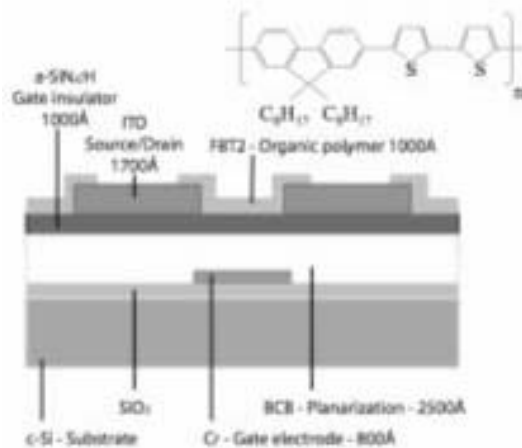


# Molecular Electronics

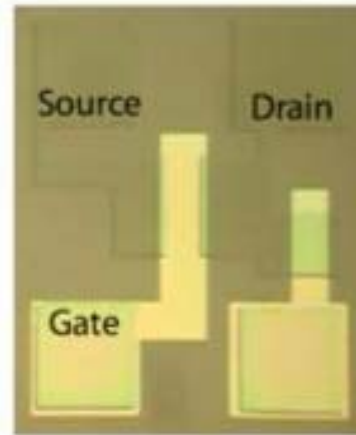
11/17/05

## Molecular electronics: definition

- Molecules are used in bulk form in a number of prototype devices:



Thin film transistors, Prof. Kaniki group



organic LED  
flexible display  
Universal Display Corp.

Covered by EECS 513: Flat Panel Displays

- Limit our discussion to situation where:
  - Small number (< ~ 1000) of molecules per device.
  - Each molecule plays an *active* role.
  - further focusing on small organic molecules ,  
macromolecules (eg, carbon nanotubes) already discussed

## The promise of molecular devices

- Smallest component size. Highest density.
- Chemical synthesis means producing  $\sim 10^{23}$  components *in parallel*. Possibly low-cost.
- All molecules of type *A* should act *exactly* the same, with no statistical variations from molecule to molecule.
- Have designer toolkit – over 100 years of synthetic chemistry background to draw upon, plus computational ability to predict energy levels and electronic structures.
- Molecules are intrinsically small, on a par with sizes of interesting phenomena (room T SET devices, etc).

Created a big splash a few years ago.

## Big concepts

Three key ideas that are fundamental departures from traditional electronics industry methodologies:

- single-molecule functionality
- self-assembly
- fault tolerance / adaptability

Engineer single molecules to replace *many* components – better than just miniaturization.

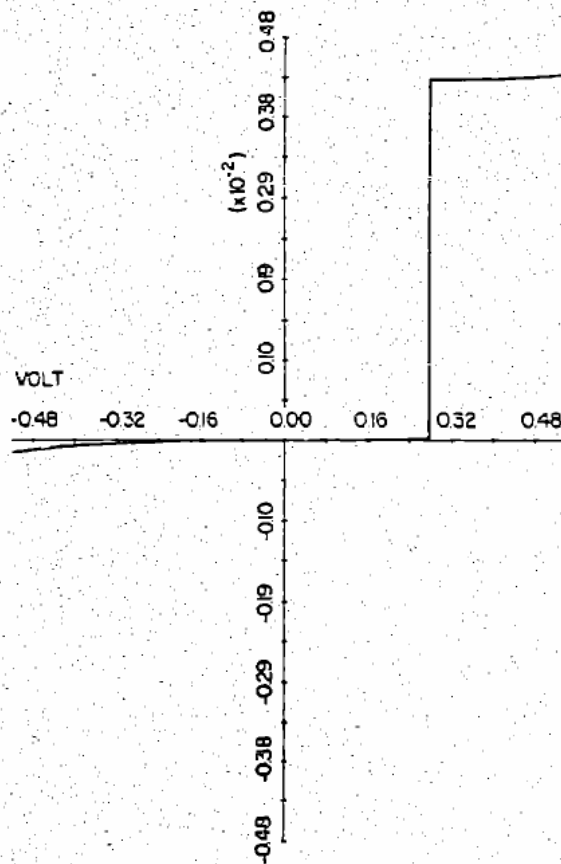
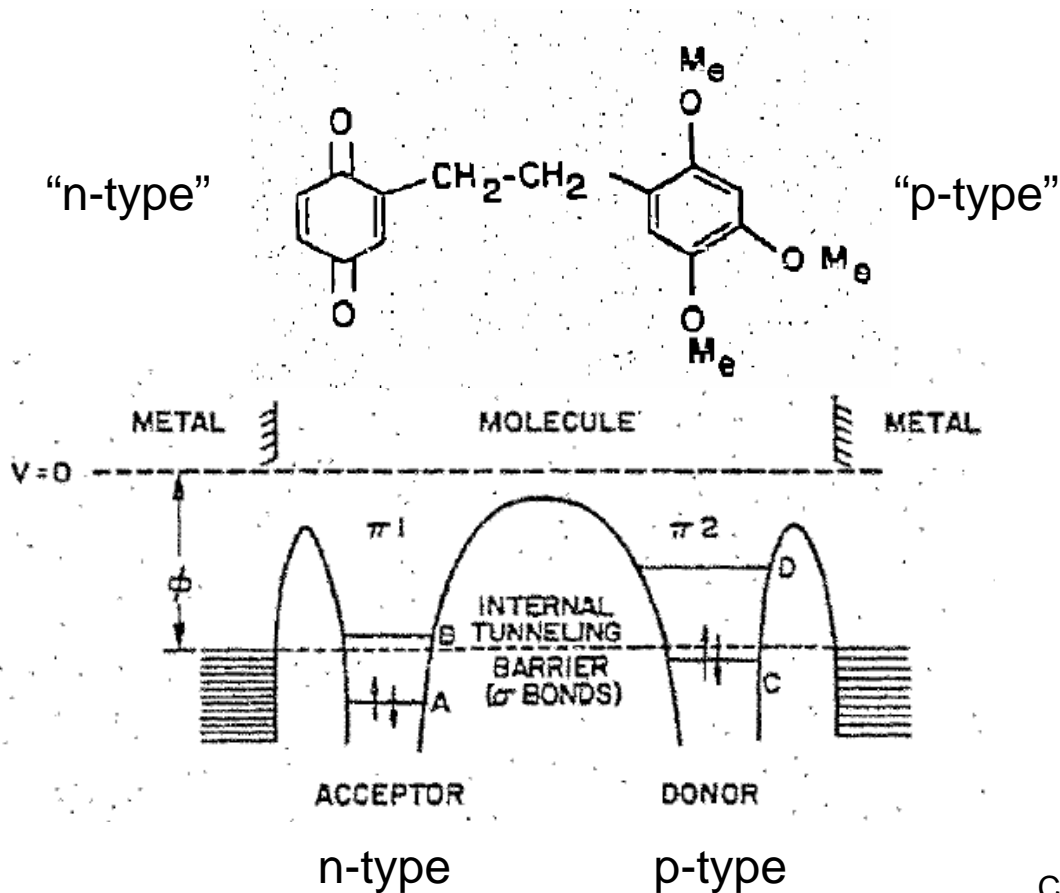
Emulate biology – use self-assembly and self-organization to avoid having to engineer assembly of  $10^{23}$  components.

Design architecture to handle large numbers of defective elements and adapt “on-the-fly” to component failures *in-situ*.

# Origins of molecular electronics

*"It seems to us reasonable to examine the potential use of molecules as components in electronic circuitry...."*

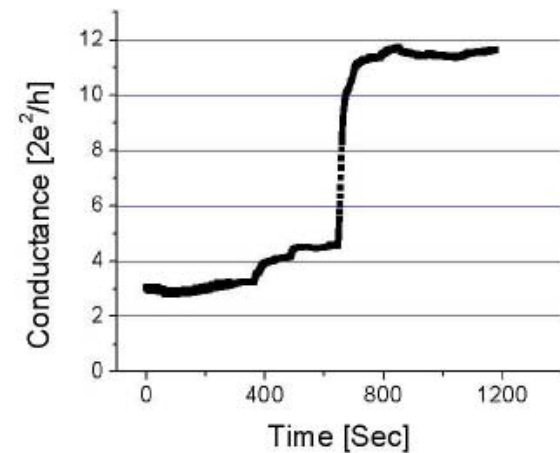
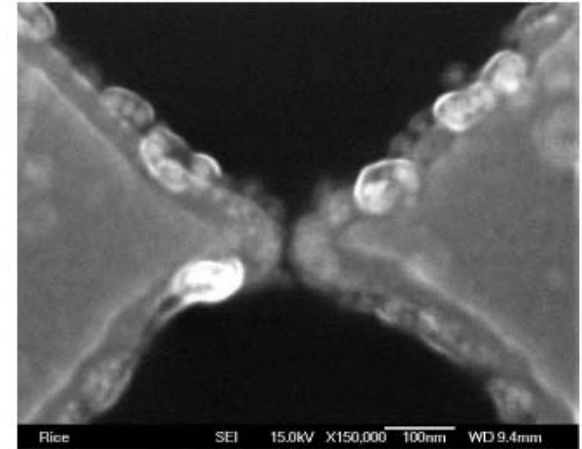
Aviram and Ratner (1974) proposed using single molecule as a diode.



## Connecting individual molecules - needs S/D separation $\sim 1$ nm

- electrodeposition

- Start with electrodes (say 10 nm apart) made by lithography.
- Reduce metal from solution (or rearrange existing metal) while monitoring SD conductance in real time.
- In very careful situations, can stop process when detecting *tunneling current*.
- Signature that electrodes must only be  $\sim 1$  nm apart....



Natelson, Rice

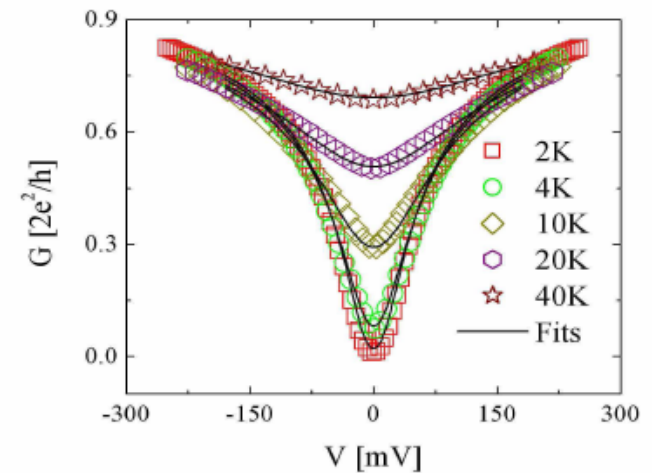
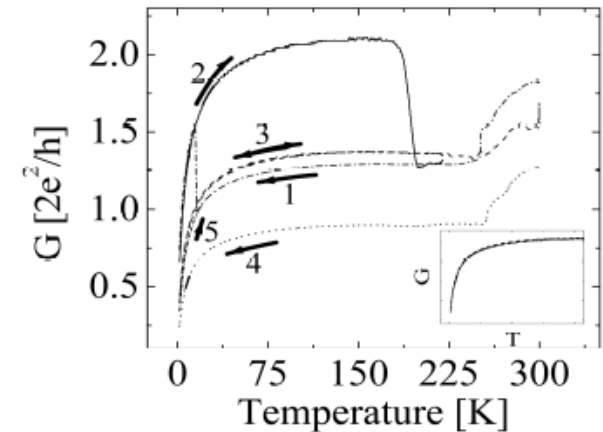
# Electrodeposition

## Downsides:

- Long term stability at room temperature poor.
- Cleanliness and microstructure of metal not well characterized or controlled.
- Strong indications that, at atomic scale, deposited metal is not necessarily a good metal!

## Bottom line:

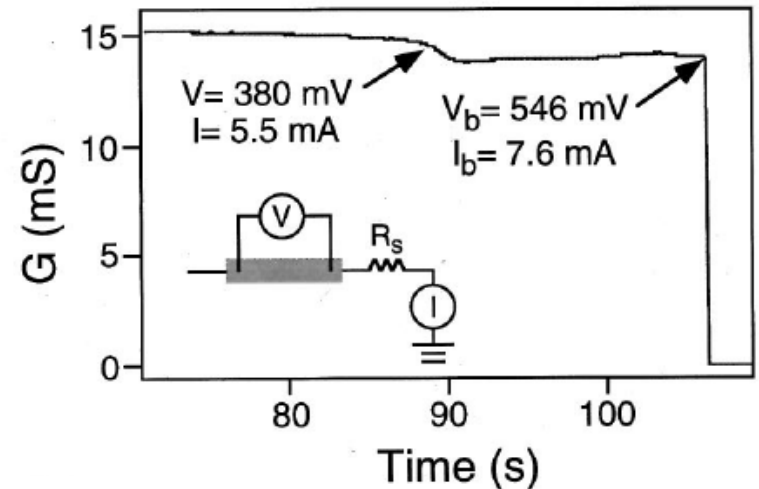
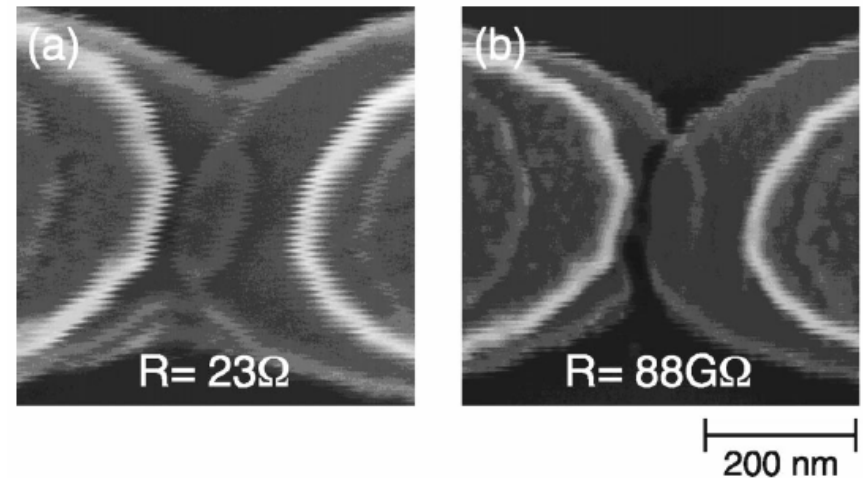
Hard to attribute observed effects to molecules.  
Not a good choice.



# Electromigration

- Start with continuous metal wire.
- (At low  $T$  and UHV), flow current through wire until it breaks due to electromigration.
- Resulting in nm size gap.
- Decorate broken wire with molecules.
- Good metal, clean.
- Still have stability problems when sample is raised back up to higher temperatures.

Park *et al.*, APL **75**, 301 (1999).

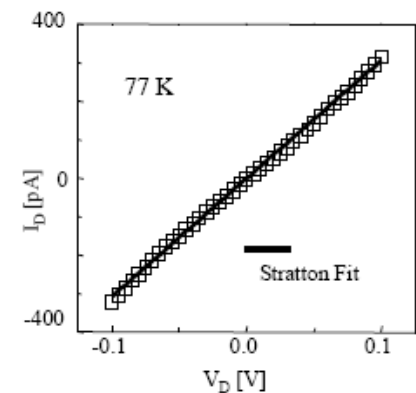
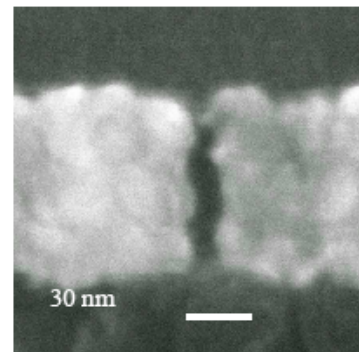
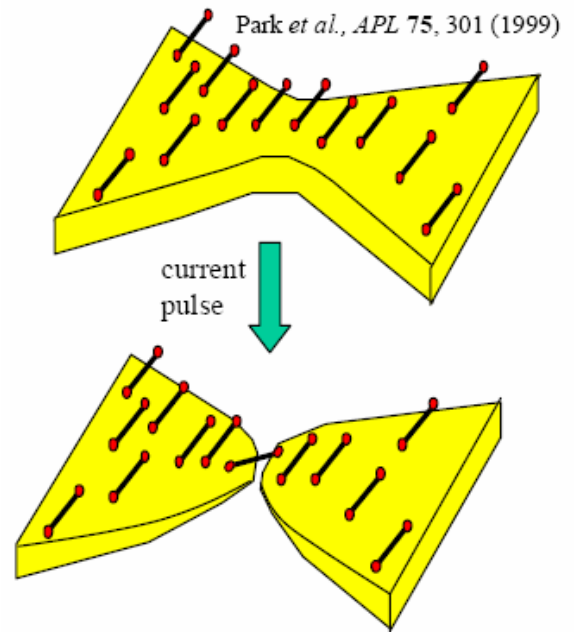




## Electromigration - variations

- Start with nanofab. electrodes (1 nm Ti, 15 nm Au).
- Decorate surface with molecules (spin out of solution, or self-assemble).
- Use electromigration to produce nanoscale gap, ideally bridged by a molecule of interest

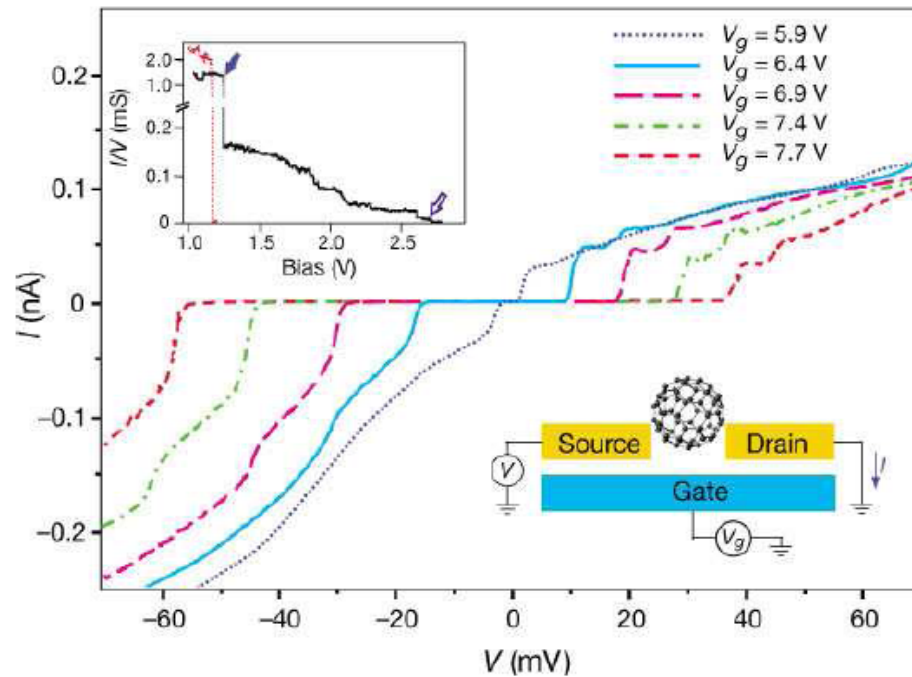
Improved yield



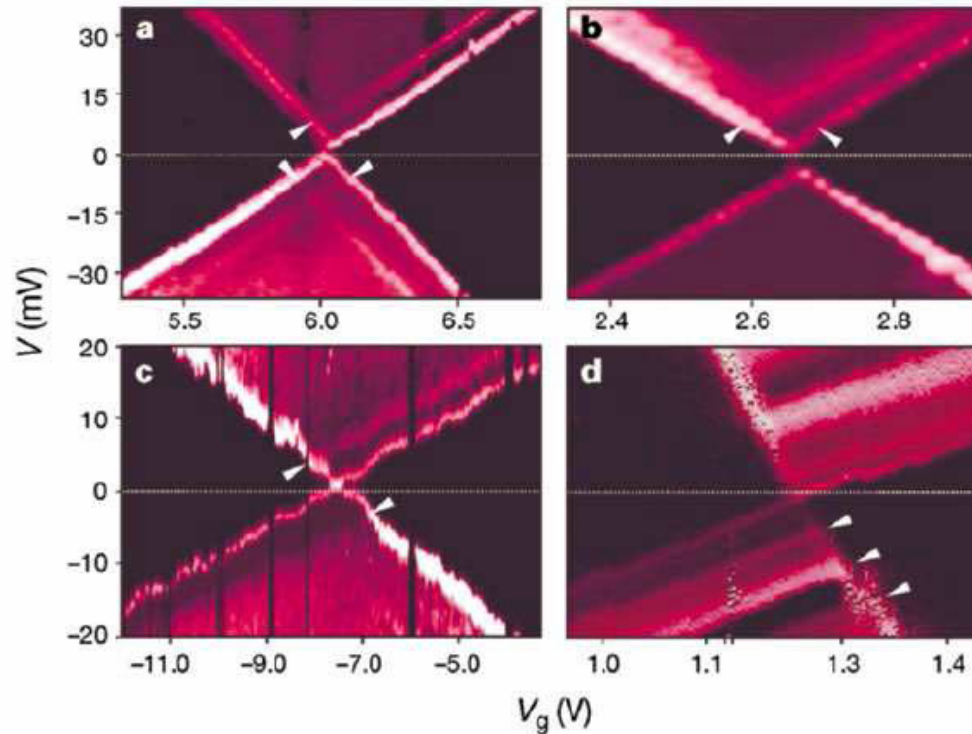
# $C_{60}$ SET

First serious test:

A 3-terminal molecular device using  $C_{60}$   
with back gate.  
Success rate  $\sim 10\%$ .



## $C_{60}$ SET



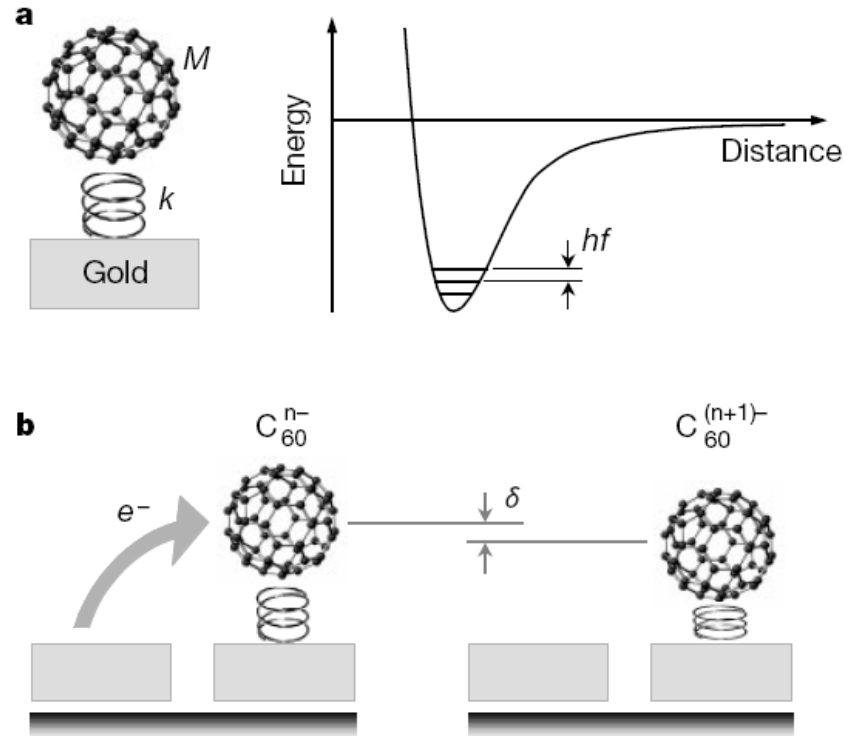
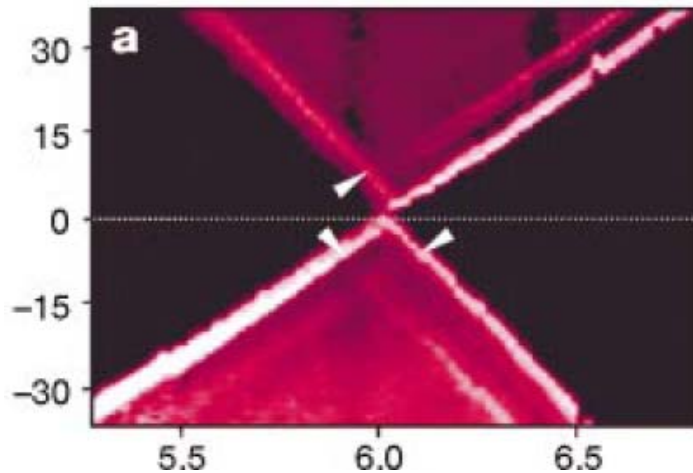
- Coulomb blockade “diamond plot” - changing charge on  $C_{60}$  by 1 electron.
- Coupling to gate varies from device to device.
- Signature of additional excitation with  $\sim 5$  meV energy.

# $C_{60}$ SET

Proposed explanation for that excitation:

Vibrational mode of  $C_{60}$  bound to Au.

Adding or removing an electron excites the vibrational modes (forces exerted by image charge)



## Challenges:

Devices at this scale, made with not well-controlled methods, are dreadful to debug.

- Low yields of small gaps (10-15%)
- How can you tell what you have? No control of final molecular / metal configuration.
- intentionally reduce device yield ( $y$ ) to reduce probabilities of having more than one molecules connected ( $\sim y^2$ )
- find common features on all possible devices, and neglect effects observed only occasionally (can see just about everything once or twice).
- Use a “designer molecule” that allows you to clearly identify molecular conduction and distinguish it from others

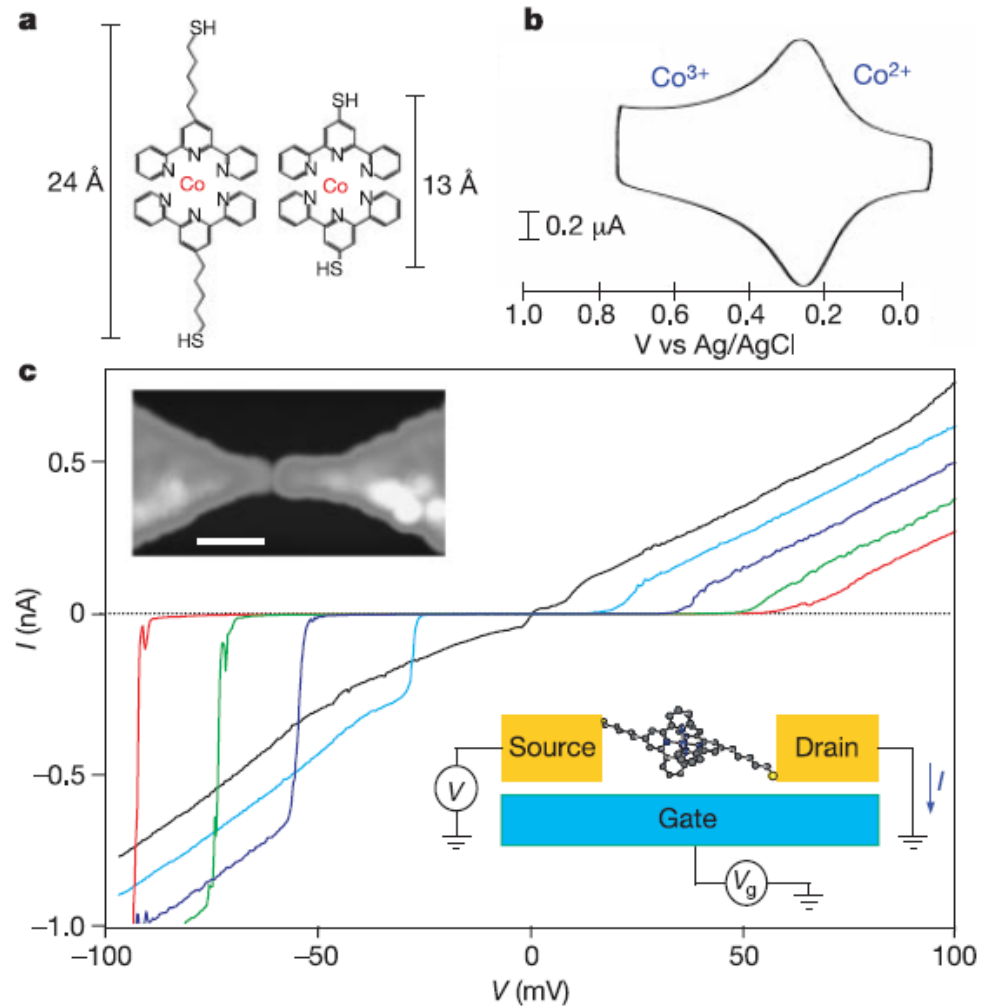
One commonly used trick, thiol (-HS) groups bond well to Au.

## Designer molecule example:

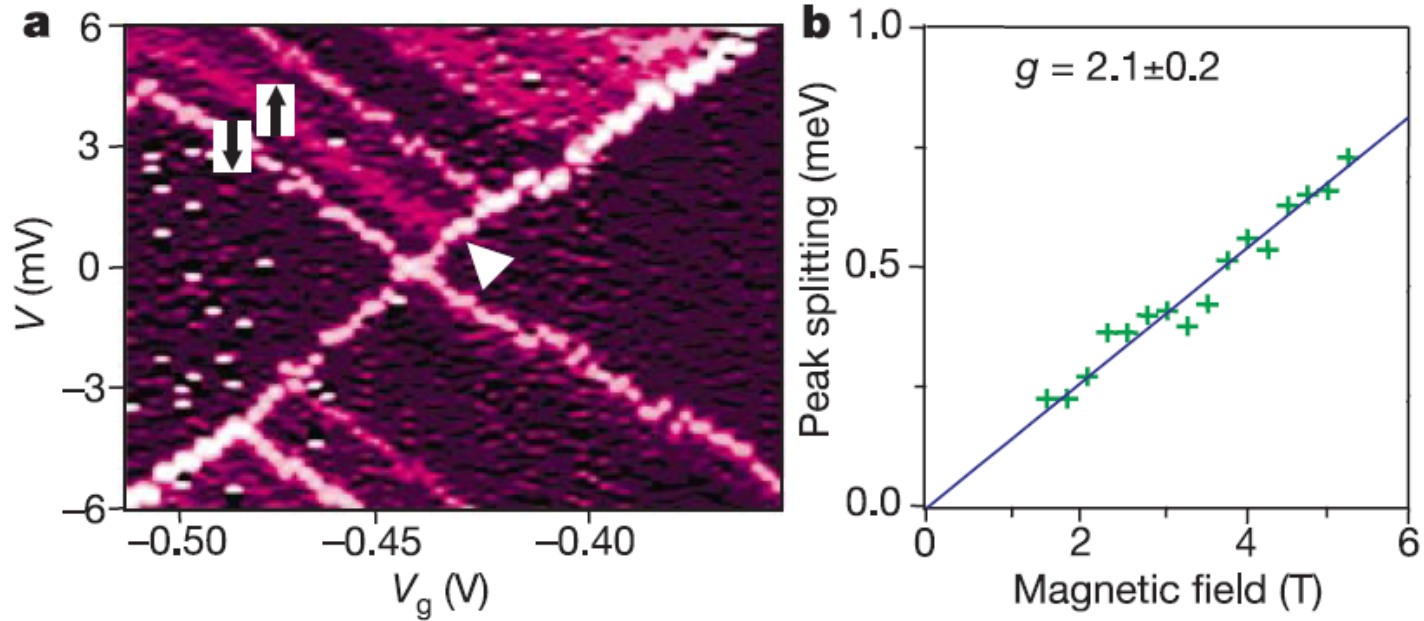
Molecule is a metal complex between two linkers.

Co ion can exist in two charge states, one of which has *even* number of electrons (total spin 0), the other with an *odd* number of electrons.

Plan: use magnetic field to figure out if they're really looking at the molecule....



Designer molecule example:

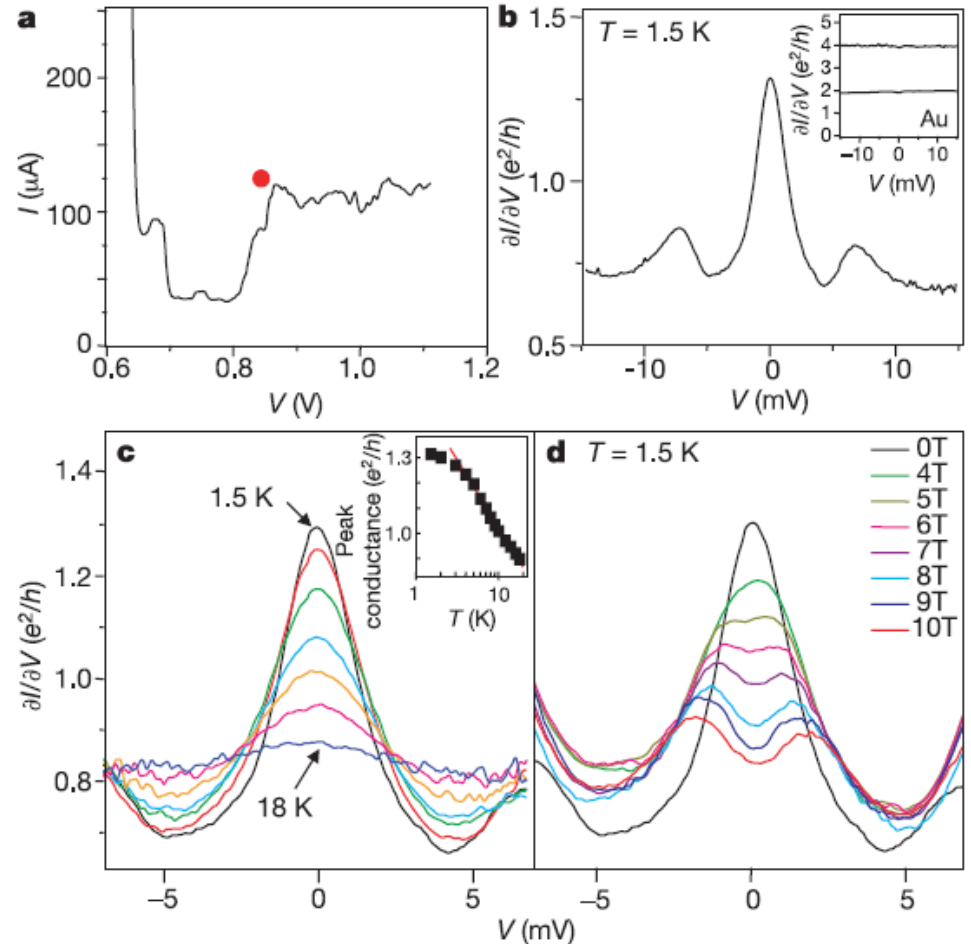
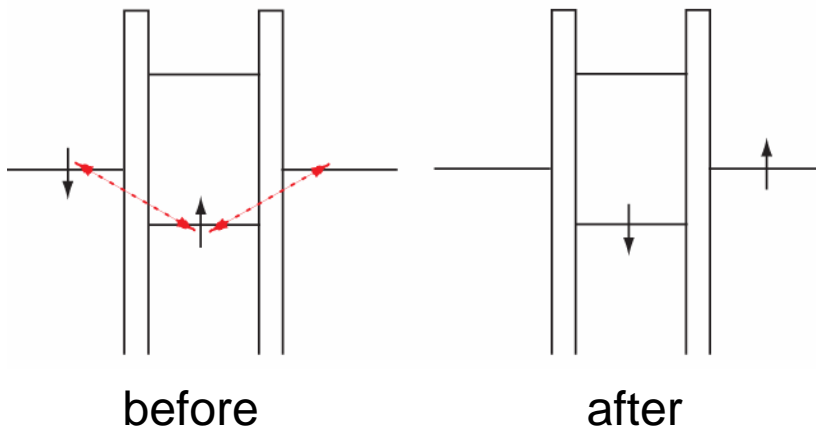


- “Extra” level appears because “free” spin on Co ion can be either aligned or antialigned with applied magnetic field.
- This level shifts linearly with applied field: Zeeman effect!
- Other evidence: Kondo effect....

# Kondo effect

Park *et al.*, *Nature* **417**, 722 (2002)

A virtual process involving flipping of a localized spin can lead to a resonant enhancement of transmission at the Fermi level.



Result:

- A peak in conductance near zero bias.
- Peak grows logarithmically as temperature is lowered.
- Peak should Zeeman split in an applied magnetic field.
- Strongly affected by coupling between contacts and metal dot, (only observed on molecules with short linker molecule chains).

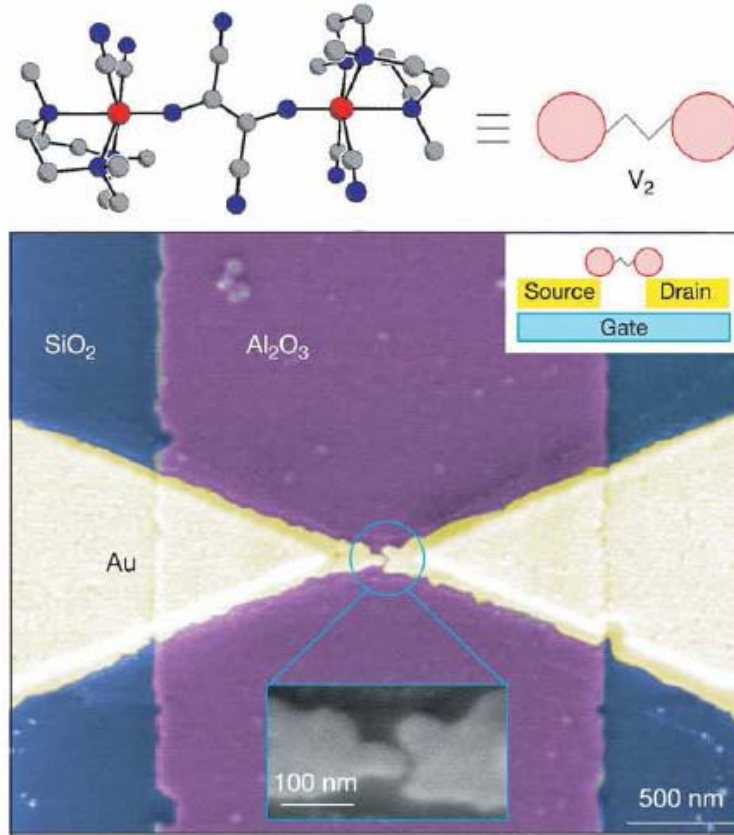


## Designer molecule example:

Liang *et al.*, *Nature* **417**, 725 (2002)

New molecule includes two vanadium ions that can have either spin 0 or spin 1/2 depending on charge state.

Plan: Total spin of molecule should vary as charge of molecule is varied.



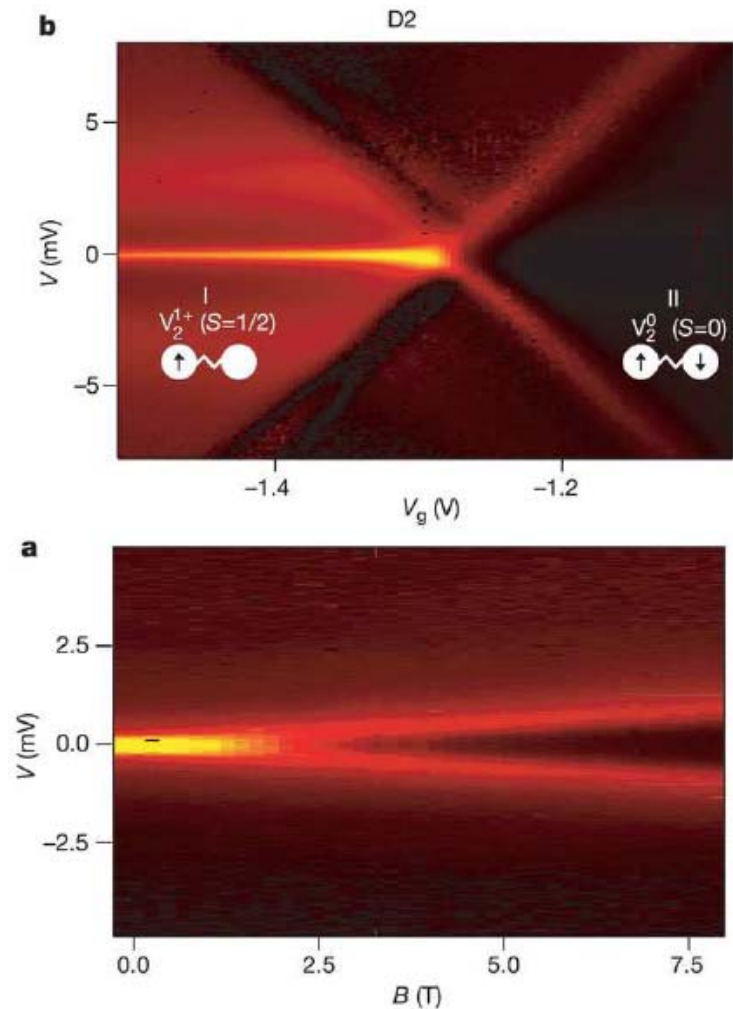
## Designer molecule example:

Kondo effect is again observed.

This paper appeared back-to-back in Nature with the previous paper we just discussed.

The point of both: strong evidence that they are really looking at transport through a single molecule of interest.

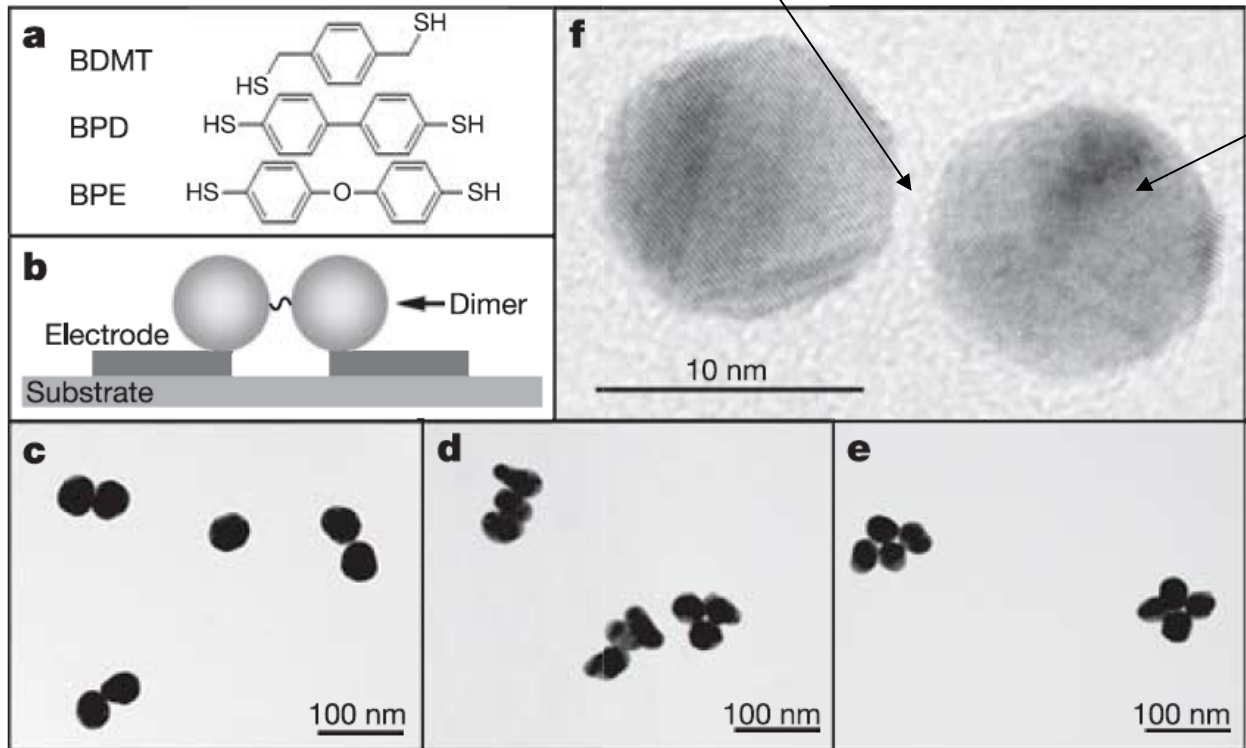
Highest Kondo temperature devices due to the small size of the molecules



Liang *et al.*, *Nature* **417**, 725 (2002)

# Smart variation

Dadosh, Nature, **436**, 677 (2005)



- Mixing nanoparticles with molecules to form dimers
- Nanoparticles help making the contacts
- Nanometer gaps no longer necessary
- Less likely to have multiple molecules being connected by a single device

## Electrical break junction summary

- Individual molecules can be connected and tested
- Charging energies exceeding room temperature are possible.
- New, interesting phenomena observed
- An alternative route to study properties of the molecules

### Problems:

- Typically only works as Coulomb blockade devices due to bad contacts
- Low device yield
- Large scale applications?

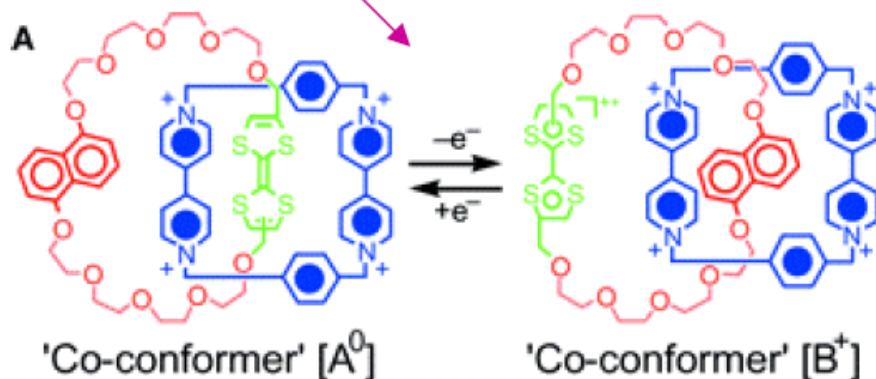
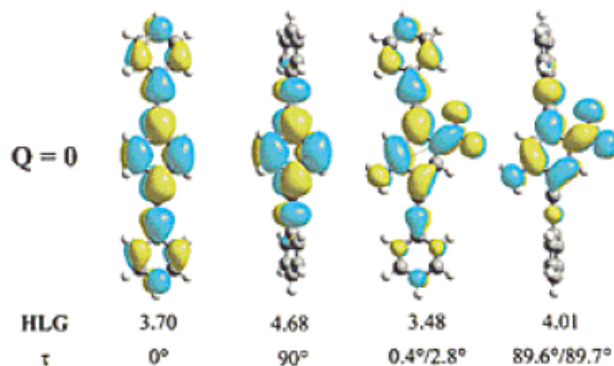
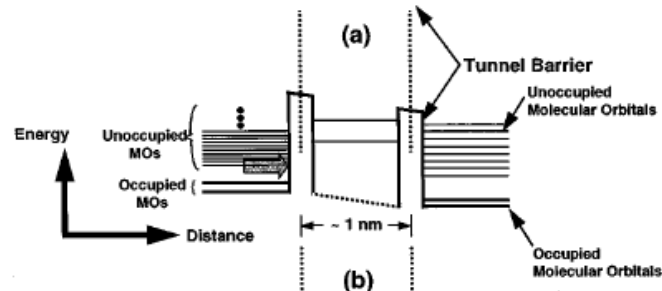
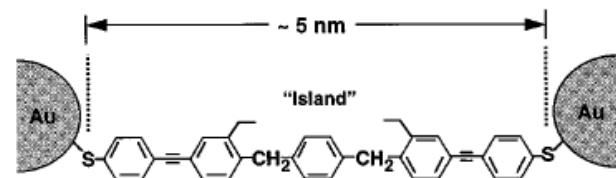
### Other approaches

- Mechanical break junctions
- Nanopores
- Scanned probe microscopy
- Crossbar structures

# Molecular electronics: beyond Coulomb blockade

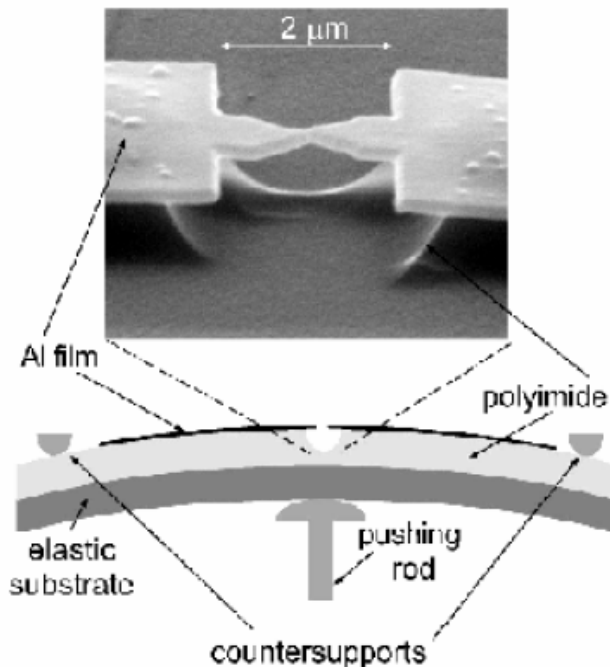
What kind of physics could lead to useful / interesting molecular devices, beyond the Coulomb blockade effects we've been examining?

- Resonant tunneling diodes / transistors
- Switching / memory based on wavefunction engineering
- Switching / memory based on steric properties



## Mechanical break junctions

Basic idea:

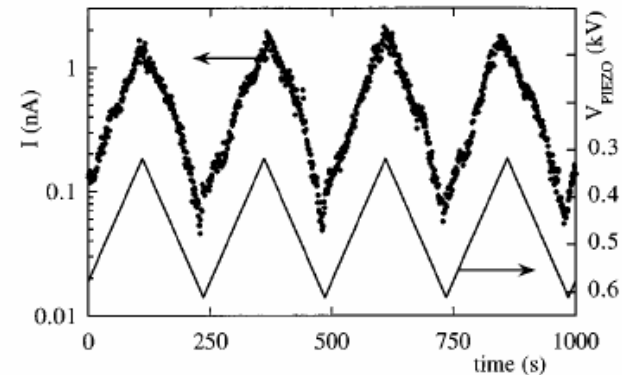


Images from van Wees group,  
Netherlands

Mechanical advantage: lateral motion from bending can be  $\sim 1000x$  smaller than vertical motion.

Breaking can be done in UHV to avoid contamination.

Bare metal tunneling current allows calibration of position.



Zhou *et al.*, APL 67, 1160 (1995).

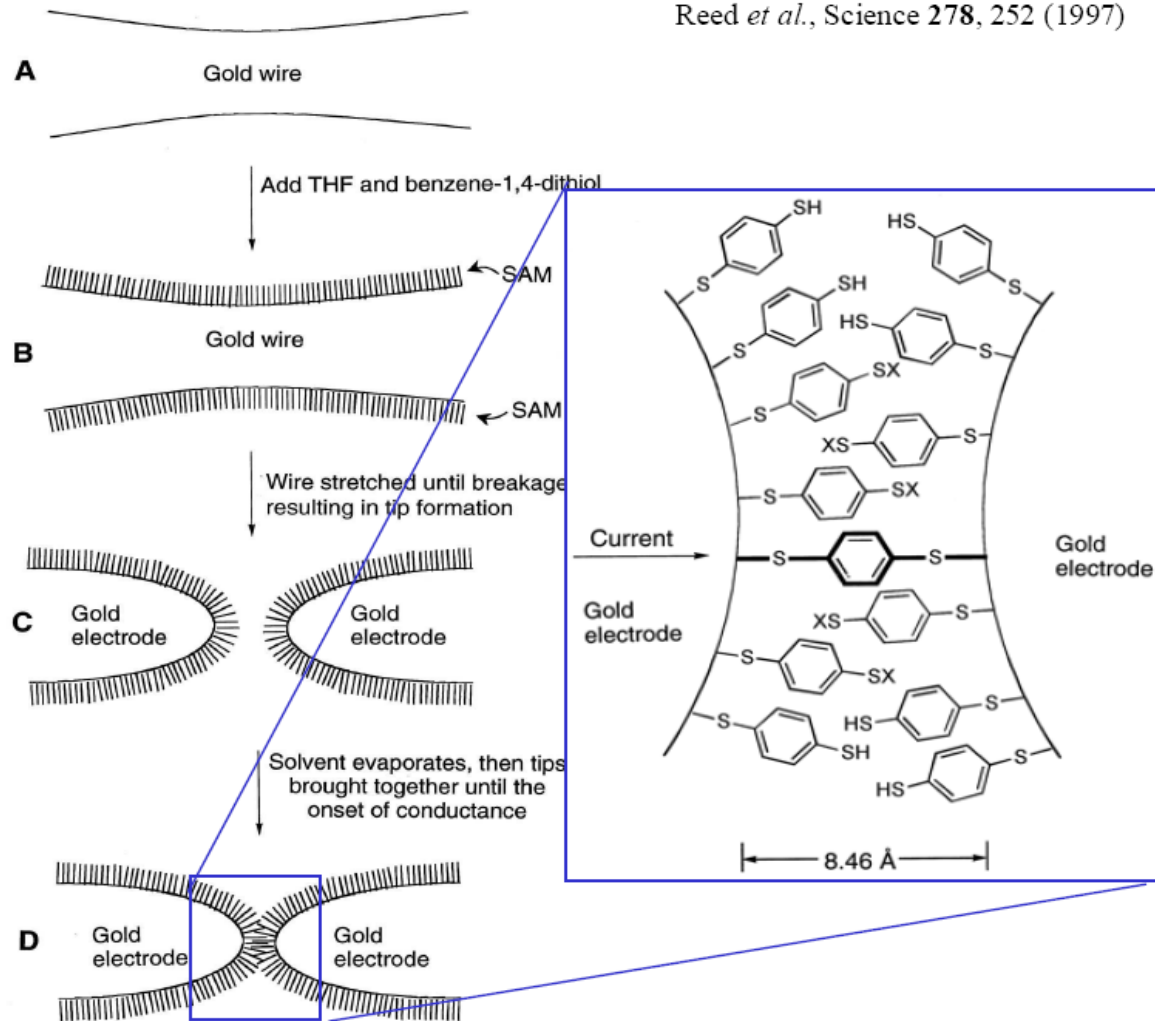
# MBJ: Reed group at Yale

Start with unbroken wire, precoated with self-assembled monolayer (SAM) of interesting molecule.

Break in UHV and allow molecules to rearrange.

Bring junction back together for measurements, knowing what piezo voltage corresponds to the correct interelectrode spacing.

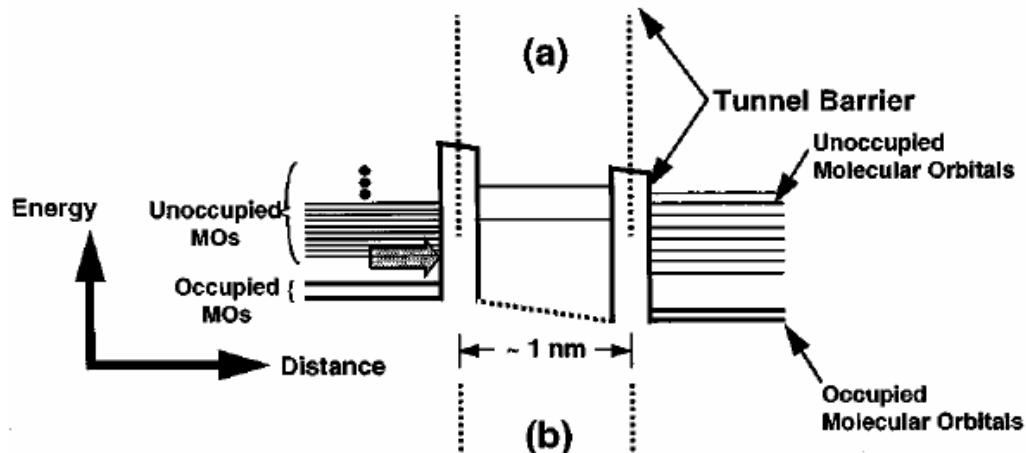
Reed *et al.*, Science **278**, 252 (1997)



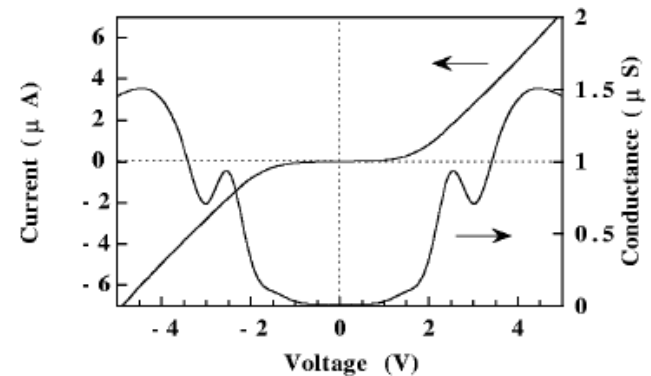
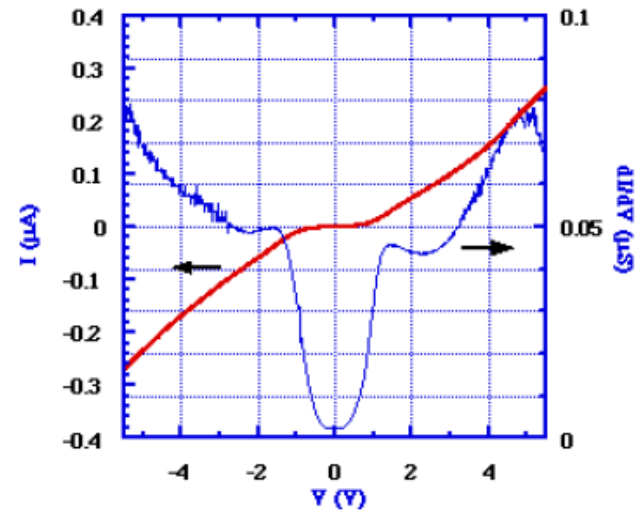
# MBJ: Reed

## Results:

- Differential conductance (blue trace) has features that can be identified with resonant tunneling through molecular levels.
- Theory must account for specific bonding of S to Au to get shape close
- Theory still overestimates conduction by  $\sim 20\times$ .



Reed *et al.*, Science **278**, 252 (1997)



di Ventra *et al.*, PRL **84**, 979 (2000)



## MBJ summary

- Highly productive research technique for examining single molecules.
- Shows that single molecule conduction is possible, though generally poor.
- Single molecule conduction depends crucially on atomic-scale details of bonding and metal surfaces.

### Problems:

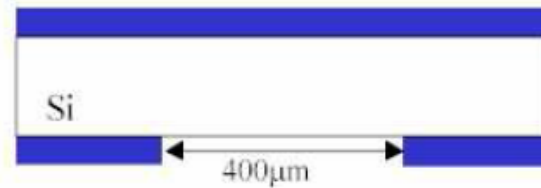
- Mechanical stability essential.
- Very difficult to do temperature sweeps - everything moves due to differential contraction. This is a problem b/c standard way of deducing conduction mechanisms uses  $G(V, T)$ .

# Nanopores

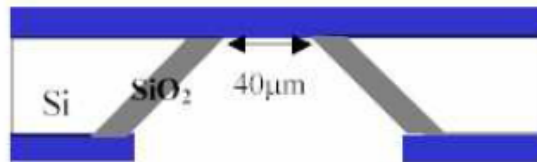
Images from Reed group, Yale



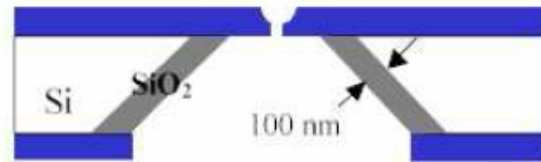
a. LPCVD to grow SiN membranes



b. Photolithography & RIE to open the back side window



c. KOH to etch through the silicon and wet oxidation to grow SiO<sub>2</sub> on the sidewall

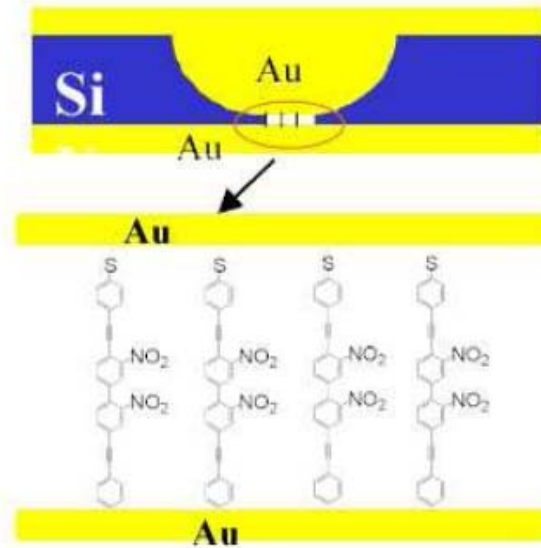
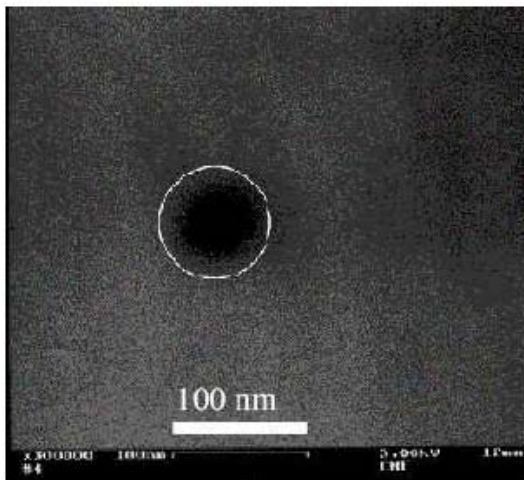
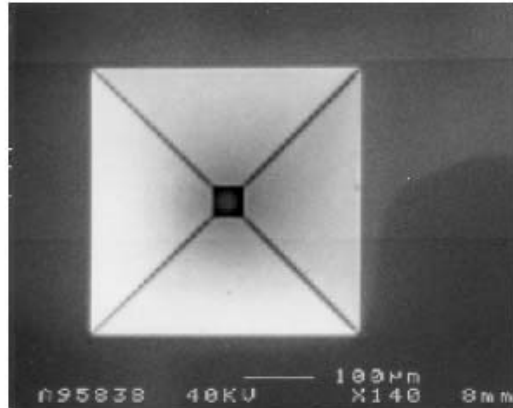


d. Ebeam lithography & RIE to open the nanopore on the front side membrane

Not a single molecule technique - more like  
~ 1000 in parallel.  
Originally developed to study ~ 10-30 nm  
diameter metal junctions.

# Nanopores

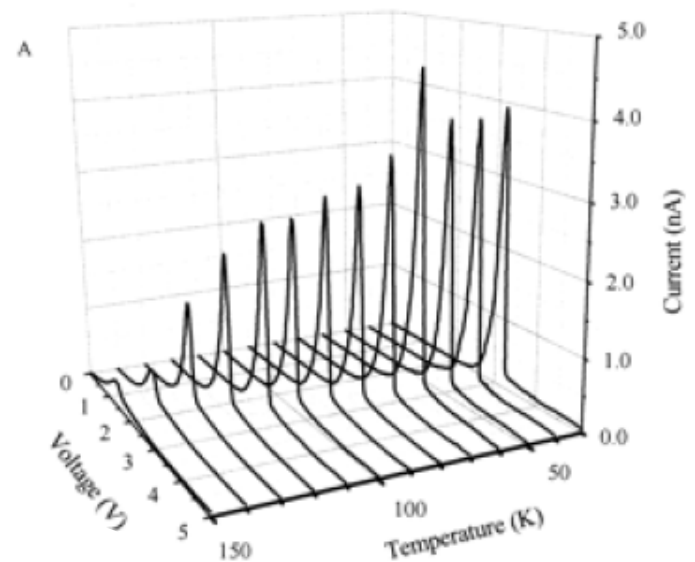
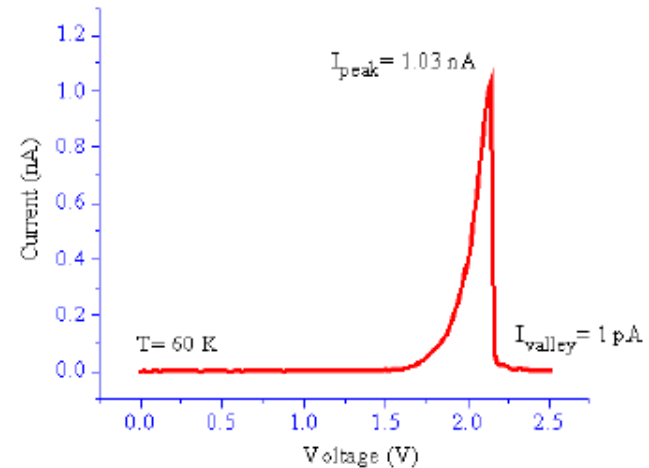
Images from Reed group, Yale



Requires self-assembly followed by evaporation of top electrode.  
No one knows what interface looks like.  
Yield very very low (~ 1-2 %).

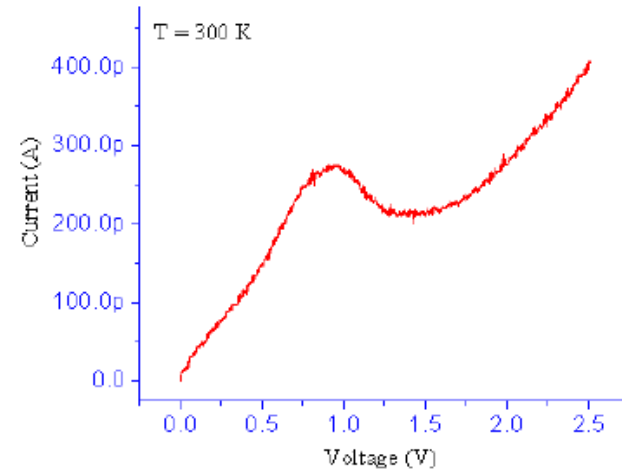
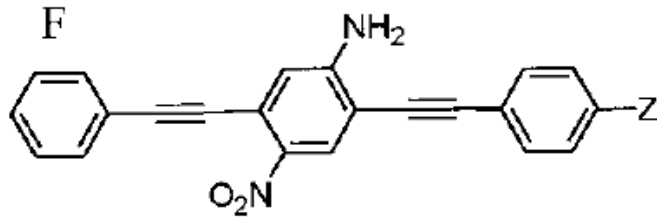
## Nanopore devices: NDR

- Nanopore devices made with above molecule exhibit negative differential resistance, as shown.
- Mechanism not clear: temperature dependence is significant and steep.
- Proposed mechanism: changes in resistance in different charge states



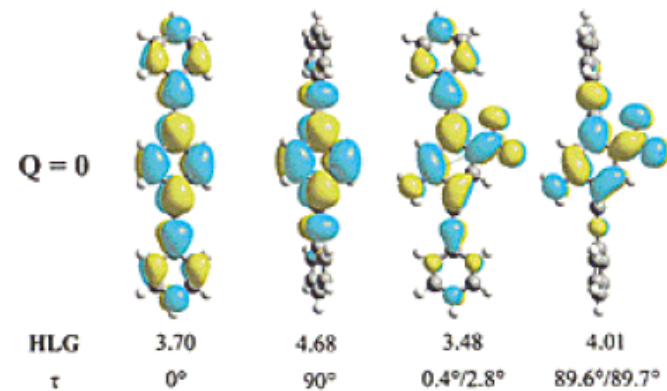
Chen *et al.*, Science **286**, 1550 (1999)  
Seminario *et al.*, JACS **122**, 3015 (2000)

## Nanopore devices: NDR



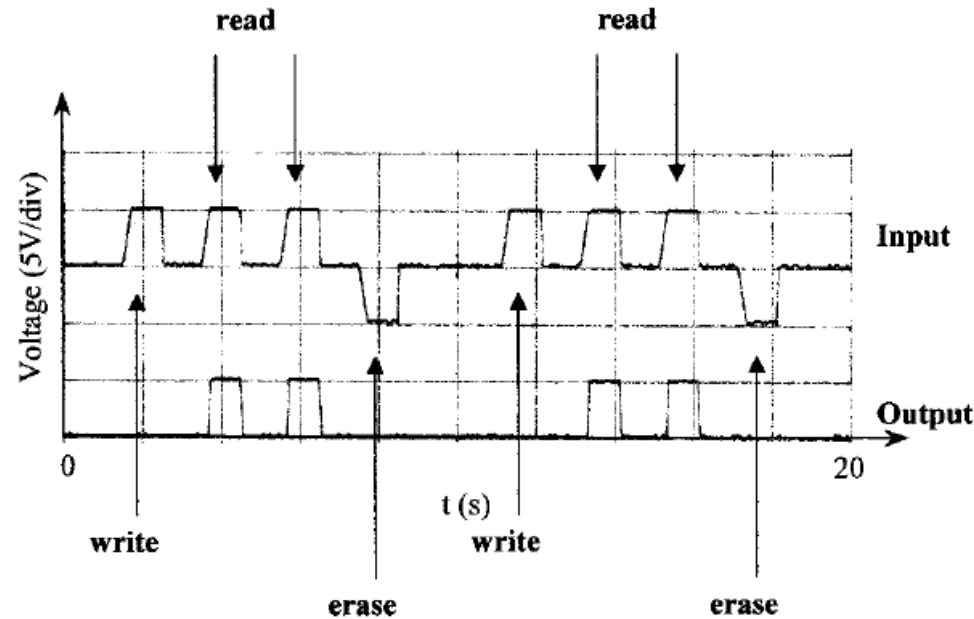
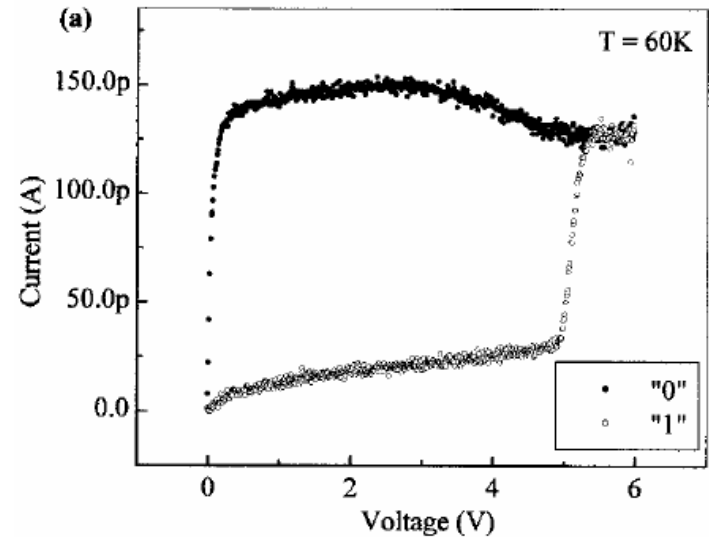
With modification of molecule,  
can see NDR that persists up to  
room temperature.

Other possible mechanism  
besides simple electronic  
structure:  
orientation of phenyl rings.



## Nanopore devices: memory

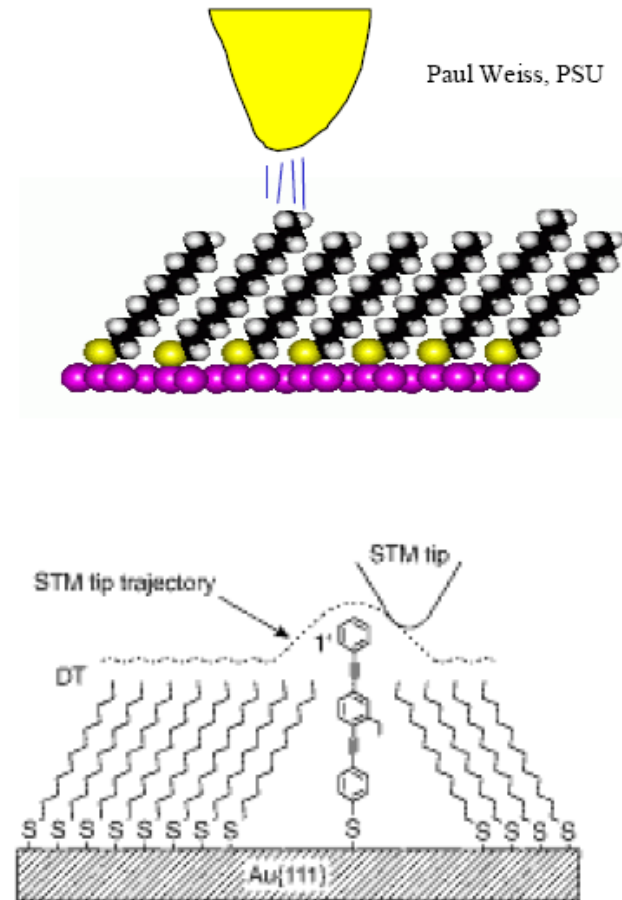
- Hysteretic  $I/V$  curves.  
Initial ramp up: “high” conductance state.  
Ramp back down: “low” conductance state, until reset.
- Prototype memory demonstrated
- Potential mechanisms:
  - wavefunction oriented (shape of electron distribution in HOMO and LUMO)
  - steric (reorientation of side groups)
  - metal filament formation?



## Scanned probe microscopy: STM

Another means of looking for interesting molecules and testing their (2-terminal) conductive properties is to use scanned probe microscopes.

- Allows highly controlled positioning of electrodes previously decorated with molecules.
- Can obtain  $I$ - $V$  curves for single molecules.
- Can quickly examine many molecules

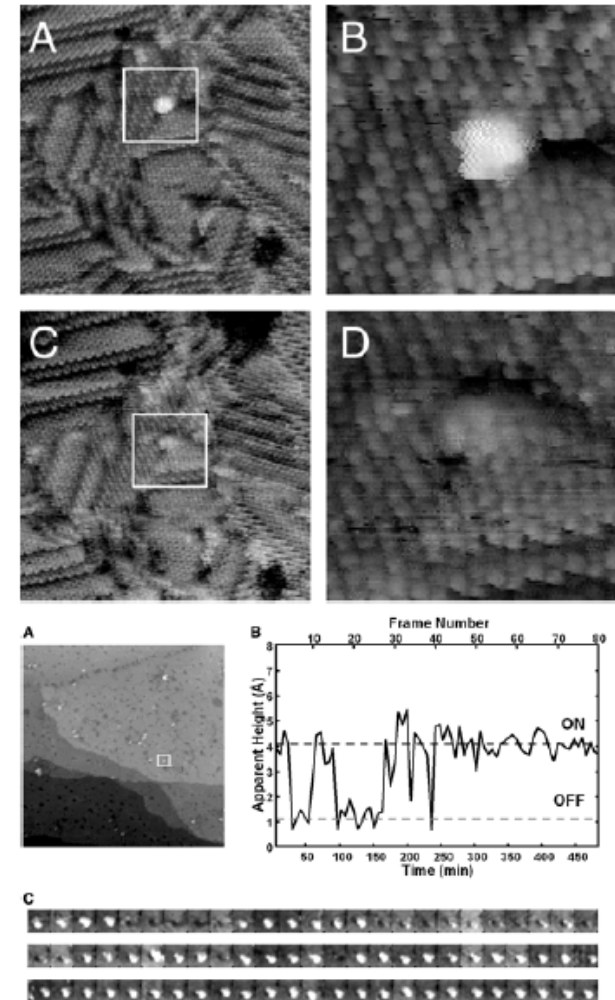


Phenylene ethynylene oligomers isolated in matrices of alkanethiolate monolayers.

Downsides:

- Mechanical stability.
- Difficult to do  $T$ -dep. measurements.
- Interpretation of contacts difficult- tunneling conductance is supposed to be proportional to product of local single-particle density of states of tip and surface.
- As result, tricky to deconvolve topography from electronic properties.

One occasion it's not too hard: time varying behavior



Switching caused by conformational changes rather than charge transfer as previously argued.



## Scanned probe microscopy: AFM

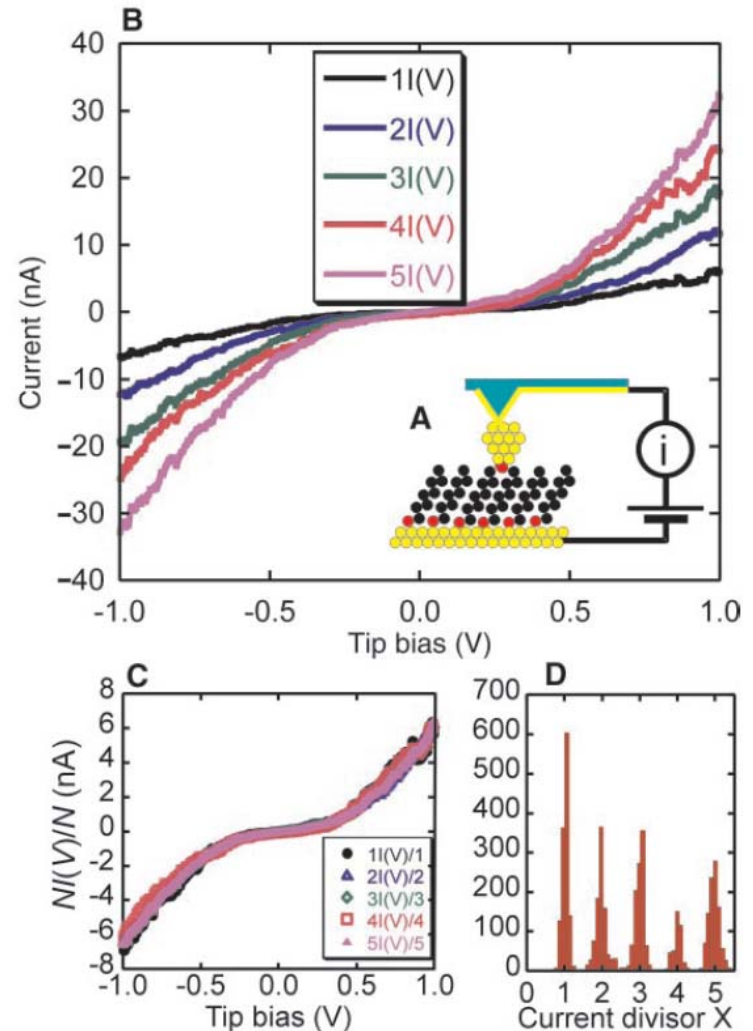
Conducting AFM is also a useful tool.

Downside: contact area is typically significantly larger than single molecule.

Upside: can vary contact force and see what happens.

- 5 distinct groups representing nanoparticles contacting with 1-5 molecules.

- Tricky to reconcile this with the data shown previously demonstrating that contact geometry has huge influence.



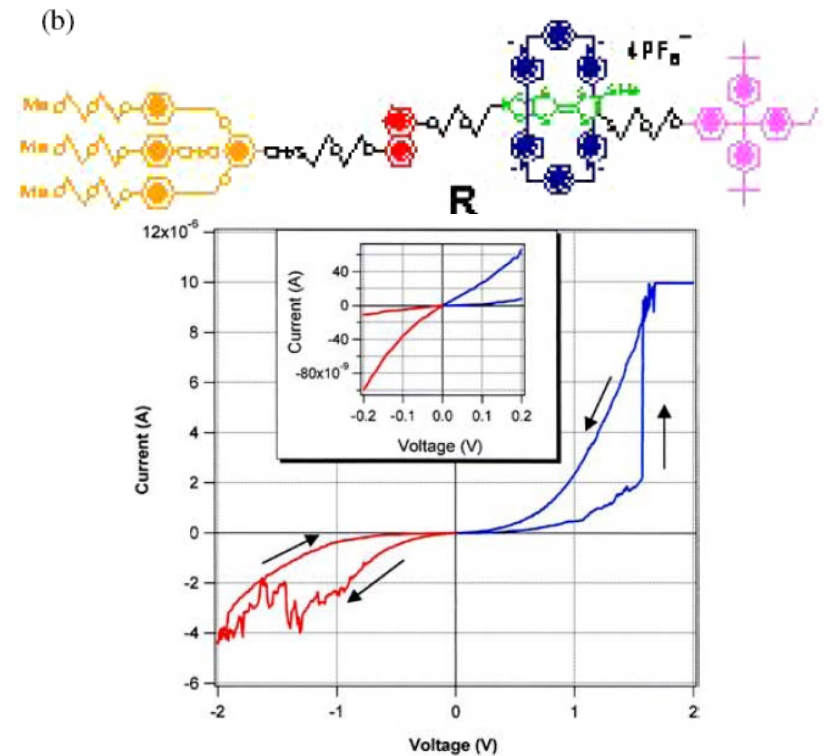
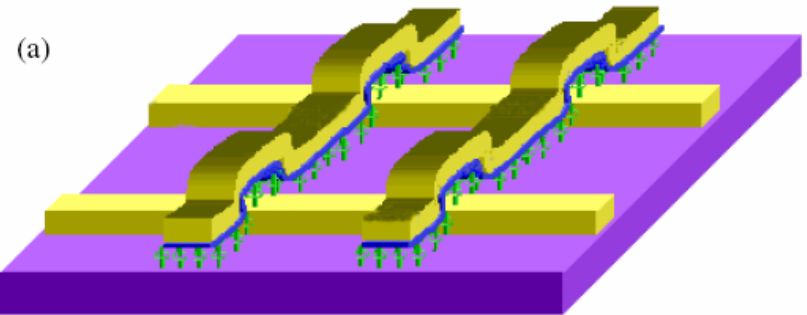
## Nanopore and SPM summary

- Nanopores have produced some impressive results
  - NDR, memory w/  $T$ -dependent measurements of  $\sim 1000$  molecules in ||.
- Problem is, yields are terrible, and diagnostics on final molecule condition is essentially impossible.
- SPM techniques are much faster, and confirm some of the nanopore work (NDR, switching of conductance states).
- Unfortunately, SPM has its own set of experimental issues.
- *Mechanisms behind these results still argued.*

# Crossbar structures as non-volatile memories (NVMs)

- Suffer from same diagnostic concerns as nanopore devices, though much easier to fabricate (larger overlap).
- Molecules have hysteretic  $I/V$  curves - may be used for nonvolatile memory.
- Limited to 2-terminal devices without gain, but that's not so crucial for nonvolatile memory schemes.

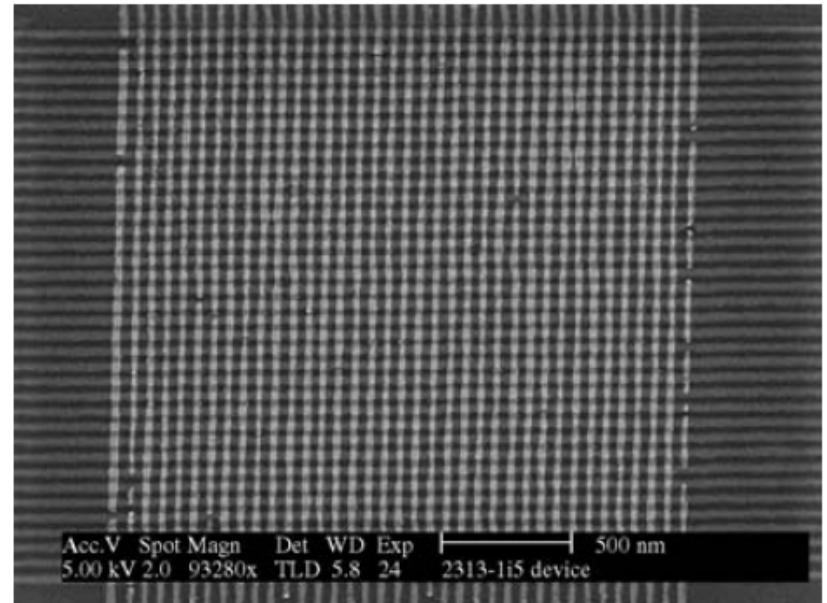
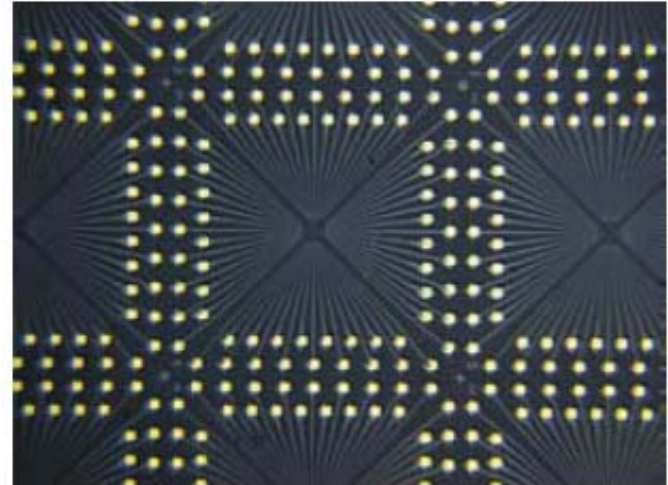
*Other types crossbar memories, see groups 1&2's presentations in week 5*



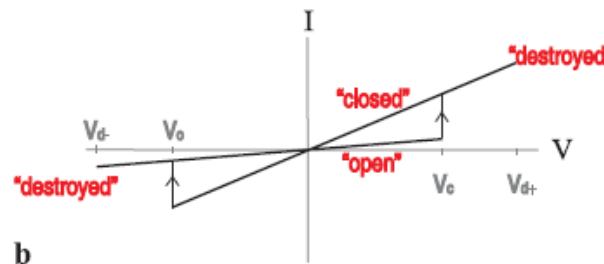
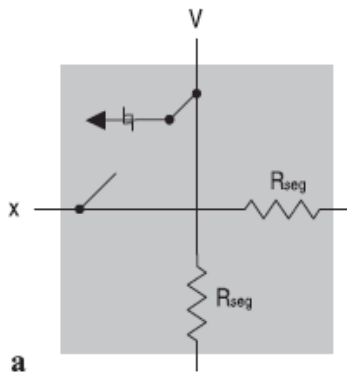
Heath, UCLA (now at Caltech)  
Williams, HP

## Molecular crossbar structures as NVMs

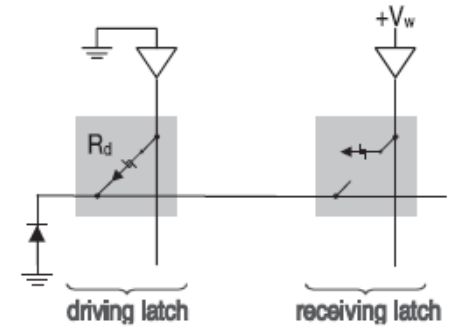
- Combine nanoimprint lithography with this sort of device design.
- Result: 1k-bit (34x34) nonvolatile memory 28 Gbits/cm<sup>2</sup> (30-nm half-pitch), >10 times capacity of commercially available NVM
- integrated multiplexer for readout.
- Predict possible market ready products w/in 5-10 years.



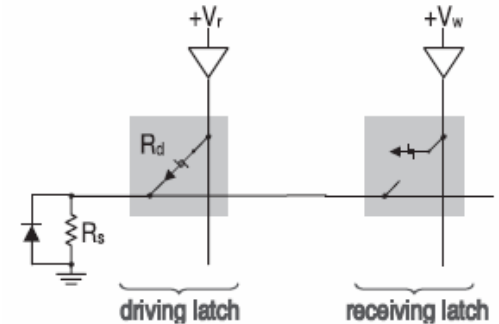
General logic operations can be achieved with *reconfigurable, hysteretic, 2D crossbar (switch) arrays*



$V_{d-}$	-3.0 V
$V_o$	-1.75 V
$V_c$	1.25 V
$V_{d+}$	2.0 V
$R_{open}$	1 Gigohm
$R_{closed}$	1 Megohm
$R_{seg}$	100 ohms



a non-inverting configuration

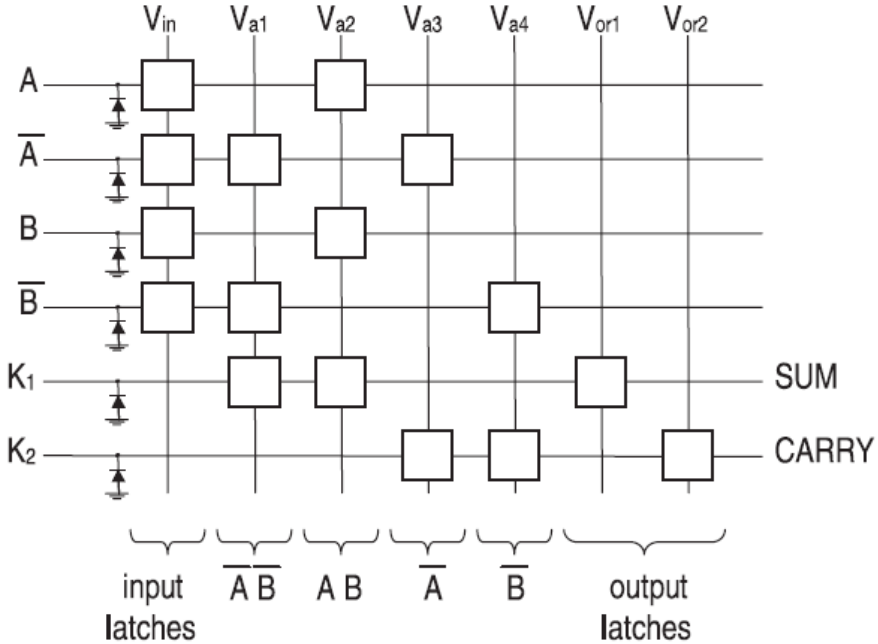
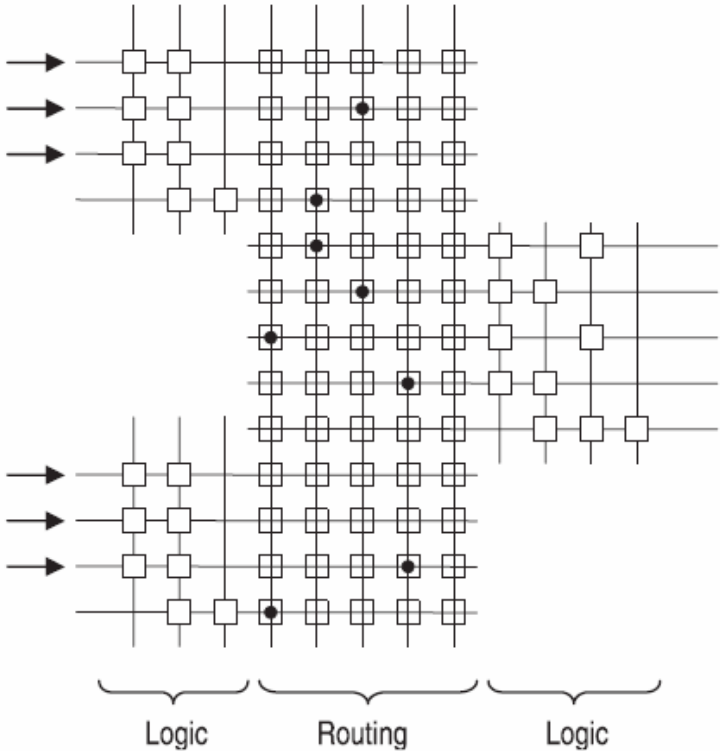


b inverting configuration

- Logic 1, 0 represented by the “open” and “close” states of the switch
- Each switch acting as a “latch”
- *Non-molecule based approaches may be more promising*

# General logic operations

Snider, Appl. Phys. A 80, 1165 (2005)



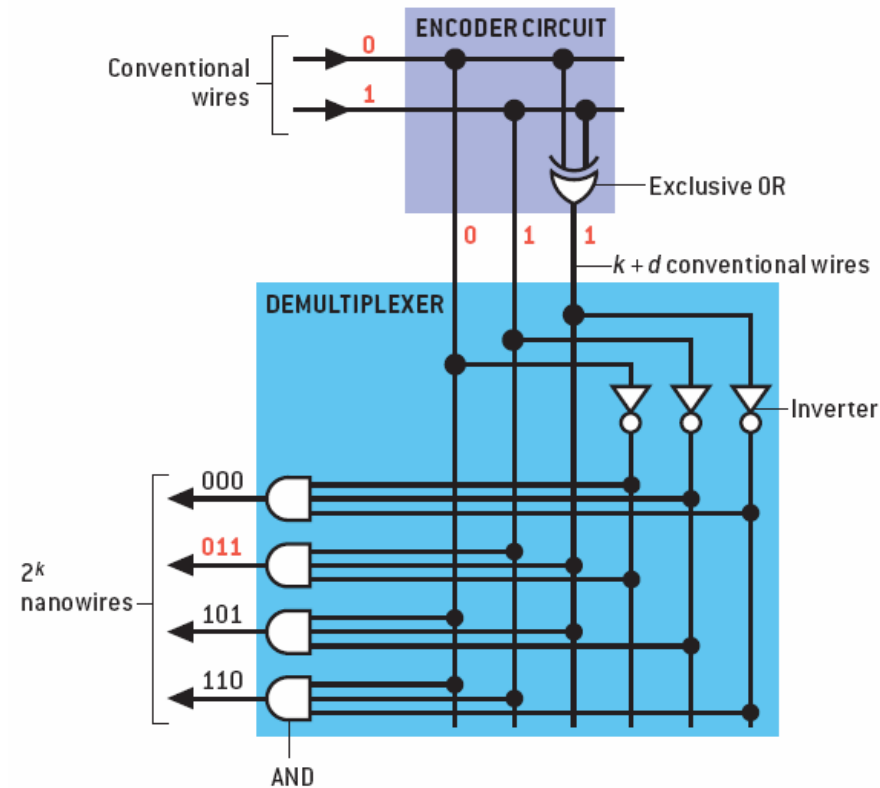
Half-adder circuit

Combining multiple crossbars to implement more complex logic functions.

# Dealing with defects

## Large number of defects in these nanodevices

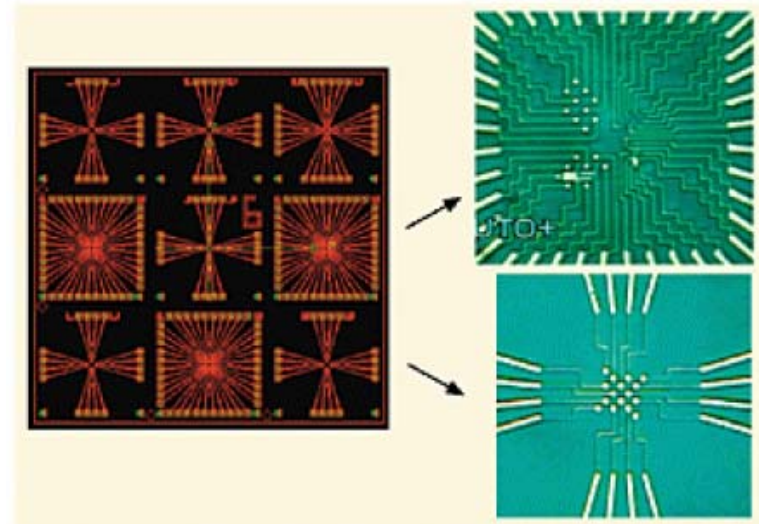
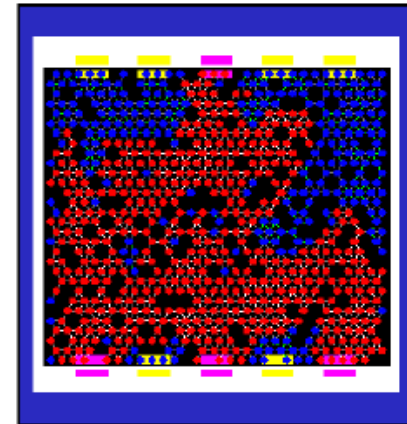
- Redundancy: instead of trying to make each device perfect, make redundant imperfect devices with high connectivity
- Shifting difficulty in hardware to software: build the generic computer (however imperfectly), find the defects, configure the resources with software, compile the program, and then run it. Think how a field programmable gate array (FPGA) works.



Coding with redundancy

## Nanocell concept

- Self-assemble large number of functionalized nanoparticles + molecules (e.g. NDR and memory molecules) across an array of leads.
- Training + field programming: apply voltage pulses; measure currents; train system to have desired functionality (!).

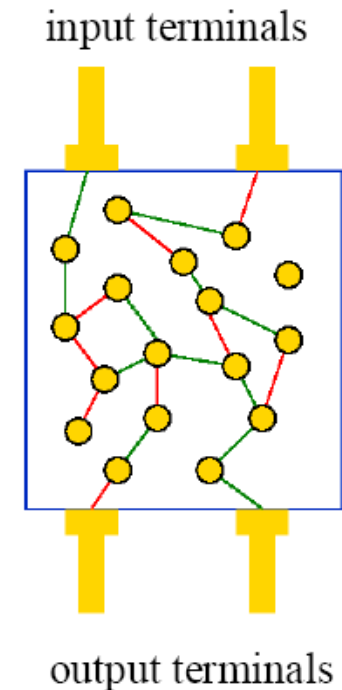




## Nanocell concept

- Every device is unique (analogous to detailed wiring of brain). *Einstein or monkey?*
- Architecture that permits on-the-fly adaptation and training would be inherently robust + defect tolerant.
- A *huge* departure from standard electronics manufacturing practice!

Molecular Electronics Corp. / Motorola paradigm:  
self assembly + software  
architecture to allow training of circuits.



## Summary and prospects

- Several research tools exist to study and utilize a single molecule or a small number of molecules.
- Details (contacts, quantitative results with predictive power) are still lacking.
- Basic physics responsible for certain interesting properties (NDR, switching) still under debate.
- We're a long way from practical molecular electronic devices, though applications in niche markets may be on the horizon.
- Knowledge learned, such as the crossbar structure, may provide a promising solution to past Moor's law, even though molecular electronics may not be the best choice.