

## **Chemical Nanotechnology: Molecular Electronics**

- What is *Molecular Electronics*?
- How do we measure a molecular electronic device?
- Molecular Components
  - Wires
  - Diodes
  - Switches
- Beyond Molecular Electronics

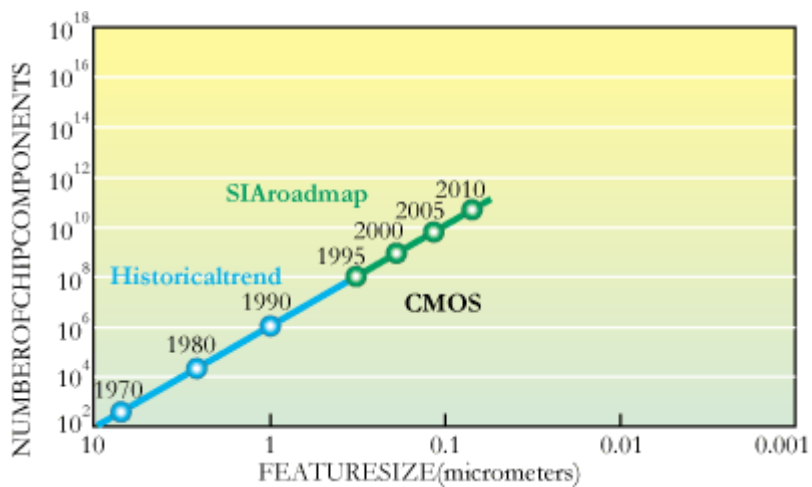
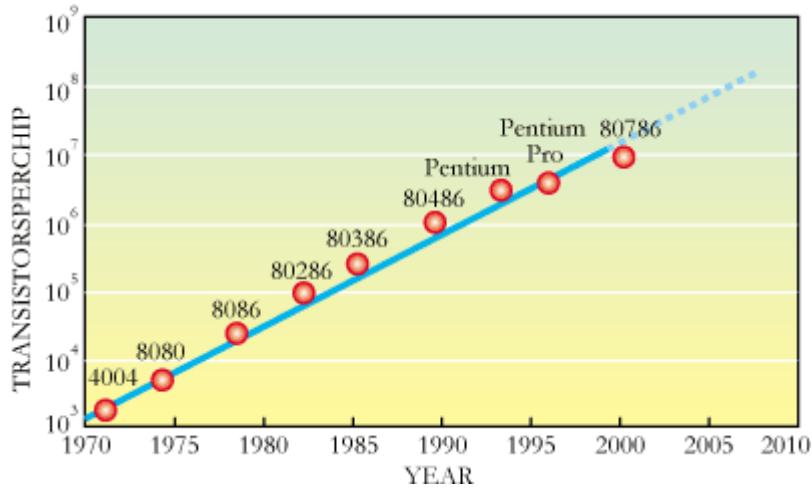
**James G. Kushmerick**

National Institute of Standards and Technology

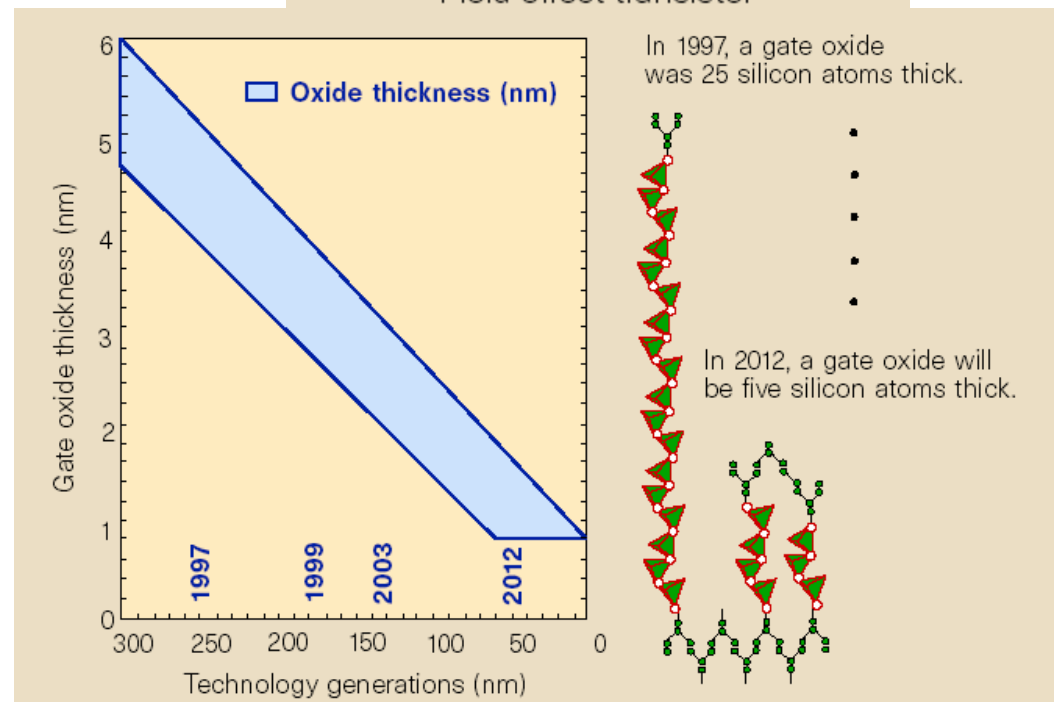
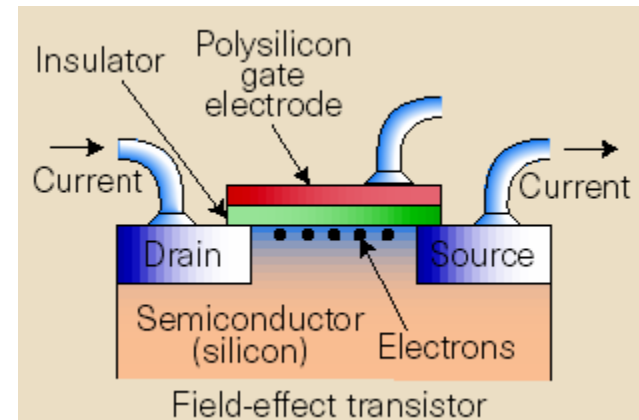
Gaithersburg, MD

[james.kushmerick@nist.gov](mailto:james.kushmerick@nist.gov)

# Moore's Law and Feature Size

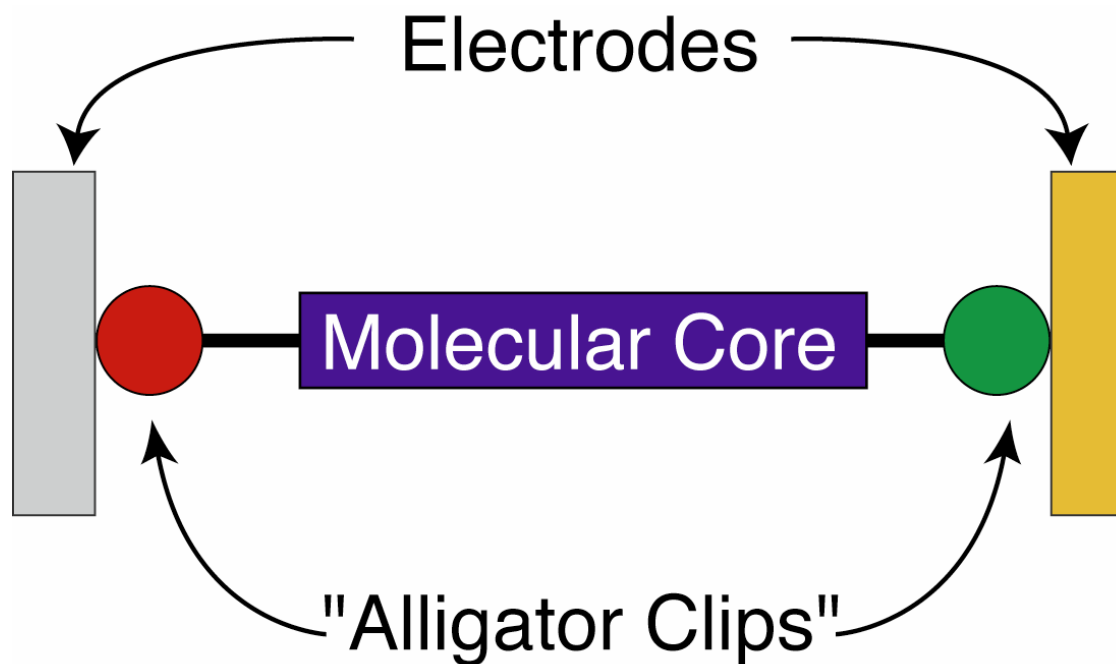


*Physics Today*



*Nature* **399** (1999) 729.

## Basic 2 Terminal Molecular Electronic Device



**Definition:** Molecular electronics endeavors to use the non-linear current-voltage characteristics of individual molecules or molecular assemblies as active components in electronic circuits.

## **Why is NIST interested in Molecular Electronics?**

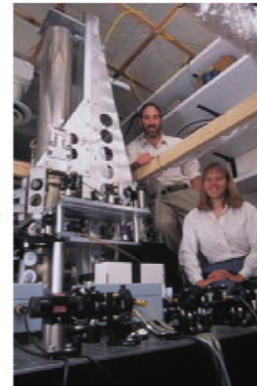
# NIST enables innovation in...

## ...standards

pendulum clock  
1 s in 3 years  
(1904)

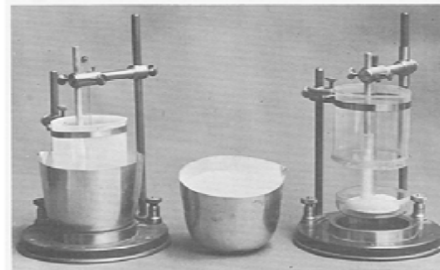


second

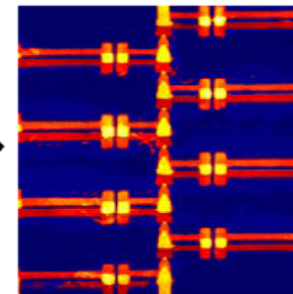
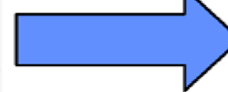


NIST F1  
atomic clock  
1 s in 30 million  
years  
(1999)

silver voltameter  
current standard  
(1910)



ampere



single  
electron  
counter  
(20xx)

physical artifact  
(1889)



kilogram



electronic  
kilogram  
(20xx)

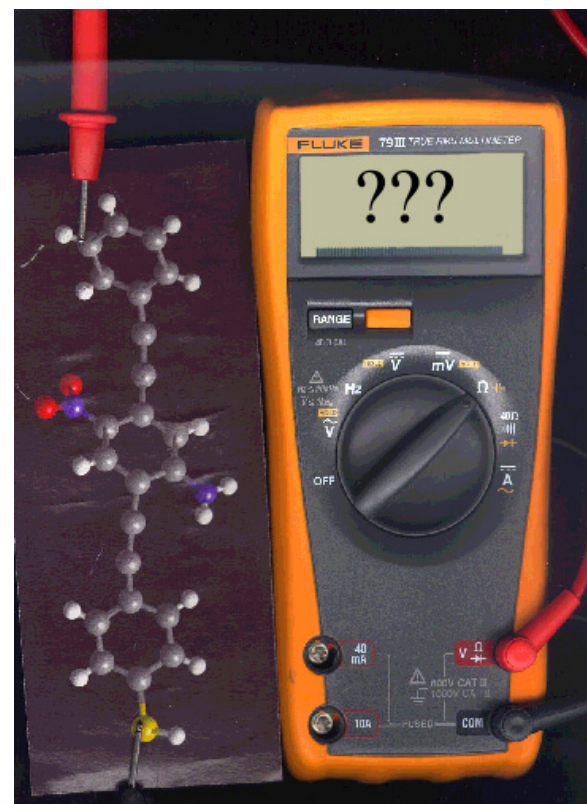
# A Role for NIST

To develop the standards and measurement infrastructure necessary to predict, measure, and control the flow of charge through molecules and ensembles of molecules.

“Moletronics Metrology”

“To knowledge by measurement.”

— Kammerlingh Onnes, Leiden Univ.

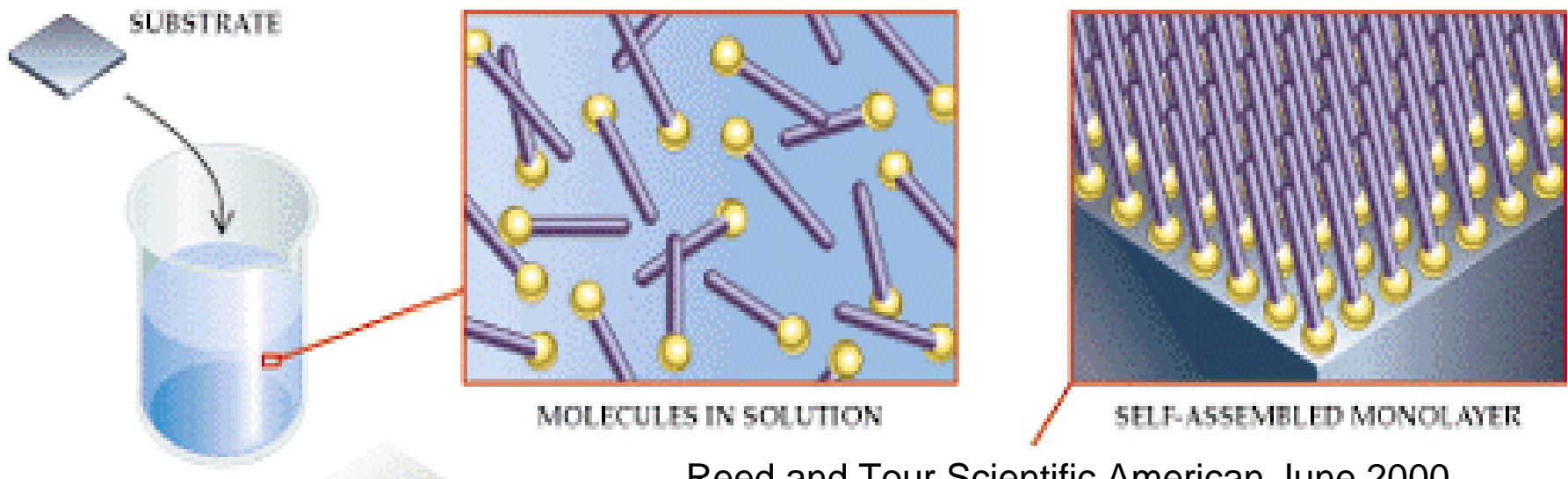


**How do we measure a molecular electronic device?**

How do we **build** a molecular electronic device?



# Molecular Self-Assembly

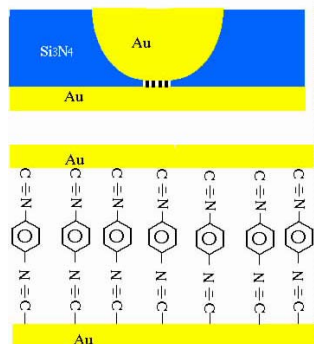


Reed and Tour Scientific American June 2000

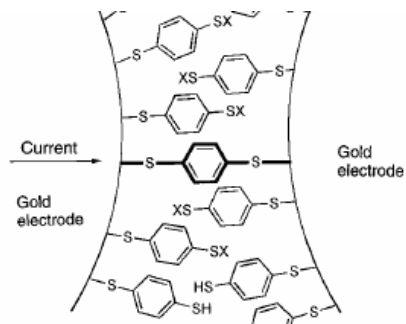
**“Connect” molecular electronic structure to the metallic band structure**

# Electronic Characterization Methods

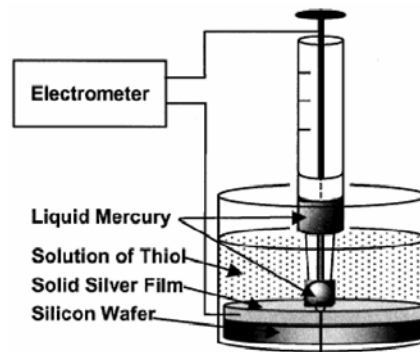
## Nanopore



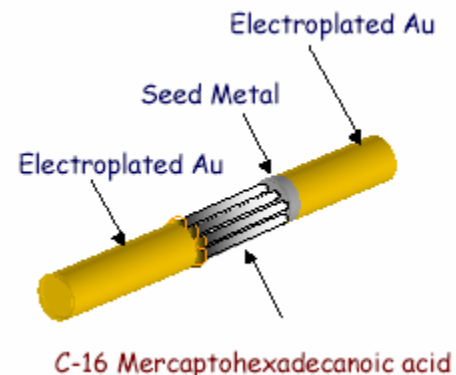
## Break Junction



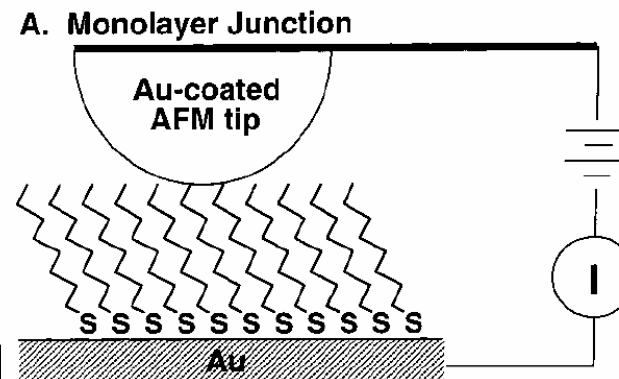
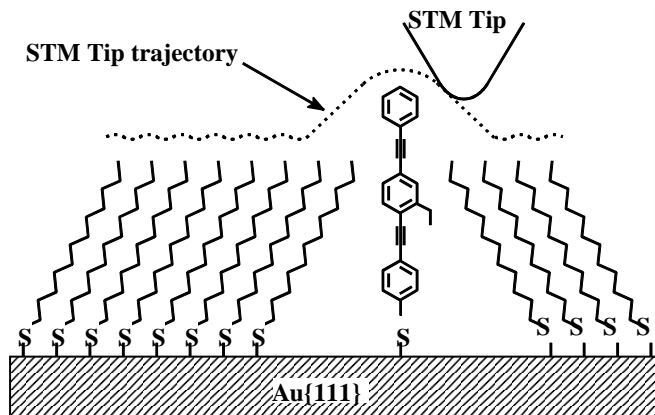
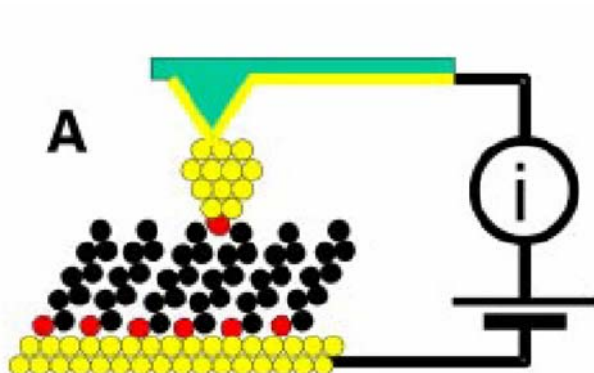
## Hg Drop



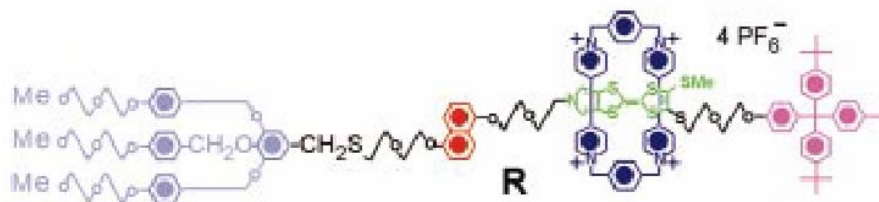
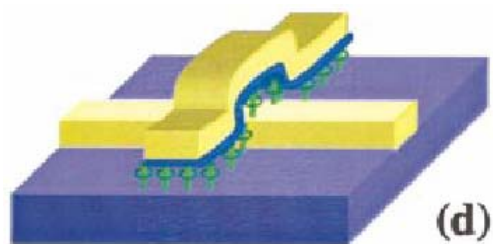
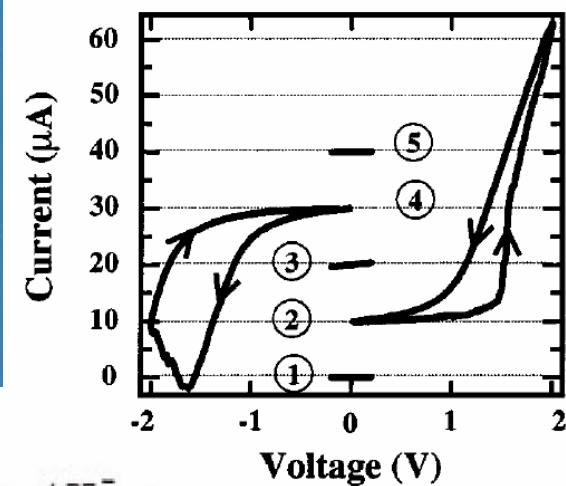
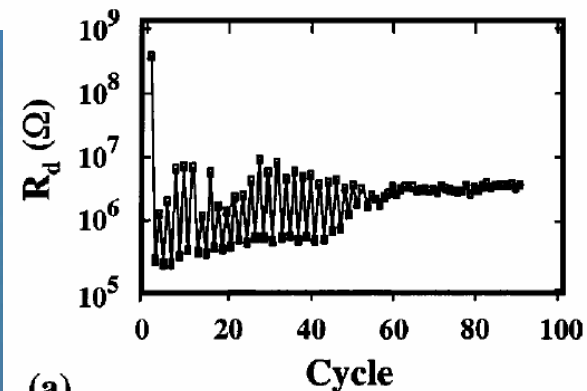
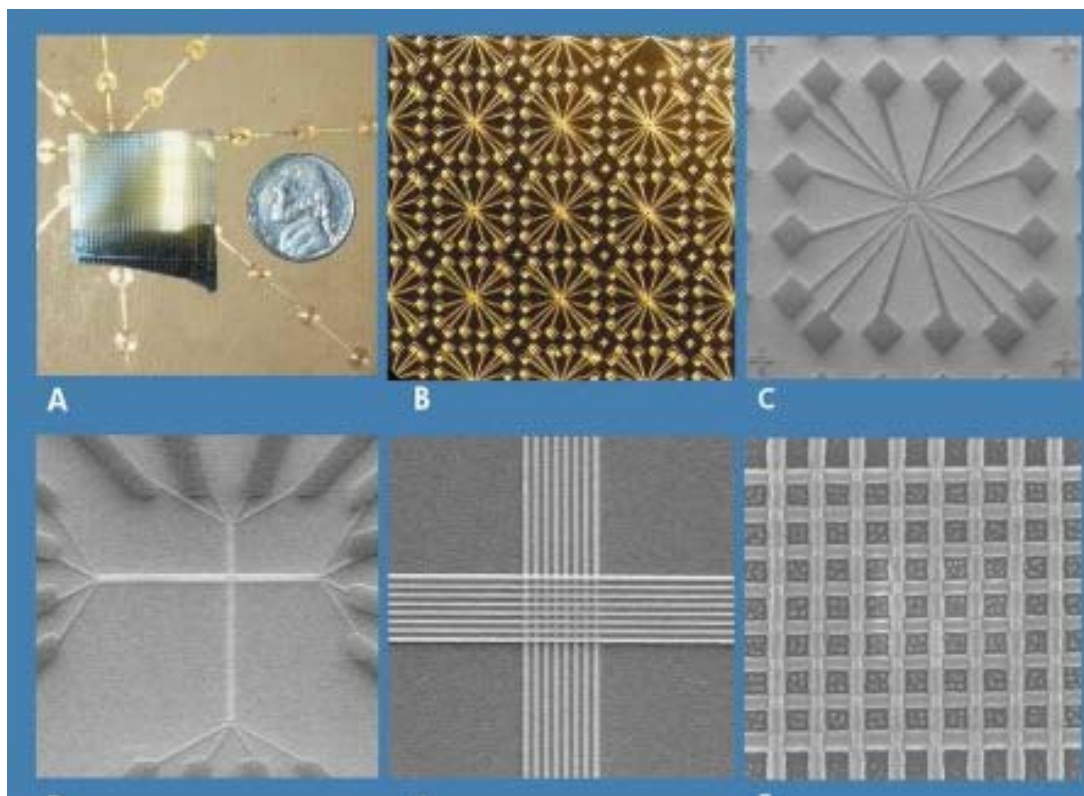
## Nanowire Devices



## Scanning Probes



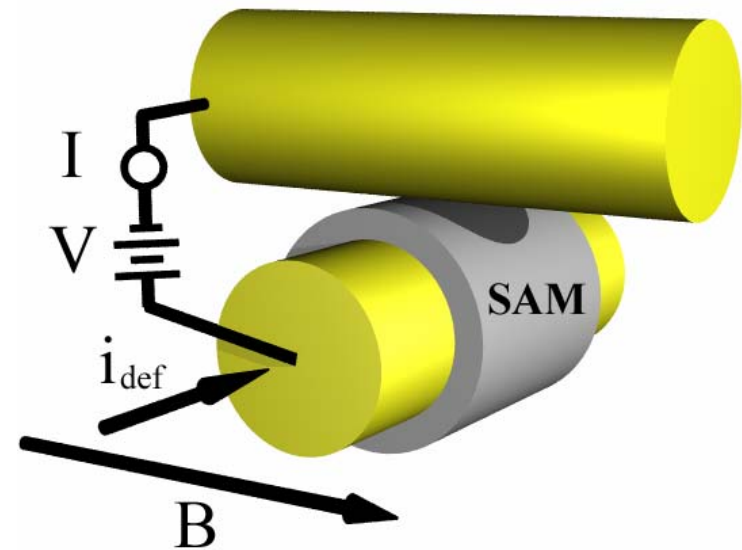
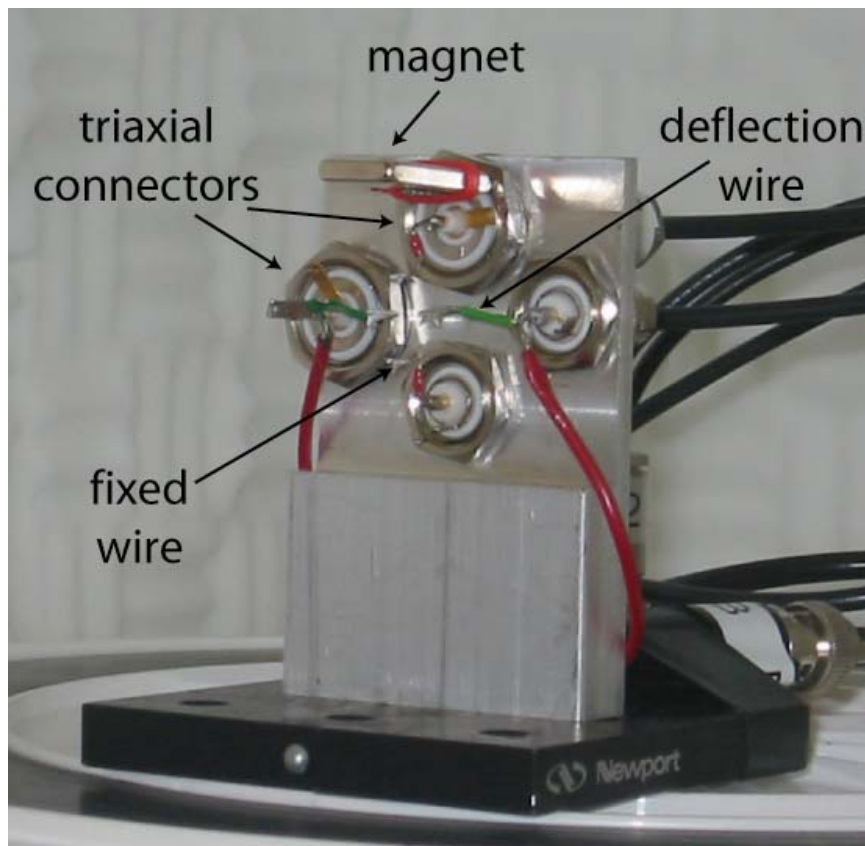
# 64-Bit Molecular Memory



HP Labs *Applied Physics Letters* **82** (2003) 1610-1612.

## Crossed-Wire Tunnel Junction

- Simple experimental apparatus
- Wide variety of wires available (Au, Pd, Pt, ...)
- Junction contains  $\sim 10^3$  molecules
- No metallization after SAM deposition

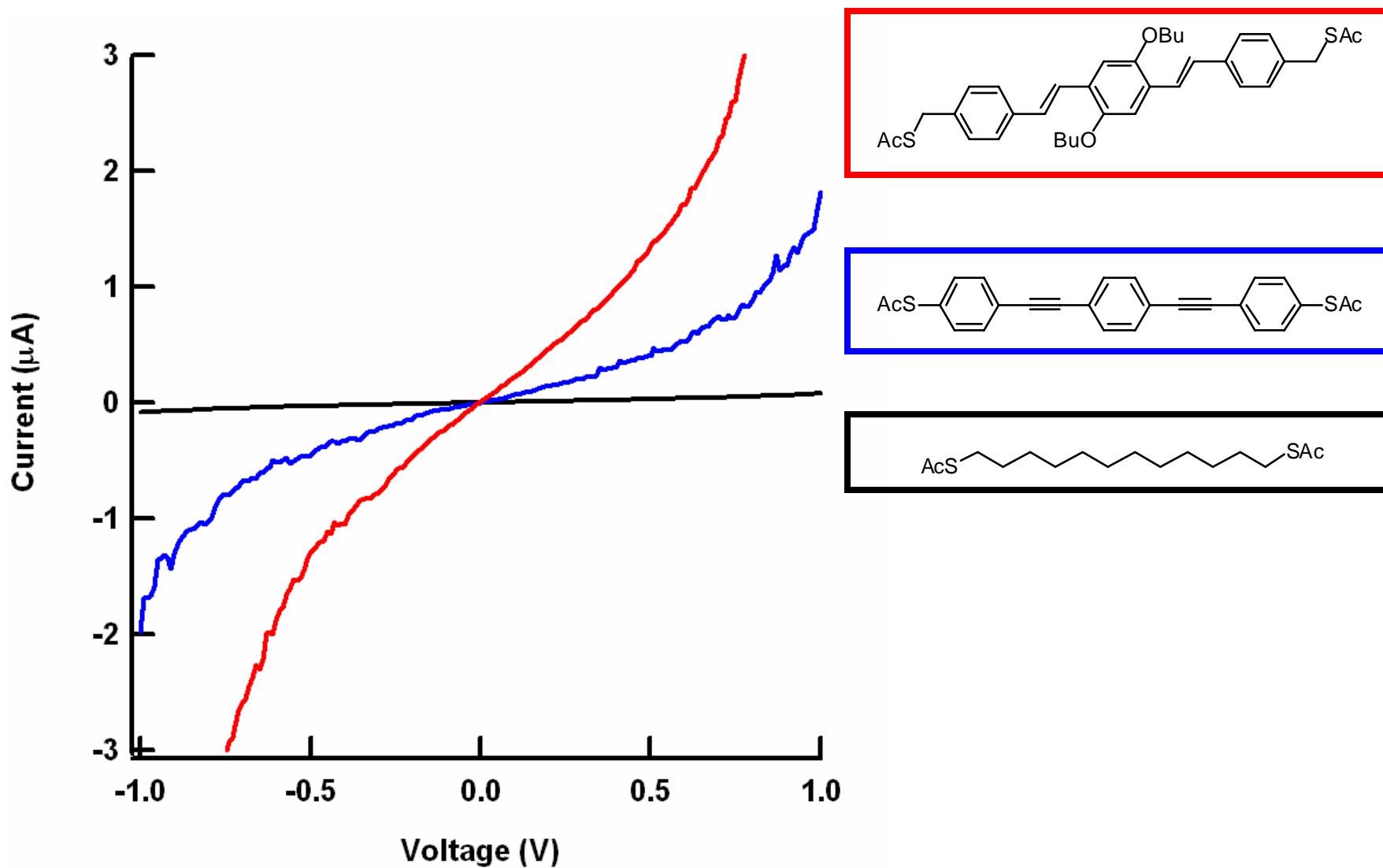


Initial work by Gregory, S. *Phys. Rev. Lett.* **1990**, 64, 689-692.

## **Molecular Components**

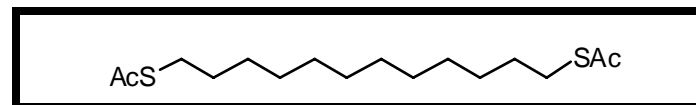
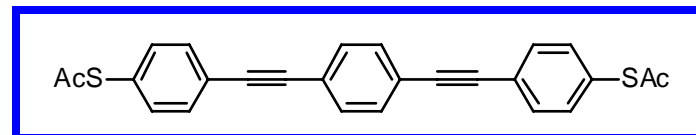
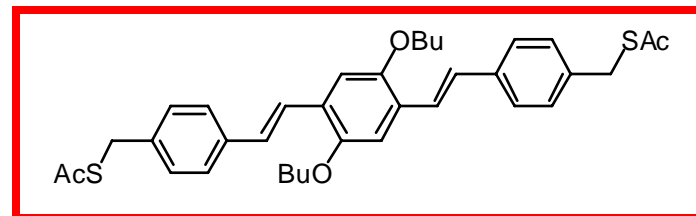
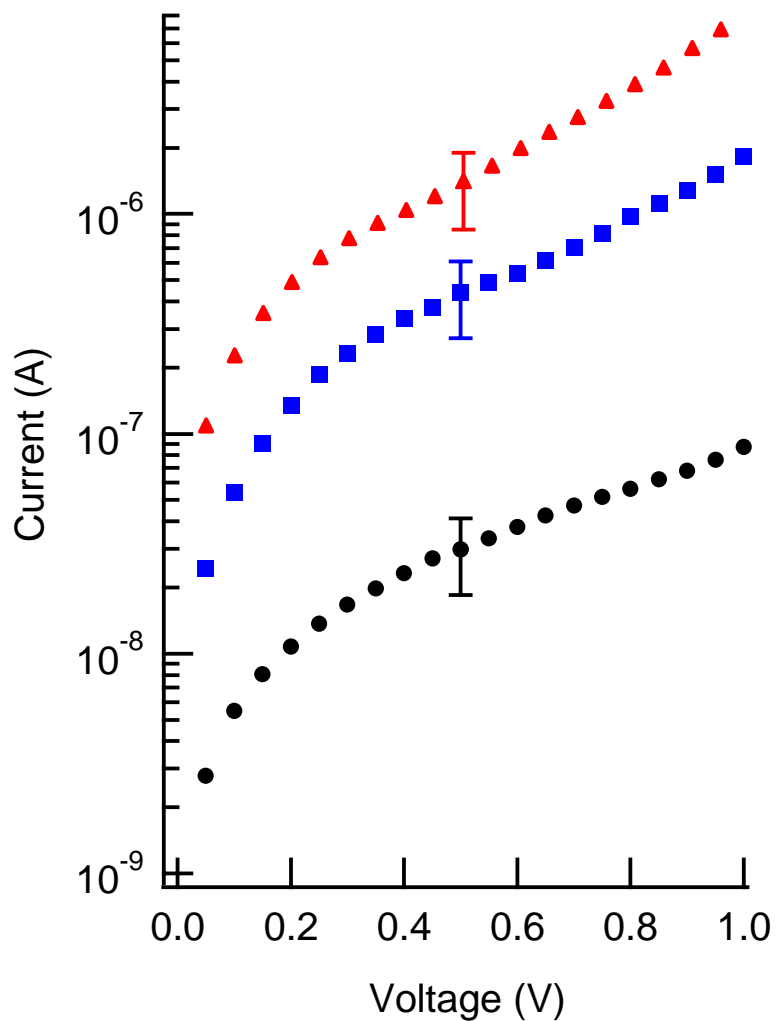
### **Wires**

## Structure Dependence of Charge Transport

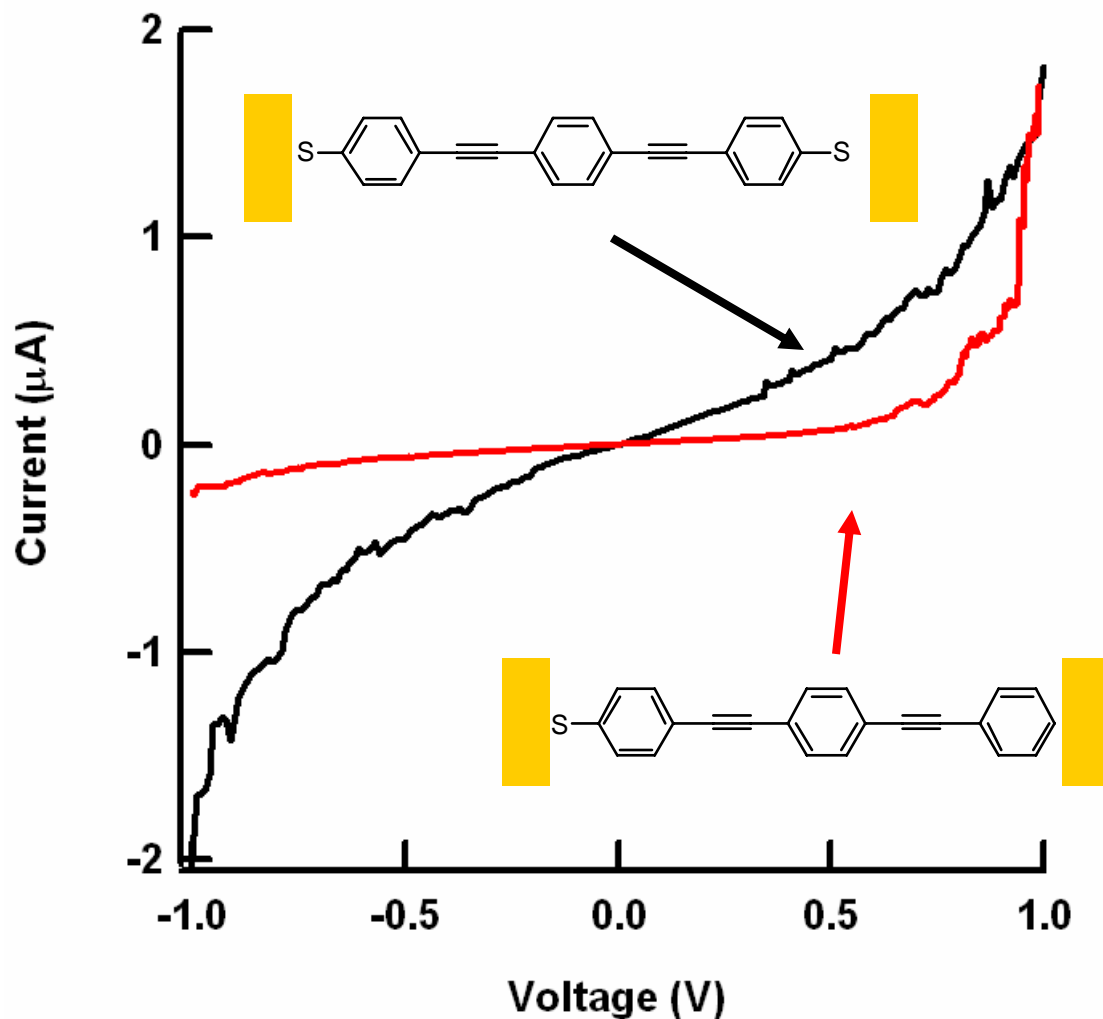


JACS 124 (2002) 10654-10655.

## Structure Dependence of Charge Transport



# Contact Induced Rectification

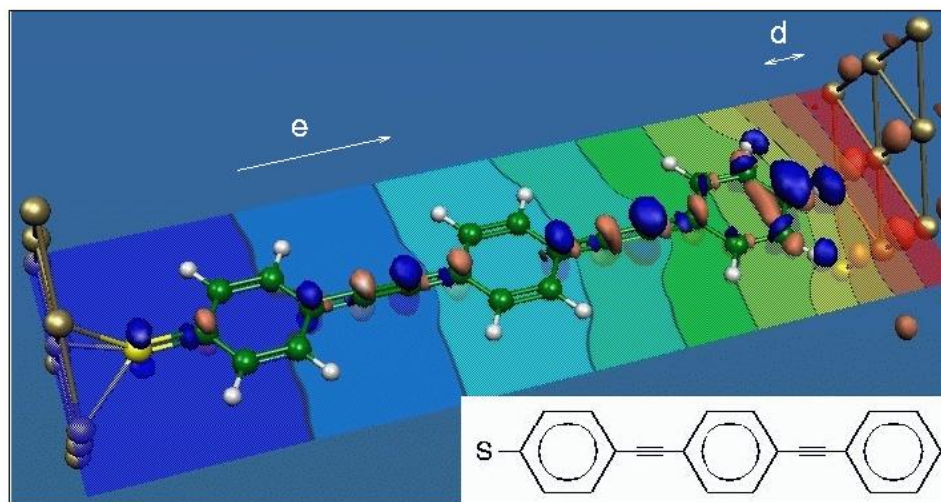
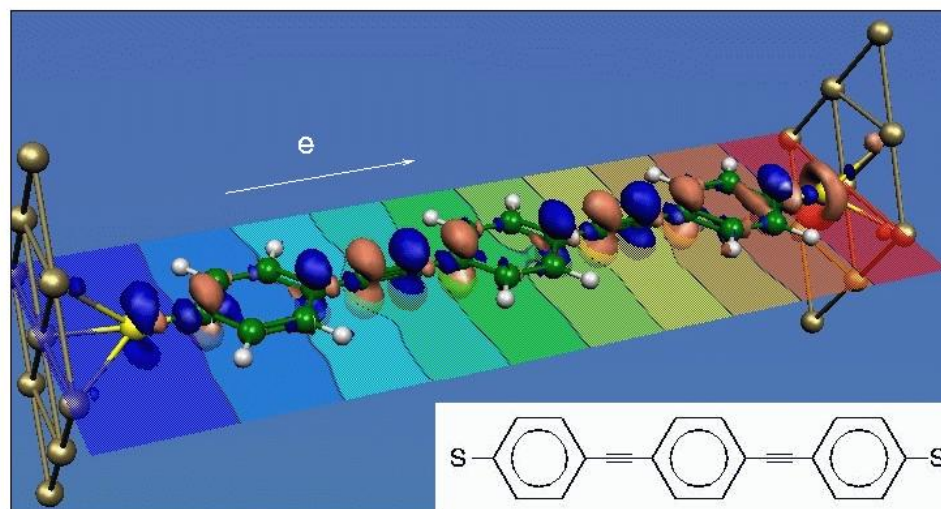


**Differences in metal-molecule coupling lead to diode-like behavior of molecular junction**



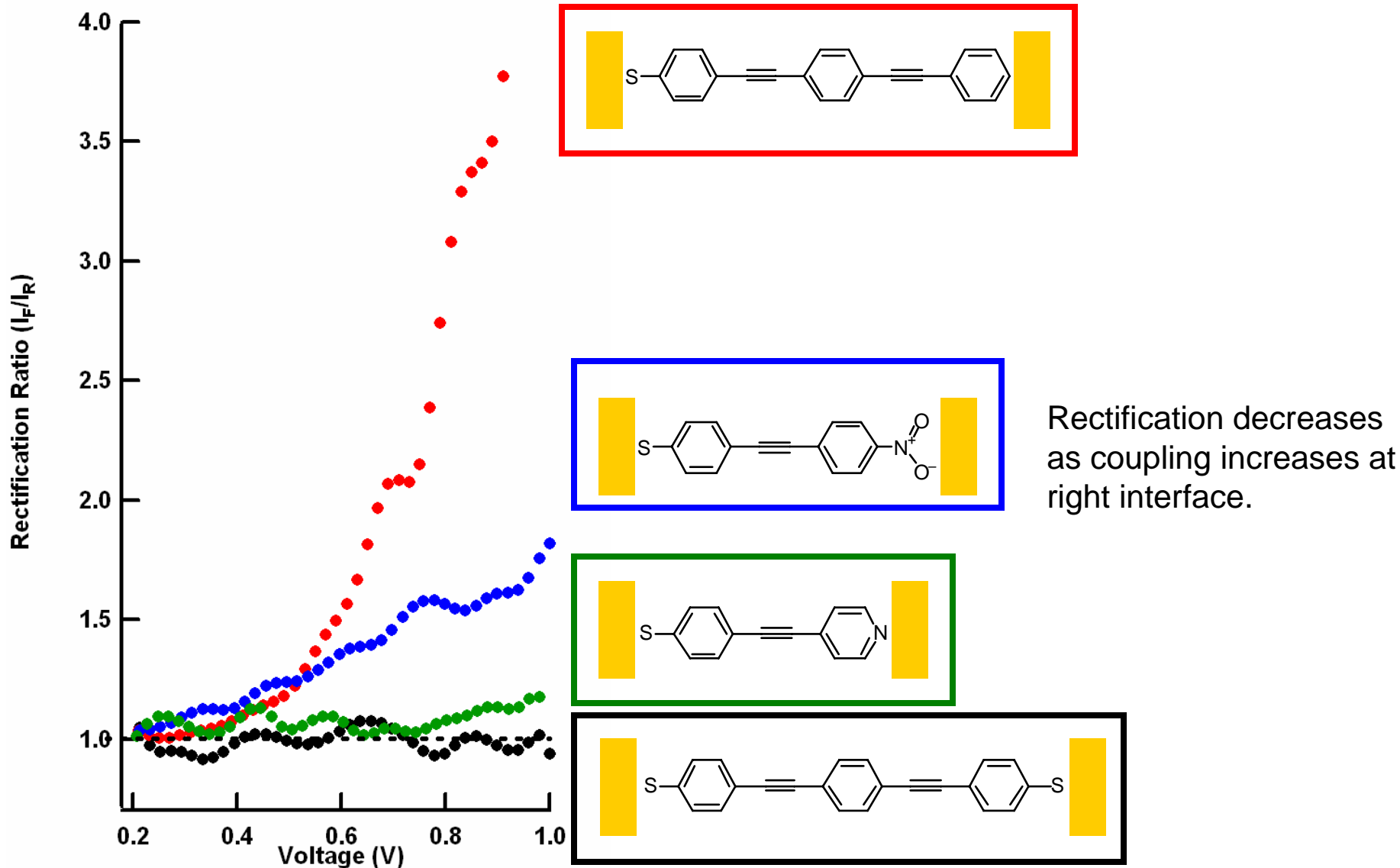
# First Principles Calculations

Large potential drop at non-bonding contact.



Taylor, Brandbyge and Stokbro *Physical Review Letters* **89** (2002) 138301.

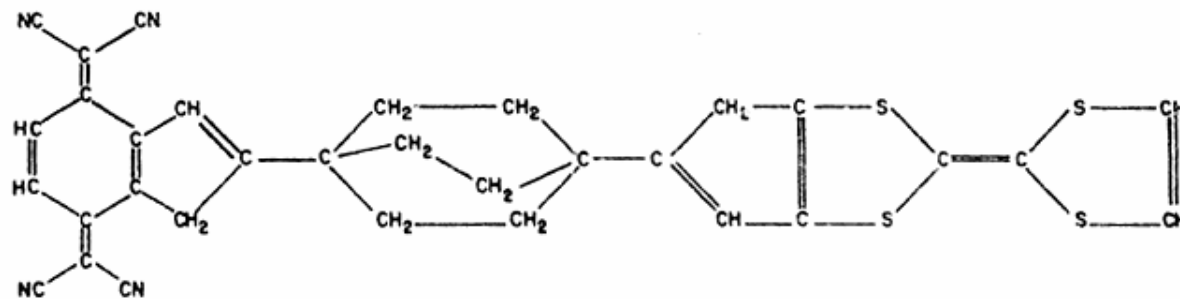
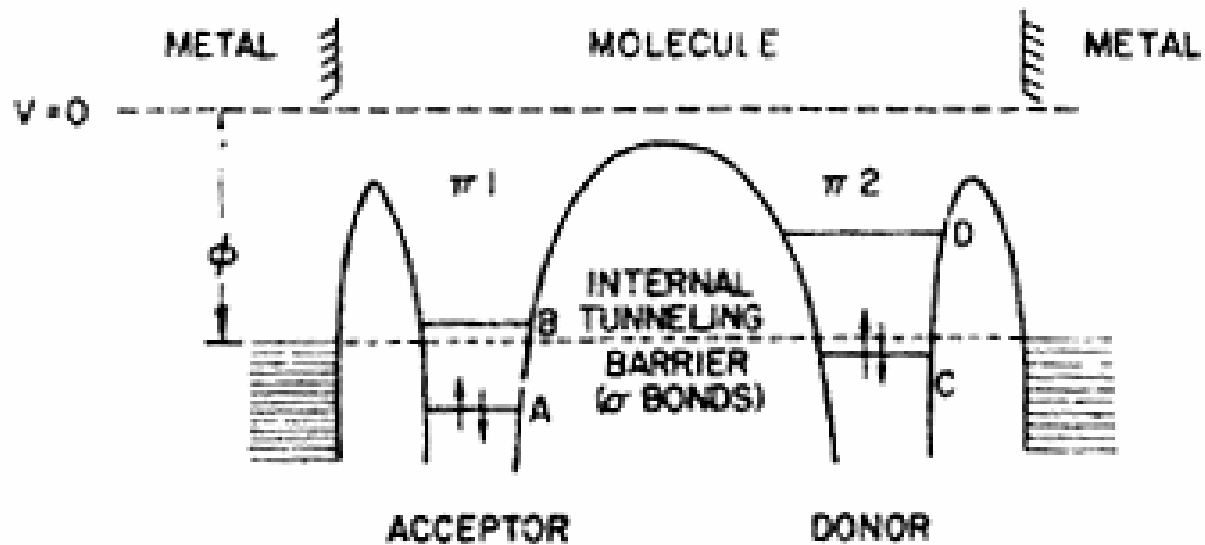
# Role of Metal-Molecule Contacts



## **Molecular Components**

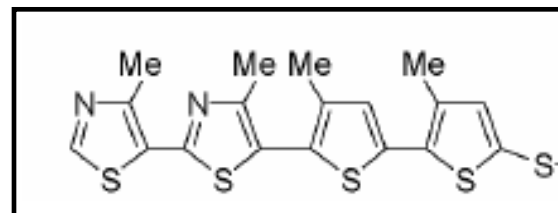
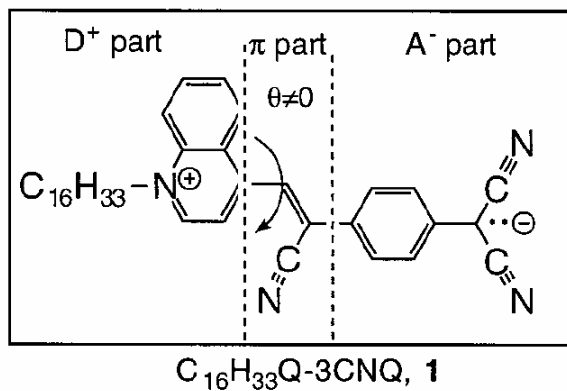
### **Diodes**

# Aviram-Ratner Rectifier



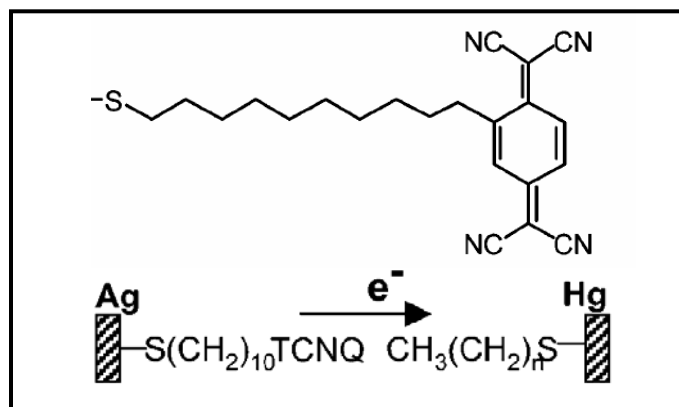
Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, 29, 277-283.

# Molecular Rectifiers



Ng, M.-K.; Lee, D.-C.; Yu, L.  
*JACS* **2002**, *124*, 11862-11863.

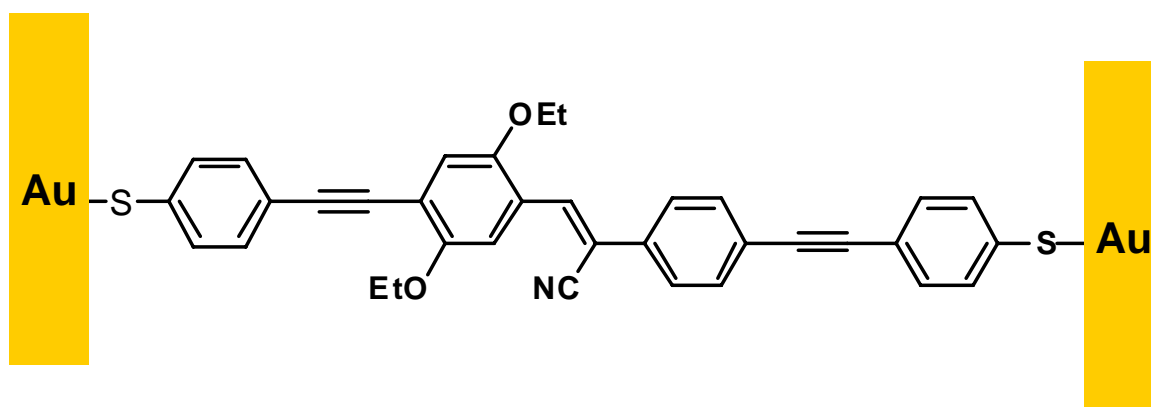
Metzger, R. M. *Acc. Chem. Res.* **1999**, *32*,  
 950-957.



Chabinyk, M. L.; Chen, X.; Holmlin, R. E.; Jacobs,  
 H.; Skulason, H.; Frisbie, C. D.; Mujica, V.; Ratner,  
 M. A.; Rampi, M. A.; Whitesides, G. M. *JACS* **2002**,  
*124*, 11730-11736.

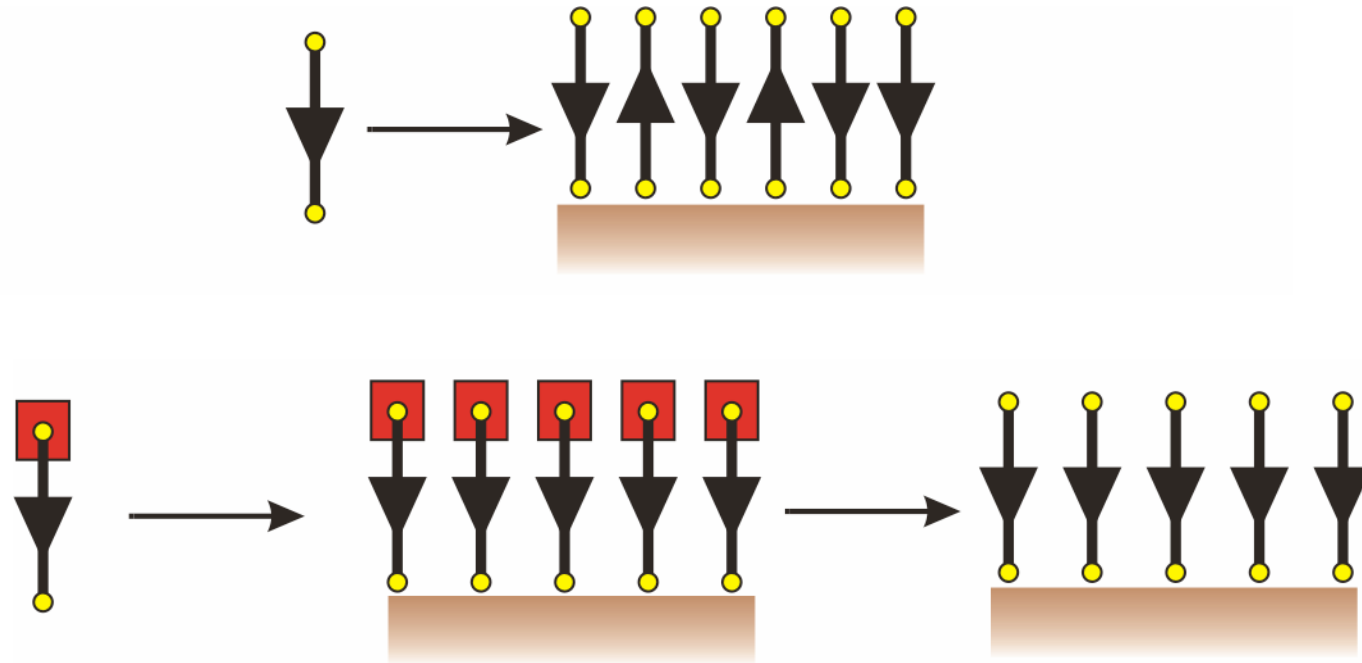
All previous demonstrations of  
 molecular rectification have  
 asymmetric metal-molecule  
 contacts

## Breaking Internal Symmetry



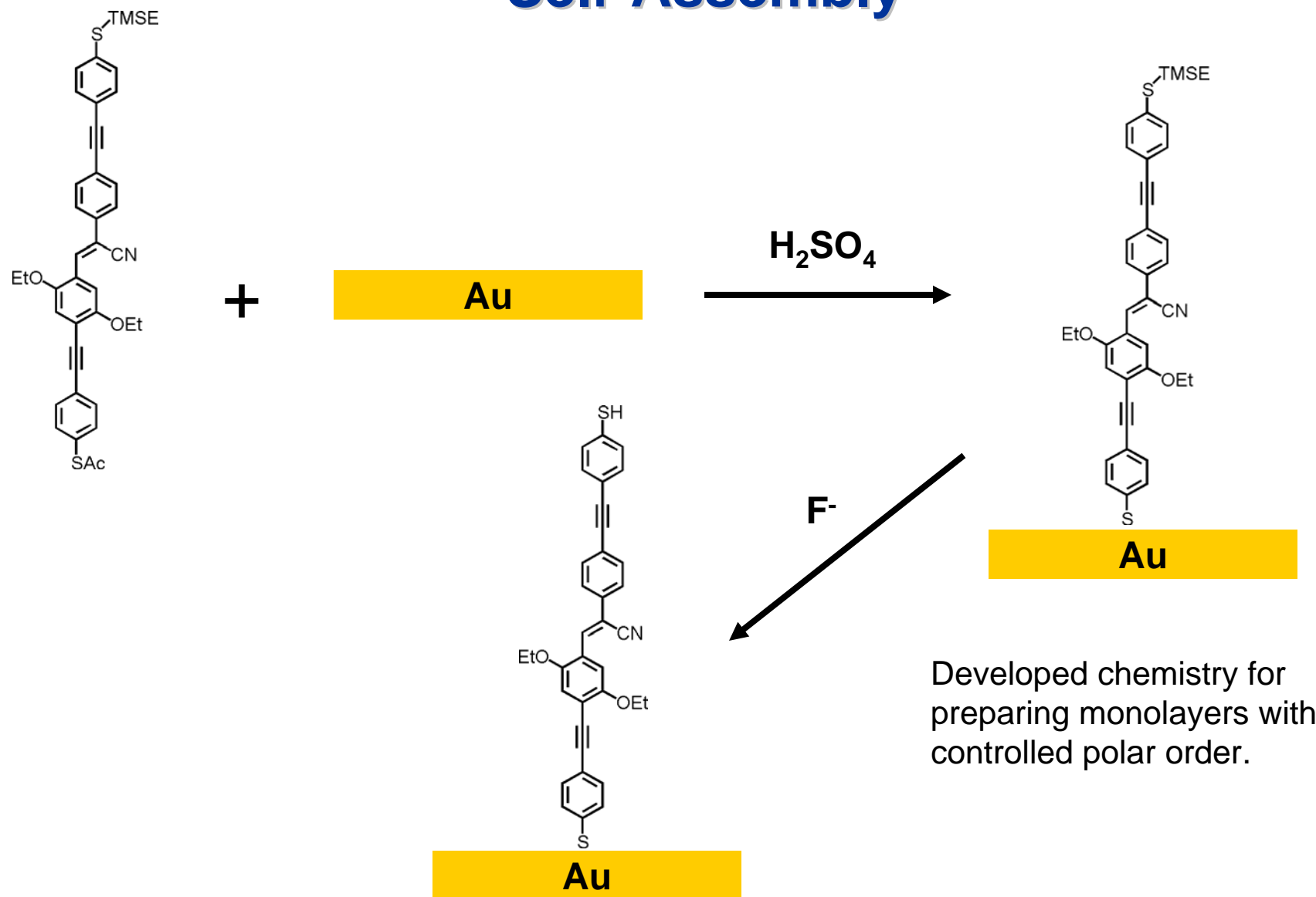
**Need to control self-assembly to create a monolayer with a single molecular orientation!**

## Controlling Self-Assembly



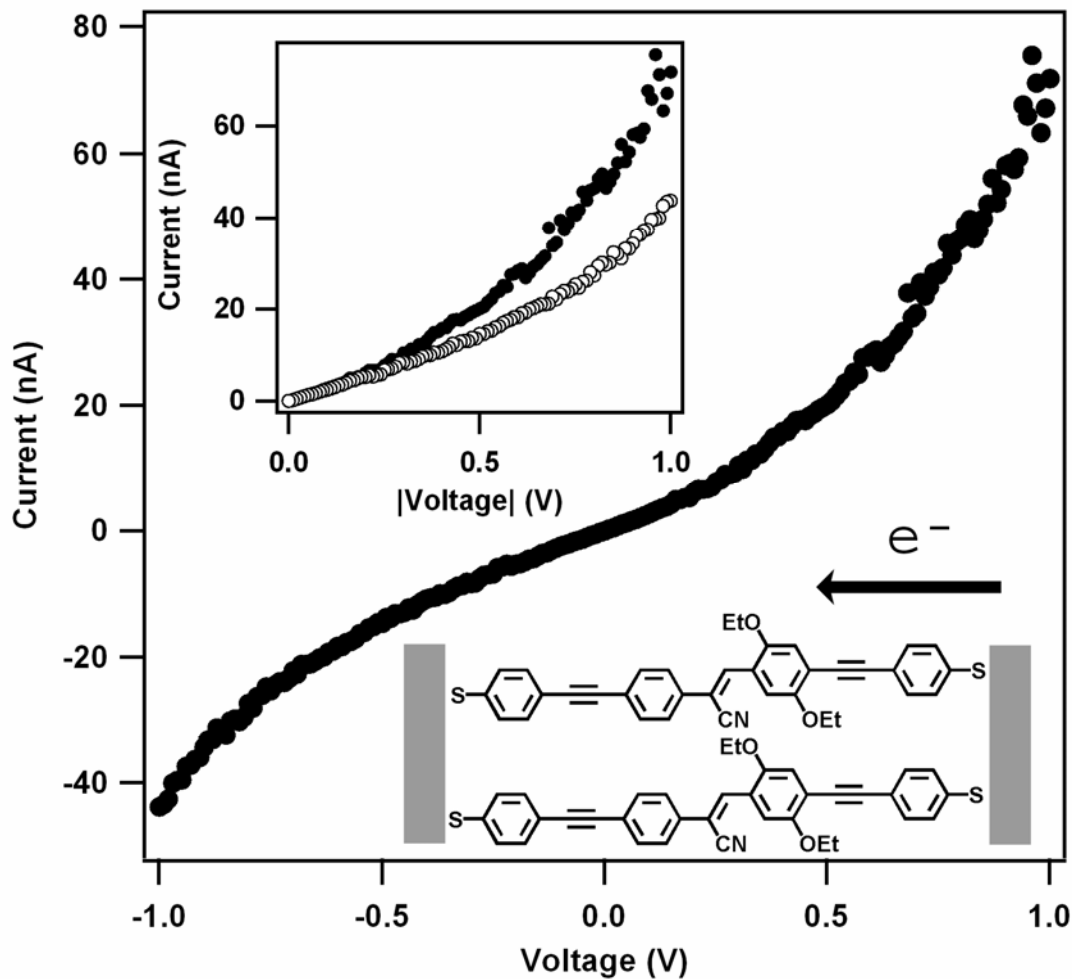
**Need to control self-assembly to create a monolayer with a single molecular orientation!**

# Sequentially Deprotected Self-Assembly





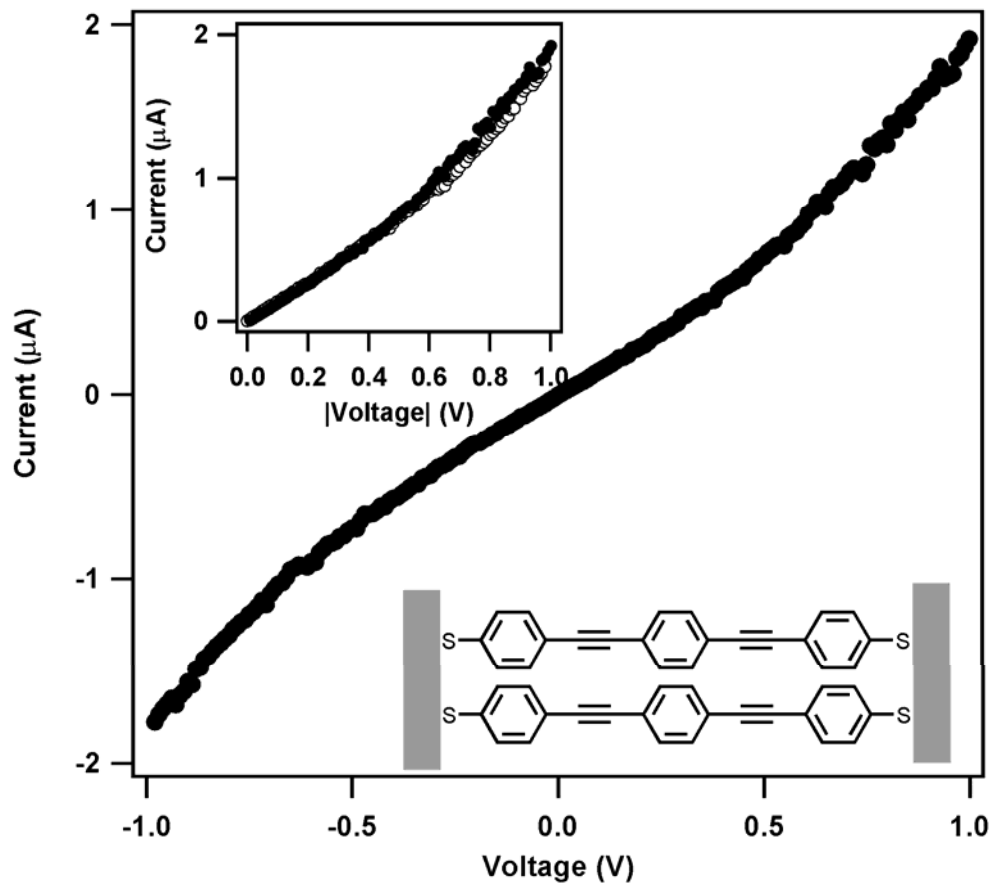
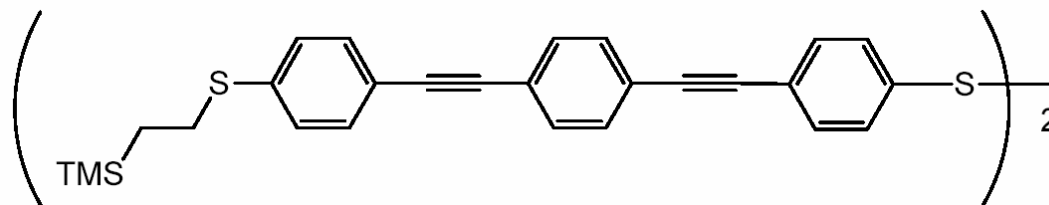
# Minor I-V Asymmetry



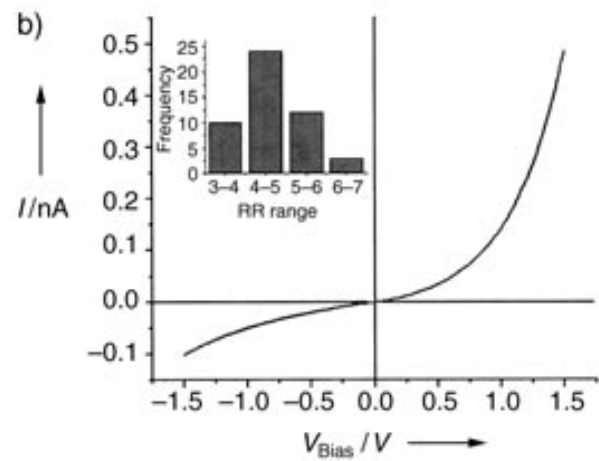
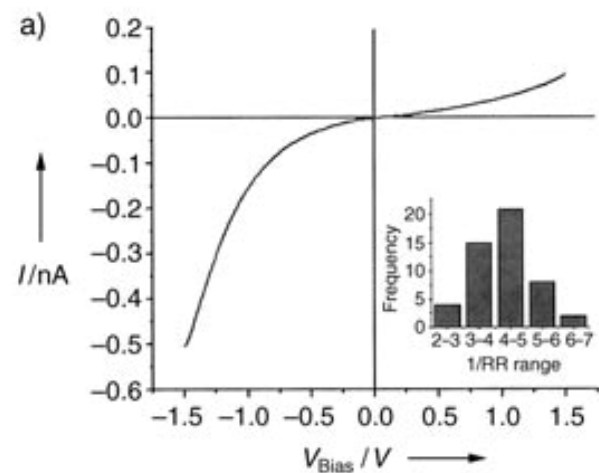
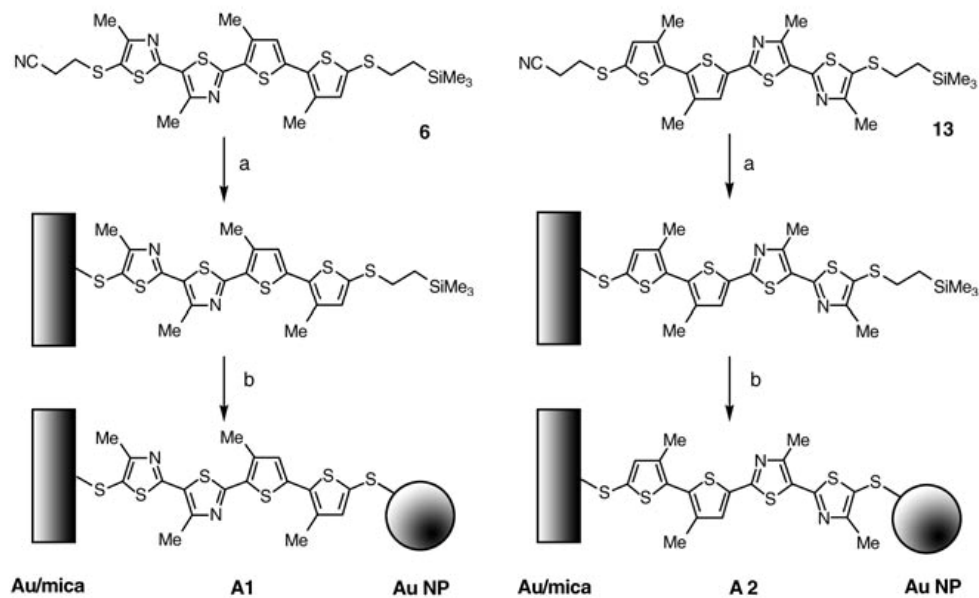
Monolayer junction with controlled polar order results in I-V characteristics asymmetric with respect to bias voltage polarity.

Molecular structure dictates difference in charge transport depending on direction of current flow.

# No Asymmetry in OPE



Measured I-V asymmetry not a result of TMSE protection/deprotection chemistries

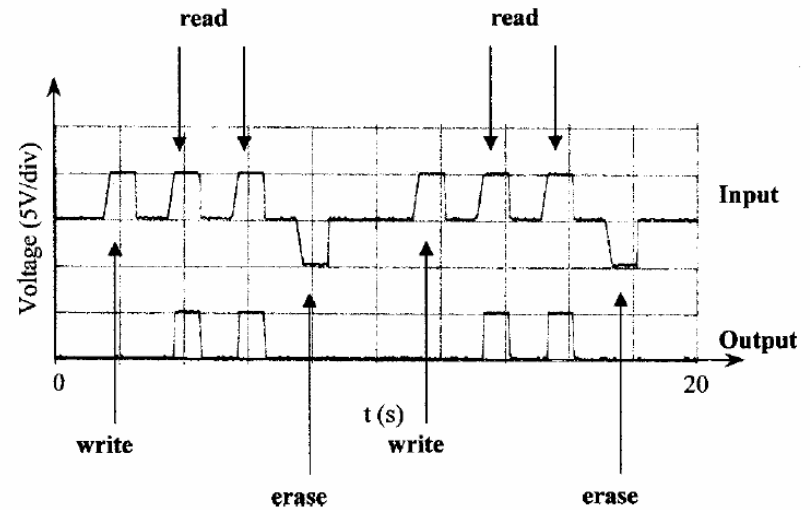
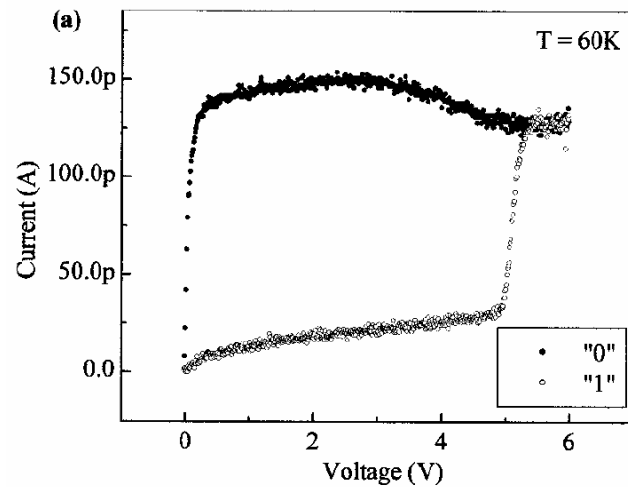
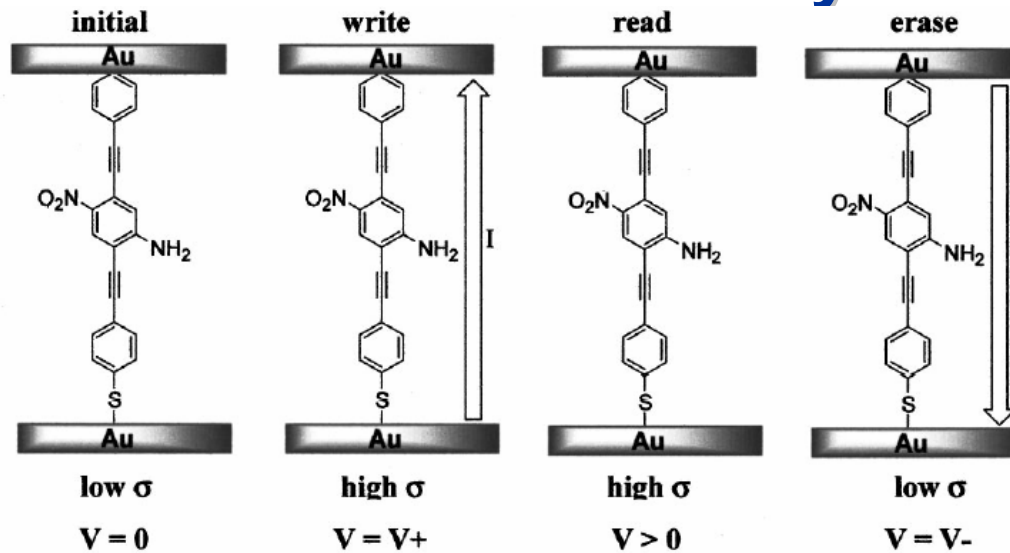


P. Jiang, G. M. Morales, W. You and L. Yu, *Angewandte Chemie* **43** (2004) 4471-4475.

## **Molecular Components**

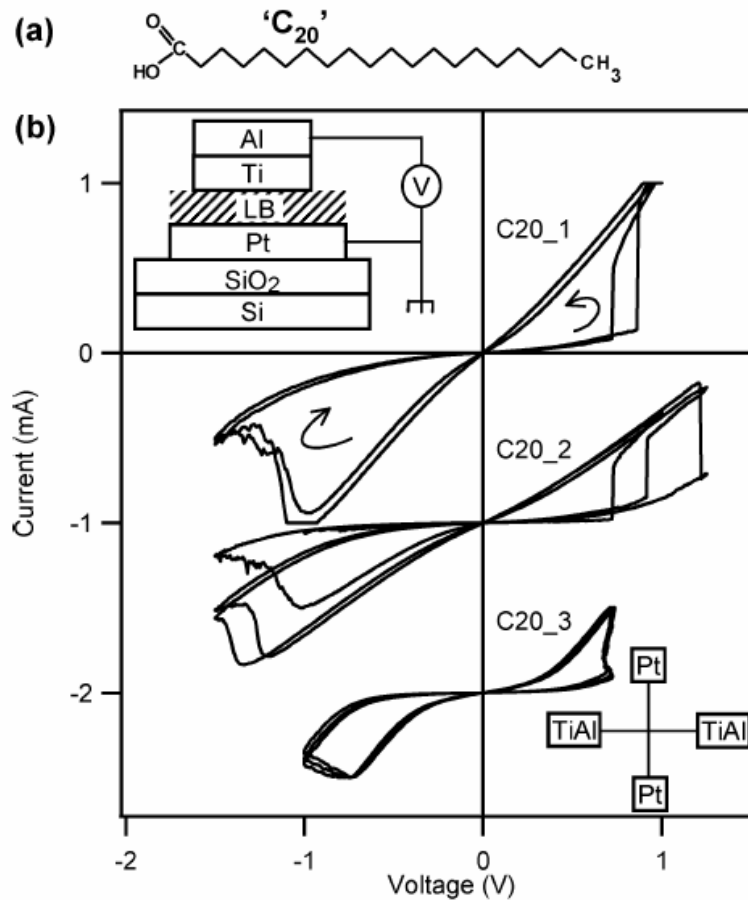
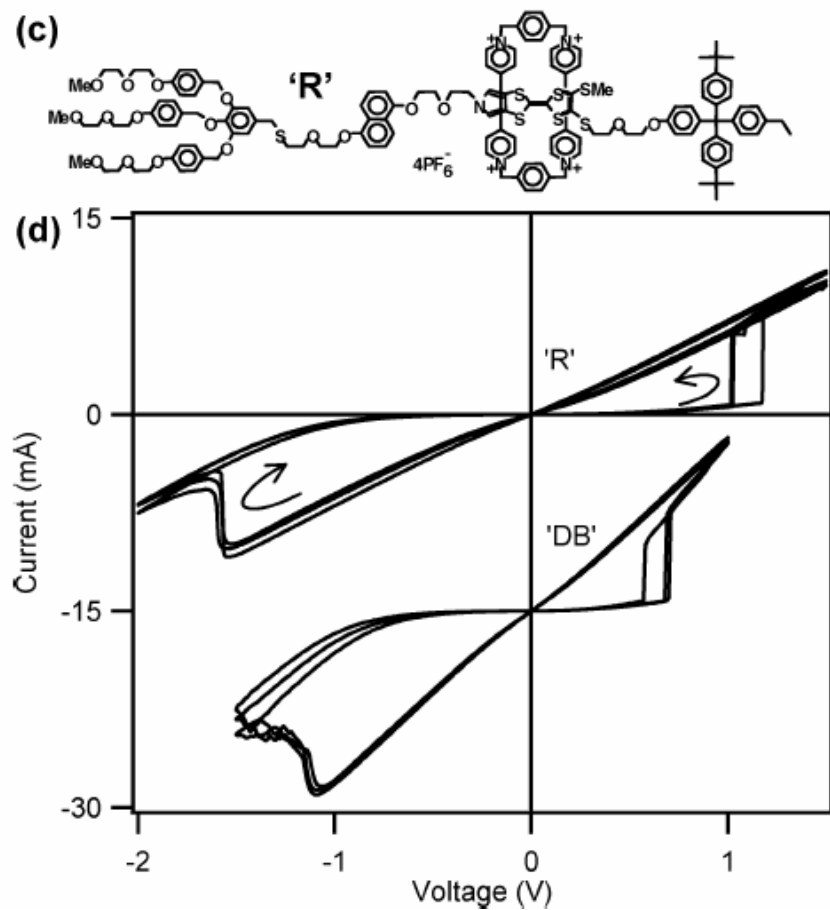
### **Switches**

# Molecular Memory

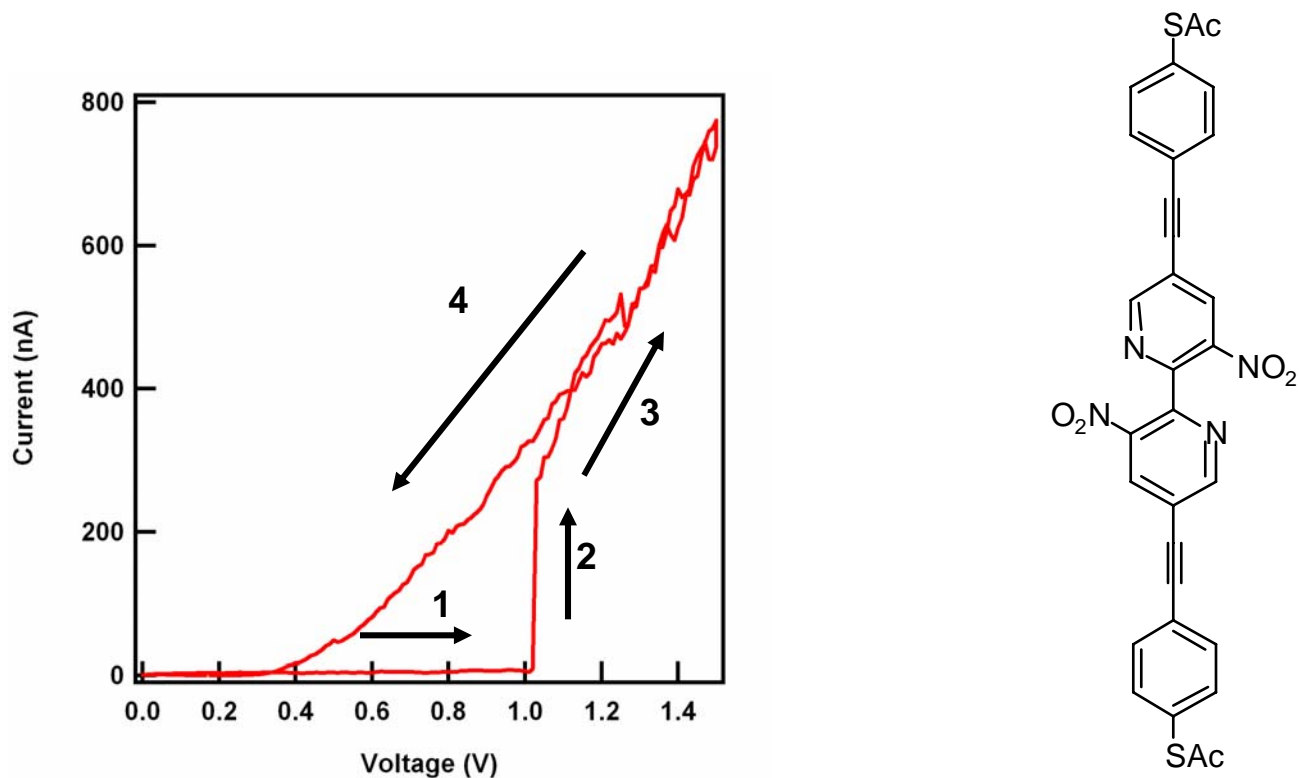


Reed *et al.* *Applied Physics Letters* **78** (2001) 3735-3737.

# Is the Molecule Switching?

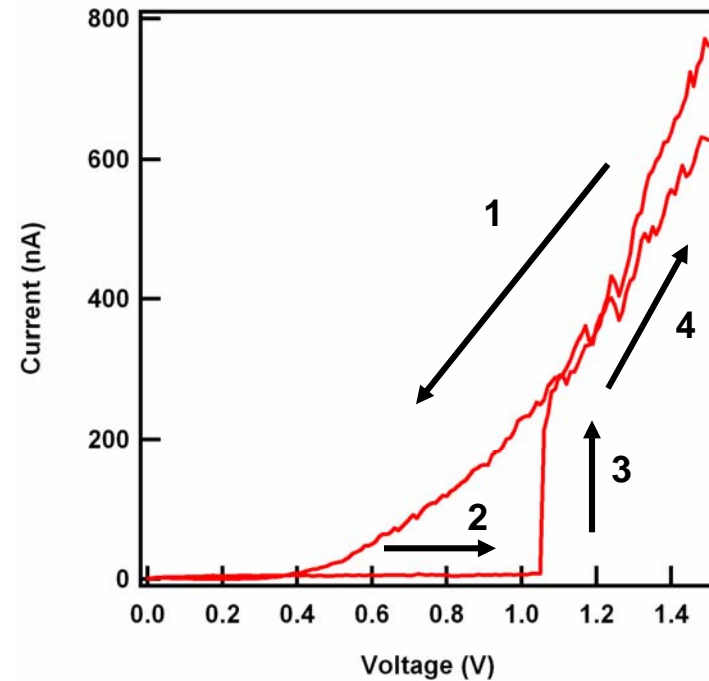
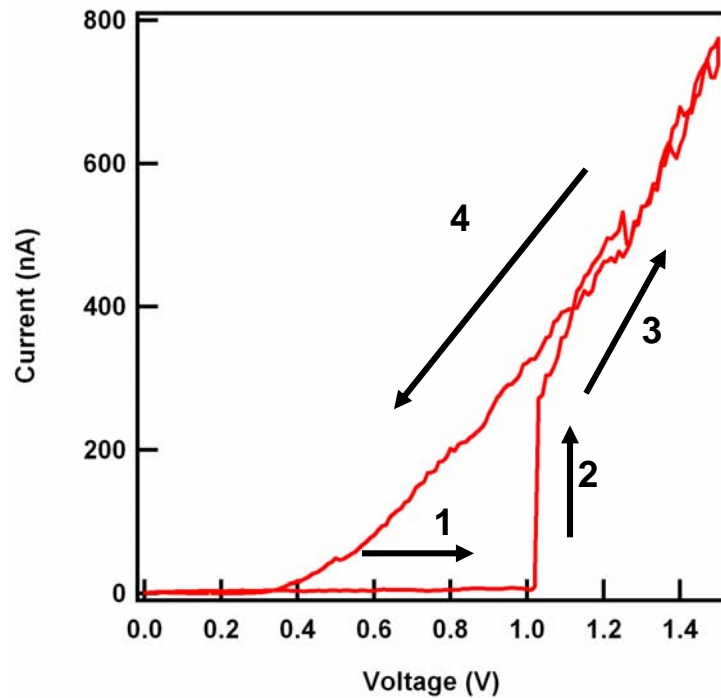


# A Molecular Switch



On-Off ratio of ~40 to 1 at 1V.

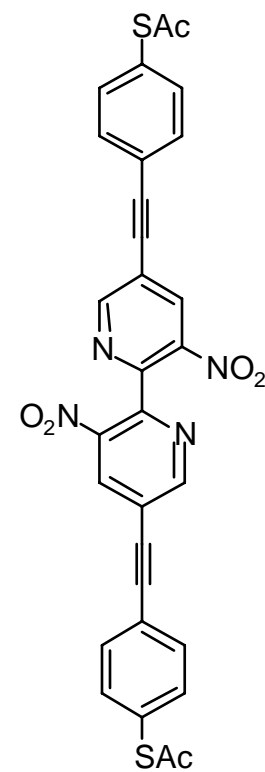
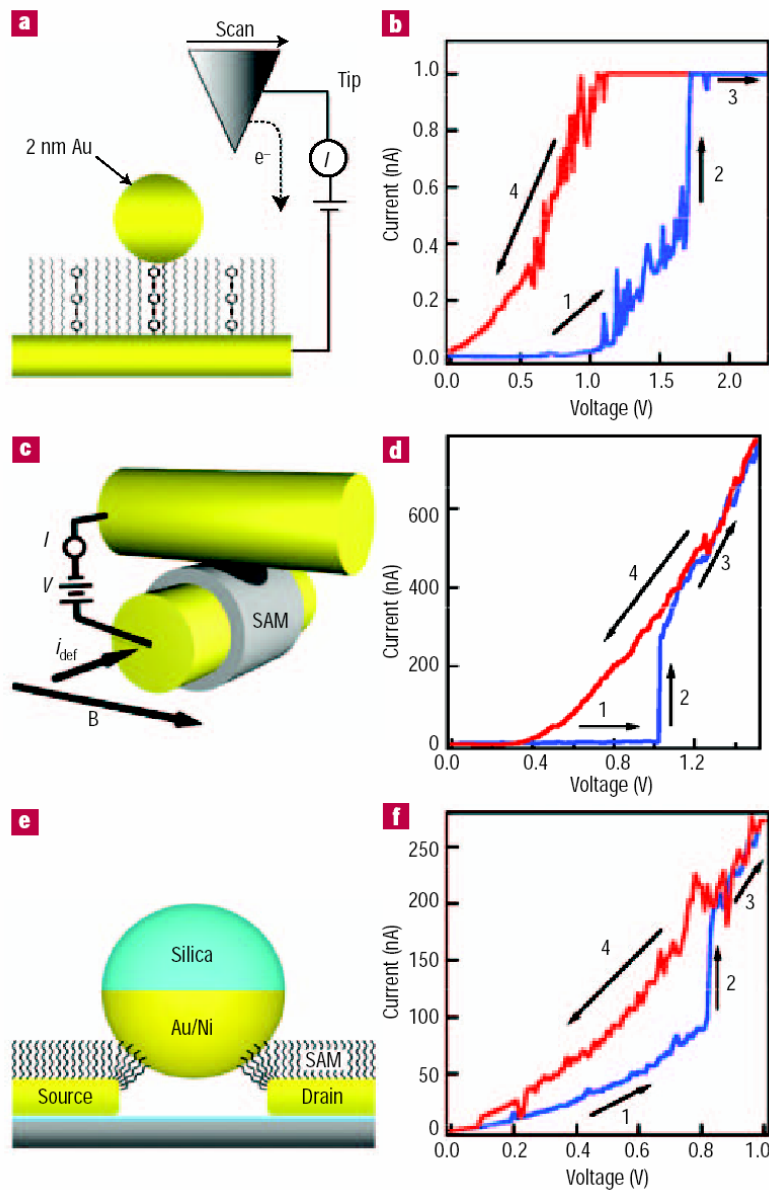
# Reversibility



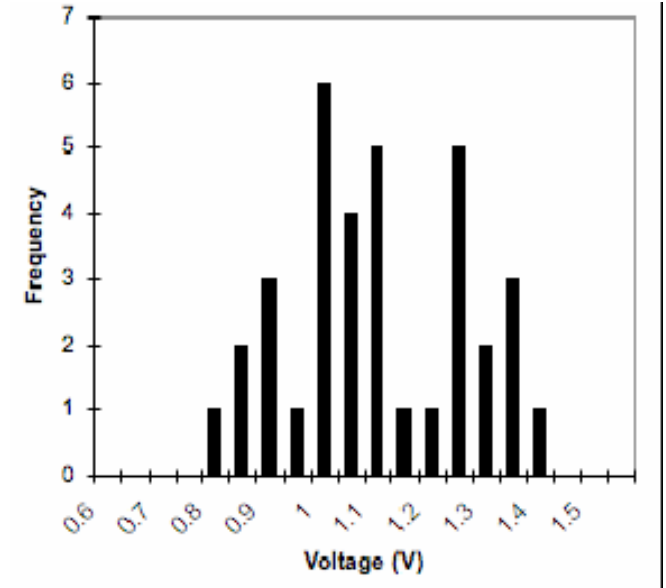
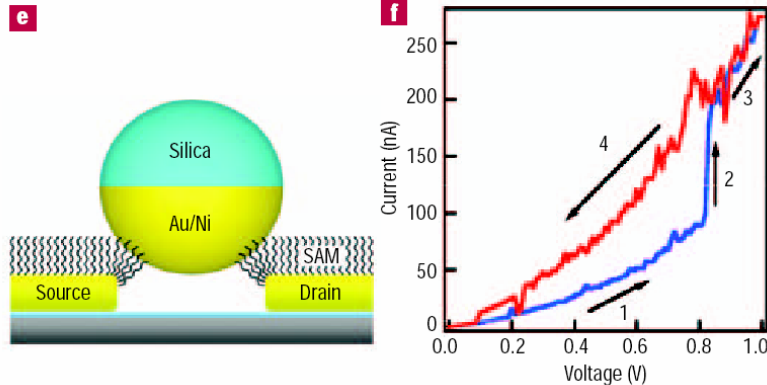
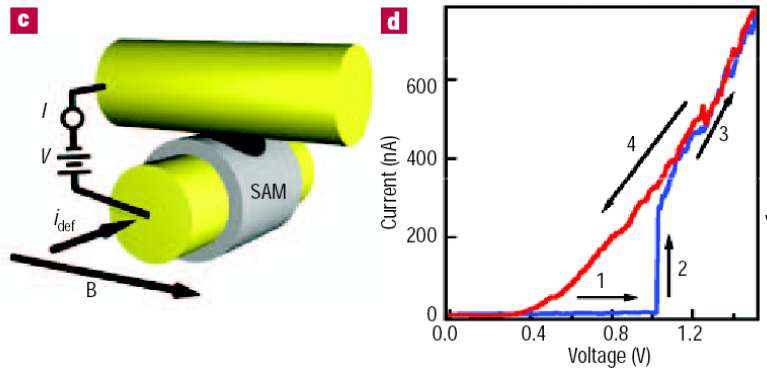
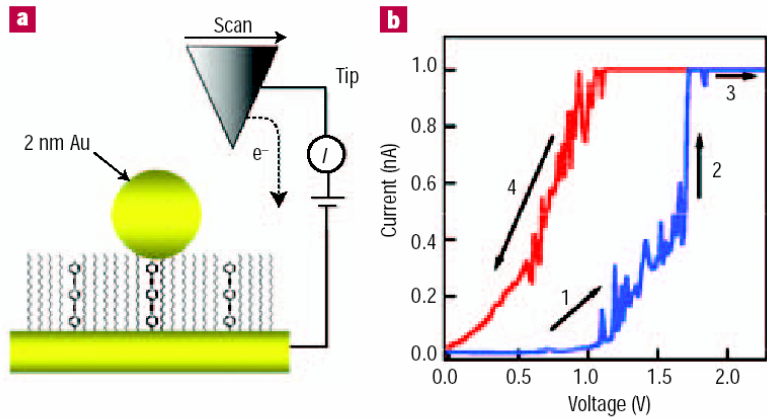
Can start with junction in either the high or low state.  
 Junction “resets” from high to low state near 0 V.



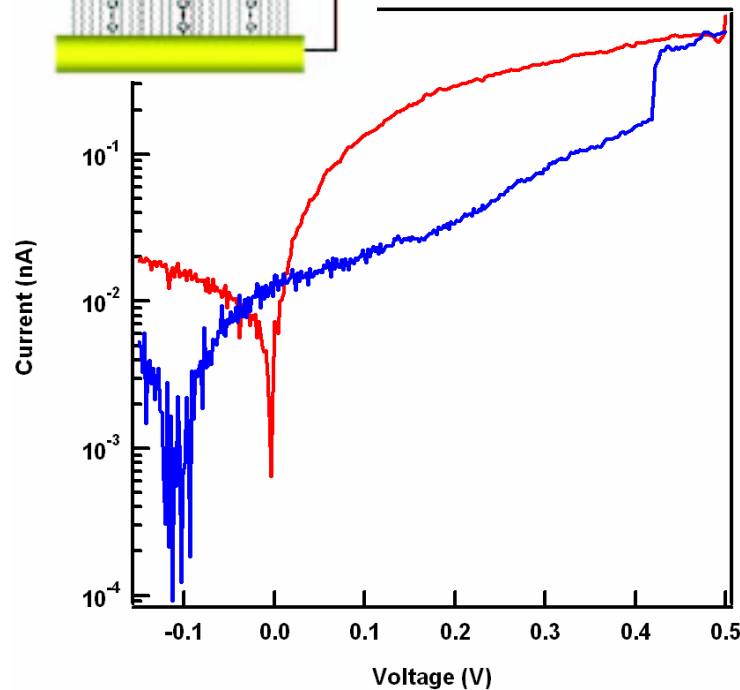
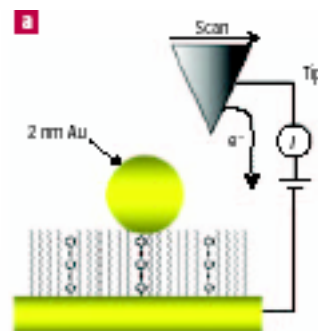
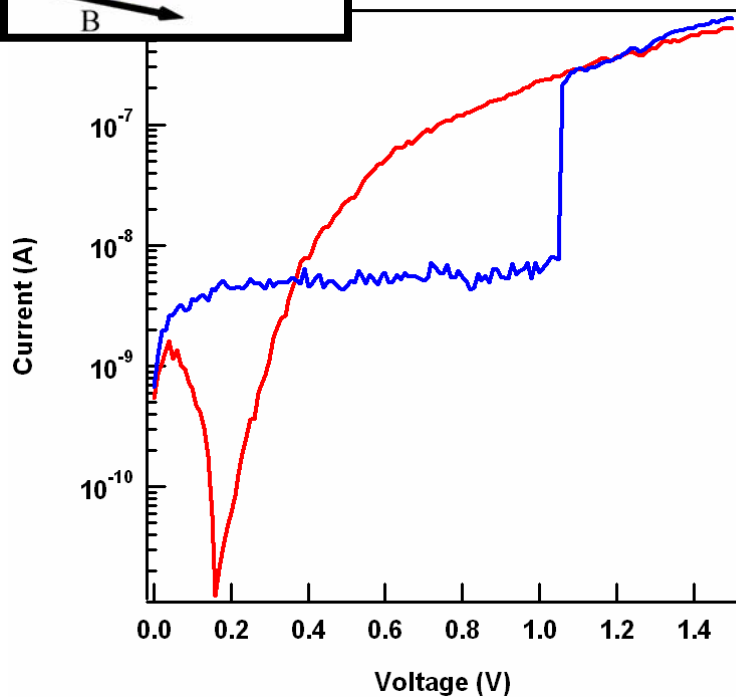
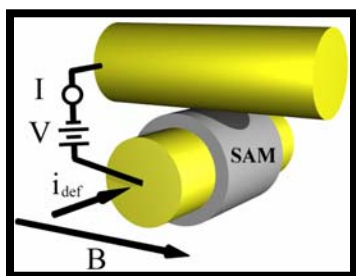
# Molecular Memory Studied by Three Techniques



# Switch Voltage Variability

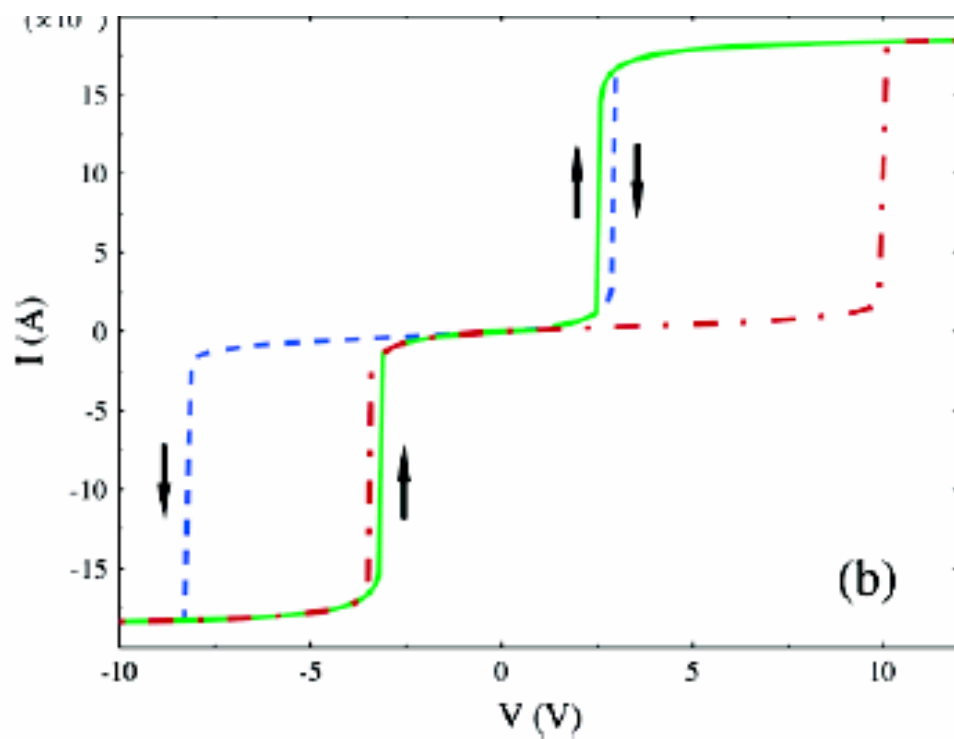
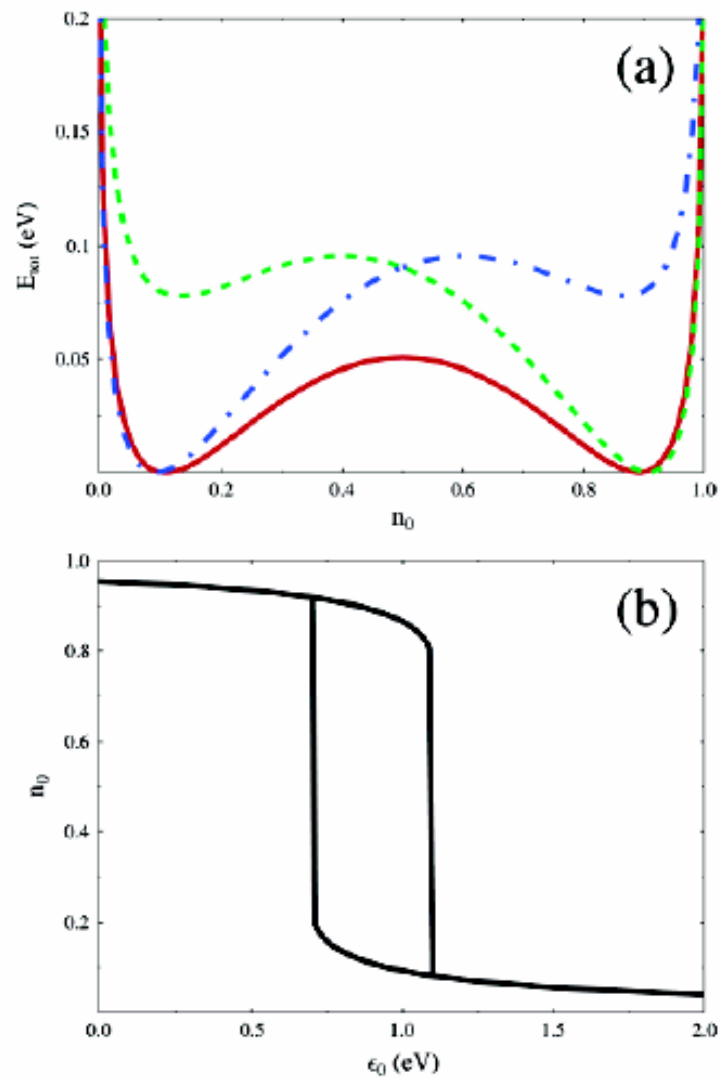


# Possible Switching Mechanism



Bias offset suggests charging in molecule or film

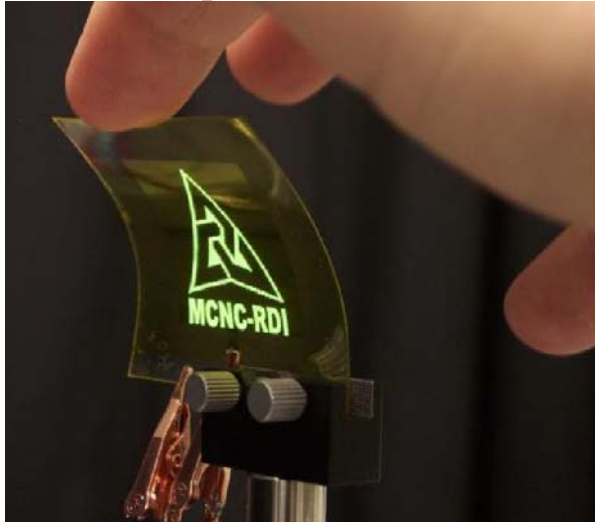
# Polaron Model



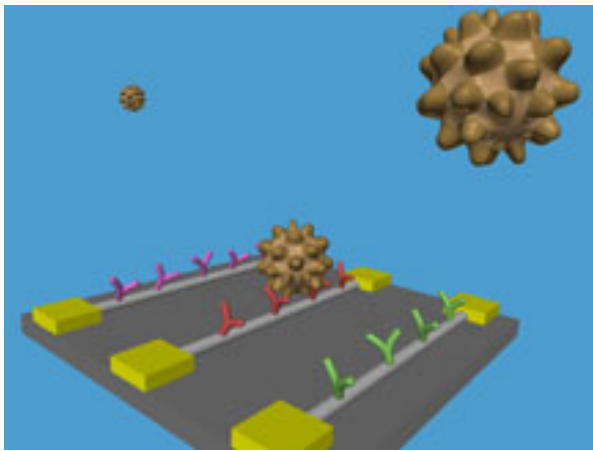
# **Beyond Molecular Electronics**

*Will this really replace your computer?*

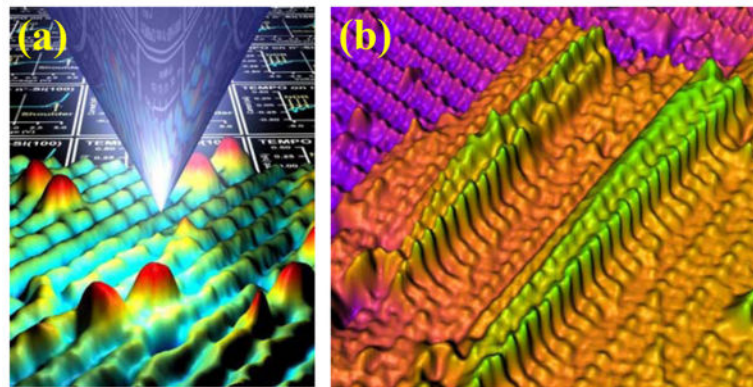
## Implications Beyond Molecular Electronics



- Improved thin film FETs and flexible displays
- New chem-bio sensors
- Hybrid silicon molecule electronics



Lieber (Harvard)



Hersam (Northwestern)

## Acknowledgements

### *NIST Colleagues:*

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R. van Zee  
C. Richter

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A. Blum (NRL)	D. Seferos (UCSB)
S. Pollack (NRL)	C. Daniel Frisbie (Minnesota)
R. Shashidhar (Geo-Centers)	Bong Soo Kim (Minnesota)
J. Lazorcik (Geo-Centers)	D. Allara (PENN State)
D. Long (Geo-Centers)	T. Mallouk (PENN State)
M. Ratner (Northwestern)	T. Mayer (PENN State)
	J. Tour (Rice)

