

# Molecular and Polymer Nanodevices

Nikolai Zhitenev

1. (Ultimate) Limitations of Silicon-based electronics
2. Molecular switches
3. Polymer and other switches
4. Summary and outlook

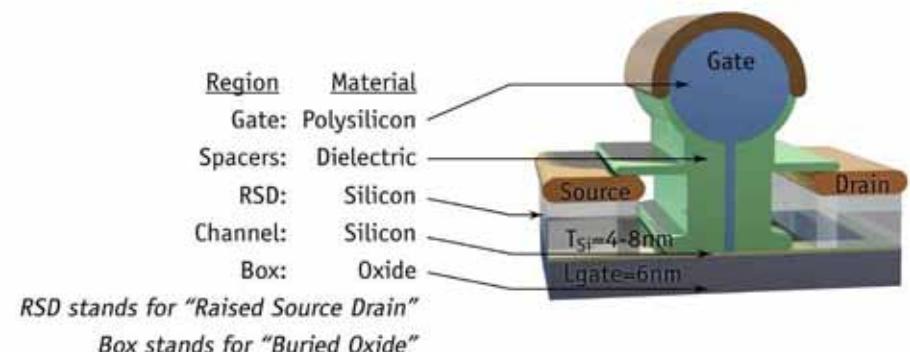
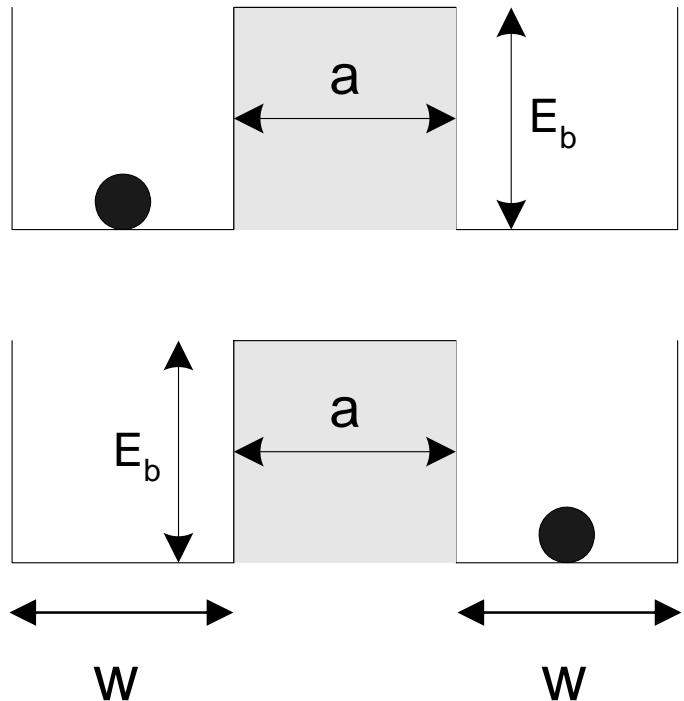


Center for Nanoscale Science and Technology

**Lucent Technologies**  
Bell Labs Innovations



# (Ultimate) Limitation: Computational State decays because of Electron Tunneling

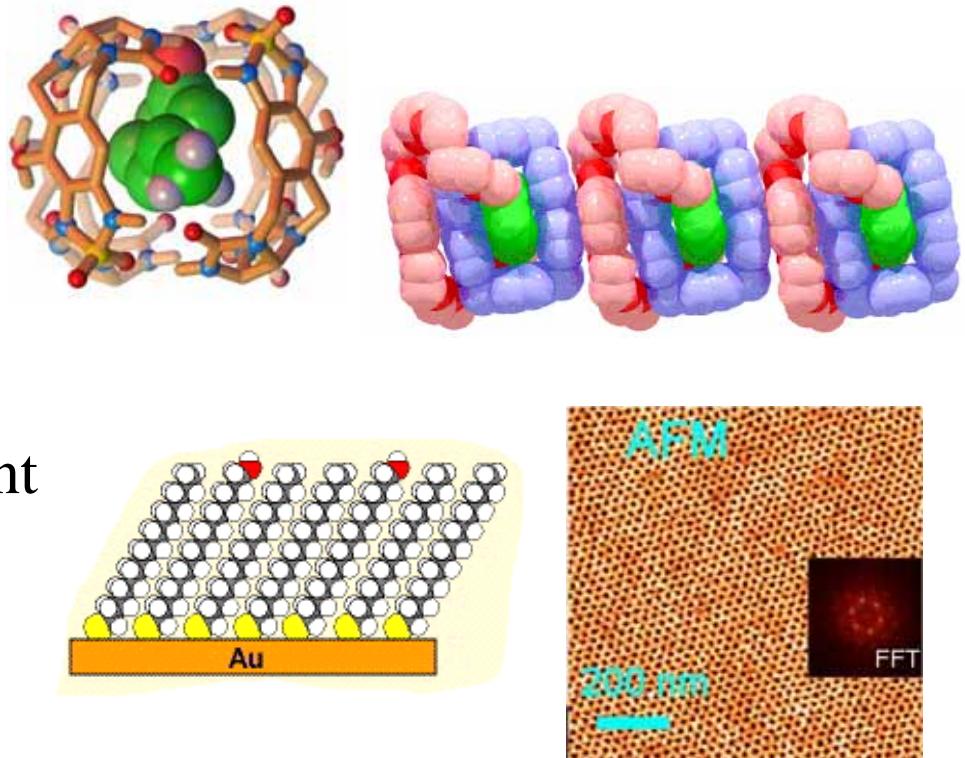


*Semiconductor Research Corporation*

*2006 hypothesis:* Devices having feature sizes less than 5 nm should utilize particles whose mass is greater than the mass of an electron.

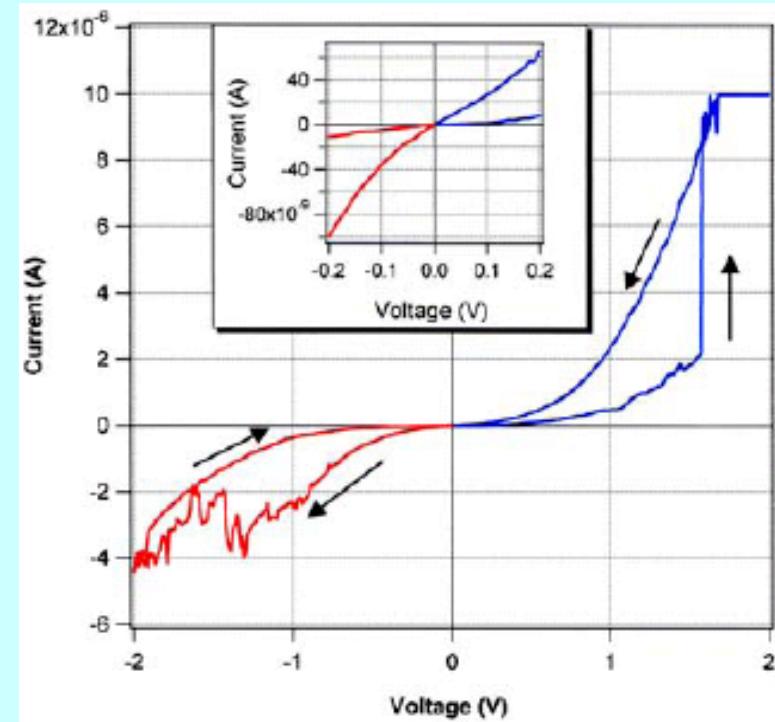
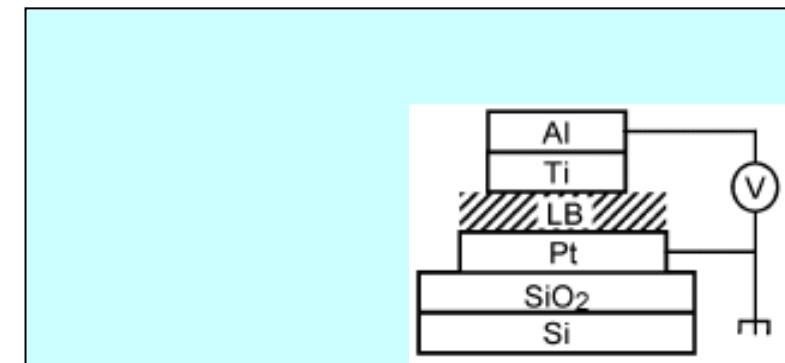
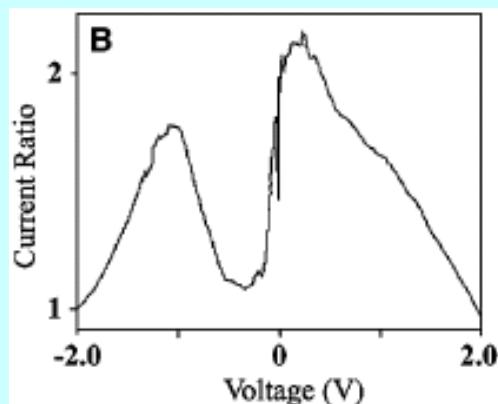
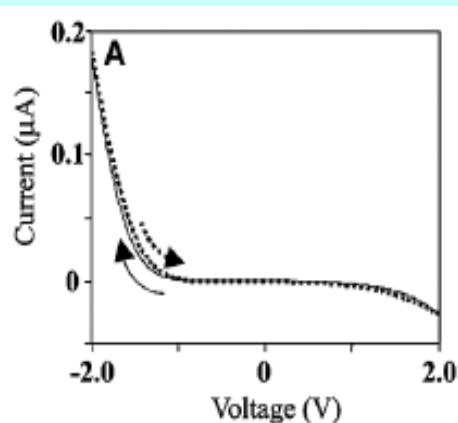
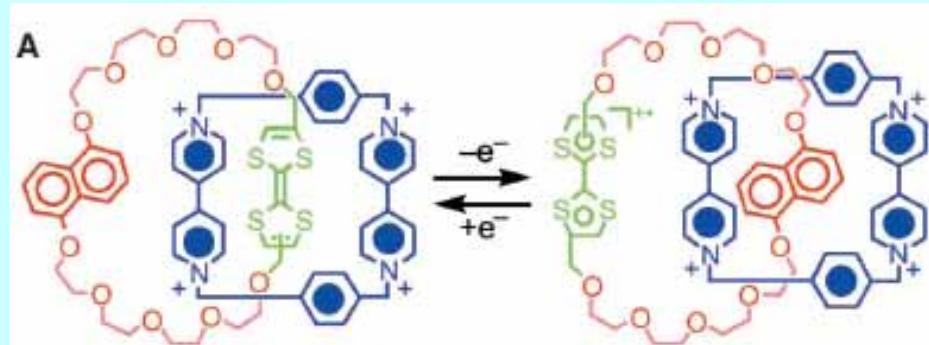
# Why molecules?

1. Small
2. Exactly reproducible
3. Enormous variety,  
sophisticated electronic  
structure
4. Self-assembly (on different  
levels)
5. New types of devices



# Electronically Reconfigurable Switch (LB monolayer)

Collier et al., Science 2000

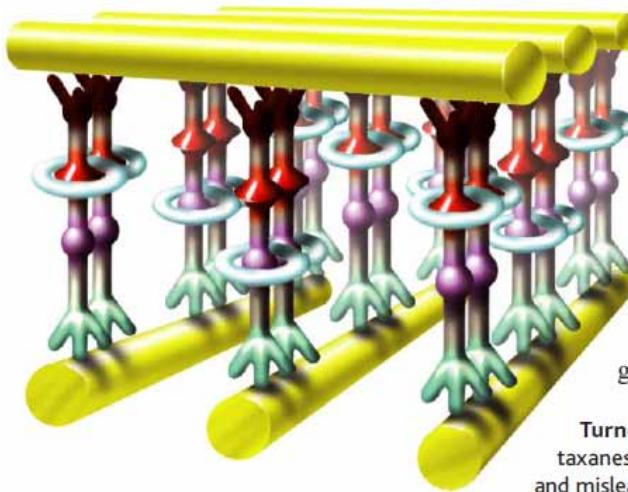


HP Labs



In 2001, scientists assembled molecules into basic circuits, raising hopes for a new world of nanoelectronics

## Molecules Get Wired



21 DECEMBER 2001 VOL 294 SCIENCE —ROBERT F. SERVICE

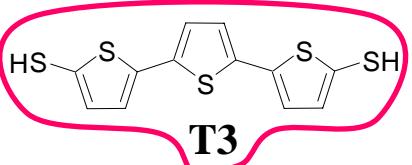
### Molecular Electronics

## Next-Generation Technology Hits an Early Midlife Crisis

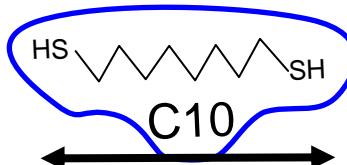
Researchers had hoped that a new revolution in ultraminiaturized electronic gadgetry lay almost within reach. But now some are saying the future must wait

24 OCTOBER 2003 VOL 302 SCIENCE —ROBERT F. SERVICE

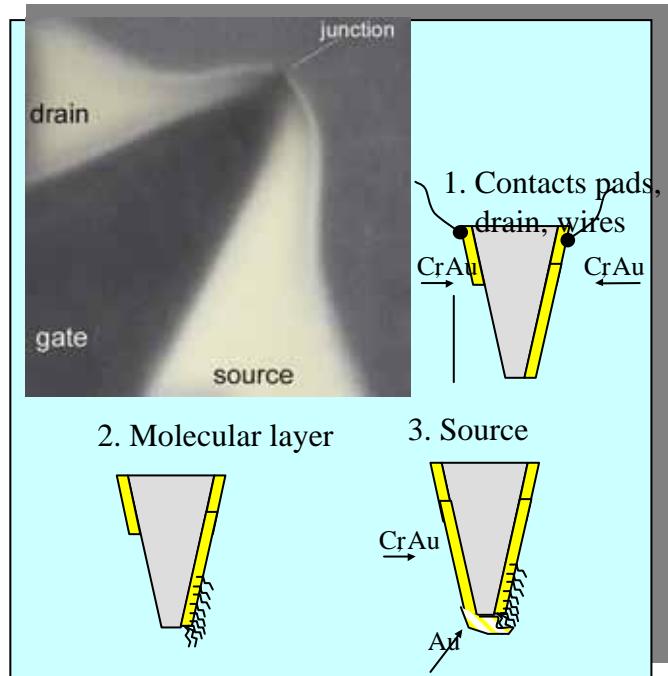
Conjugated :



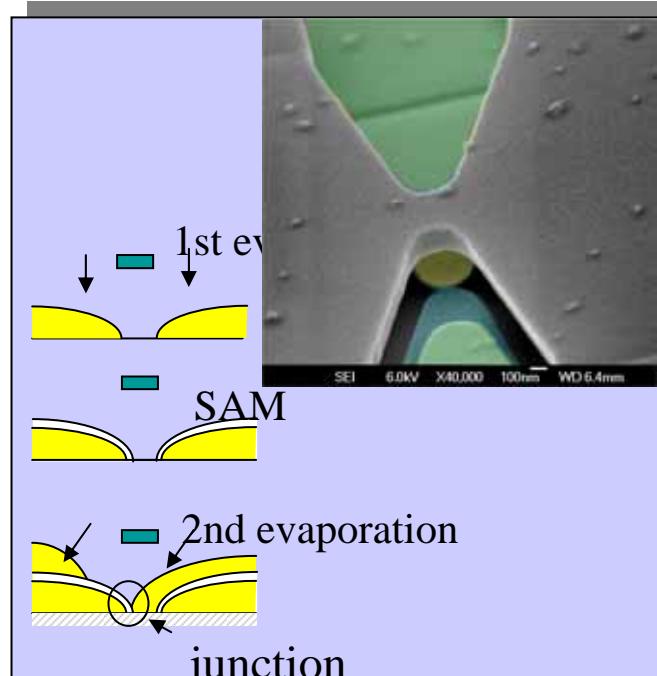
Saturated:



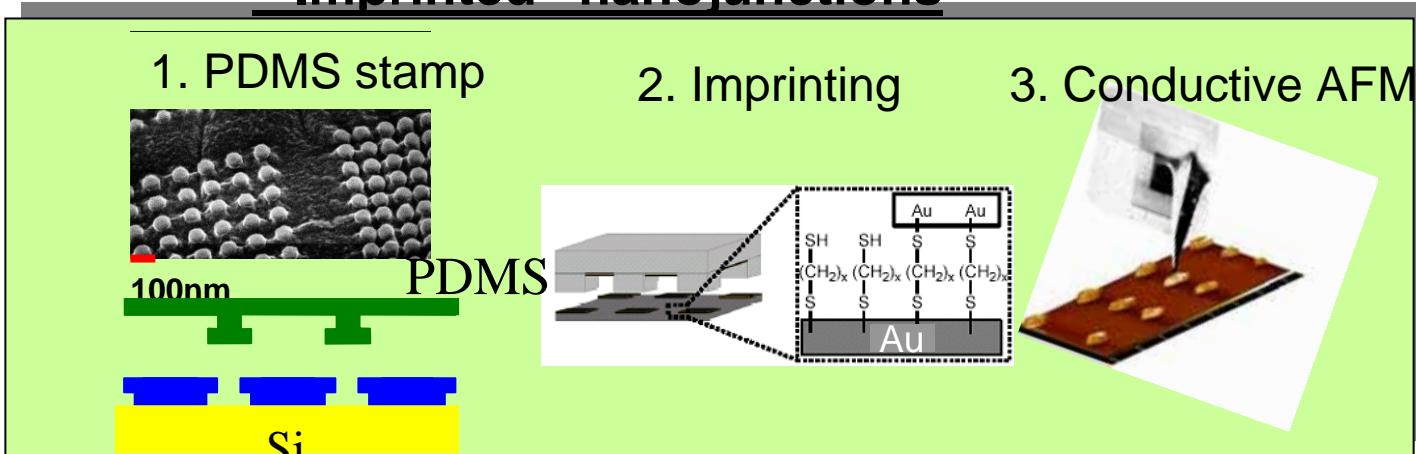
## ~"Single-molecule" junctions



## "Fixed-area" nanojunctions

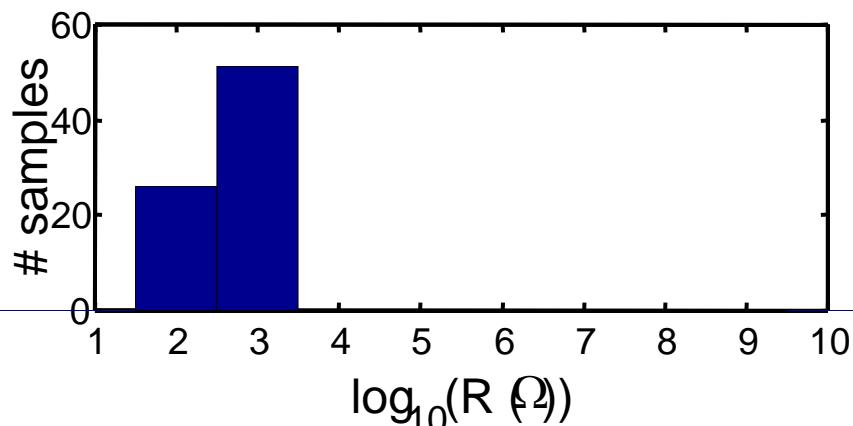
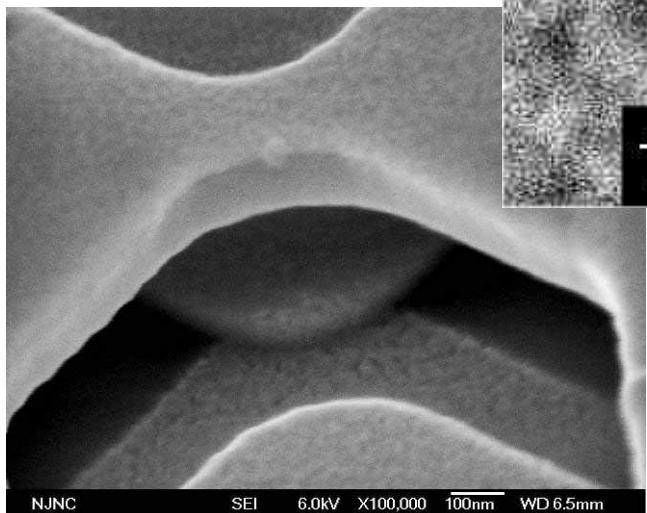


## "Imprinted" nanojunctions



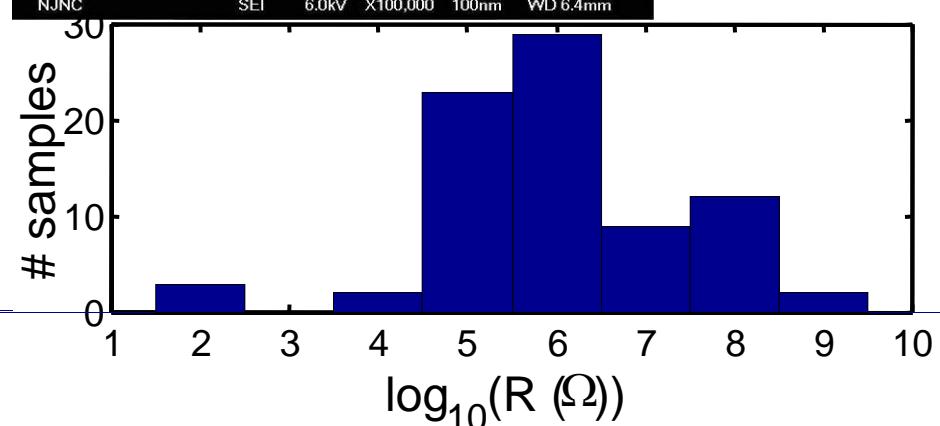
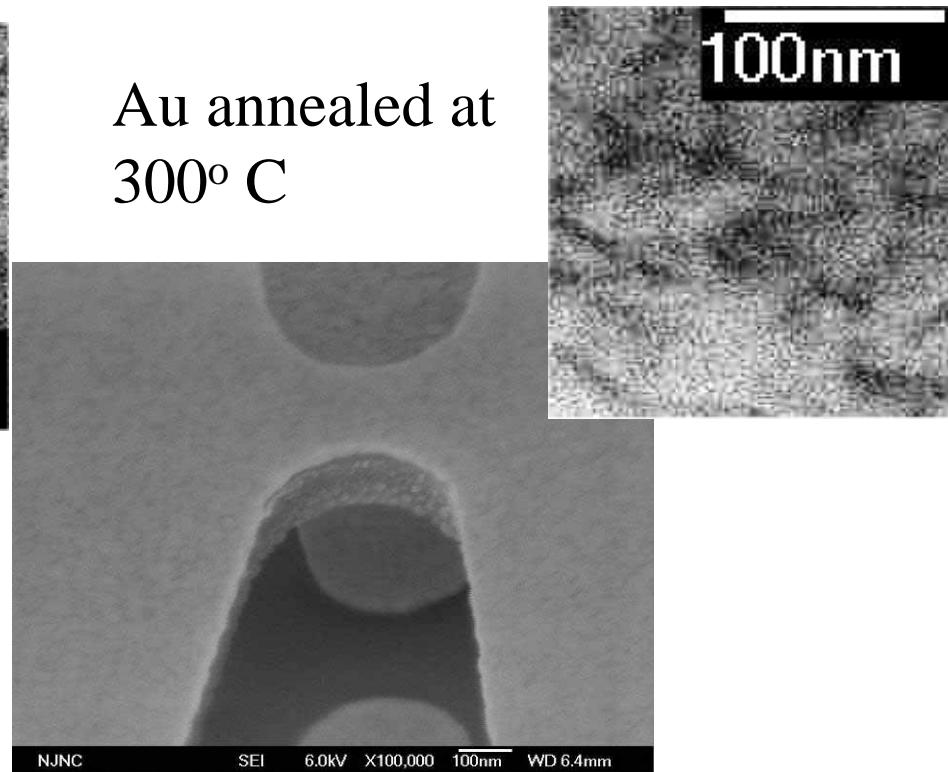
# Topography of bottom electrode:

Au as deposited



100 % junctions are “shorted”  
((Au)- (T3)-(Au))

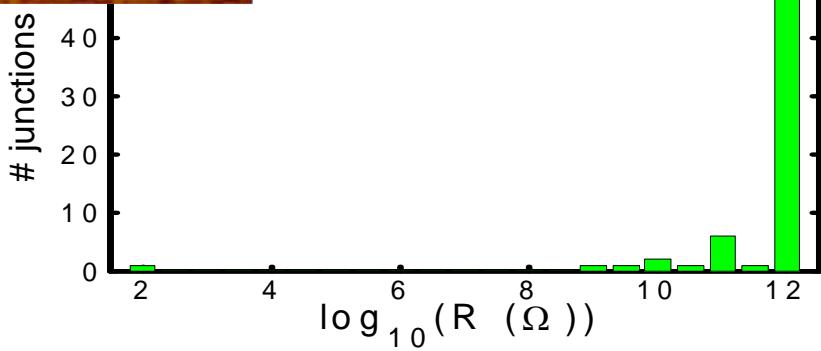
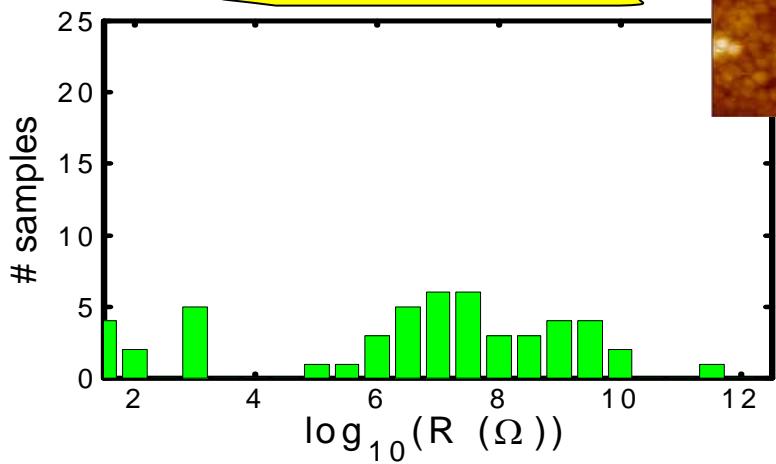
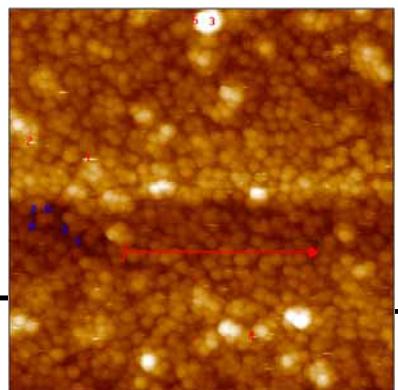
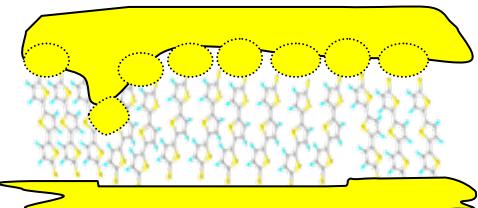
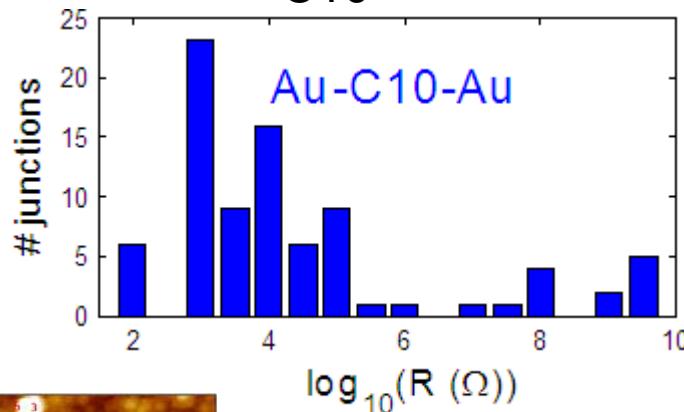
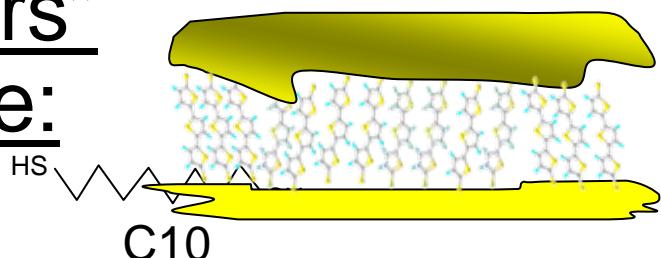
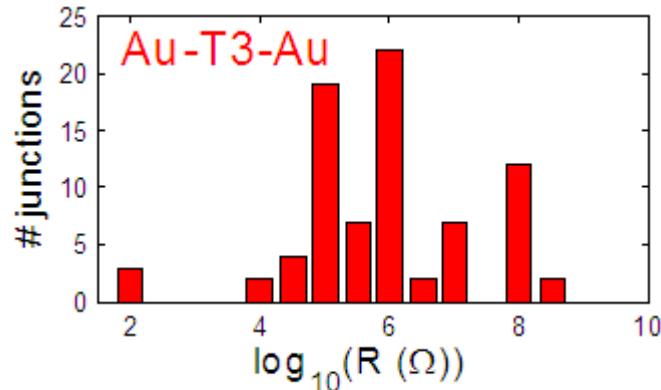
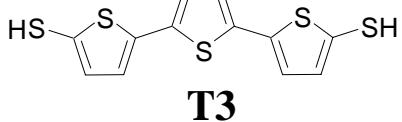
Au annealed at  
300° C



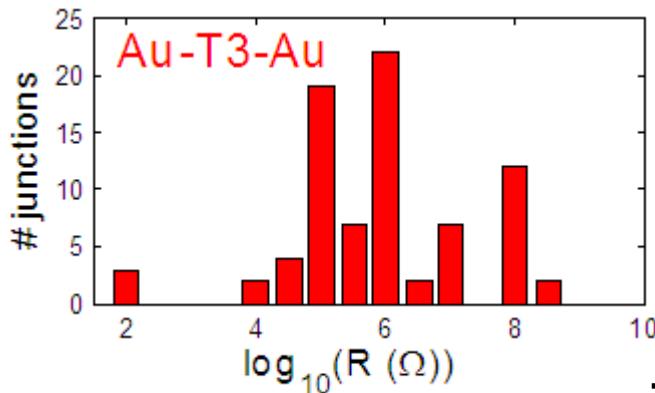
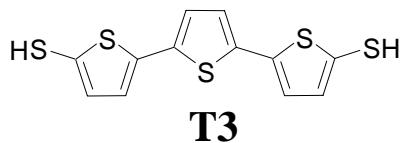
~100 % junctions are “good”  
((annealed Au)- (T3)-(Au))

# Molecular “wires” vs “barriers”

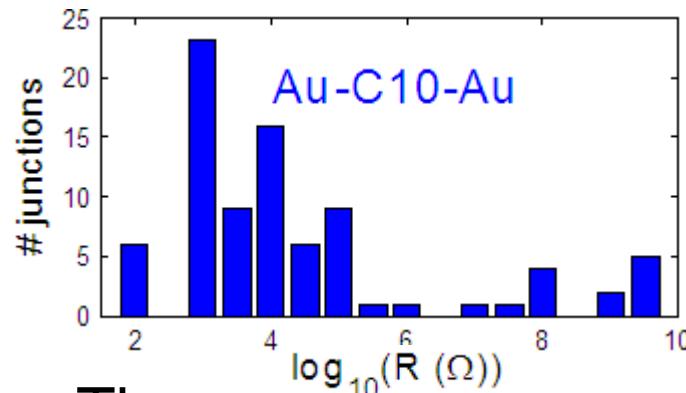
## Topography of top electrode:



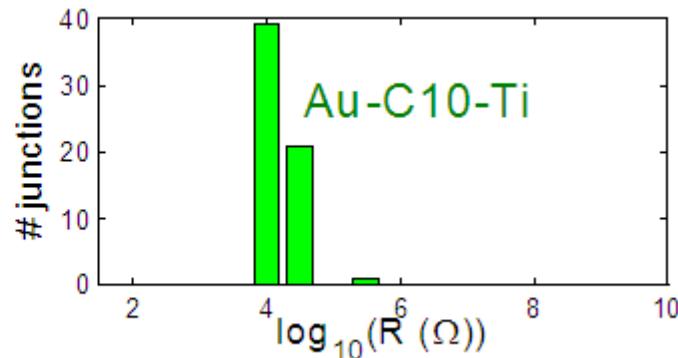
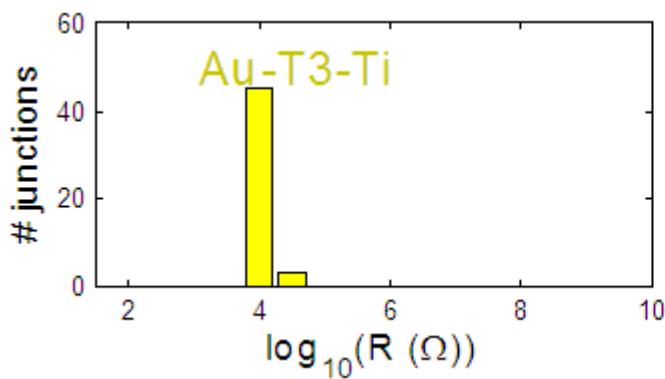
# Chemical reactivity of electrodes:



Top: Au



Top: Ti



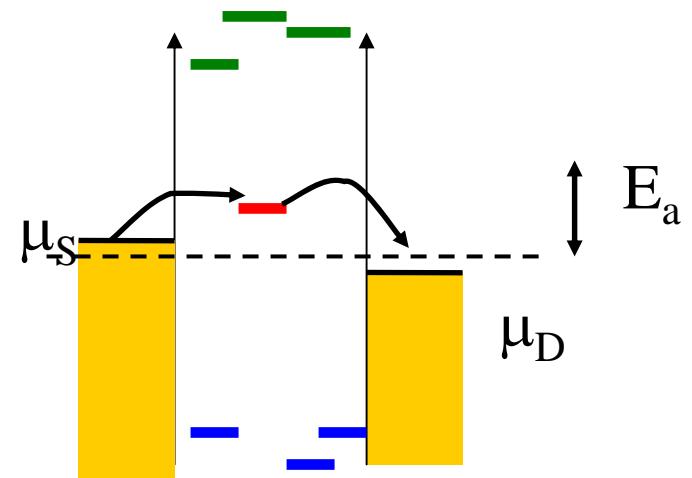
Weakly  
reactive  
metal



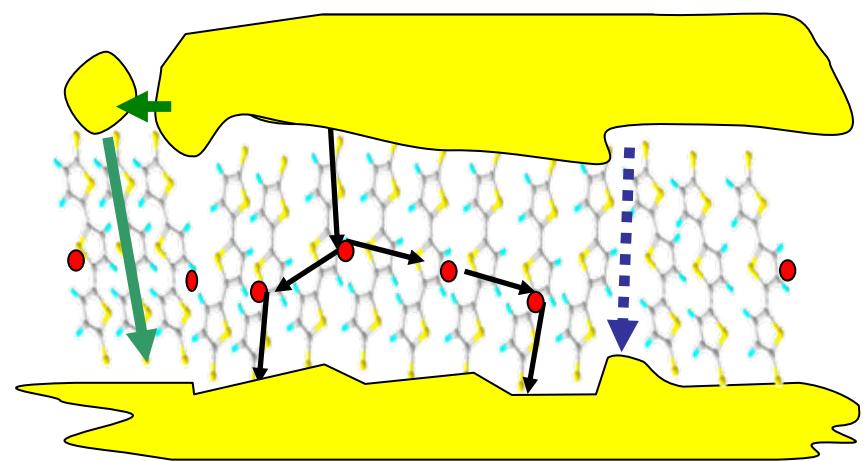
Strongly  
reactive  
metal

# Problems with “short molecule” devices:

1. Typical metal-molecules devices are EXTREMELY LOW conductive – energy level mismatch



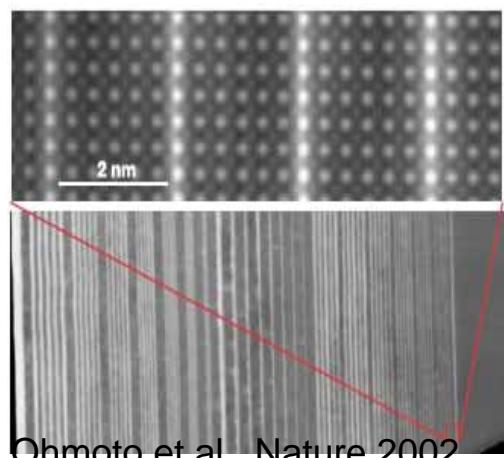
2. Conductance is dominated by *DEFECT* states (NOT molecular states)



# “Ideal” or “Idealized” Systems vs. Reality

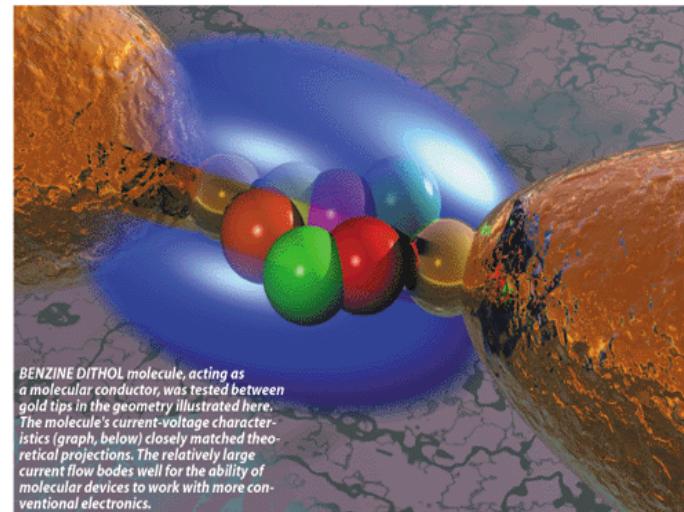
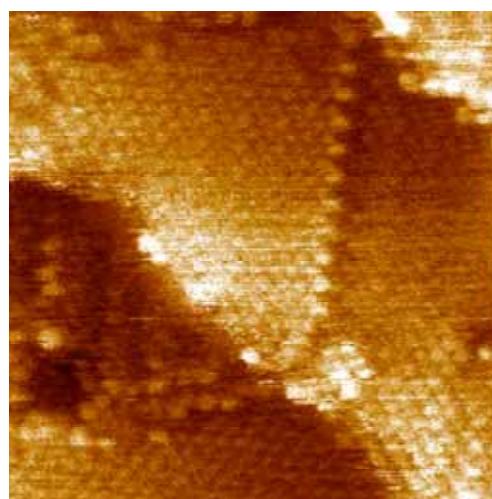
Epitaxial systems:

Oxide superlattices

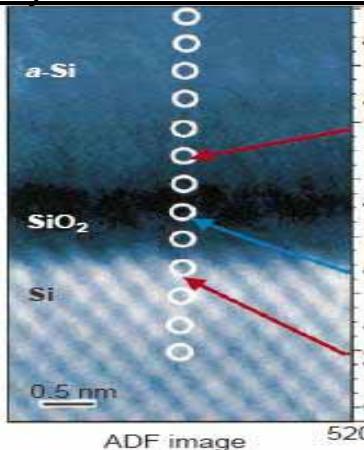


Ohmoto et al., Nature 2002

Molecular layers on metals:

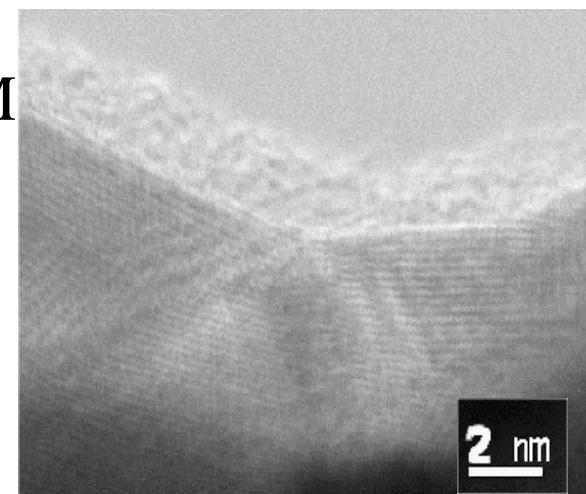


Reality in nanoscale devices = > disorder, dopants, material reactions



Muller et al.,  
Nature 1999

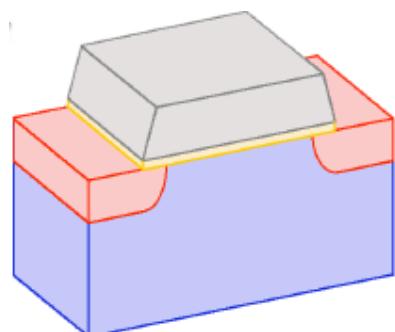
SAM



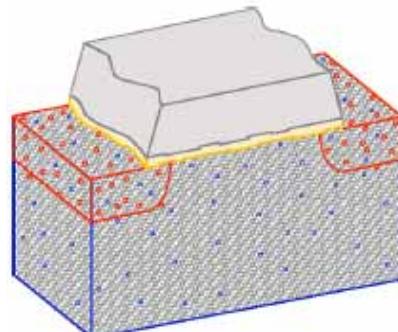
Au

## Problem: Defects

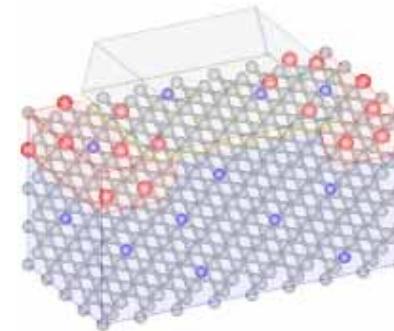
# Sometimes: not enough DEFECTS



A 100 nm MOSFET

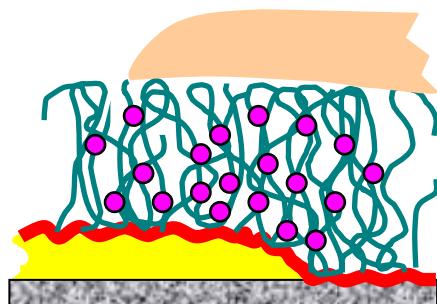


A 22 nm MOSFET

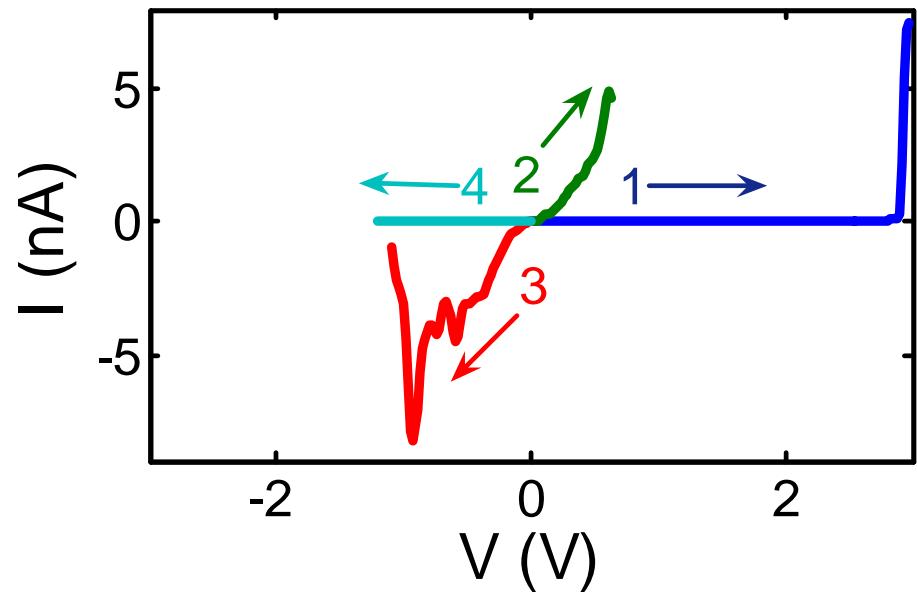


A 4.2 nm MOSFET

# Possible Solution: plenty of “DEFECTS”

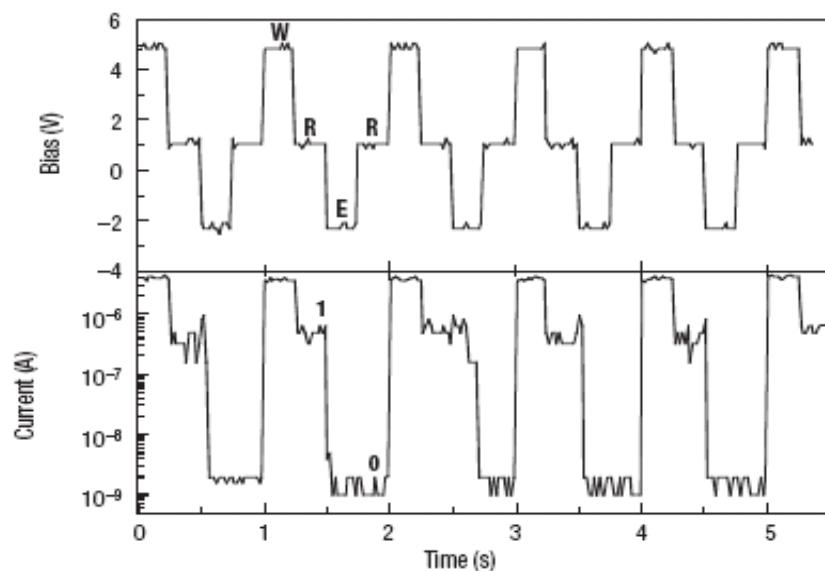
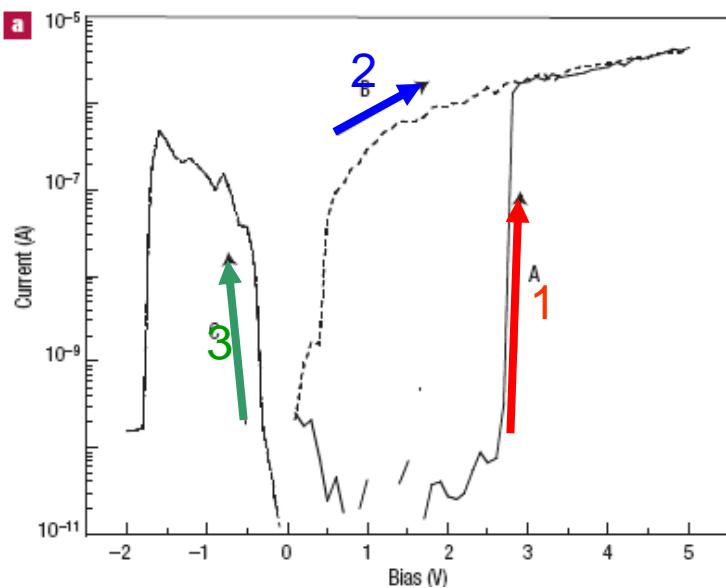
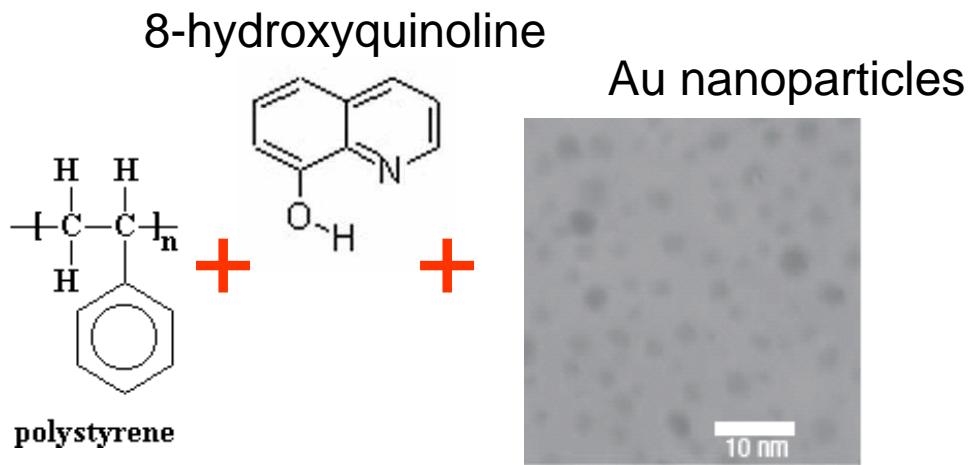
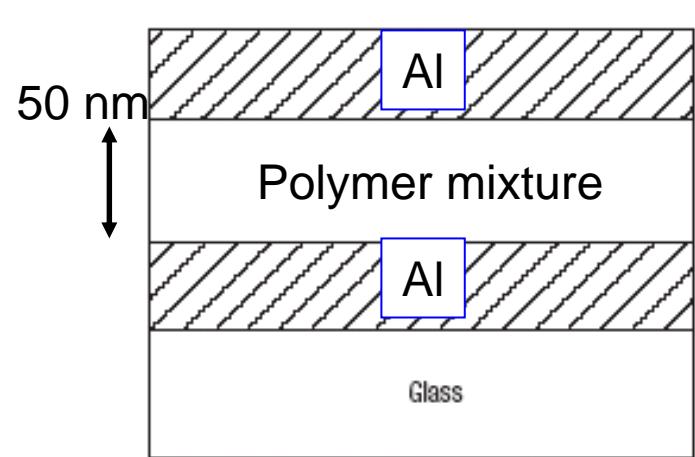


High density of ions enables  
Bistable Switching in tiny  
device!



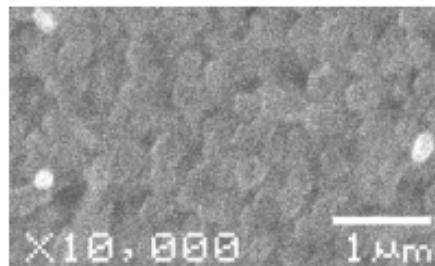
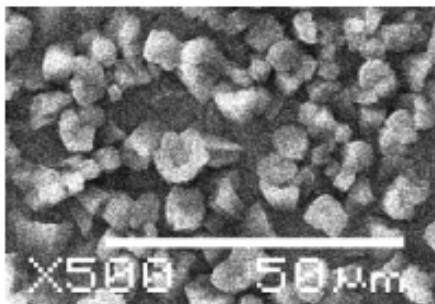
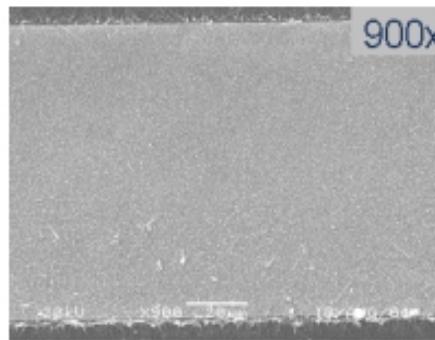
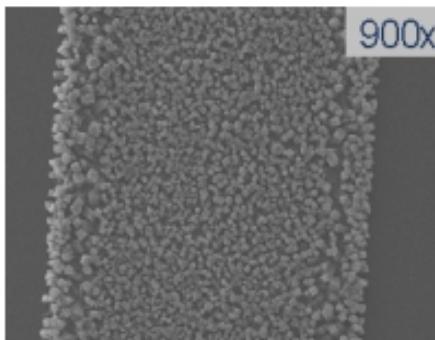
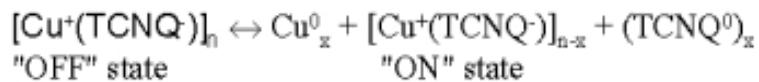
# Programmable polymer thin film and non-volatile memory device

Ouyang et al, Nature Materials 2004



# Charge-transfer organic for memory (IMEC)

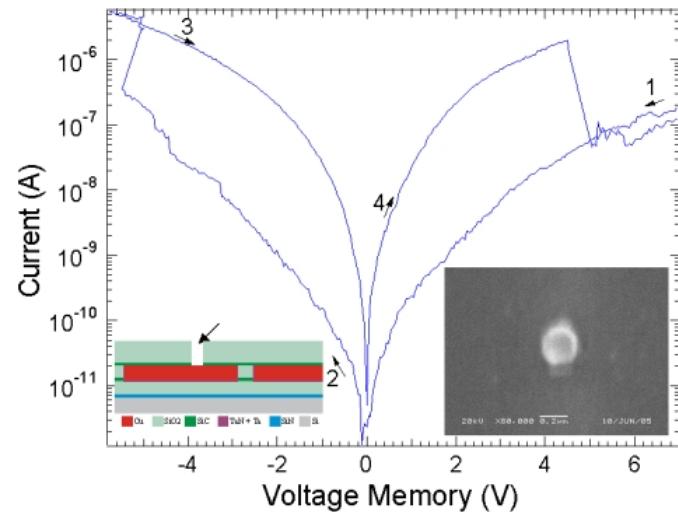
## CuTCNQ

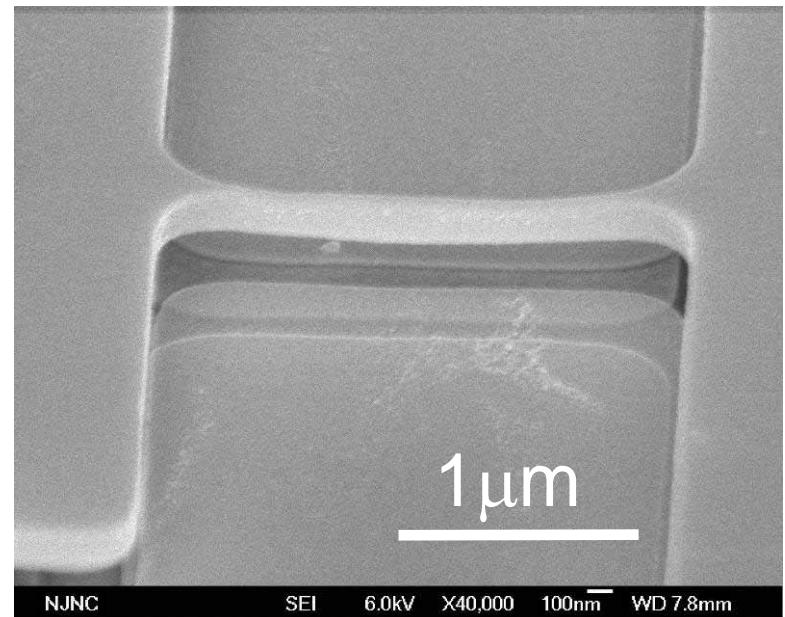
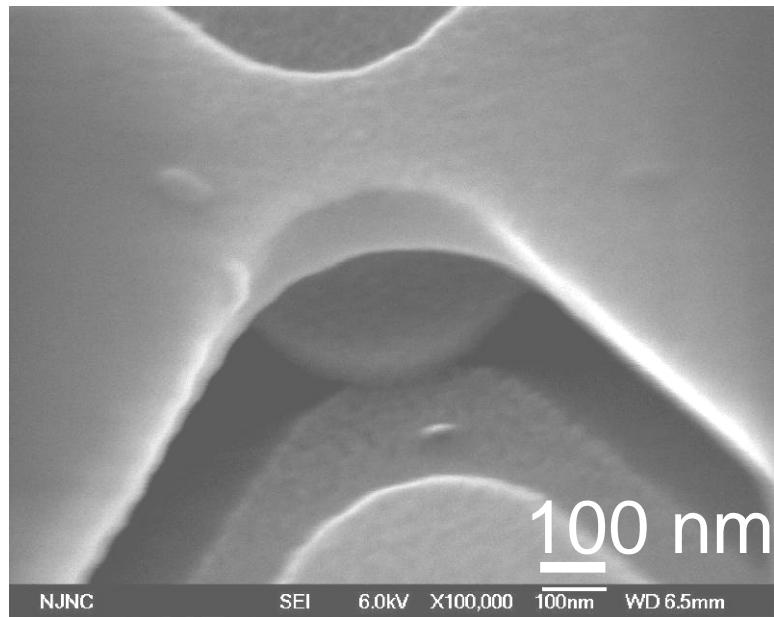
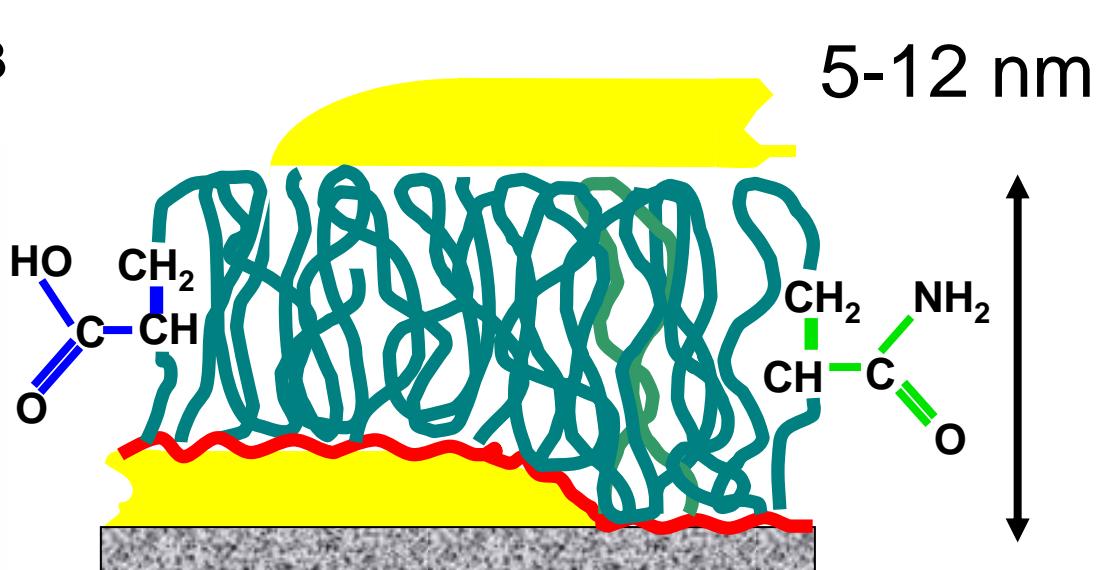
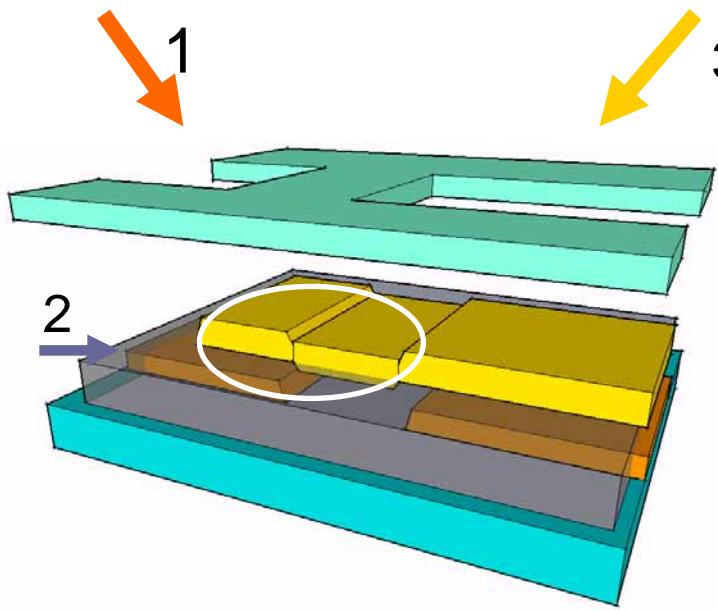


acetonitrile (RT)  
(literature procedure)

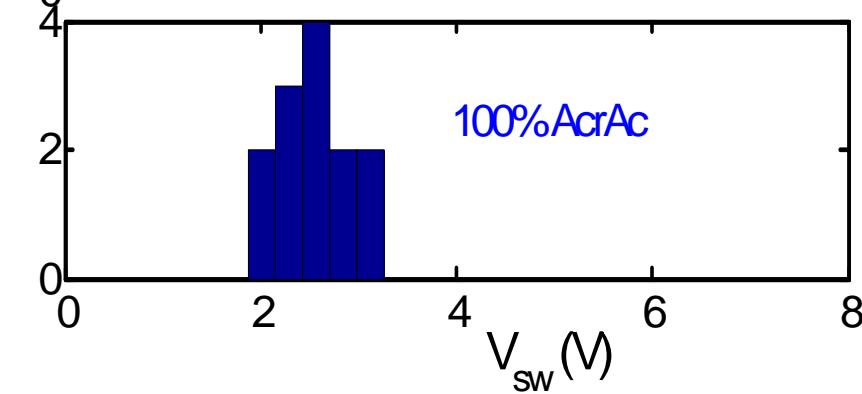
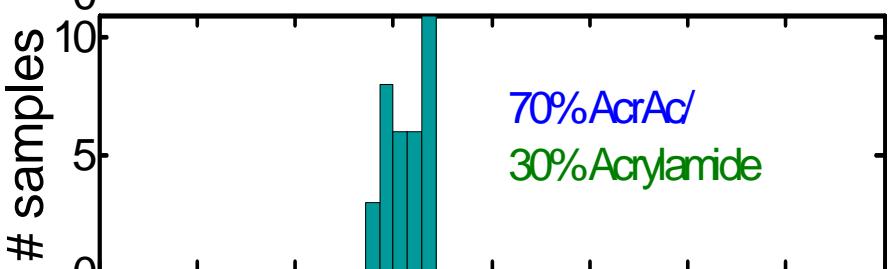
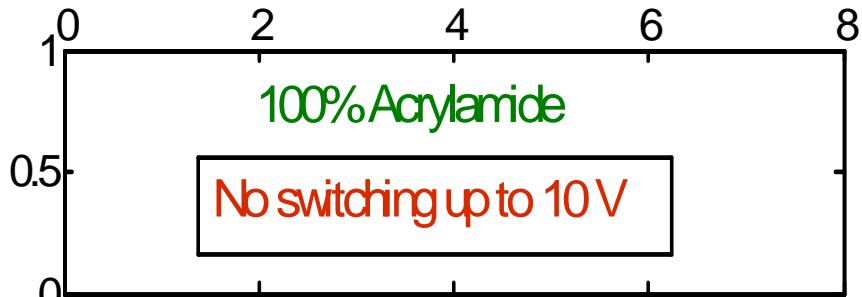
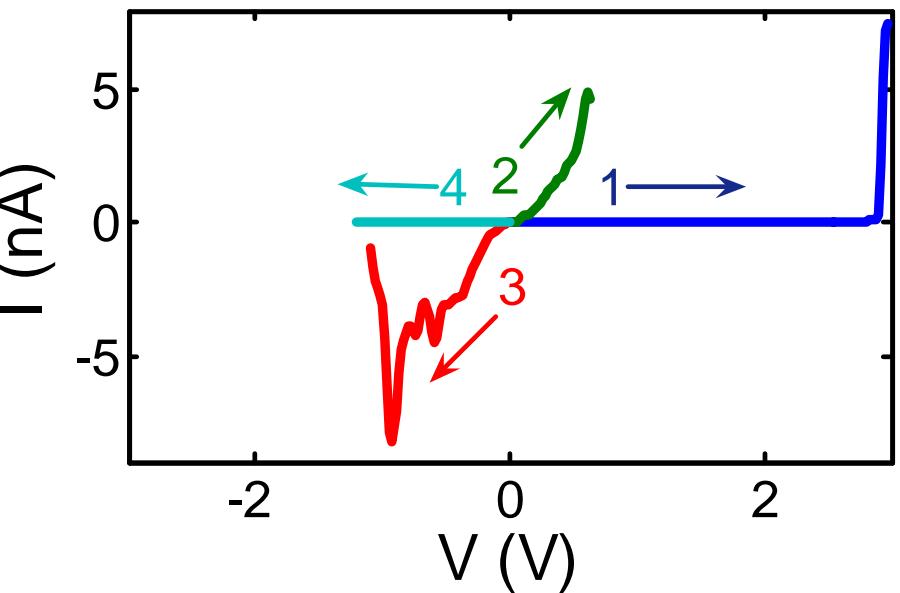
n-butyronitrile (110°C)  
(IMEC work)

Template growth of CuTCNQ *inside* vias  
Improved reproducibility, 0.25 μm diameter via, R = 220 kΩ



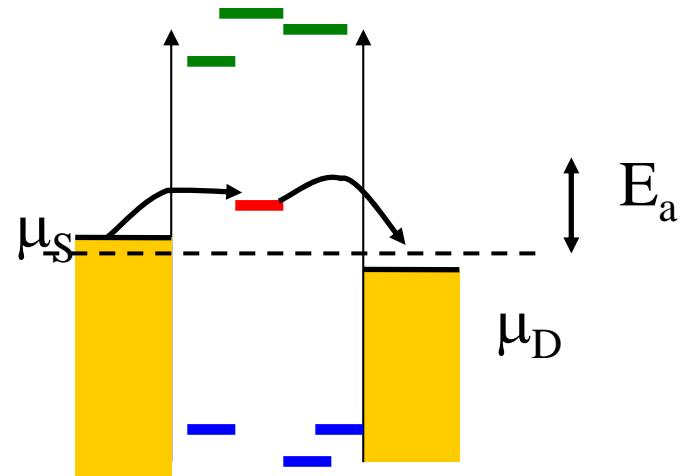


# Electrical switching

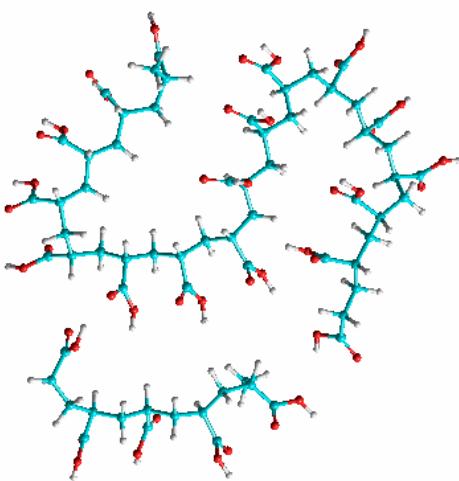


## MODEL:

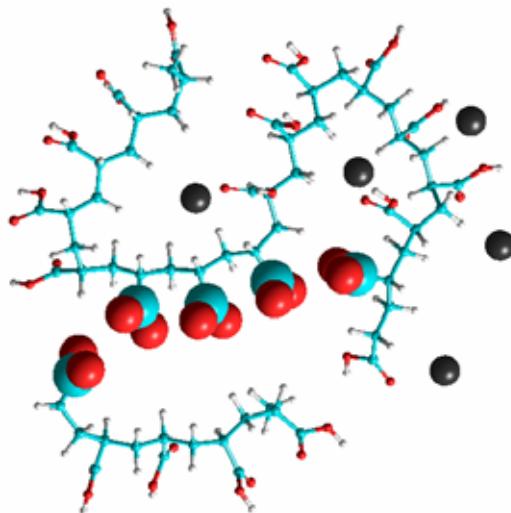
- 1) Electronic states are created by COO<sup>-</sup> ions
- 2) Conducting chain formation



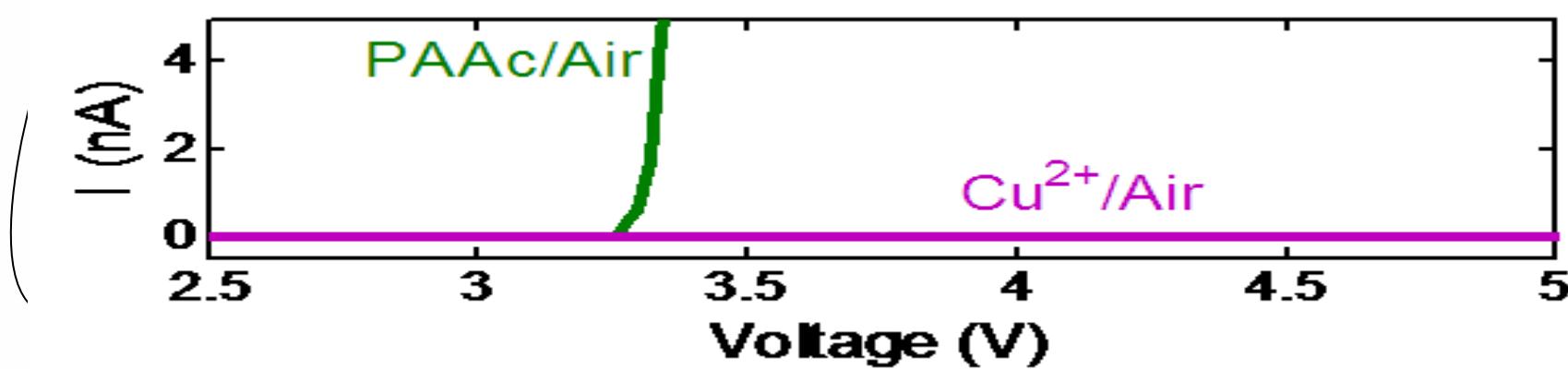
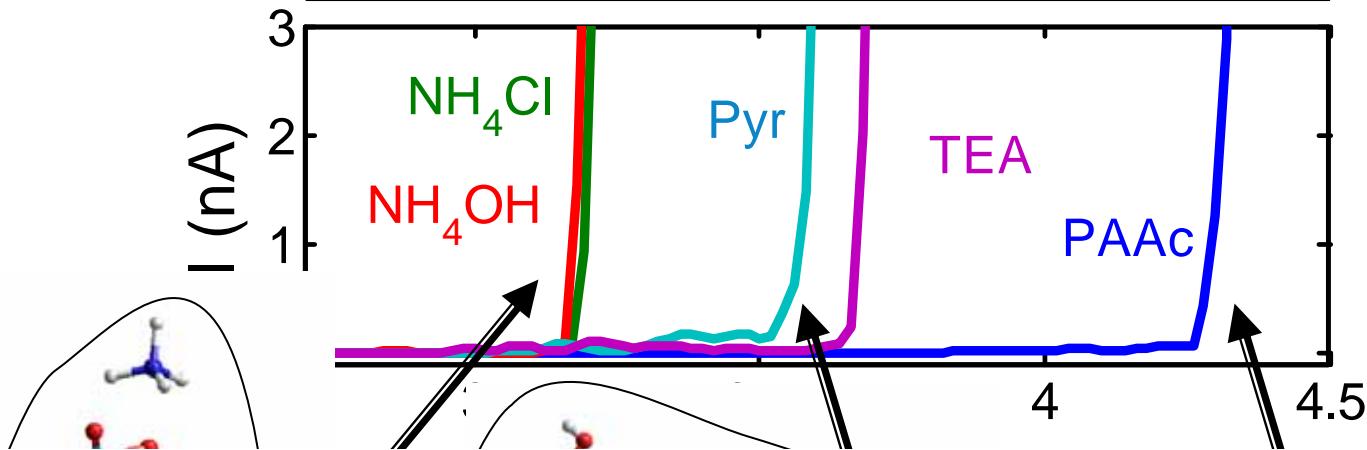
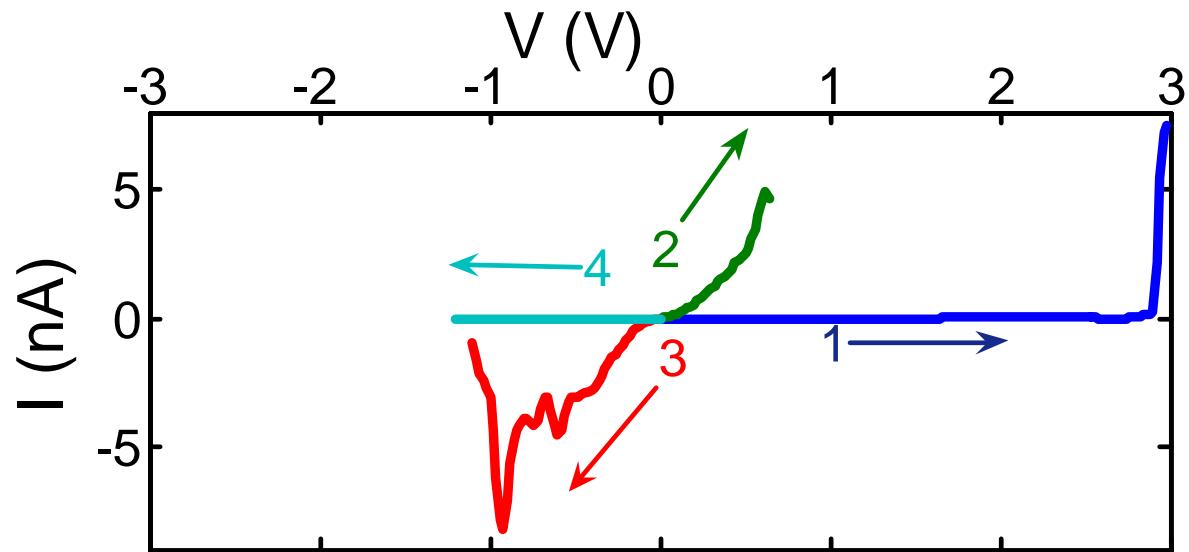
Initial state



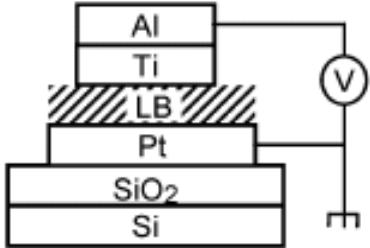
Conducting channel



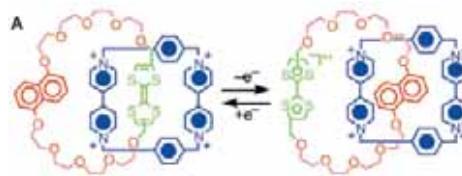
Metastable state stabilized  
by conformational change



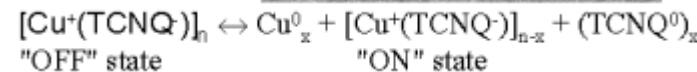
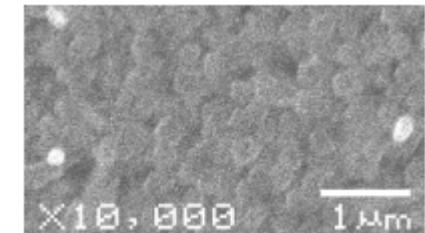
Chemical  
Modifications  
of COOH  
change  
electrical  
properties



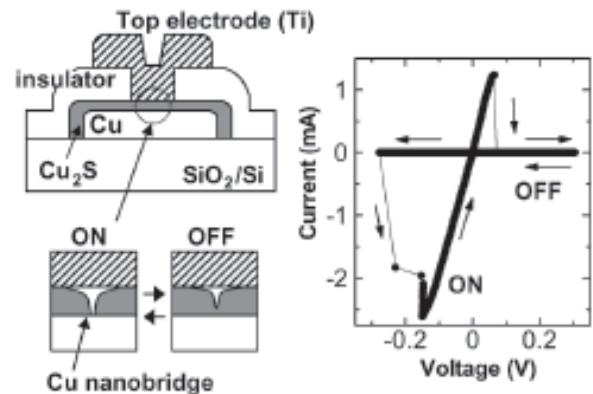
# Electrochemistry of metal filaments (HP Labs)



# Single-molecule Switching (UCLA/Caltech)



# Solid Electrolytes (NEC)

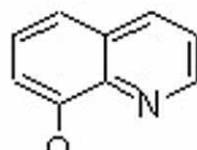


# Bistable switches

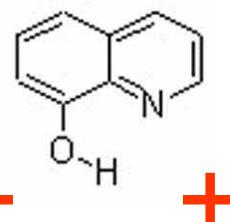
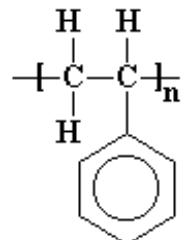
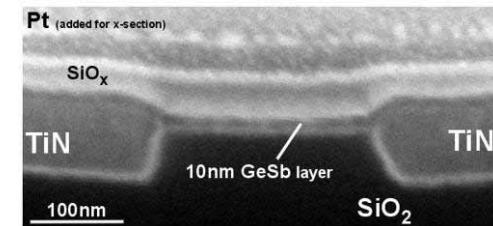
## Charge transfer salts (IMAC)

## Phase-change memory (IBM)

## Polymer mixtures (UCLA)



## Au nanoparticles



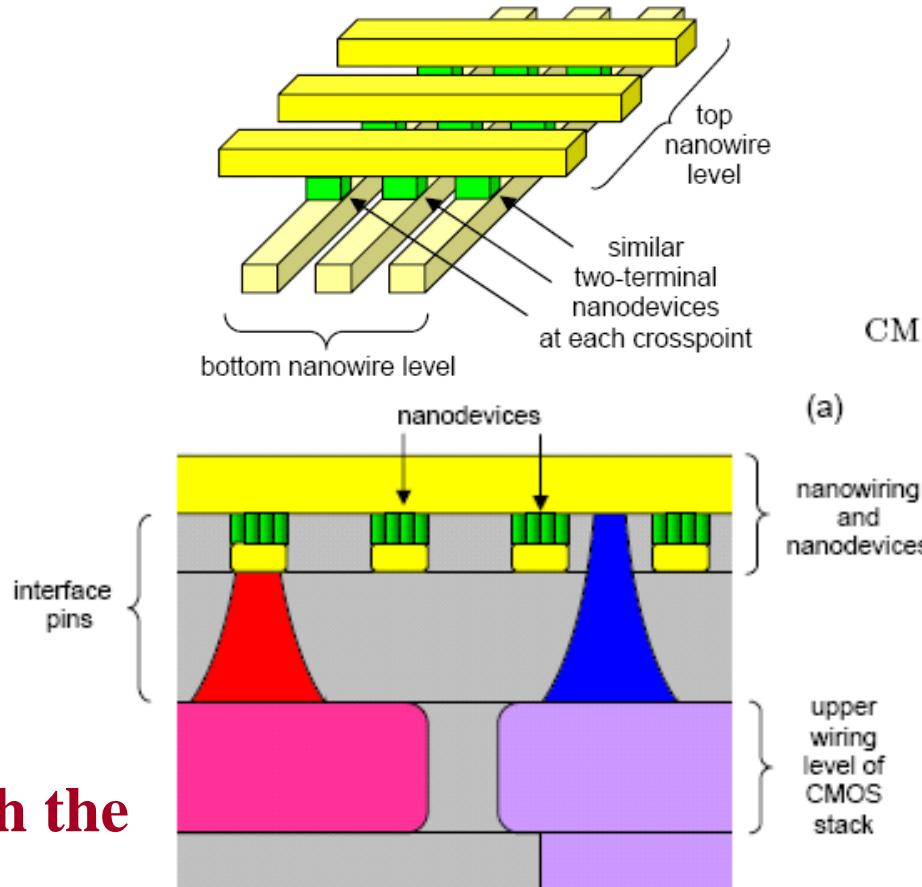
### polystyrene

# Summary

1. Opportunities beyond Silicon: **Ion / Atom** based **Switches**
2. Problems with atomically precise devices: **Defects**
3. Possible Solution: **Engineering** devices with **high “Defect” density**
4. Applications

## 4. Applications

- a) Memory
- b) Memory + Logics
- c) New architectures
- d) New Functionality



**When will computer hardware match the  
human brain?**

