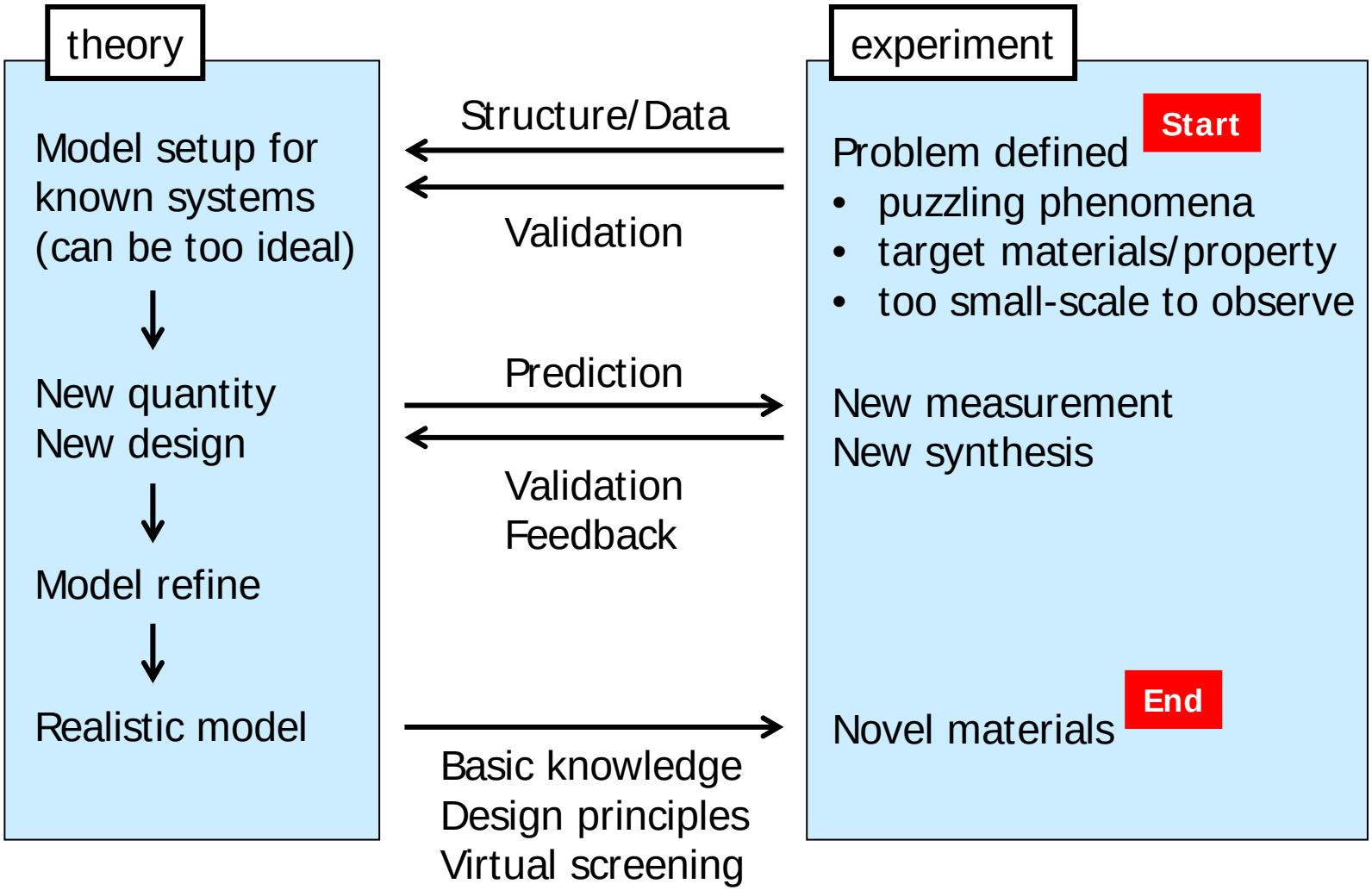
[2]Rotaxane Molecular Switch: Contributions from Molecular Modeling

Yun Hee Jang

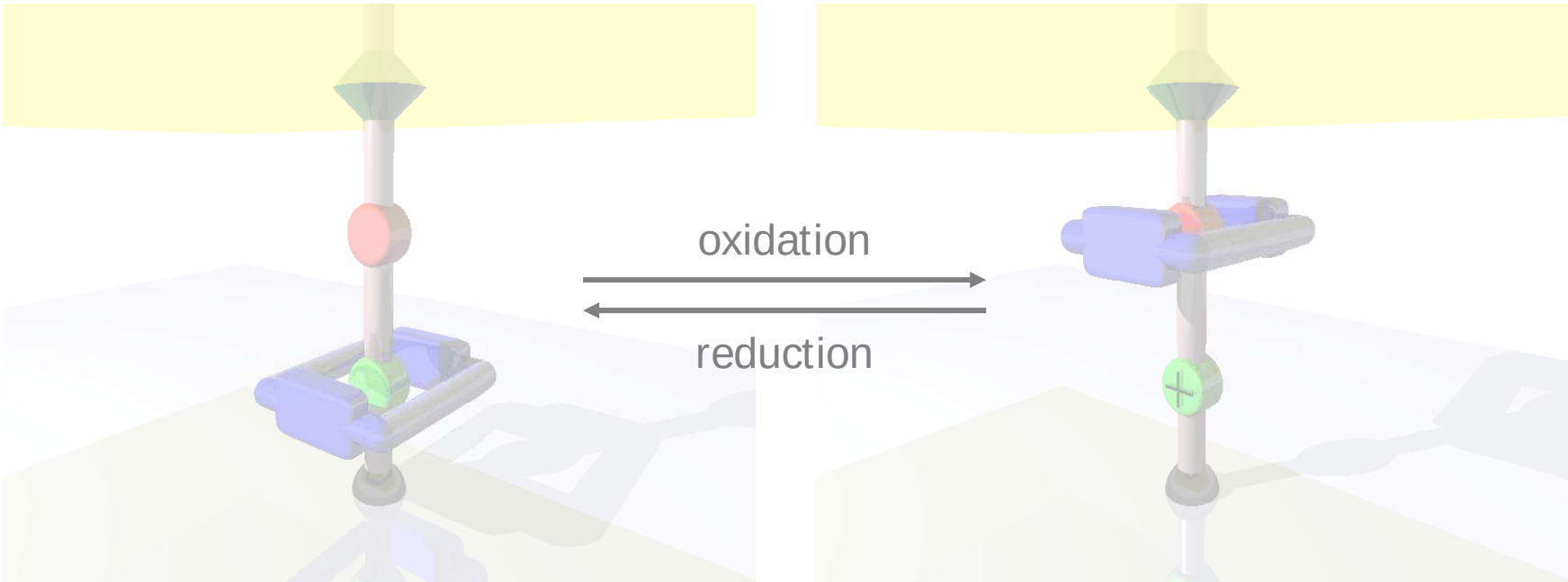
Department of Materials Science and Engineering,
Gwangju Institute of Science and Technology (GIST), Gwangju, Korea
and
LEMA, Université François Rabelais, Tours, France

June 23, 2006
CASCI MODOT (Université François Rabelais, Tours)

Ideal interplay between theory and experiment



[2]Rotaxane Molecular Switch: Contributions from Theory



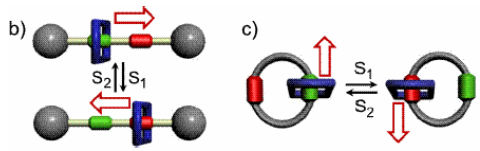
Acknowledgement:

- Yong-Hoon Kim, Seung Soon Jang,William A. Goddard III (Caltech)
- Hsian-Rong Tseng, Amar H. Flood, J. Fraser Stoddart (UCLA)
- David R. Steuerman, Jang Wook Choi, James R. Heath(Caltech)
- Bo W. Laursen, Kasper Norgaard, Thomas Bjornholm (U Copenhagen)

Outline

- Rotaxanes and Catenanes

  Molecular electronics and other applications



- Electronic structure (Design principle):

  Quantum mechanics calculation

- SAM structure on Au surface:

  Molecular dynamics simulation

- Current-voltage (I - V) curve calculation between Au electrodes

  Periodic quantum mechanics calculation

  + Surface Green's function formalism

Stoddart-Heath Type [2]Rotaxane and [2]Catenane

Rotaxane / Catenane
(dumbell / ring-shape)

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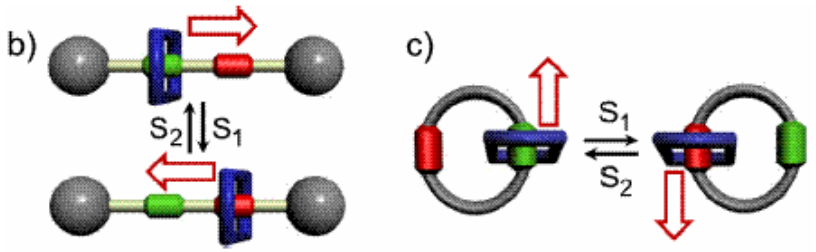
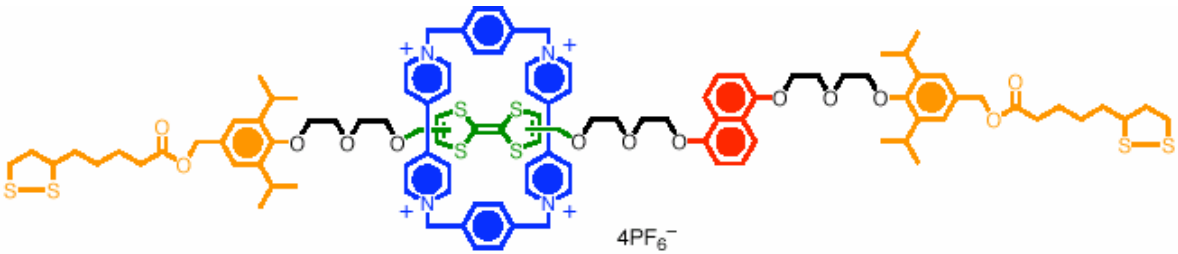
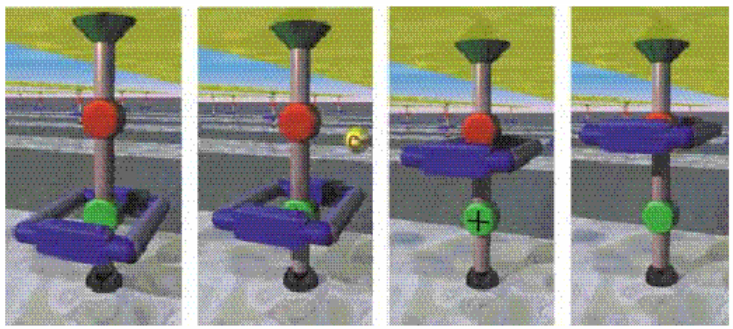
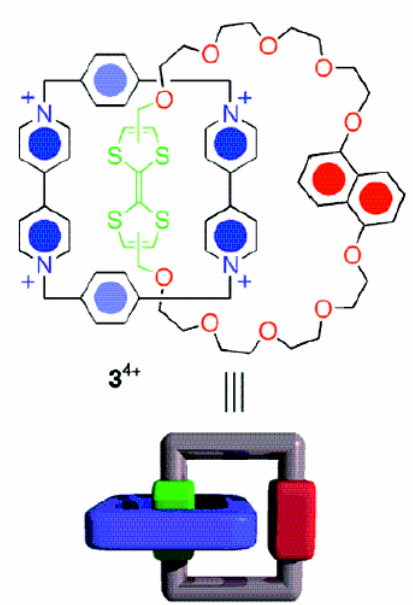
a shuttle moving back and forth between stations







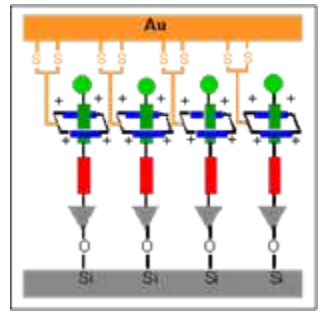


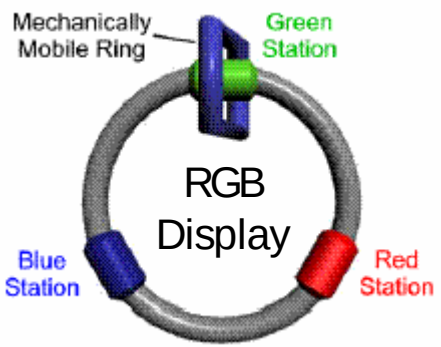
Shuttle : CBPQT = cyclobis(paraquat-*p*-phenylene)
Station 1: TTF = tetrathiafulvalene
Station 2: DNP = 1,5-dioxynaphthalene

"Molecular Design" of rotaxane/ catenane for various functions

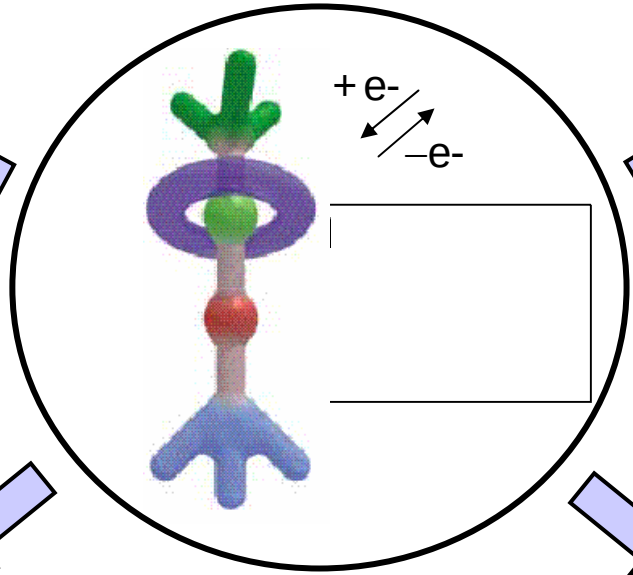
Input

Electrochemical
Photochemical
Chemical





Output: color change



SAM on surface for coherence

Molecular machine / muscle

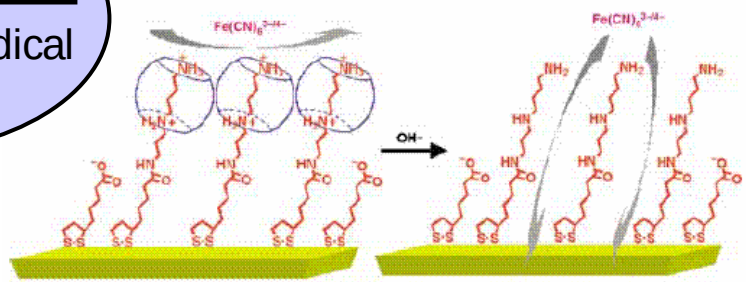
Output: position change

Output: thread-dethread

Output: conductivity change

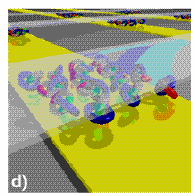
Sensing & Gating

Analytical / Medical application



Self-assembled between electrodes

Molecular electronics



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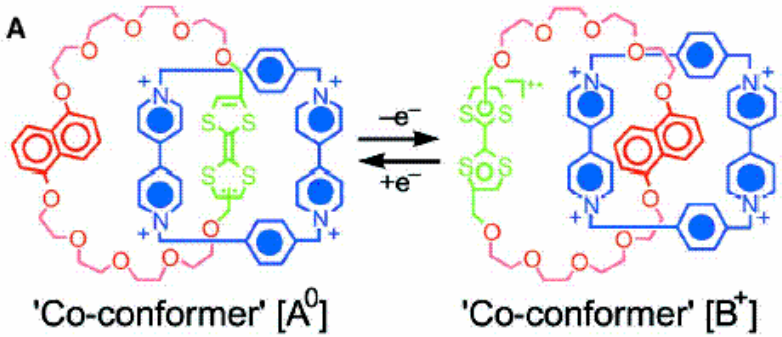
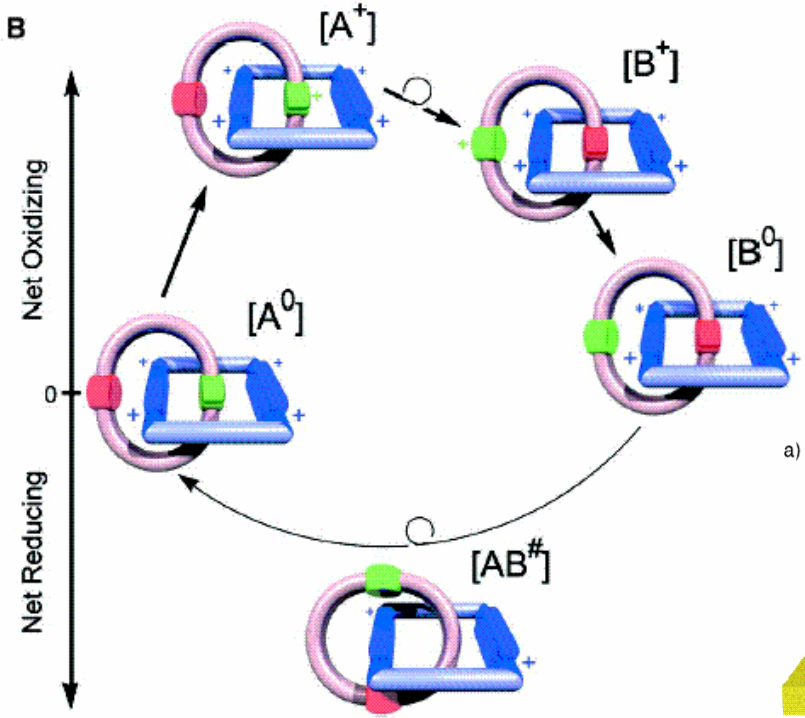
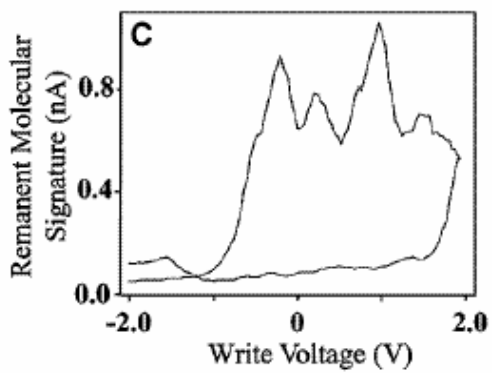
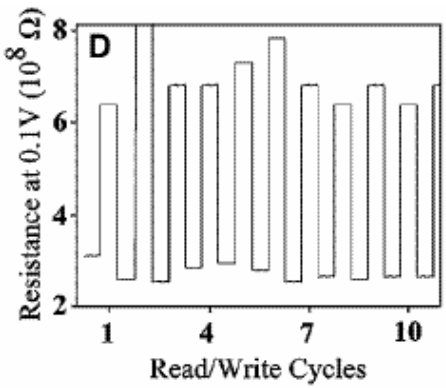
A [2]Catenane-Based Solid State Electronically Reconfigurable Switch

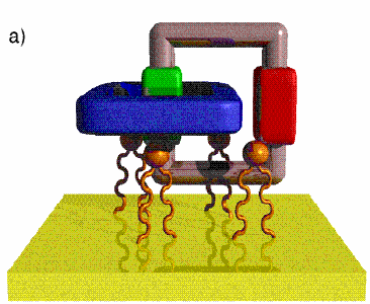
Charles P. Collier, Gunter Mattersteig, Eric W. Wong, Yi Luo, Kristen Beverly, José Sampaio, Françisco M. Raymo, J. Fraser Stoddart,* James R. Heath*

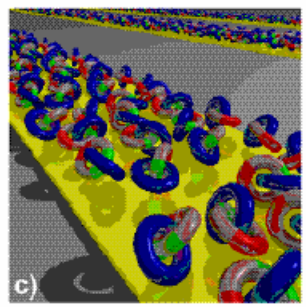


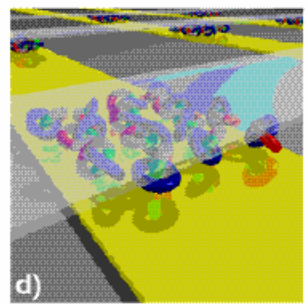








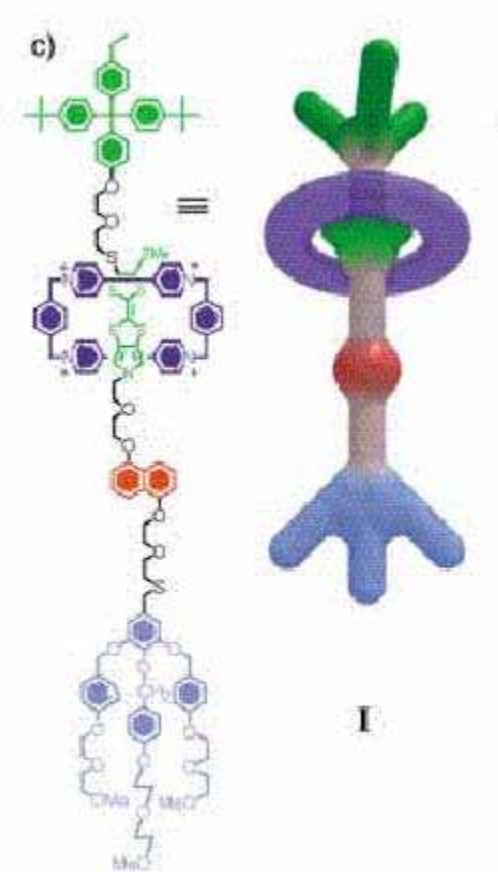


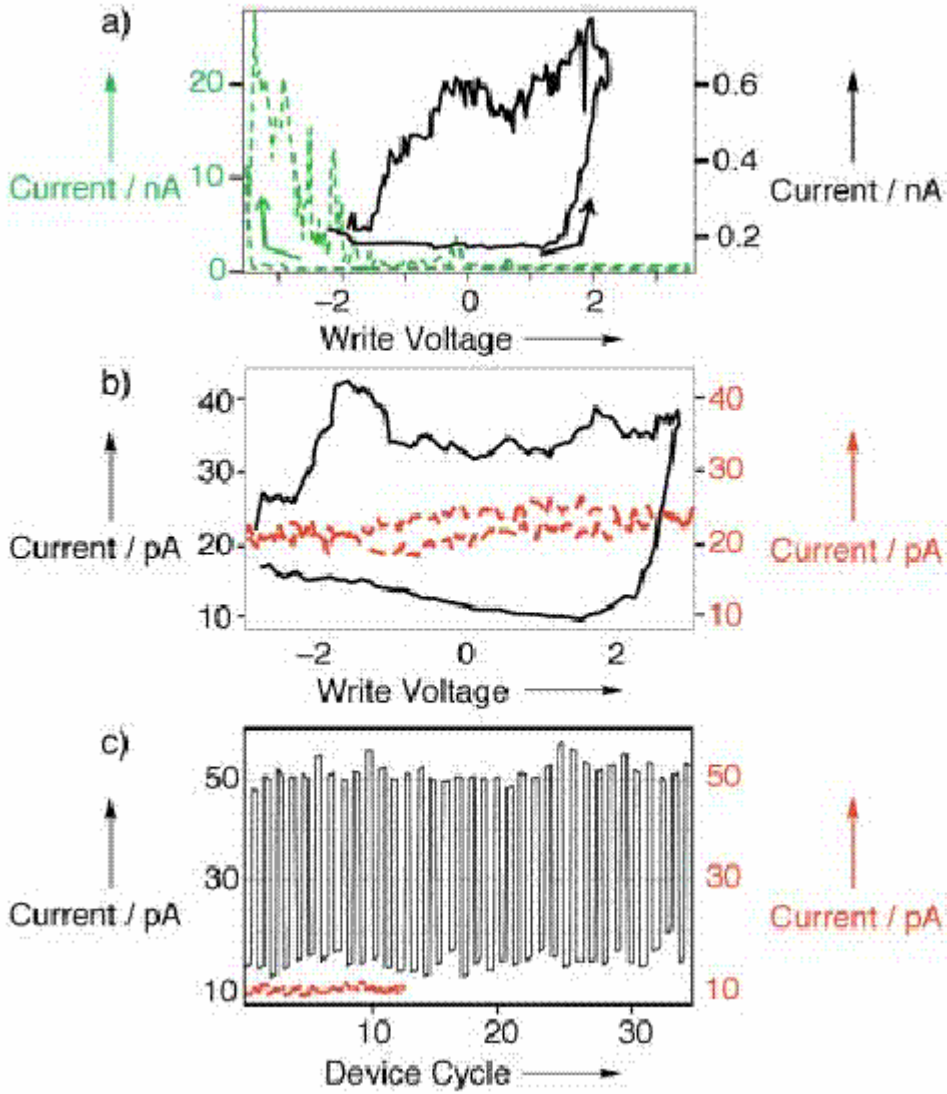


Two-Dimensional Molecular Electronics Circuits

Yi Luo, C. Patrick Collier, Jan O. Jeppesen, Kent A. Nielsen, Erica Delonno, Greg Ho, Julie Perkins, Hsian-Rong Tseng, Tohru Yamamoto, J. Fraser Stoddart,* and James R. Heath*[a]

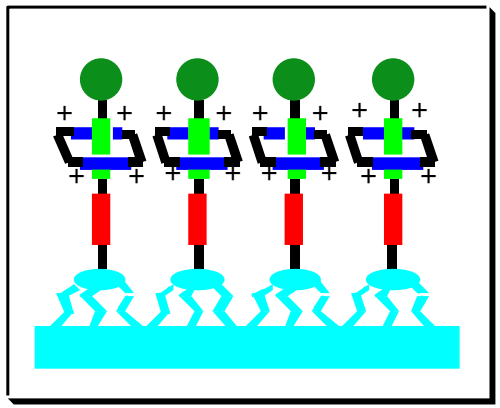
CHEMPHYSCHEM **2002**, *3*, 519 – 525



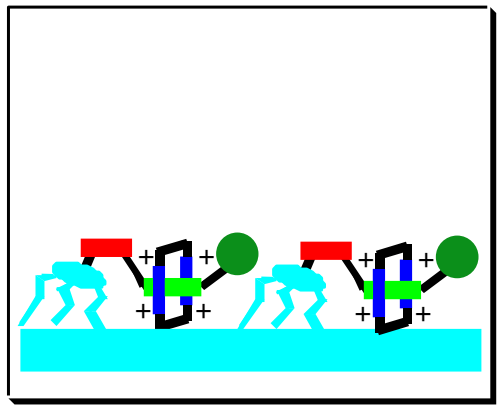


Toward better arrangement of rotaxane-soldiers

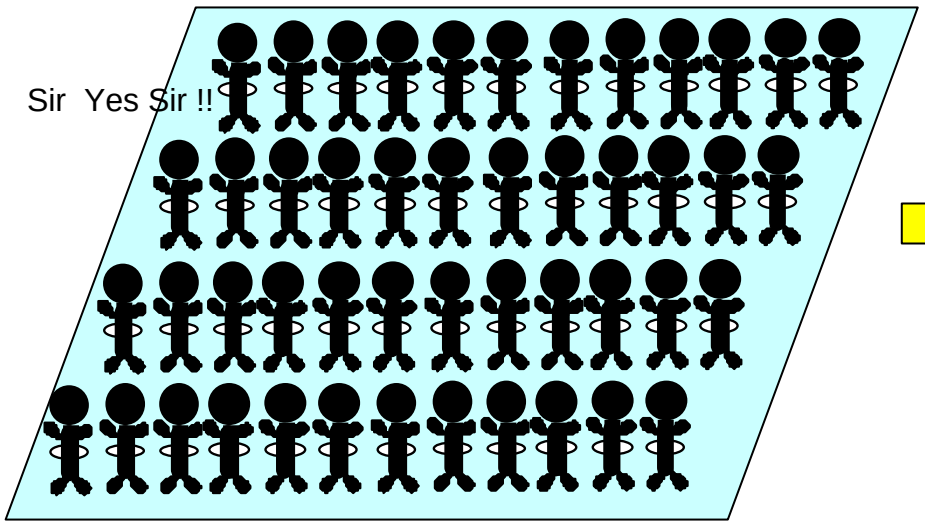
Ideal

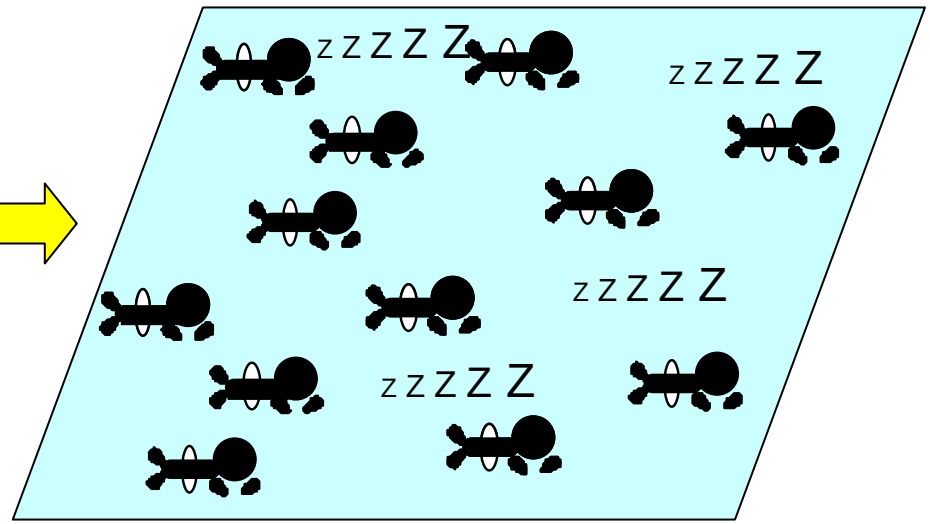


Could be ...



Sir Yes Sir !!





We need to order them to stand shoulder-to-shoulder sticking straight out from the surface.

Luo – Collier – Jeppesen – Nielsen – Delonno – Ho – Perkins – Tseng – Yamamoto – Stoddart – Heath

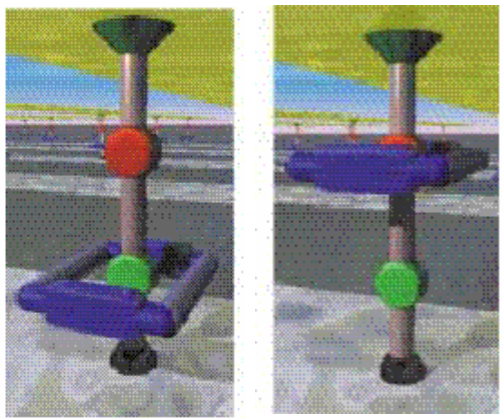
Goal

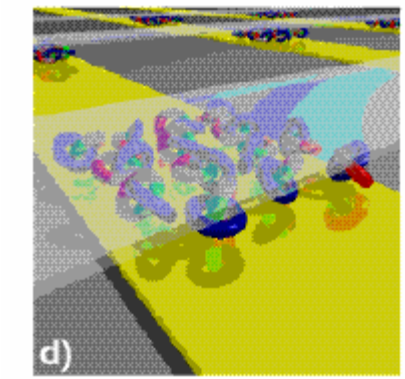
Model molecular junctions between electrodes

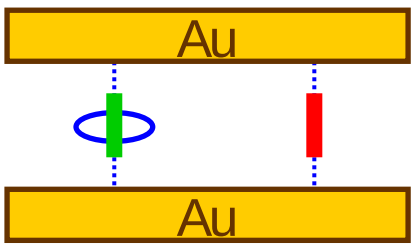
Predict current-voltage *(I-V)* characteristics

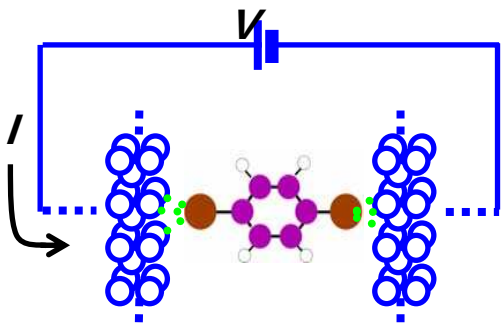
Periodic quantum mechanics + surface Green's function formalism

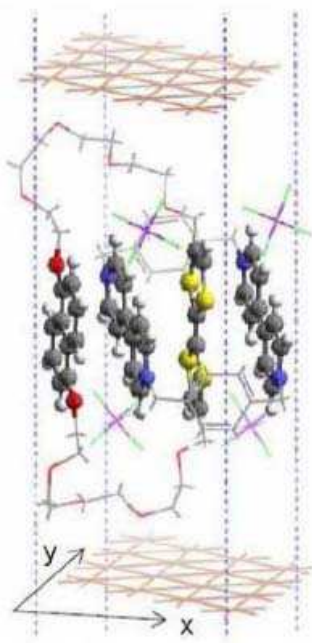
→ Switching mechanisms & Design principles



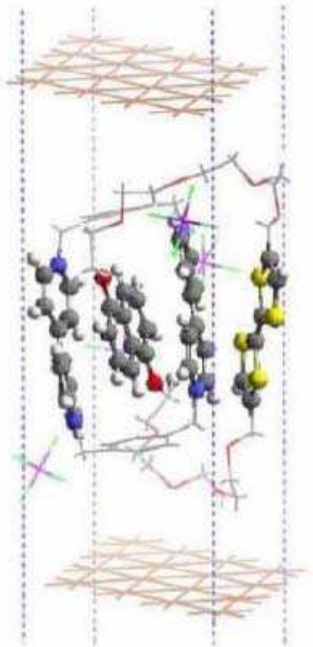








CBPQT@TTF
"Green" state



CBPQT@DNP
"Red" state

Hierarchical multi-scale modeling

- Rotaxanes and Catenanes

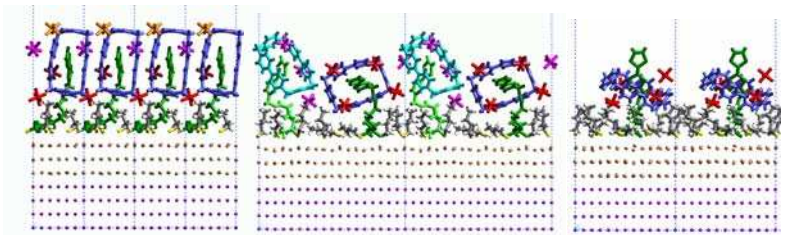
  Molecular electronics and other applications

- Electronic structure (Switch mechanism):

  Quantum mechanics calculation

- SAM structure on Au surface:

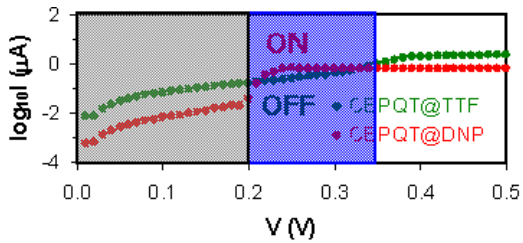
  Molecular dynamics simulation



- Current-voltage *(I -V)* curve calculation between Au electrodes

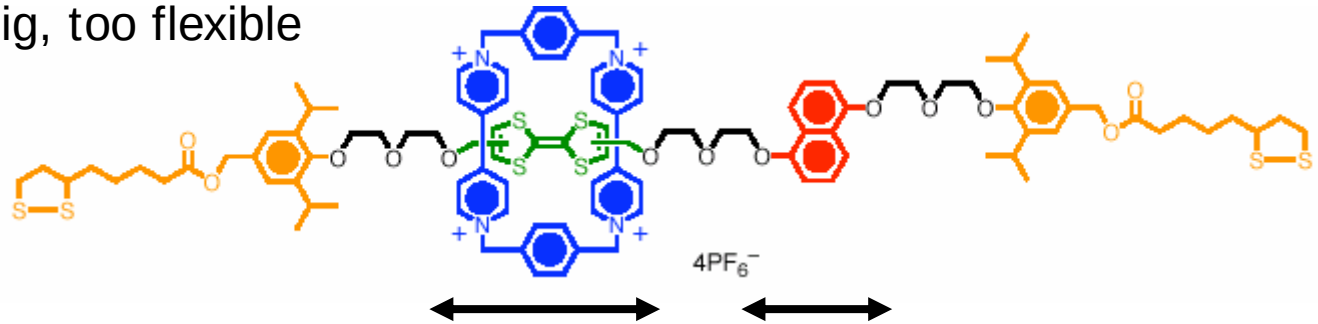
  Periodic quantum mechanics calculation

  \+ Surface Green's function formalism



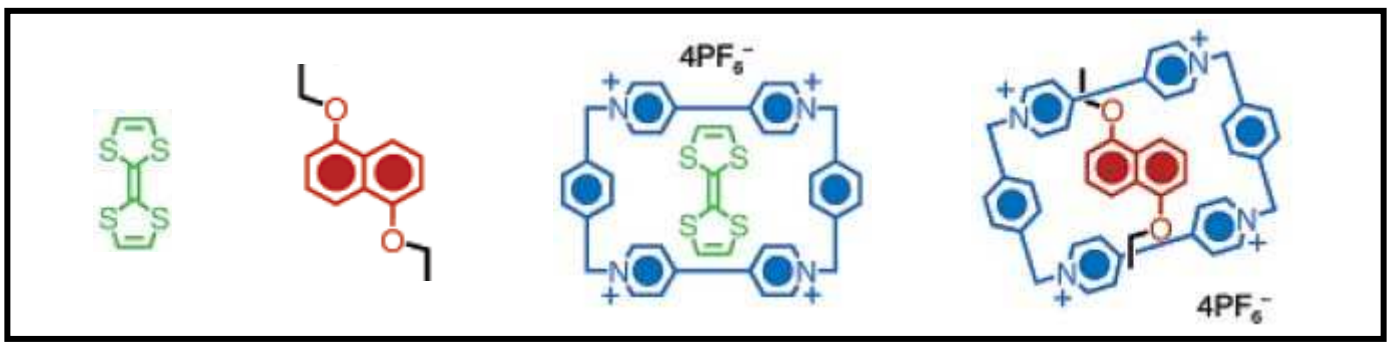
Step 1. Electronic Structure and Switching Mechanism
Quantum Mechanics Calculation

Too big, too flexible



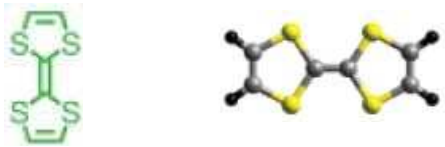
Start from the key π-components "bottom up"

*** Around E_F, only π-orbitals: σ-character components (linker & anchor) irrelevant**

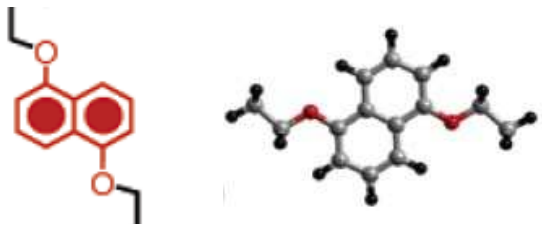


YHJ, Hwang, Kim, Jang, Goddard III, J. Am. Chem. Soc., 126, 12636 (2004)

Free stations (finger)

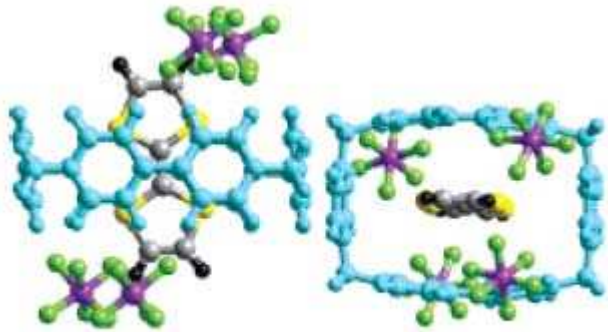


TTF

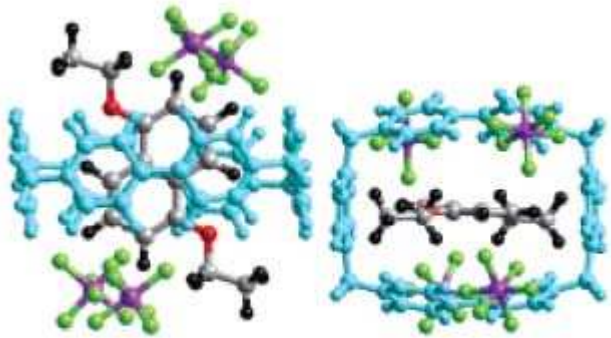


DNP

Shuttle-station complexes



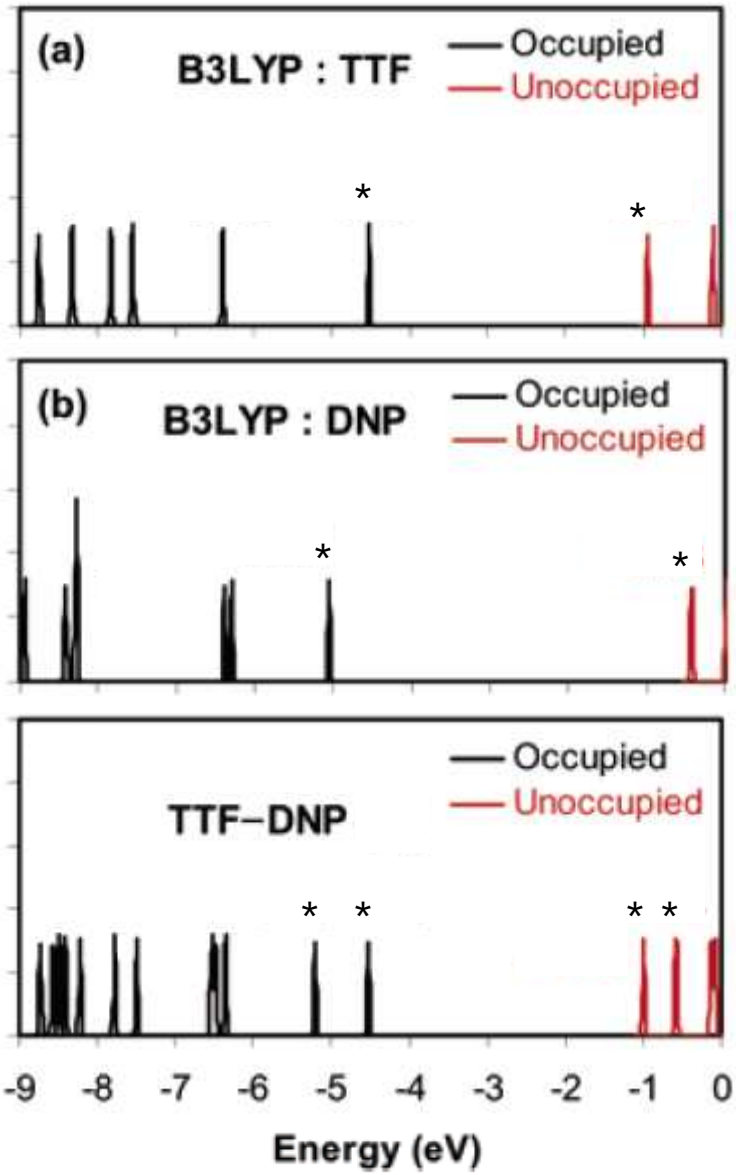
$(TTF)(CBPQT)(PF_6)_4$



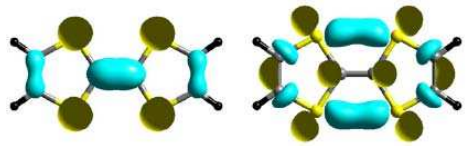
$(DNP)(CBPQT)(PF_6)_4$

Crystal structure → Geometry optimized at B3LYP/ 6-31G level**

Density of states (energy levels)



Frontier molecular orbitals



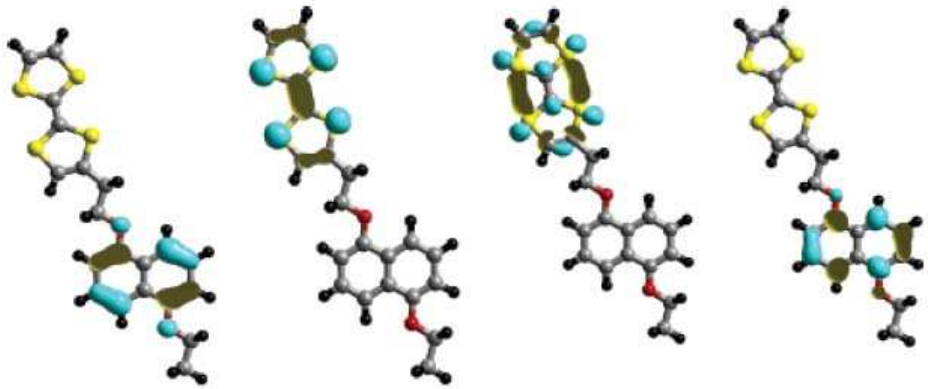
HOMO (π; −4.52 eV) LUMO (σ; −0.95 eV)

higher

HOMO (π; −5.06 eV)

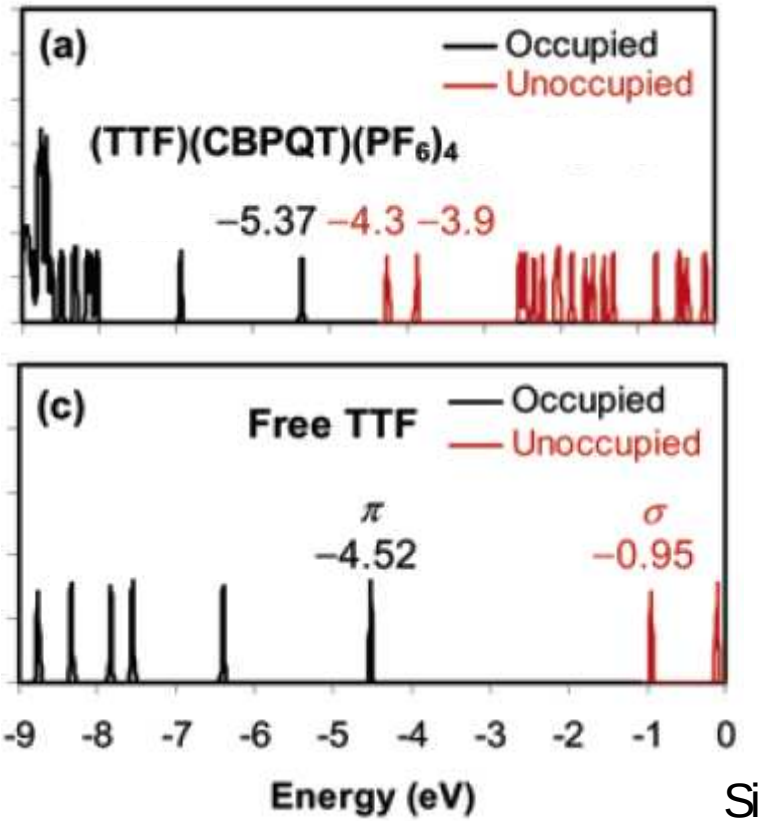
LUMO (π; −0.43 eV)

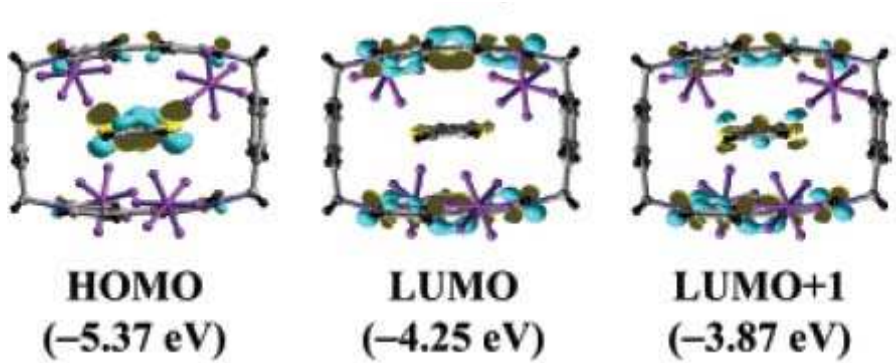
Simply add up



HOMO−1 (−5.20 eV) HOMO (−4.52 eV) LUMO (−1.00 eV) LUMO+1 (−0.58 eV)

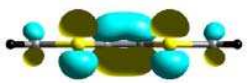
Shuttle-Station Complex: $(TTF)(CBPQT^{4+})(PF_6^-)_4$





From shuttle

Smaller HOMO-LUMO gap (green)



HOMO (π; −4.52 eV)

Significant downshift of HOMO due to net positive field by $CBPQT^{4+}$

The same goes for the other complex $(DNP)(CBPQT^{4+})(PF_6^-)_4$.

- **[2]rotaxane electronic structure ≈ a sum of two stations: bottom-up**
- **HOMO(TTF) is higher than HOMO(DNP) (first oxidation site).**
- **CBPQT provides low-lying LUMOs (smaller HOMO-LUMO gap).**
- **CBPQT lowers HOMO of the station where it sits on.**

Good agreement with experiment:

Reduction potential E^0 (vs SCE in V in acetonitrile)

Bottom-up model	E^0_1	E^0_2	E^0_2	E^0(expt) [a]
2: TTF	0.32	0.90	-	0.3-0.4; 0.7-0.8
3: DNP	1.18	-	-	1.1-1.3
4: C(TTF)P	0.83	2.44	-	0.7-1.0
5: C(DNP)P	1.49	-	-	1.65, >1.30
TTF + DNP	0.32	0.90	1.17	0.2-0.4, 0.7-0.8, 1.1-1.2
C(TTF)P + DNP	0.81	0.90	-	0.7-1.0, 0.7-1.0

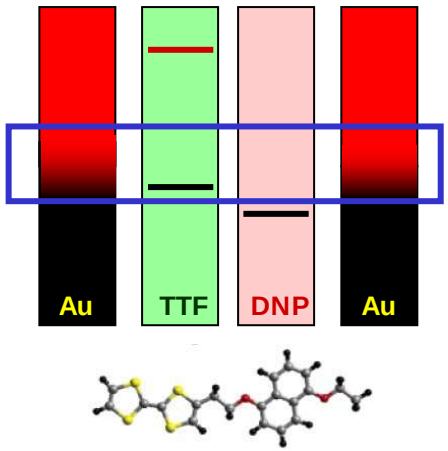
YHJ, Goddard III, J. Phys. Chem. B, 110, 7660 (2006)

Implication of QM to switching mechanism

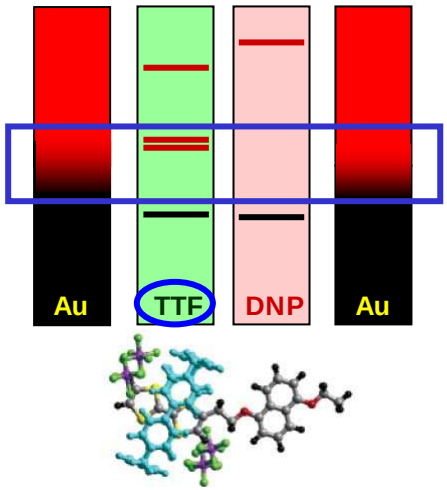
(TTF)–(DNP)
"finger only"

CBPQT

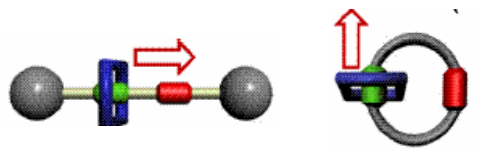
[2]rotaxane
[2]catenane



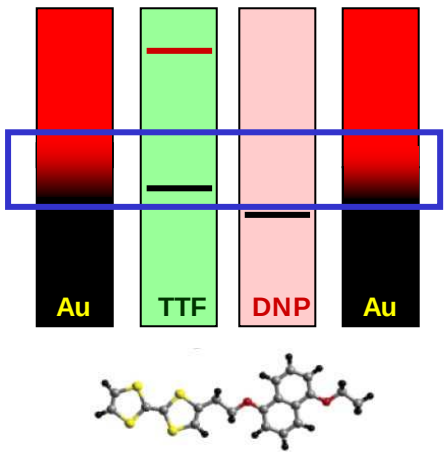
CBPQT
@TTF



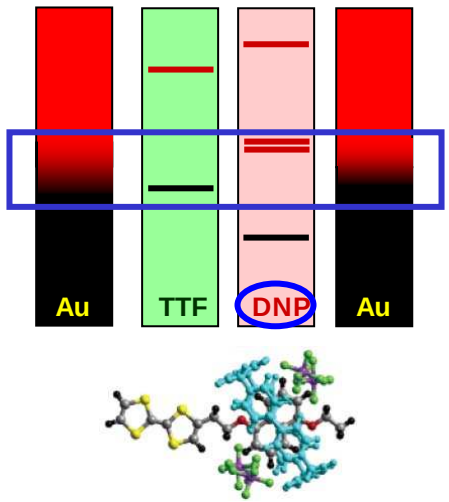
$(TTF)(CBPQT)(PF_6)_4$–(DNP)
"CBPQT@TTF"



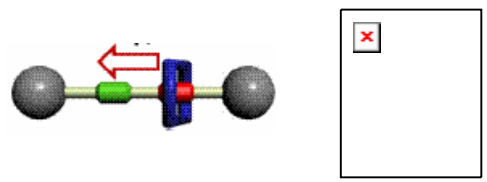
No HOMO level close to E_F



CBPQT
@DNP



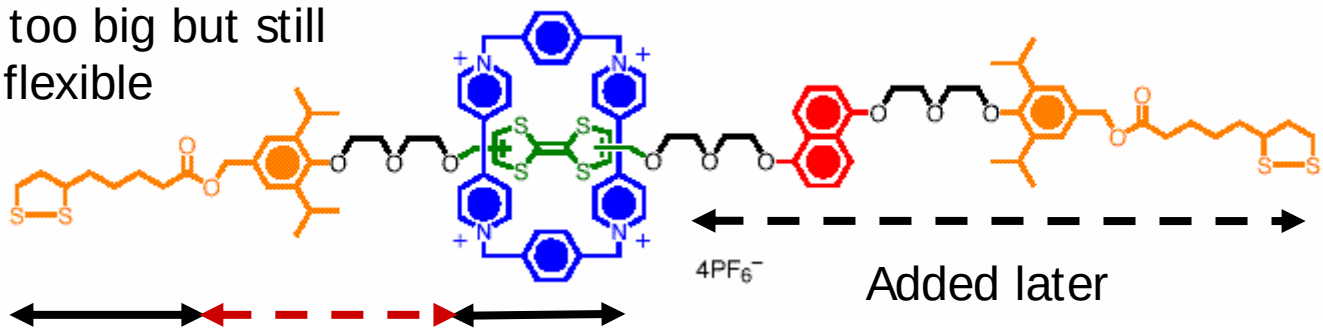
(TTF)–$(DNP)(CBPQT)(PF_6)_4$
"CBPQT@DNP"



TTF HOMO level close to E_F

Step 2. Self-Assembed Monolayer on Au(111)
MD Simulation at Various Coverages

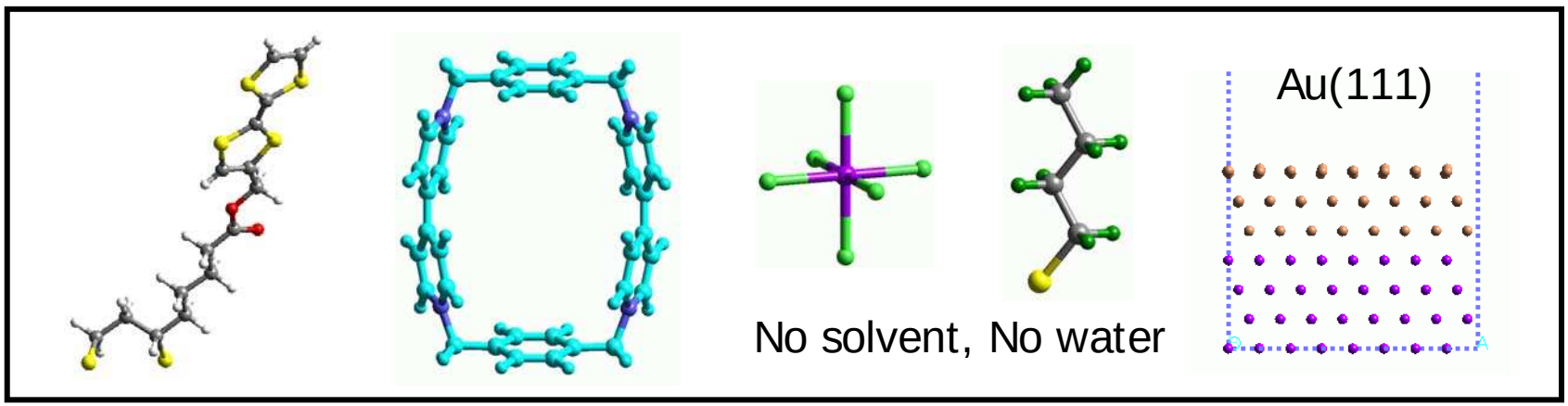
Not too big but still
too flexible



Bryce, et al. (2001)

Simplified half
(no folding issue)

"Bottom up"



YHJ, Jang, Goddard III, J. Am. Chem. Soc., 127, 4959 (2005)

Force field

$$E = E^{nonbond} + E^{valence}$$

$$E^{nonbond} = E^{coulomb} + E^{vdW}$$

$$E^{valence} = E^{bond} + E^{angle} + E^{torsion} + E^{inversion}$$

$$E_{ij}^{coulomb}(R) = C_0 \frac{q_i q_j}{\varepsilon R_{ij}}$$

$$E_{ij}^{vdW}(R) = D_0 \left\{ \left[\left(\frac{6}{\varsigma - 6} \right) e^{\varsigma \left(1 - \frac{R}{R_0} \right)} \right] - \left[\left(\frac{\varsigma}{\varsigma - 6} \right) \left(\frac{R_0}{R} \right)^6 \right] \right\}$$

$$E^{bond}(R) = \frac{1}{2} K_R (R - R_0)^2$$

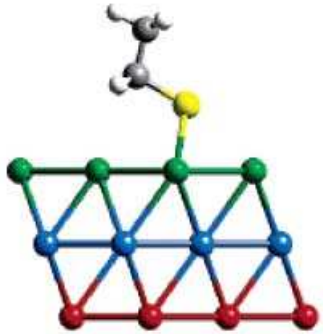
$$E^{angle}(\theta) = \frac{1}{2} \frac{K_\theta}{\sin^2 \theta_0} (\cos\theta - \cos\theta_0)^2$$

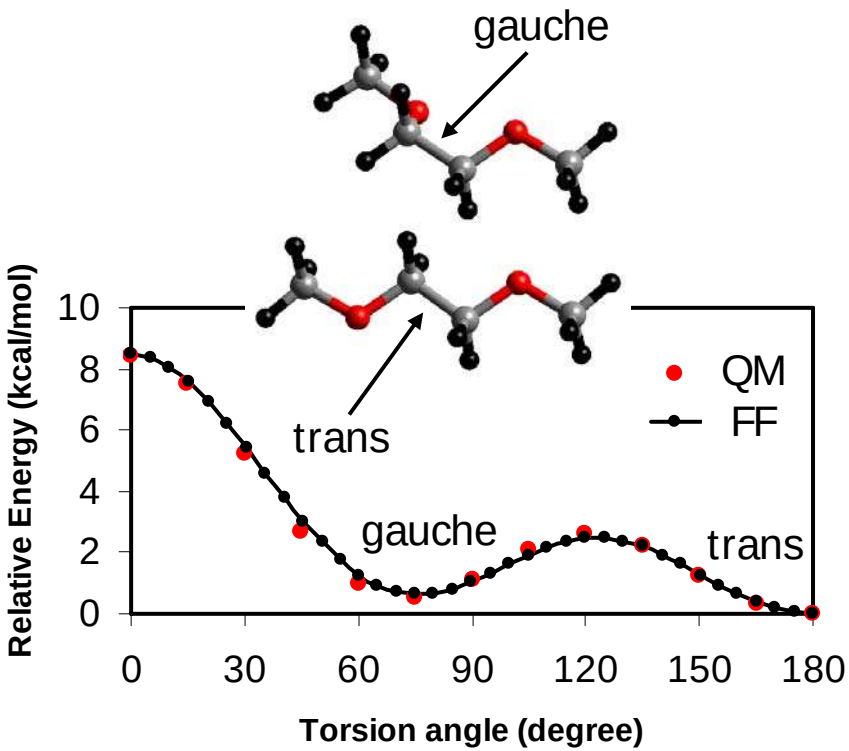
$$E_{Oh}^{angle}(\theta) = \frac{1}{2} \frac{K_\theta}{N^2} \left[1 - B(-1)^N \cos(N\theta) \right] \quad (N = 4)$$

$$E^{torsion}(\varphi) = \frac{1}{2} \sum_n K_{\varphi,n} [1 - d \cos(n\varphi)]$$

$$E^{inversion}(\omega) = \frac{1}{2} \frac{K_\omega}{\sin^2 \omega_0} (\cos\omega - \cos\omega_0)^2$$

- Dreiding FF
- QM component charges
- QM-fitted parameters for Au-S
- QM-fitted ethylene oxide torsion
- Validated with experimental crystal structure (density) and binding energy



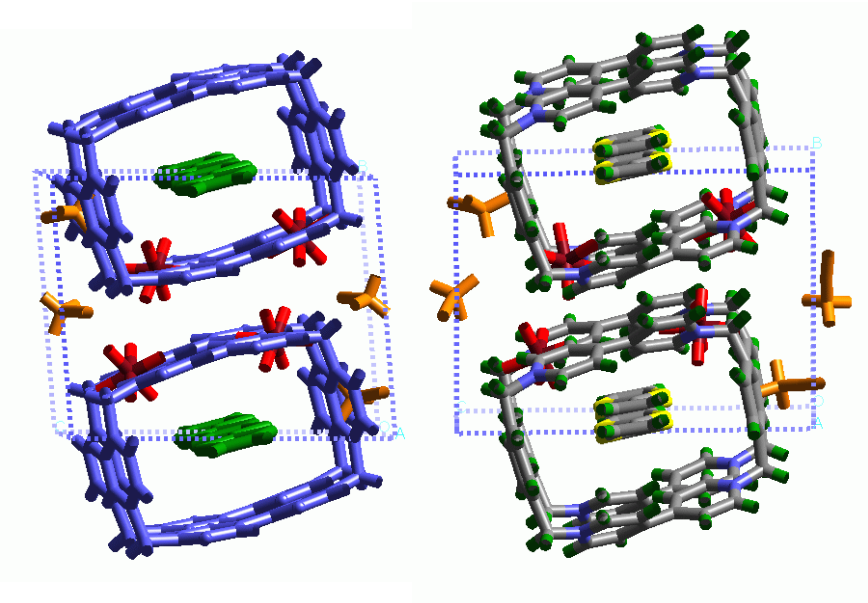


Force field validation: Crystal structure of components

VOLMEO

(TTF • $CBPQT^{4+}$ • 4 PF_6^- • 4 CH_3CN)

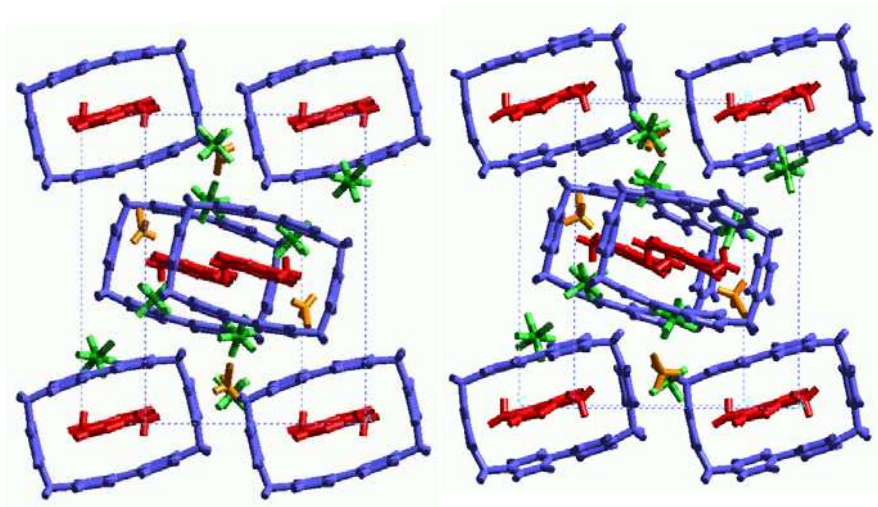
R = 0.094; Philp, JCS, Chem. Commun. (1991)



KI RTEK

(DNP • $CBPQT^{4+}$ • $4PF_6^-$ • $2CH_3CN$)

Reddington, Chem. Commun. (1991)

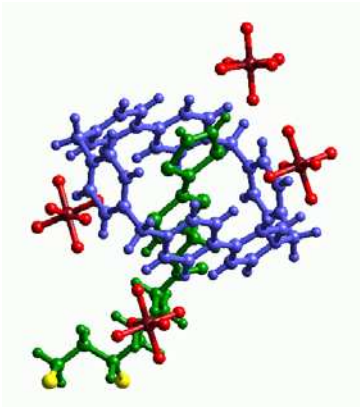


X-ray structure vs average from MD

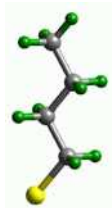
Density	1.59	1.546 (3 % ↓)	1.58	1.586 (0.4 %↑)
(g/cm^3)	@ 295 K	@ 295 K	@ 295 K	@ 295 K

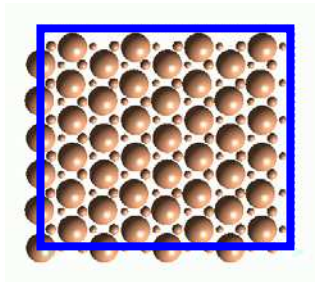
Low-end coverage SAM (1/48): 1 + 14 BuS on Au(6×4r3)

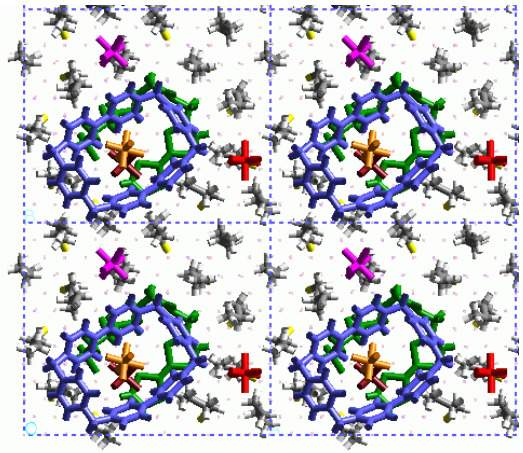
(θ(S) = 0.33; 16 sites for S)



Surface diluent

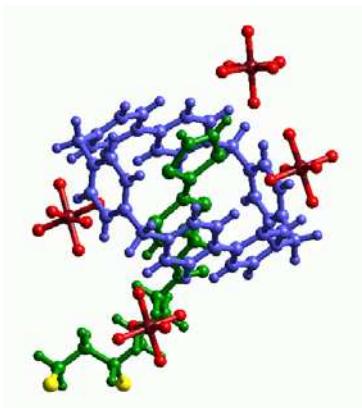




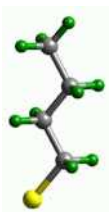


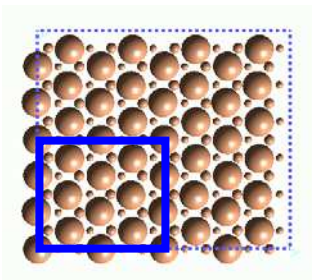
High-end coverage SAM (1/12): 1 + 2 BuS on Au(3×2r3)

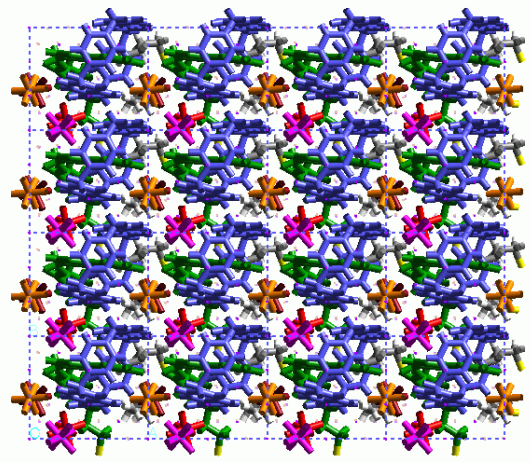
(θ(S) = 0.33; 4 sites for S)



Surface diluent



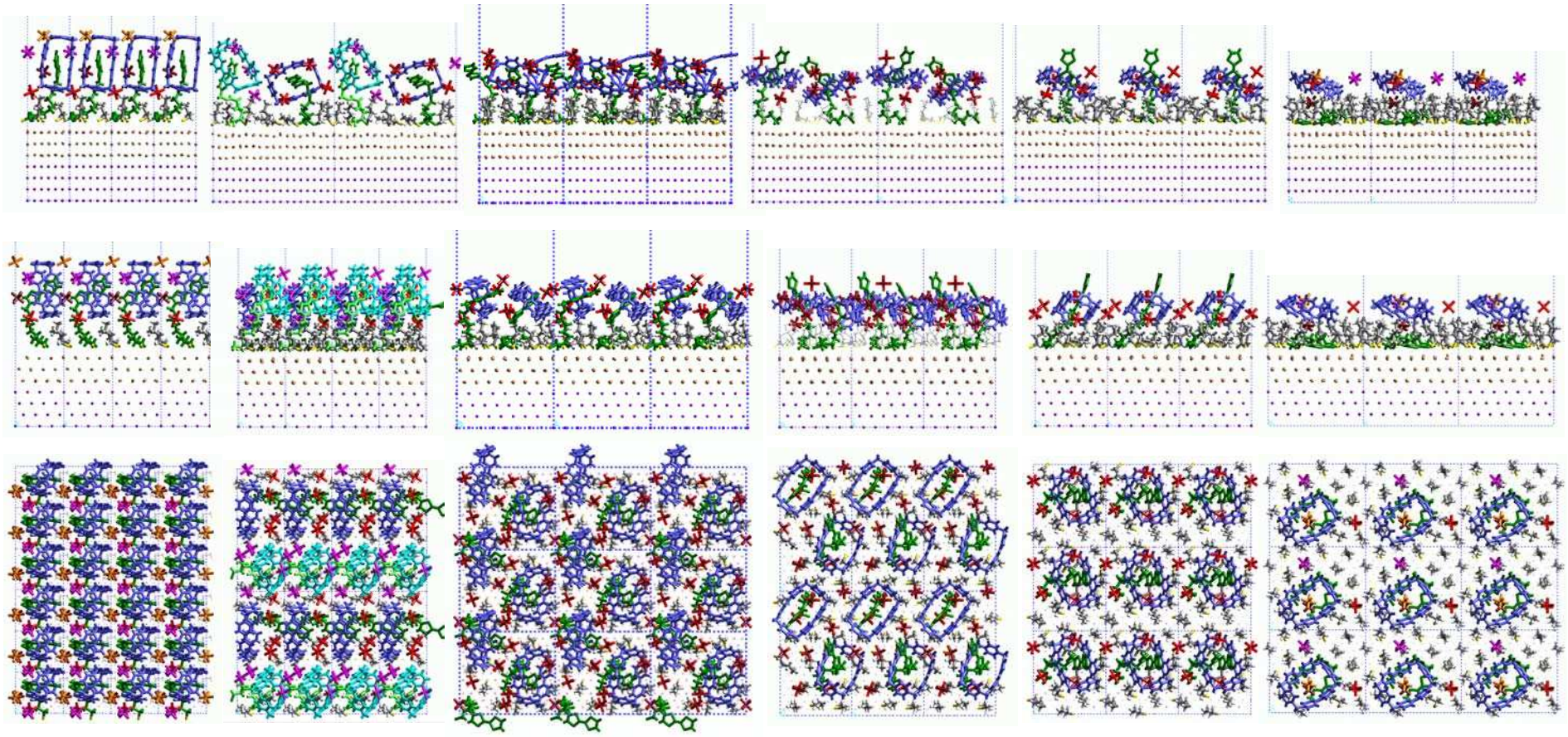




* Vacant adsorption sites passivated by coadsorbing butanethiol. Constant number of S per area

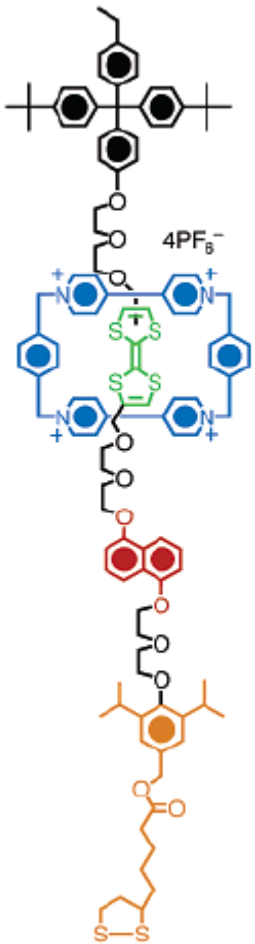
SAM at various coverages [$n(1)/n(Au_{surf})$ and footprint]

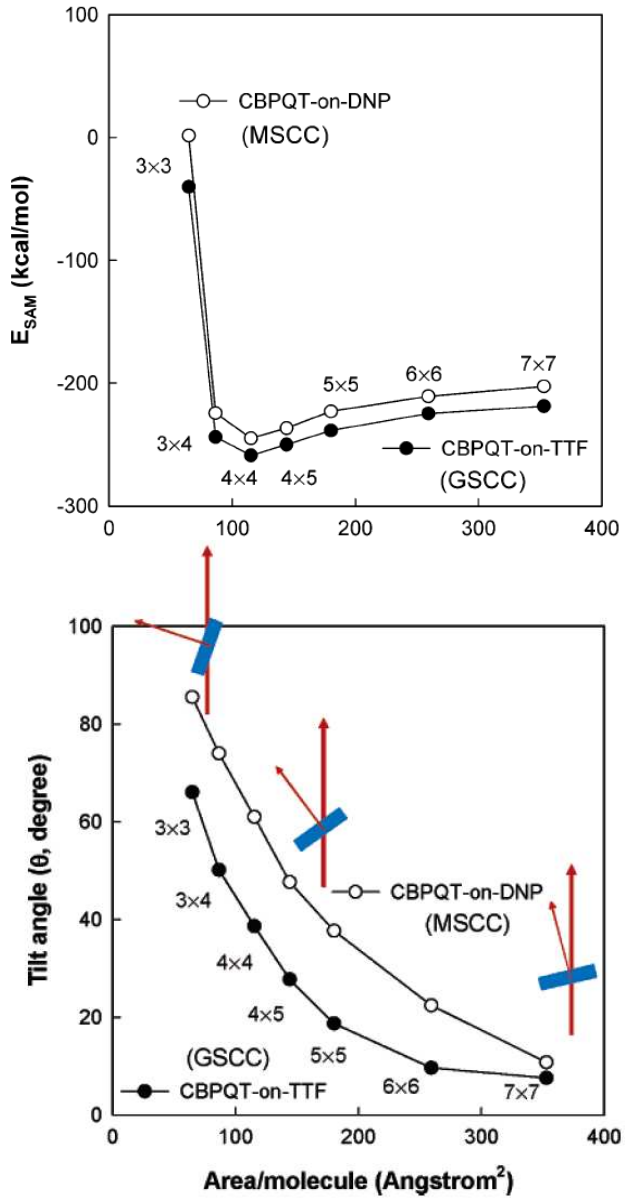
1/ 12	**1/ 18**	**1/ 24**	**1/ 27**	**1/ 36**	**1/ 48**
(3×2r3)	c(9×2r3)	c(6×4r3)	c(9×3r3)	(6×3r3)	(6×4r3)
0.86	1.30	1.73	1.94	2.59	3.46 nm^2/**1**



Up along *x* **Up along *y*** **Tilt around *y*-axis** **lie down** Complexed Uncomplexed

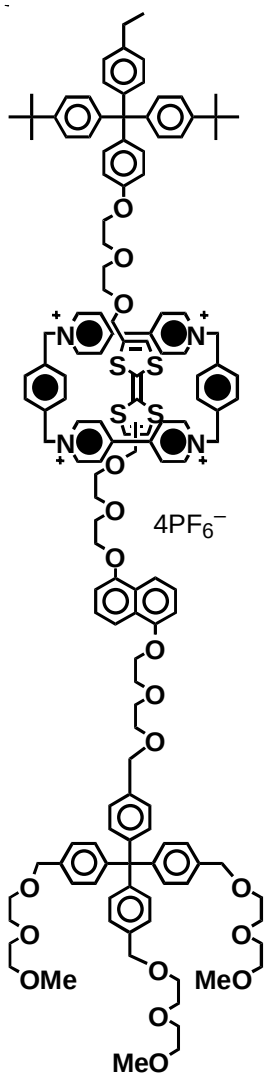
Full [2]rotaxane: the same behavior



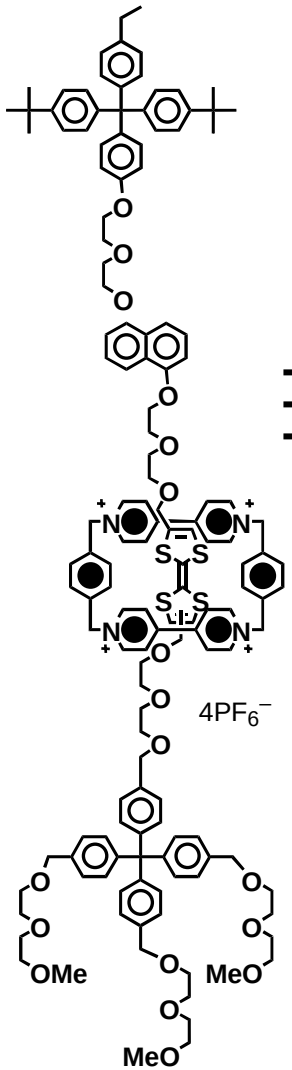


Jang, YHJ, Kim, Goddard III, et al. J. Am. Chem. Soc., 127, 1563 (2005)

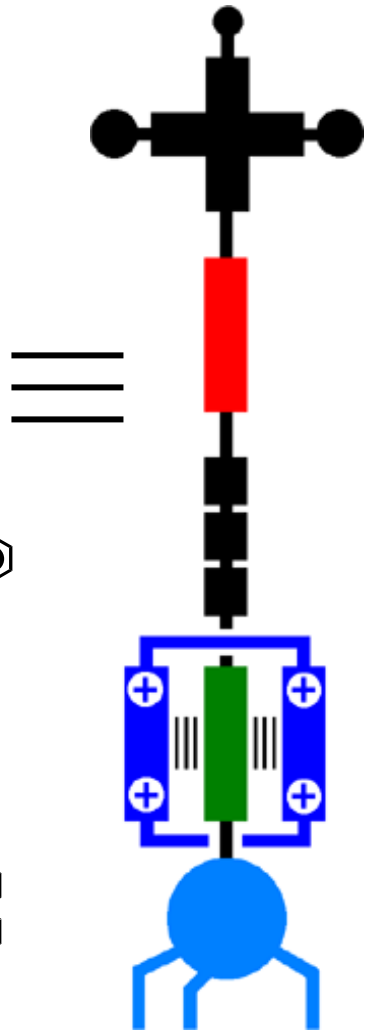
Related experiment: Langmuir isotherm

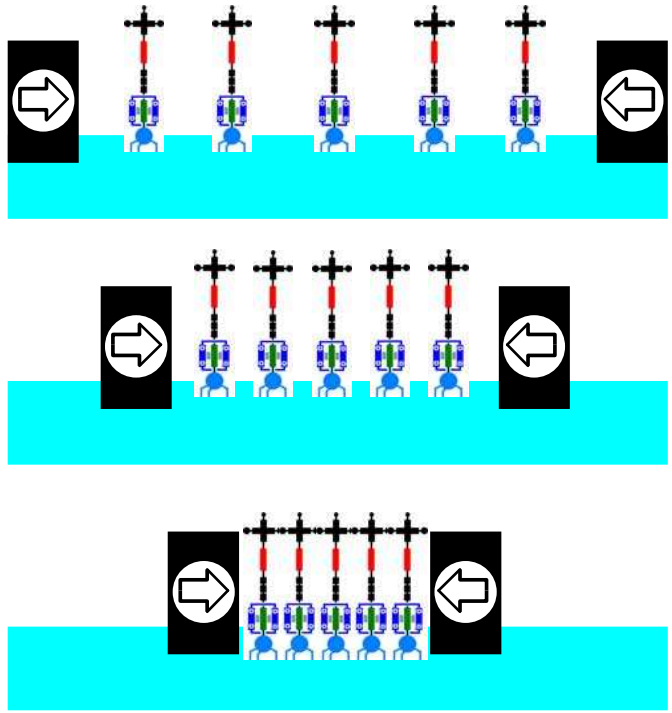


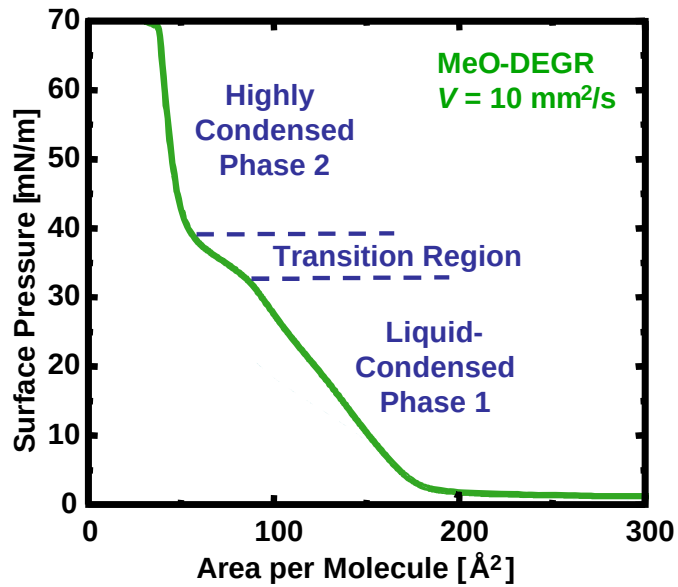
MeO-DEGR• 4PF6



iso-MeO-DEGR• 4PF6

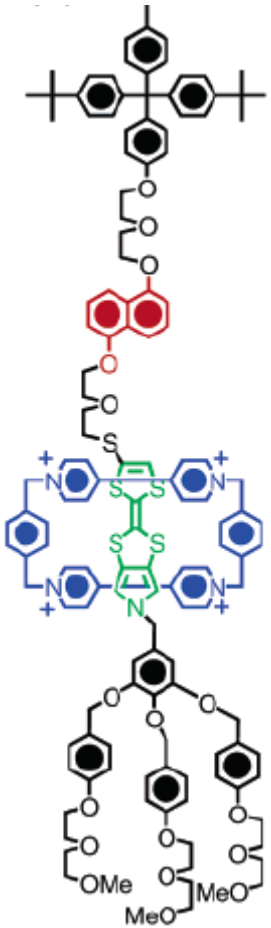


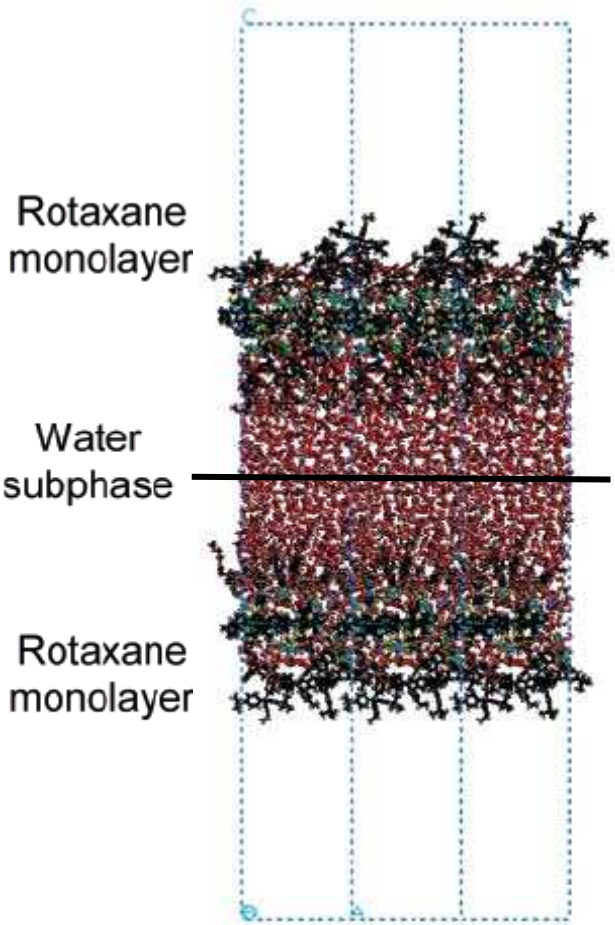




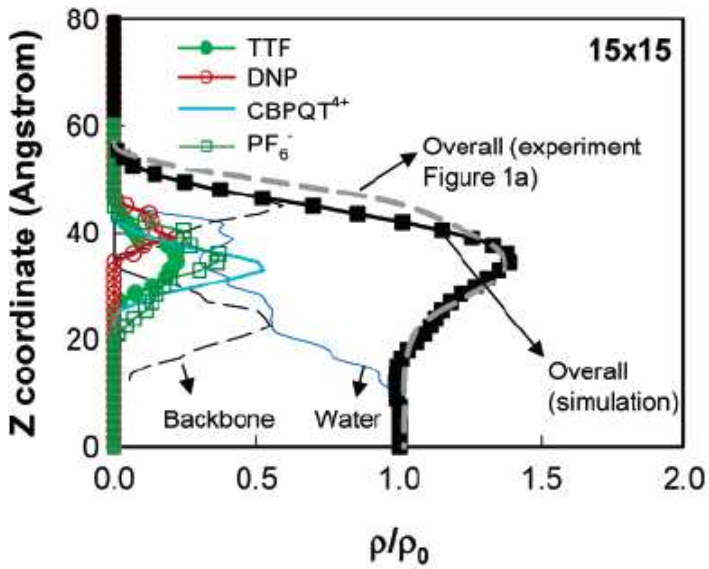
Langmuir monolayer at air/ water interface

Simulated electron density z-profile vs x-ray reflectivity experiment





Equilibrated



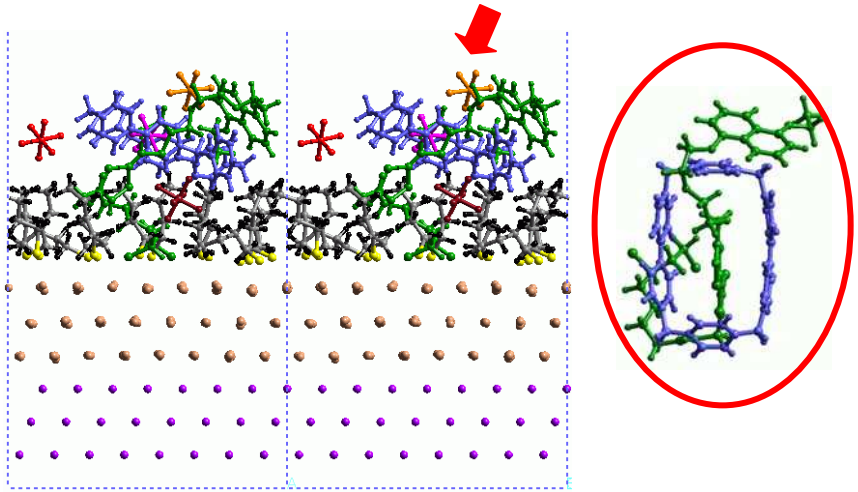
From component analysis:

Water may remain inside SAM after transferred on electrode.

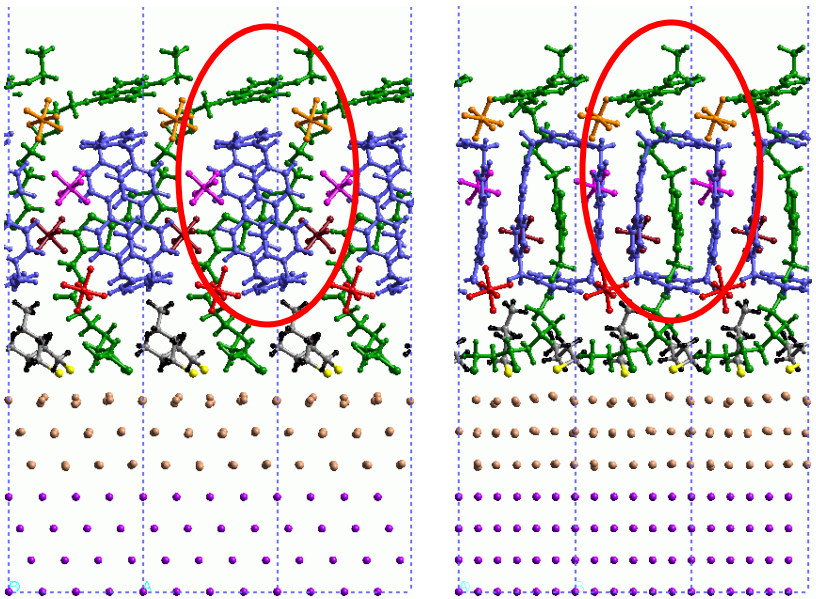
Jang, YHJ, Kim, Goddard III, Choi, Heath, Laursen, Flood, Stoddart, Norgaard, Bjornholm
J. Am. Chem. Soc., 127, 14804 (2005)

Full [2]rotaxane:

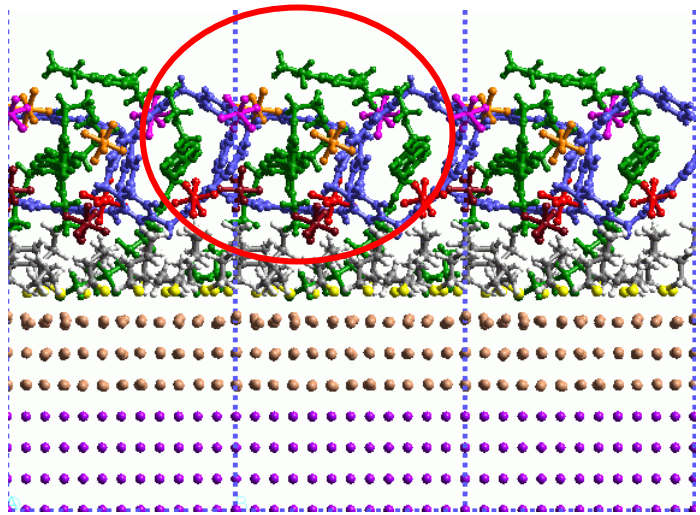
π-π contact between stations preferred at all coverages



1/ 48 (footprint 3.46 nm^2)



1/ 12 (footprint 0.86 nm^2)



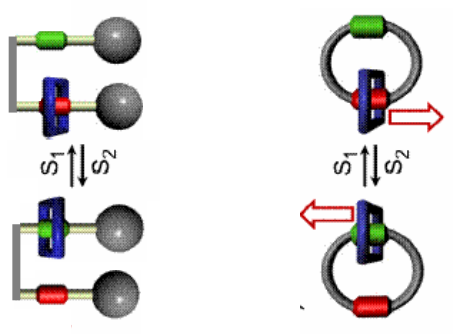
1/ 24 (footprint 1.73 nm^2)

Finding

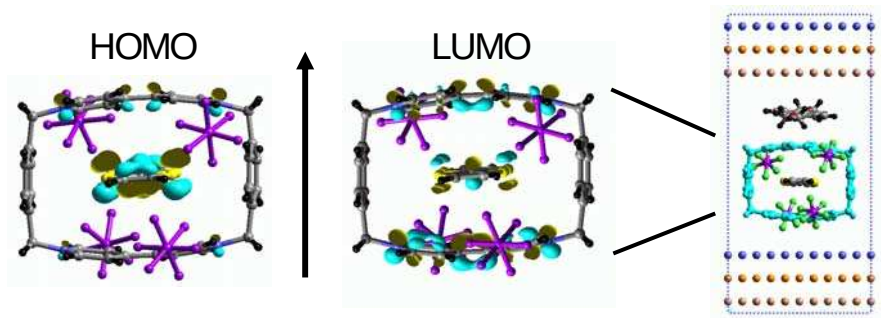
- **CBPQT changes orientation at higher coverages.**
- **Folding & π-π contact between stations**
- **Water still remains after transfer of Langmuir monolayer to electrode**

Implication from MD

- **Rotaxane ~ Catenane?**



- **Conducting thru π-π stack (as in DNA)?**

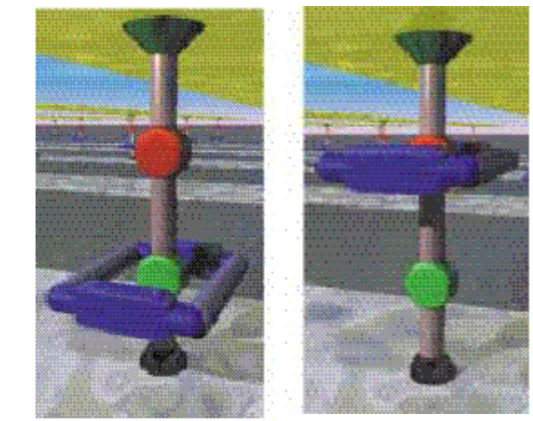


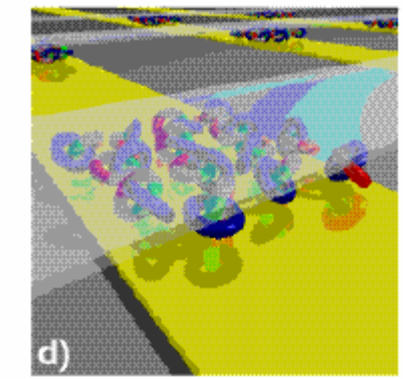
- **Shuttling-&-switching possible at this tight network?** Other mechanisms?

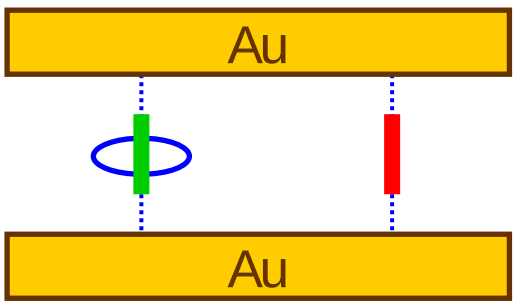
- **Refined model with water inside is needed.**

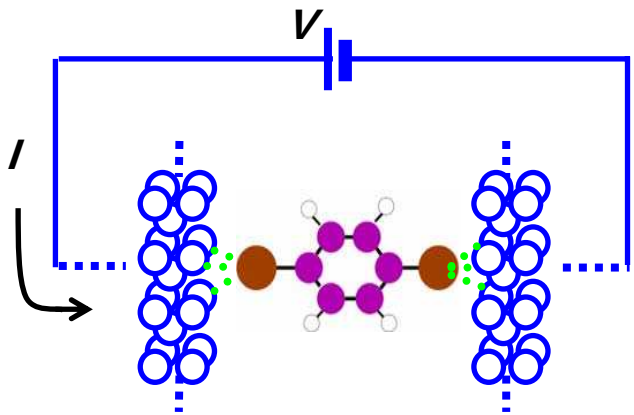
Step 3. Molecular junction between Au electrodes
Current-Voltage *(I-V)* Characteristics

Periodic QM (DFT) with surface Green's function formalism









Kim, Jang, YHJ, Goddard III, Phys. Rev. Lett., 95, 156801 (2005)

I-V: DFT + Green's Function + Landauer formalism

Density-functional theory (Hohenberg-Kohn-Sham)

"Extended molecule" + separate bulk electrode calc. -> *H*, *S*

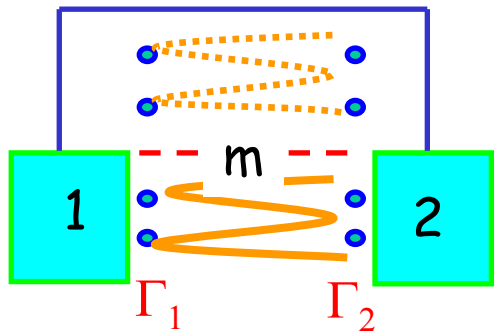
Non-Eqm. Green's ftn. Formalism (Fisher-Lee)

$$G_m = (E_m S_m - H_m - \Sigma_1 - \Sigma_2)^{-1}$$

$$\Gamma_{1,2} = i\left(\Sigma_{1,2} - \Sigma_{1,2}^{+}\right)$$

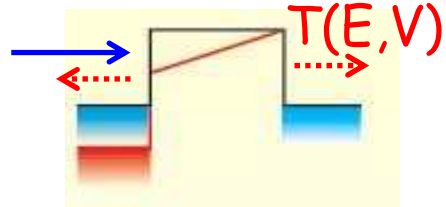
self-energy broadening

$$T(E,V) = \mathrm{Tr}\left(\Gamma_1 G \Gamma_2 G^{+}\right)$$

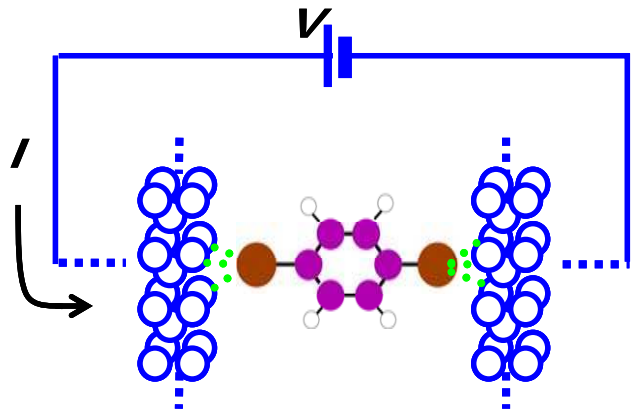


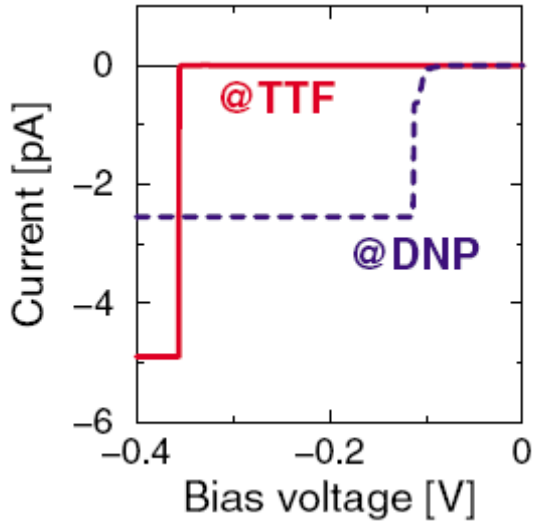
Ballistic transport theory (Landauer, Buttiker)

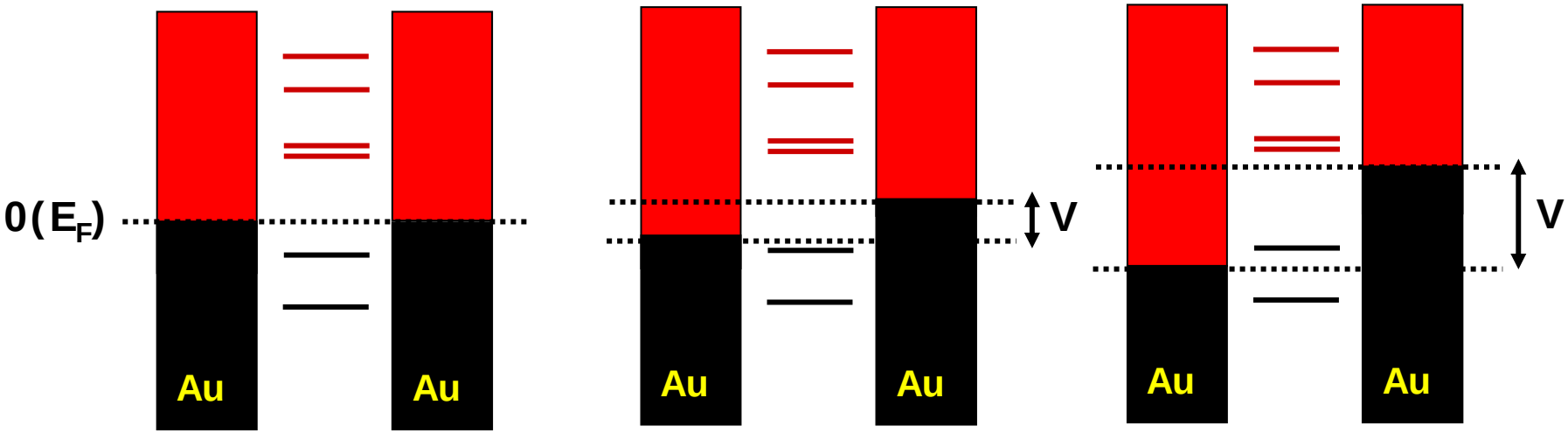
$$I = \frac{2e}{h}\int_{-\infty}^{\infty} T(E,V)\left[f_1(E-\mu_2) - f_2(E-\mu_1)\right]dE$$



Calculated with *SeqQuest* periodic DFT code (Peter Schultz, Sandia)







V= 0

I = 0

Small V

I = 0

Large V

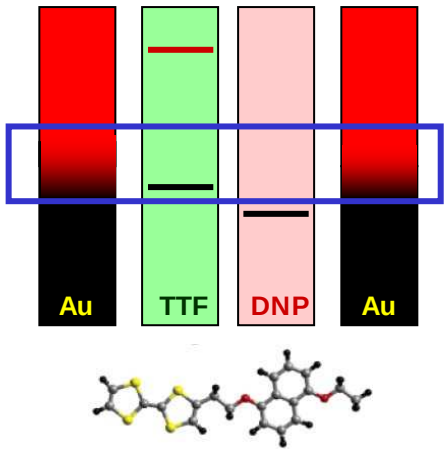
I ≠0

Implication of QM to switching mechanism

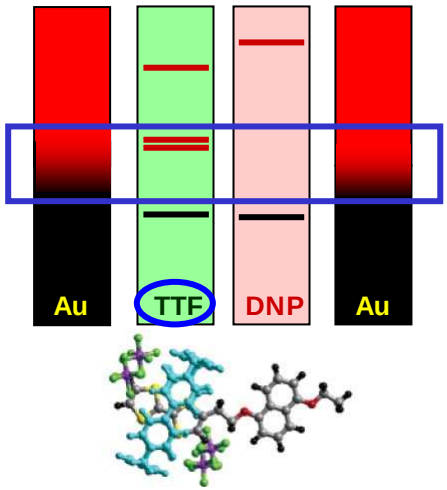
(TTF)–(DNP)
"finger only"

CBPQT

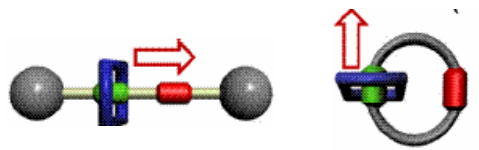
[2]rotaxane
[2]catenane



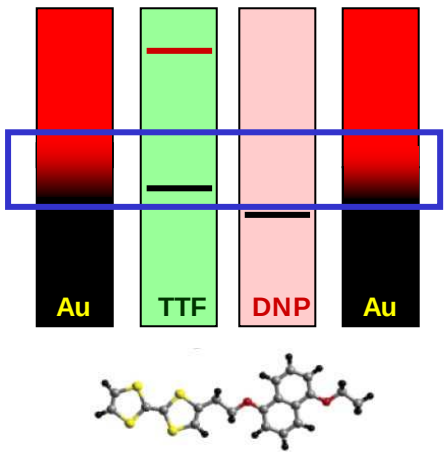
CBPQT
@TTF



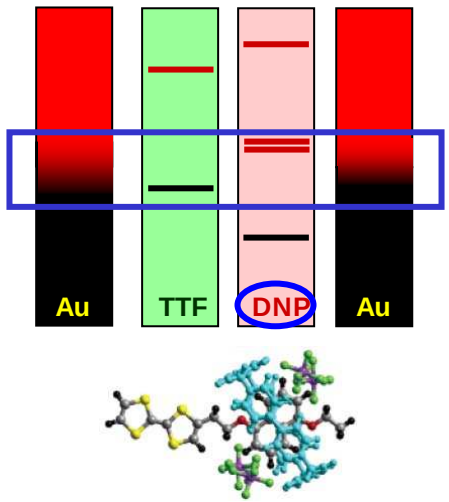
$(TTF)(CBPQT)(PF_6)_4$–(DNP)
"CBPQT@TTF"



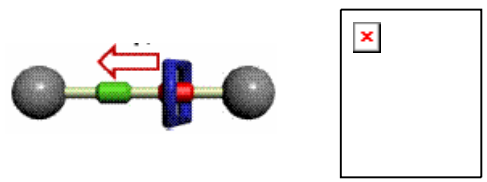
No HOMO level close to E_F



CBPQT
@DNP



(TTF)–$(DNP)(CBPQT)(PF_6)_4$
"CBPQT@DNP"

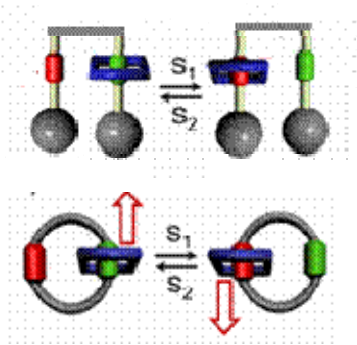


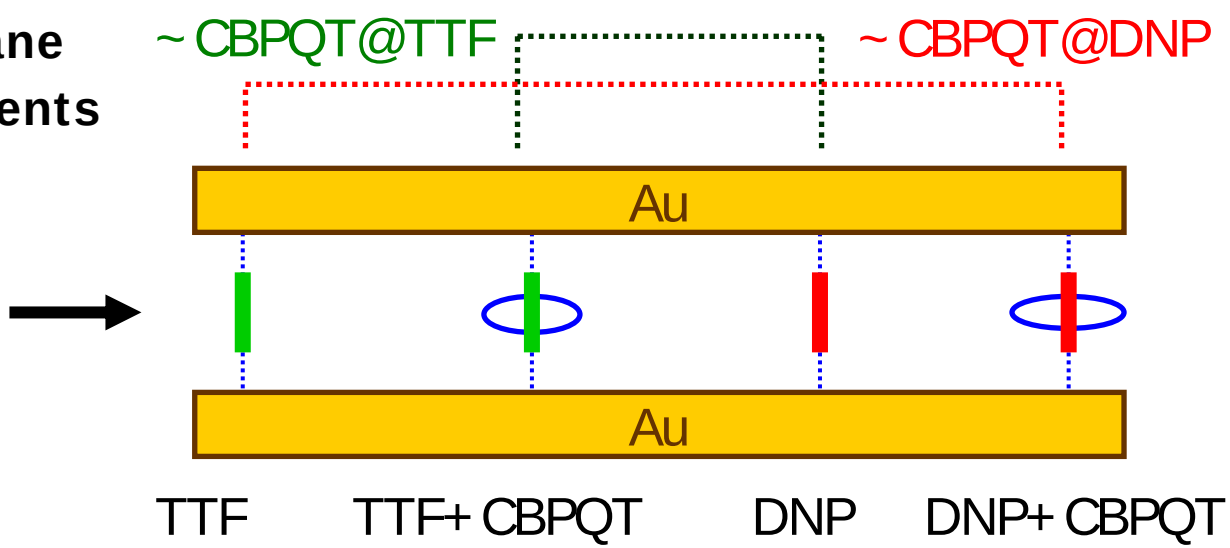
TTF HOMO level close to E_F

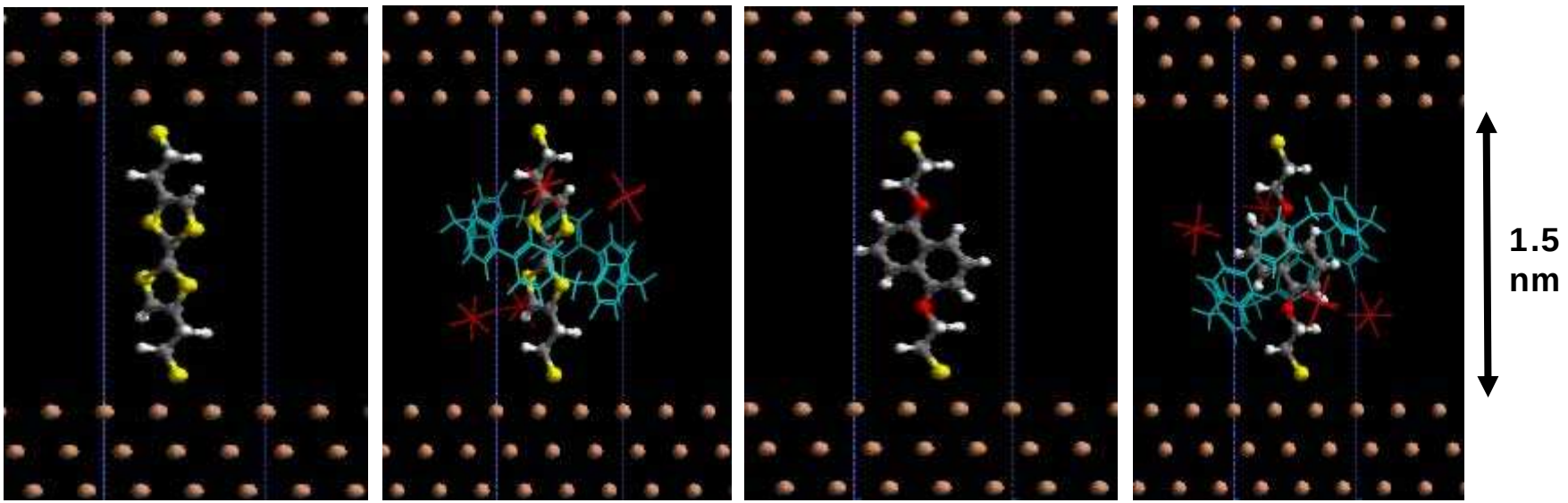
Key components between Au(111) slabs

Rotaxane ~ Catenane

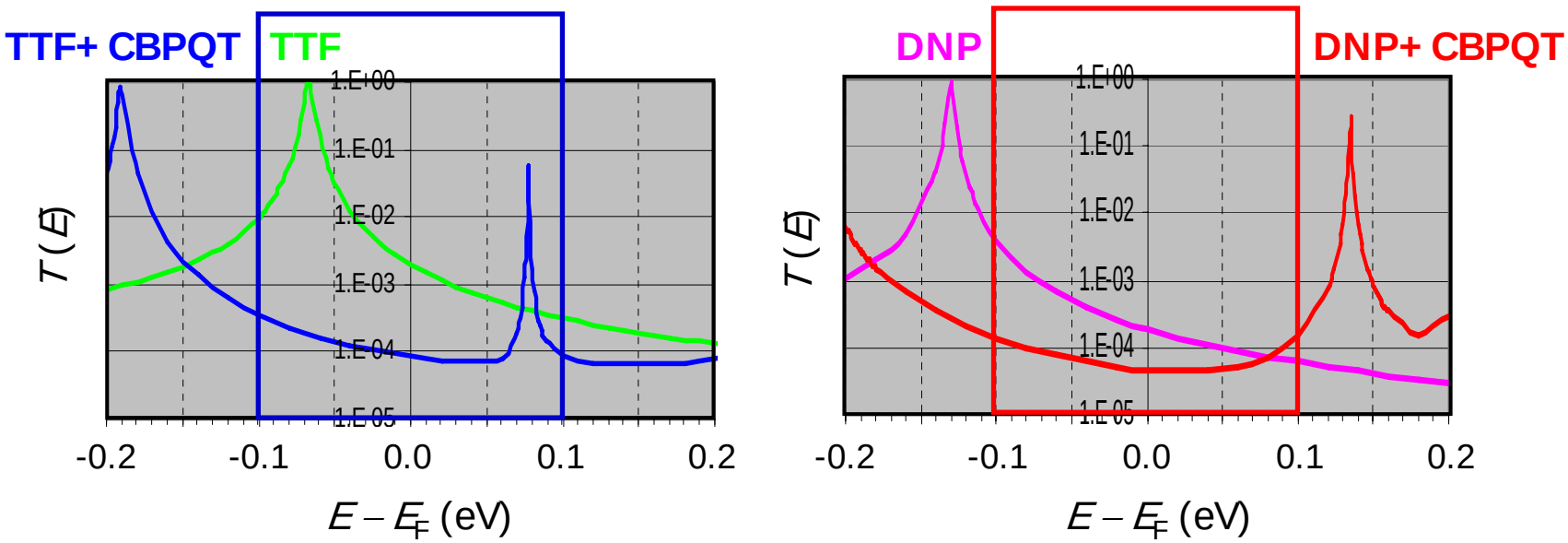
~ sum-up of components

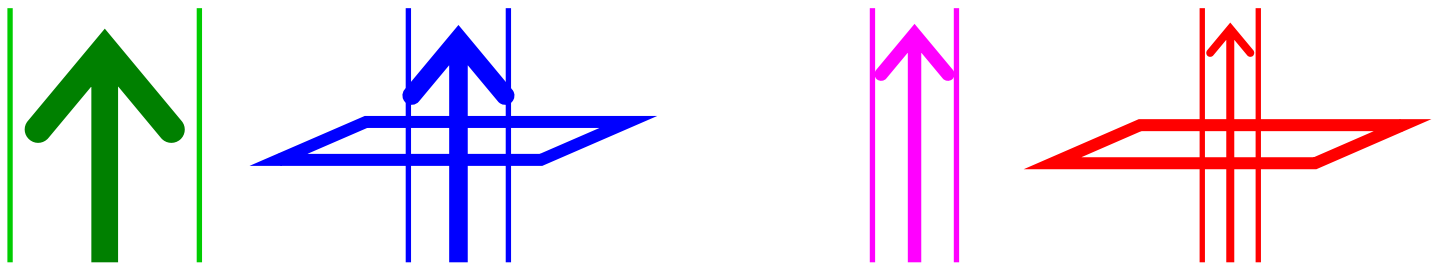






Transmission within the energy window





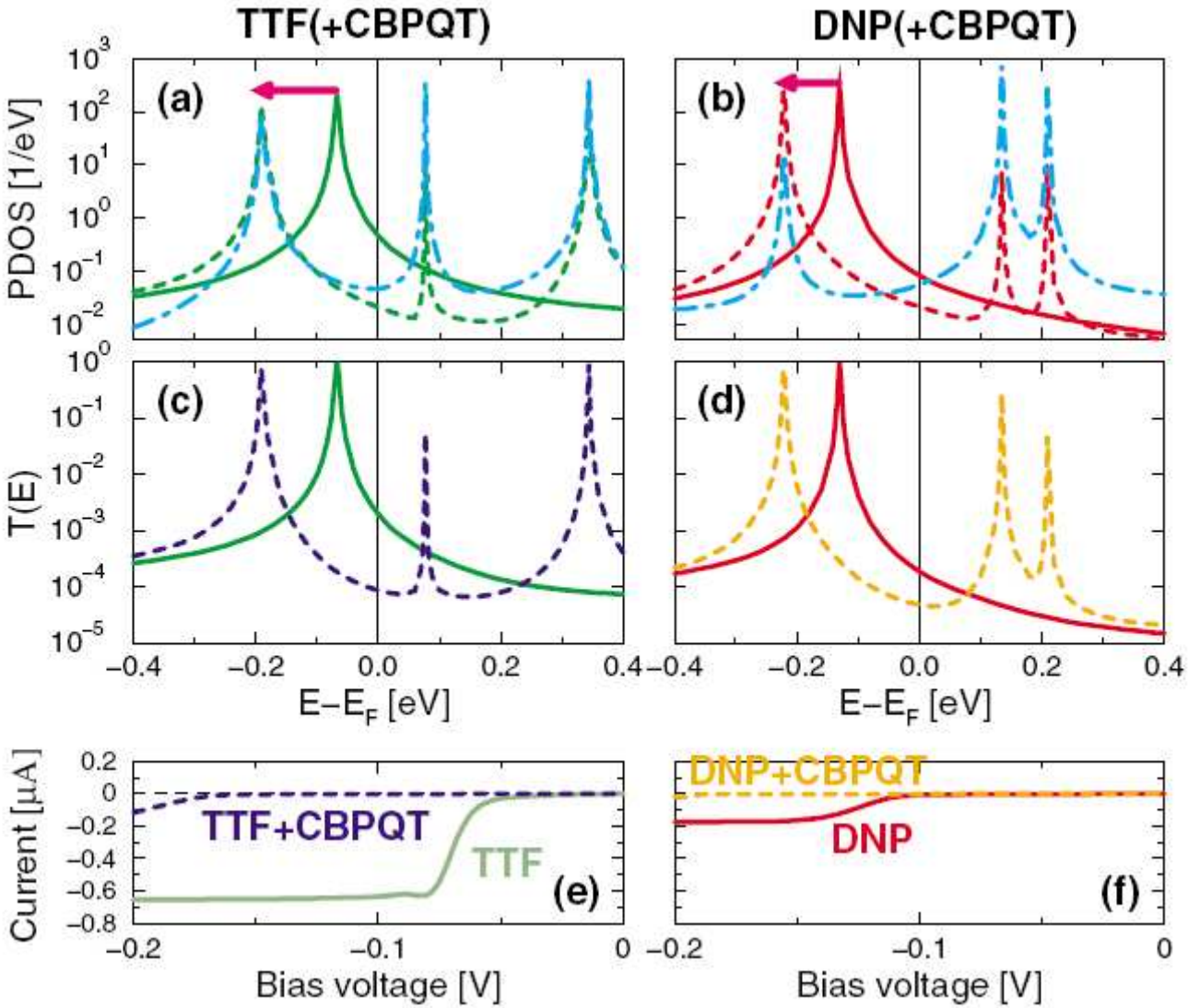
TTF TTF+ CBPQT DNP DNP+ CBPQT

~ CBPQT@DNP

Switch ON

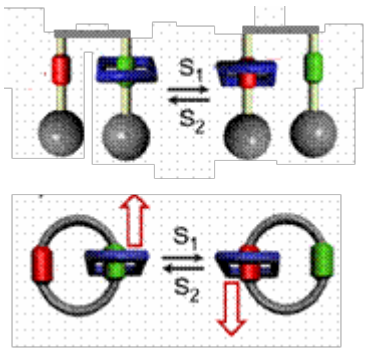
~ CBPQT@TTF

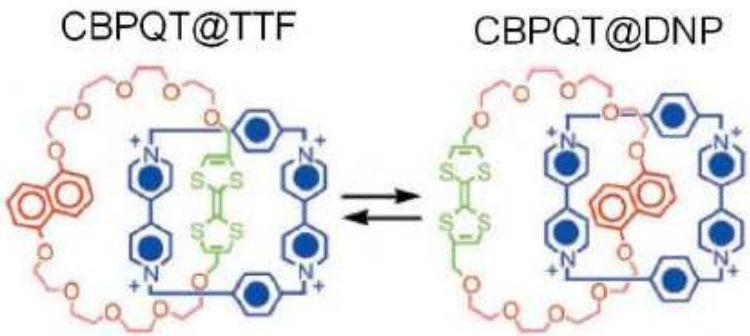
Switch OFF

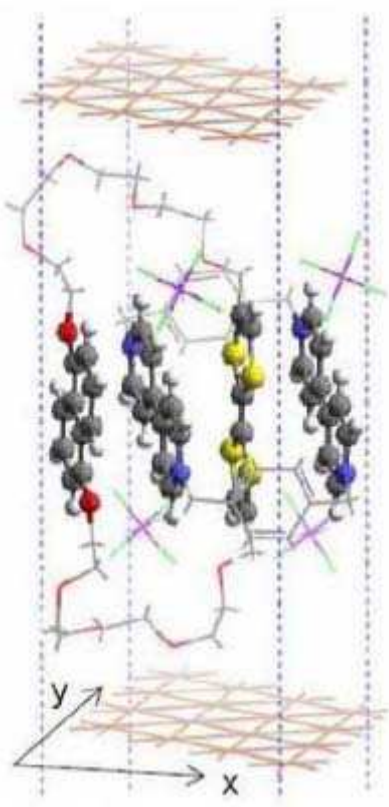

TTF(+CBPQT)
DNP(+CBPQT)
(a)
(b)
(c)
(d)
(e)
(f)
PDOS [1/eV]
T(E)
E−E_F [eV]
Current [μA]
Bias voltage [V]
TTF+CBPQT
TTF
DNP+CBPQT
DNP

Model junction: [2]Catenane between Au(111) slabs

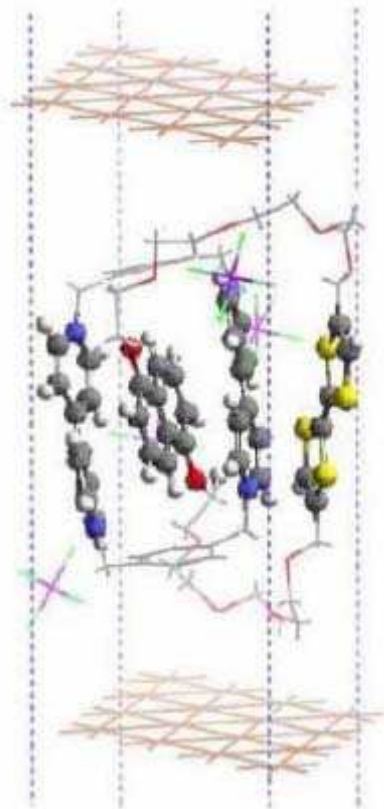
Folded rotaxane ~ Catenane



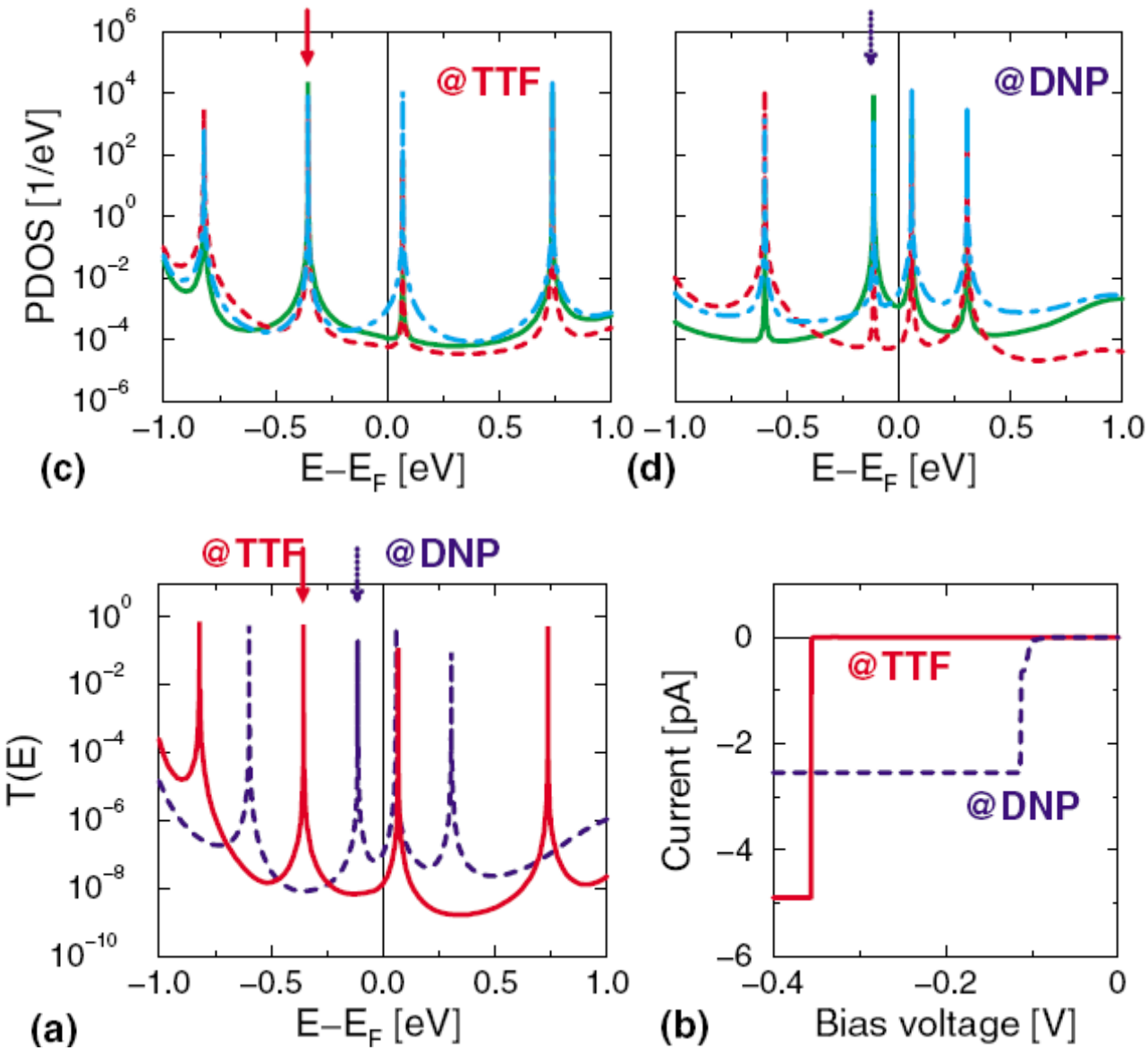




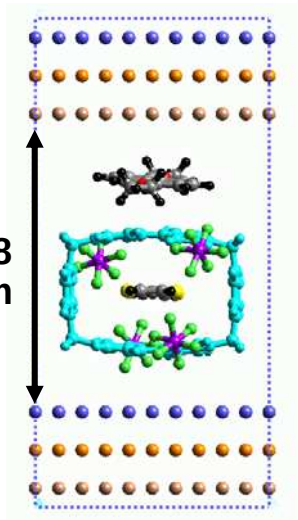
CBPQT@TTF
"Green" state



CBPQT@DNP
"Red" state

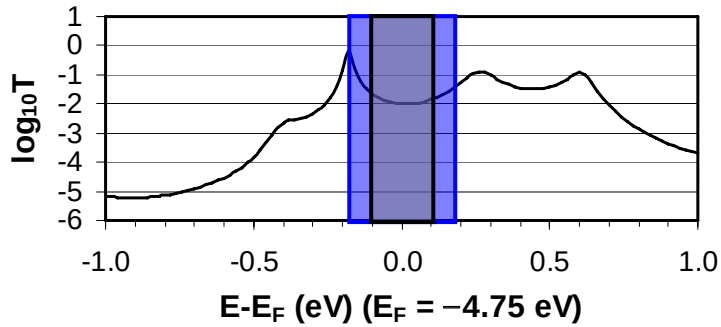

@TTF
@DNP
PDOS [1/eV]
E–E_F [eV]
(c)
(d)
T(E)
(a)
Current [pA]
Bias voltage [V]
(b)

Model: π-stacked components between Au(111)

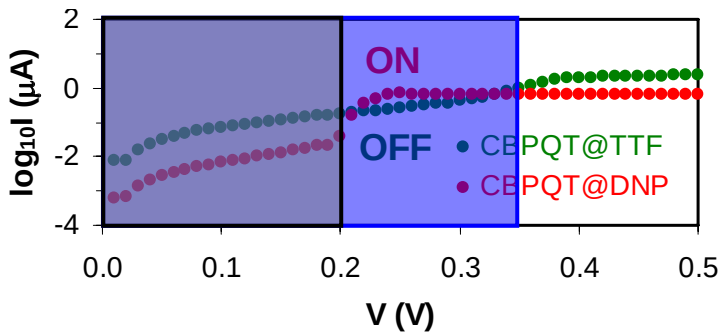


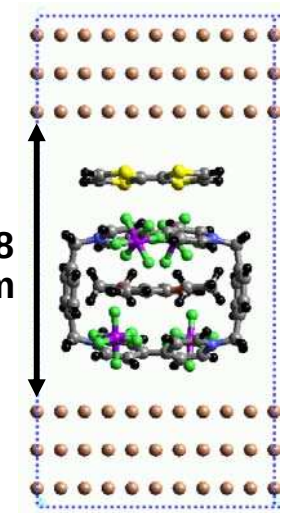
(TTF)(CBPQT)$(PF_6)_4$:(DNP)

"CBPQT@TTF"



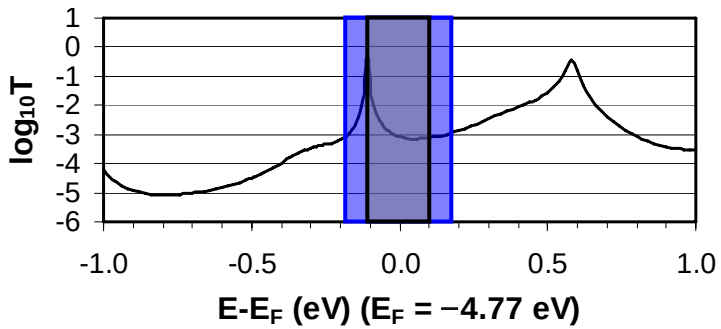
0.2 – 0.3 V
(choice in experiments)
CBPQT@DNP: Switch ON
CBPQT@TTF: Switch OFF
ON/OFF ratio ~ 5
(agreement with experiments)





(TTF):(DNP)(CBPQT)$(PF_6)_4$

"CBPQT@DNP"



Summary

(1) Electronic structure of key components: QM

→ Role of the ring 1: provide low-lying LUMO

→ Role of the ring 2: stabilize energy level of station

→ π-orbitals dominant around HOMO-LUMO

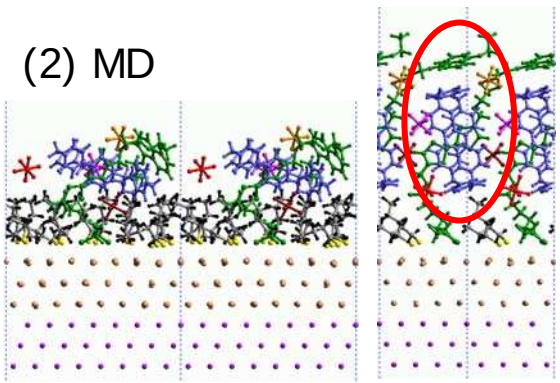
(2) SAM packing on Au(111): MD simulation

→ Coverage-dependent conformation

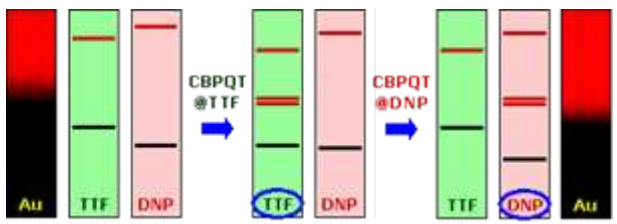
(3) *I-V* Calculation: periodic QM + Green's function formalism

Au(111) – Model catenane/fully-folded-rotaxane – Au(111)

(2) MD



(1) QM



(3) Periodic QM + *I-V*