Gated devices using self-assembled monolayers

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1. Conductance of molecules: theory and experiment

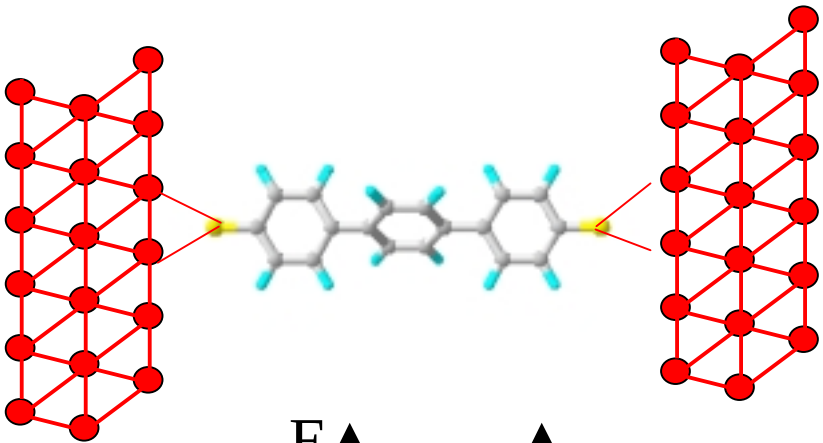
2. Molecular junctions on quartz tips & in planar geometry.

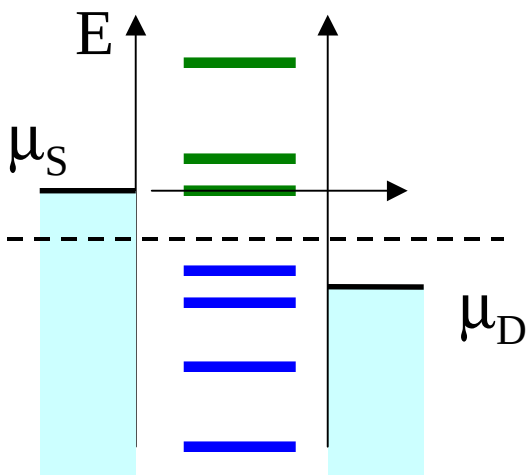
3. Scanning probe characterization of SAM and molecule-metal contacts .

Lucent Technologies
Bell Labs Innovations

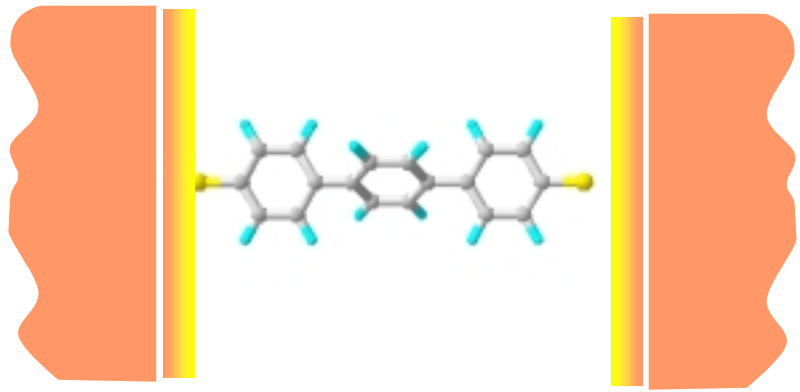
Transport through molecules:

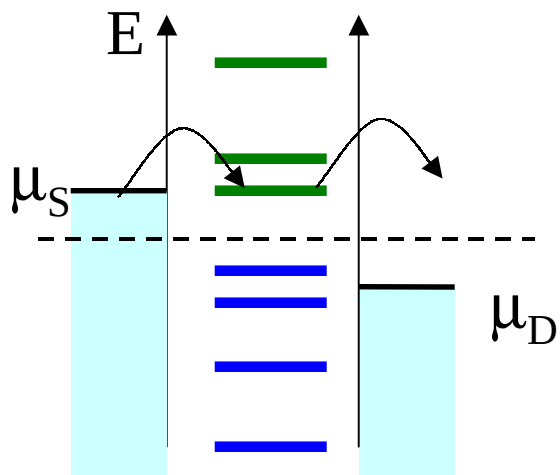
Tunneling electron shoots through molecule
(Coherent transport)





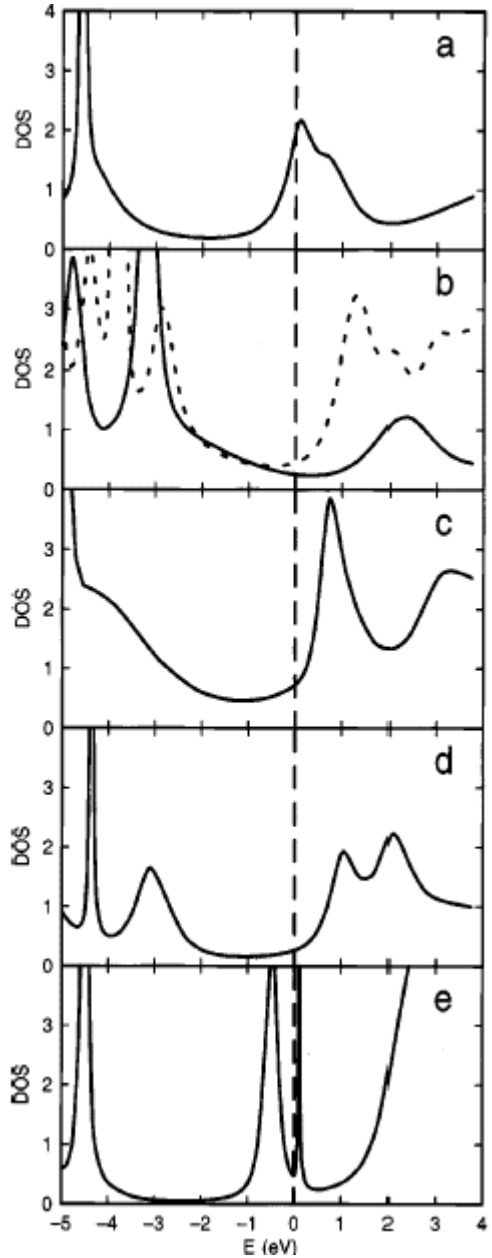
Tunneling electron dwells on molecule
(Incoherent transport)





Example of calculations: short molecules between Au leads:

	G ($2e^2/h$)	L (nm)	LUMO-E_F (eV)	DOS(E_F) (states/eV)
	1.01	0.57		2.0
	0.47	0.46	2.3	0.3
	0.21	0.78	0.73	0.7
	0.12	0.57	1.0	0.3
	0.08	1.03	0.11	0.5
	0.09	0.89	1.3	0.45

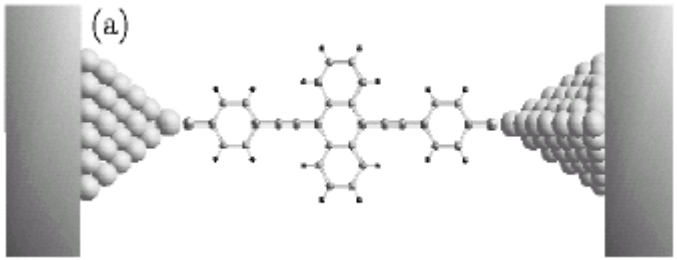


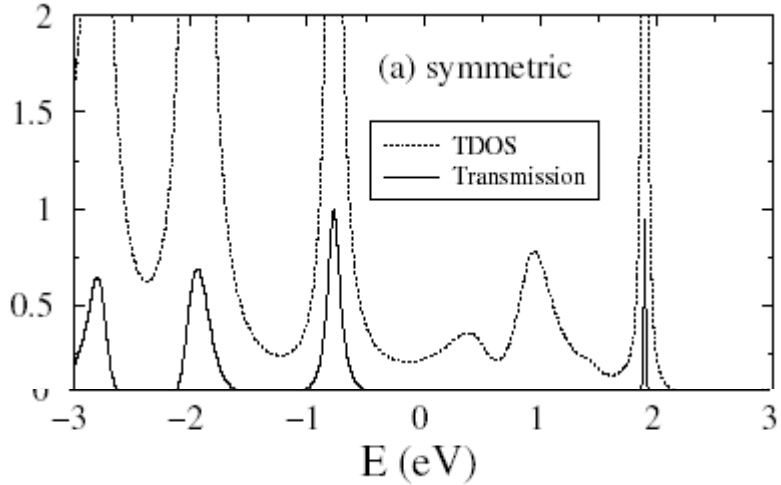
N. D. Lang and Ph. Avouris

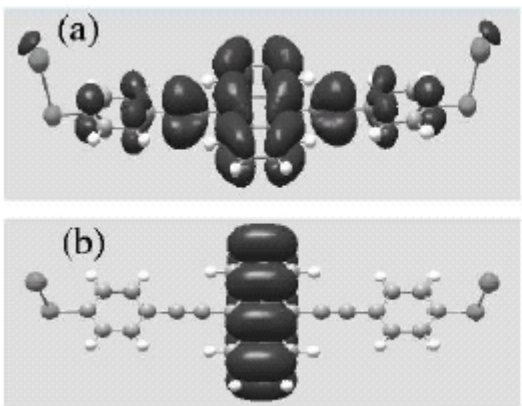
PHYSICAL REVIEW B, VOLUME 64, 125323

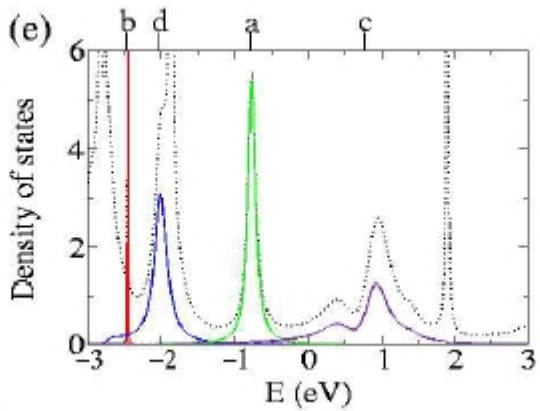
Example of calculation: longer molecules between Au leads

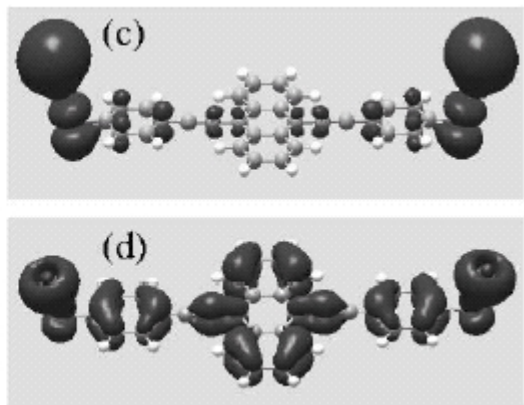
J. Heurich, J.C. Cuevas, W. Wenzel, and G. Schon
cond-matt 2002





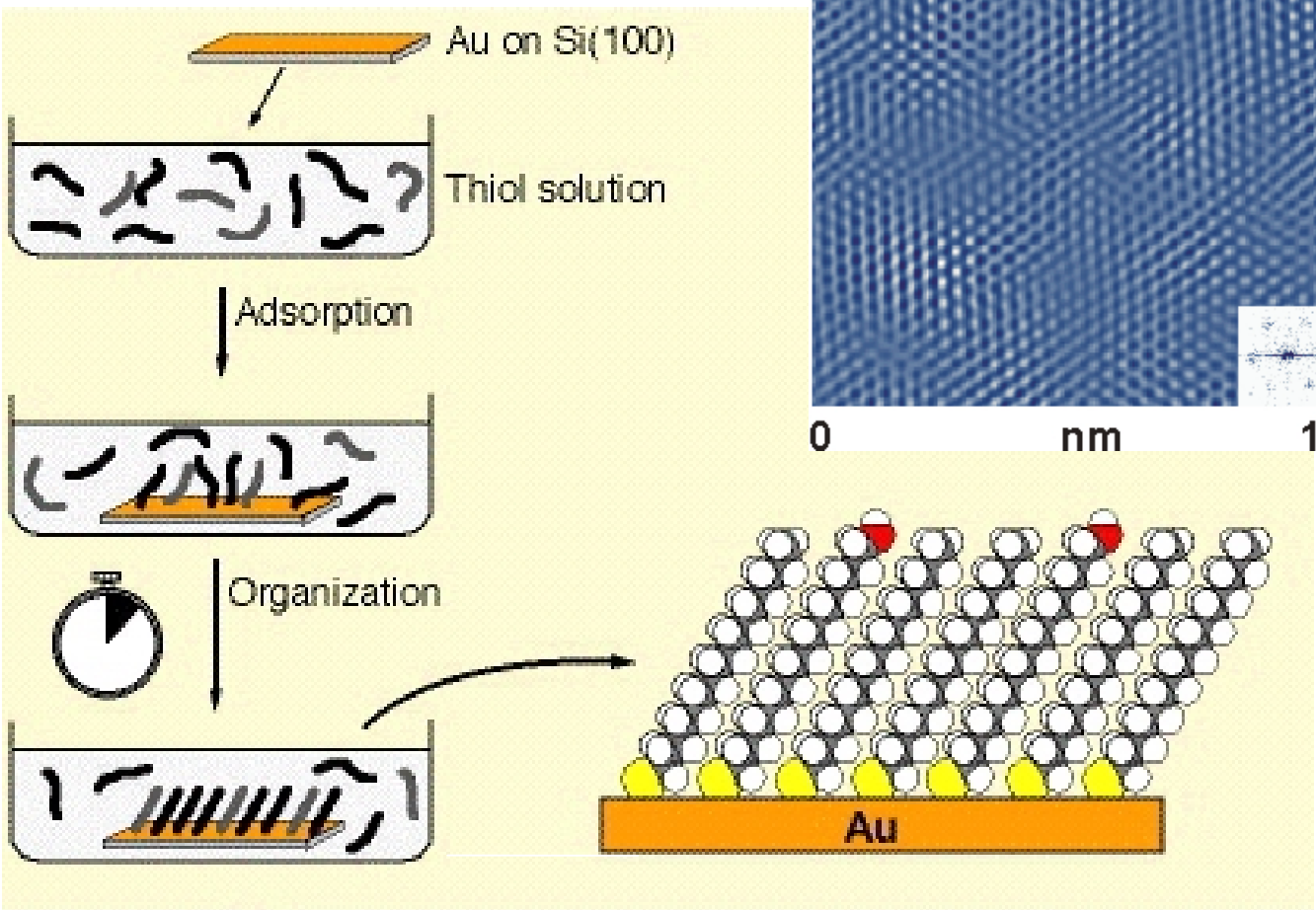






$$|\alpha_a|^2 = 0.007,\ |\alpha_b|^2 = 10^{-11},\ |\alpha_c|^2 = 0.06,\ |\alpha_d|^2 = 0.02$$

Self-Assembled Monolayers



well-ordered monolayer

Experiments: tunable contacts

Break junctions

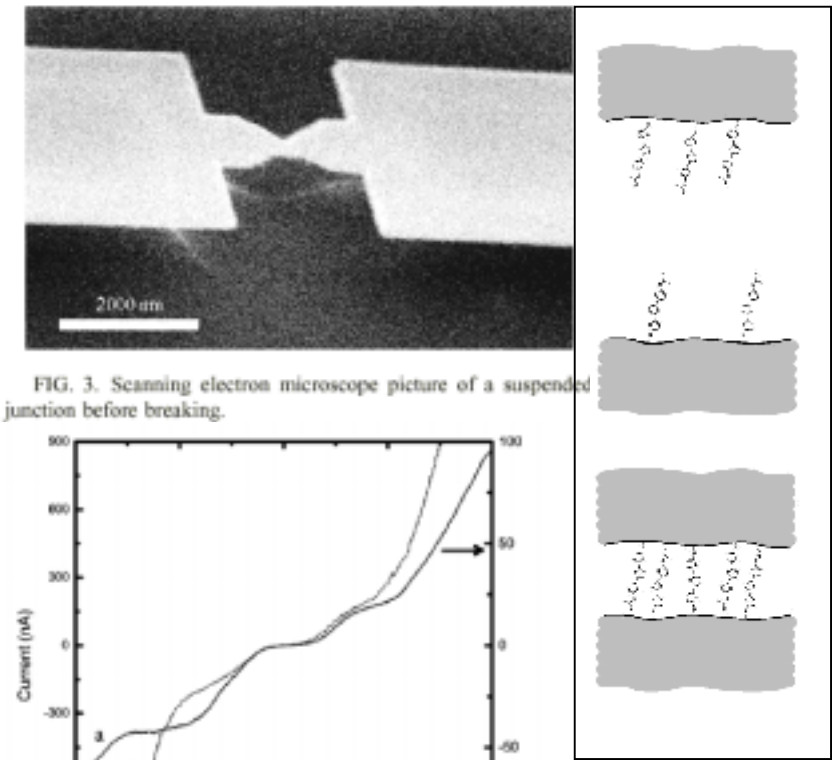


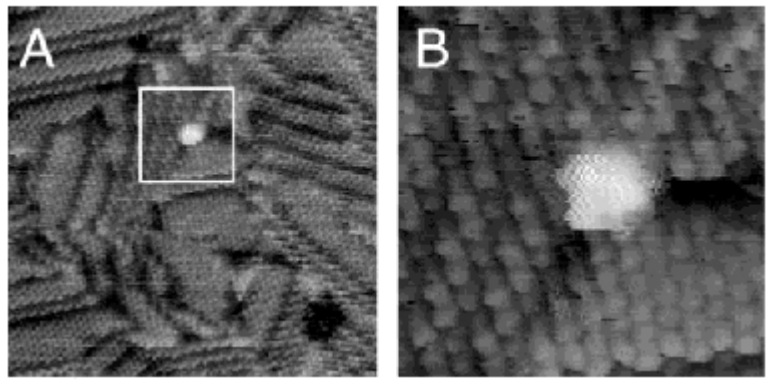
FIG. 3. Scanning electron microscope picture of a suspended junction before breaking.

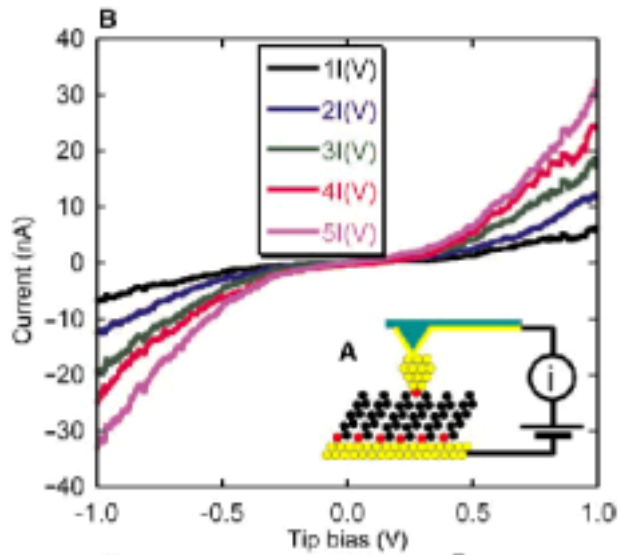
FIG. 7. Typical (a) asymmetric (solid line) and (b) symmetric (dashed line) I-V curves recorded at room temperature for gold-$T3$-gold junctions. Both curves were obtained by averaging over five voltage sweeps.

M. A. Reed *et al*., Science 1997

C. Kergueris et al, PRB 1999

Scanning probes





L. A. Bumm et al., Science 1996

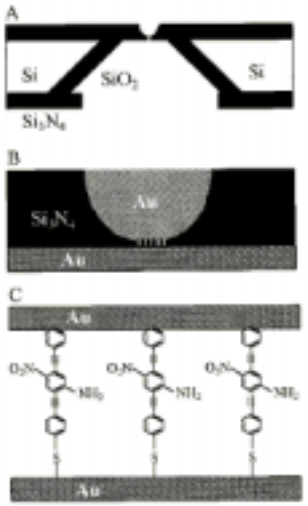
Z. J. Donhauser et al, Science 2001

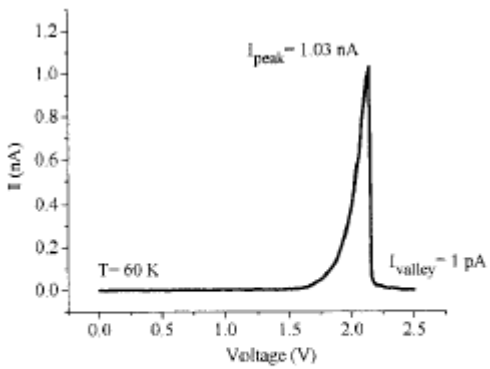
S. Datta et al, PRL 1997

X.D. Cui et al, Science 2001

Experiments: fixed contacts

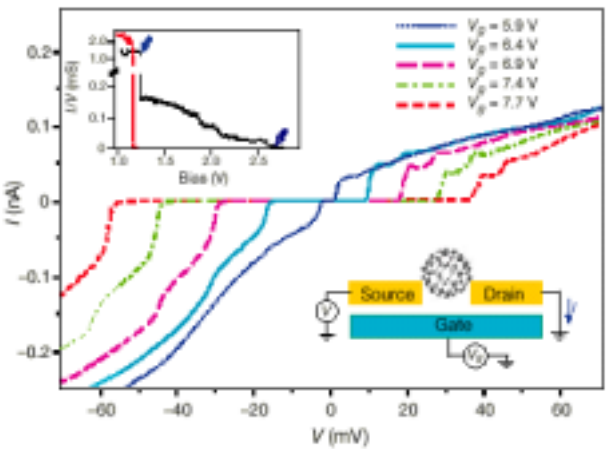
Nanopores

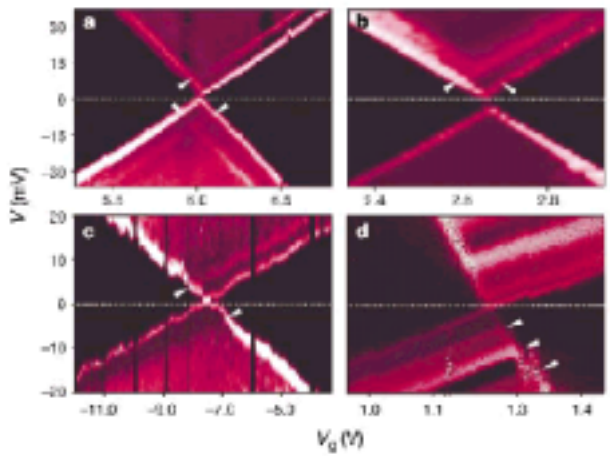




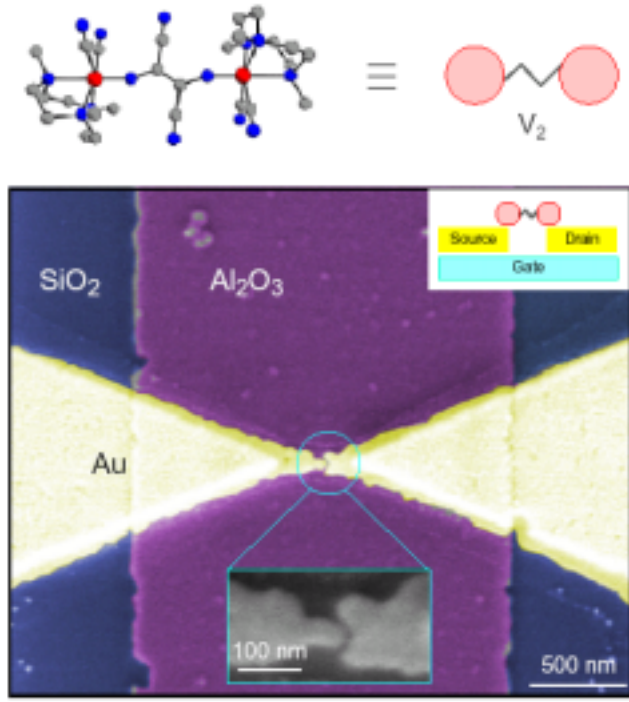
J.Chen et al, Science 1999

Trapping on lateral contacts





H. Park et al., Nature 2000



W. Liang et al., Nature 2002

J. Park et al., Nature 2002

Typical discrepancy between theory & experiment:

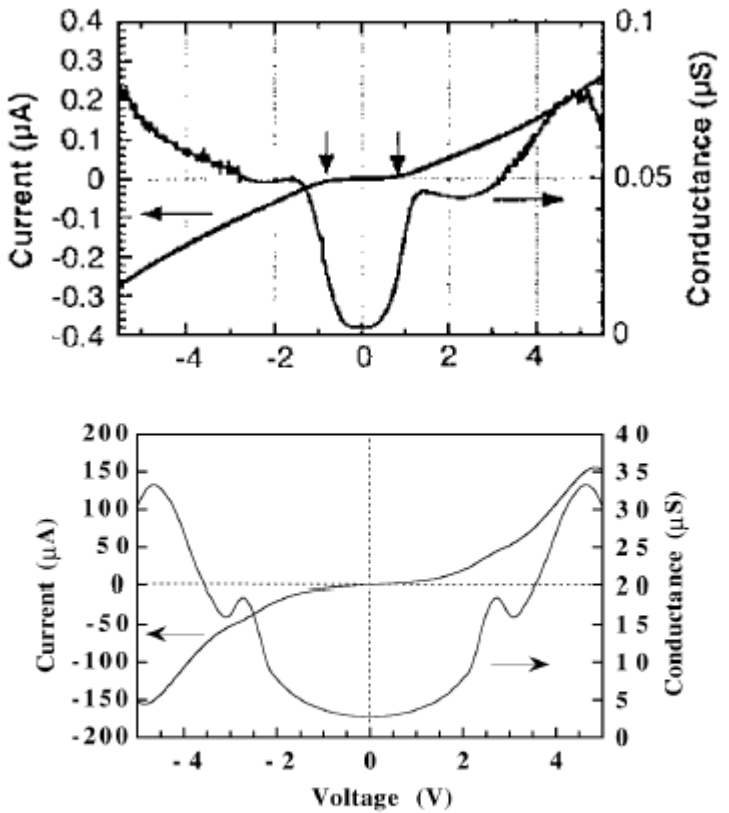


FIG. 2. Top: Experimental *I-V* characteristic of a benzene-1,4-dithiolate molecule measured by Reed *et al.* [1]. Bottom: Conductance of the molecule of Fig. 1 as a function of the external bias applied to the metallic contacts.

Experiment: Reed et al. (1997)

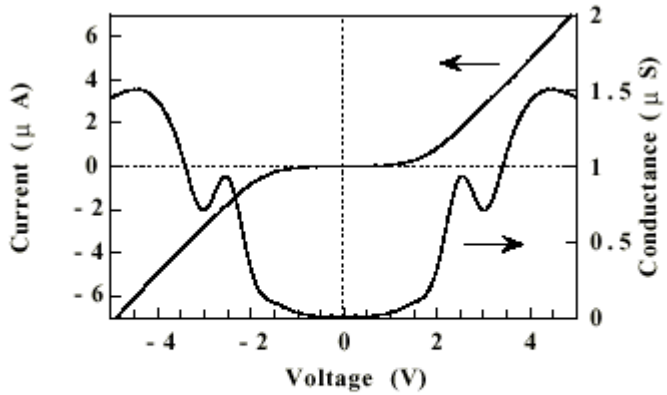


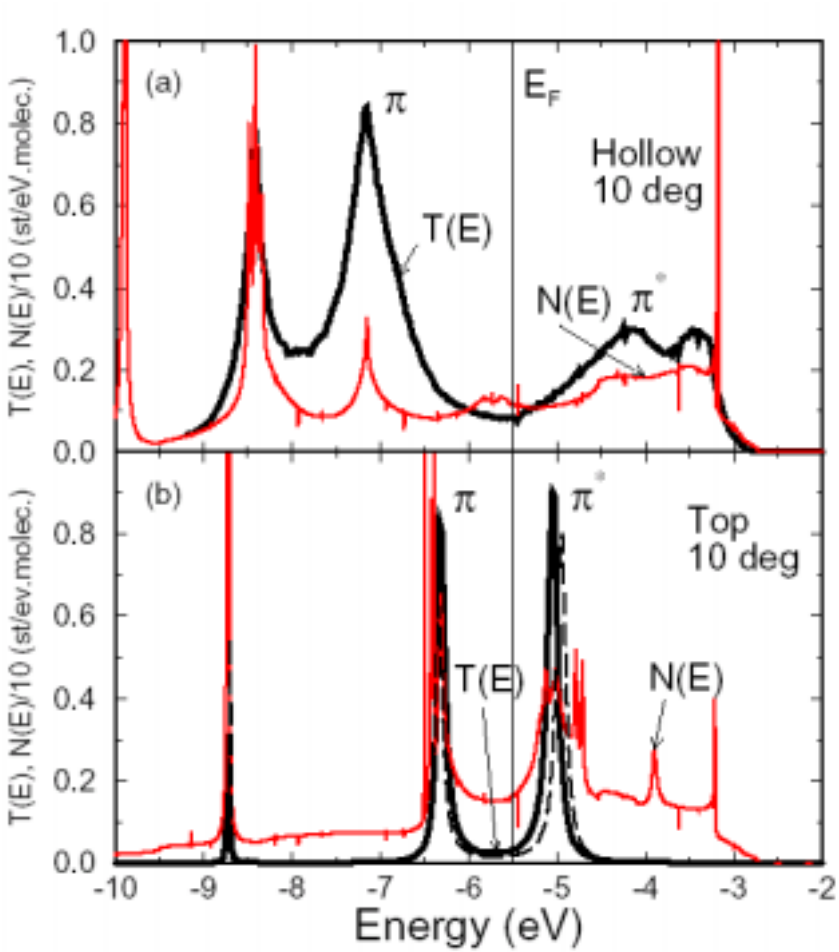
FIG. 5. Conductance of the molecule of Fig. 1 with one Au atom between the model metal surface and the sulfur for each contact as a function of the external bias applied to the metallic contacts.

calculation (:400)

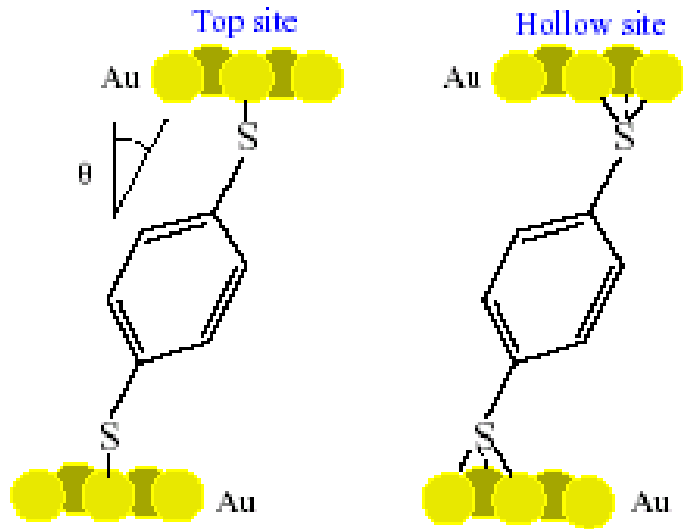
"improved" calculation (:20)

M. Di Ventra, S. T. Pantelides, and N. D. Lang, PRL 2000

Sensitivity to exact contacts configuration:



A.M. Bratkovsky and P.E. Kornilovitch, preprint

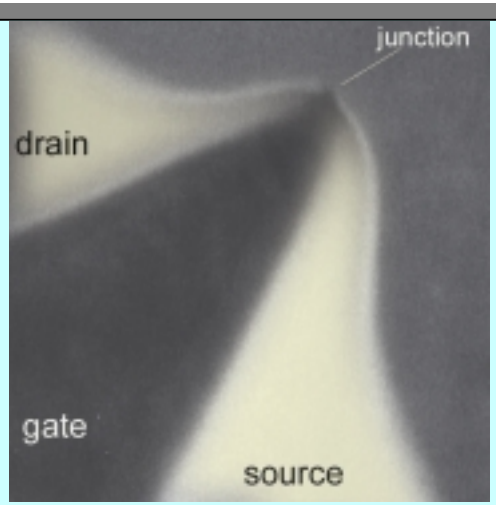


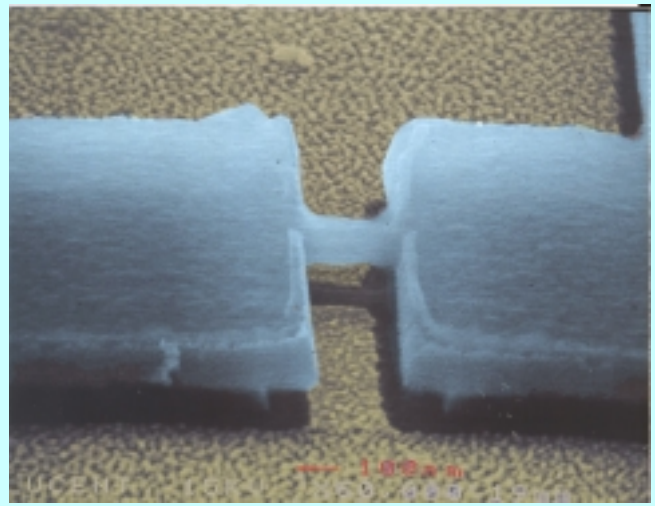
HOMO-LUMO gap in benzene ring is 6.5 V,
In BDT bonded to “top” site is 1.2 V
In BDT bonded to “hollow” site – soft gap

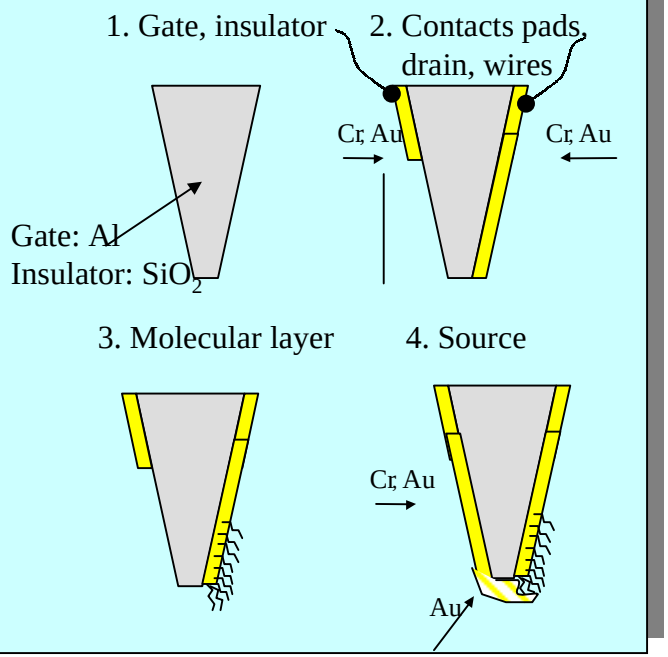
Red curve – DOS, **Black** - transmission

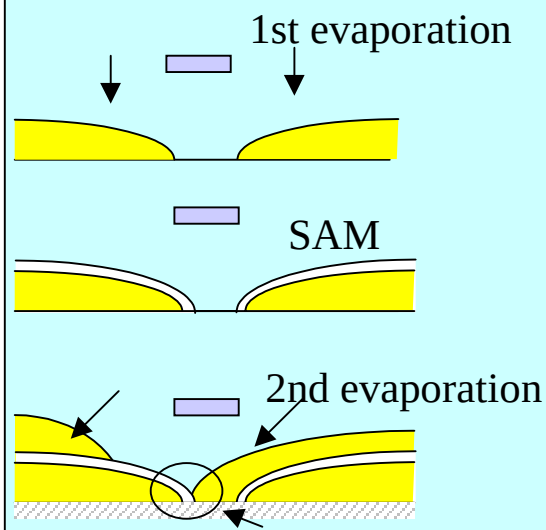
Molecular junctions on tips and in planar geometry using shadow angle evaporation

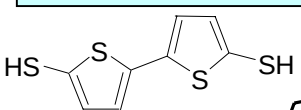
Junction fabrication



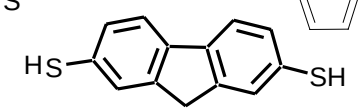




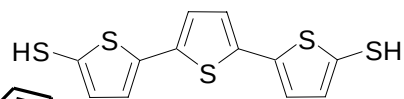




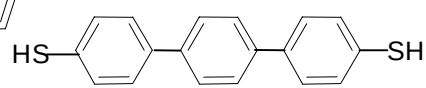
T2



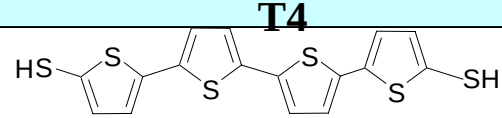
F1



T3



P3



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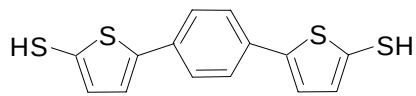
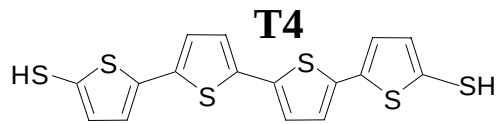
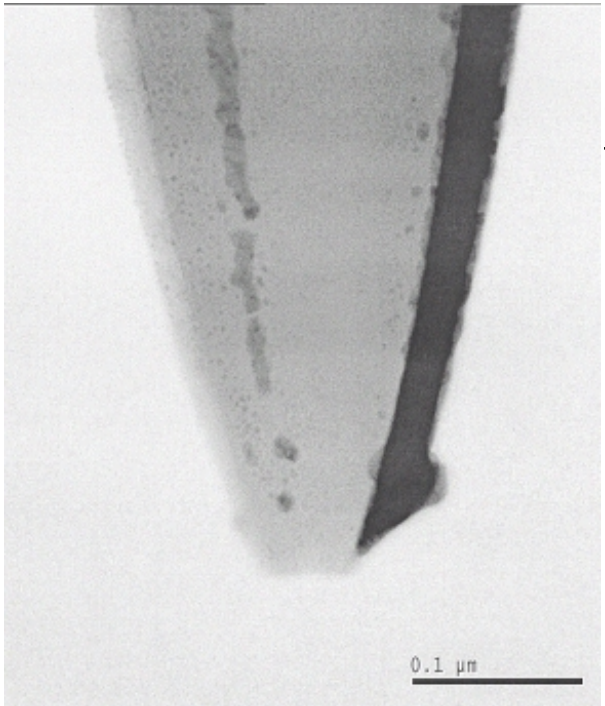


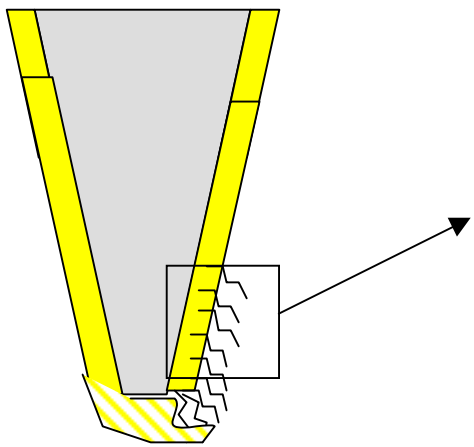
TBT

High-resolution TEM pictures

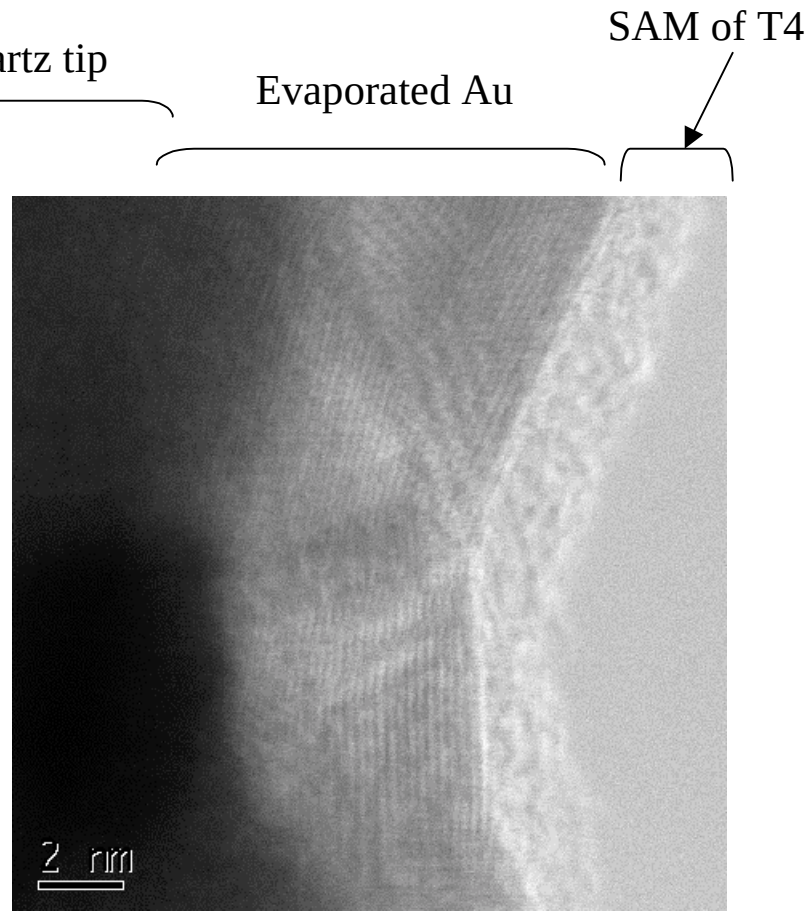




0.1 µm

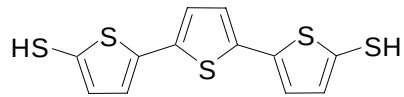


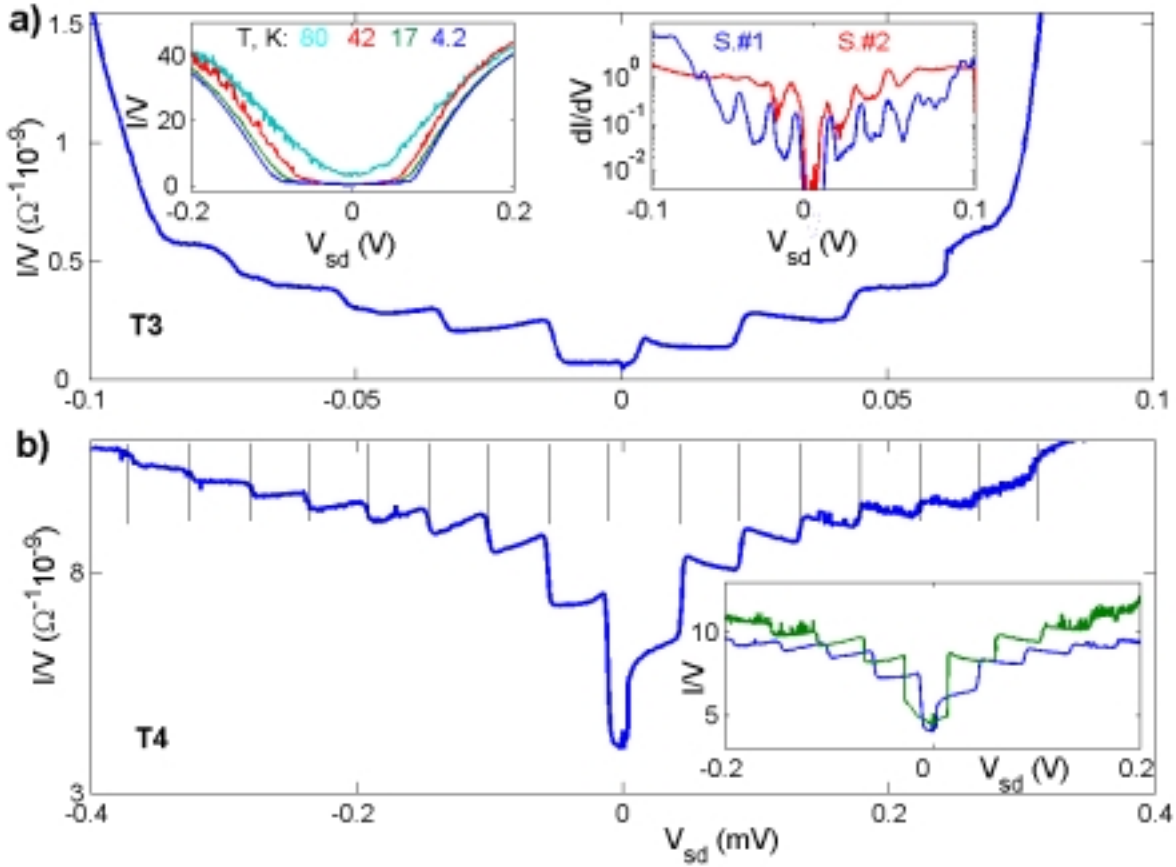
TEM by David Muller, Bell Labs

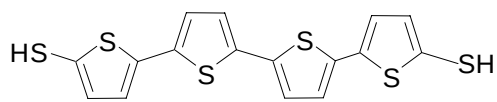


2 nm

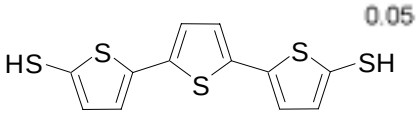
Typical IV curves

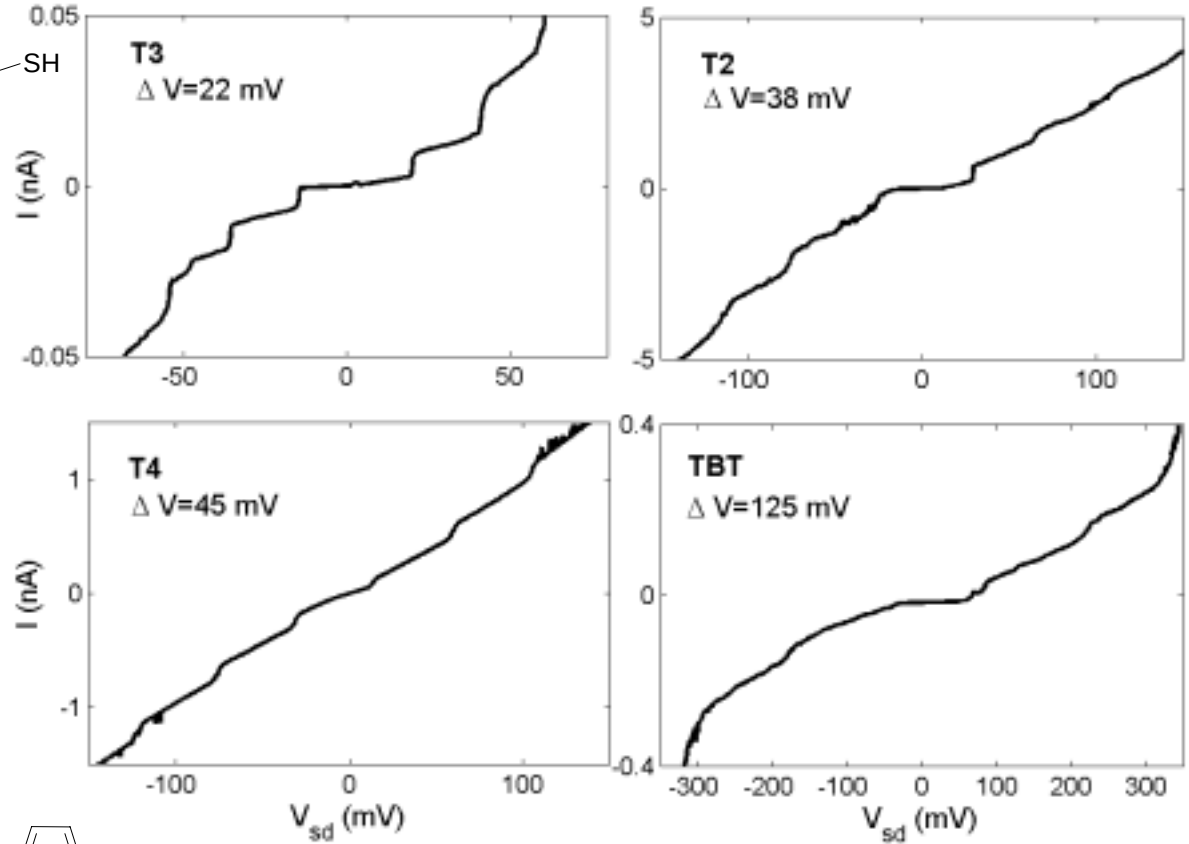


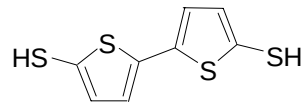


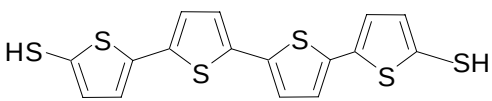


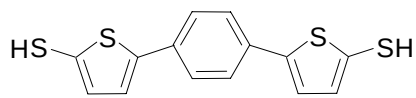
Low temperature IV curves: steps for all molecules



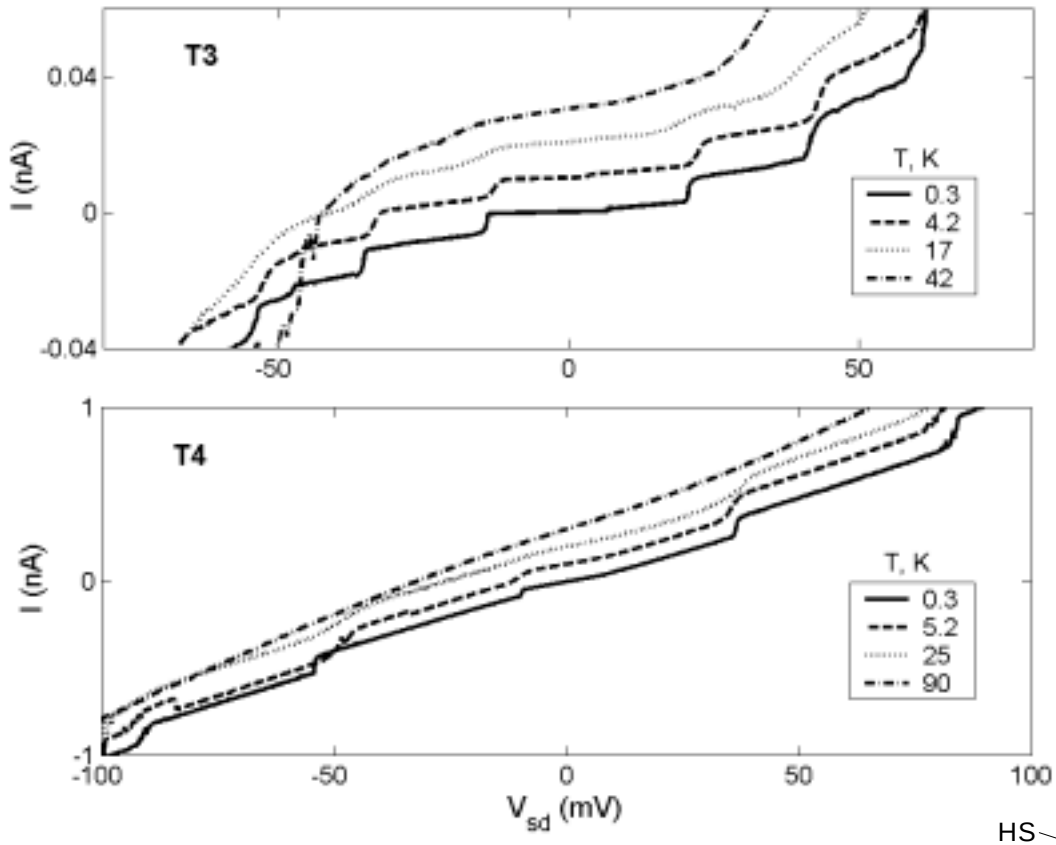


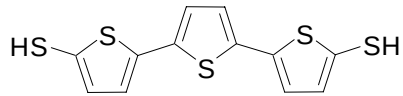


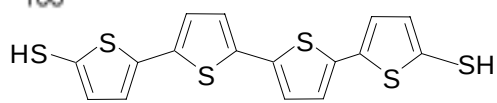




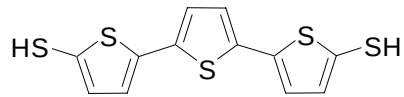
IV curves: different temperatures

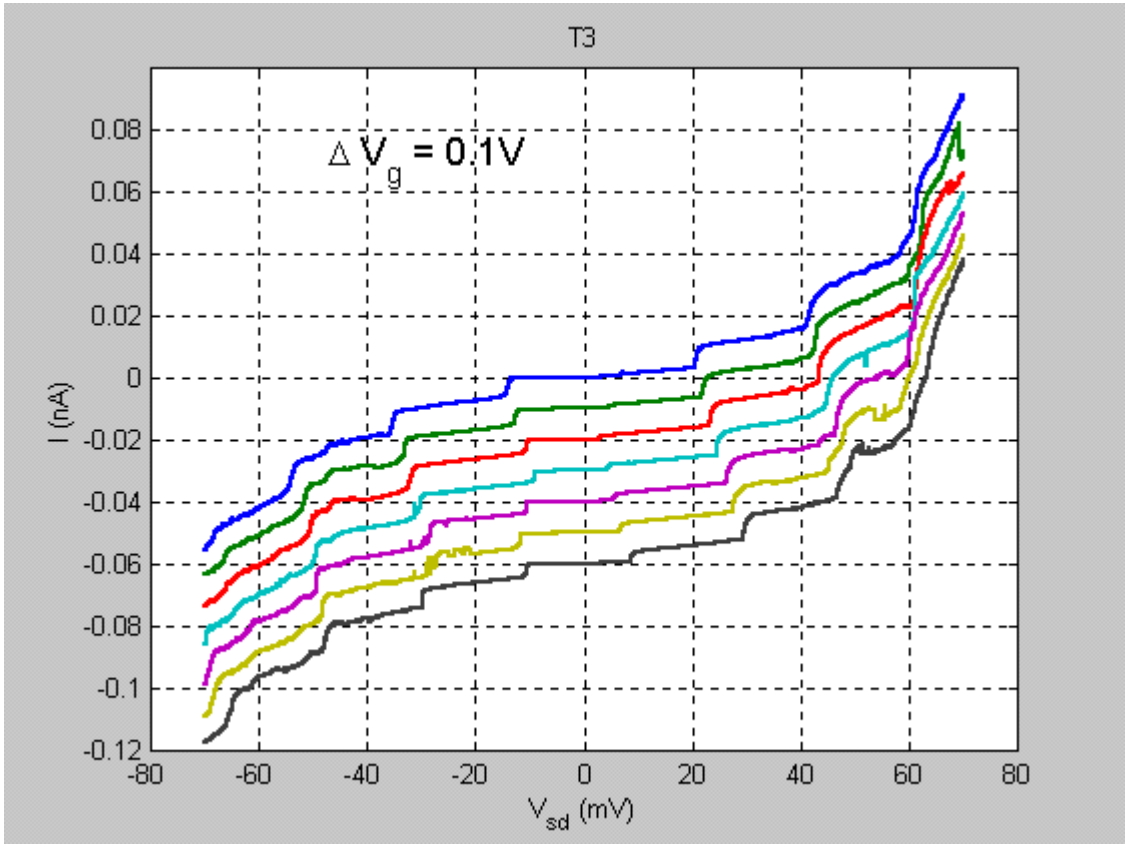




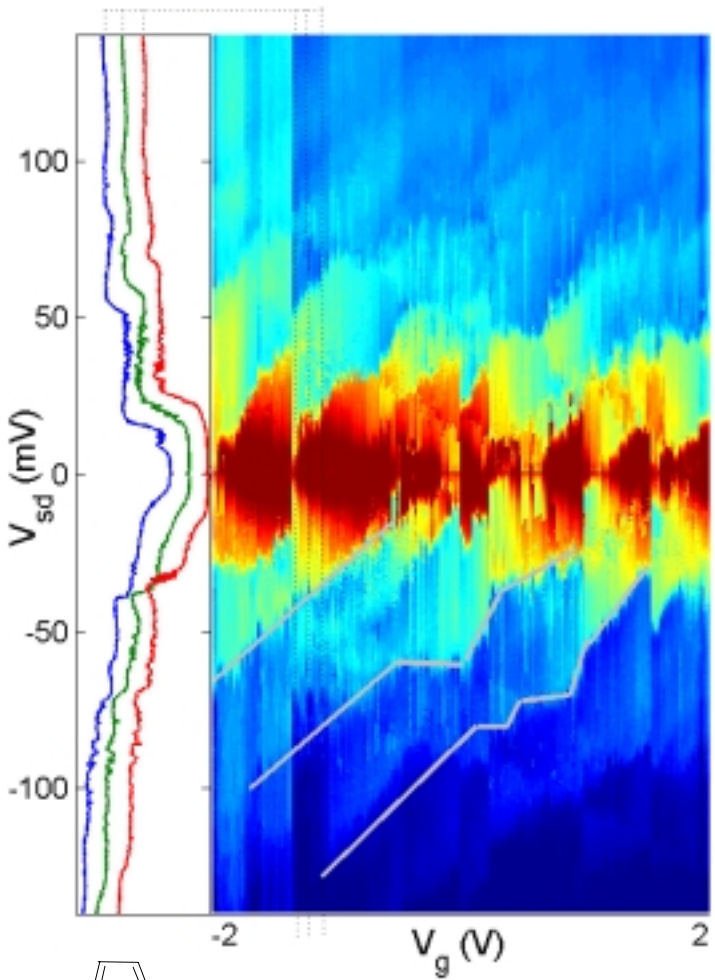


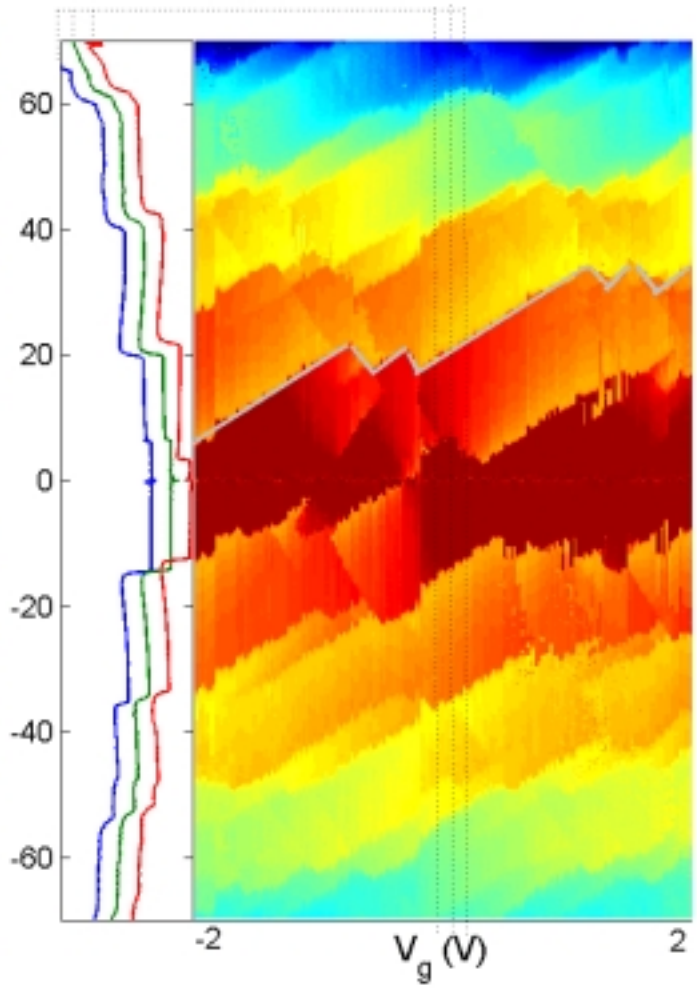
Gate potential effect:

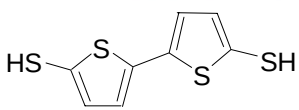




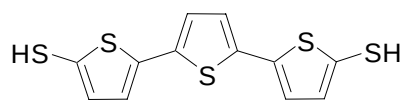
Conductance @ different V_{gate}





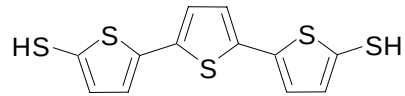


T2

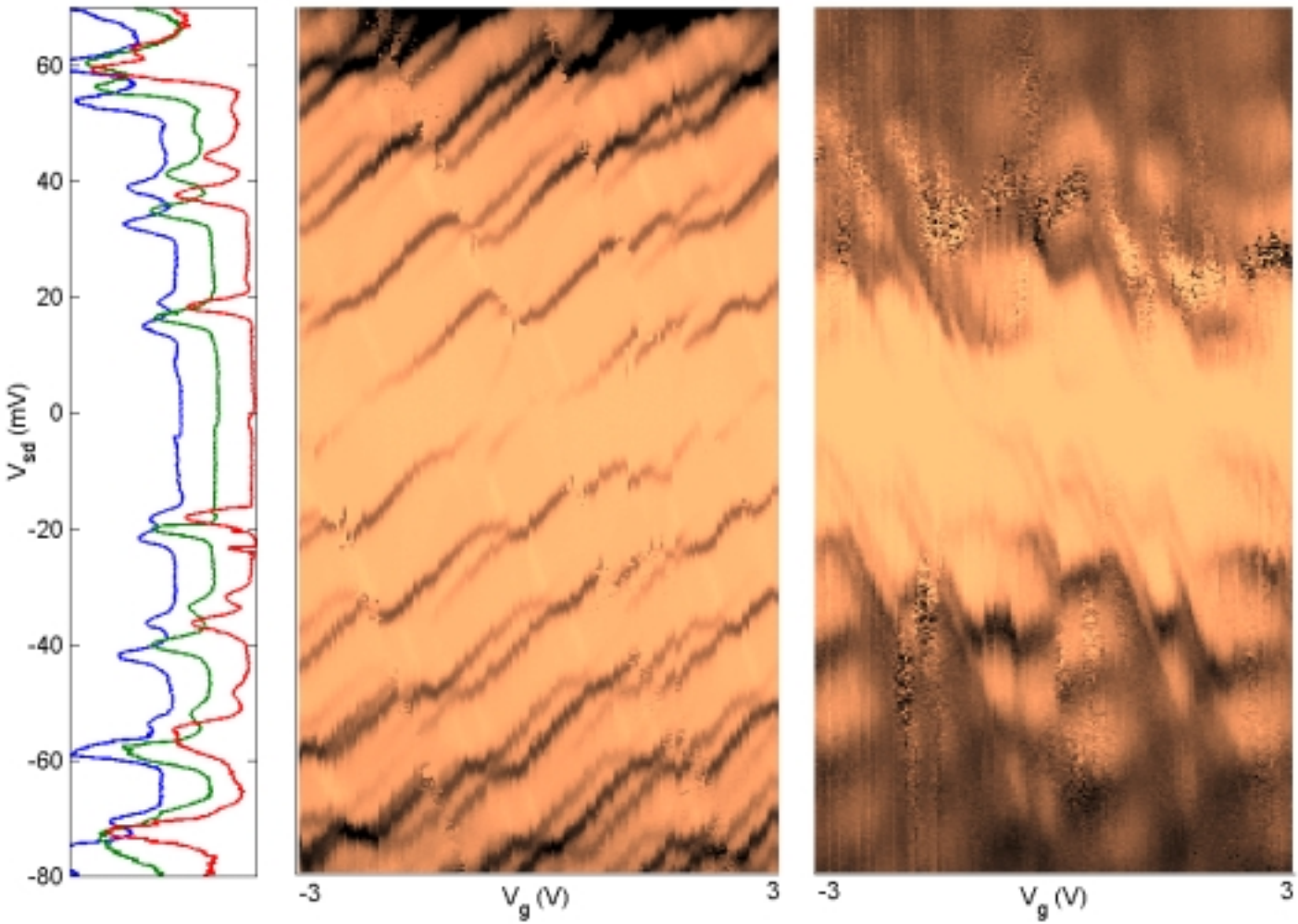


T3

Differential conductance @ different V_{gate}

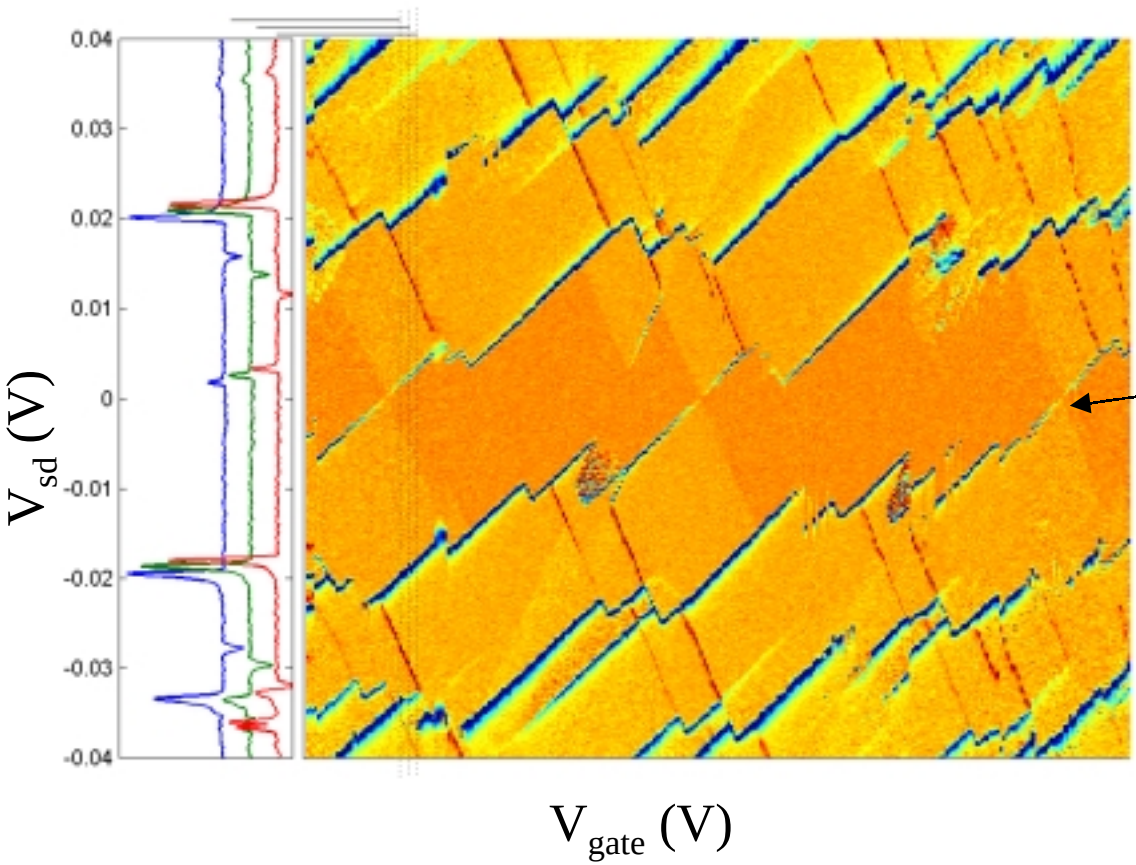


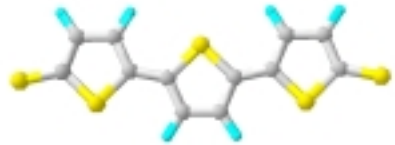
#1 #2



T=4.2 K

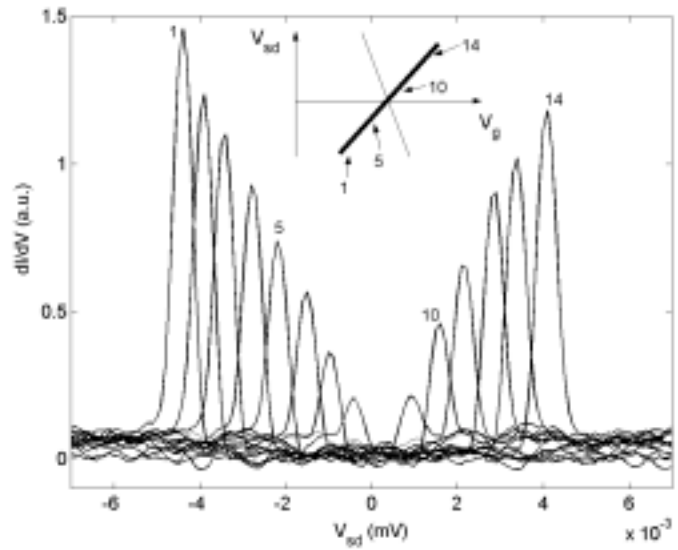
Differential conductance @ different V_{gate}

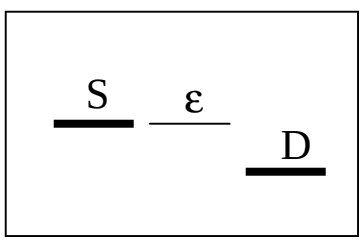




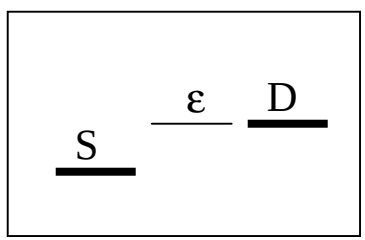
T=0.3 K

Level crossing near zero V_{sd}





Conductance resonance

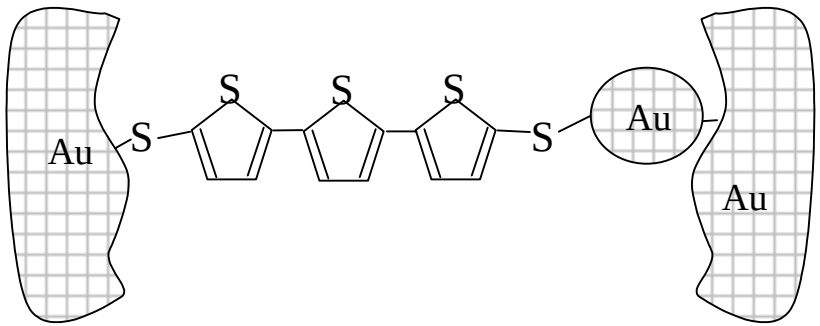


Change of slope

What is the origin of the structure?

1. Coulomb blockade on single molecule? ------ $E_{Charging}$ ~ 1-4 V

2. Metal cluster with size 5-20 nm? ------ Reproducible, molecule specific



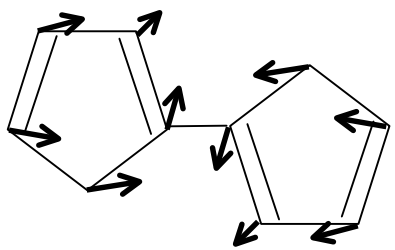
3. Coupling to molecular vibrations?

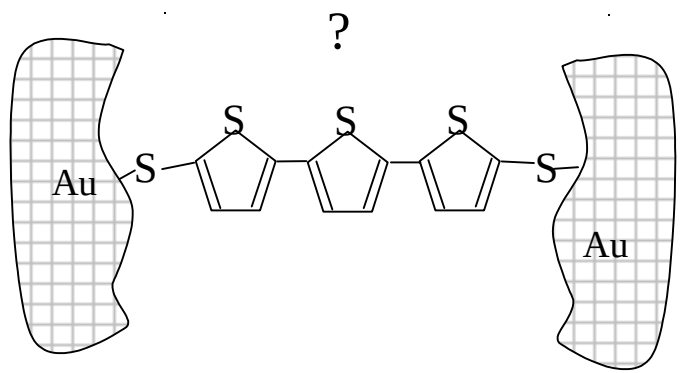
4. Metal island within self-assembled monolayer?

Vibrations:

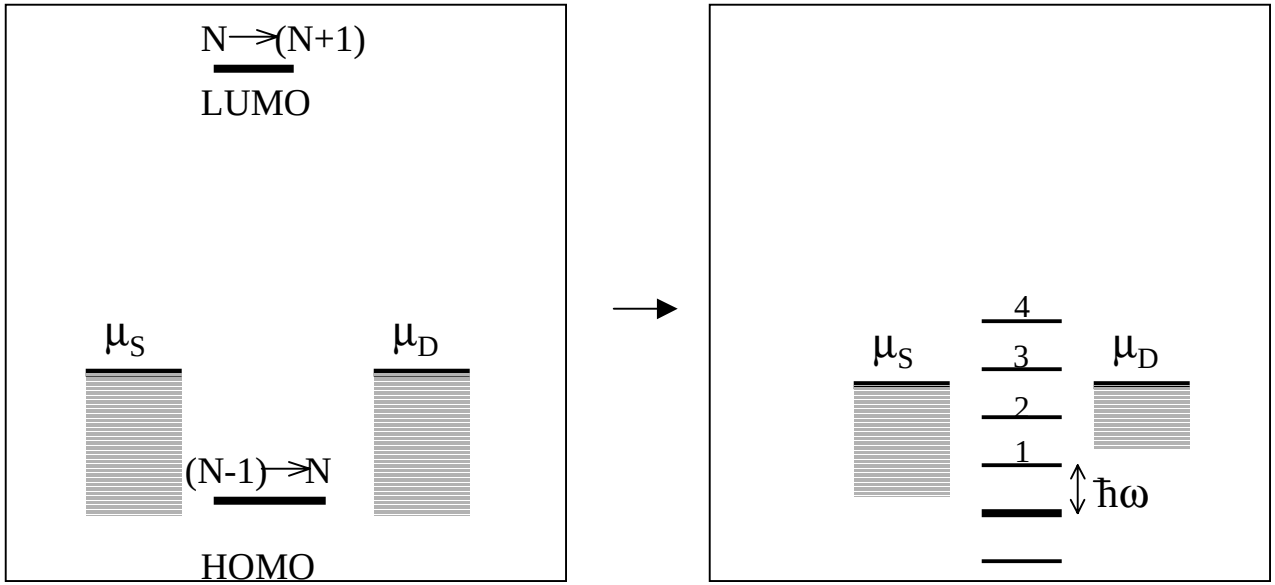
Molecule	Spacing (mV)	# resonances	# samples	E_{ph} (mV)
T2	38	10	3	36
T3	22	8	4	26.1
TBT	125	6	3	
T4	35, 45, 24	30, 22, 8	7	20.3

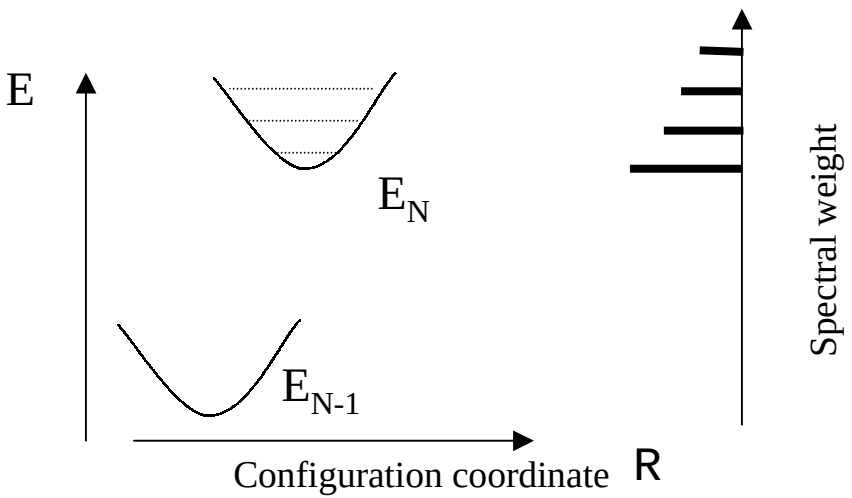
Low frequency vibration:





Tunneling through coupled electron-vibration levels:



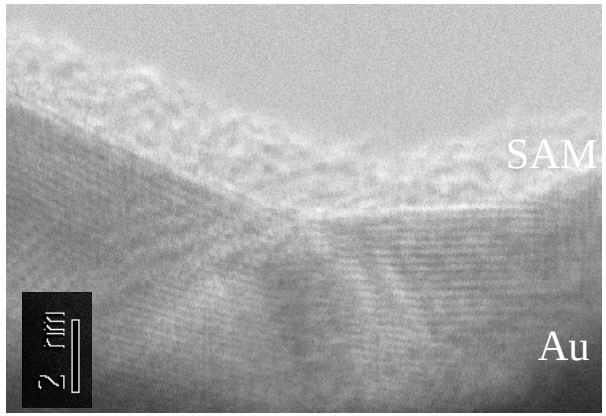


$|(N-1)> \longrightarrow |Ne> |n_{ph}>$

Problem 1: n_{ph} probability $\sim \lambda^n/n!$, λ - electron-phonon coupling (usually ~1, ~3-5 needed)

Problem 2: Tunneling though the excited states at $V_{sd}=0$ should vanish (it does in experiment but rather "slow")

‘Metal’ island within SAM

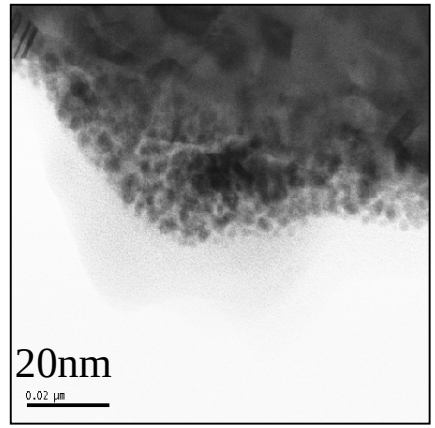


5 nm, 10^2 molecules

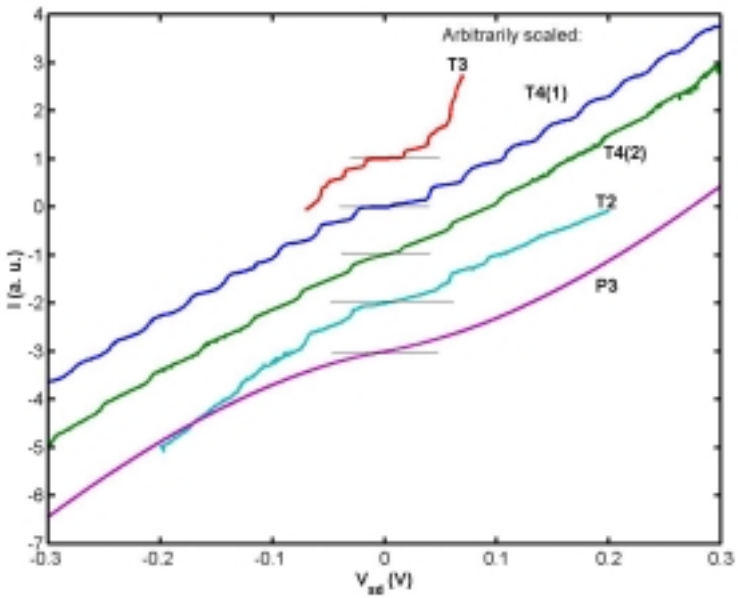
20 nm, $>10^3$ molecules

Size of ‘metal’ island must be determined by molecule-specific delocalization length within SAM (polaron formation?)

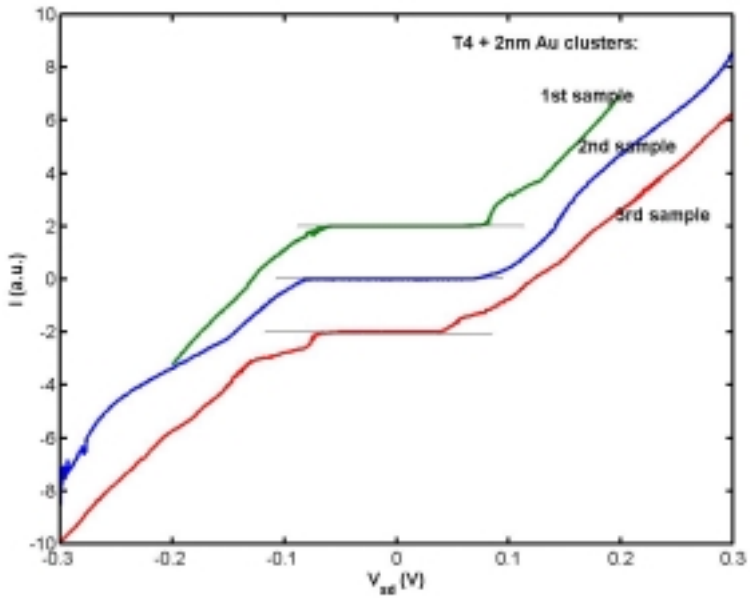
Soft gap vs. Coulomb-blockade gap:



Au-molecule-Au junctions:

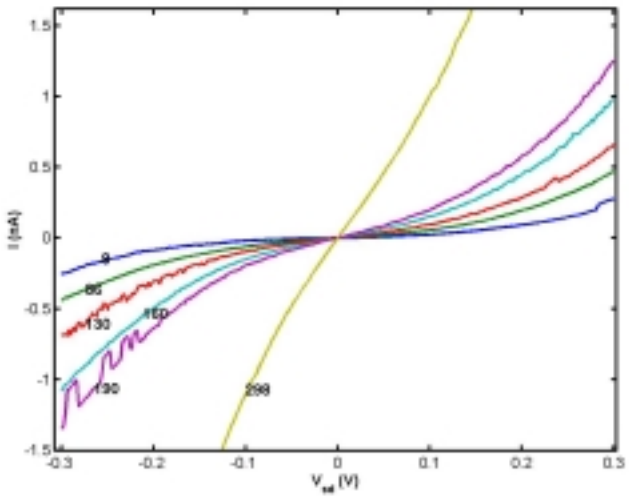


Au-molecule-2nm Au clusters-Au junctions:

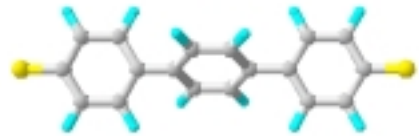


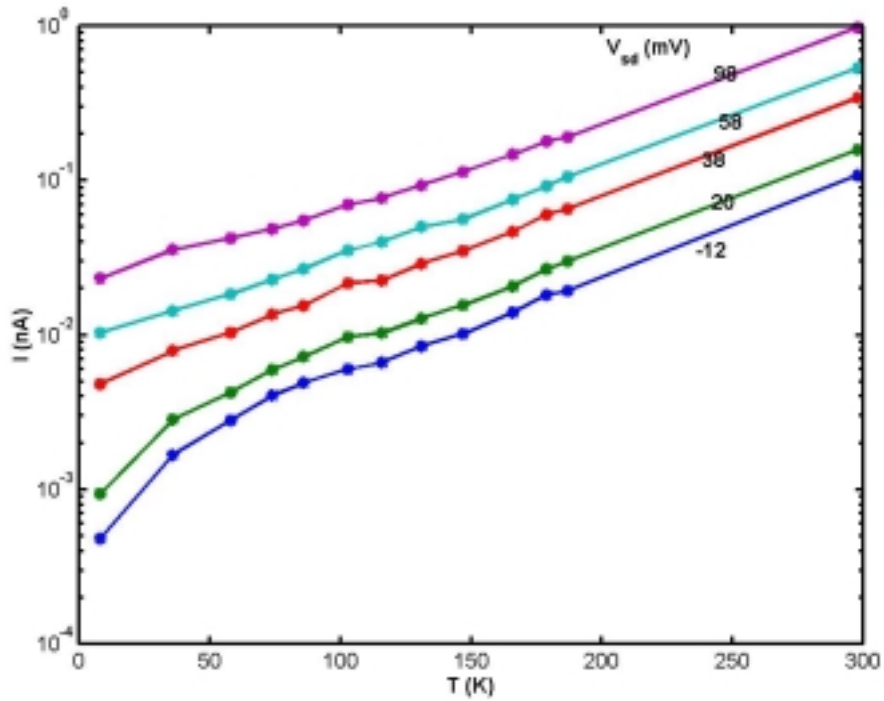
T4+Au cluster

Temperature dependence:



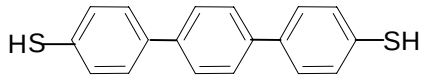
P3



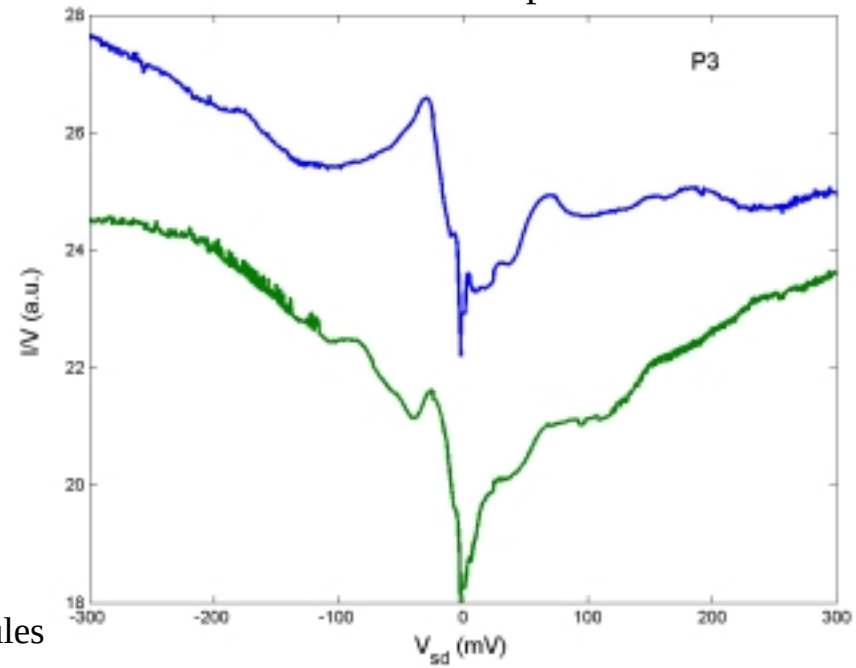


$I \sim f(V_{sd})\exp(kT)$???

Phenyl rings:

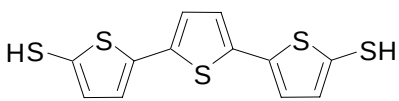


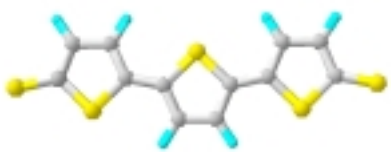
P3: two samples



No sharp steps
No periodic structure
No gate dependence

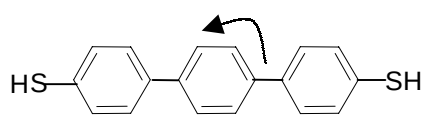
Thiophene: planar molecules

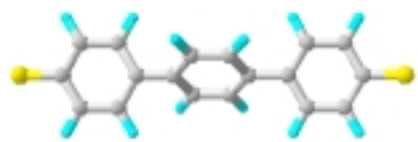




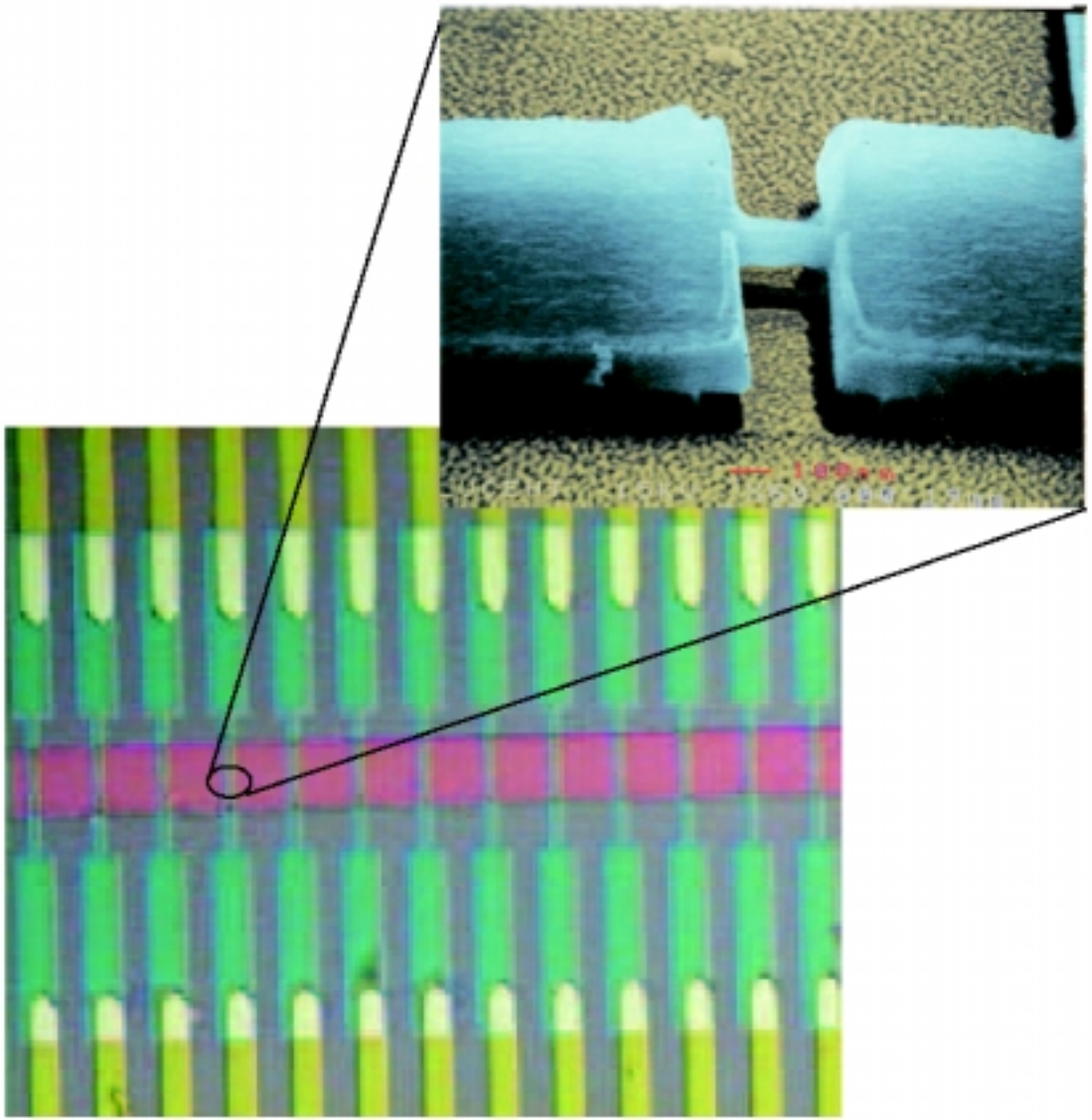
Inner ring rotated

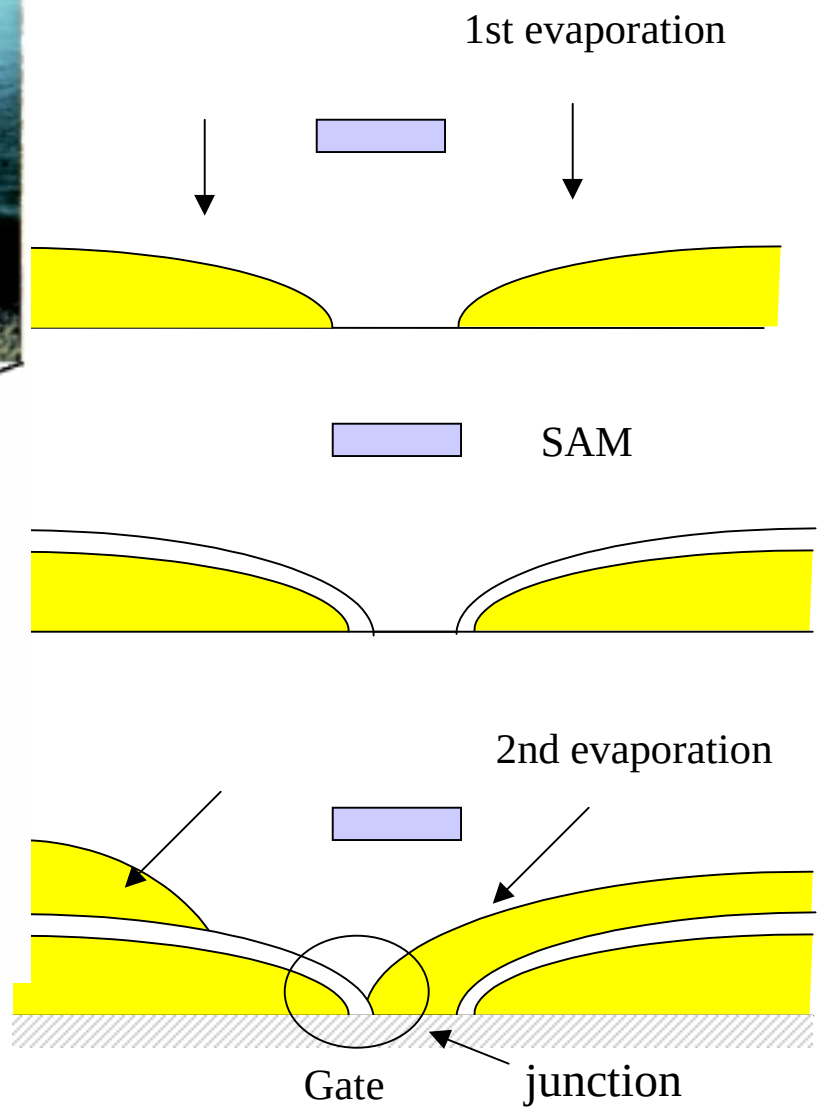
45°





Shadow mask for molecular junctions in planar geometry



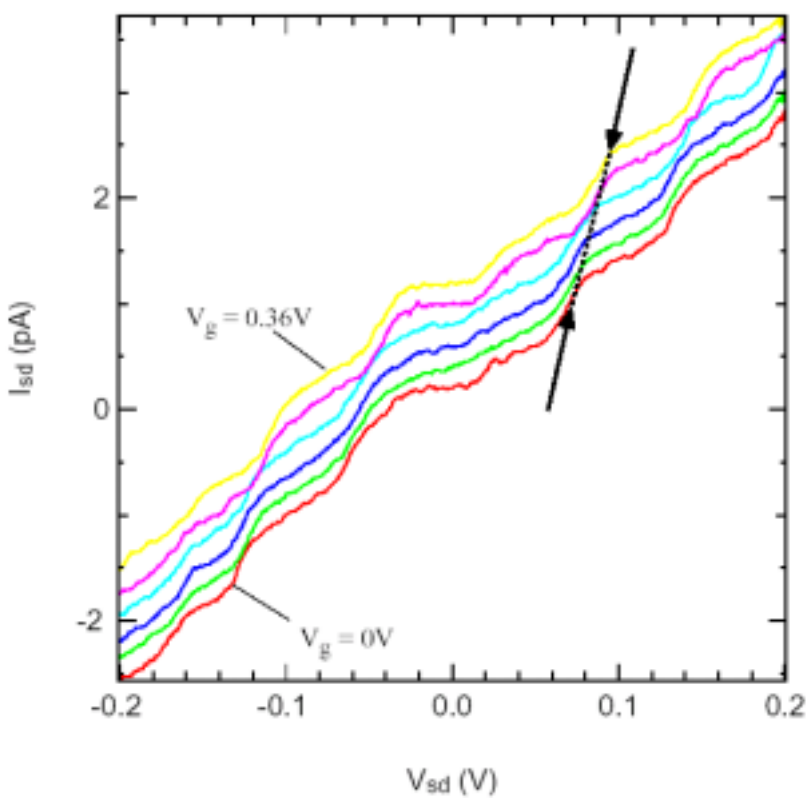


Planar junctions: ~100 x 100 nm^2, P3 molecules

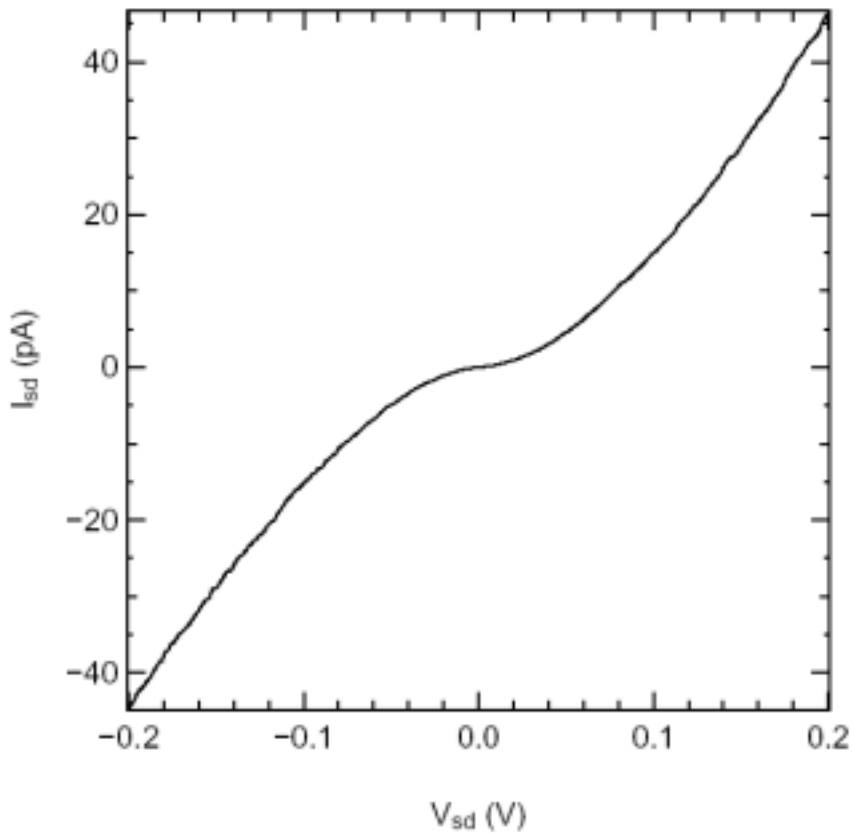
Main surprise: junctions are larger, conductance is still low $<10^{-8}$ Ω^{-1}

Results: IV curves vary broadly, can be separated in two groups

IV curve with features, some show gating



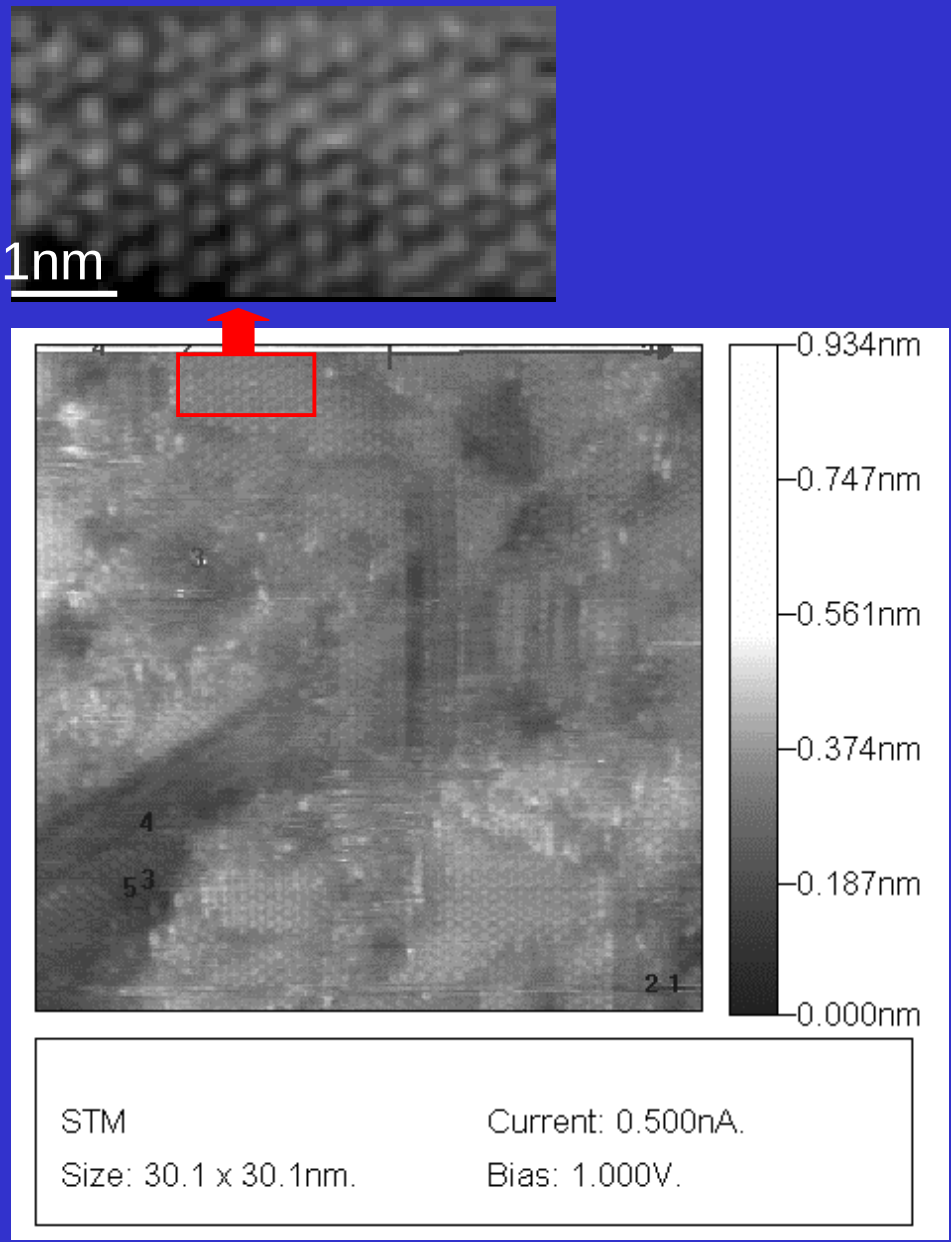
Weak non-linearity, “soft” gap



Scanning probe studies of conjugated molecules and metal-molecule contacts

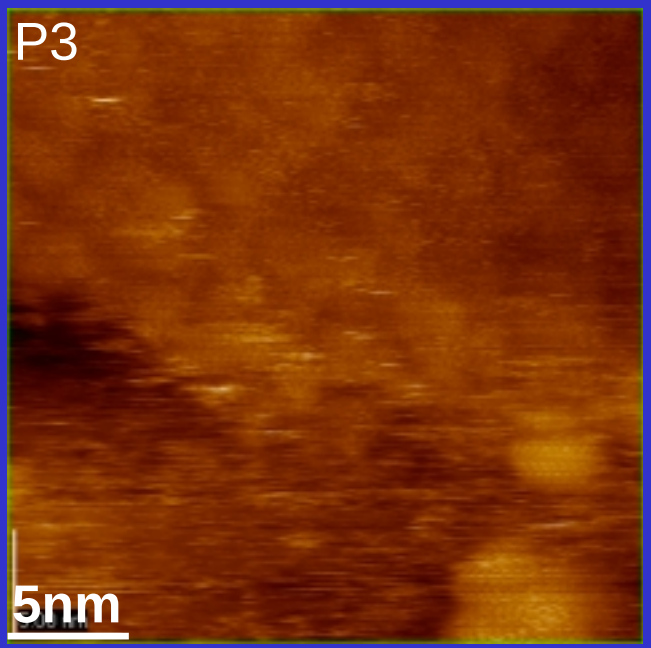
Jeol JSPM-5200

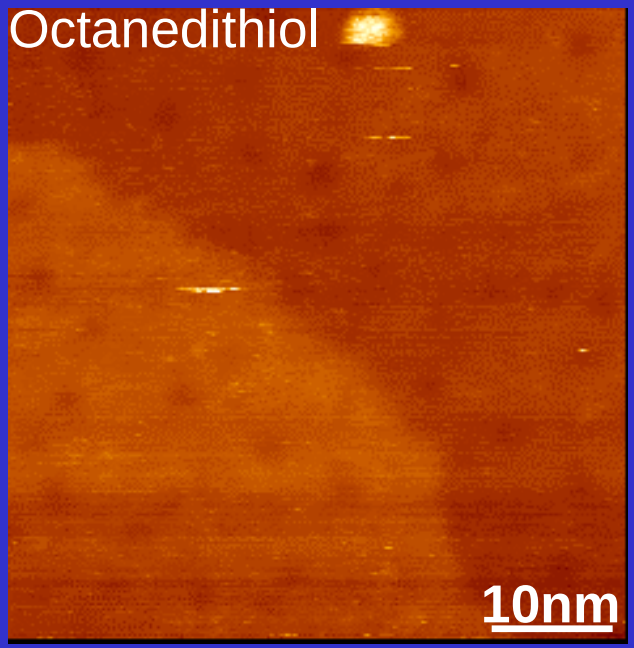
Lowest current: 1 pA

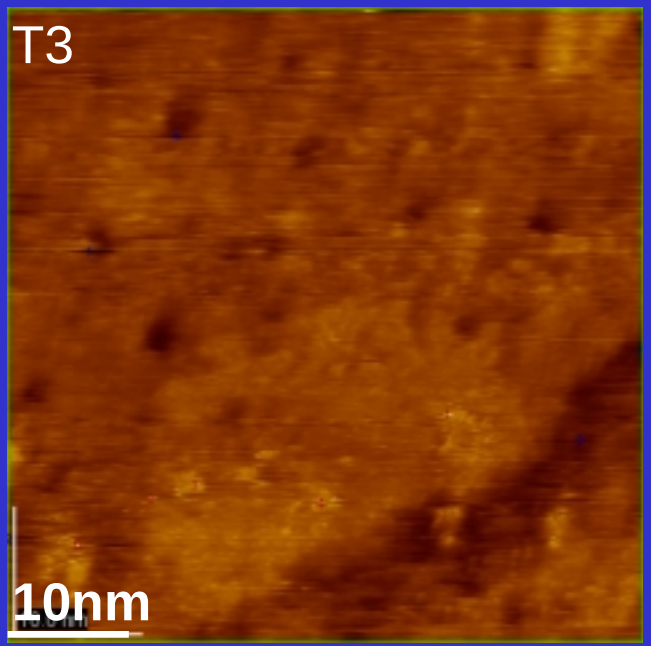


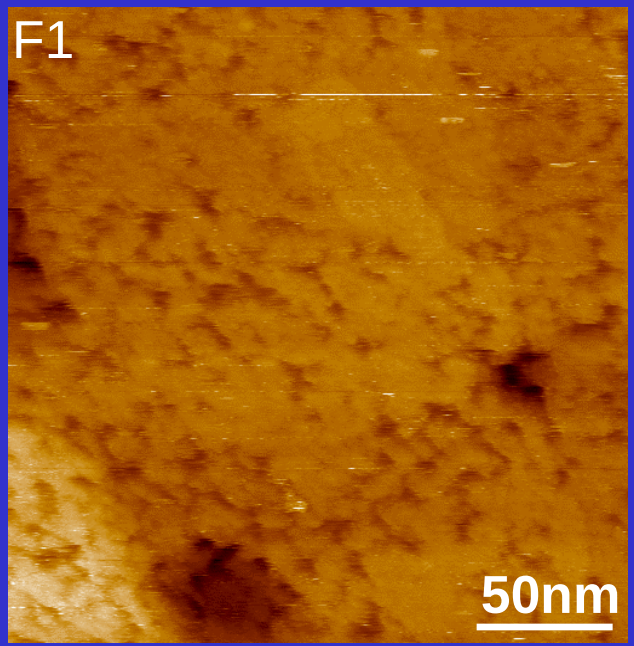
C8:P3 – 1000:1, RT, Nitrogen

STM images of dithiols:









P3: Inner ring rotated

Octanedithiol, T3, F1:
planar geometry

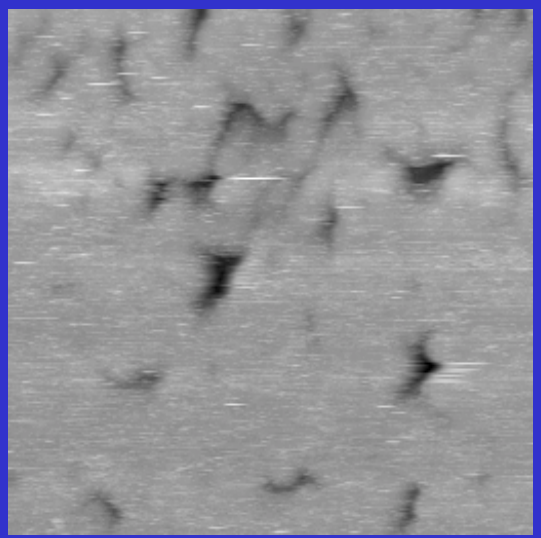
*Planar molecules form better quality SAM

Solution-based passivation with metal ions: Au, Cu, Pt

1) to passivate the surface: better structure and IV measurements
2) to reveal defects & provide height contrast

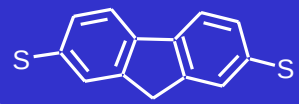
P3

P3: concentrated Au cyanide, 1min

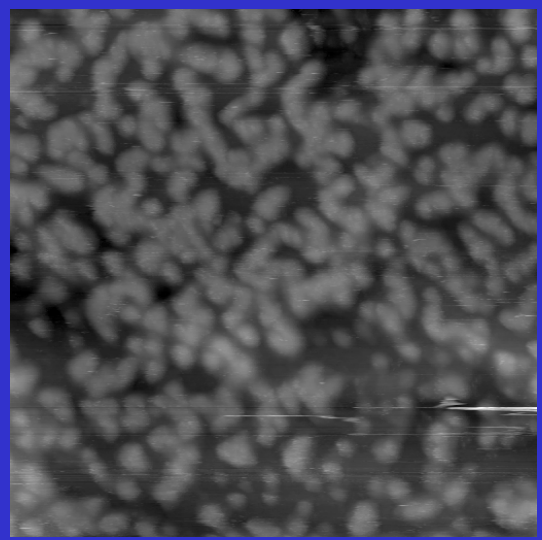


200 nm

F1, diluted Au cyanide, 10 s

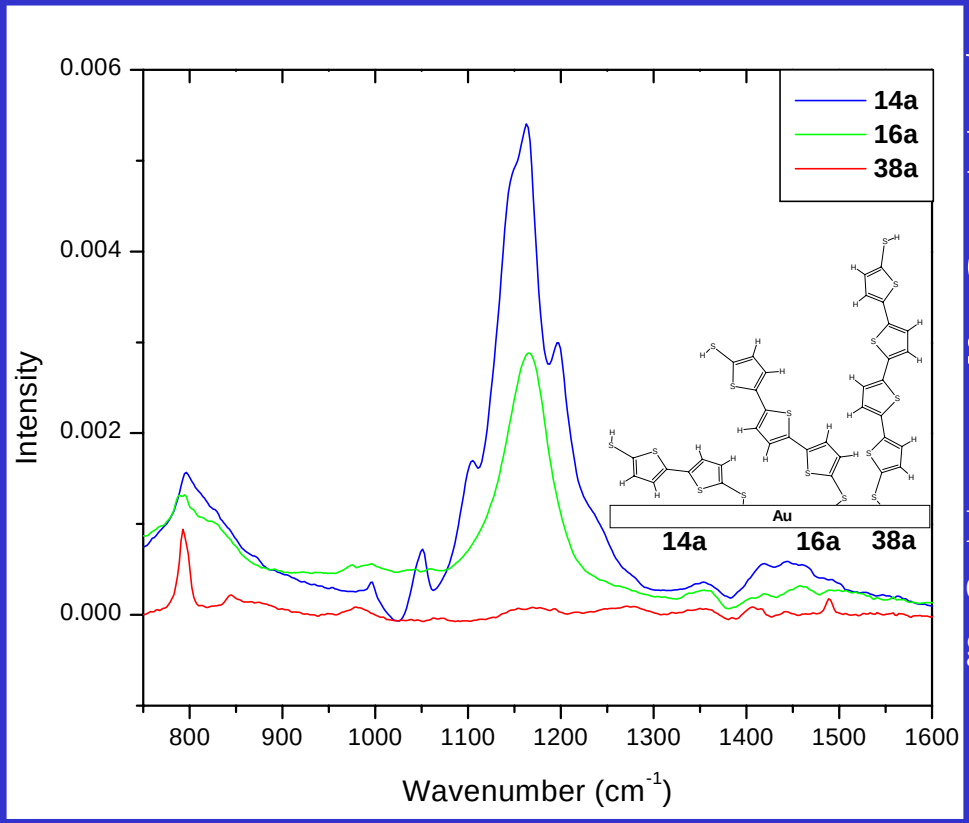


F1



200 nm

- No molecular order yet
- The depth of defects is close to the length of molecule
- Defect density can be low enough not to have shorts on 100 nm scale



Yve Chabal's group at Rutgers:

GI-FTIR spectra of the C–C stretch modes of

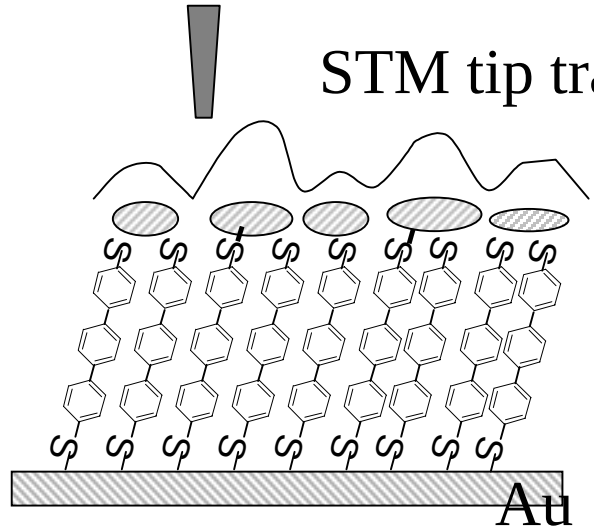
T2(**14a**), T3 (**16a**) and T4(**38a**).

Inset shows schematically the orientation of **14a**, **16a** and **38a** on the gold surface.

	P3	F1	T2	T3	T4
Oxidation Potential	1.38	1.33	1.31	0.98	0.81
Melting point	175-178	142-143	133-135	143-144	225-226

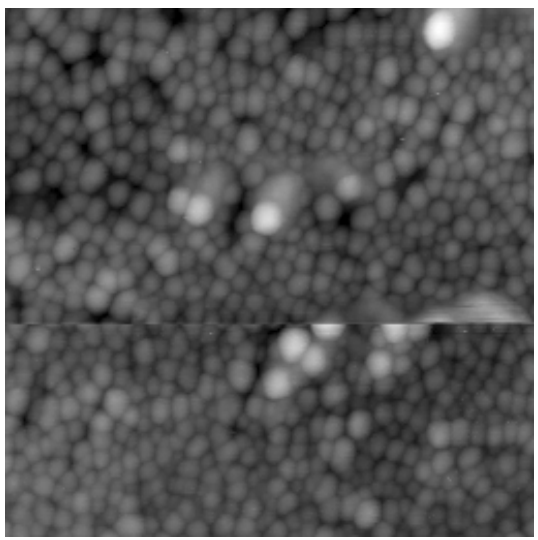
Contact to molecules:

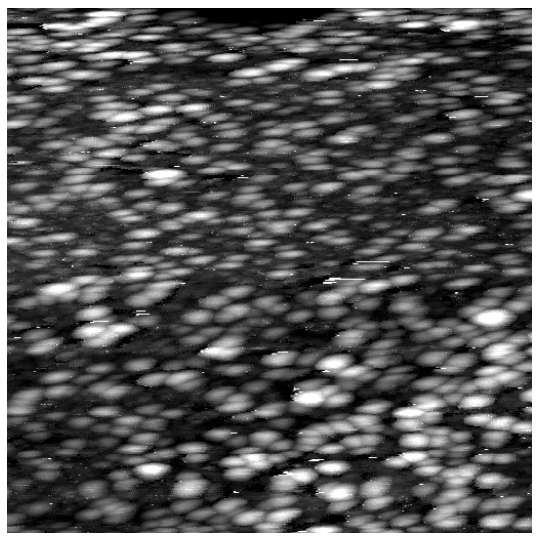
STM tip trajectory: height+ conductance

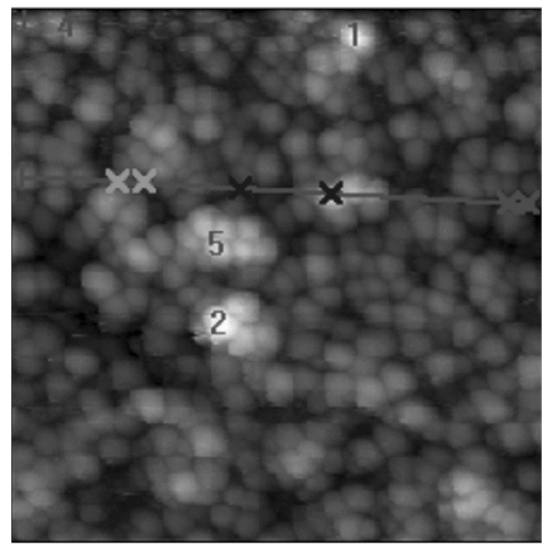


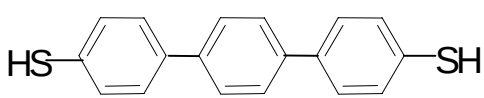
0.3 nm Au on top of SAM with conjugated molecules

100x100 nm^2



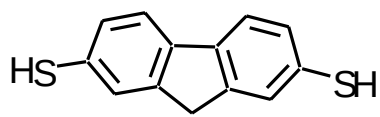






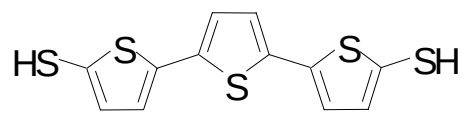
P3

Height 0.3 nm –no bonding



F1

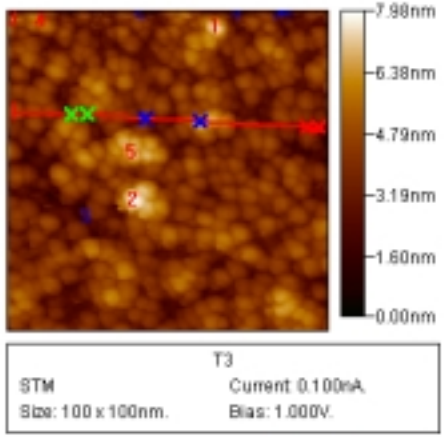
Au diffusion to bonding centers



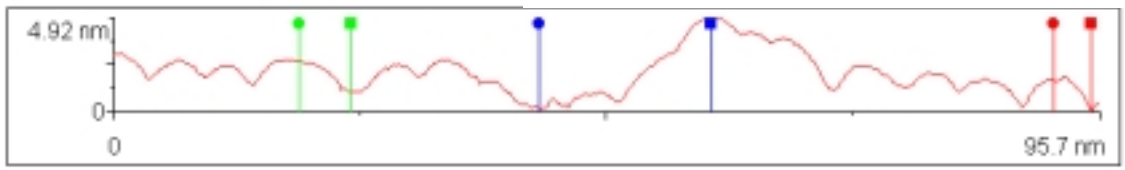
T3

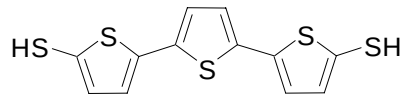
Height 1.5 nm –good bonding

T3/0.3nm Au



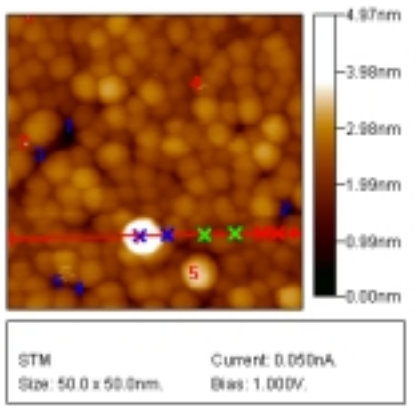
Well-bonding case: 0.3 nm evaporated,
~1.5 nm visible cluster size



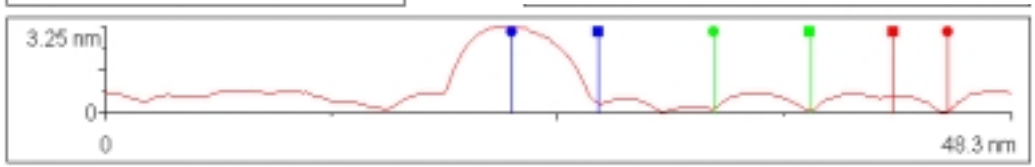


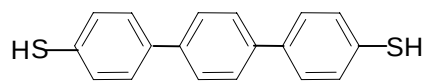
T3

P3/0.3nm Au



Poor bonding: 0.3 nm evaporated,
most clusters ~0.3-0.5 nm





P3

Conclusions

1. Making molecular device is still tricky – shadow masking, trapping, printing…but possible without shorts

2. Molecule-metal contact remains the least defined link in devices.

Better control of interface during device fabrication:

- atomically flat gold substrates: Au growth on mica, patterning, transfer to other substrates
- Second bond: comparing different metal deposition (evaporation, electrochemistry, stamping)
- correlation between scanning probe techniques and devices