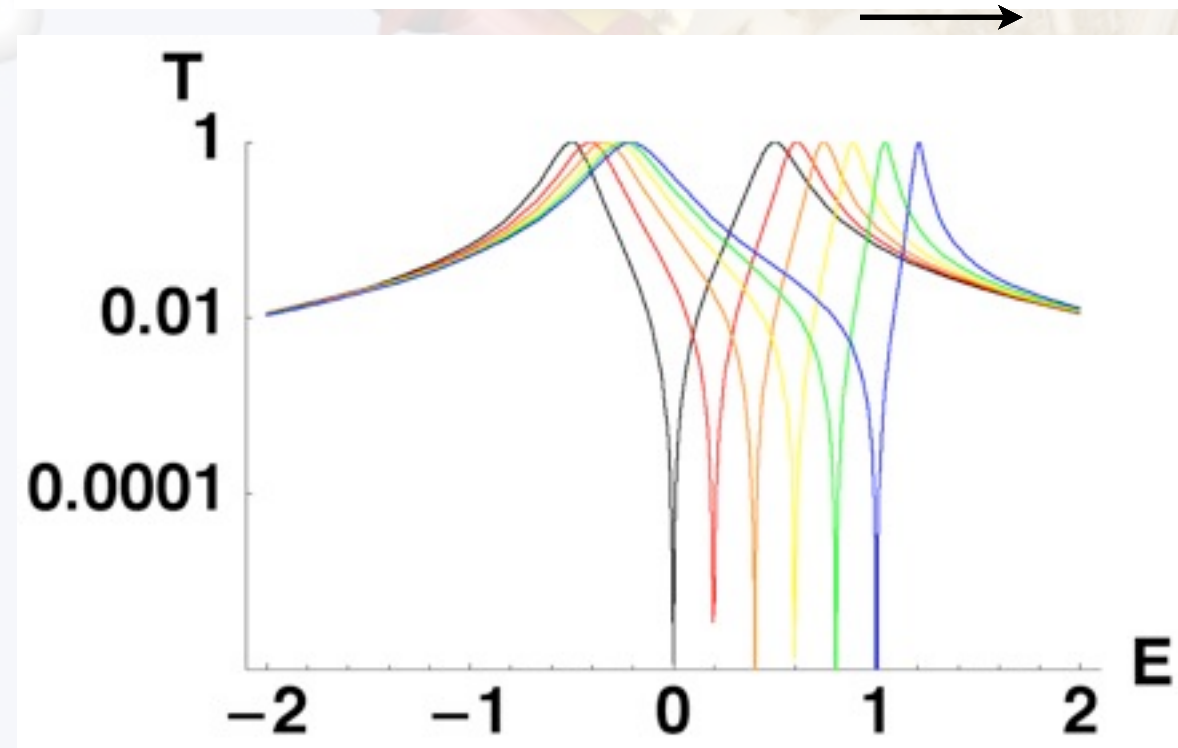




$$T = 0 \quad E = \alpha'$$

$$\alpha = 0, \alpha' = 0 - 1.0$$

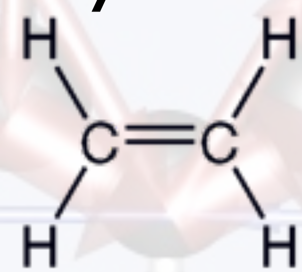




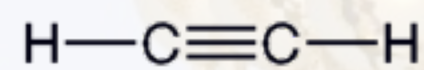
A little aside σ and π bonds

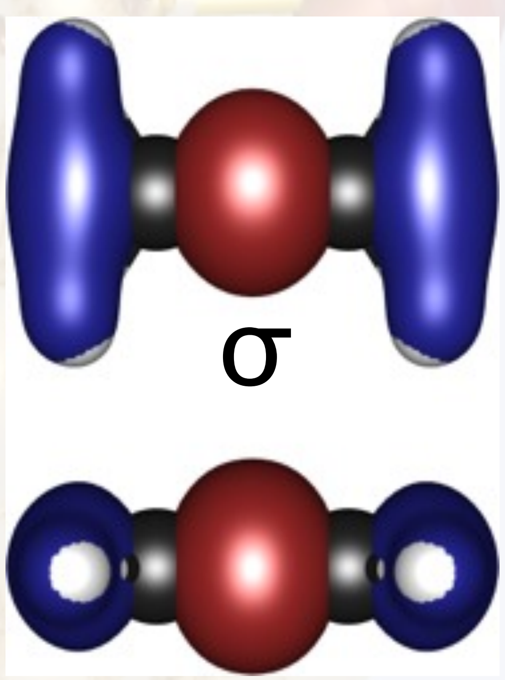
- A molecular orbital can be classified as:
  - σ if the interaction occurs along the line connecting two nuclei
  - and π when the interaction occurs in 2 regions one directly above and one directly below the line connecting two nuclei
- A Hückel Hamiltonian generally includes only the π system

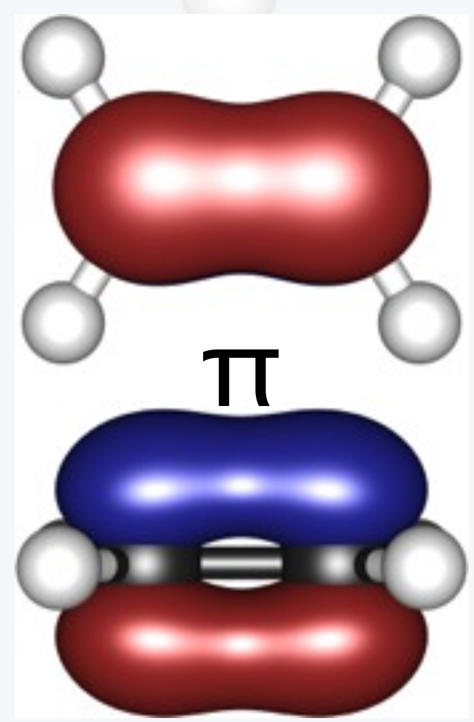
$$H = \begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix} \rightarrow$$

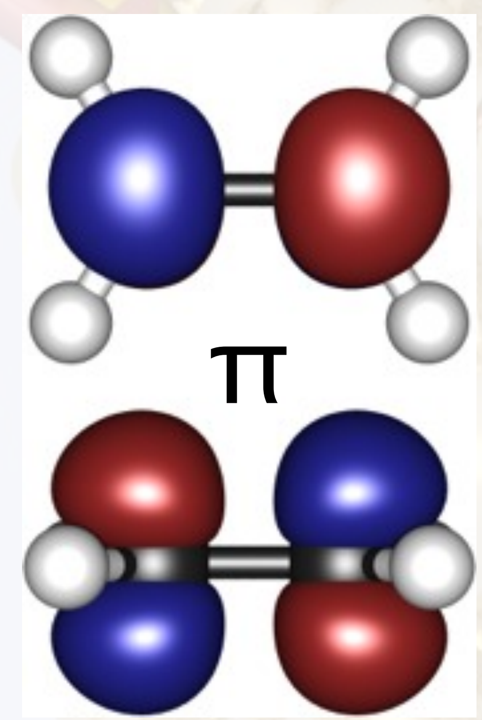


or

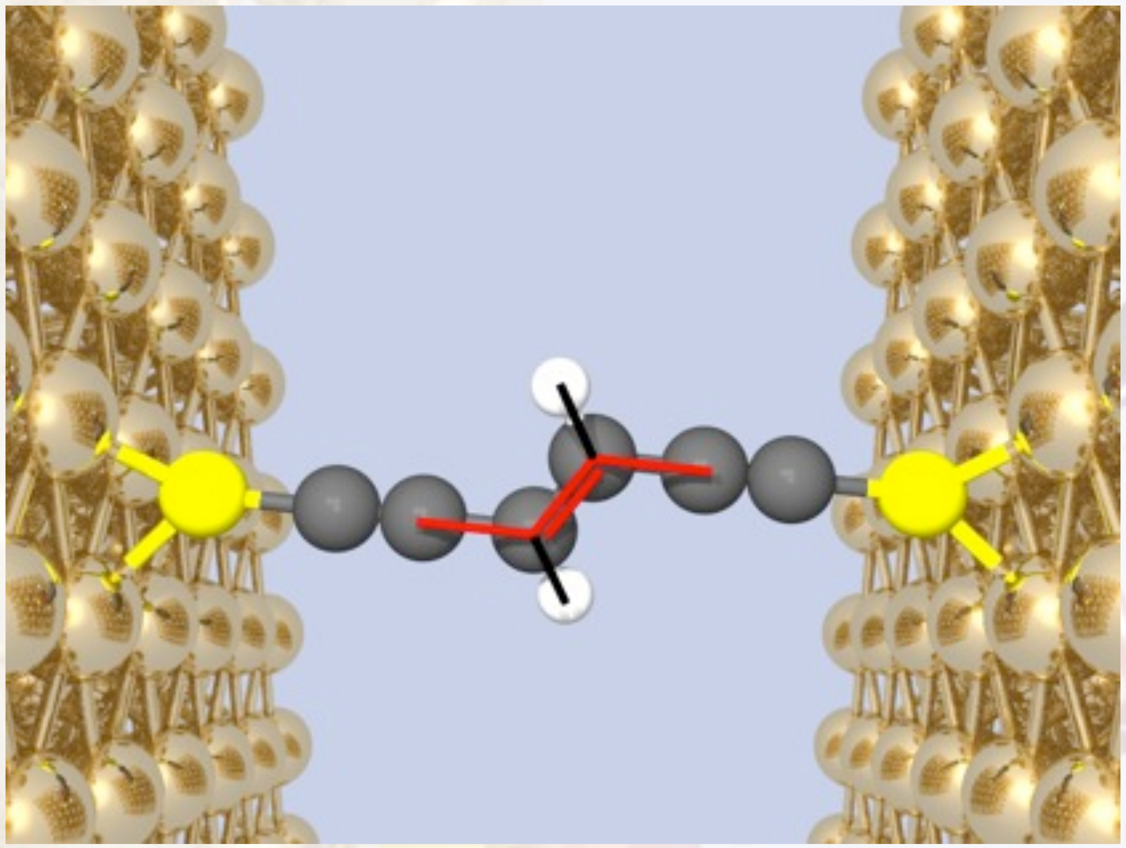


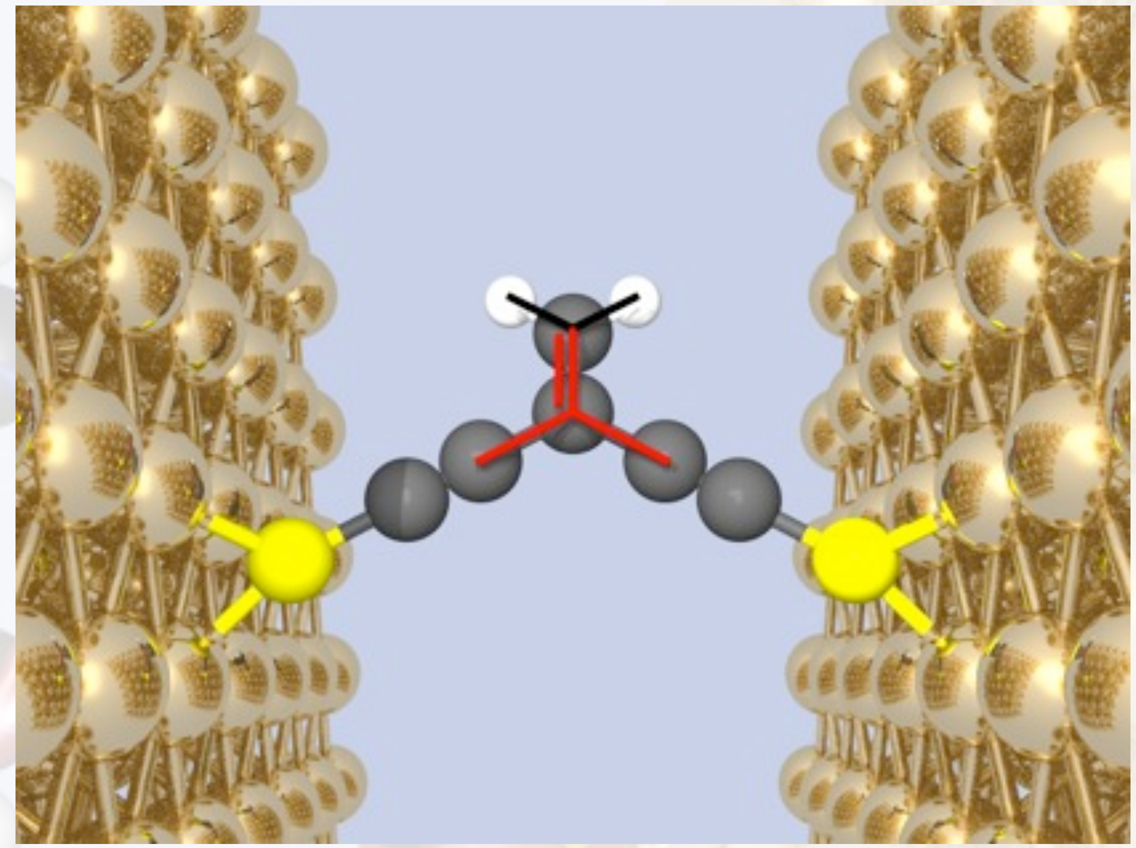






The molecular analogue: cross-conjugated molecules

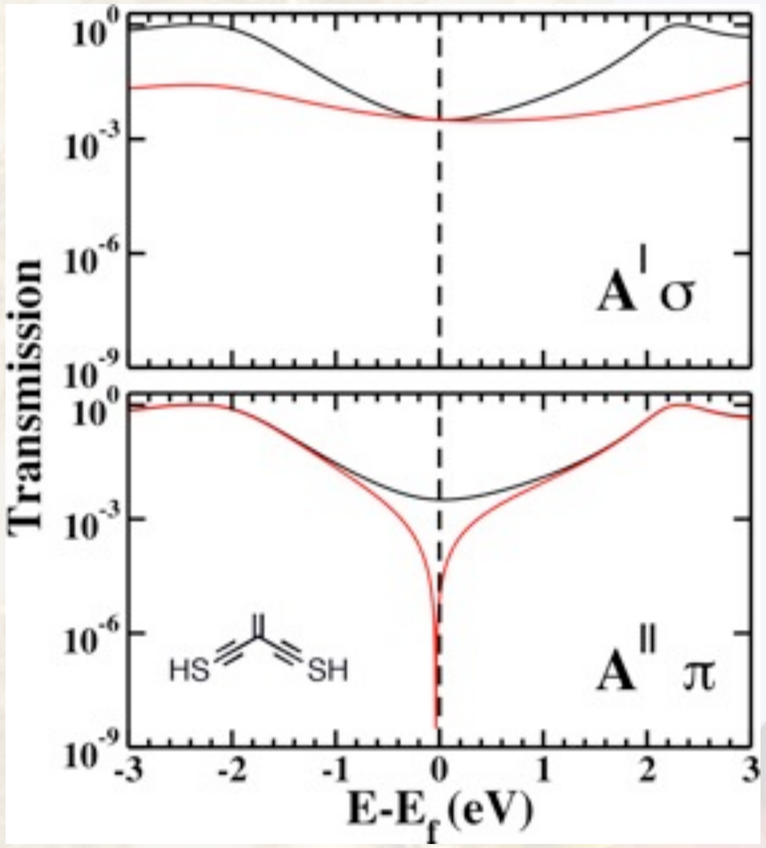


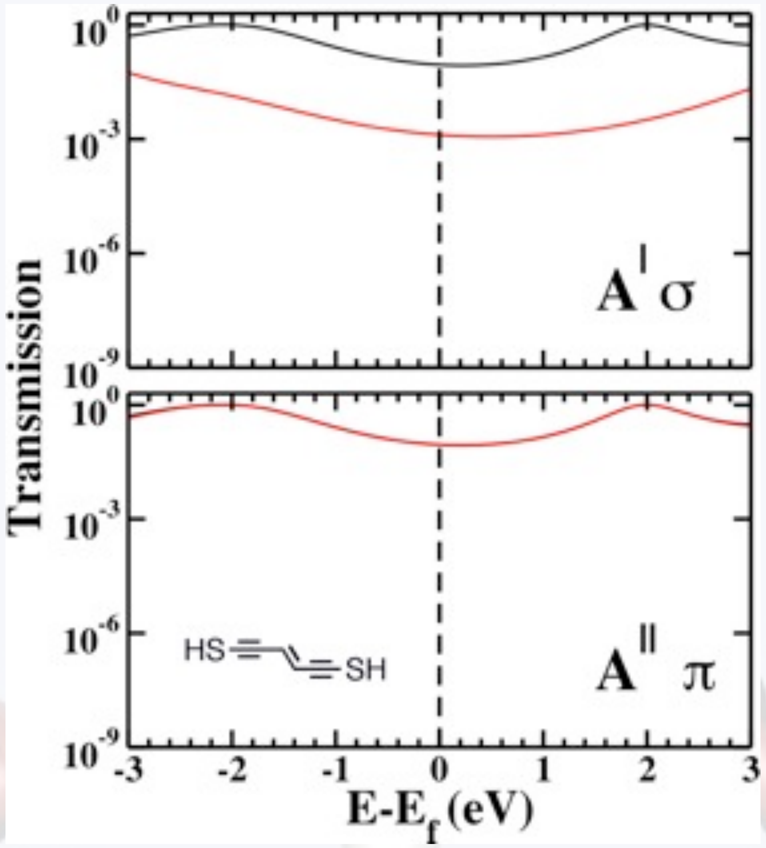


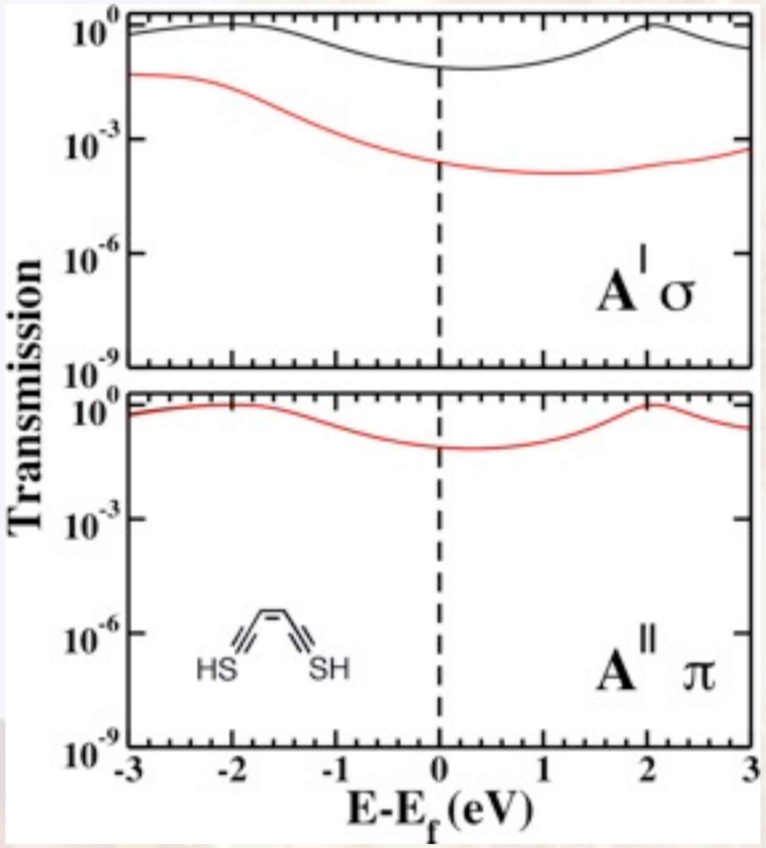
"a compound possessing three unsaturated groups, two of which although conjugated to a third unsaturated center are not conjugated to each other."

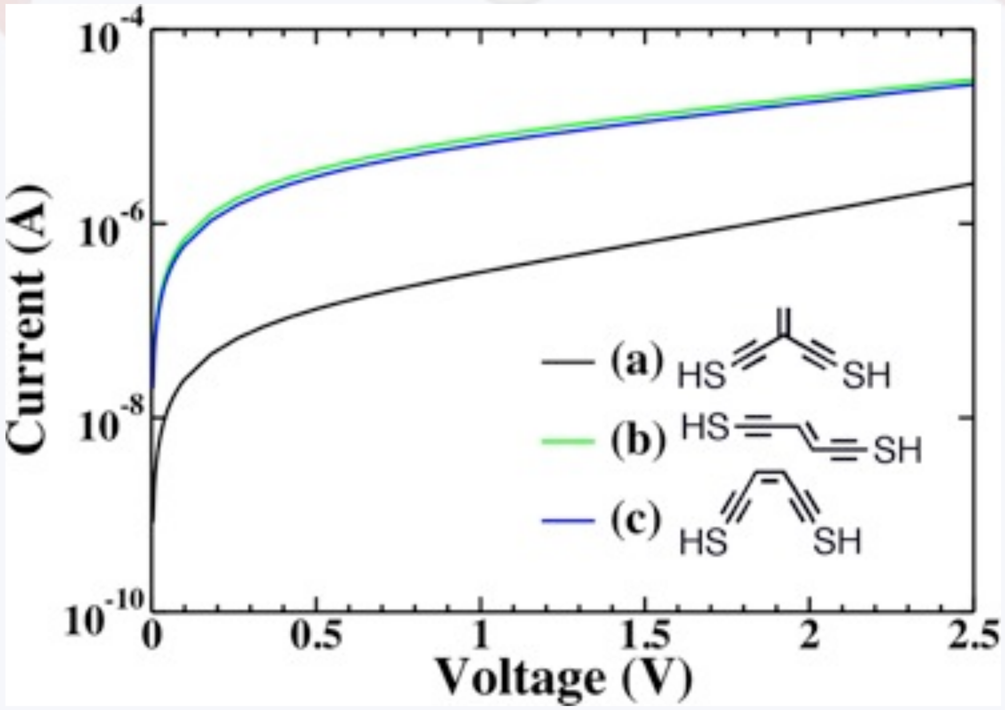
N. F. Phelan, M. Orchin, *J. Chem. Educ.* **45**, 633 (1968)

A simple comparison



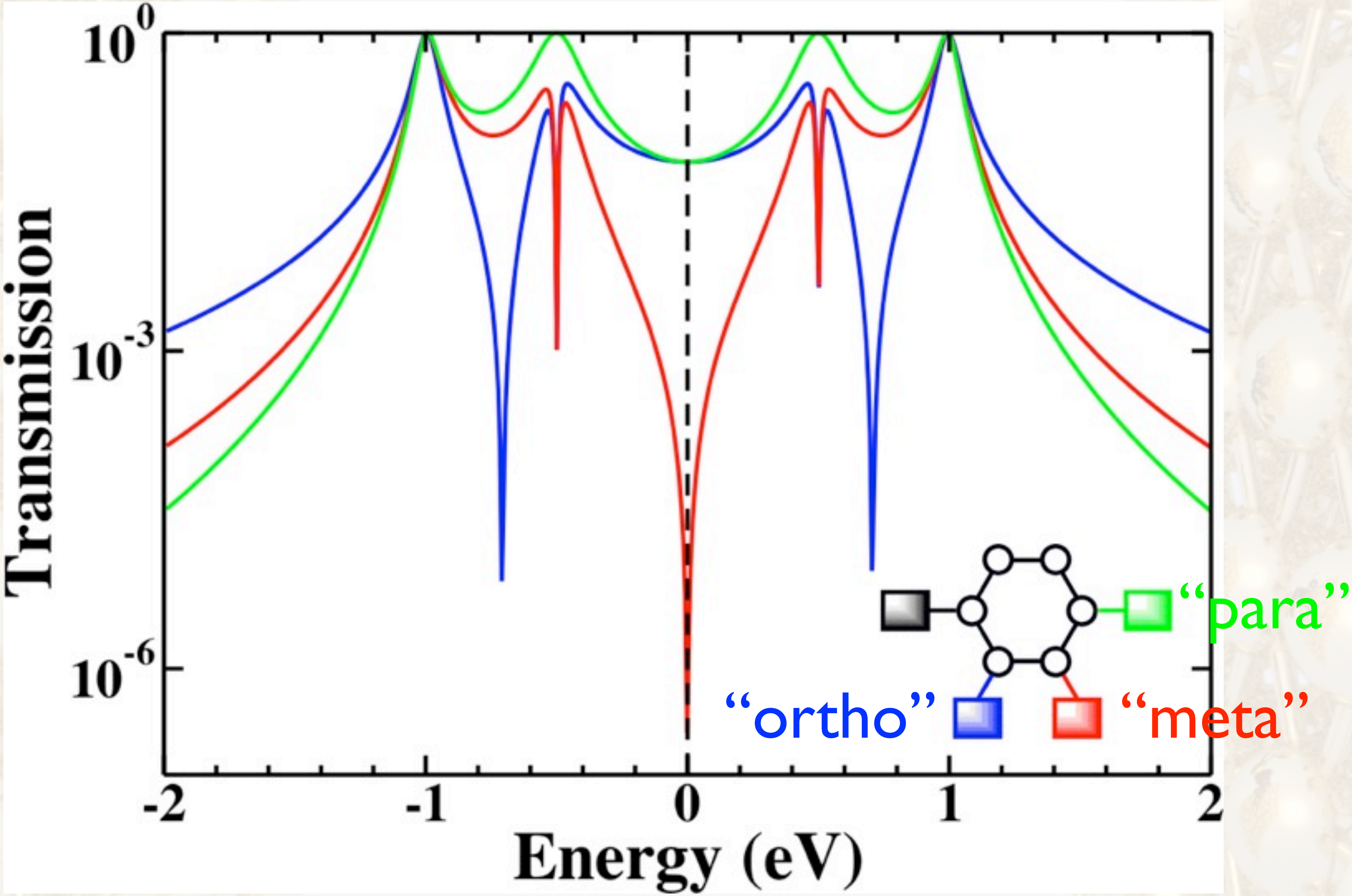






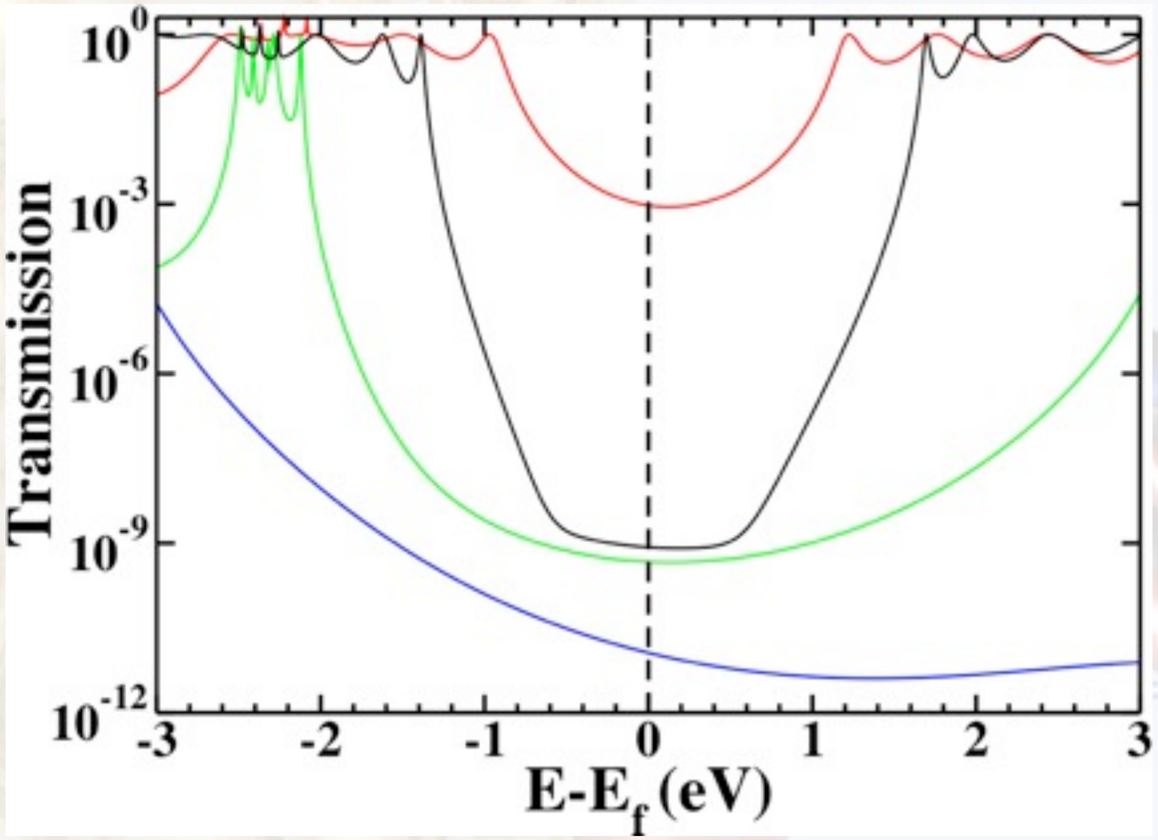
JACS **130**, 17301 (2008)

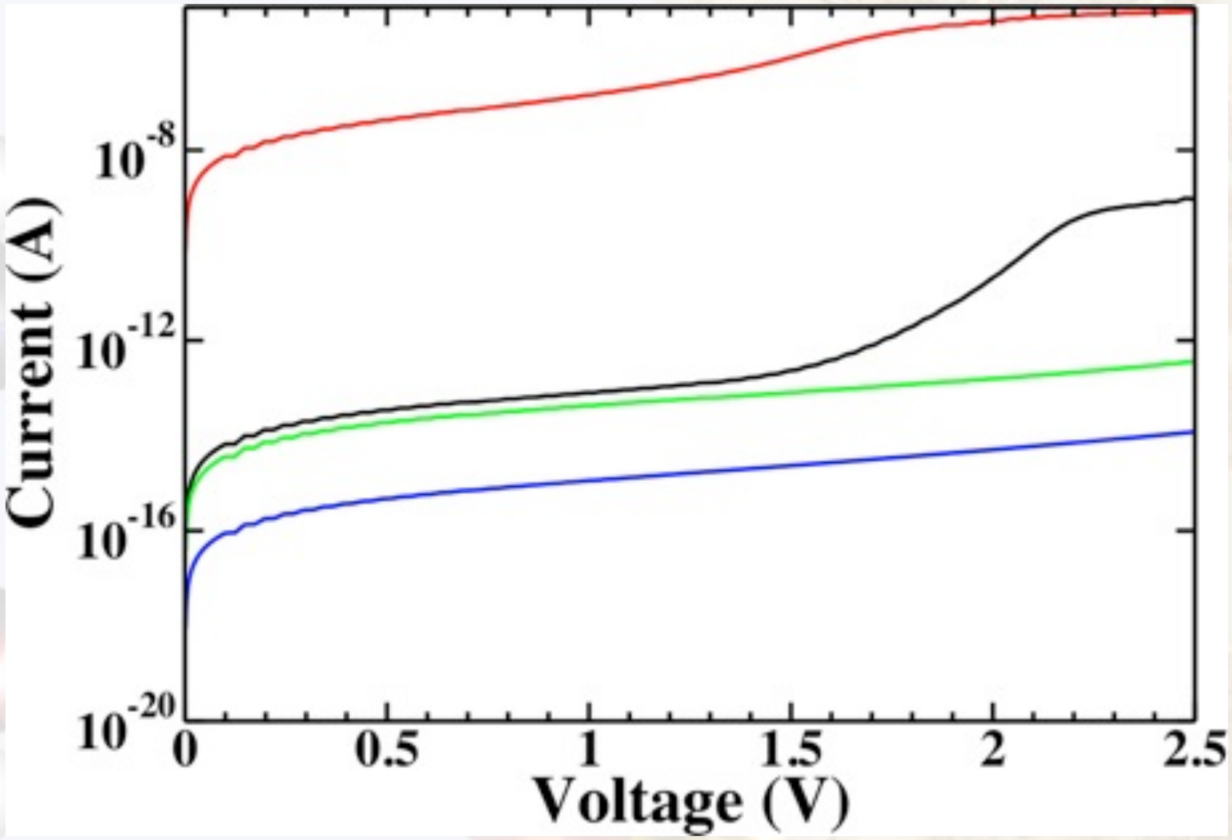
The most well-known example of interference:

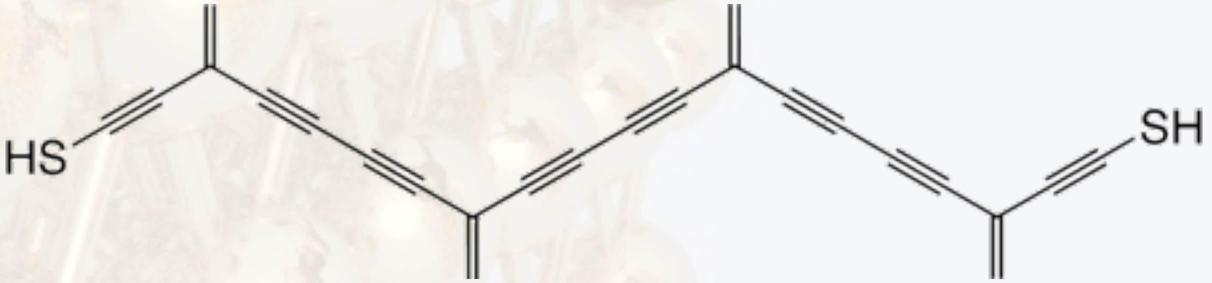


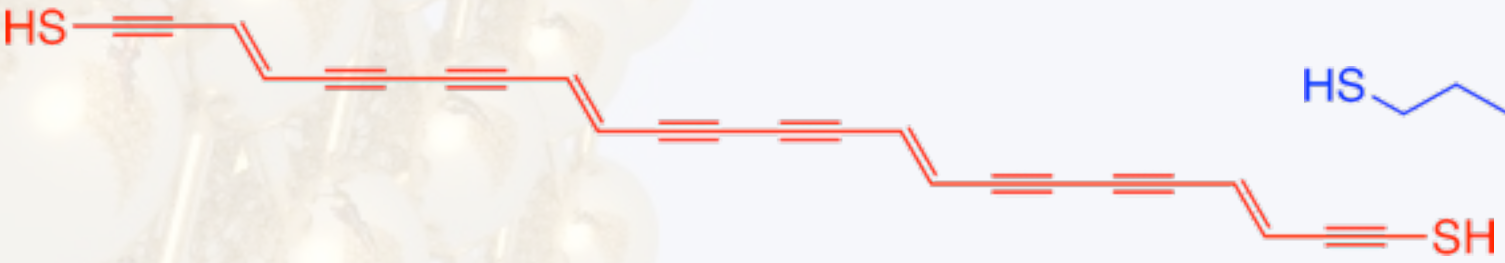
J Chem. Phys. **129**, 054701 (2008)

Some larger systems



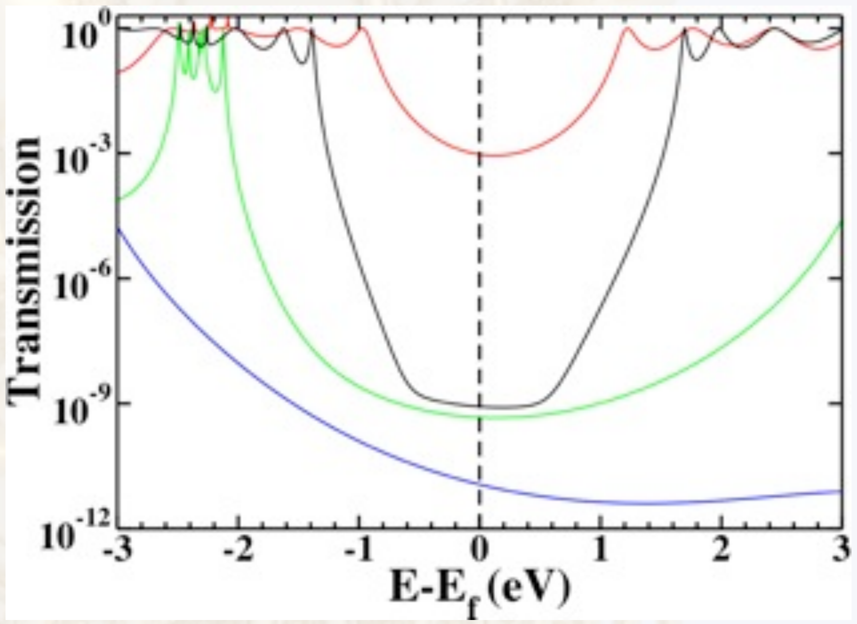




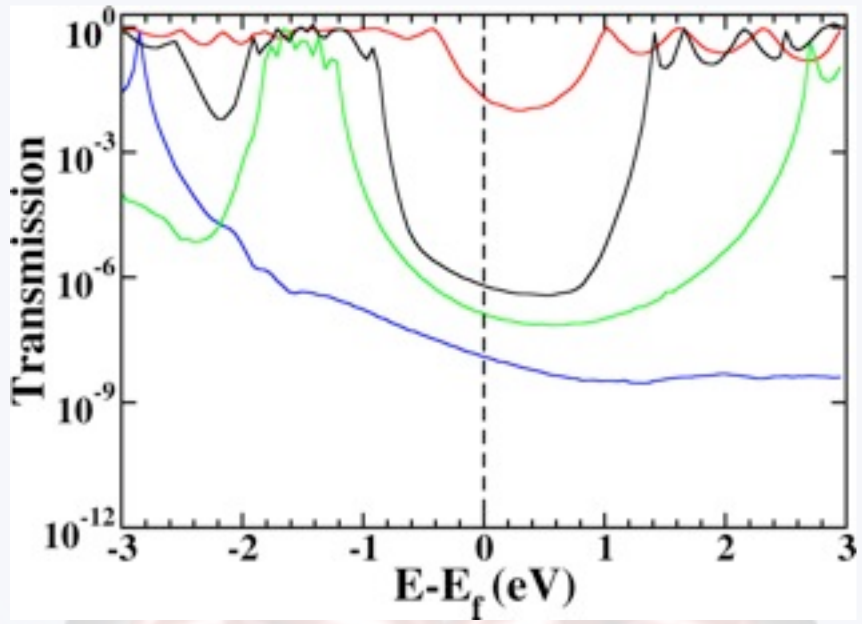


JACS **130**, 17301 (2008)

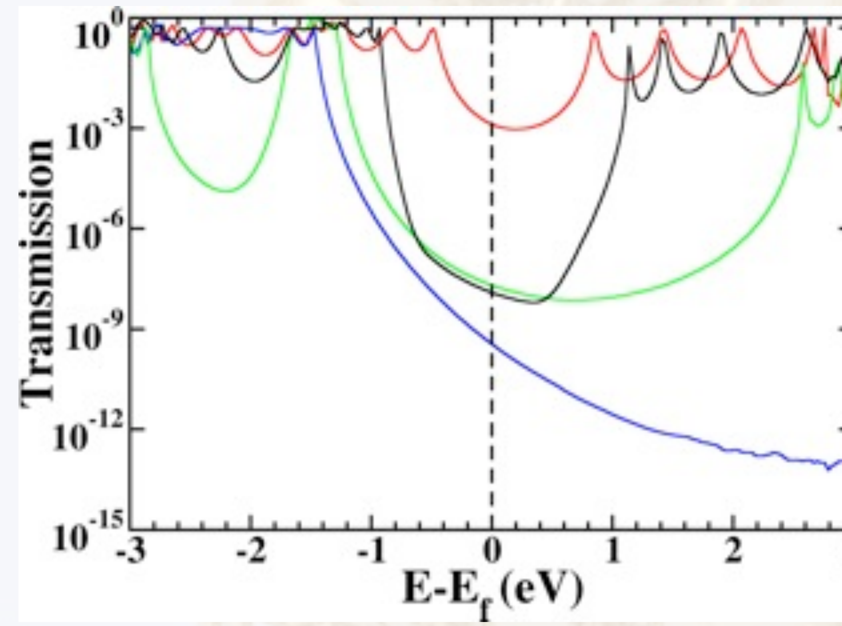
A comparison of 3 methods



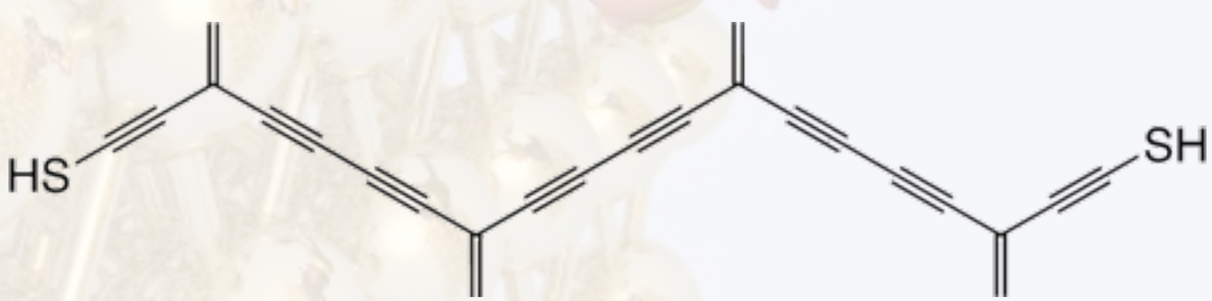
gDFTB

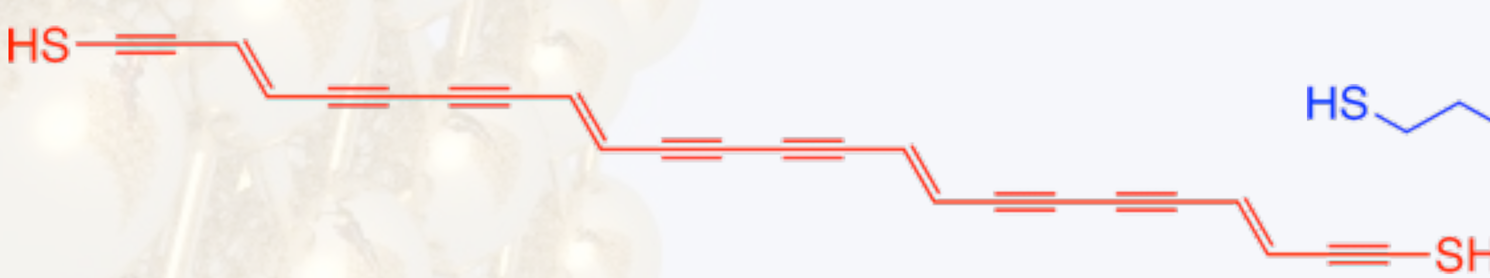


ATK



Huckel IV





JACS **130**, 17301 (2008)

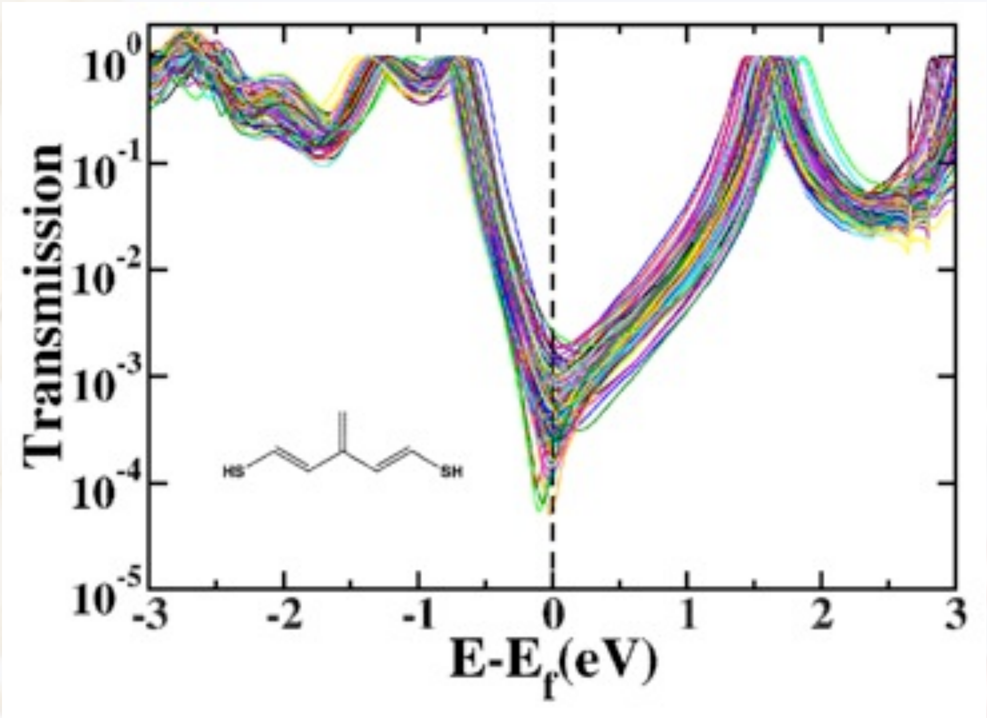
Stability is important

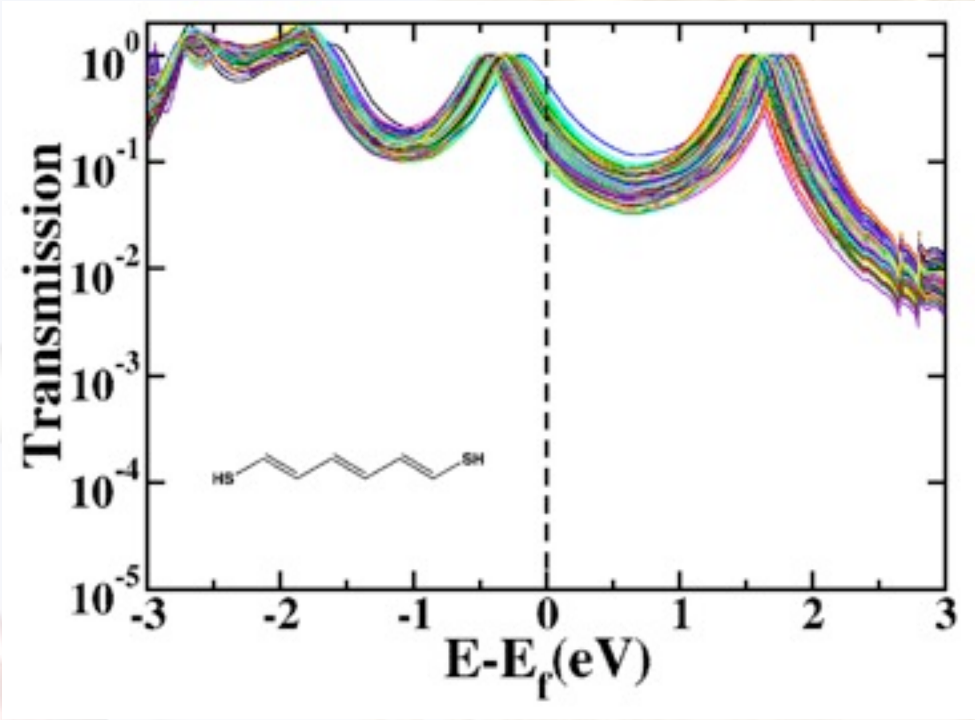
•Simulations were run in Tinker 4.0.

•Following a 1ns equilibration, 100 snapshots were taken at 1ps intervals.

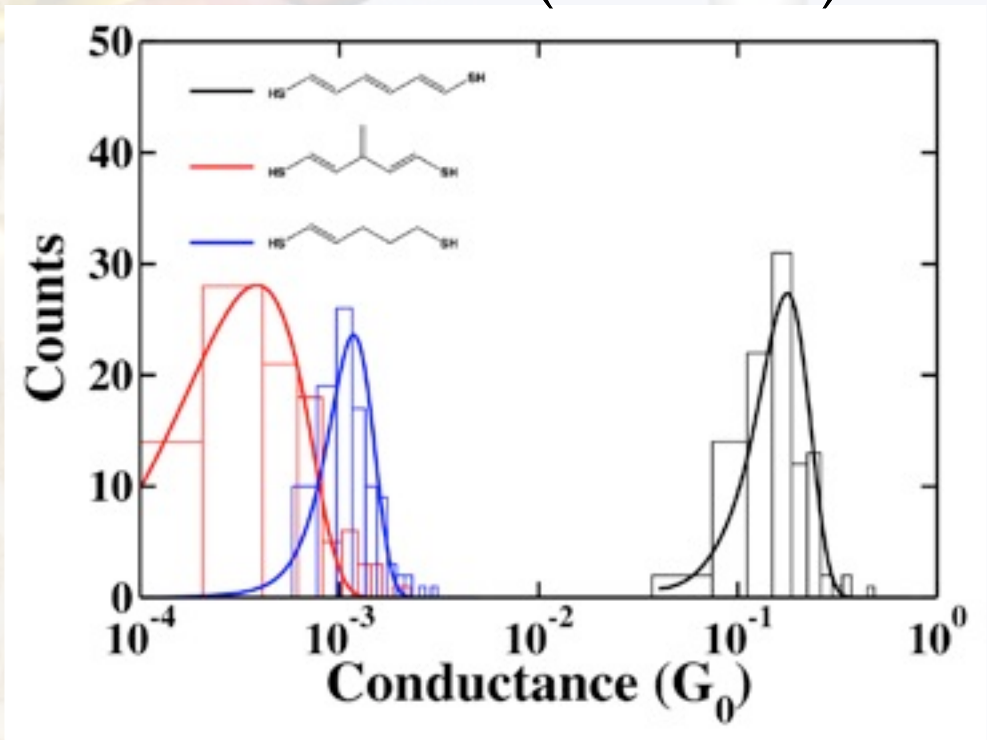
•The transmission was calculated using atk 2.0.

•The conductance distributions are shown with a Gaussian fit.

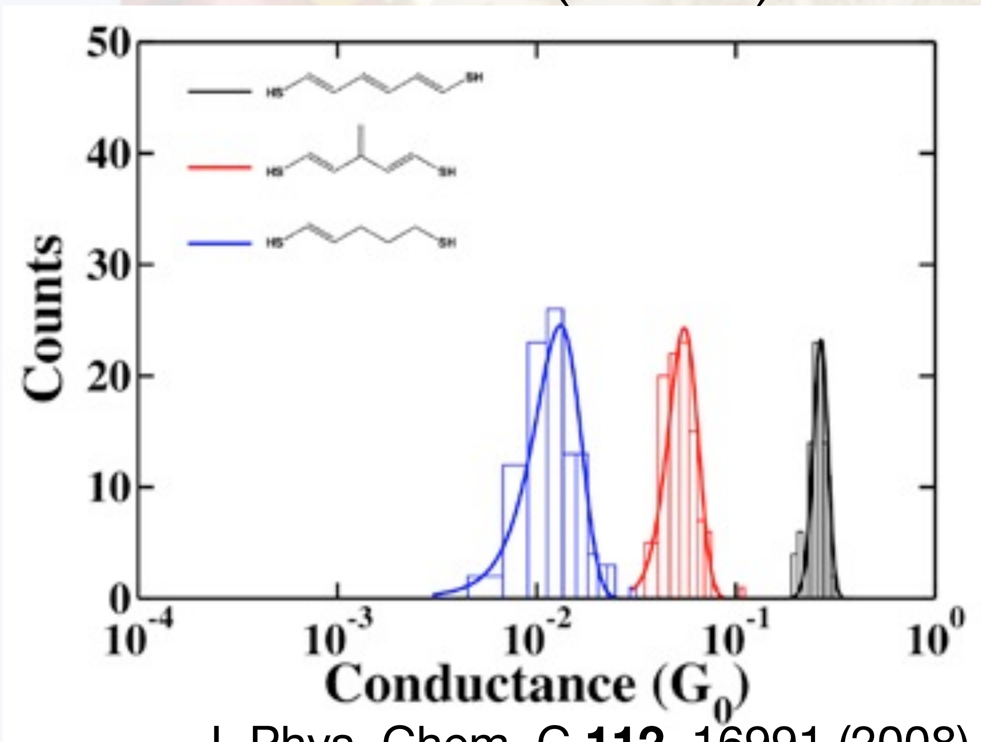




Conductance (10mV bias)

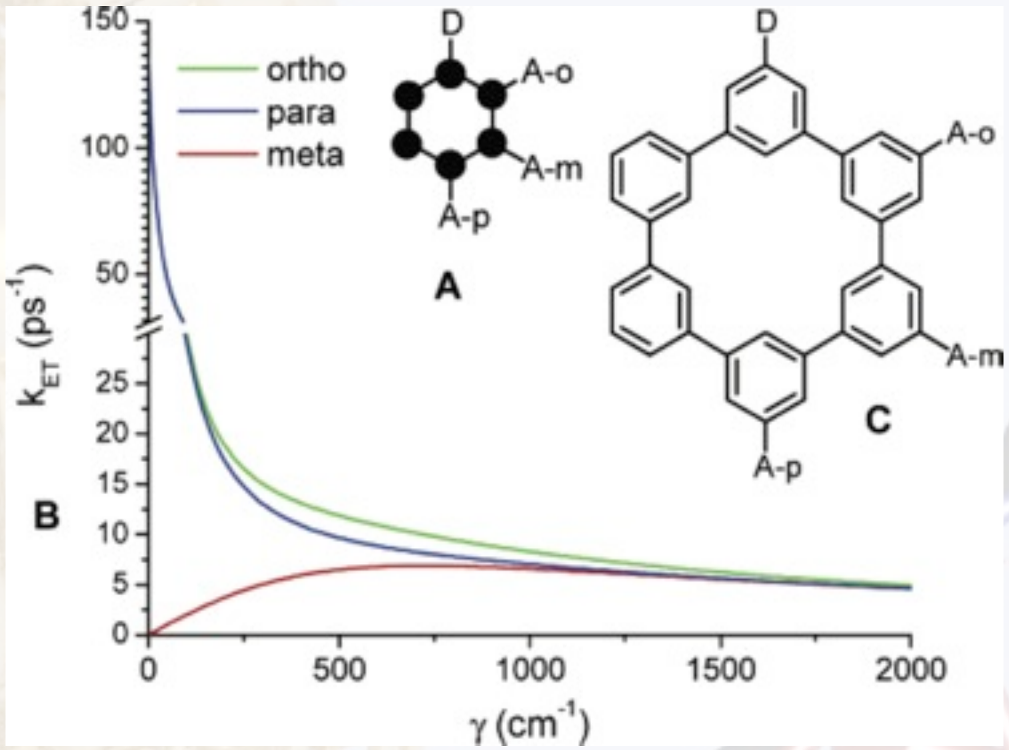


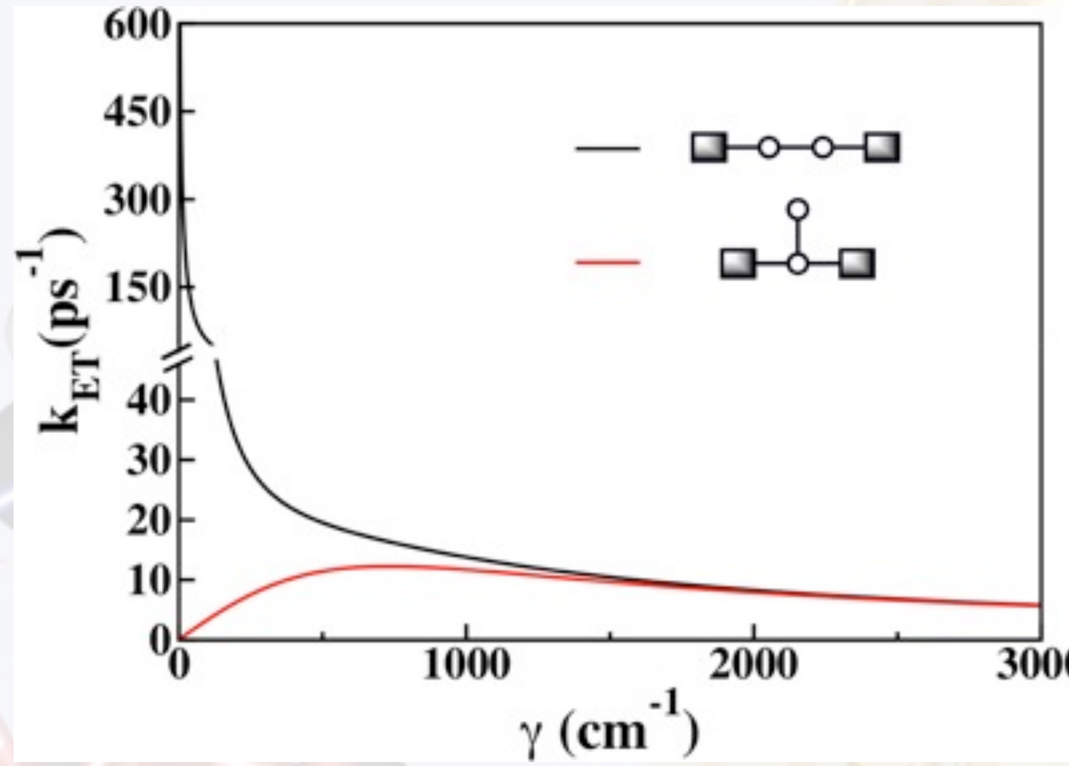
Conductance (2V bias)



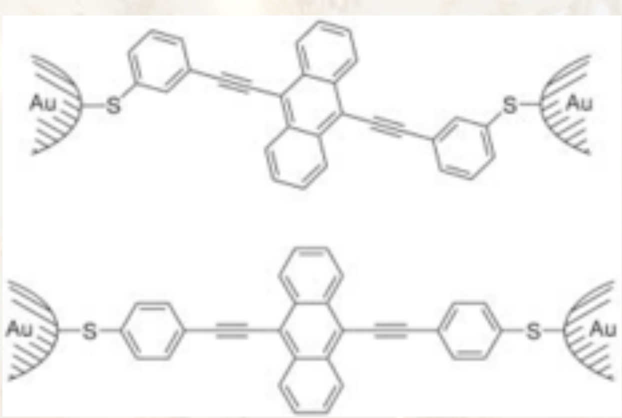
J. Phys. Chem. C **112**, 16991 (2008)

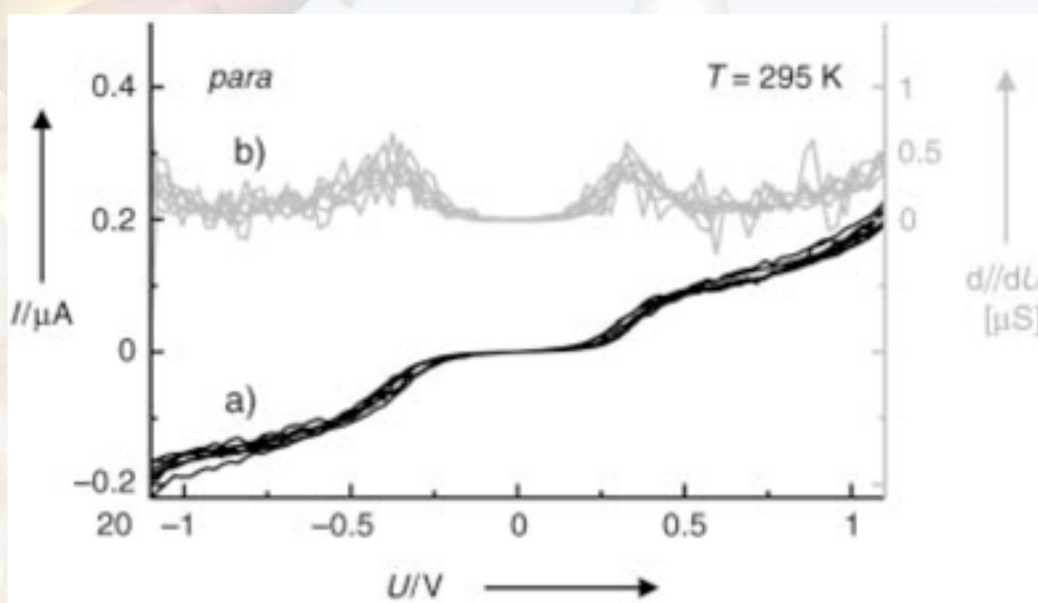
Dephasing

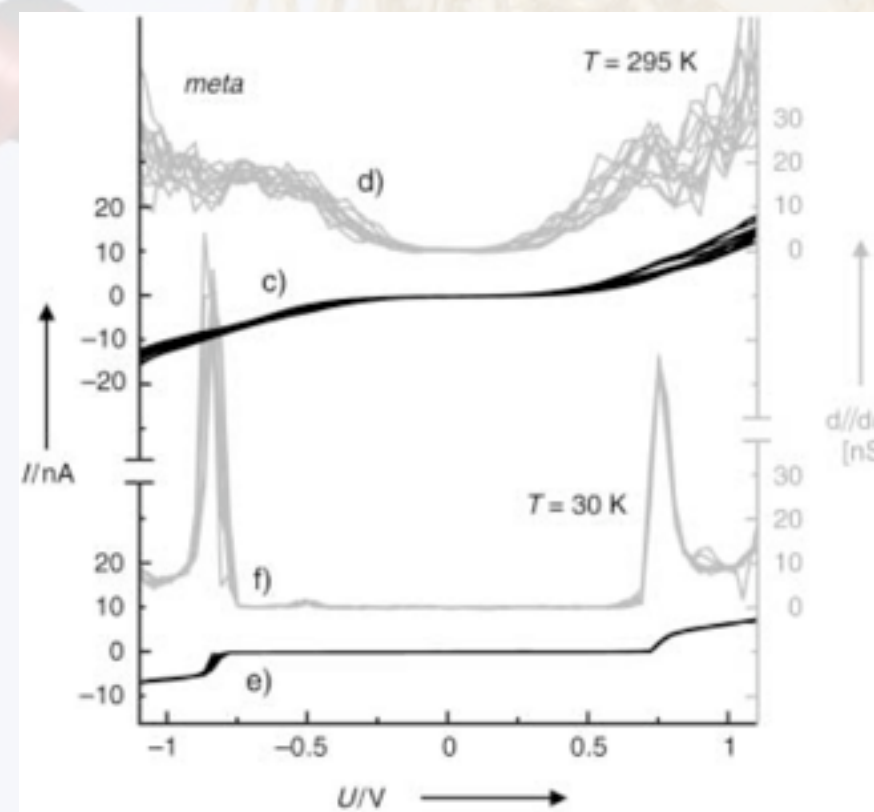




R. H. Goldsmith et al.
J. Phys. Chem. B **110,** 20258 (2006)

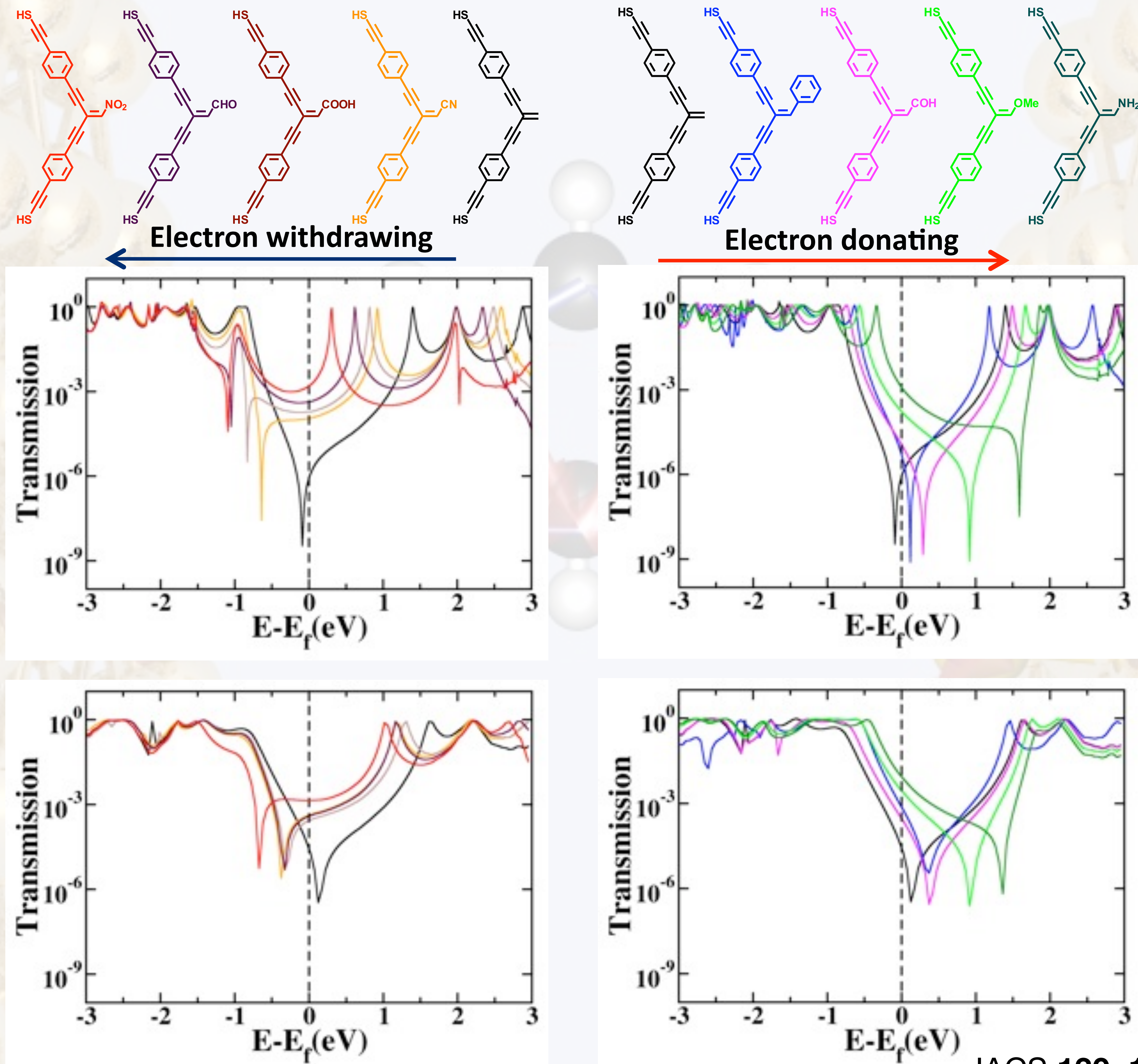






M. Mayor et al.
Angew. Chem. Int. Ed. **42,** 5834 (2003)

Tuning the interference feature

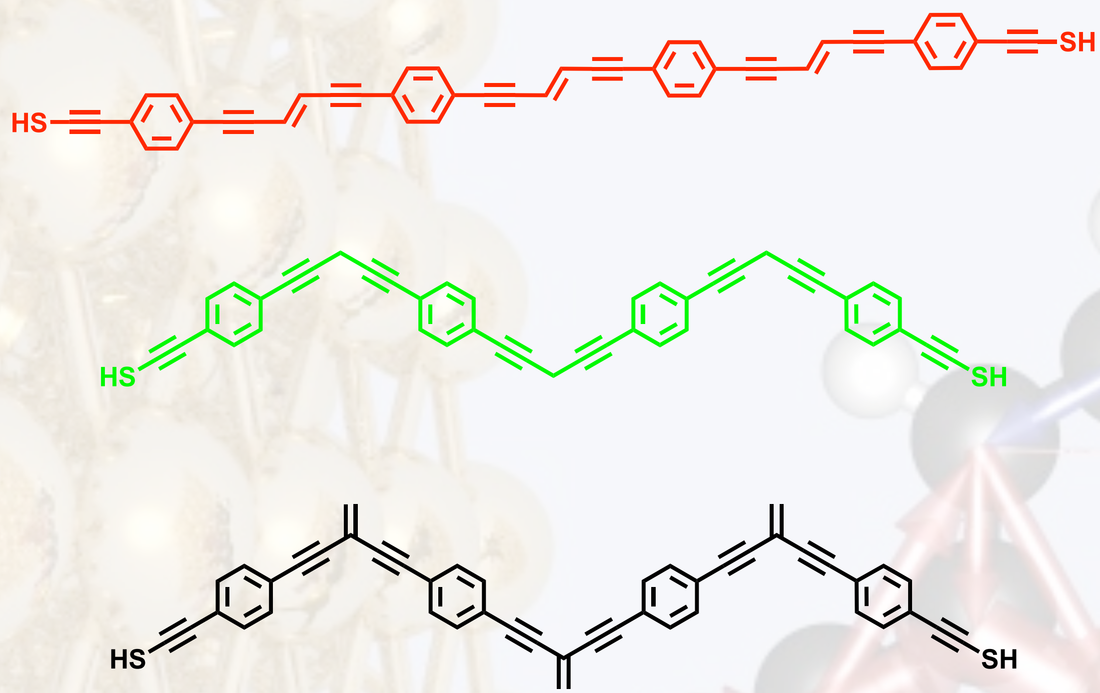


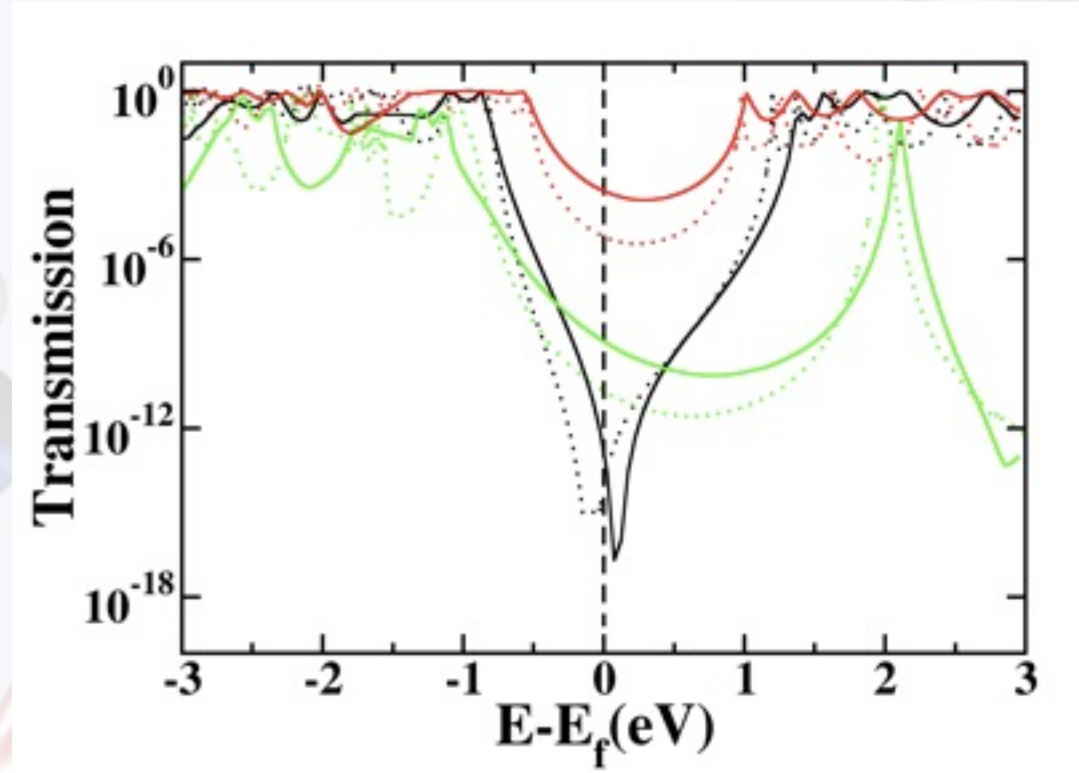
Hückel-IV

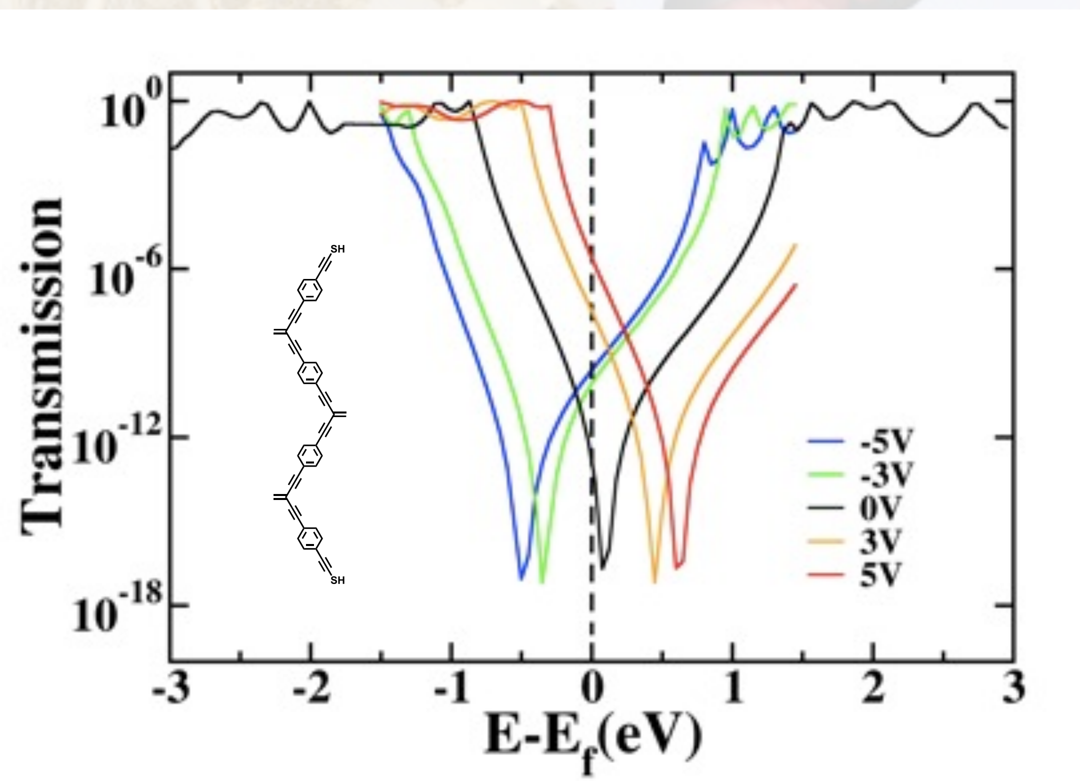
ATK

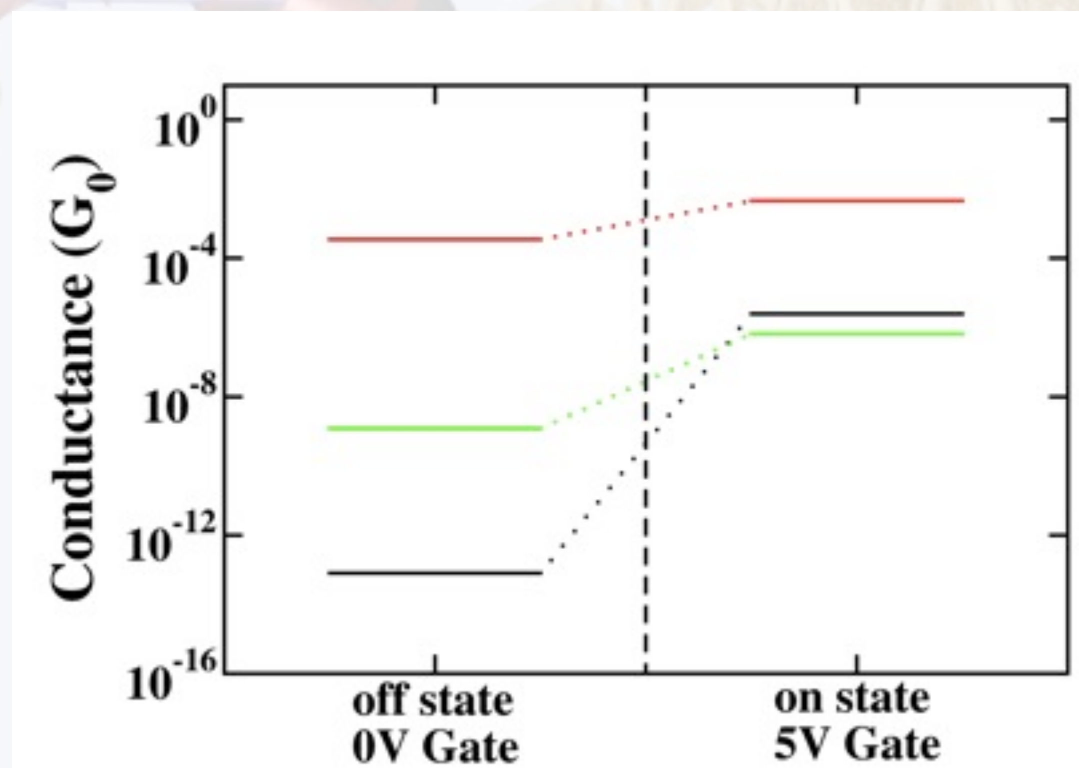
JACS **130**, 17309 (2008)

Voltage dependence



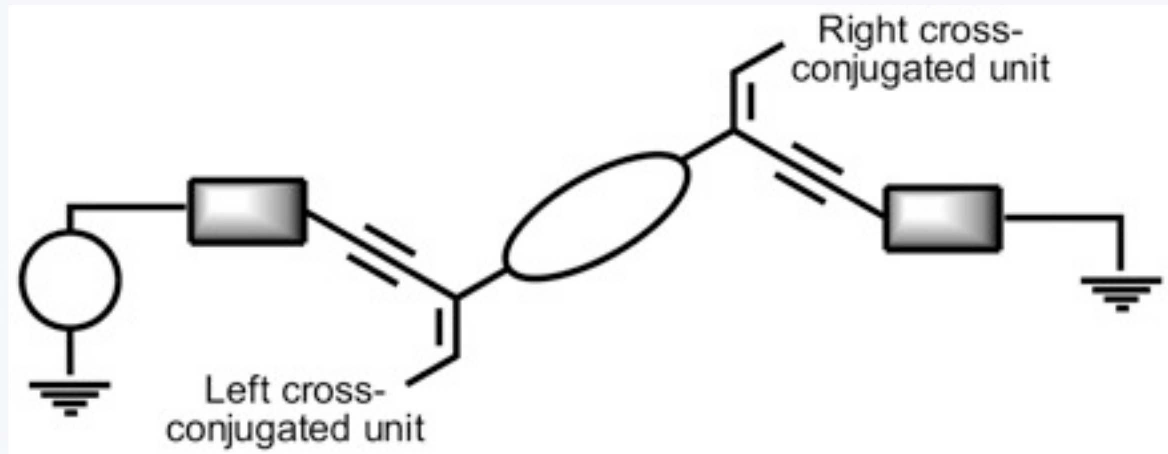


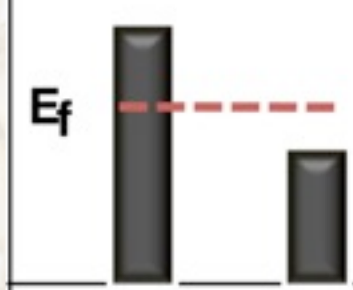




JACS **130**, 17309 (2008)

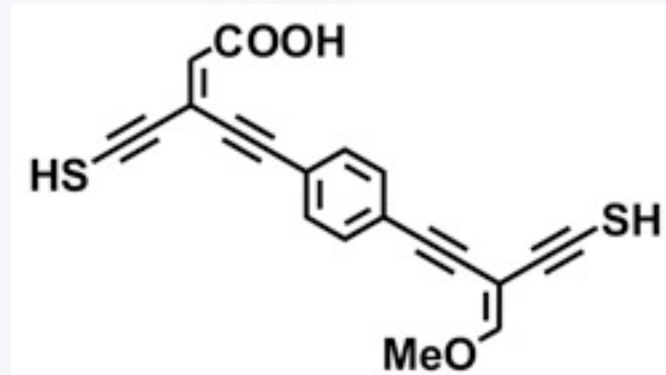
A Molecular Rectifier

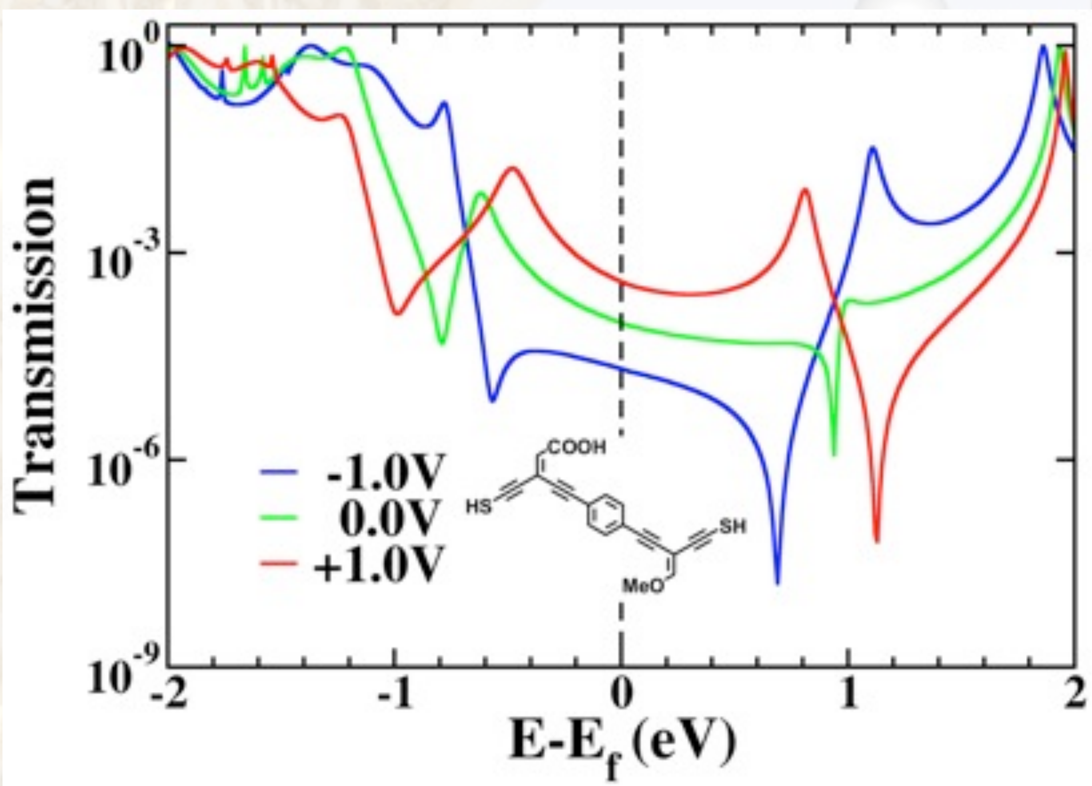


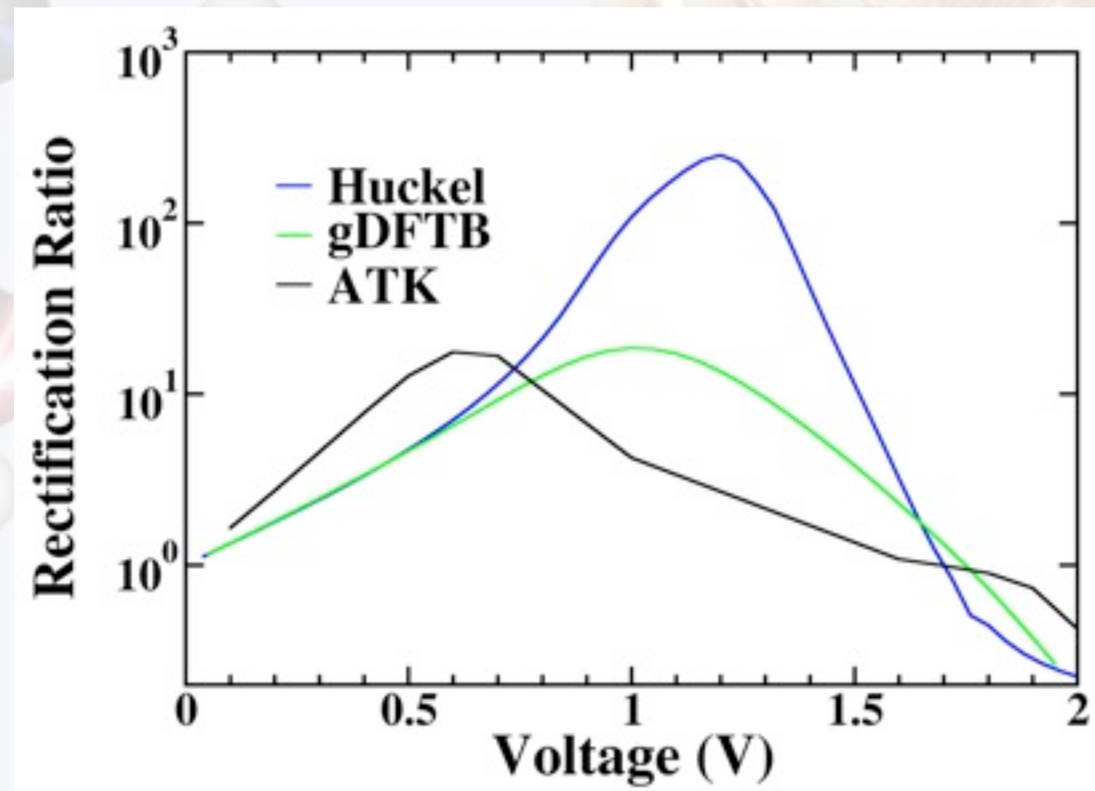
Change in interference position		
bias	Left cross-conjugated unit	Right cross-conjugated unit
	←	→
	→	←

JACS **130**, 17309 (2008)

A model system



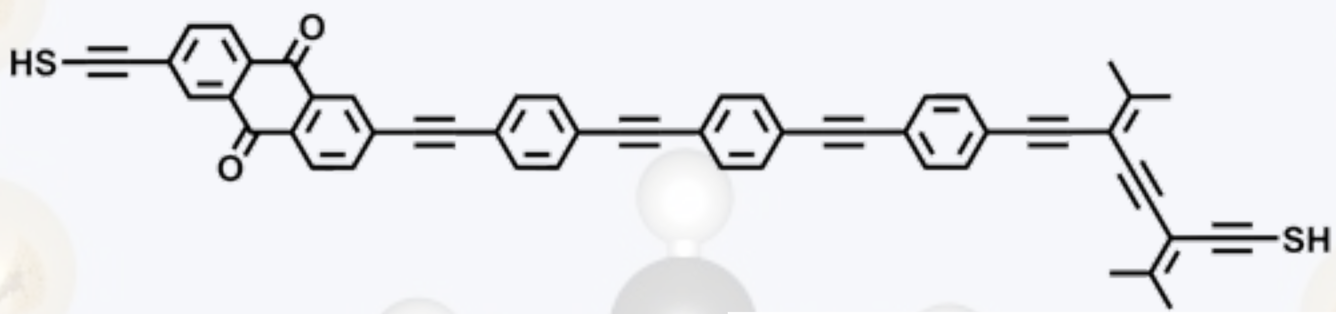


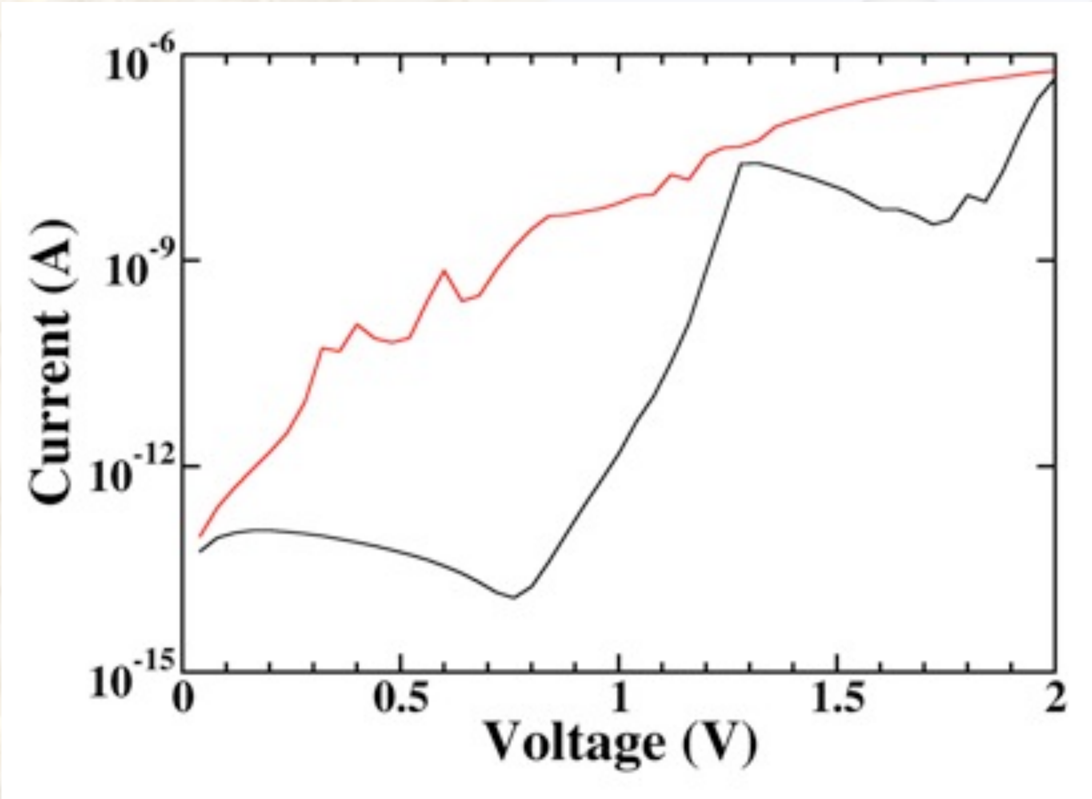


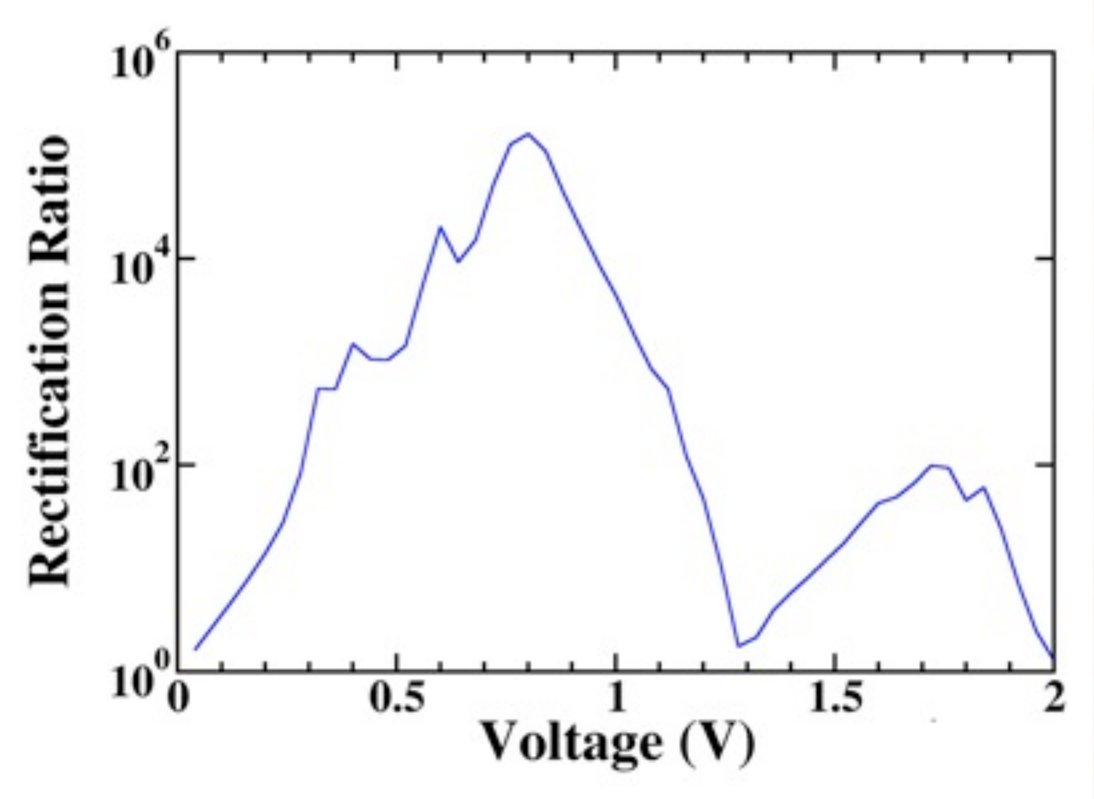
Code	Max. R. R.	Voltage
Hückel-IV	249	1.2 V
gDFTB	18.6	1.0 V
ATK	17.6	0.6 V

JACS **130**, 17309 (2008)

More striking results





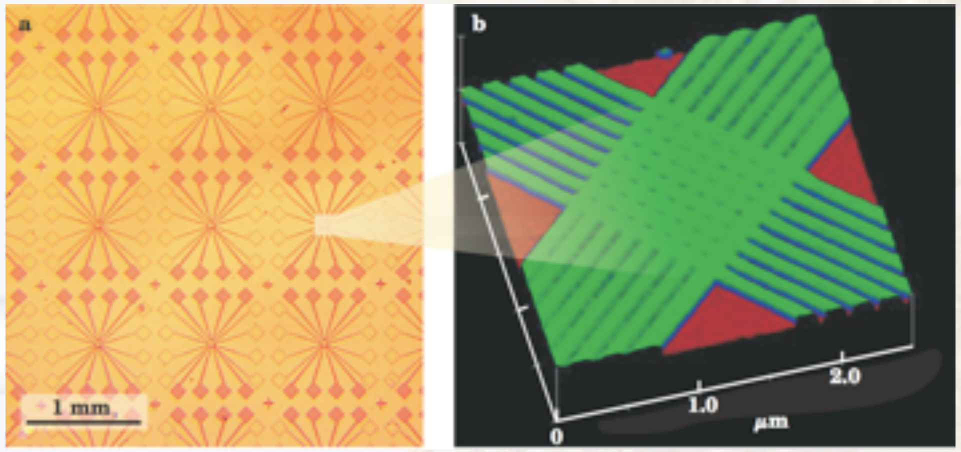


Code	Max. R. R.	Voltage
Hückel-IV	>150,000	0.8V
gDFTB	501	0.52V
ATK	83.5	1.5V

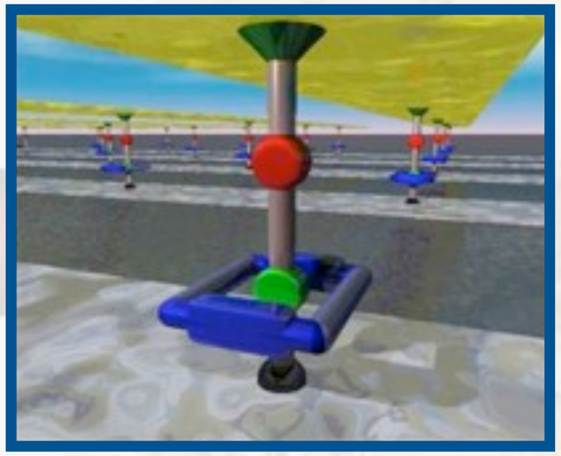
JACS **130**, 17309 (2008)

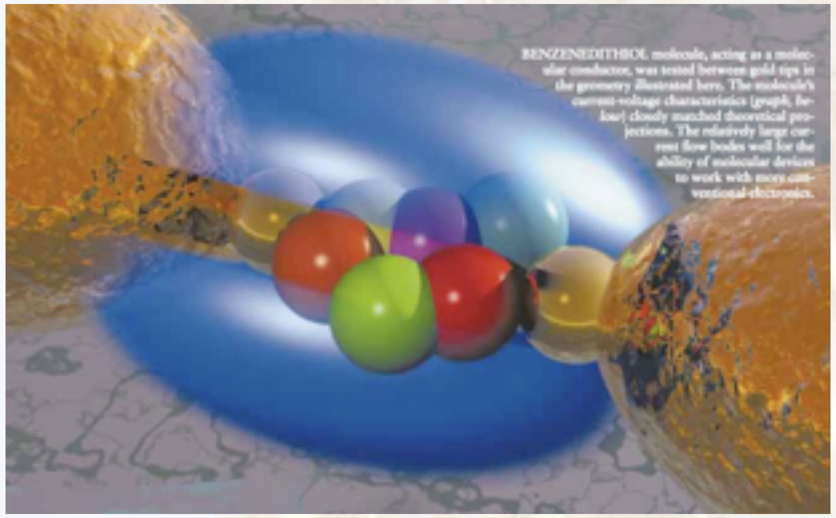
Designing molecular electronic devices....
....means assembling molecules

- Positioning single molecules between metallic electrodes is an enormous challenge.
- Controllable synthesis of really large molecules is another enormous challenge.
- Self-assembly of supramolecular structures or carefully constructed films seem to be a promising alternative.

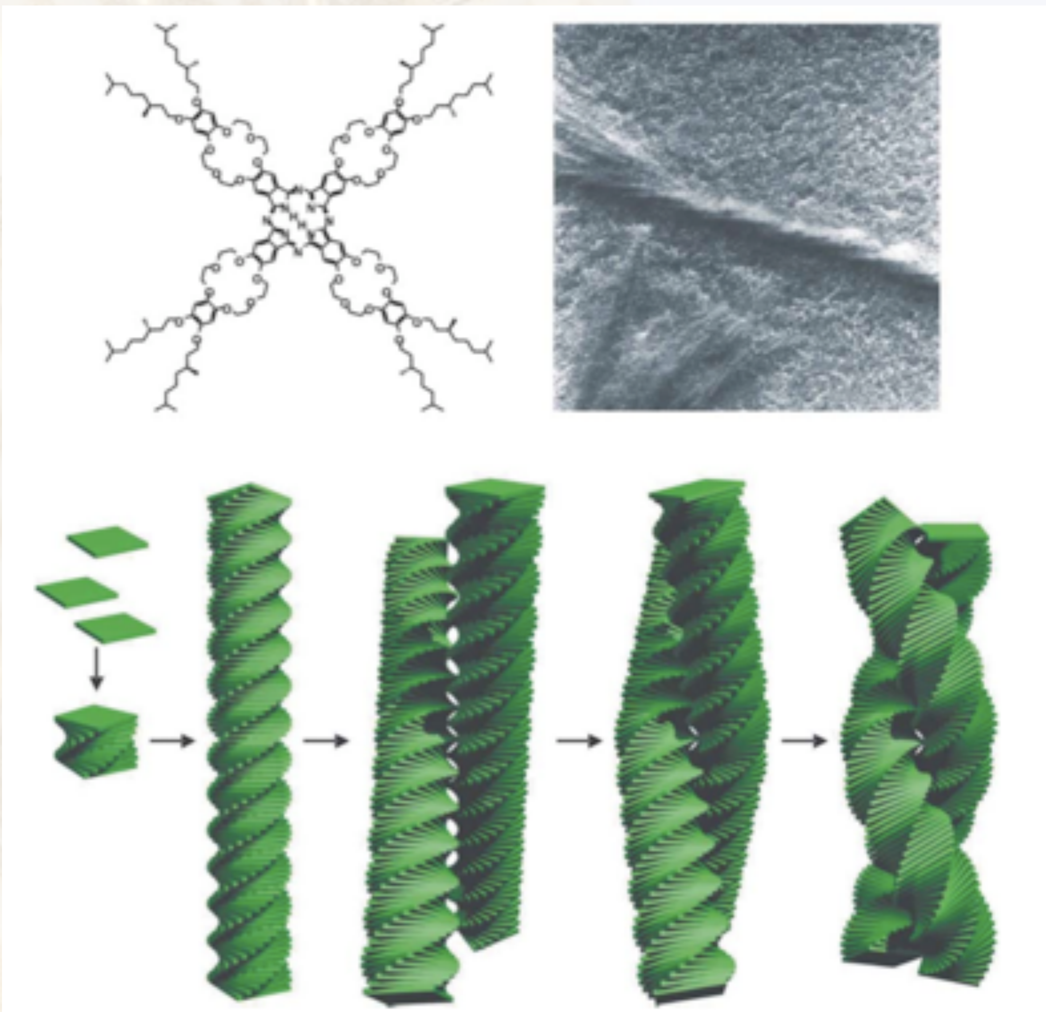


J. Heath and M. Ratner, Physics Today, May 2003


J. Heath

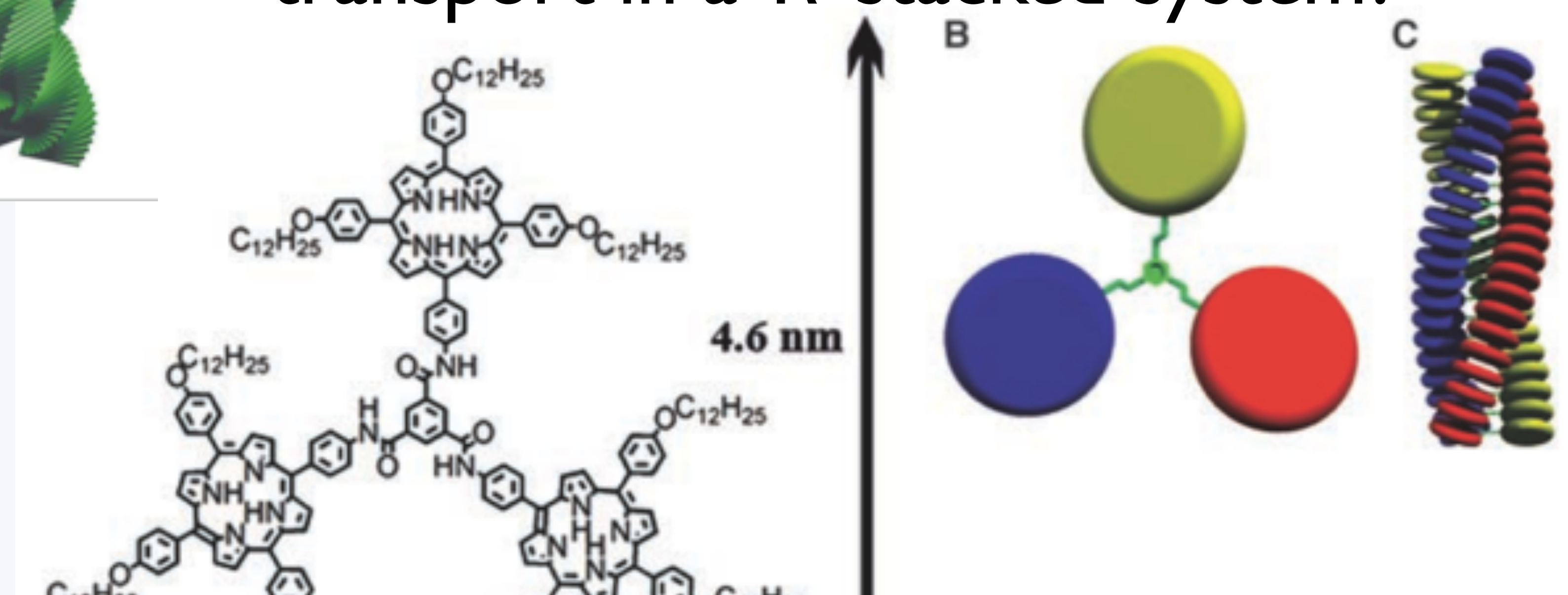

M. Reed and J. Tour Scientific American, June 2000

π-stacked structures are favorable for self-assembly



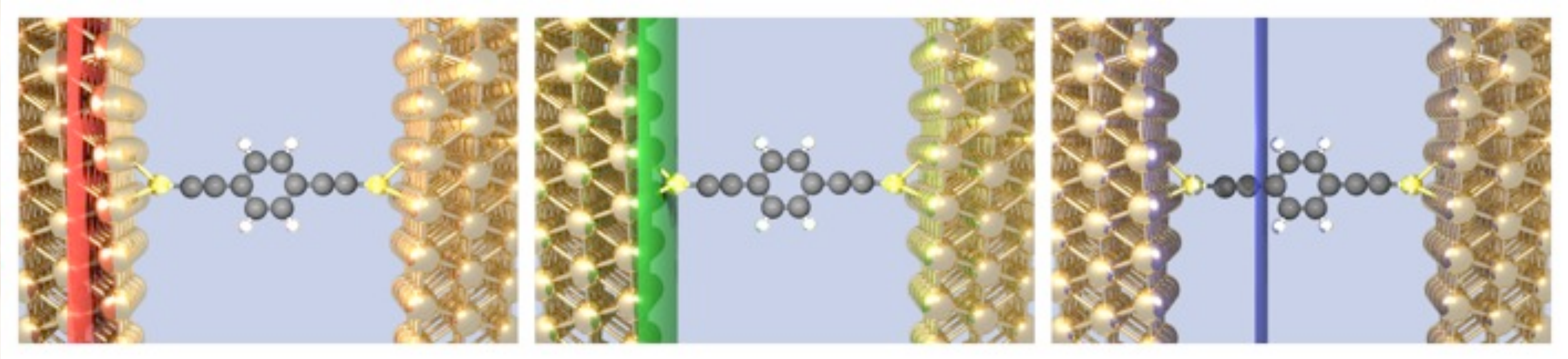
J. A. A. W. Elemans, A. E. Rowan and R. J. M. Nolte
J. Mater. Chem. (2003) **13** 2661

- Non-bonding interactions can be used to build extremely large structures.
- These structures have been suggested as architectures for charge transport.
- What is really desirable for charge transport in a π-stacked system?



R. van Hameren et al.
Science (2006) **314** 1433

Current through an arbitrary surface



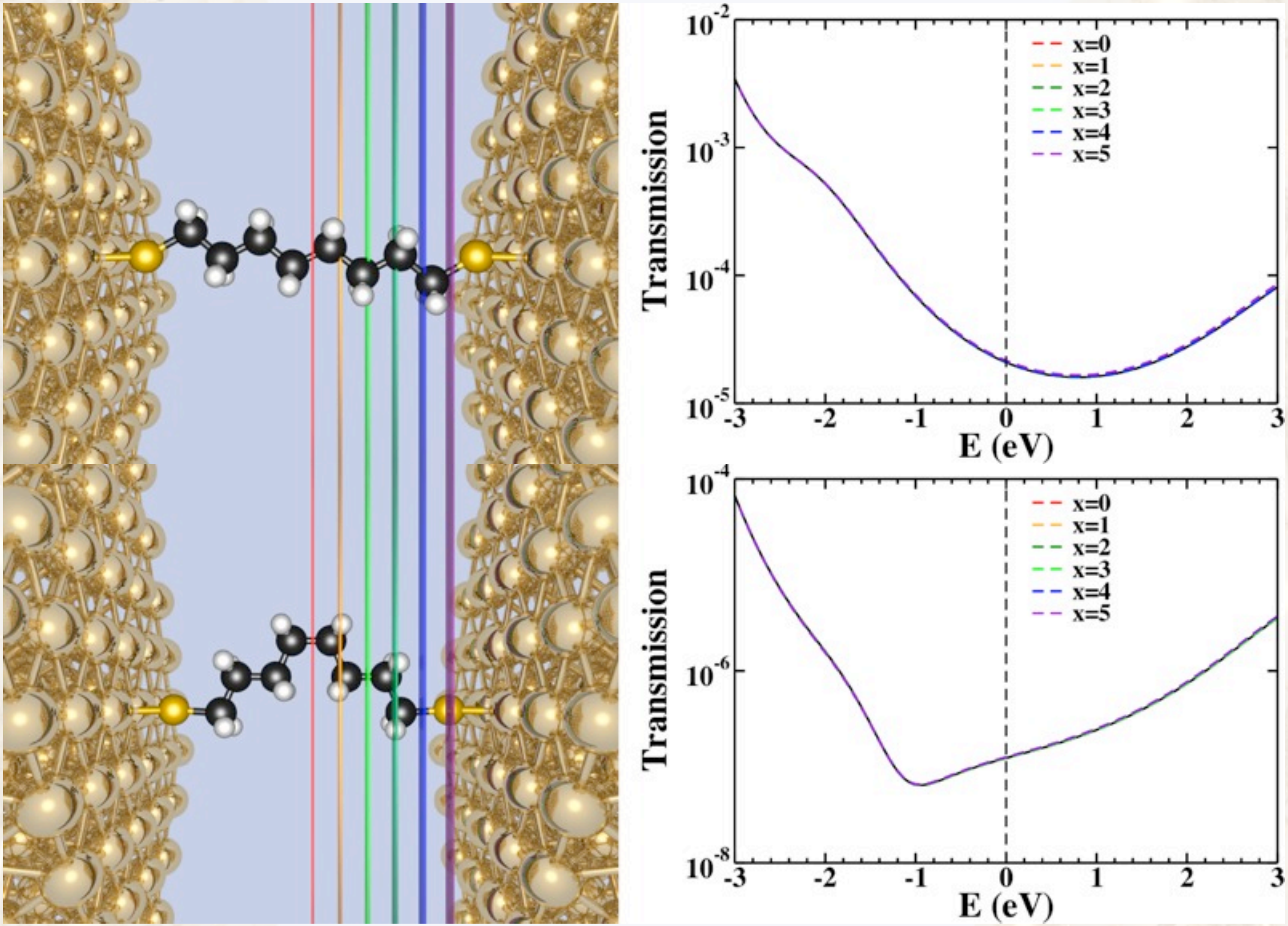
$$I_{mn} = \frac{2e}{\hbar} \int \frac{d\varepsilon}{2\pi} K_{mn}(\varepsilon) \qquad I = \frac{2e}{h} \sum_{m \in M_L} \sum_{n \in M_R} \int d\varepsilon K_{mn}(\varepsilon)$$

$$\sum_{m \in M_L} \sum_{n \in M_R} K_{mn}(\varepsilon) = (f_L(\varepsilon) - f_R(\varepsilon)) T(\varepsilon)$$

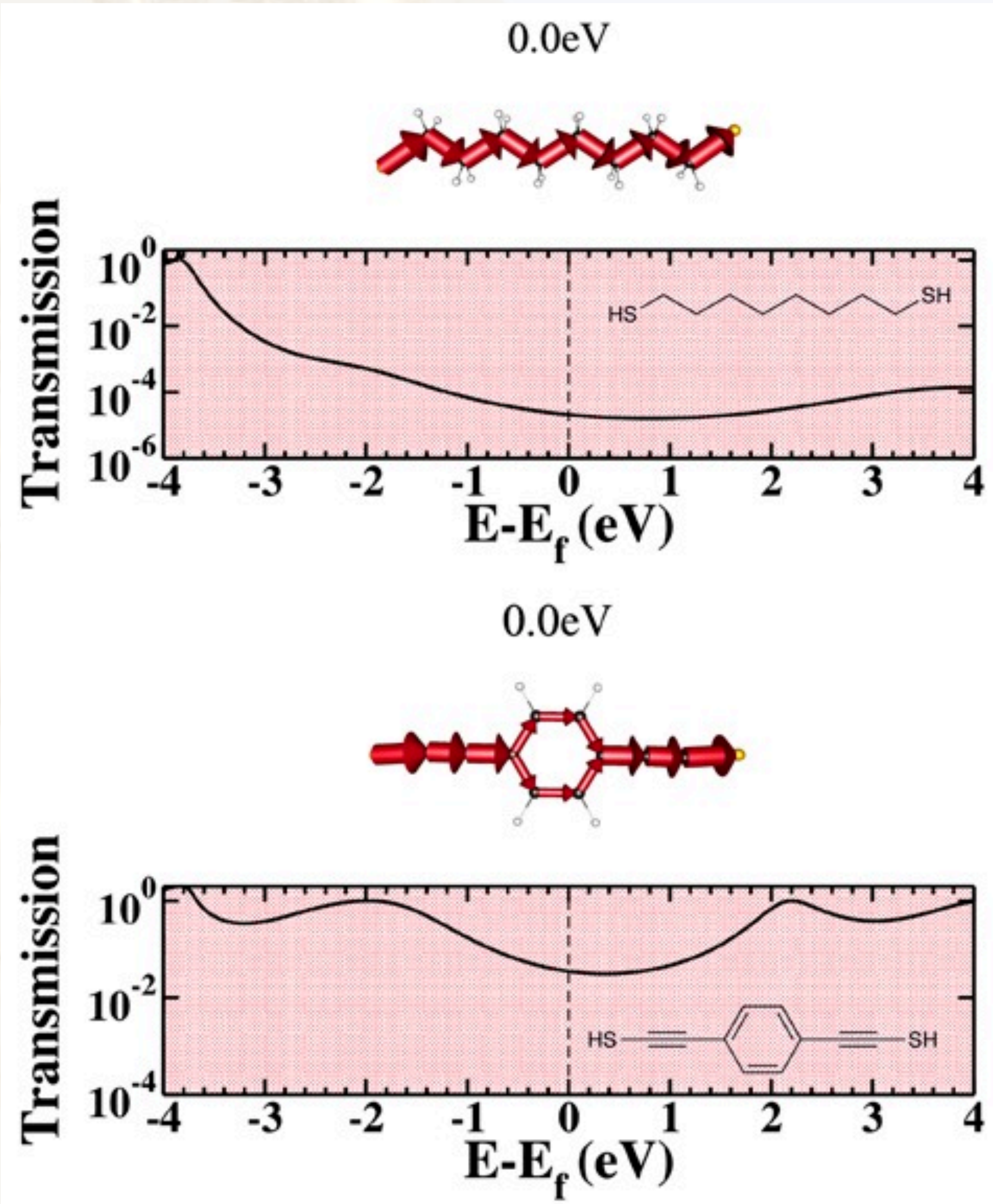
$$K_{mn}(\varepsilon) = \sum_{i \in m} \sum_{\substack{j \in n \\ n \neq m}} \sum_{kl} (i f_L (V_{ij} G^r_{jk} \Gamma^L_{kl} G^a_{li} - V_{ji} G^r_{il} \Gamma^L_{lk} G^a_{kj})$$
$$- i f_R (V_{ji} G^r_{il} \Gamma^R_{lk} G^a_{kj} - V_{ij} G^r_{jk} \Gamma^R_{kl} G^a_{lj}))$$

Nature Chem. **2**, 223-228 (2010)

Conservation



What does local transmission look like?

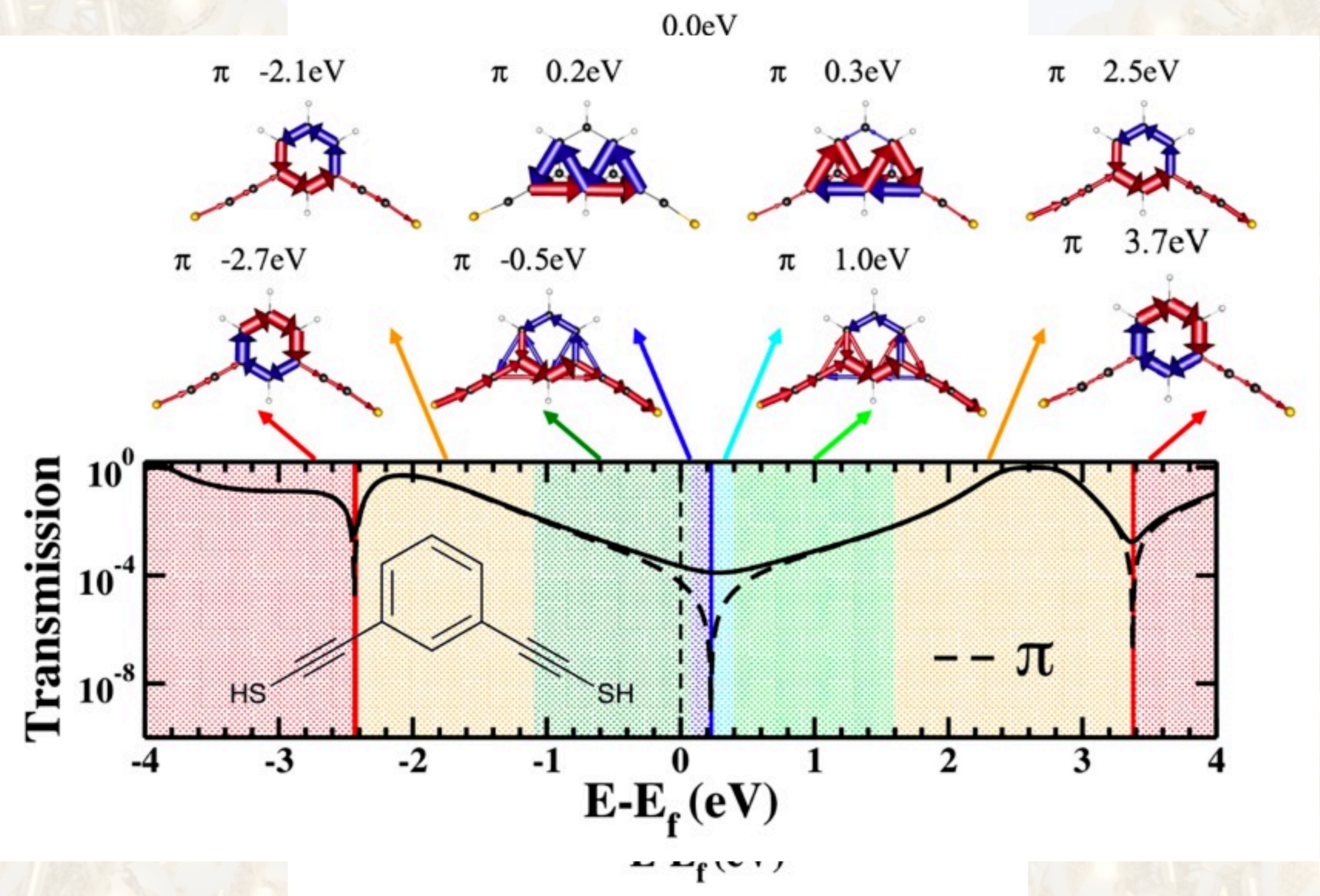


A note about local transmission plots:

- The radius of the arrow is proportional to the magnitude of the local transmission
- The arrows are normalized so the largest component in each picture is the same size.
- The arrows are only shown for elements that are greater than 10% of the maximum local transmission element.
- The arrows are sometimes coloured red and blue to indicate transmission in the forward and reverse direction.

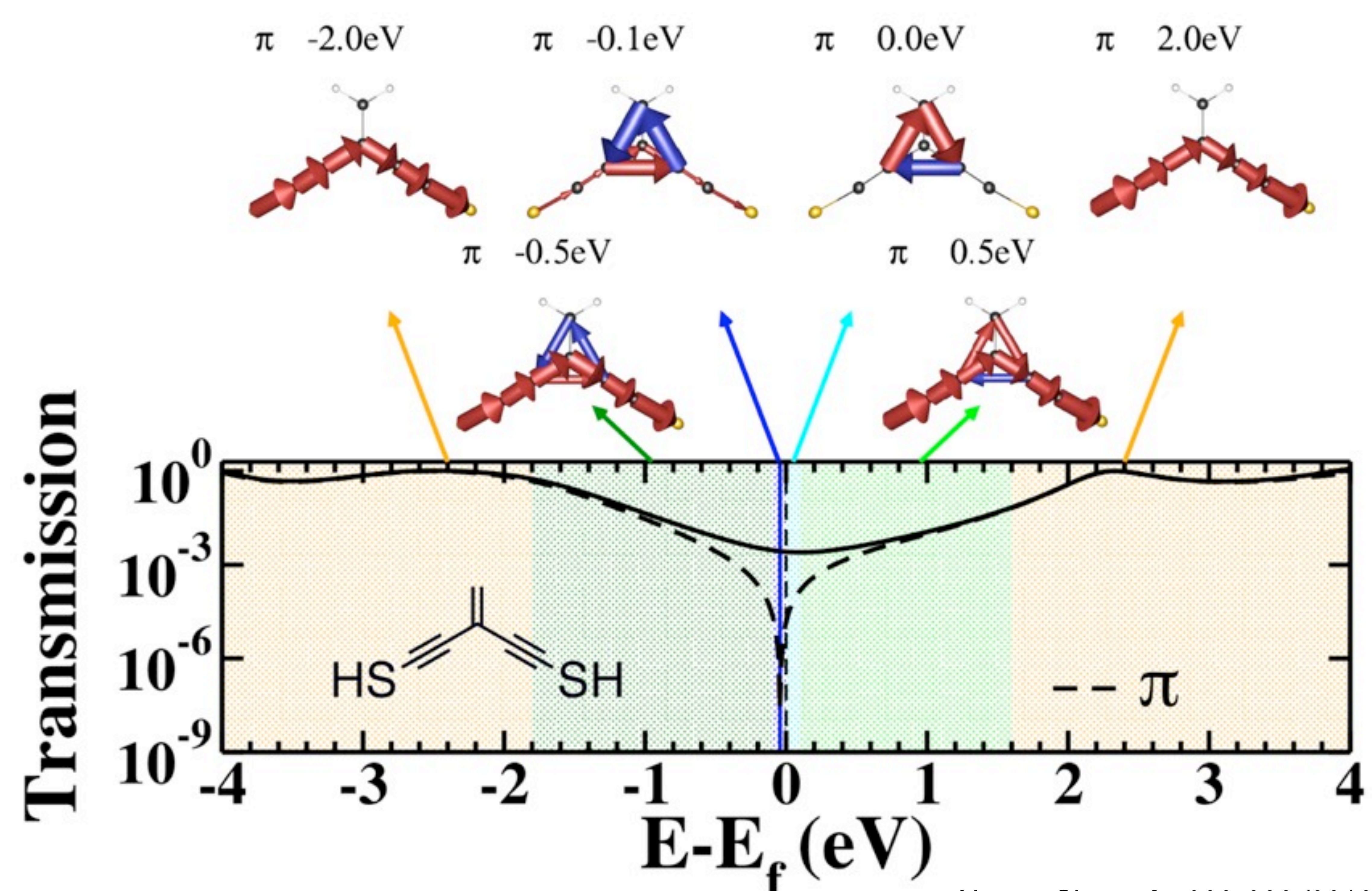
Nature Chem. **2**, 223-228 (2010)

What does local transmission look like?



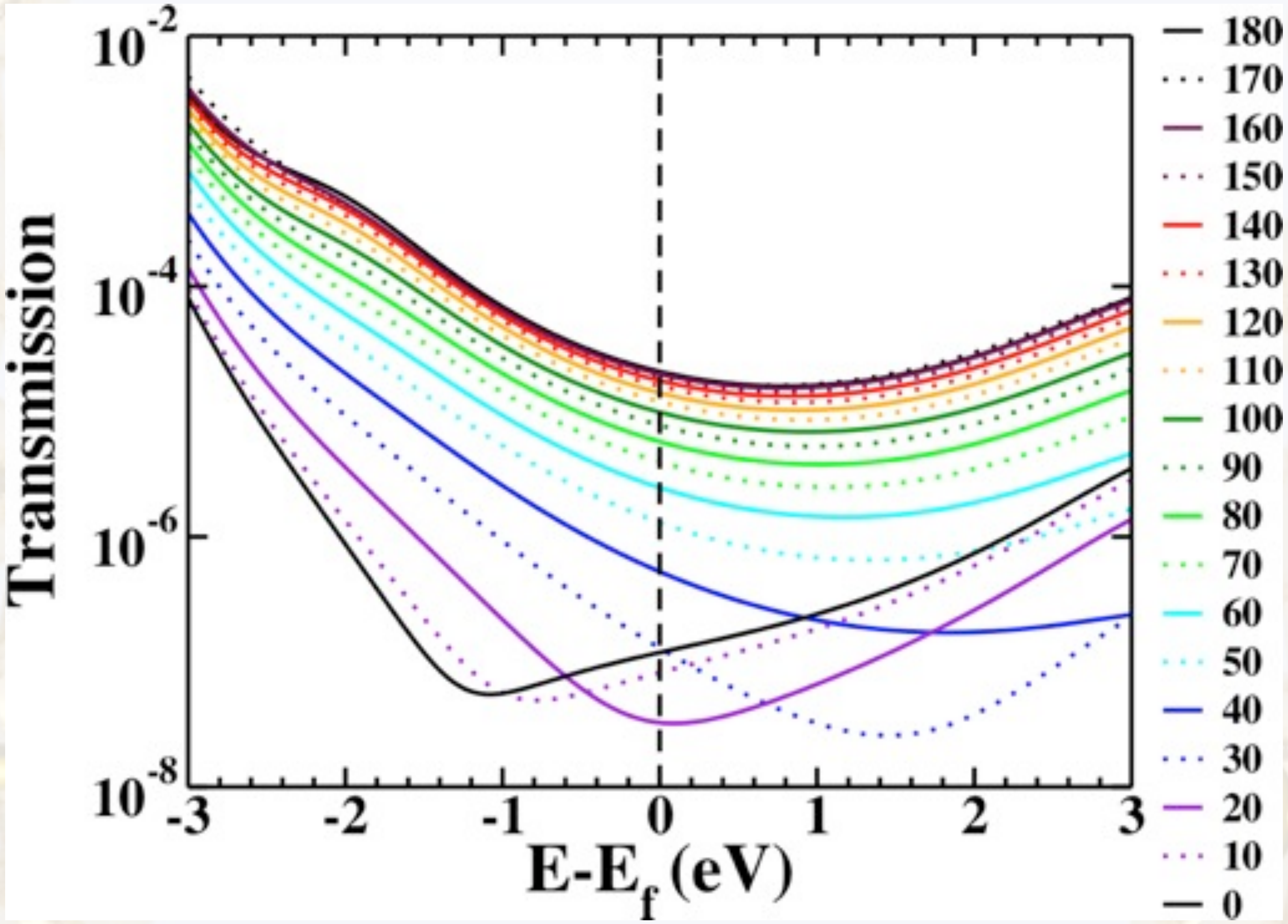
Nature Chem. **2**, 223-228 (2010)

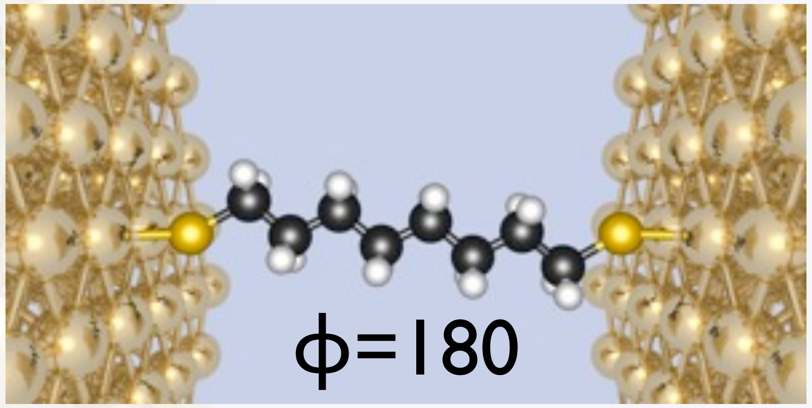
Similar behavior

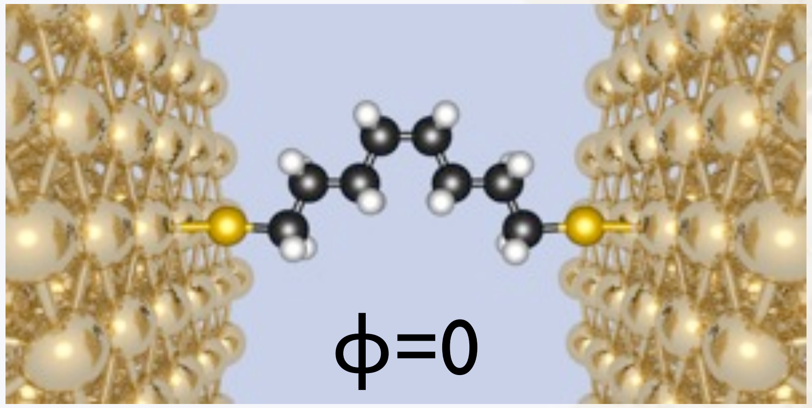


Nature Chem. **2**, 223-228 (2010)

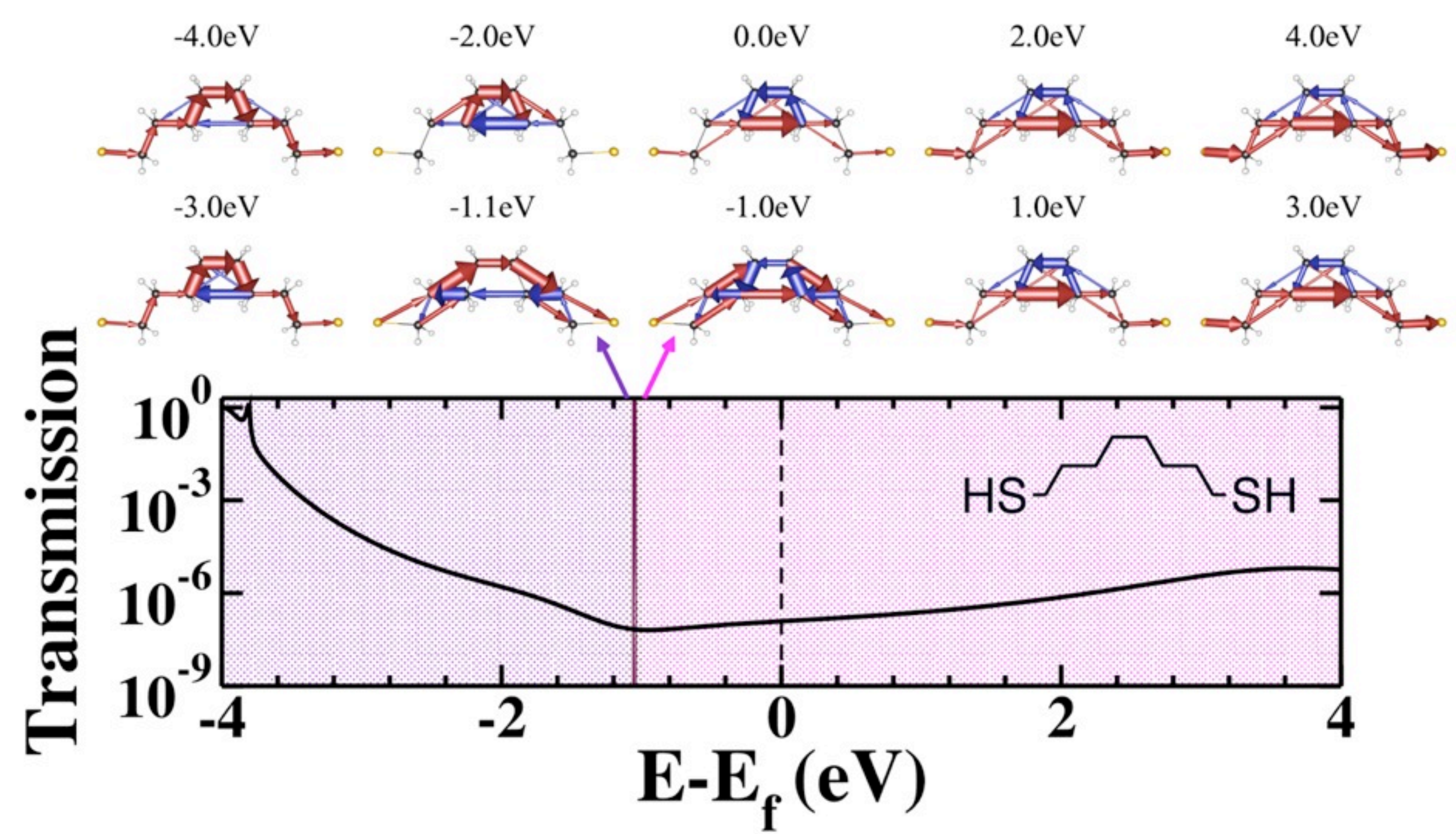
σ-systems can be unusual too





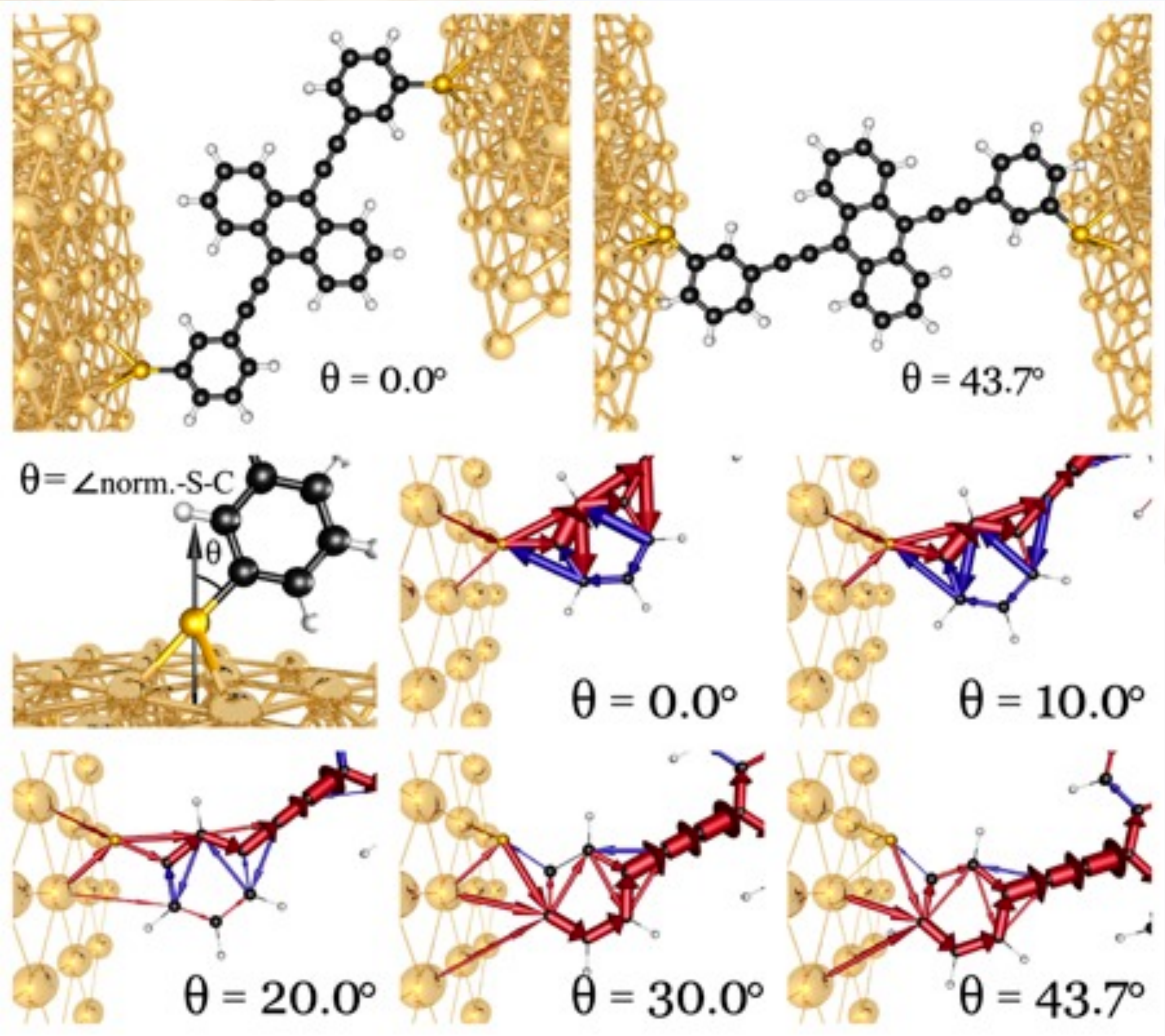


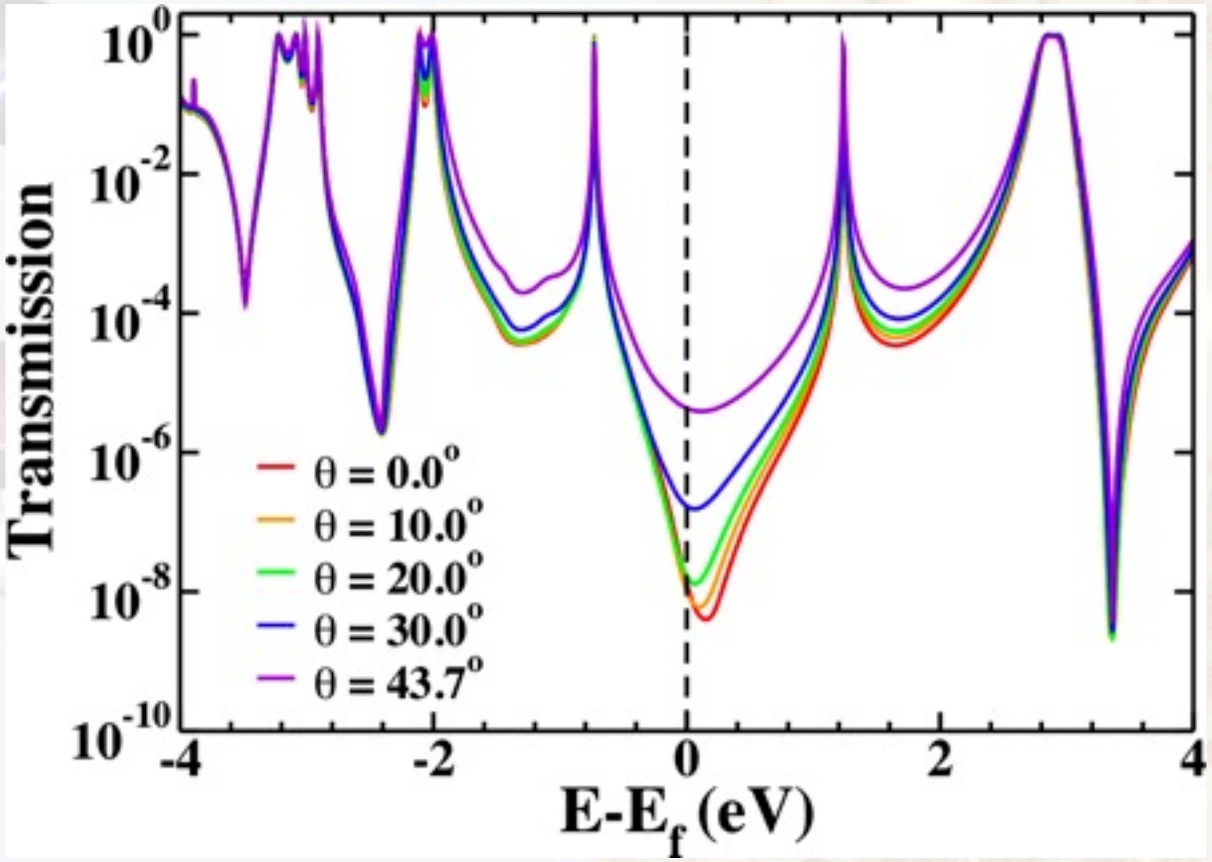
We can see the signature of interference



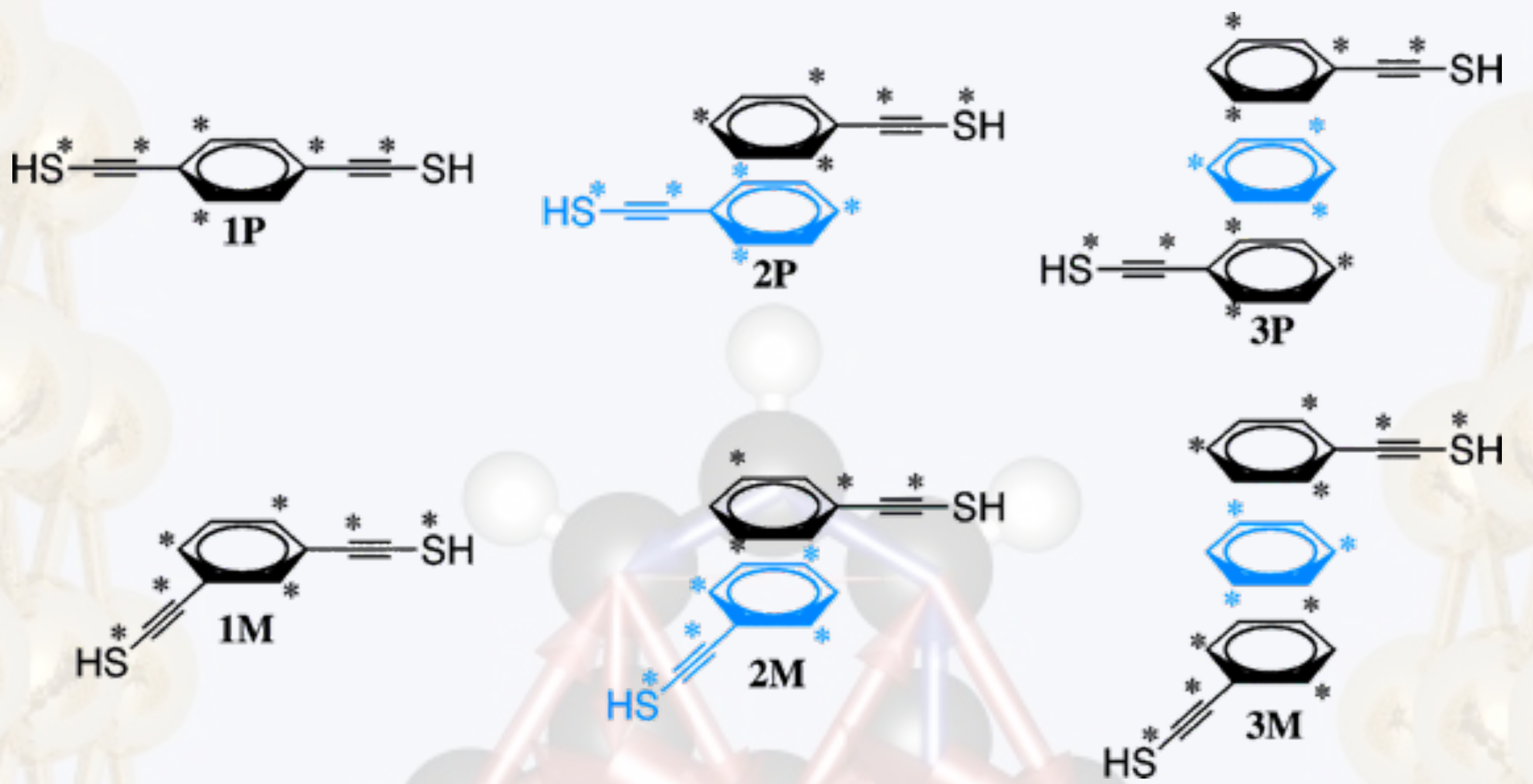
Nature Chem. **2**, 223-228 (2010)

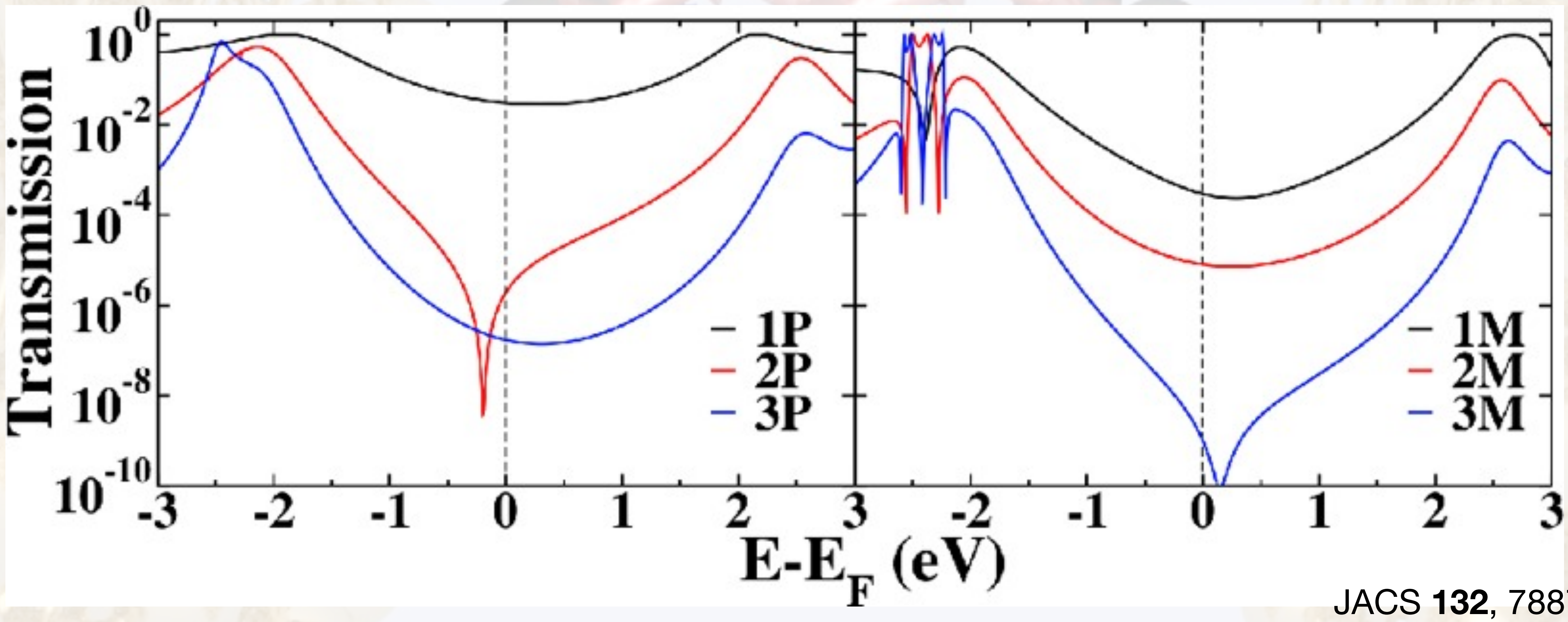
Non-bonding interactions can also hurt transport





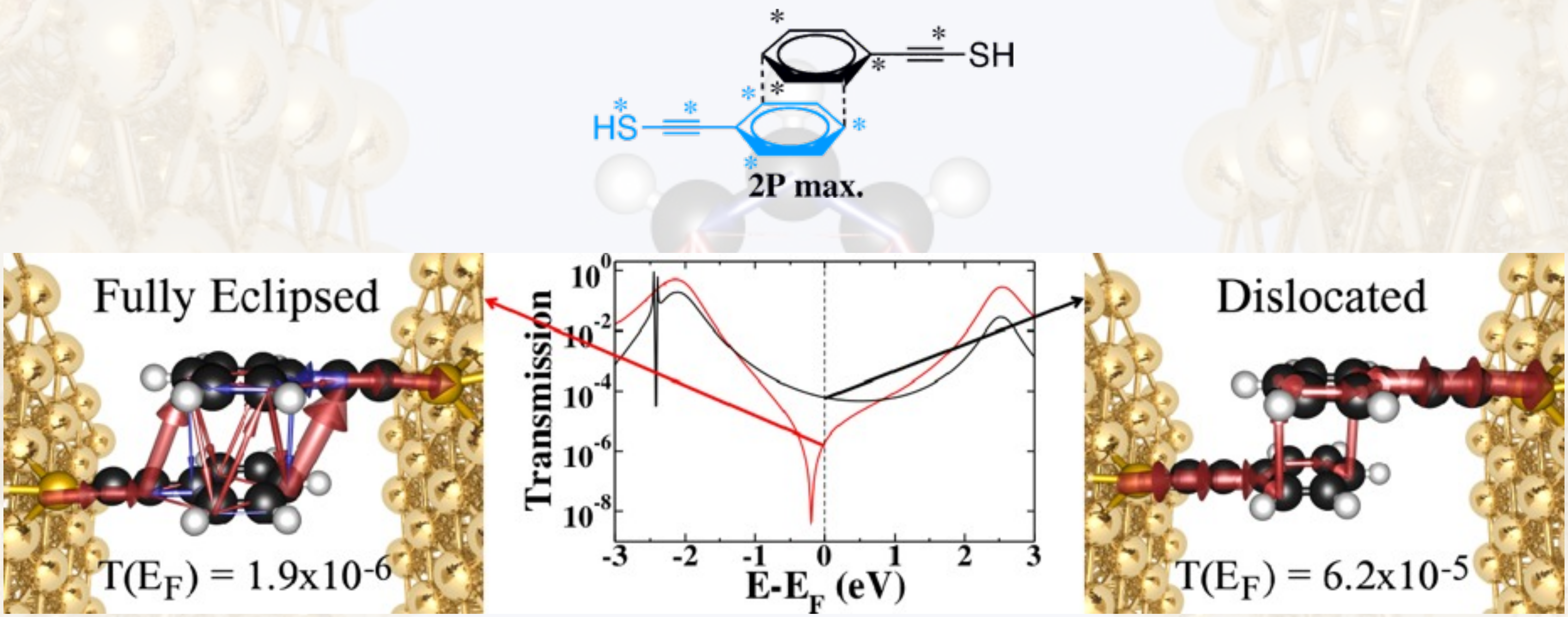
Take a simple series





JACS **132**, 7887 (2010)

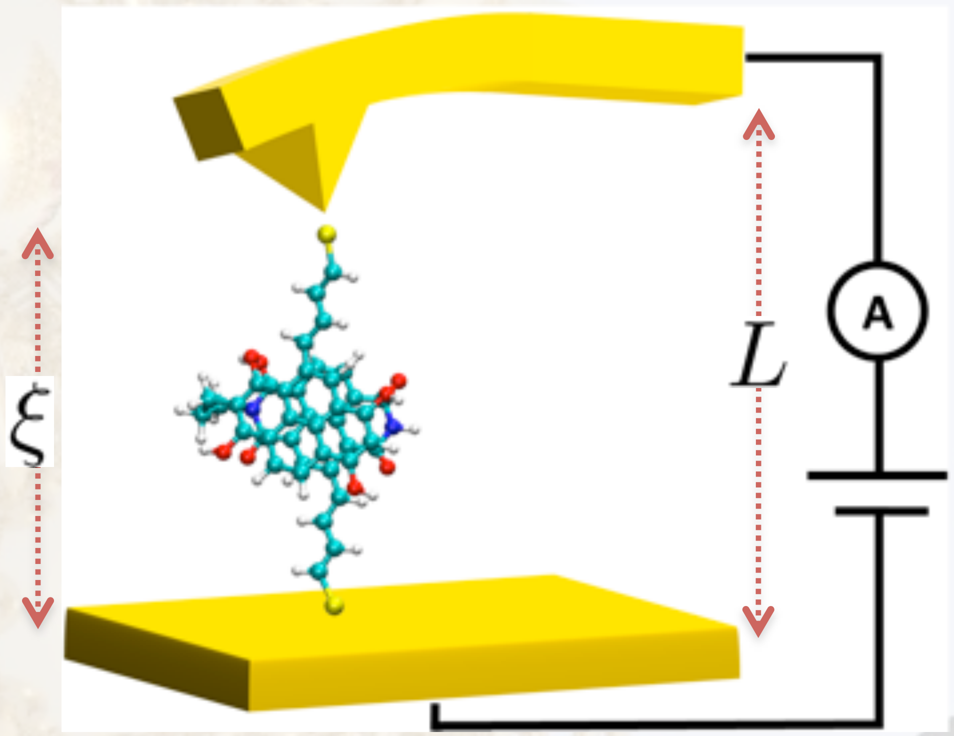
Increasing transmission by reducing overlap



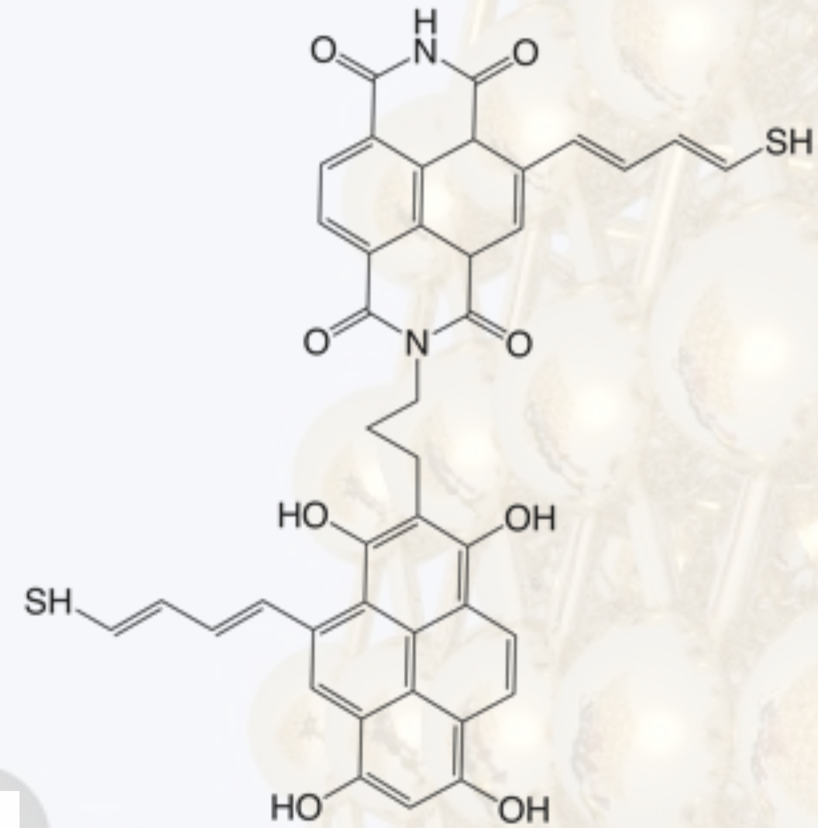
JACS **132**, 7887 (2010)

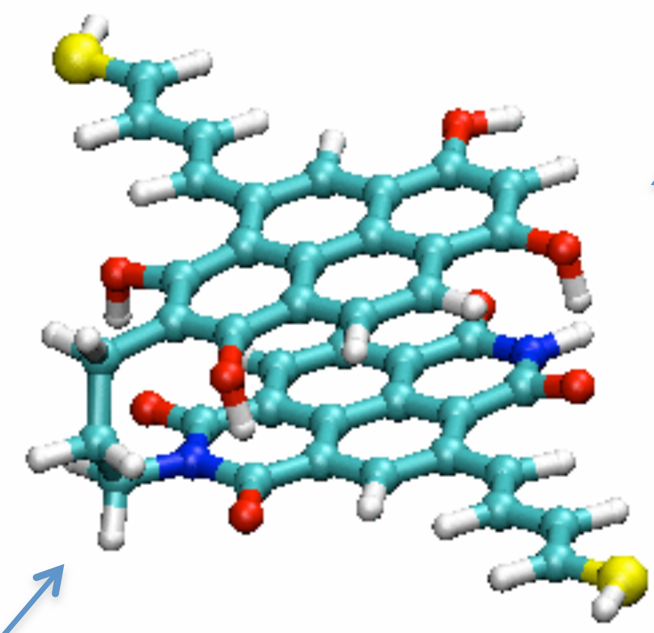
Putting it all together

conducting AFM



Au surface





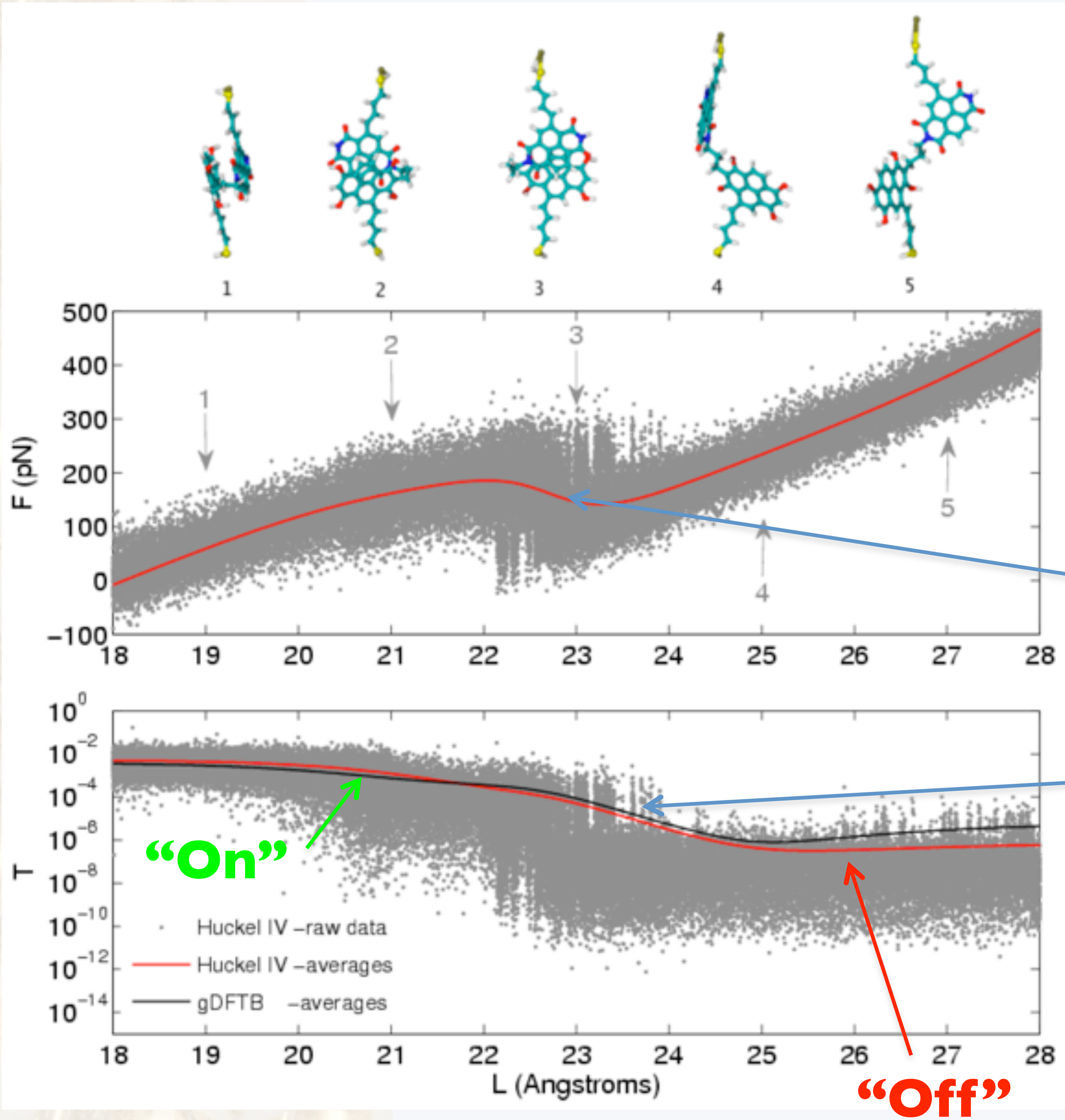
Hydrogen bonds stabilize the π-stacker

short aliphatic chain forces alignment between aromatic units

Alkene-thiols connect the stacker to the Au contacts

JACS **133**, 2242 (2011)

Mechanically activated molecular switch



pulling speed ~ 10^{-6} Å/ps
k = 1.1 N/m

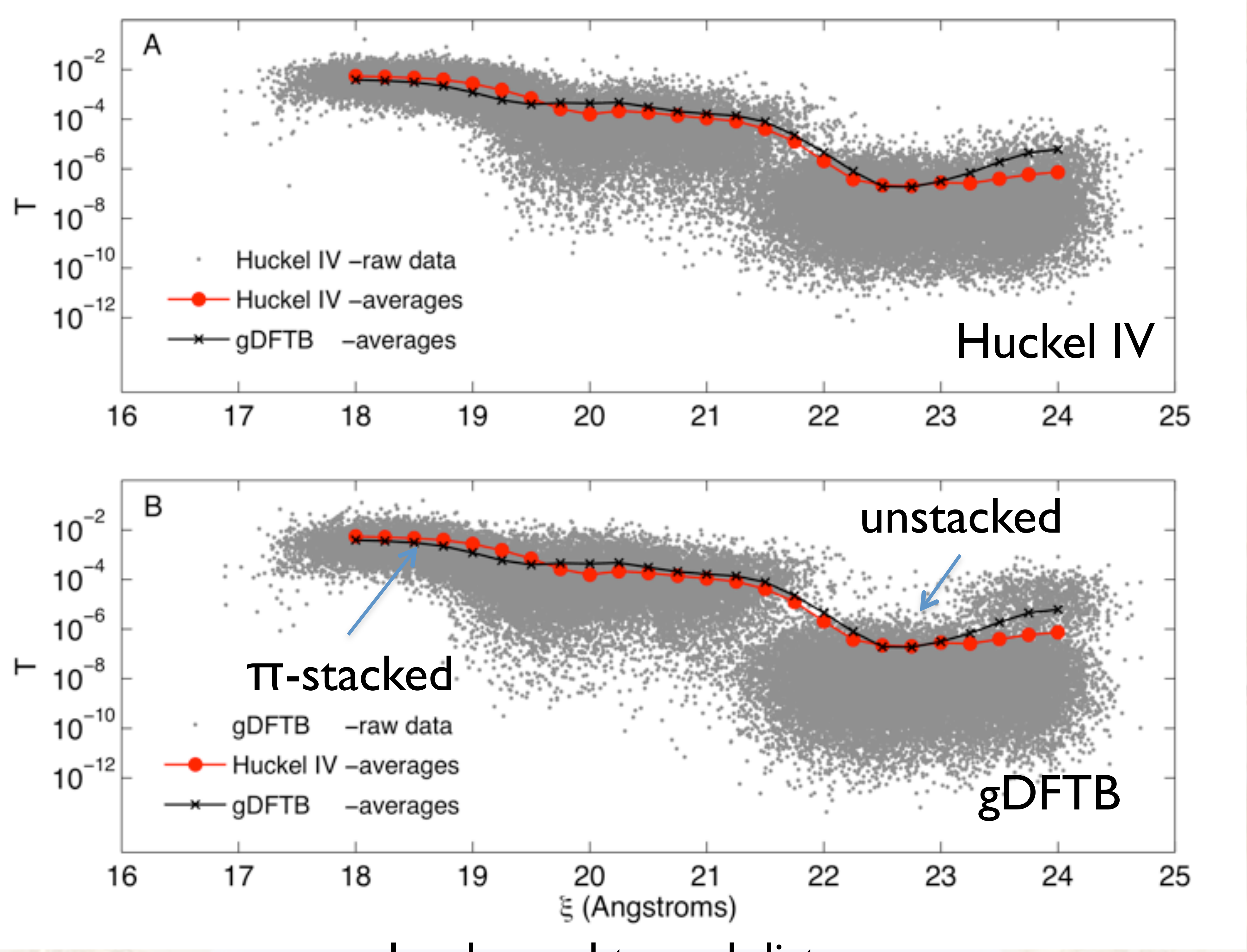
unfolding

Drop of 3-4 orders of magnitude

Note: the size of the fluctuations

JACS **133**, 2242 (2011)

Agreement between transport methods

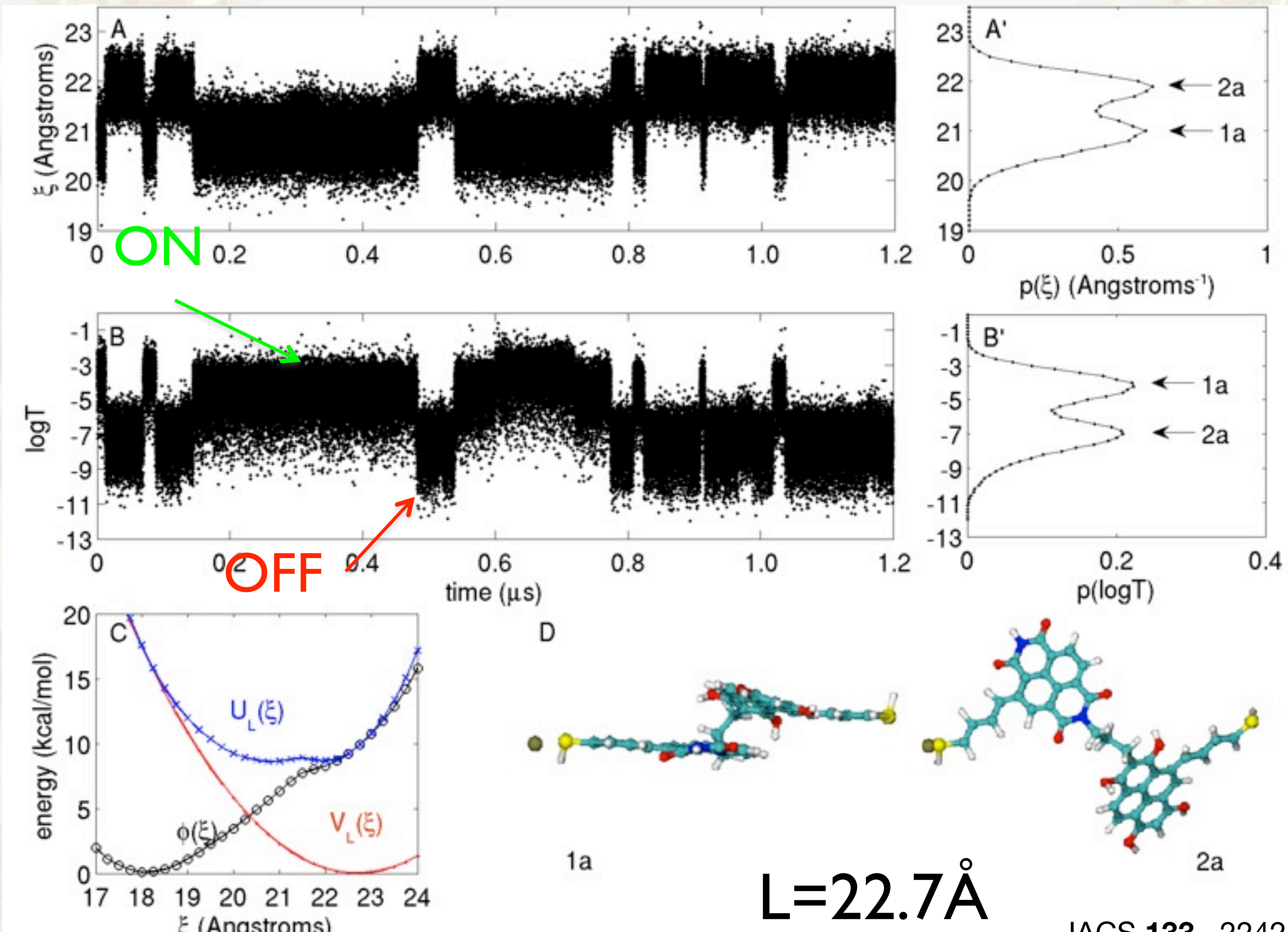


molecular end to end distance

Methods agree in average, disagree for individual conformations

JACS **133**, 2242 (2011)

Bistability leads to blinking in the conductance

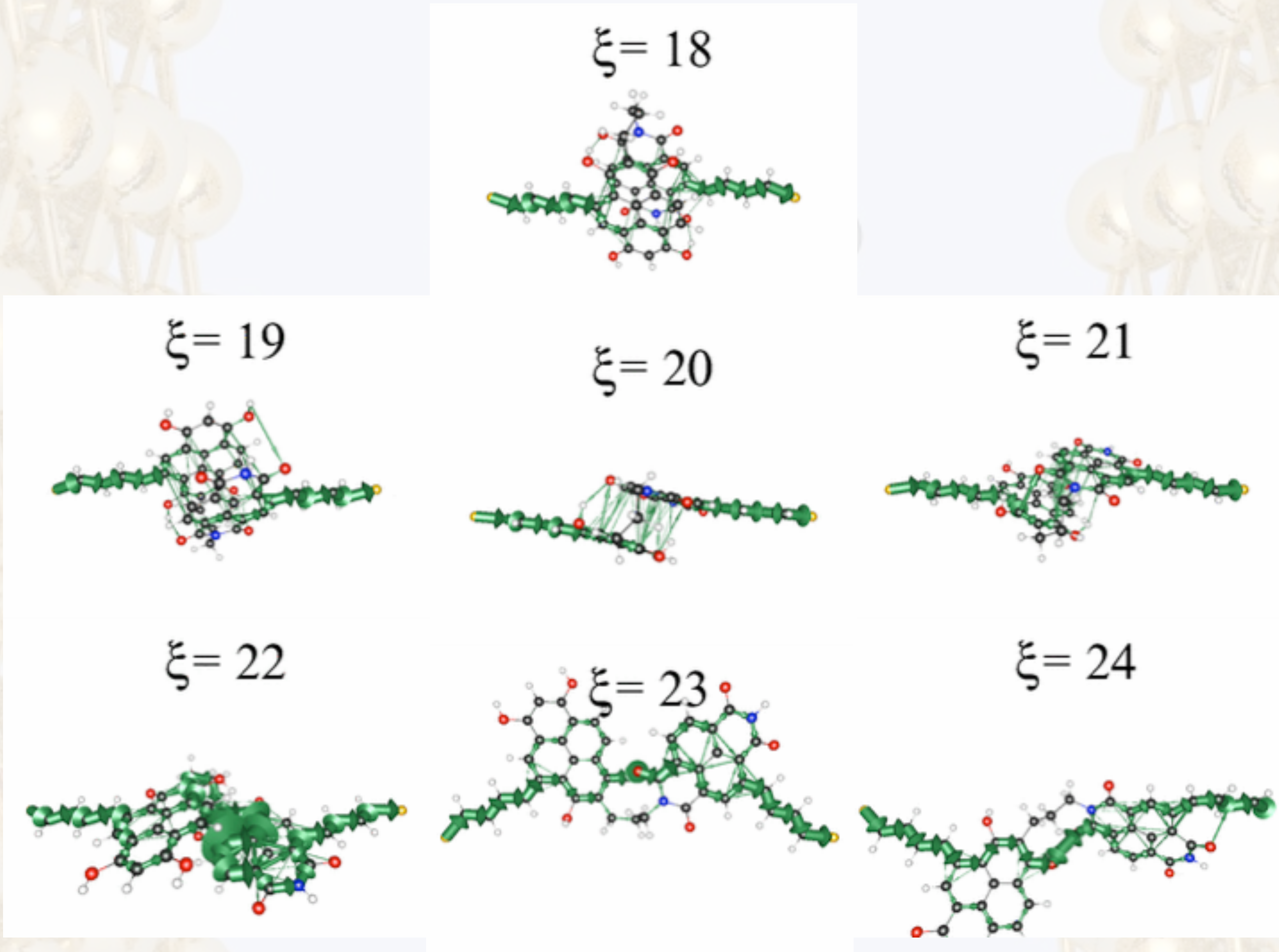


L=22.7Å

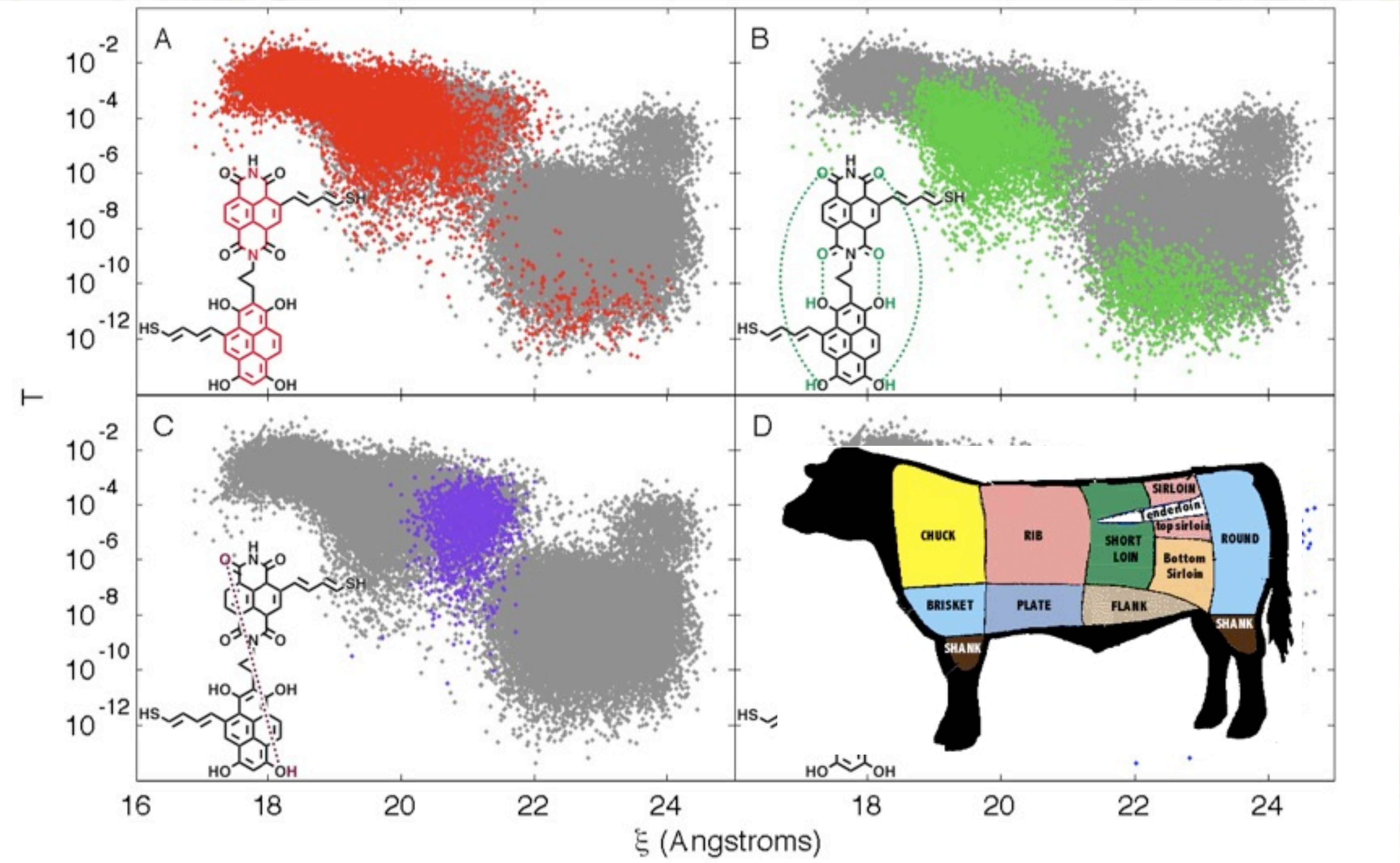
JACS **133**, 2242 (2011)

J. Am. Chem. Soc. **133**, 2242-2249 (2011)

Average transmission at fixed extension



The cow diagram: understanding transport domains



JACS **133**, 2242 (2011)

Conclusions and future work

- Finding the right molecule for the job is important for optimizing electronic function in molecular electronic devices.

- Quantum interference in molecules offers interesting possibilities for tuning electrical properties.

- This effect seems to be robust, but the question remains as to what interesting properties we might also be able to get out of the inelastic transport through these systems.

Acknowledgements

Mark Ratner

David Andrews, Carmen Herrman, Thorsten Hansen, Josh Vura-Weis, Randall Goldsmith, Ignacio Franco, Christopher George

Michael Wasielewski, Richard Van Duyne, Vladimiro Mujica, George Schatz

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DoE, NSF-Chemistry, NSF-MRSEC, ONR-Chemistry, DFG

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