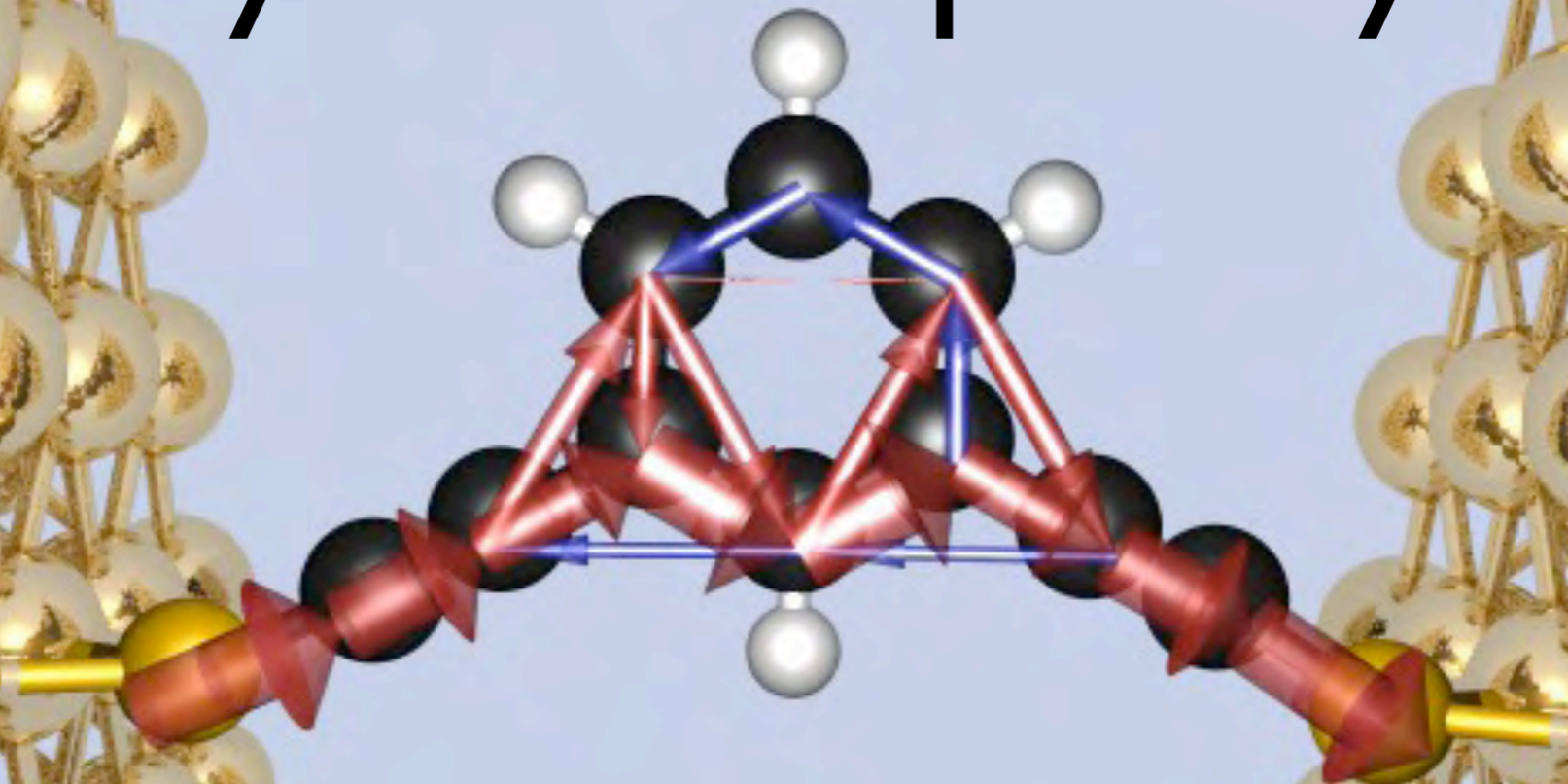
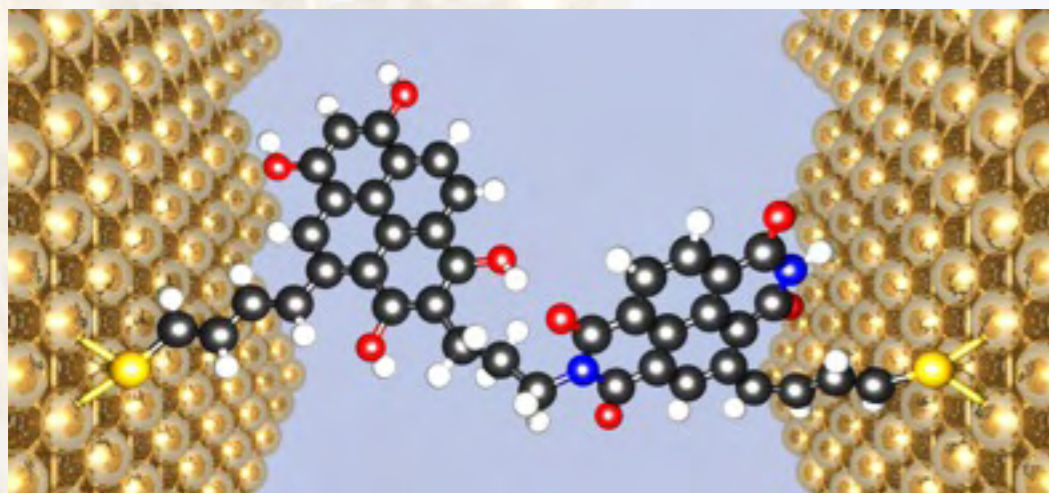


Mapping electron transport pathways in complex systems



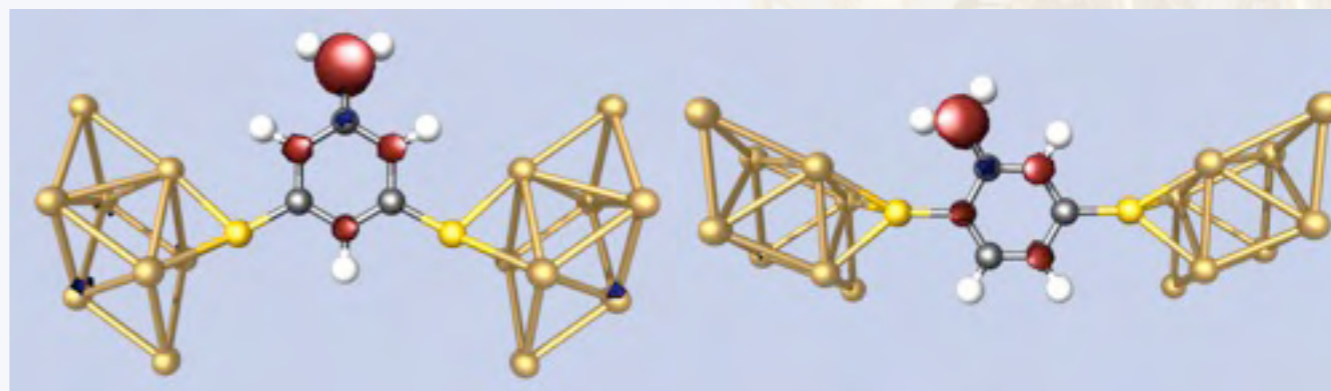
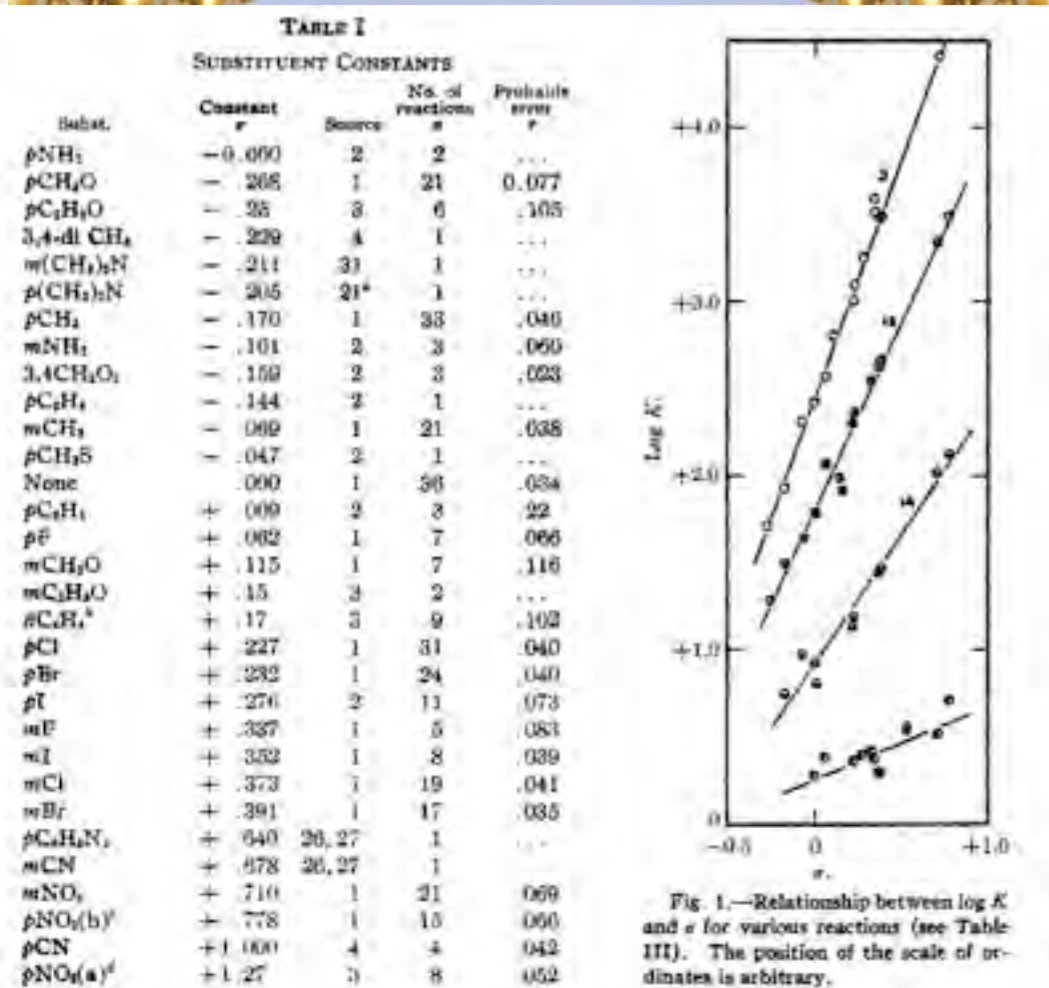
Gemma C. Solomon
Nano Science Centre and Department of Chemistry
University of Copenhagen

Local properties are central in our understanding of chemistry

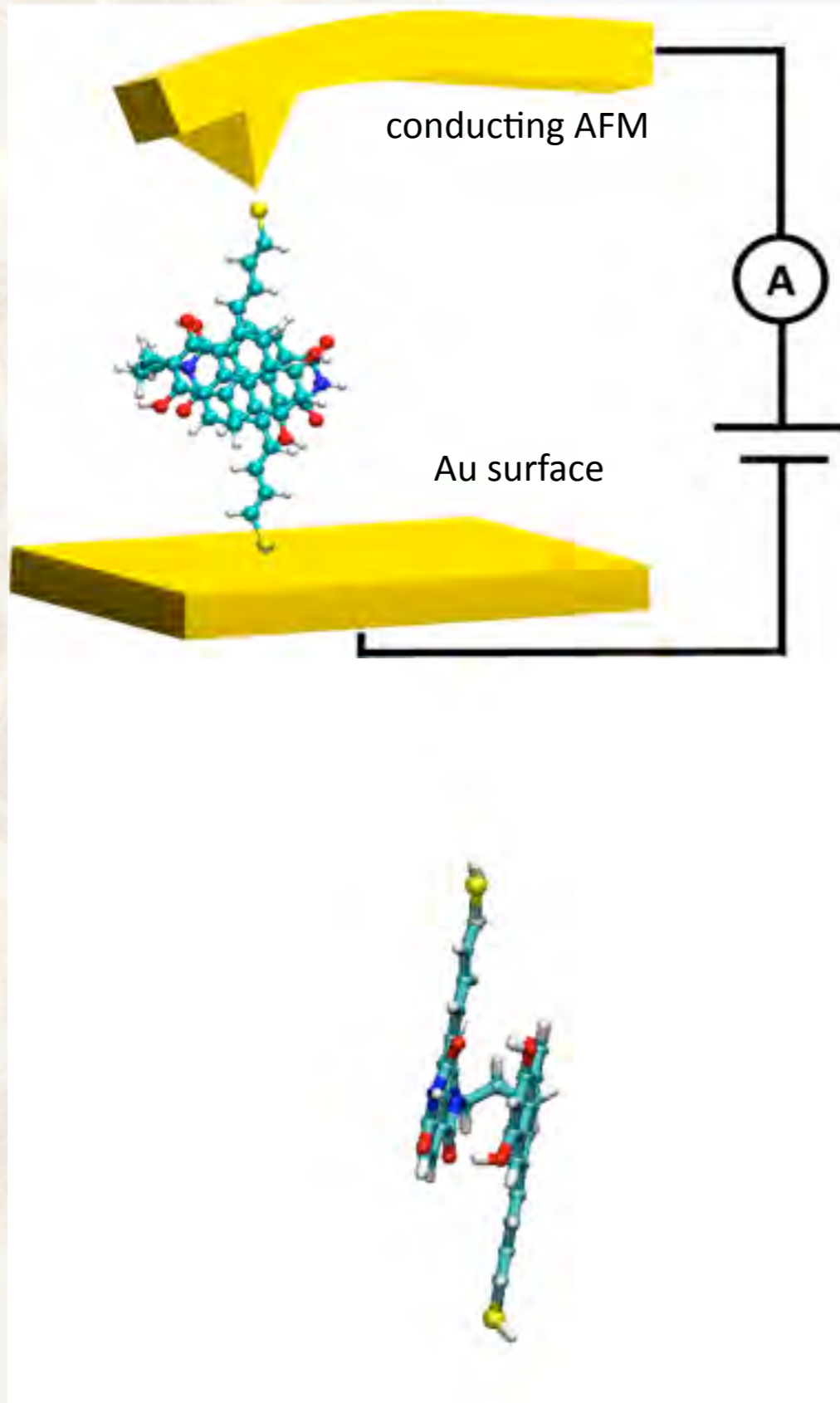


- From Hammett constants, to Mulliken charges to local spins, local properties underpin structure-function relationships in chemistry.

- For new types of physical measurements, like passing current through a molecule, we need new local descriptions.
- If we can understand how different components interact in a complex system, maybe we can design interesting devices?

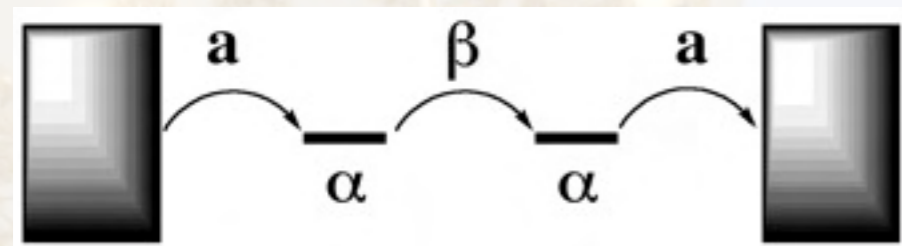


Questions:

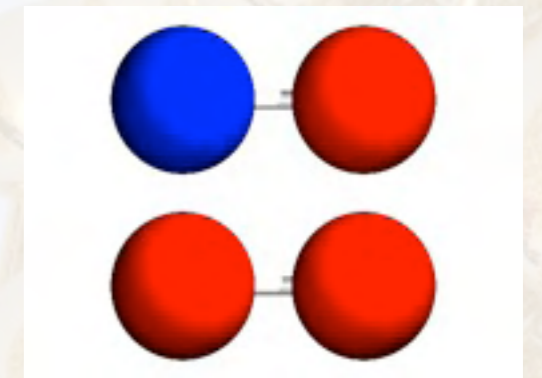


- How do different functional groups in a molecule modulate transport? Do they always participate?
- Does current through a molecule always follow the bonds?
- When might through-space interactions be important? Is overlap all that matters?
- Can we map the characteristic transport pathways through a complex molecular system?

Calculating conductance



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



$$\Gamma_L = \begin{bmatrix} 2a & 0 \\ 0 & 0 \end{bmatrix}$$

$$\Gamma_R = \begin{bmatrix} 0 & 0 \\ 0 & 2a \end{bmatrix}$$

$$\Sigma = \frac{i(\Gamma_L + \Gamma_R)}{2}$$

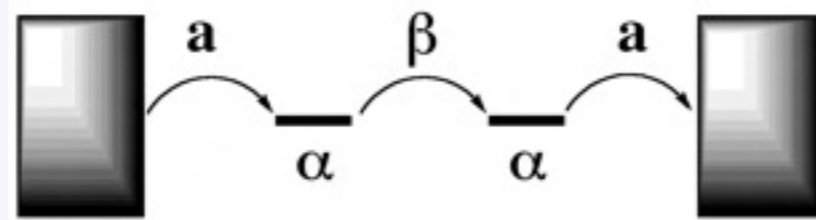
$$\begin{aligned} H' &= H - \Sigma \\ &= \begin{bmatrix} \alpha - ia & \beta \\ \beta & \alpha - ia \end{bmatrix} \end{aligned}$$

$$G^r = \frac{1}{ES - H'}$$

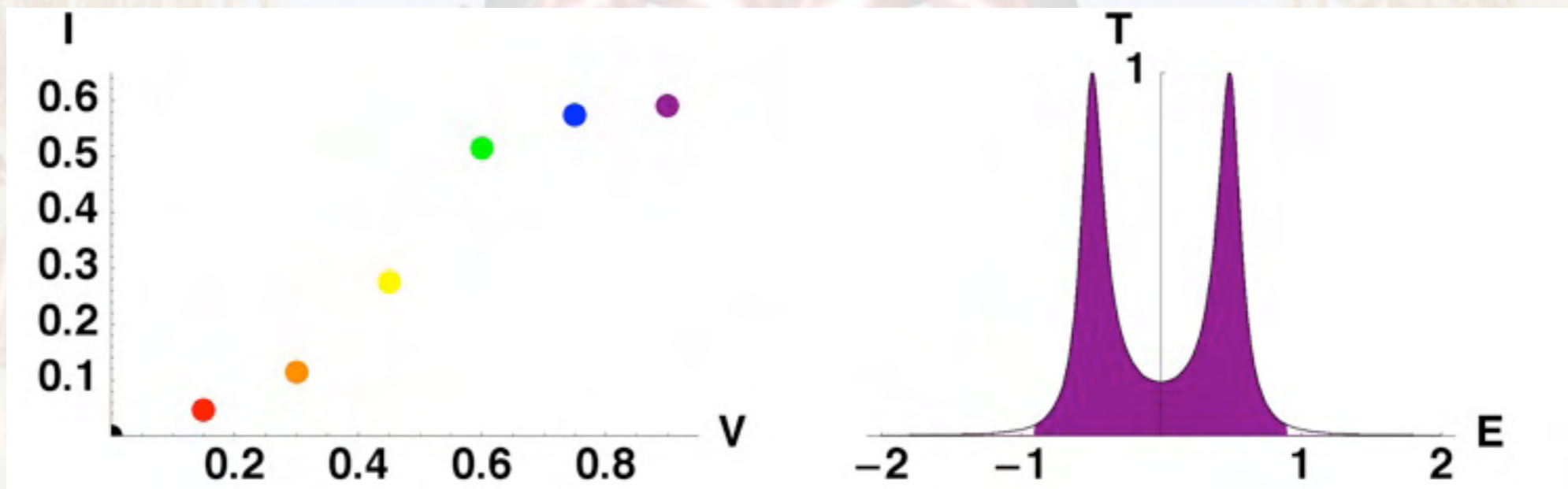
$$G^a = G^{r\dagger}$$

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

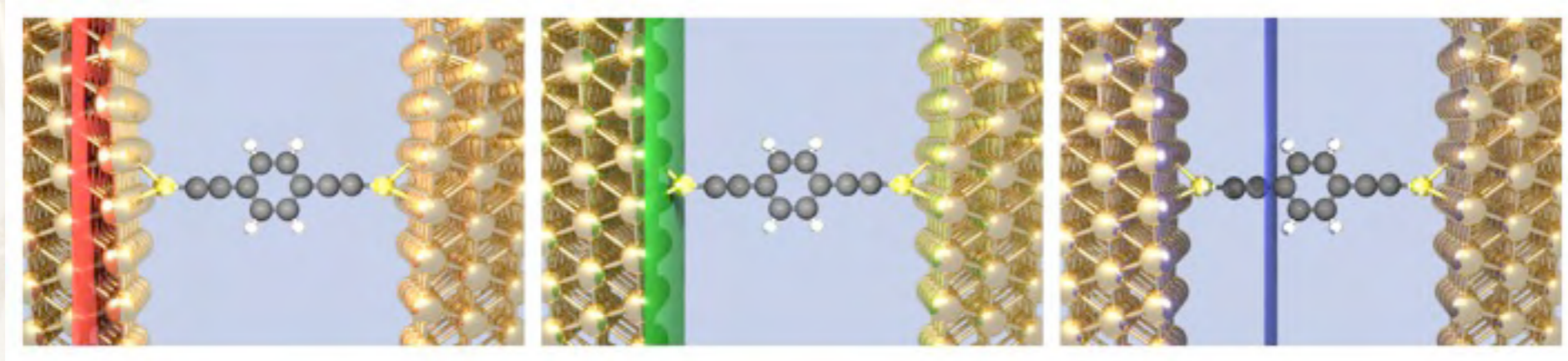
Calculating current from transmission



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



Current through an arbitrary surface

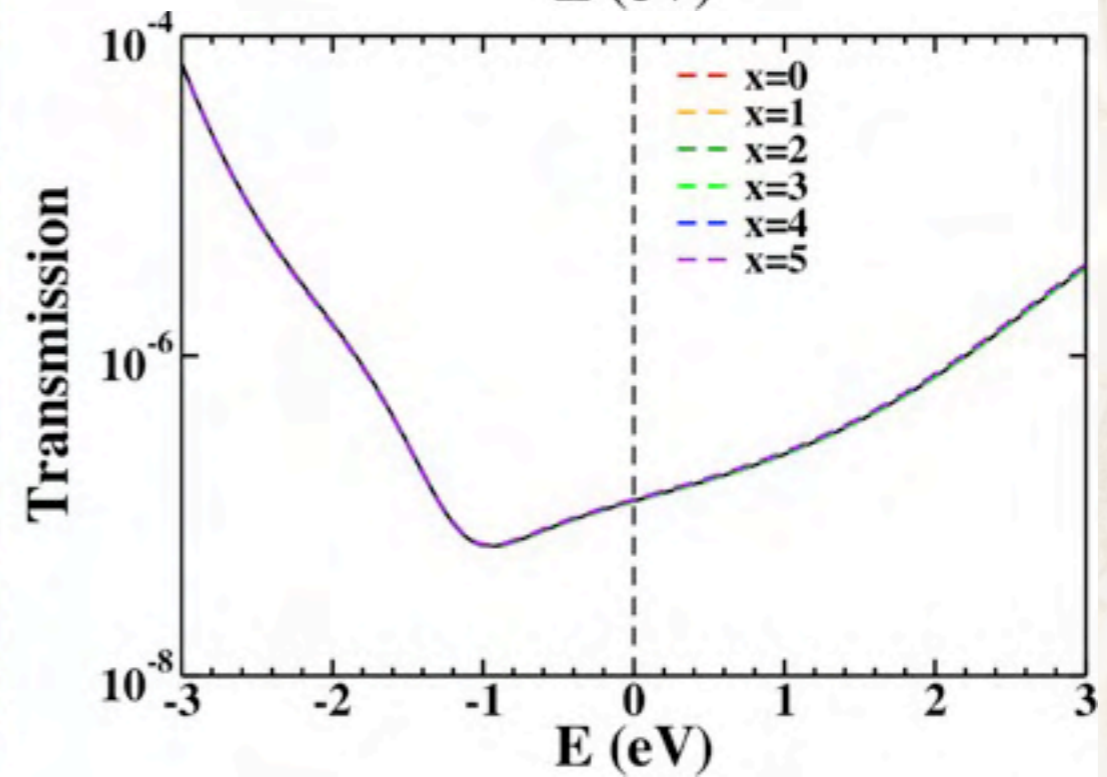
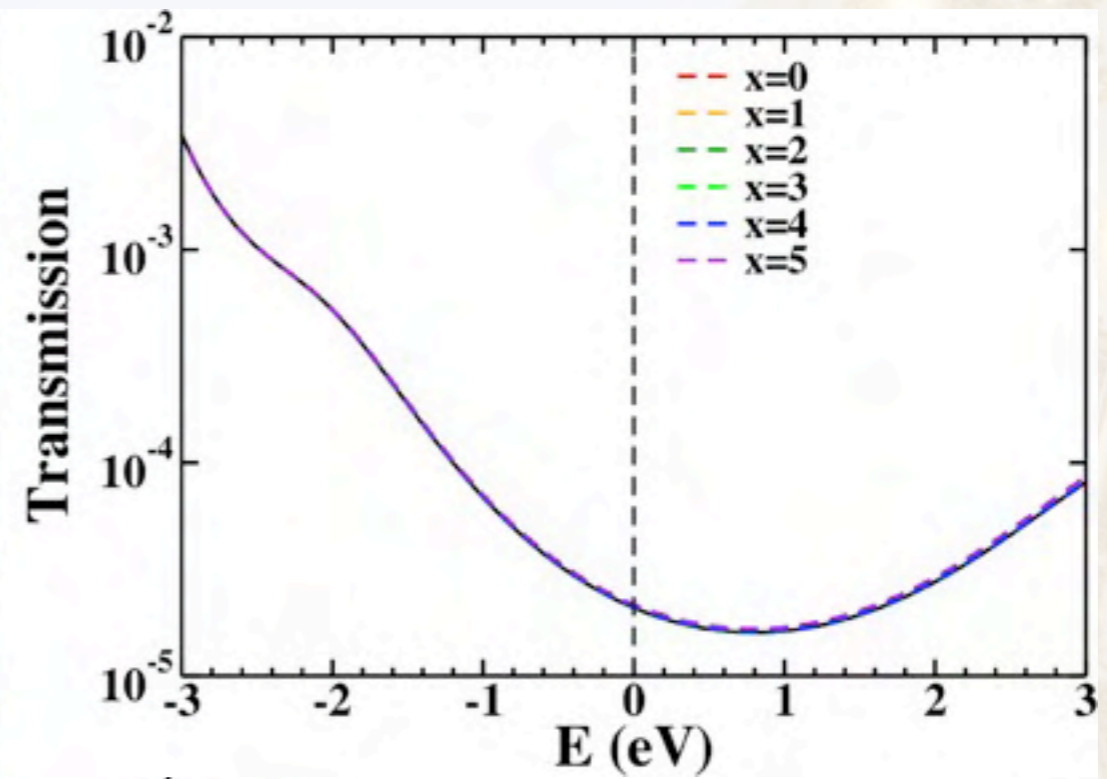
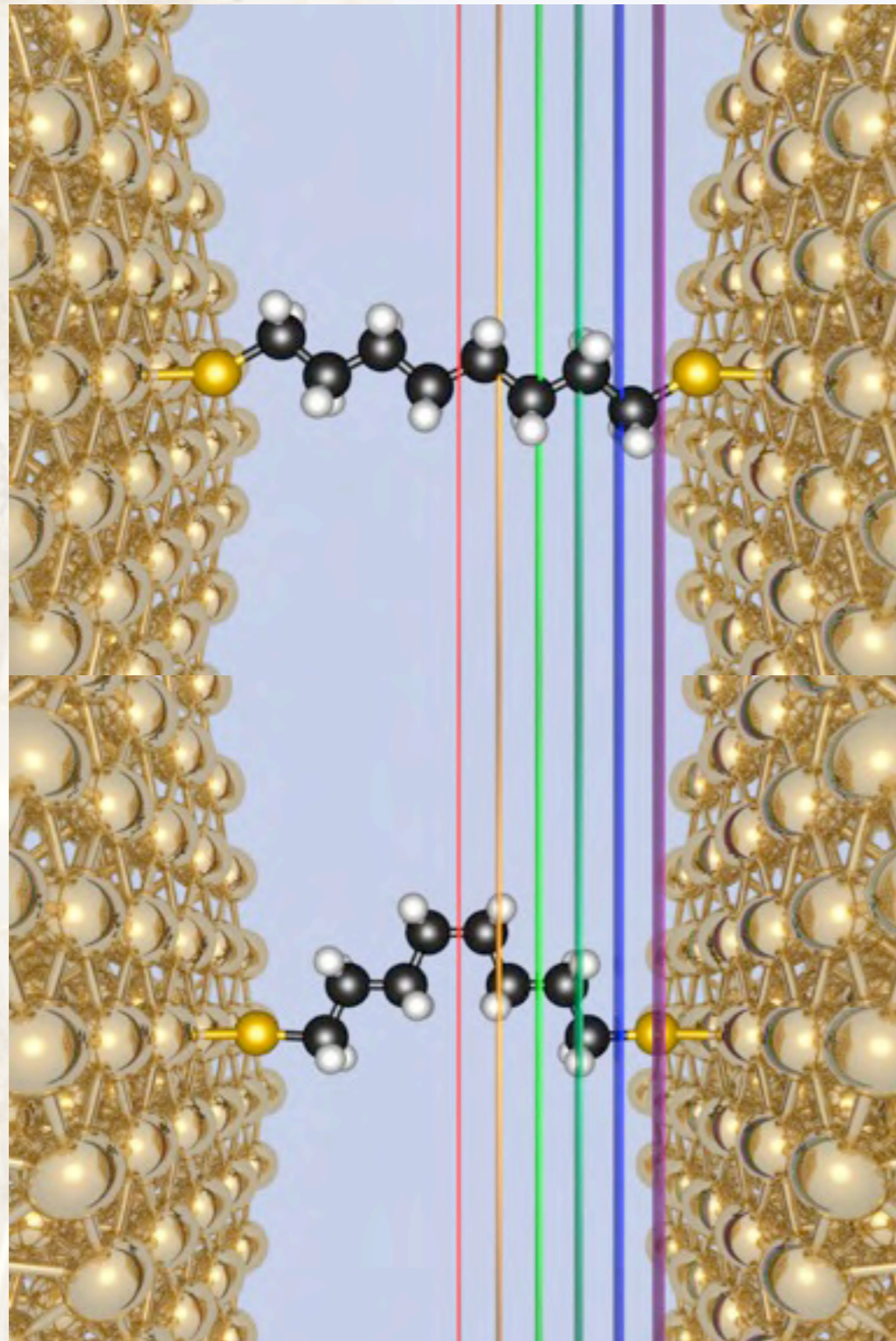


$$I_{mn} = \frac{2e}{\hbar} \int \frac{d\varepsilon}{2\pi} K_{mn}(\varepsilon) \quad I = \frac{2e}{h} \sum_{m \in M_L} \sum_{n \in M_R} \int d\varepsilon K_{mn}(\varepsilon)$$

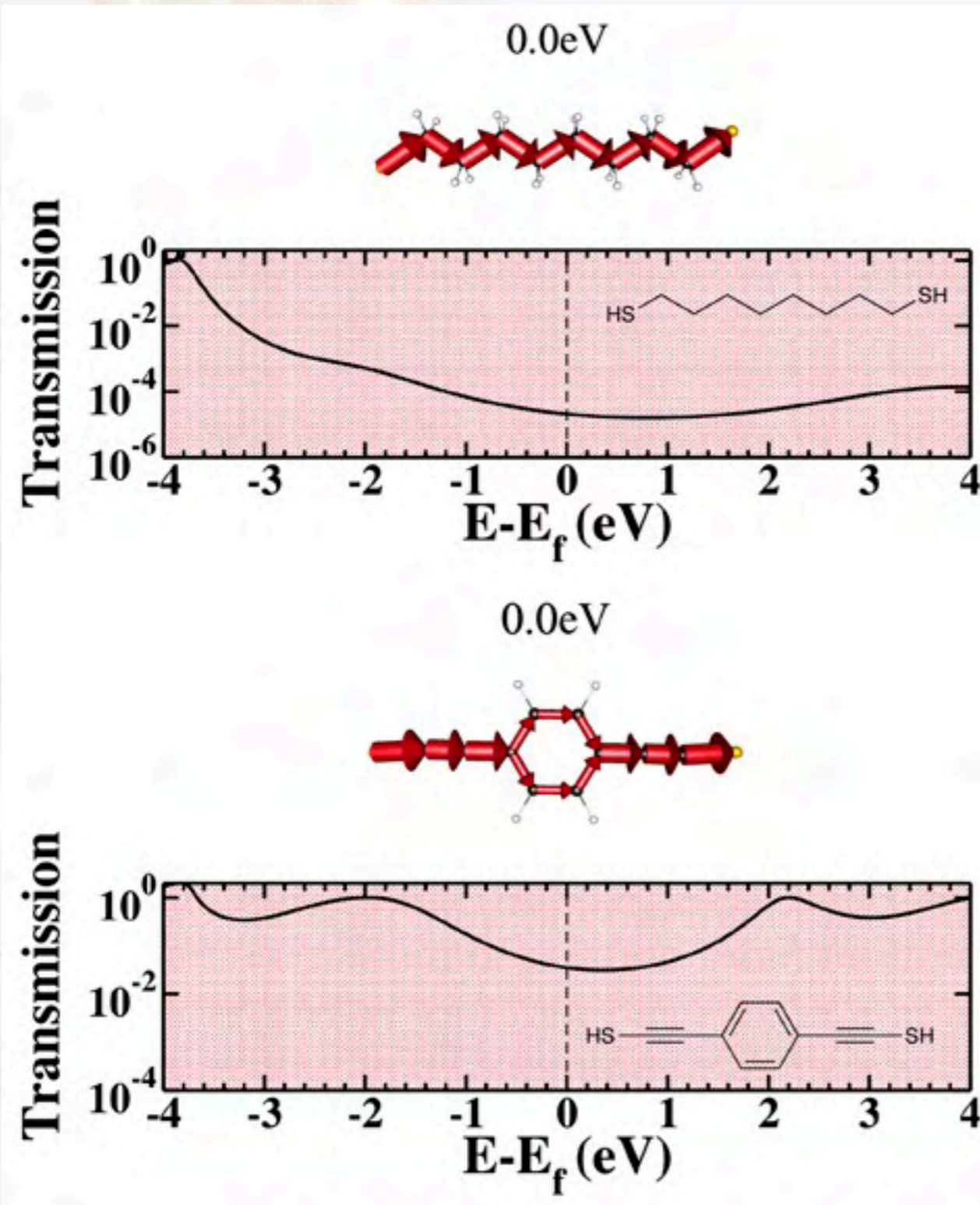
$$\sum_{m \in M_L} \sum_{n \in M_R} K_{mn}(\varepsilon) = (f_L(\varepsilon) - f_R(\varepsilon)) T(\varepsilon)$$

$$K_{mn}(\varepsilon) = \sum_{i \in m} \sum_{\substack{j \in n \\ n \neq m}} \sum_{kl} (i f_L (V_{ij} G_{jk}^r \Gamma_{kl}^L G_{li}^a - V_{ji} G_{il}^r \Gamma_{lk}^L G_{kj}^a) \\ - i f_R (V_{ji} G_{il}^r \Gamma_{lk}^R G_{kj}^a - V_{ij} G_{jk}^r \Gamma_{kl}^R G_{lj}^a))$$

Conservation



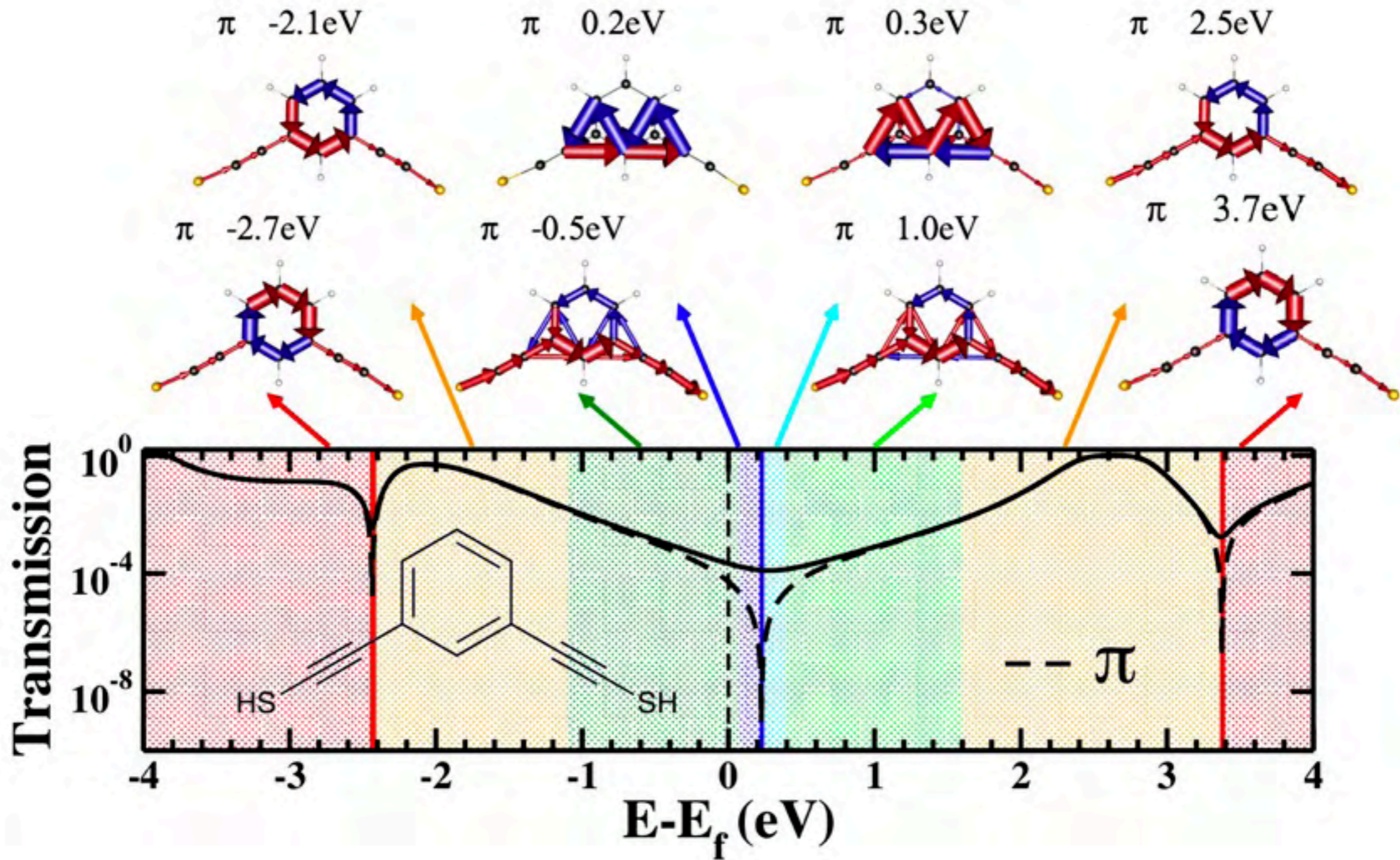
What does local transmission look like?



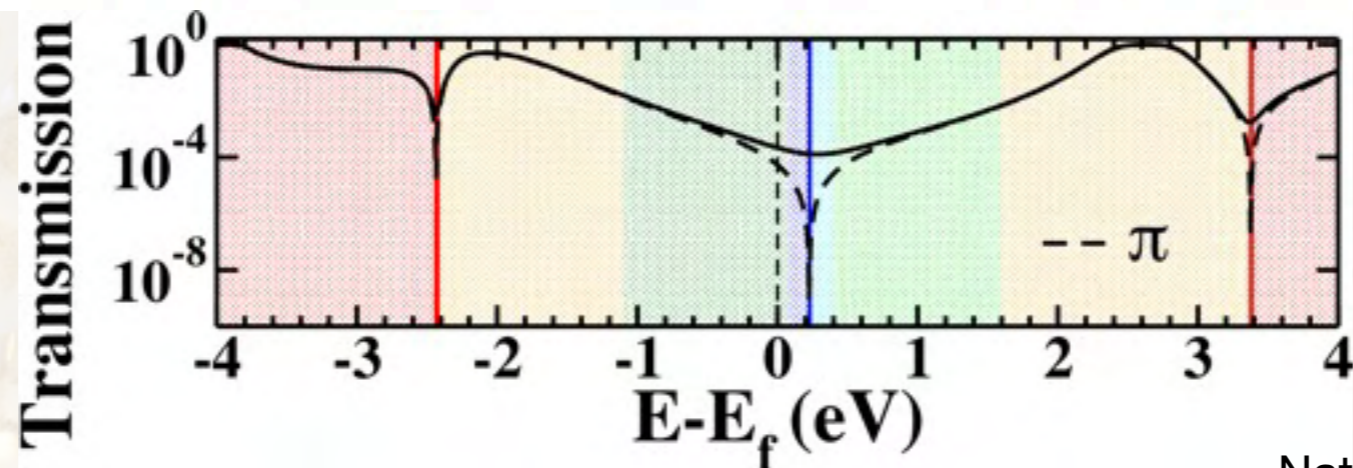
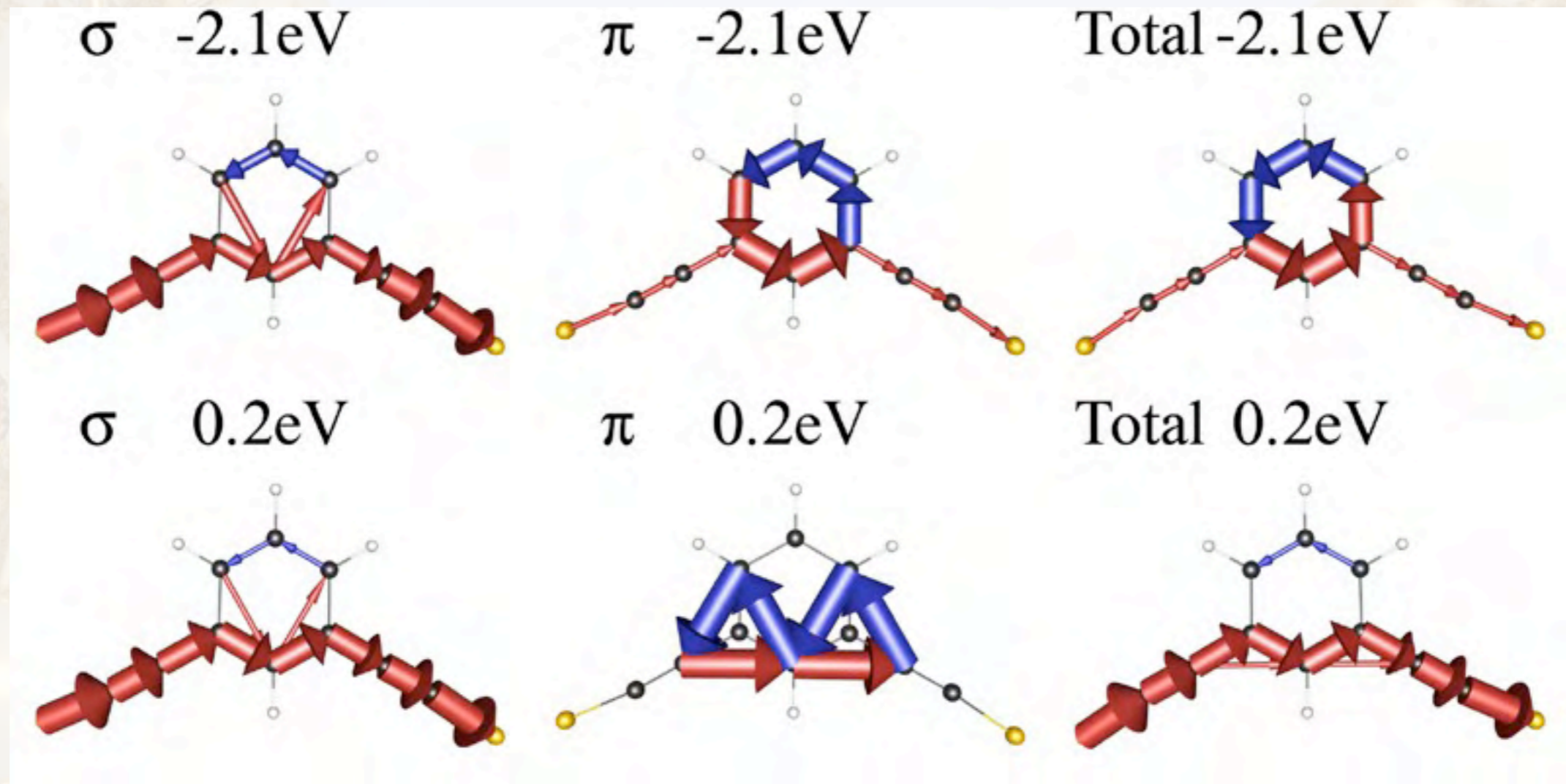
A note about local transmission plots:

- 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.

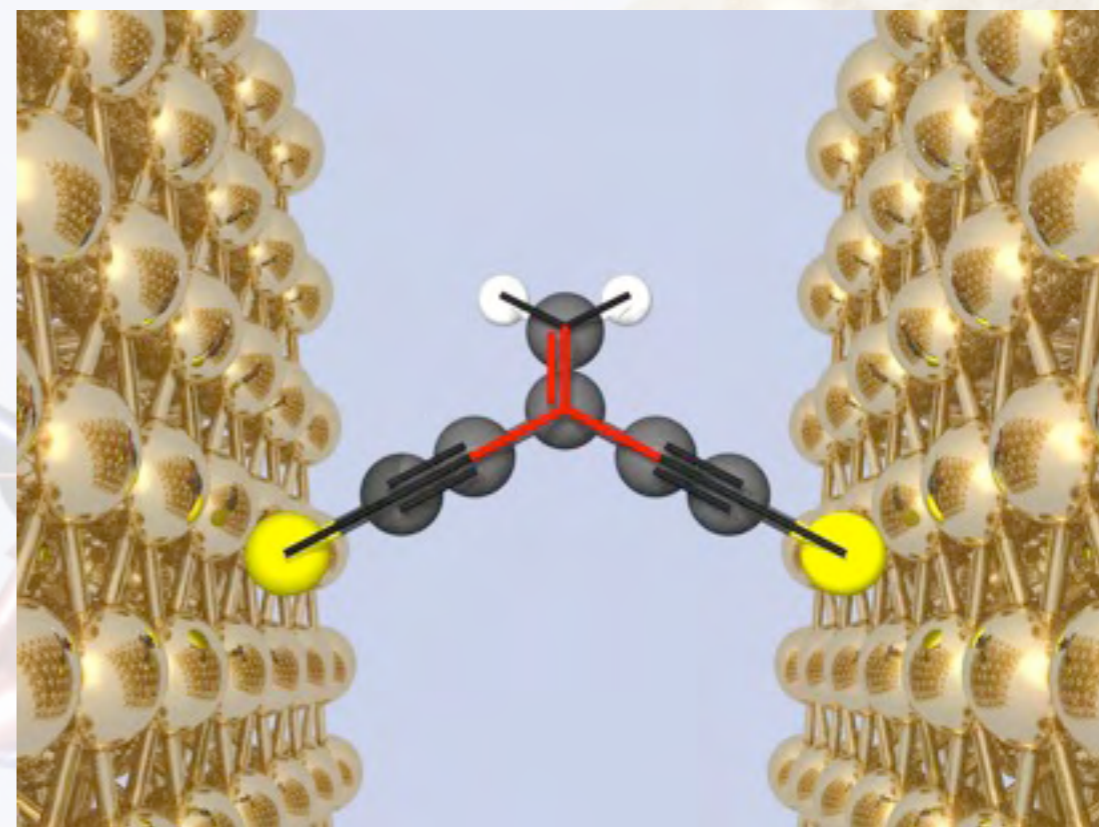
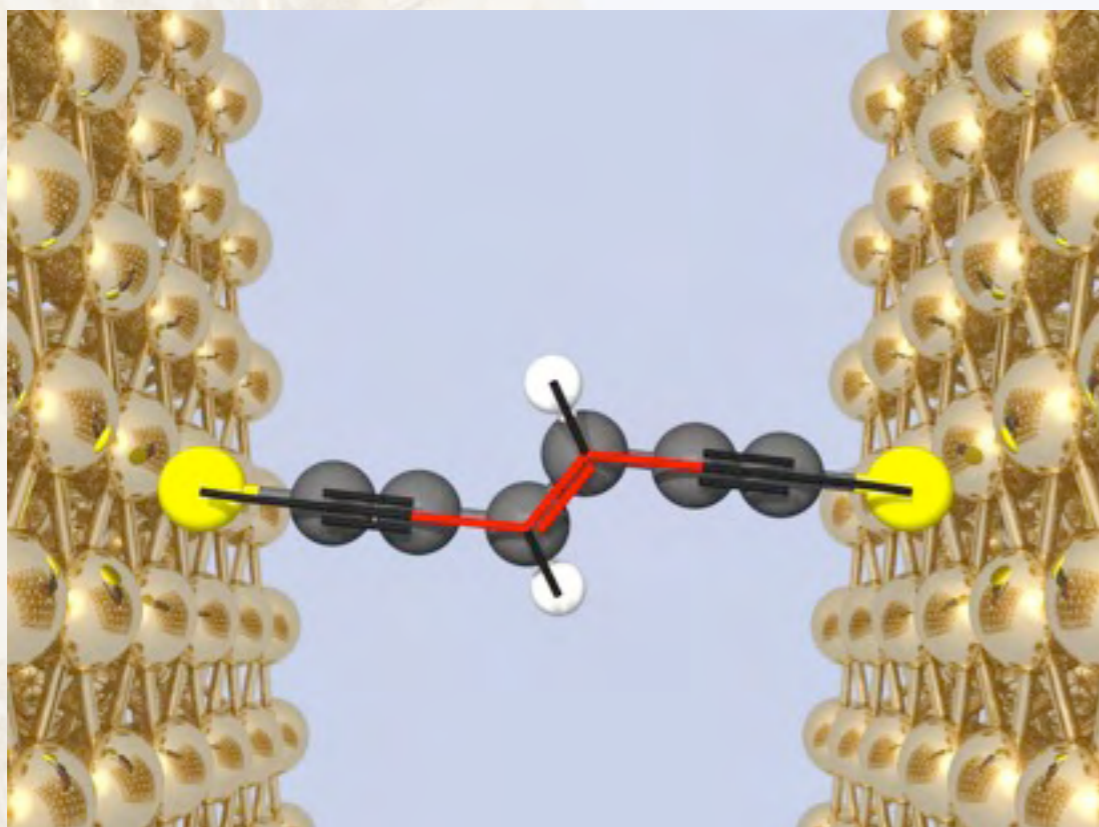
More involved local transmission



π transmission & Total transmission



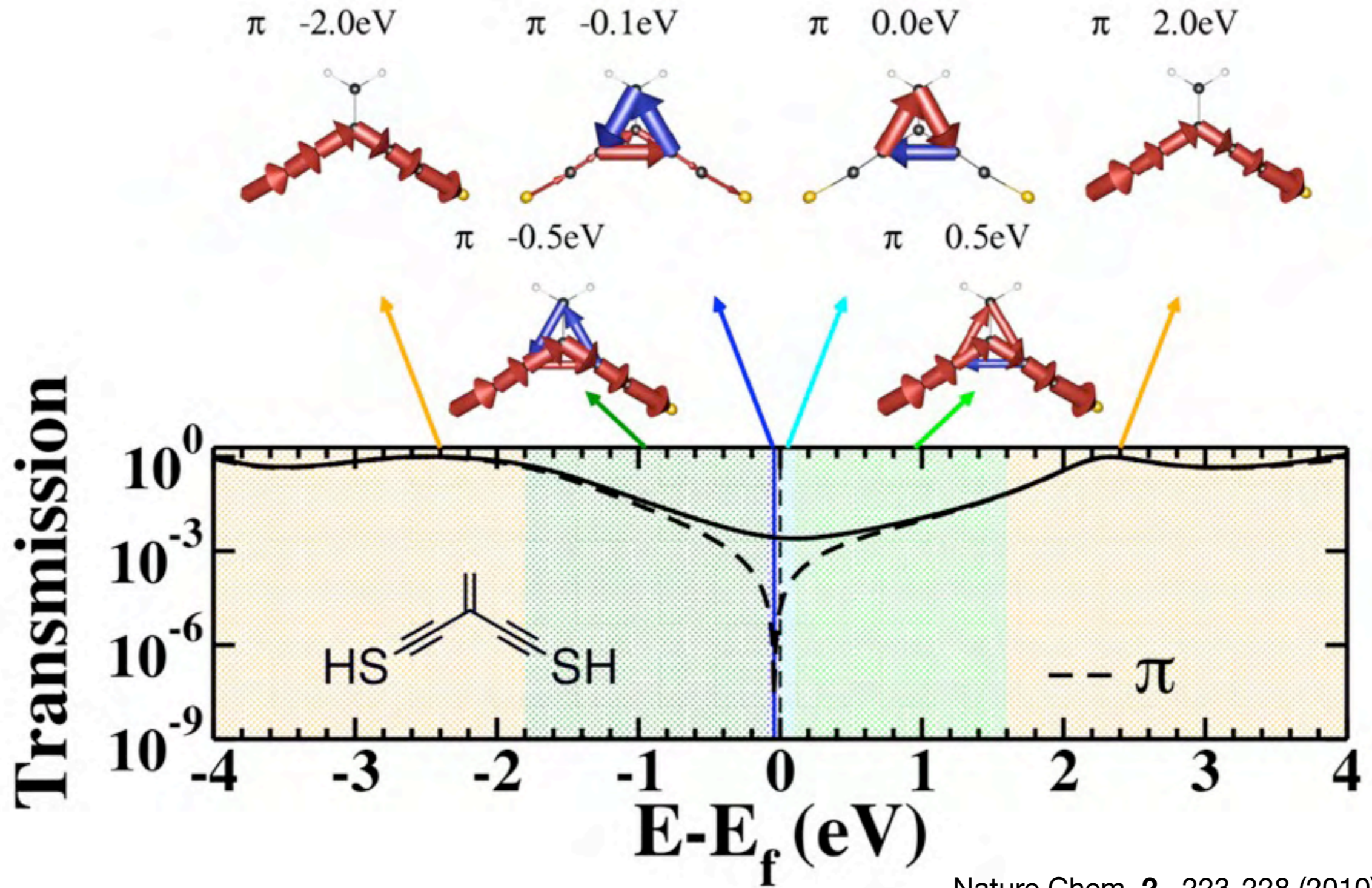
Cross-conjugated molecules



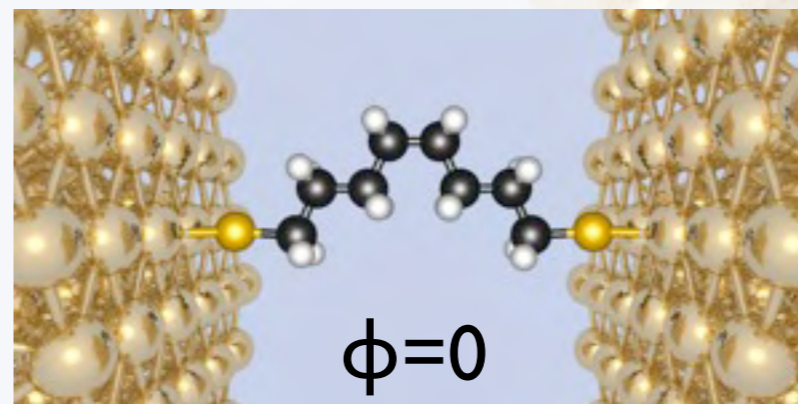
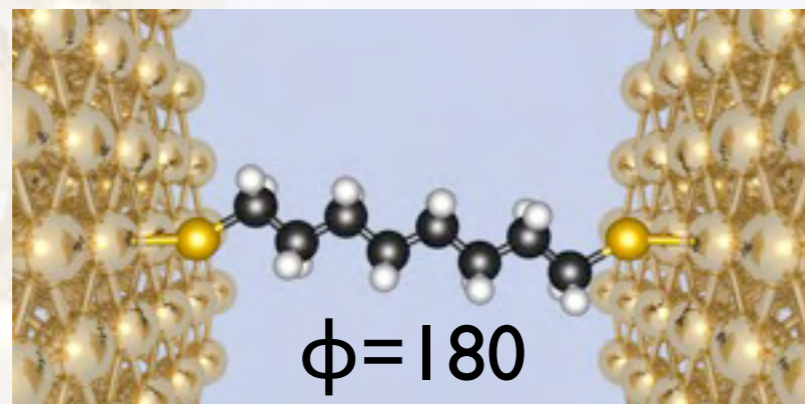
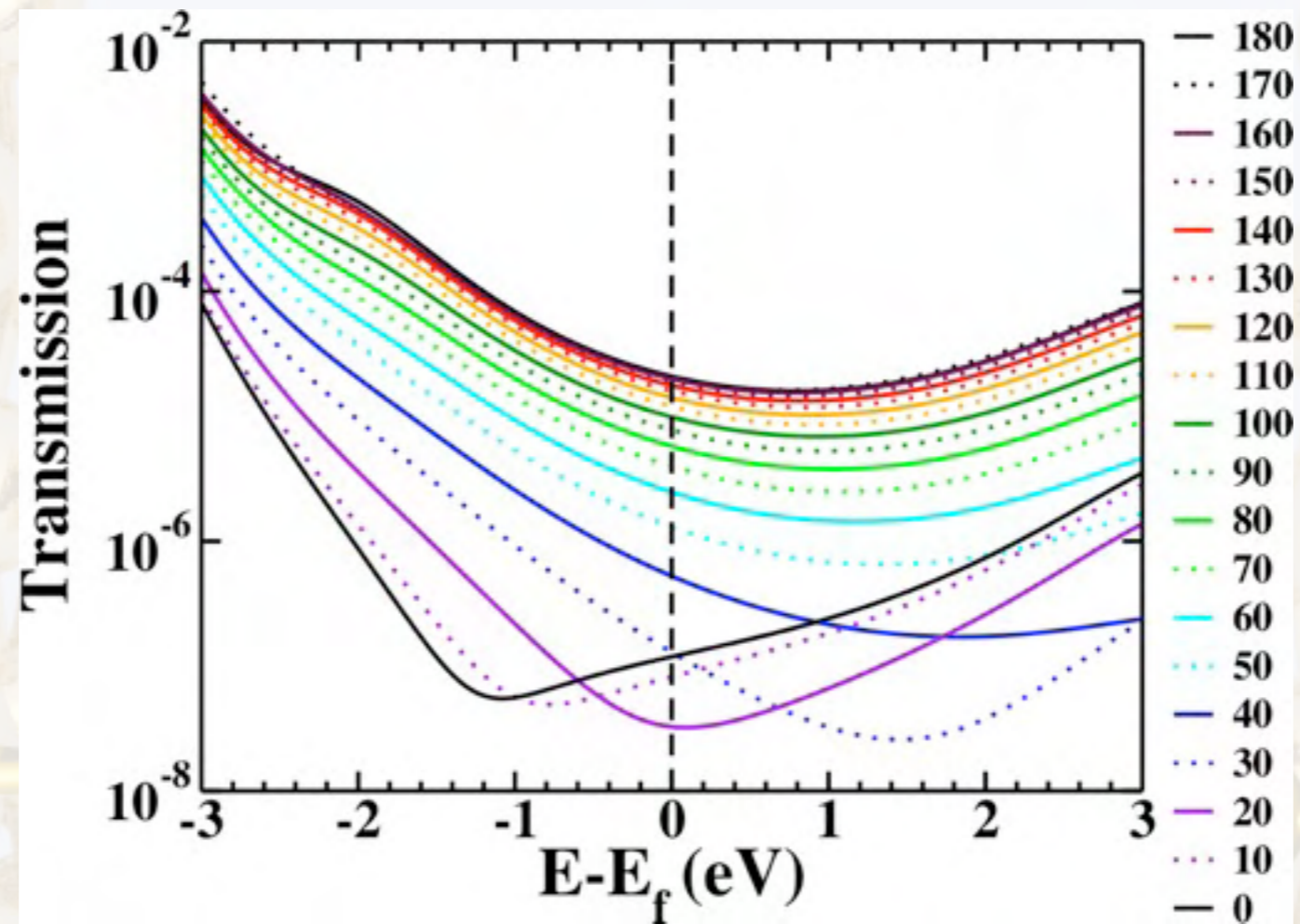
“a compound possessing three unsaturated groups, two of which although conjugated to a third unsaturated center are not conjugated to each other.”

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

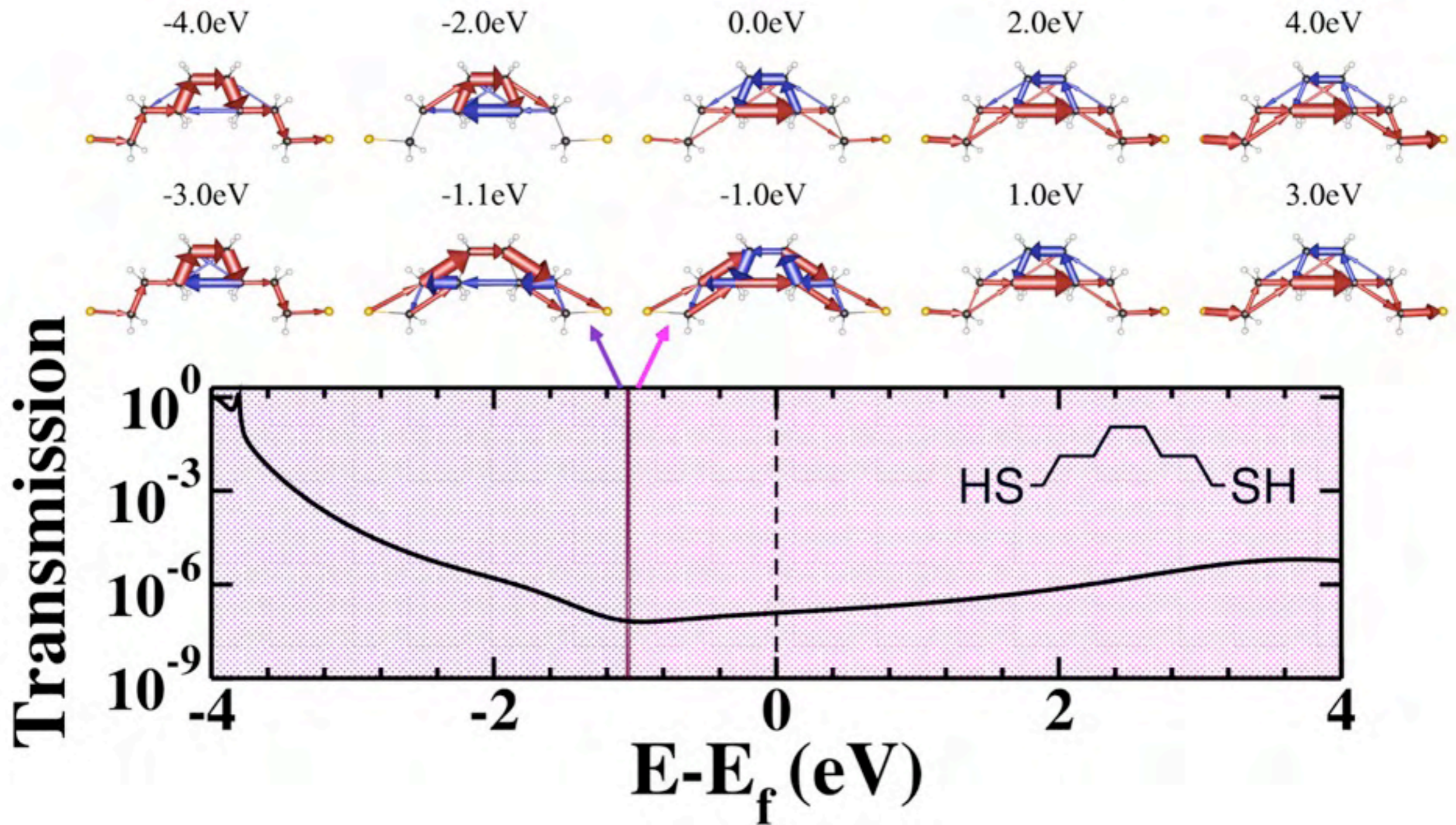
Similar behavior



σ -systems can be unusual too

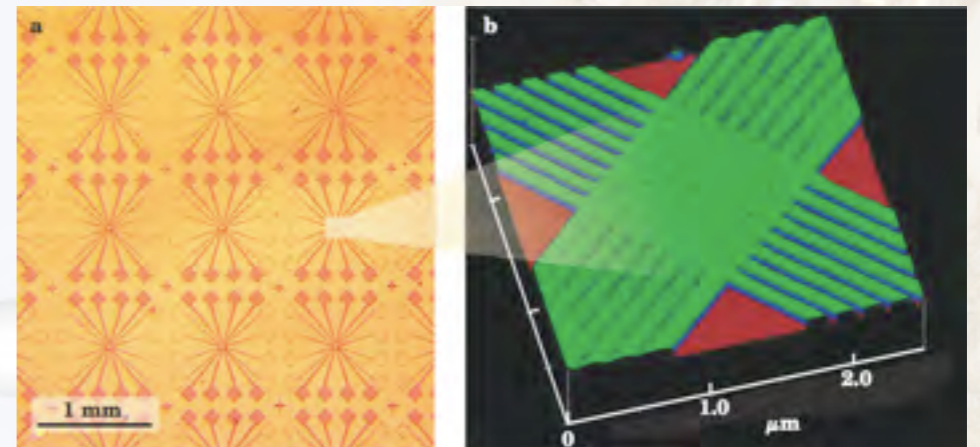


We can see the signature of interference



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

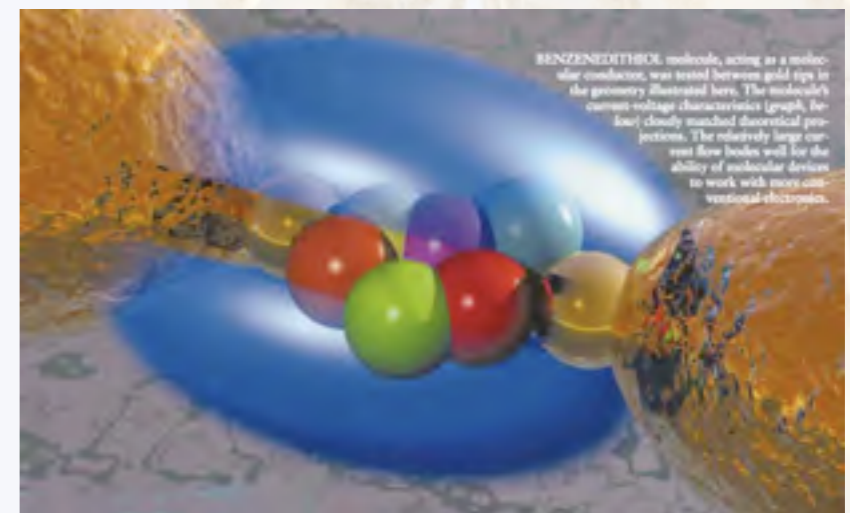
- Positioning single molecules between metallic electrodes is an enormous challenge.
- Controllable synthesis of really large molecules is another enormous challenge.
- Self-assembly of supramolecular structures or carefully constructed films seem to be a promising alternative.



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

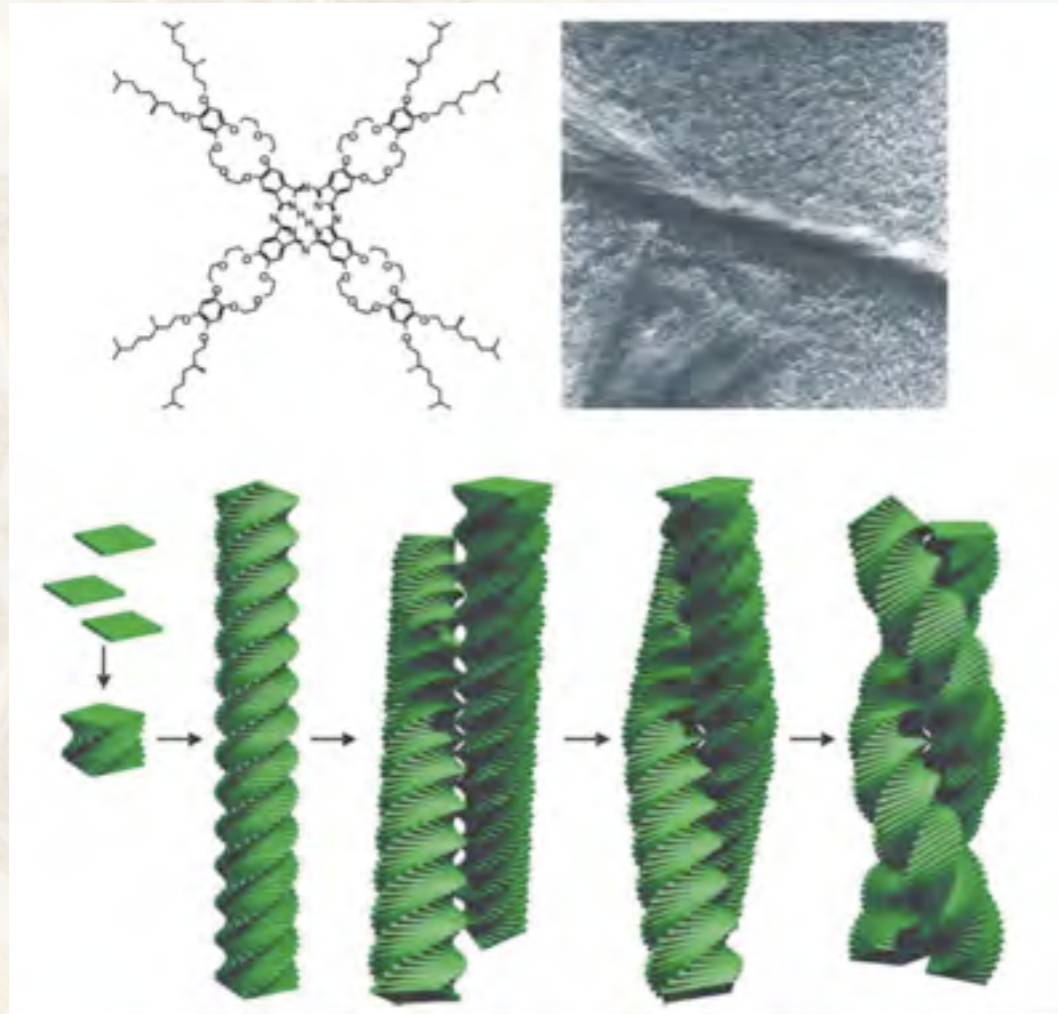


J. Heath



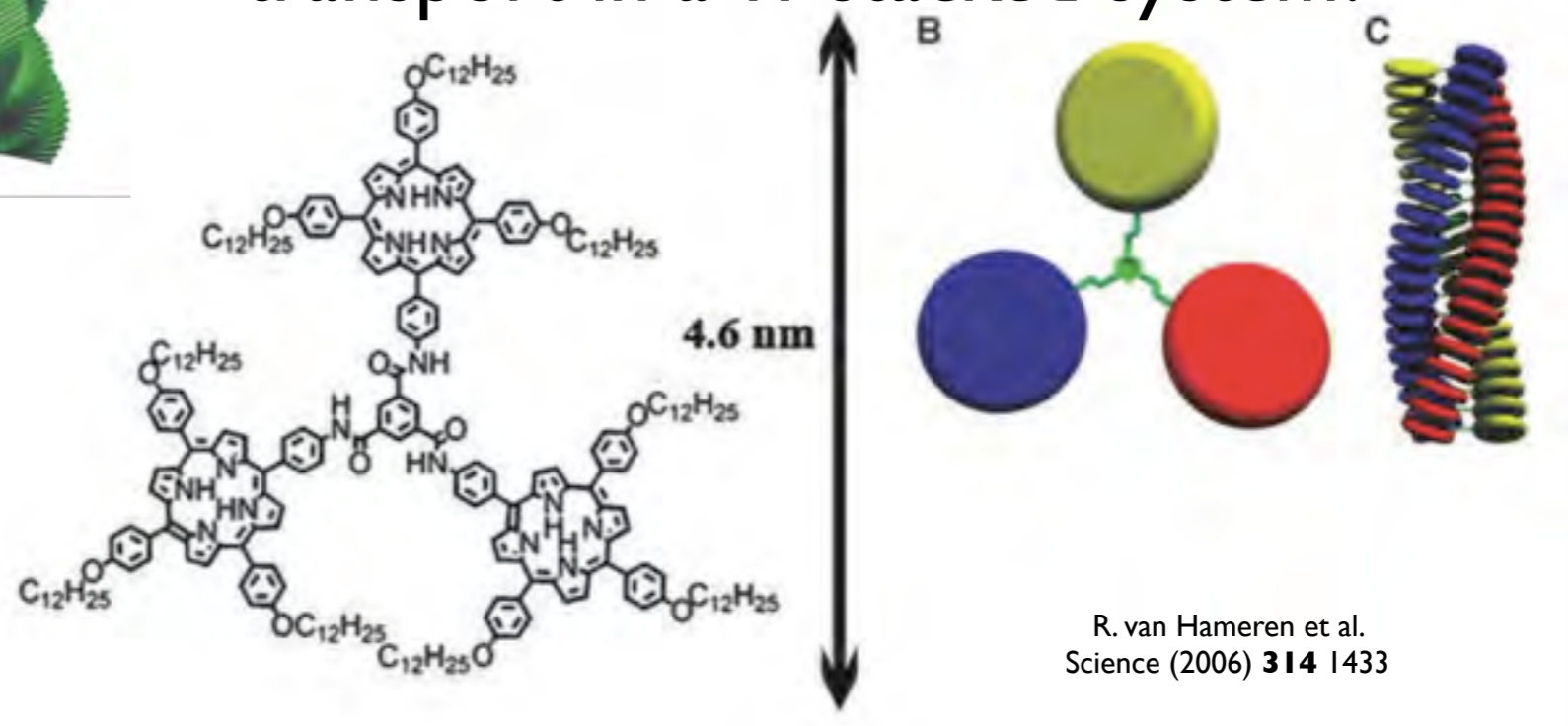
M. Reed and J. Tour Scientific American, June 2000

π -stacked structures are favorable for self-assembly

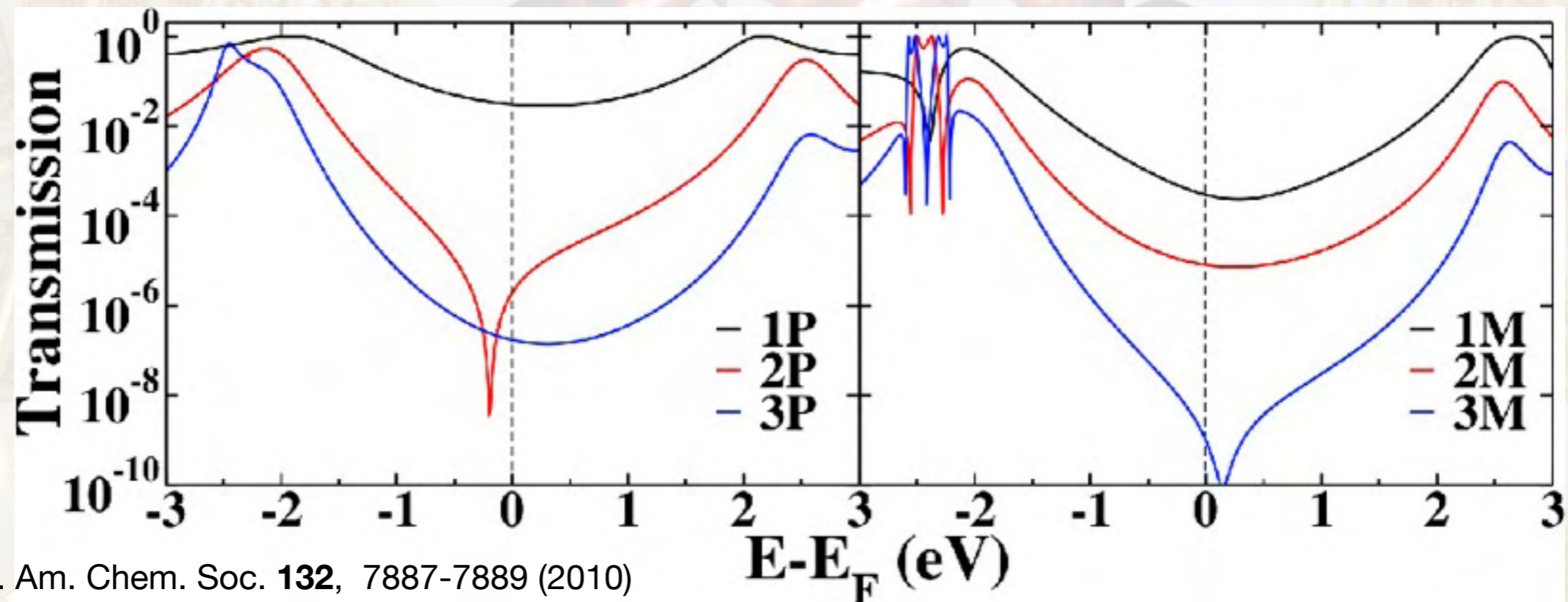
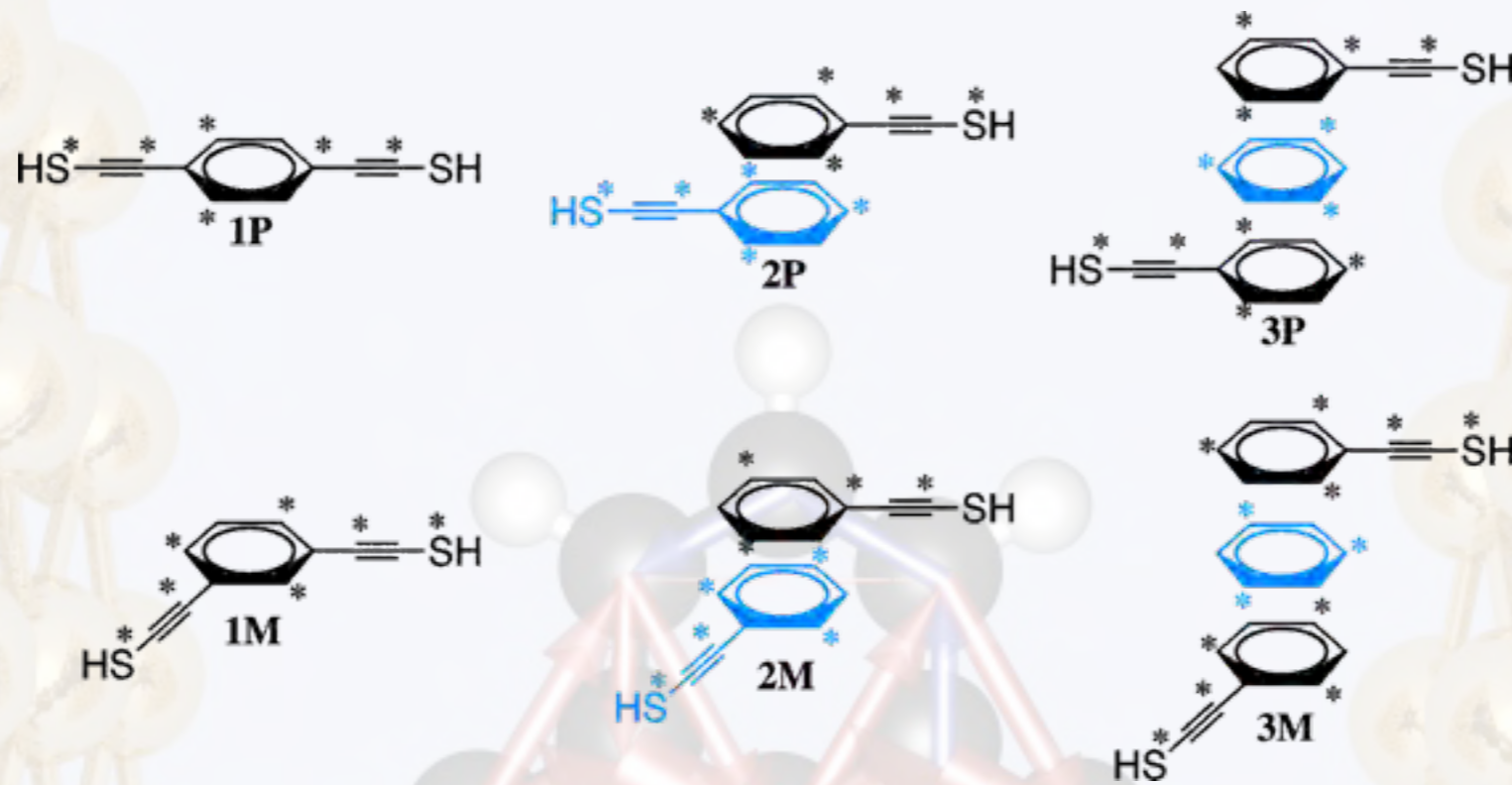


J. A. A. W. Elemans, A. E. Rowan and R. J. M. Nolte
J. Mater. Chem. (2003) **13** 2661

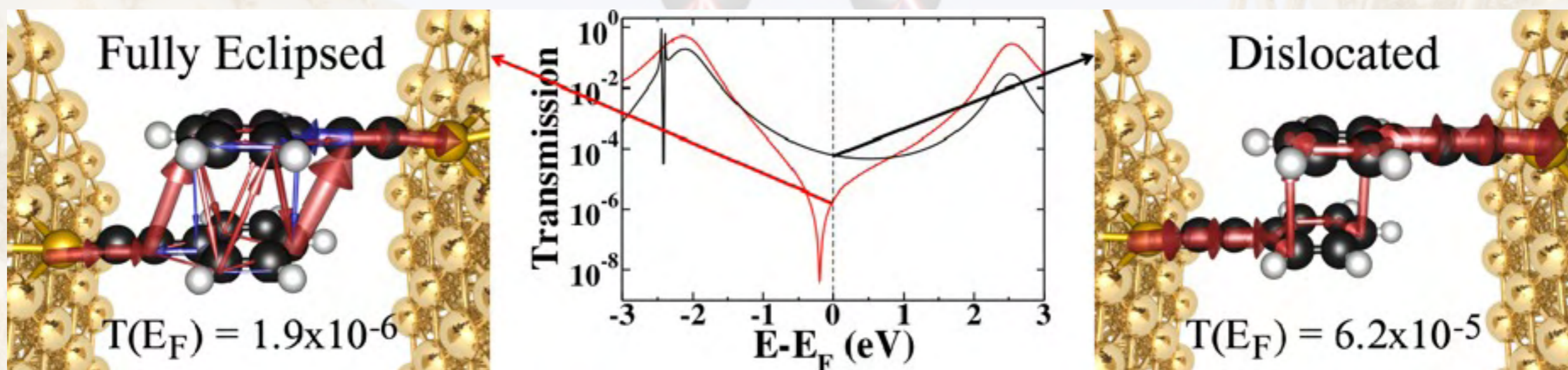
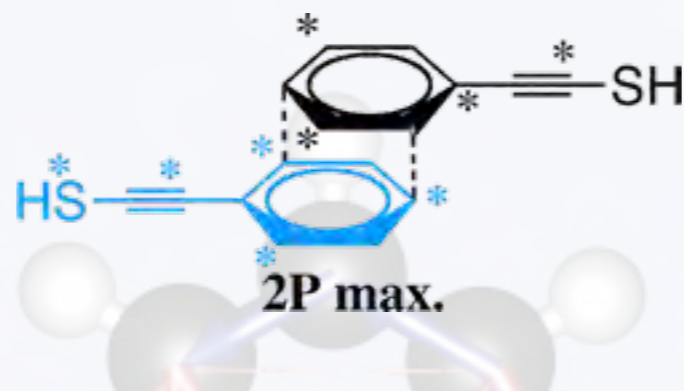
- Non-bonding interactions can be used to build extremely large structures.
- These structures have been suggested as architectures for charge transport.
- What is really desirable for charge transport in a π -stacked system?



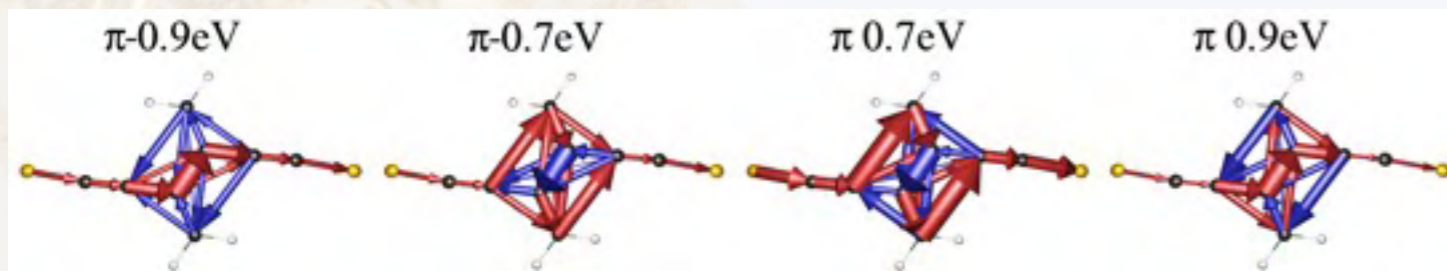
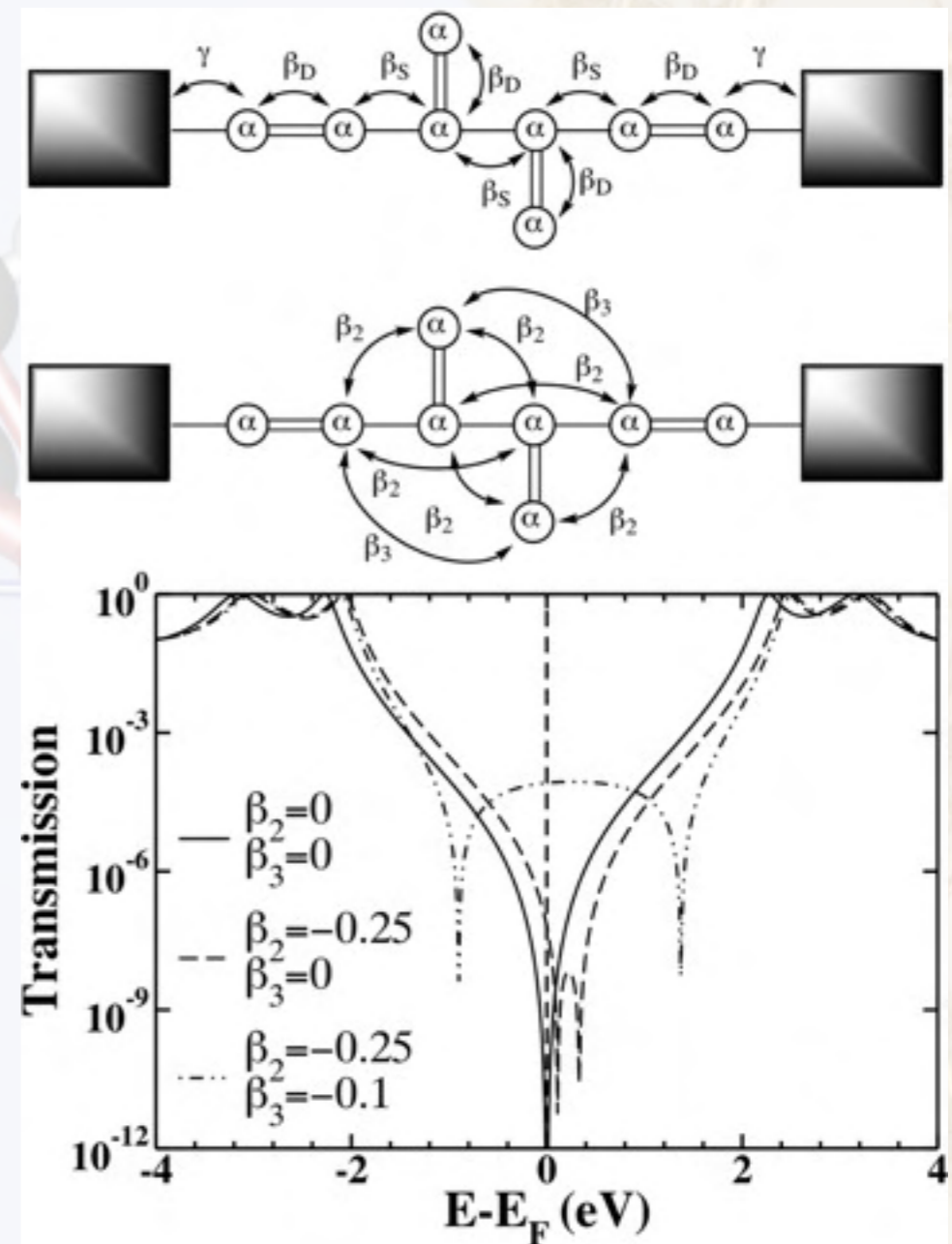
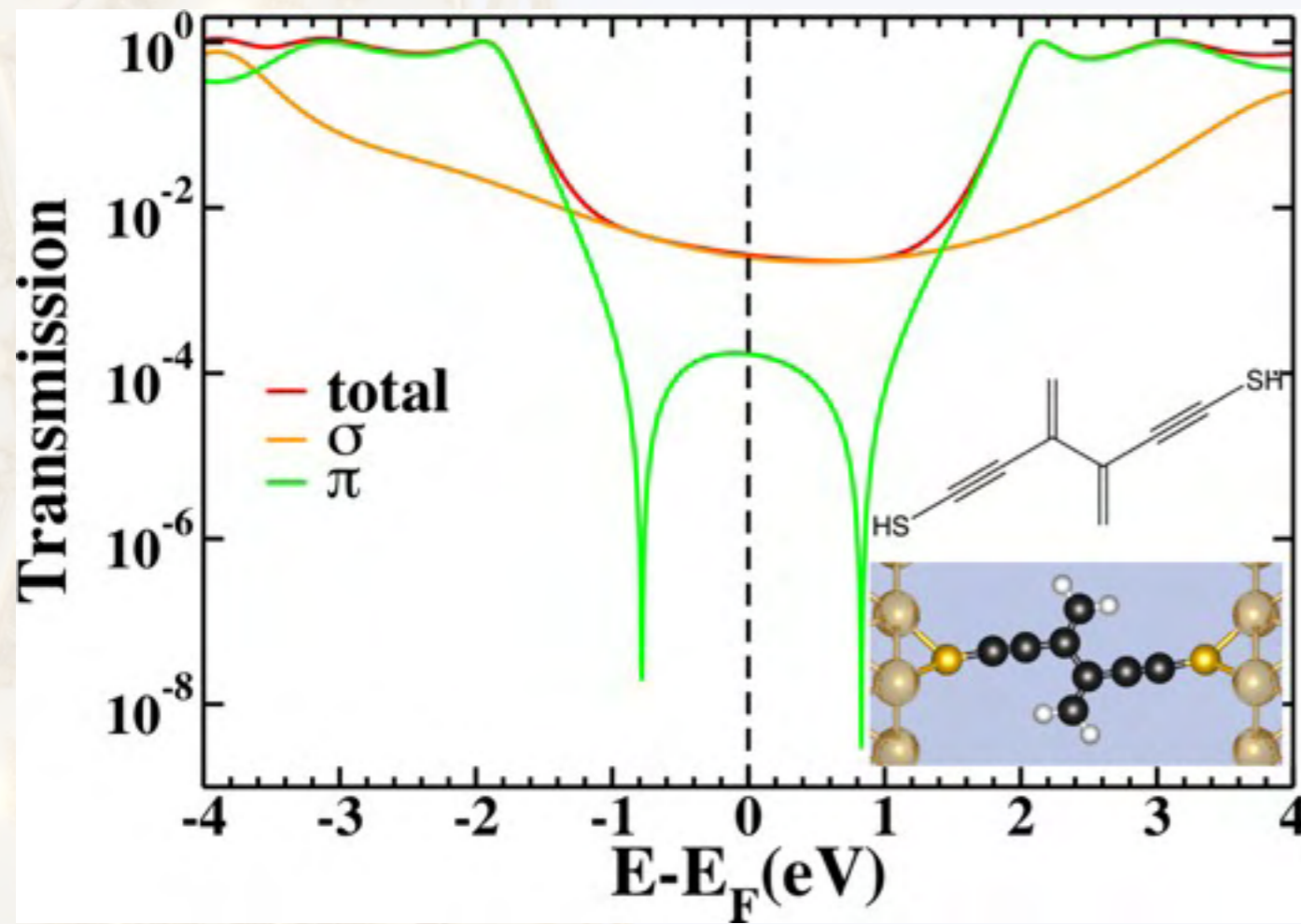
Take a simple series



Increasing transmission by reducing overlap

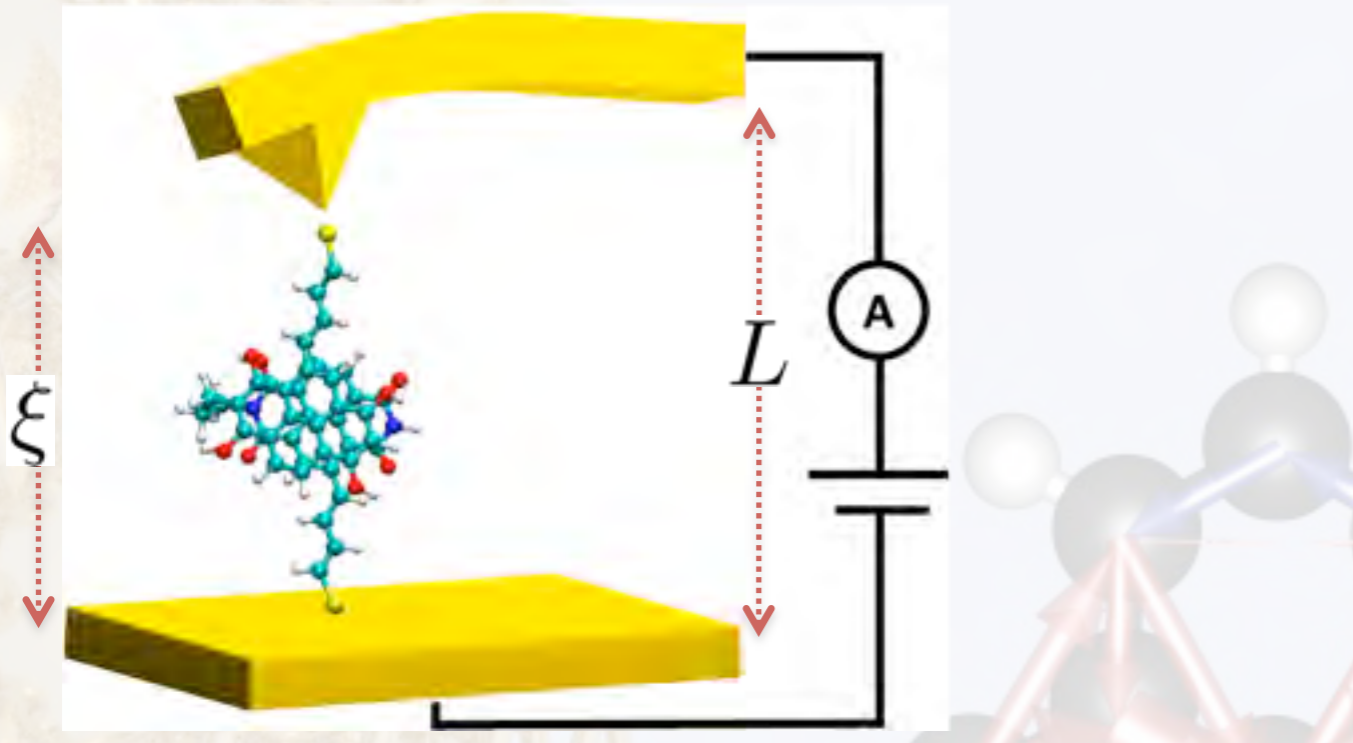


Perturbing interference features

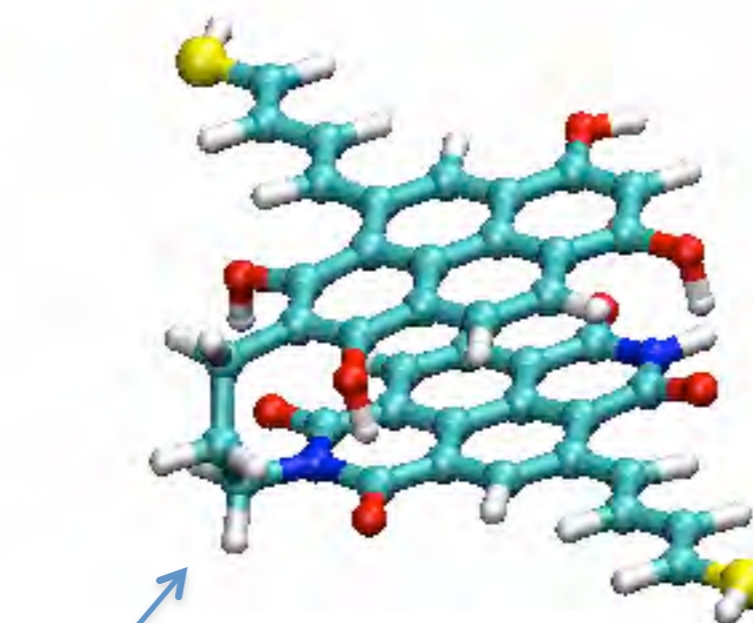
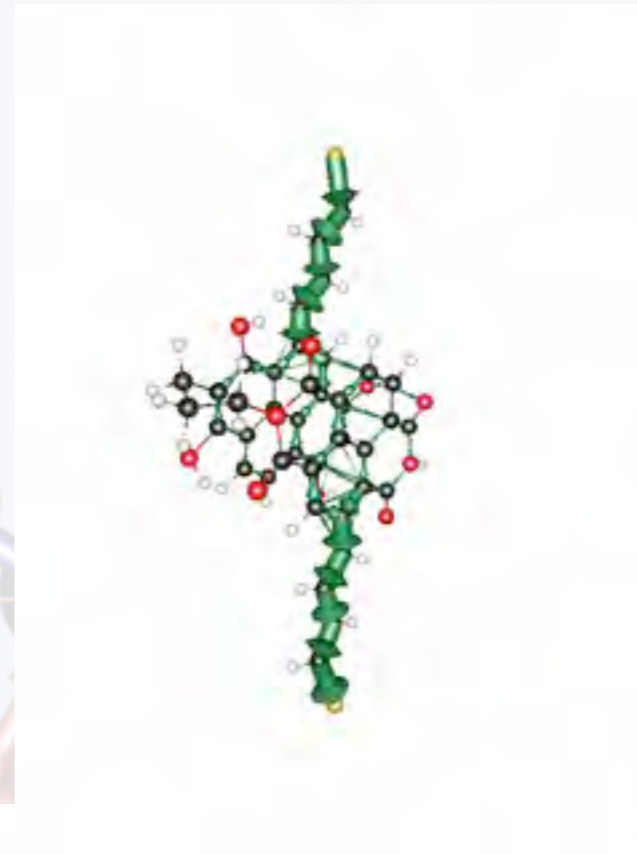


Putting it all together: the super stacker

conducting AFM



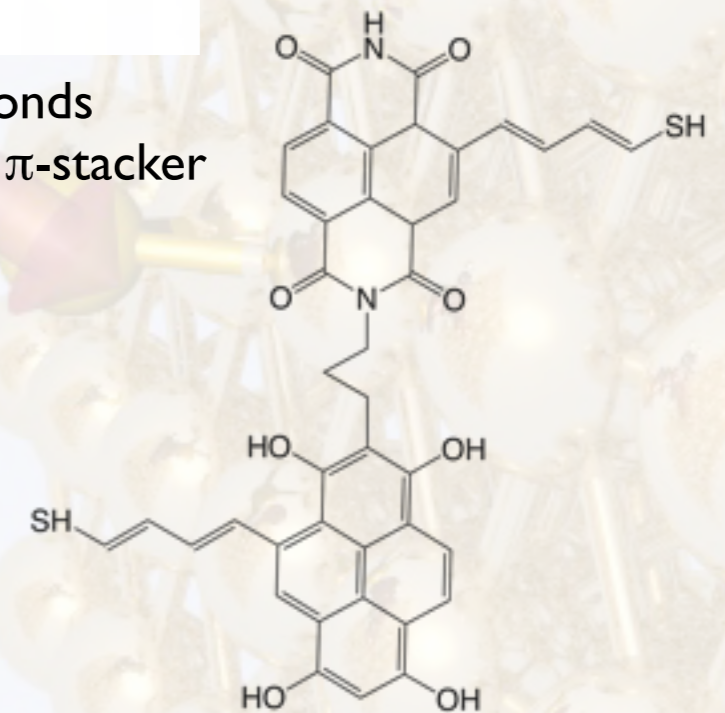
Au surface



short aliphatic chain
forces alignment
between aromatic units

Alkene-thiols connect the
stacker to the Au contacts

Hydrogen bonds
stabilize the π -stacker



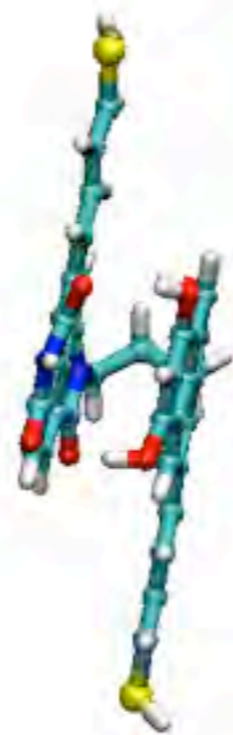
J. Am. Chem. Soc. **133**, 2242-2249 (2011)

Pulling the super stacker

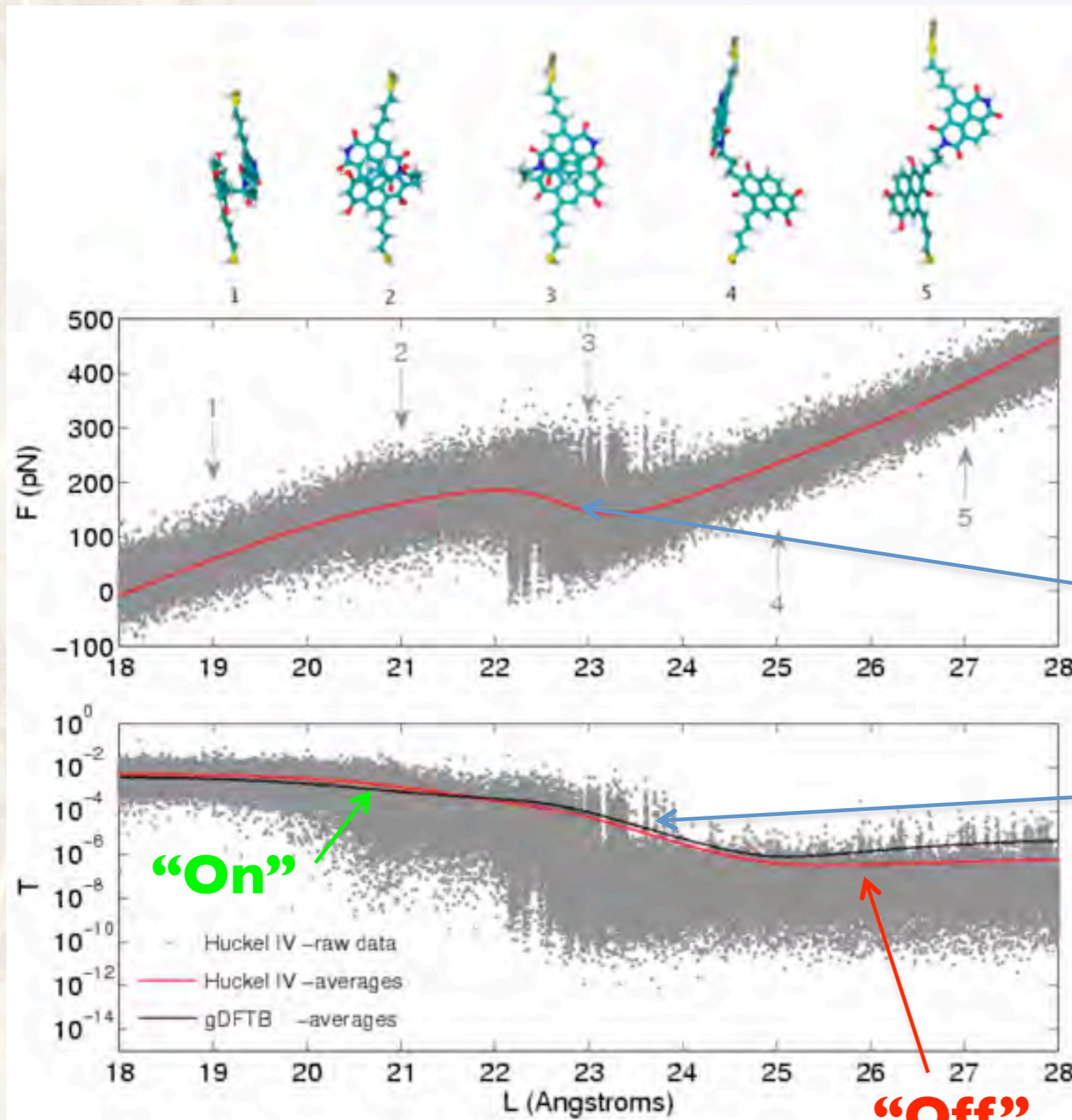
Nonequilibrium
trajectory

Pulling speed \sim
 10^{-3} Å/ps

$k = 1.1$ N/m



Mechanically activated molecular switch



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

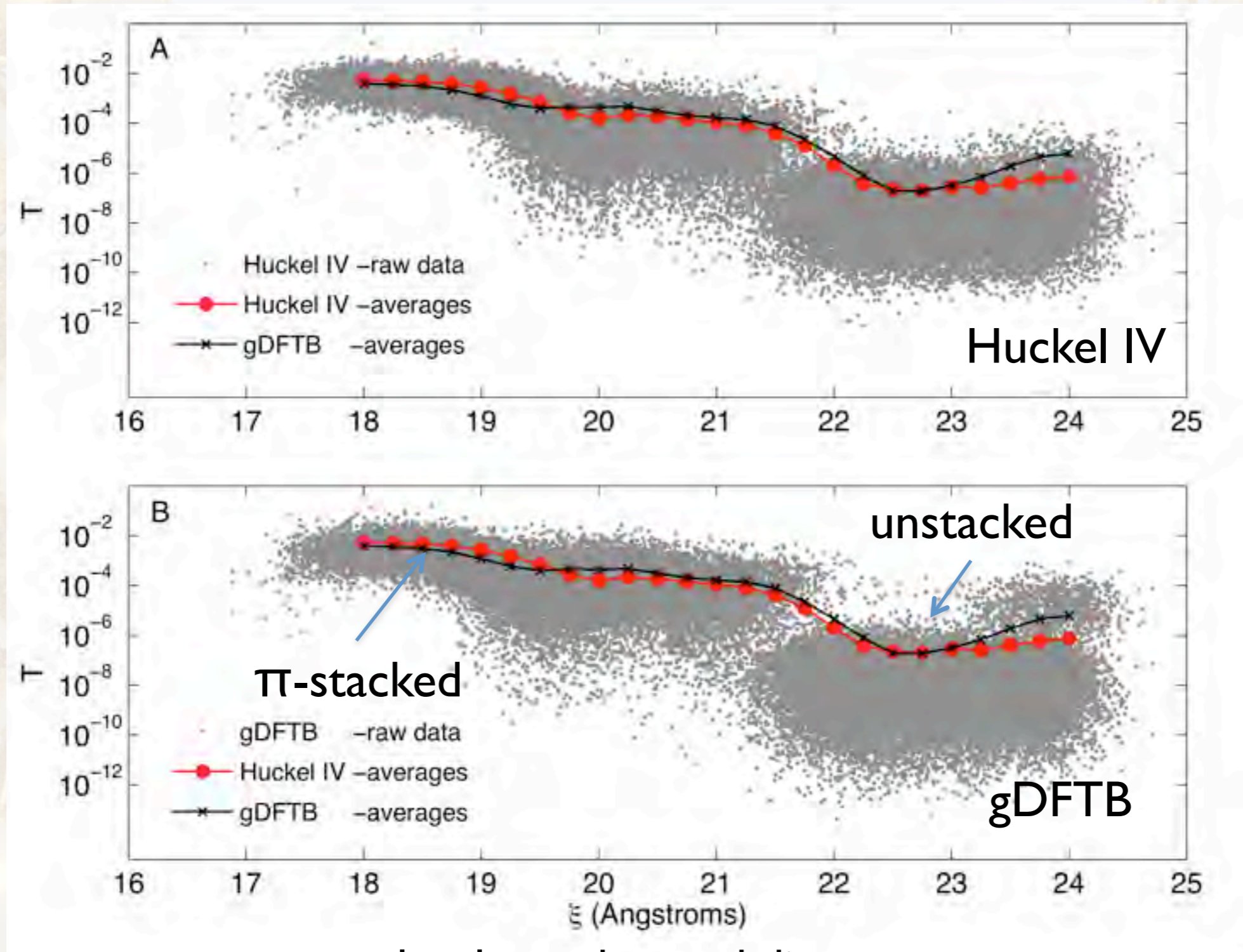
unfolding

Drop of 3-4 orders of magnitude

Note: the size of the fluctuations

“Off”

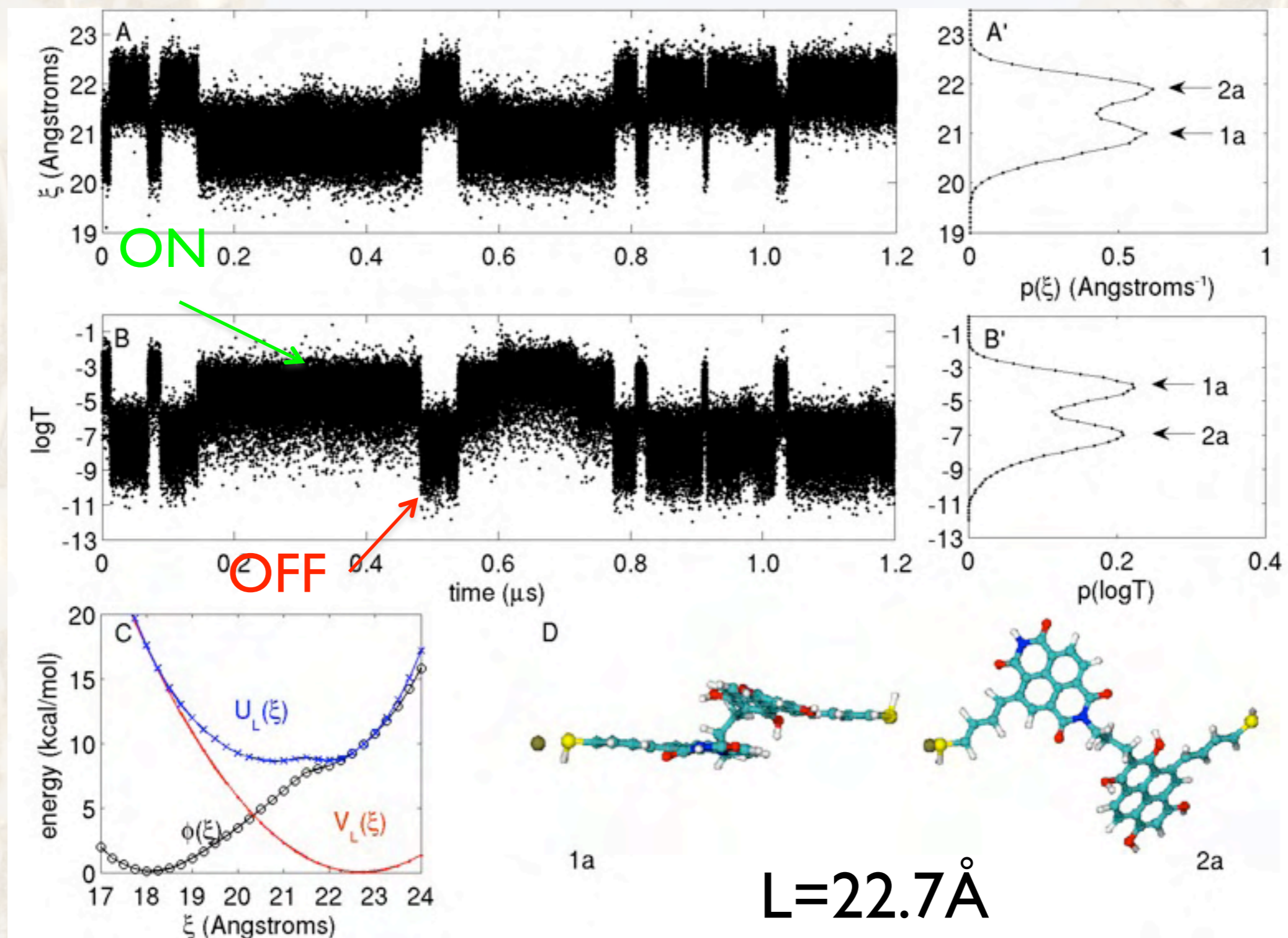
Agreement between transport methods



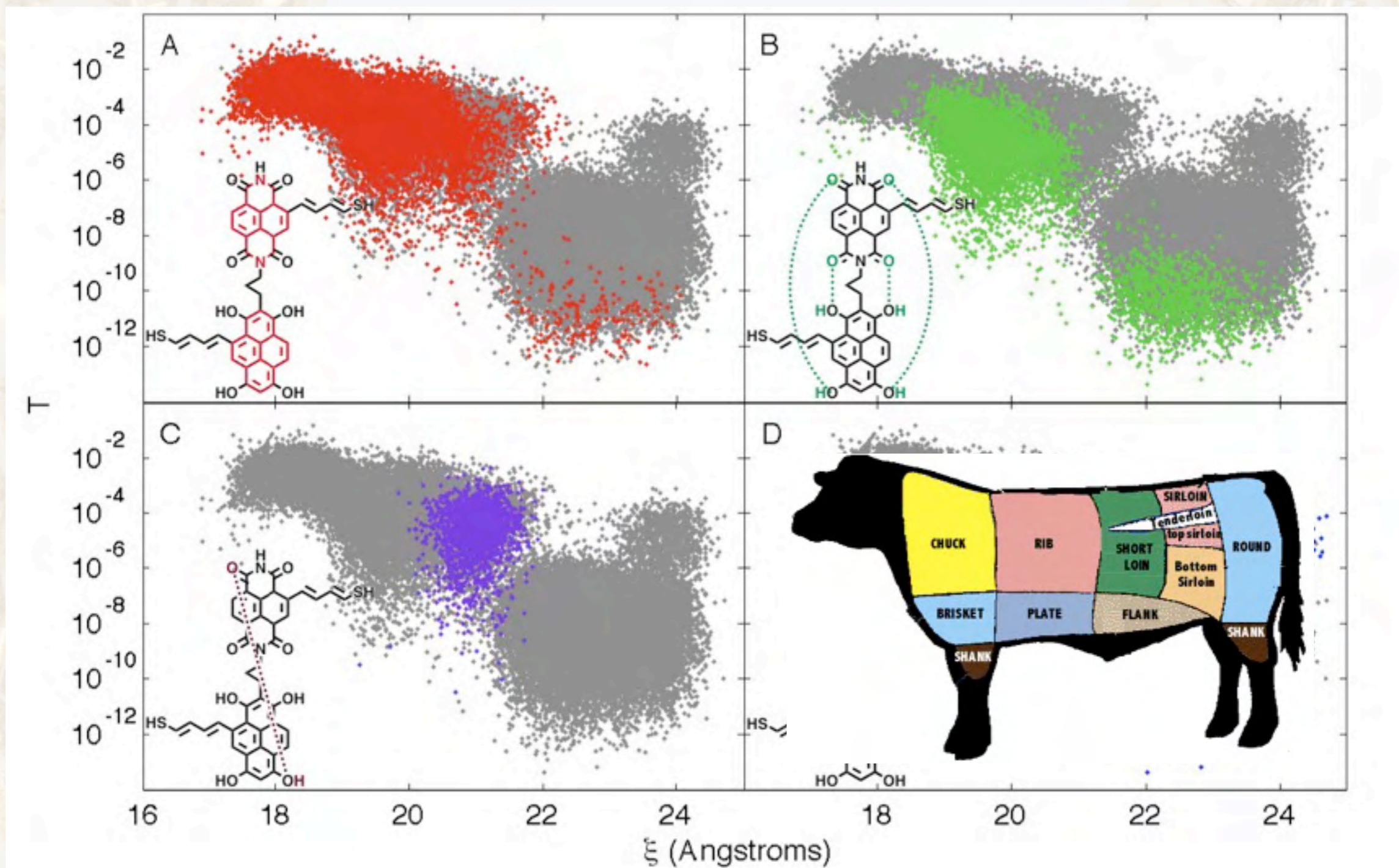
molecular end to end distance

Methods agree in average, disagree for individual conformations

Bistability leads to blinking in the conductance



The cow diagram: understanding transport domains



Acknowledgements

Anders Borges
Justin Bergfield

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

\$\$\$

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

