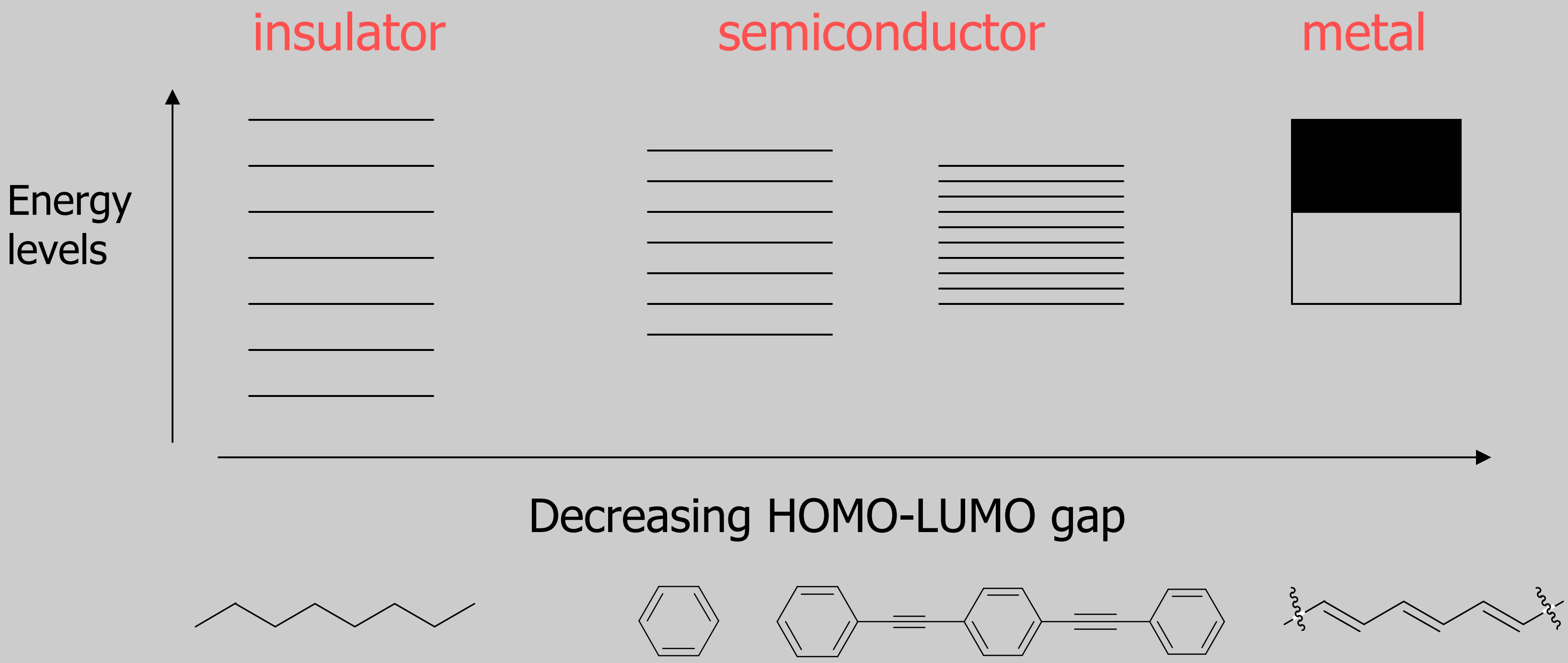
Molecular Electronics

Dr. Bin Yu

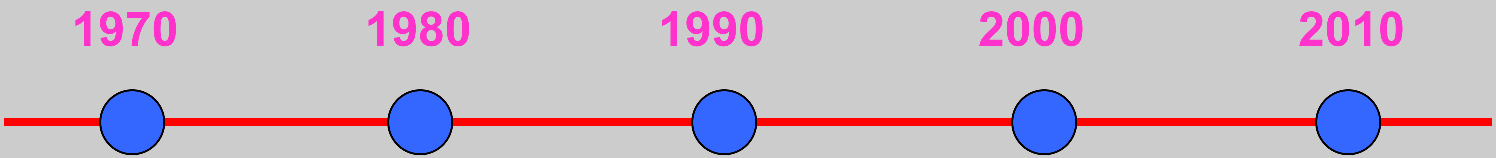
Electrical Engineering Course 379

Molecular Band Structure

- Molecules can be insulator, semiconductor and metal
- The band gap of a molecule can be tuned by its structure



Brief History of Molecular Electronics



Molecular logic and memory device demonstrated

Spiro-switch synthesized

Different variants of molecular rectifiers made

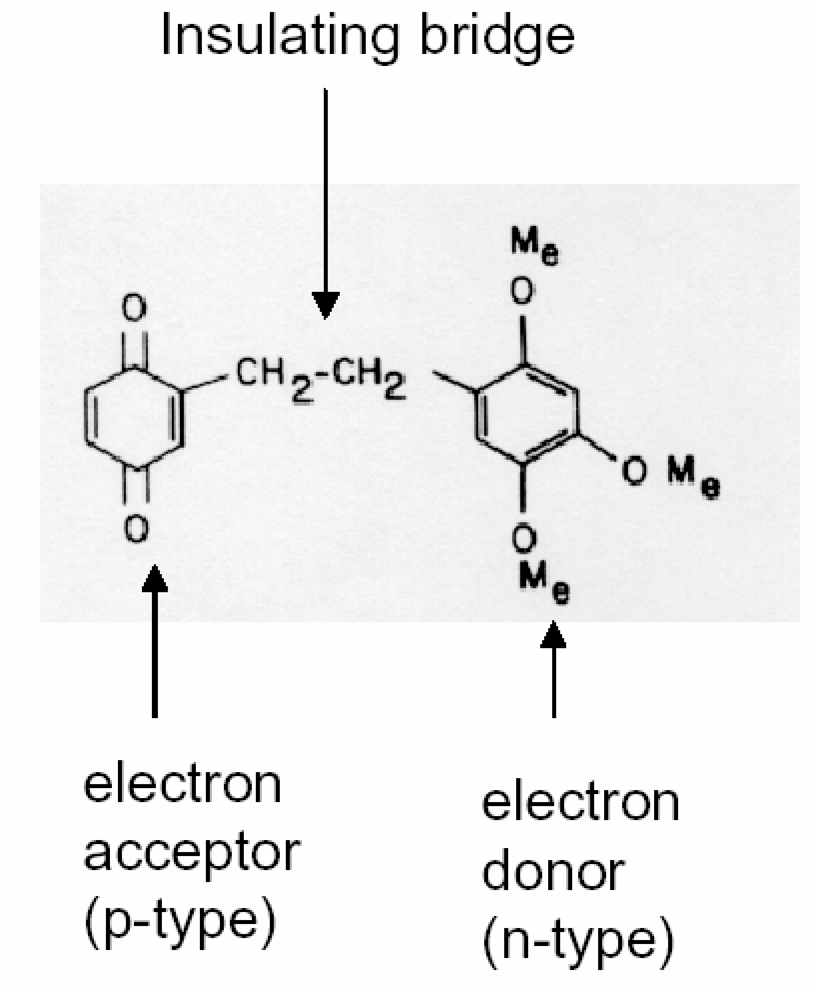
Individual molecular conductance measured

Modeling work

Sensitive new tools invented

- Theory on molecular rectification

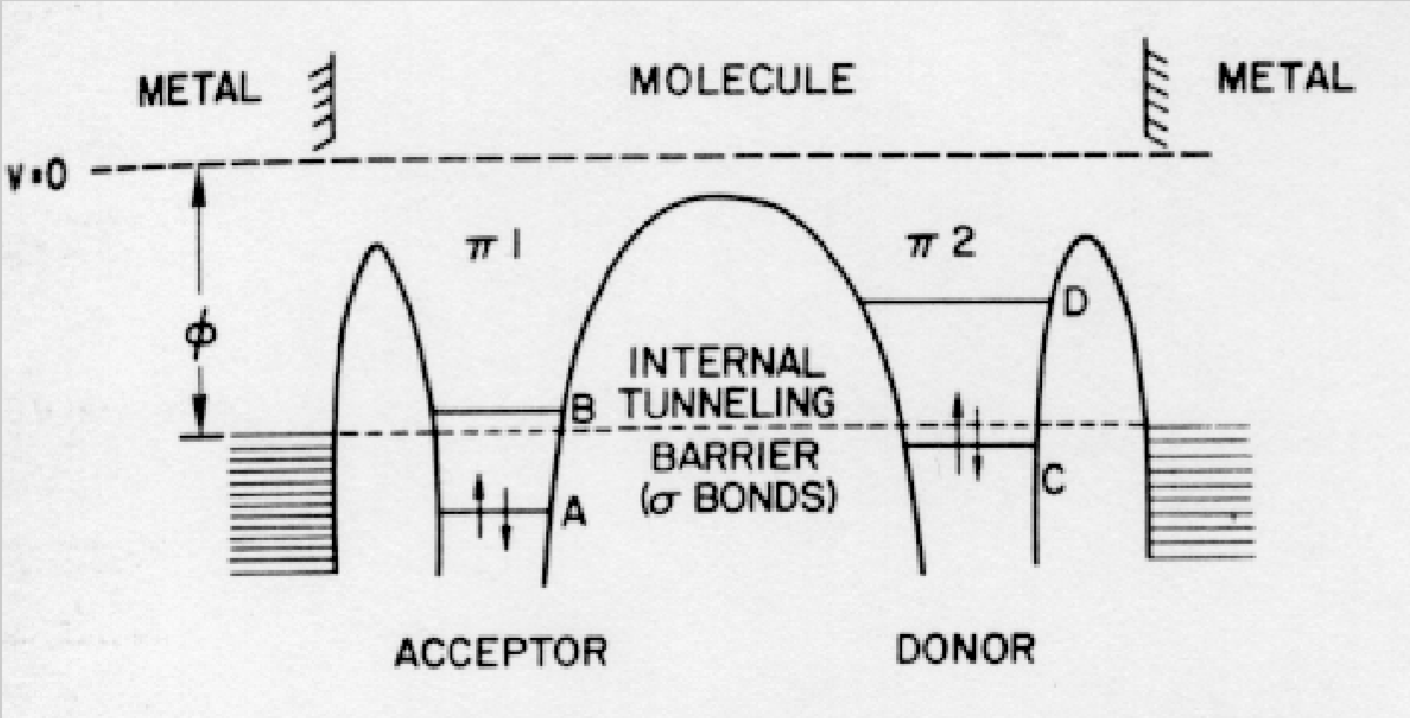
The Beginning of Molecular Electronics



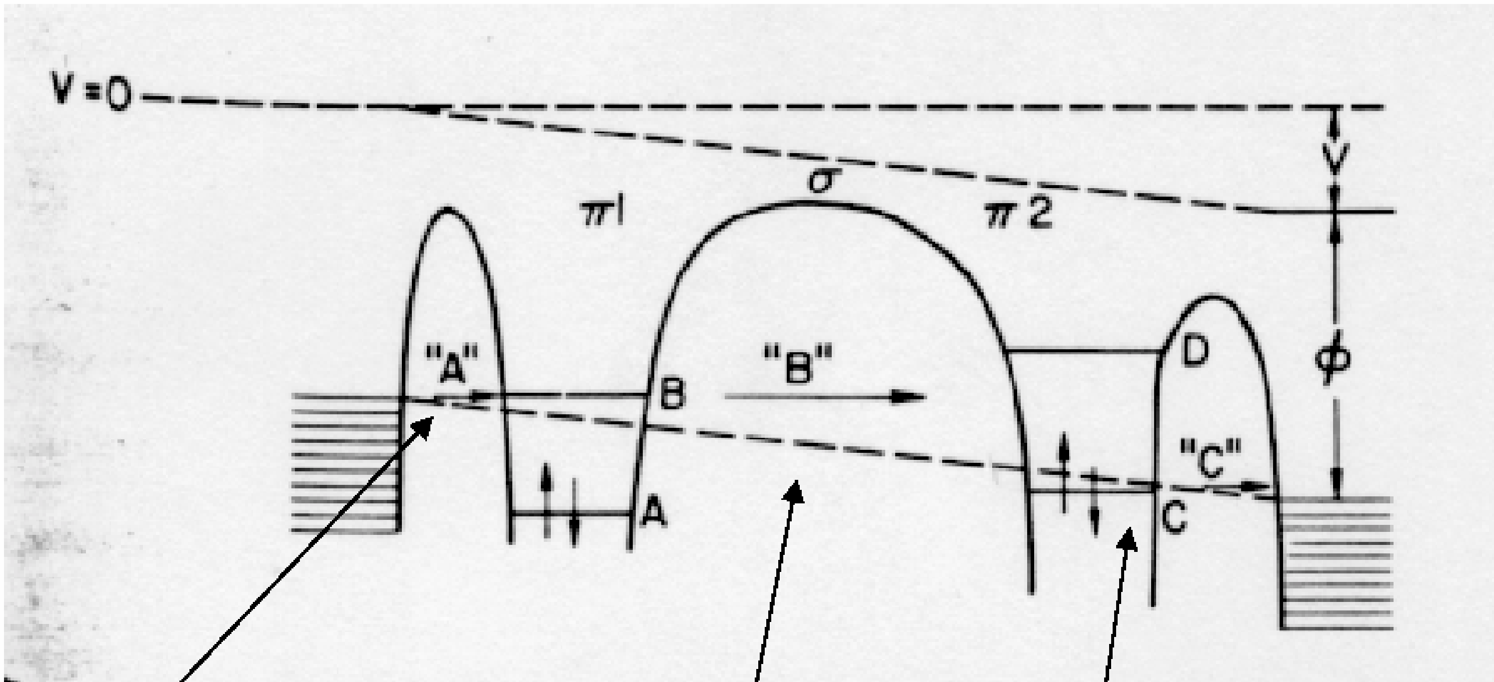
- In 1974 Aviram and Ratner predicted that molecules with a donor and acceptor would like a pn junction.

A. Aviram, Chem. Phys. Lett. 29 (1974) p.277

A Donor-Acceptor Junction



Forward Bias



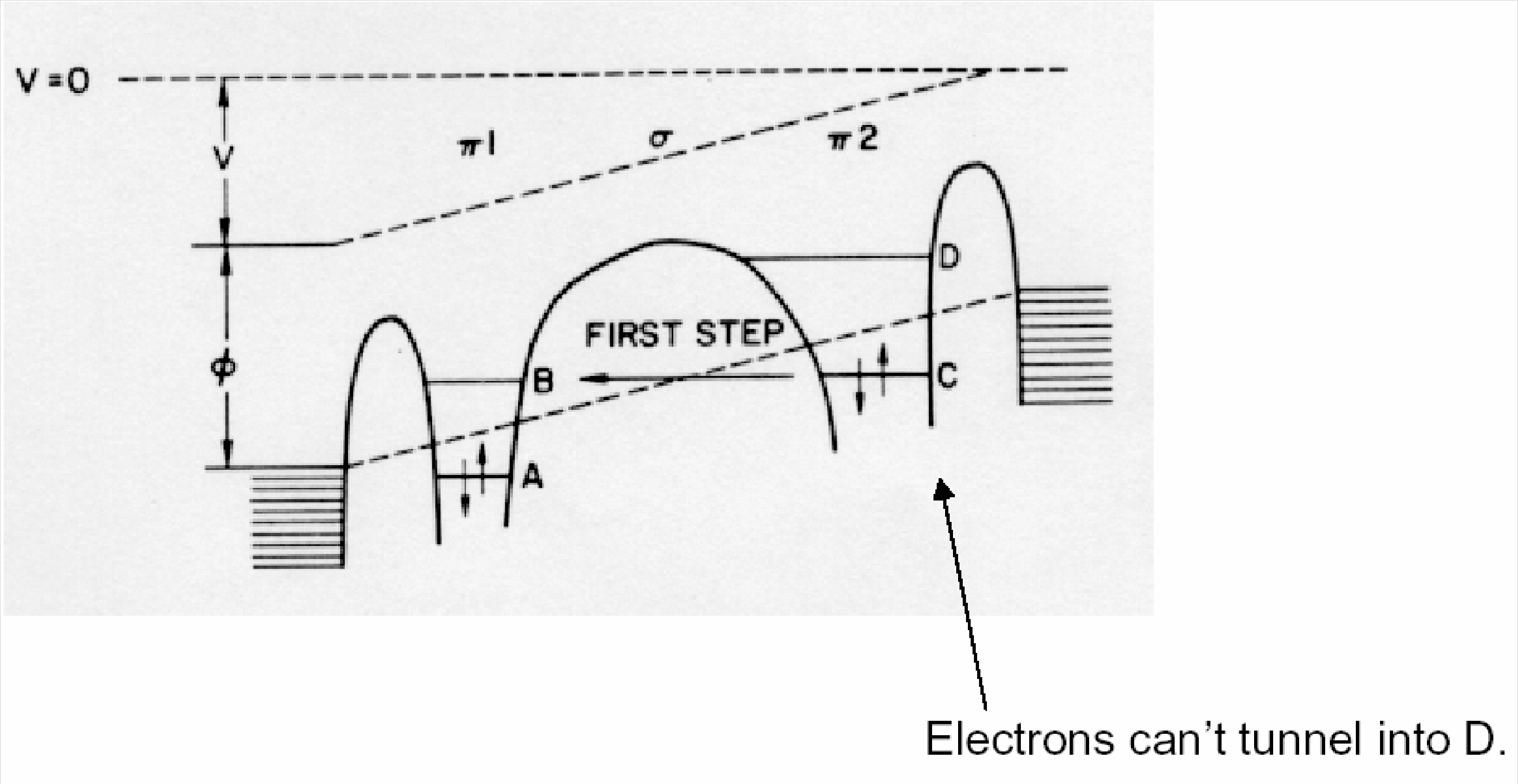
Electrons can easily tunnel across this barrier.

Electrons can tunnel from B to C if there are holes in C.

Holes can easily tunnel across this barrier.

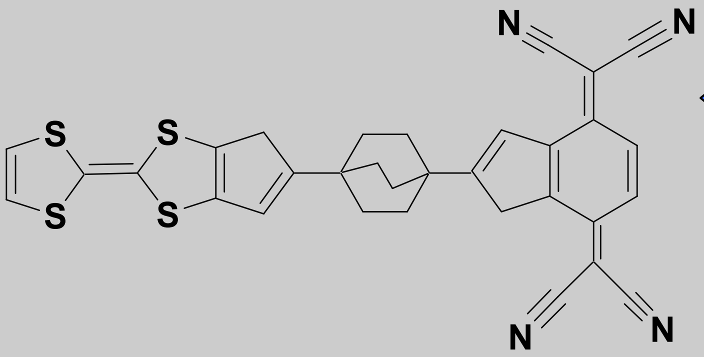
Current flows.

Reverse Bias

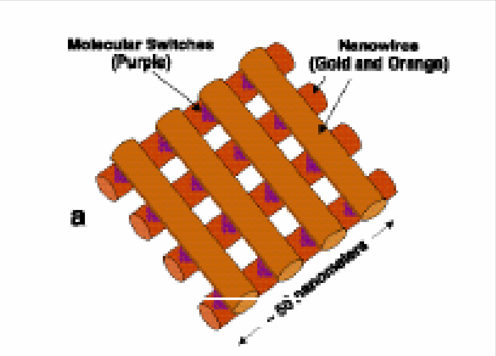


Very little current flows.

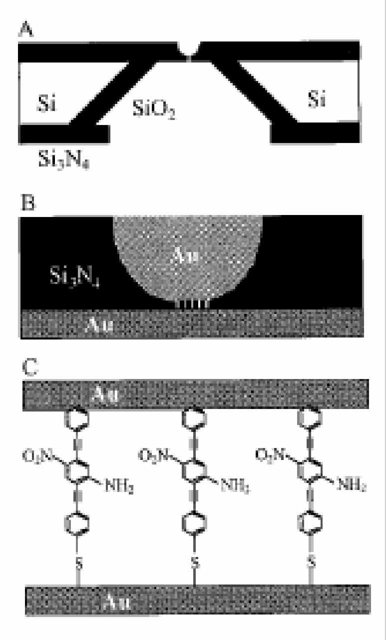
Molecule: Active Electronic Component



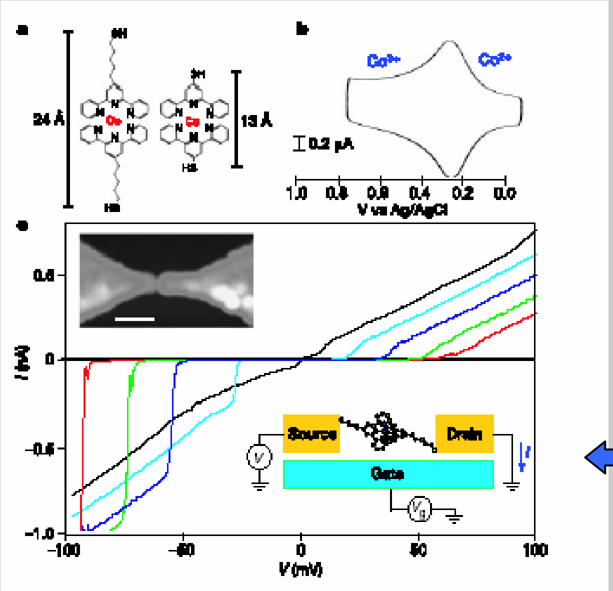
The Aviram-Ratner molecular rectifier 1974



Memory crossbar HP, 2001



Nanopore
Reed and Tour
1999



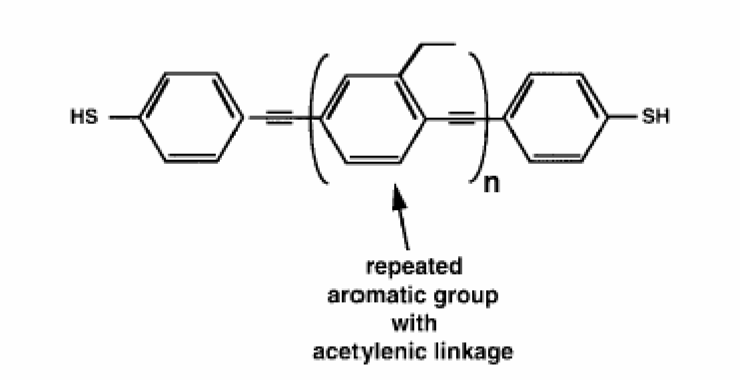
Kondo effect
McEuen and Park
2002

Why Molecule?

- 2 decades of work
- Individual molecules or supramolecular structures
- Covalently bonded molecular structures, electrically isolated from bulk substrate
- Different from “organic devices” that use bulk-effect electron transport
- Easily made identical by the trillions of billions
- Great power and variety of organic chemistry offers more options for designing and fabricating nm-scale devices than Si
- Inexpensive

Molecular Structures

- Molecular nanowires
  - A sequence of benzene-like rings connected by acetylene linkage
  - Orbital or clouds of π-electrons to form a single large orbital through the length of wire to permit mobile electrons to flow.



- Buckytubes
  - Carbob nanotubes
    - 10nm diameter CNT = > carry 10mA current

Why Molecular Devices?

- Nano-scale Dimension
  - The “last” engineering level human can handle
  - Few/single electron operation - low voltage / low power
- Uniform Components
  - Achieved by chemistry synthesis – less variation
- Tunable Functionality
  - Availability of many molecule species tailored for different device applications through surface chemistry engineering

Great potential to build ultra-dense, low-power, low-cost computing chips (logic, memory)

Molecular Transport

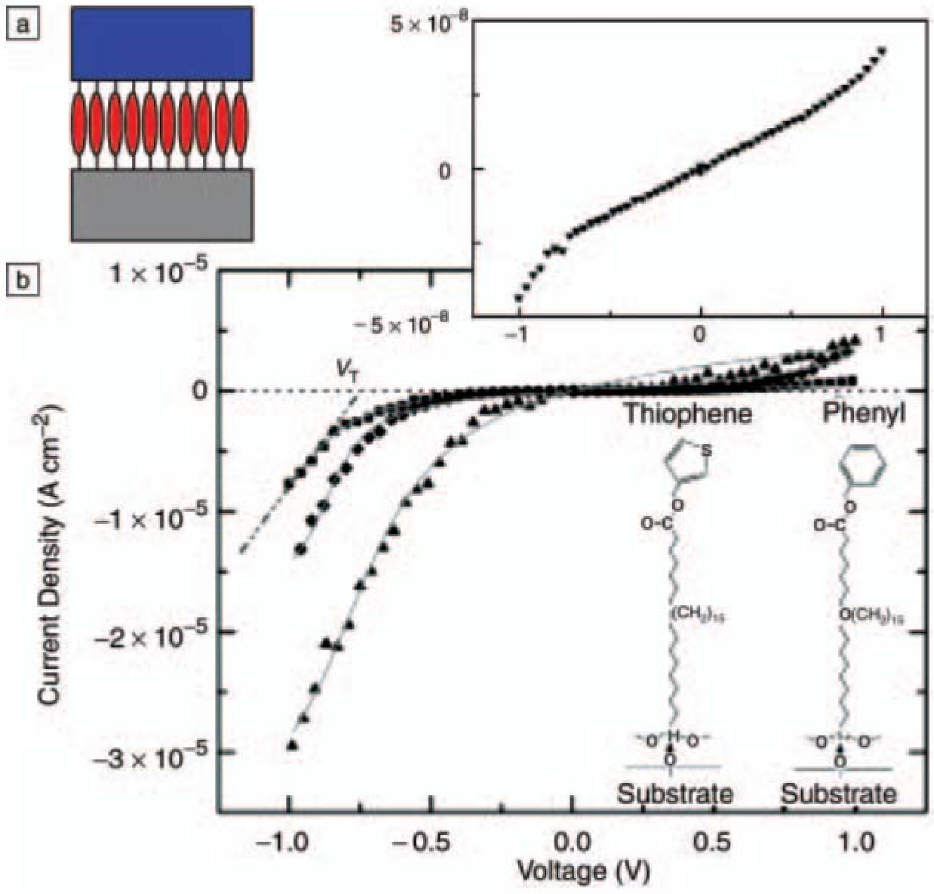
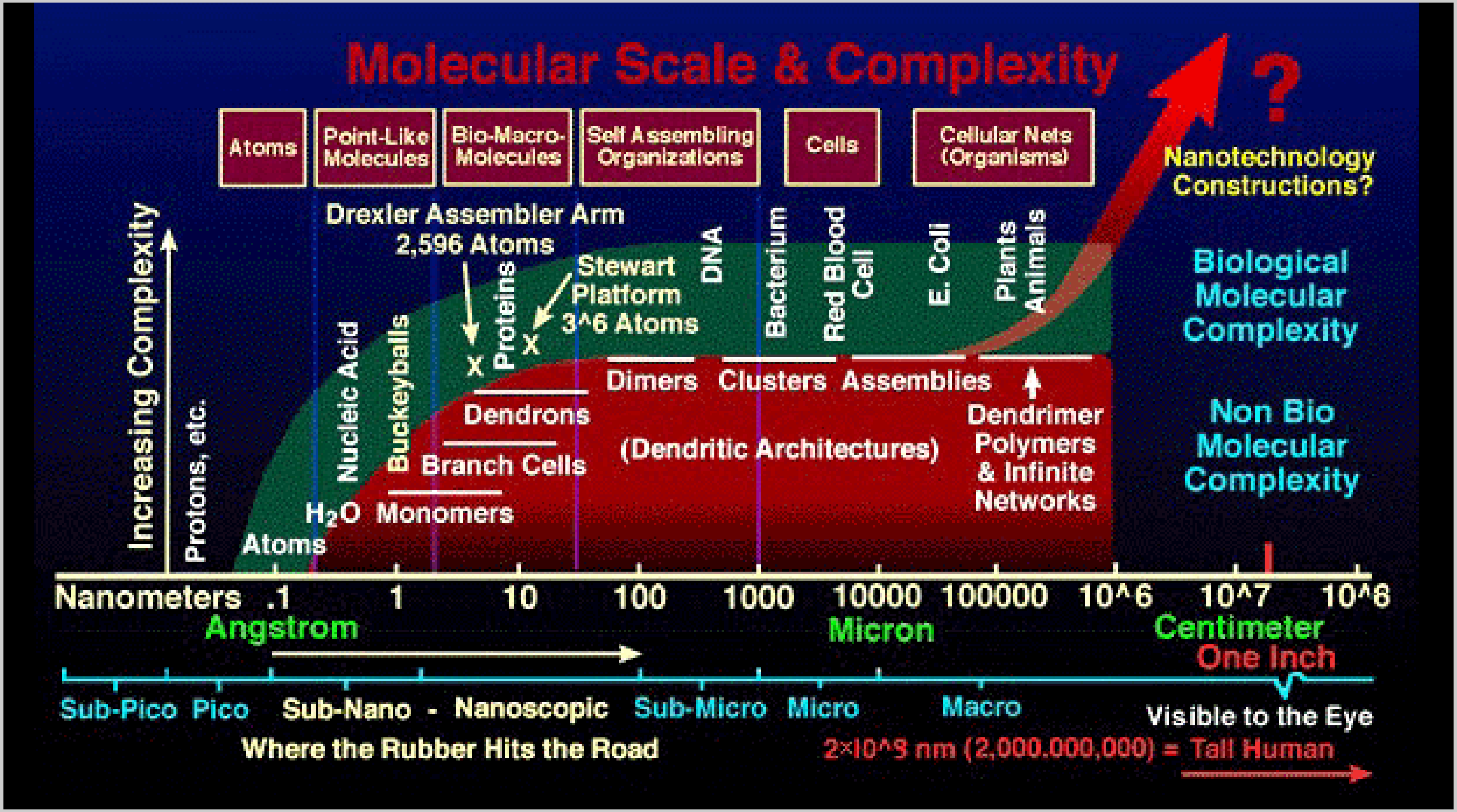
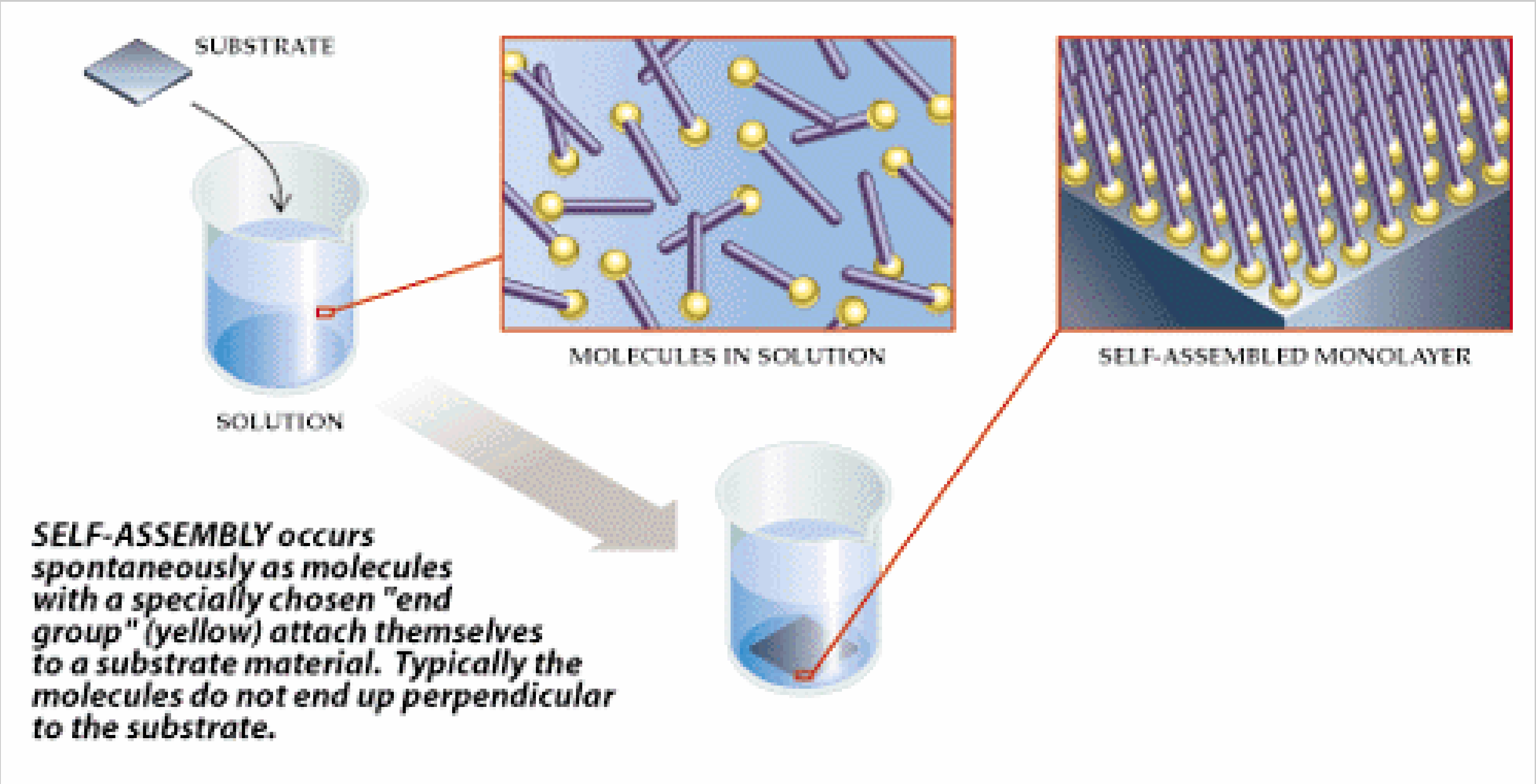


Figure 4. (a) Schematic illustration of a two-terminal vertically fabricated junction. (b) I–V characteristics showing rectification of a thiophene-terminated oct-7-en-1-trichlorosilane self-assembled monolayer (triangles), and phenyl-terminated (squares) and thiophene-terminated (diamonds) heptadec-16-en-1-trichlorosilane self-assembled monolayers, in a molecular junction between Al and n^+ Si electrodes. The top graph shows the graphical determination of the threshold voltage. V_T is taken as the intercept of the linear extrapolation of the I–V curve and the zero of the y axis. (Reprinted with permission from Reference 24.)

S. Lenfant, Nano Letters 2003


Molecular Scale & Complexity
Atoms
Point-Like Molecules
Bio-Macro-Molecules
Self Assembling Organizations
Cells
Cellular Nets (Organisms)
Nanotechnology Constructions?
Drexler Assembler Arm 2,596 Atoms
Stewart Platform 3^6 Atoms
DNA
Bacterium
Red Blood Cell
E. Coli
Plants Animals
Biological Molecular Complexity
Increasing Complexity
Protons, etc.
Nucleic Acid
Buckeyballs
Proteins
Dimers
Clusters
Assemblies
Dendrons
Branch Cells
(Dendritic Architectures)
Dendrimer Polymers & Infinite Networks
Non Bio Molecular Complexity
H_2O
Monomers
Atoms
Nanometers .1 1 10 100 1000 10000 100000 10^6 10^7 10^6
Angstrom
Micron
Centimeter
One Inch
Sub-Pico Pico Sub-Nano - Nanoscopic Sub-Micro Micro Macro
Visible to the Eye
Where the Rubber Hits the Road
2×10^9 nm (2,000,000,000) = Tall Human

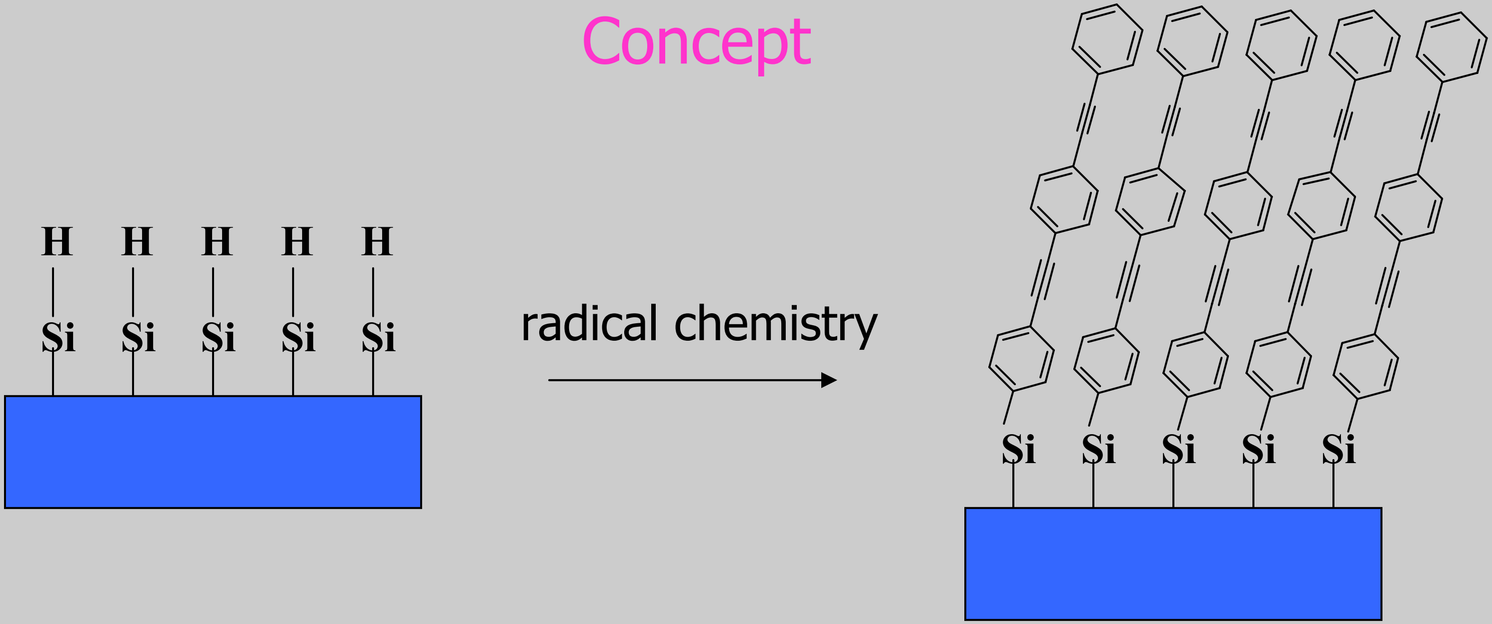
Molecular Self-Assembly



- At NASA lab, functional organic molecular monolayers can be self-assembled onto metal (Au) and semiconductor (Si, In_2O_3) surfaces

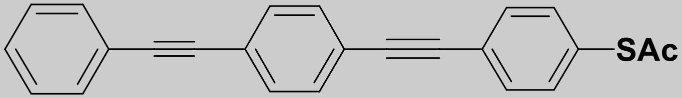
Radical Chemistry/Direct Functionalization on Si or Ge Surface

Concept

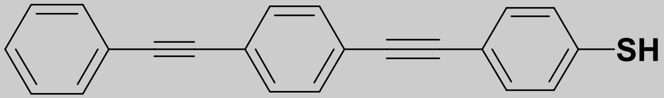


Direct attachment of conjugated systems onto Si surface will minimize coulomb blockade and give optimal electron transport behavior. In addition, the covalent nature of Si-C bond will give stable and robust devices.

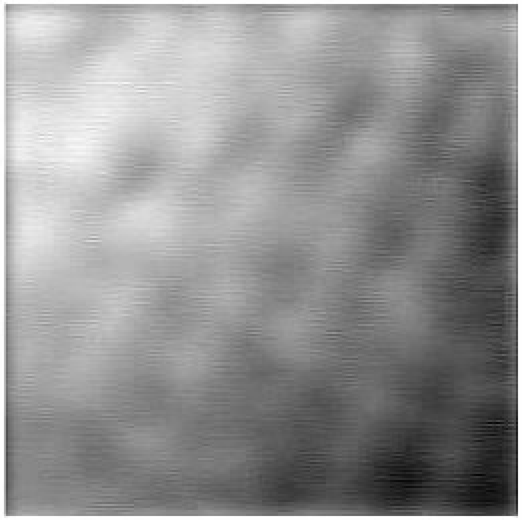
Self-Assembled Molecular Monolayer



1. Ammonium hydroxide/ tetrahydrofuran
2. Deposition on Au



1. Deposition on Au



The nature of the terminal group influences the order of the SAM.

Molecular Design Basis

Device Requirement

(1) Good self-assembly property
(2) Make good contacts
(3) Conducting
(4) Switching at low potential
(5) Magnetic property
(6) Optical/opto-electronic property
(7) Amenable to high density memory arrays
(8) Robust and stable

Chemical Synthesis

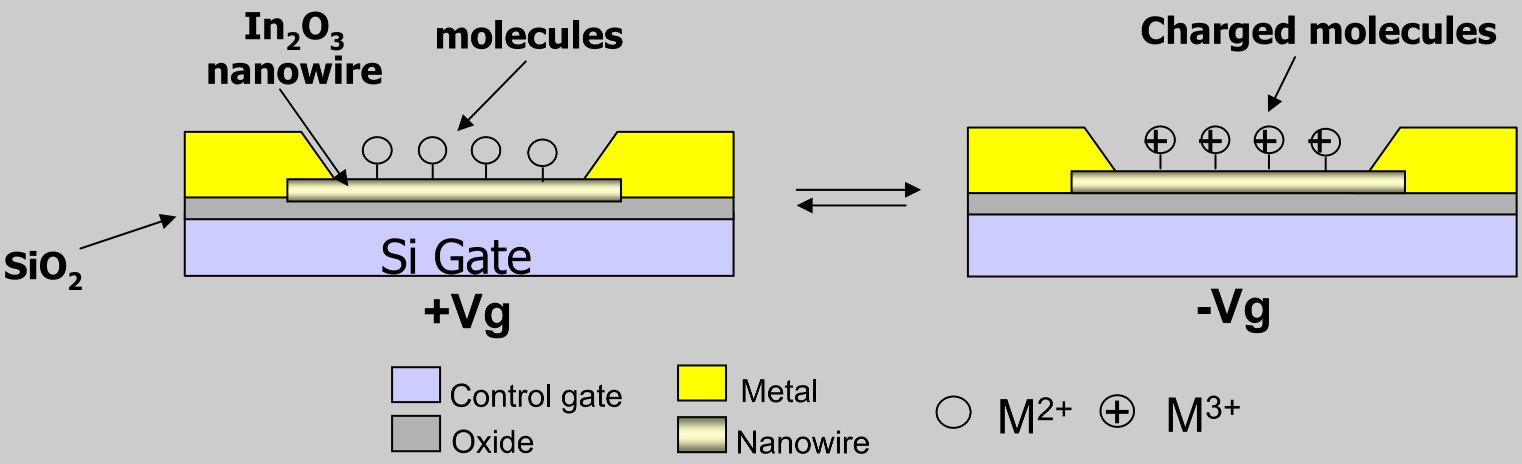
(1) Rigid rod-like structure
(2) Conjugated pi-electron system
(3) Facile redox properties
(4) Conformational barriers
(5) Metal-ligand charge transfer
(6) Transition metals with unpaired electrons
(7) Imbedded chemical interactions at strategic and periodic positions in molecules

Band gap engineering –

Molecular Memory: Issues

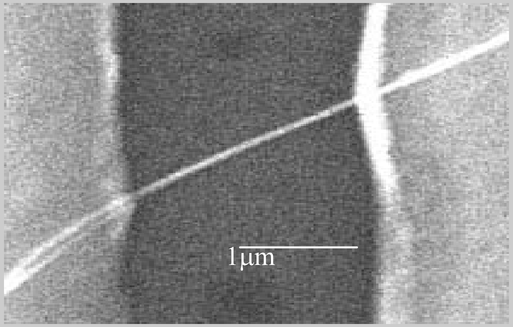
- Adhesion to ultra-small nanowire/nanotube for novel devices
- Localized charge distribution in the intermolecular direction – discrete charge storage nodes
- Molecule-semiconductor interface
  - Tunneling mechanism
  - Charge retention
  - endurance
- Quantum well effect – Coulomb Blockage?
- Thermal stability

Molecular-Nanowire Memory



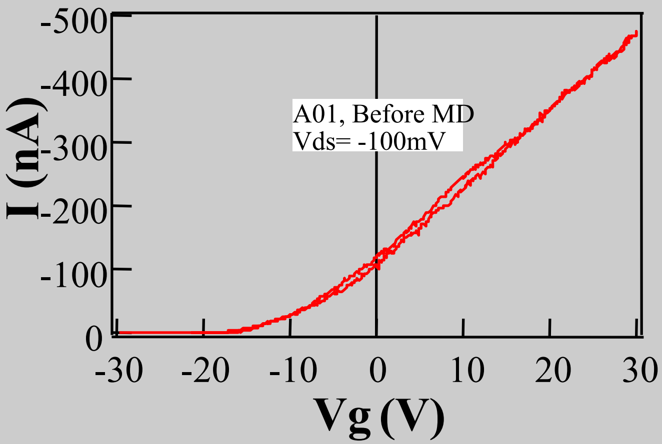
Key feature: Molecules are chemisorbed on doped In_2O_3 surface, molecular component (ligand/linker) replaces insulating oxide as charge transfer barrier.

As-fabricated device



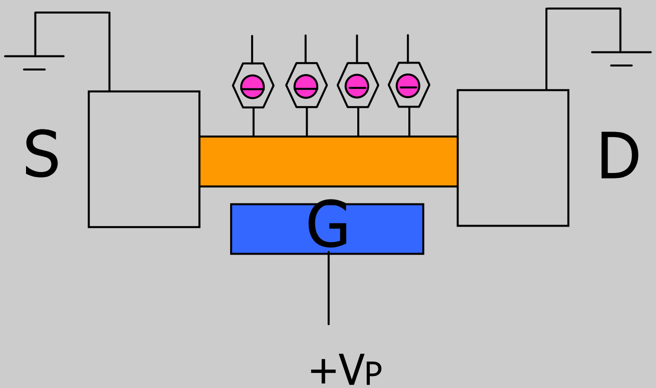
Li, et al. App. Phys. Lett. 2004.

Id-Vg

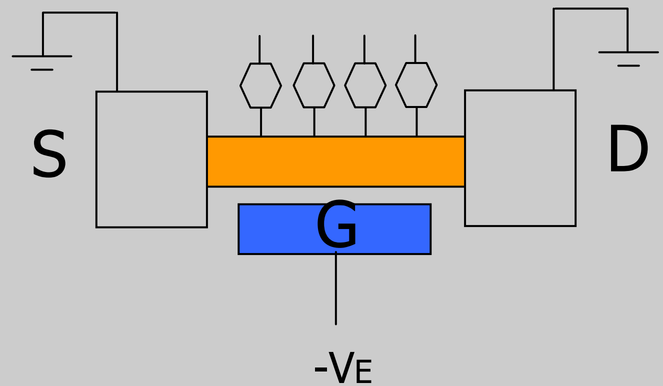


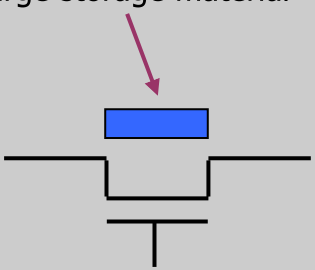
Molecular Memory

Programming (high V_{th})

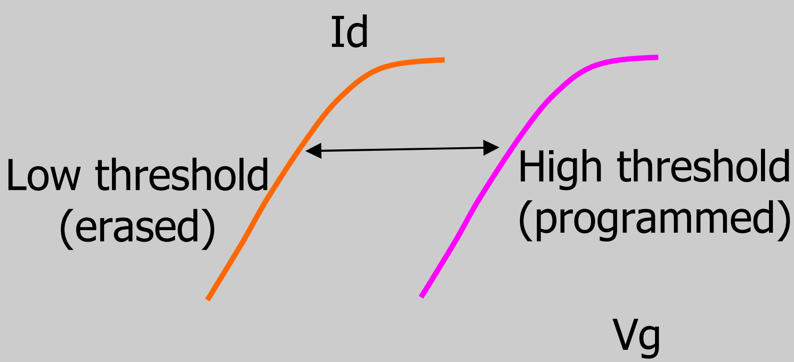


Erasing (low V_{th})



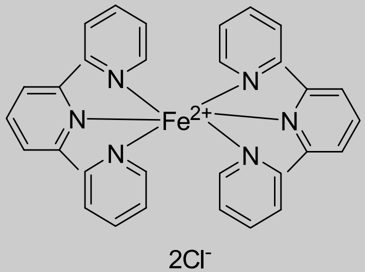


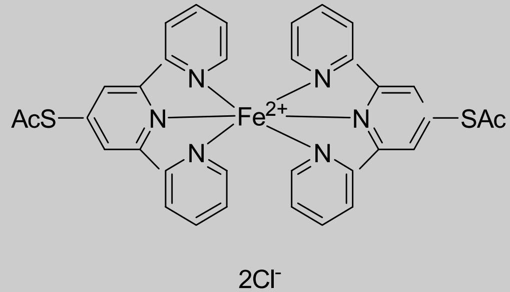
molecule memory
(non-volatile)

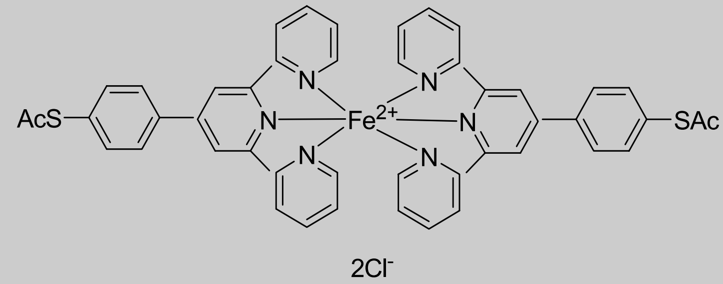


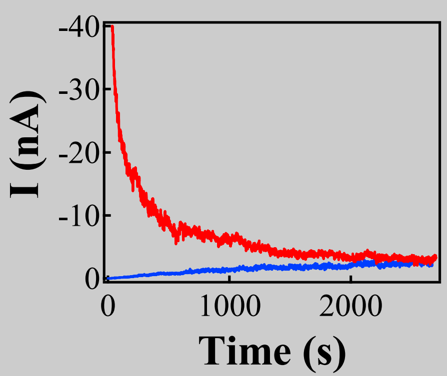
- Large gate bias for P/E
  - Positive $+V_P$ for programming
  - Negative $-V_E$ for erasure
- “Chemical gate” to modulate channel conductance

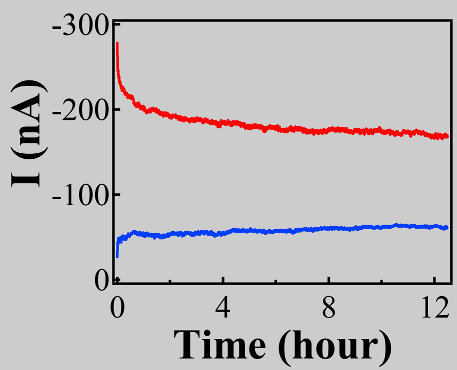
Contact and Barrier vs. Retention Time

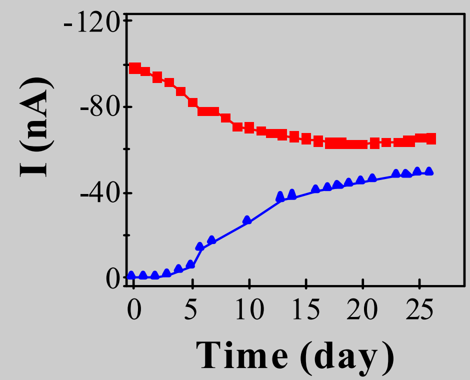












τ ~ 200 seconds

Physisorption
Poor contact
Weak barrier

τ ~ 12 hours

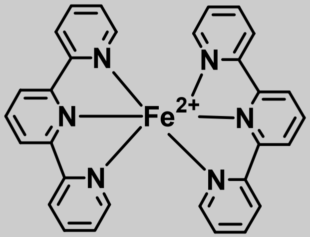
Chemisorption
Robust contact
Strong barrier

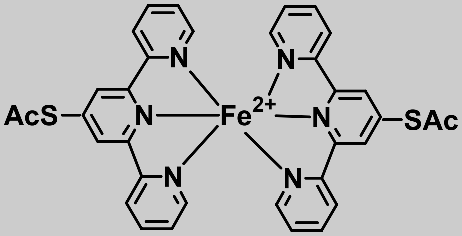
τ ~ 250 hours

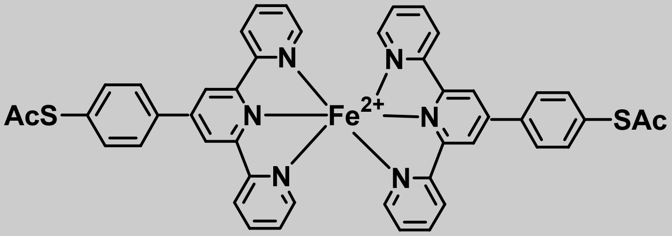
Chemisorption
Robst contact
Stronger barrier
(Conformation)

Li, et al. App. Phys. Lett. 2004.

Molecular Self Assembly on Nanowire







Physisorption
Poor contact
Weak barrier

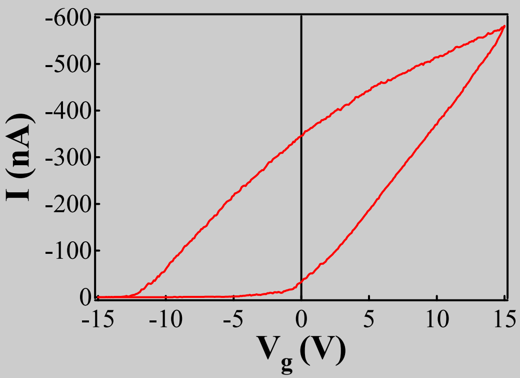
Chemisorption
Robust contact
Strong barrier

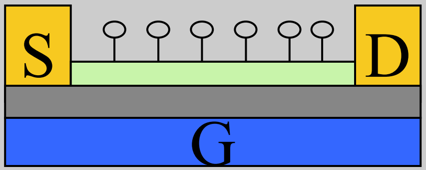
Chemisorption
Robst contact
Stronger barrier
(Conformation)

τ_{on}, τ_{off} ~ 100 seconds

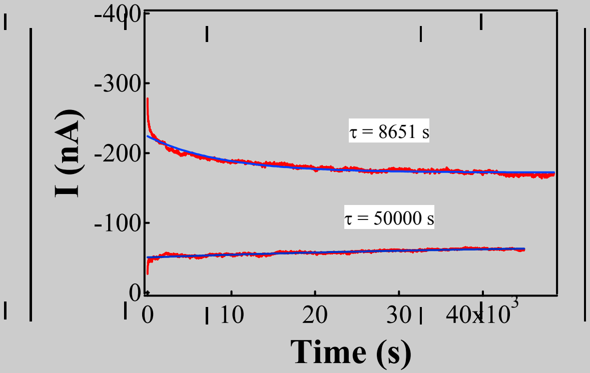
τ_{on}, τ_{off} ~ 2-3 hours

τ_{on}, τ_{off} ~ 600 hours

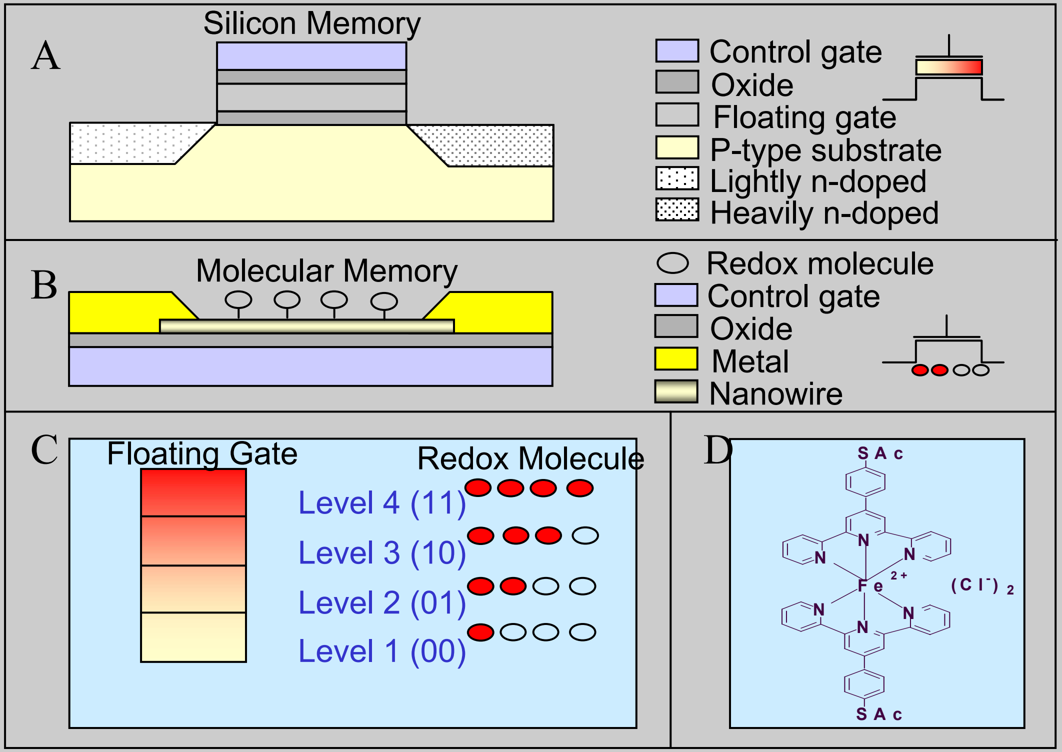


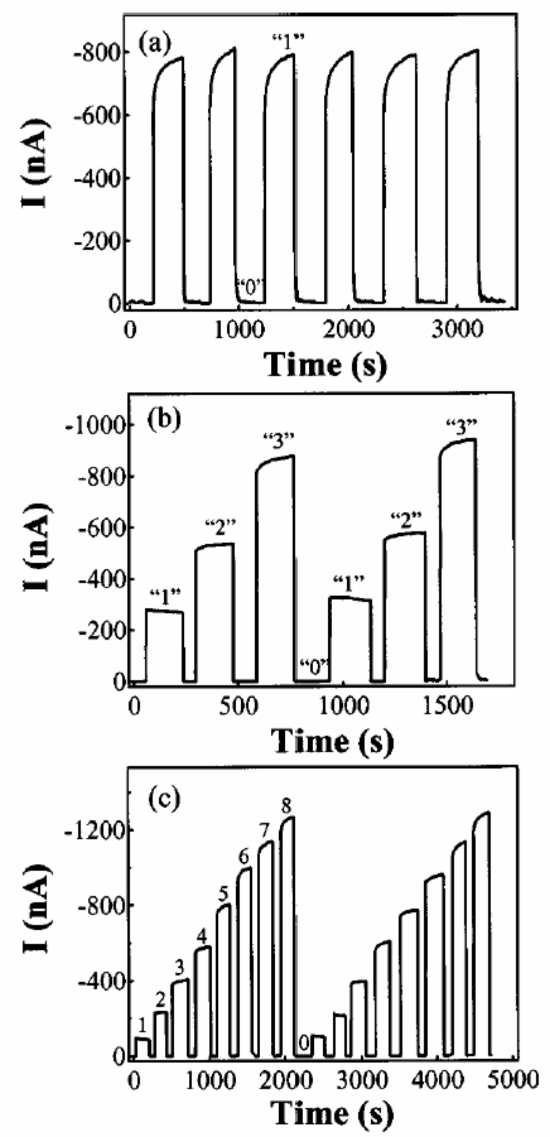


(W. Fan, NASA)



Multi-Level Molecular Memory

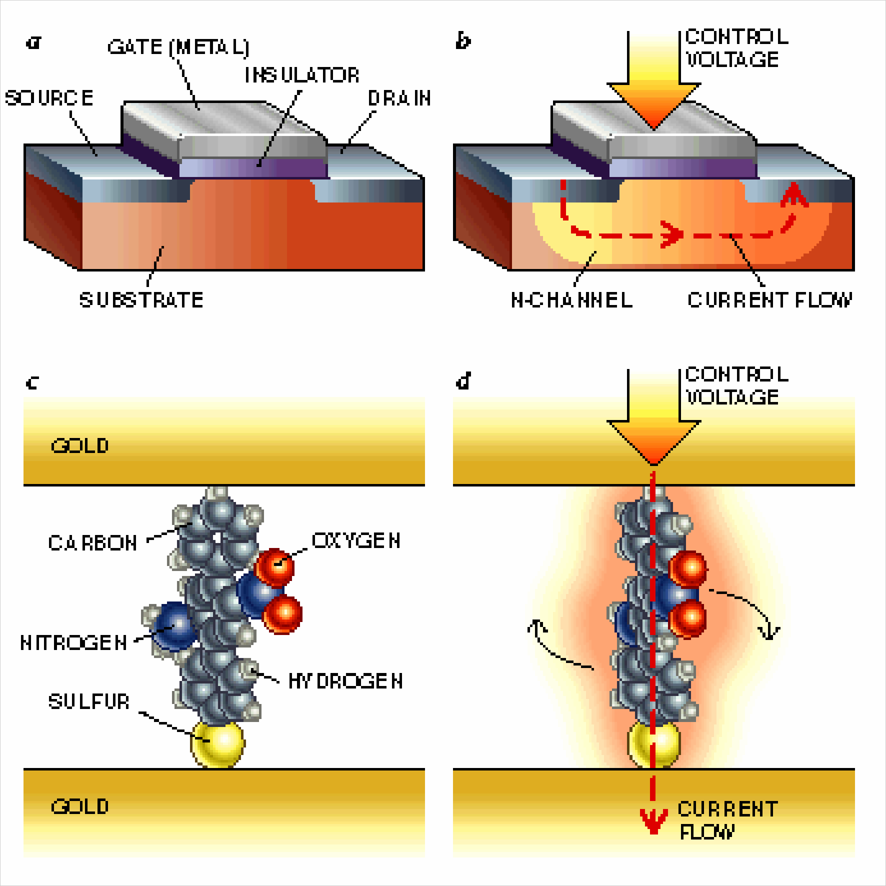




- Multilevel charge storage in redox molecules
- Nonvolatile nature (charge retention ~ 600 hours)

(NASA/USC, APL, March 2004)

Molecular Switch



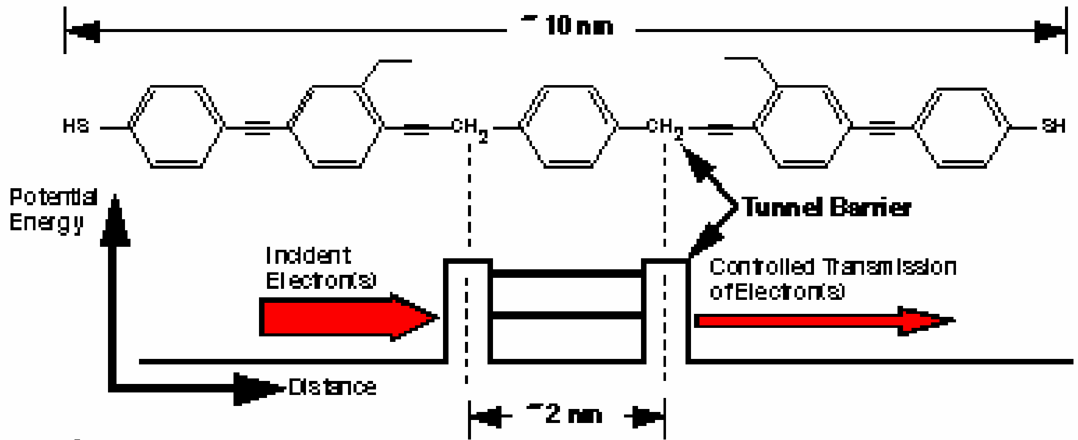
A molecule based on three benzene rings

With a specific voltage applied, the E-field twists the molecule and permits current to flow.

Molecular QM Devices

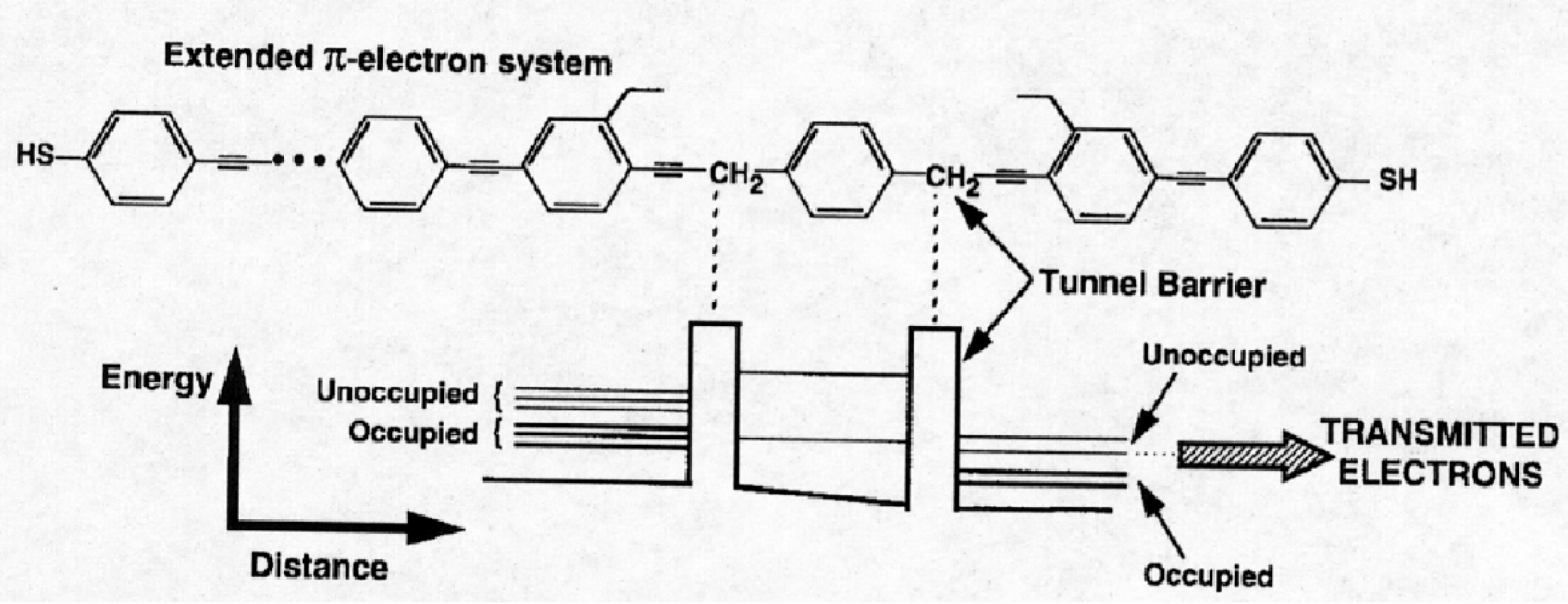
Molecular Electronic Wires and Nanometer-Scale, Quantum-Effect Switches

- Molecule can act as wire or as resonant tunneling diode
- Methylene groups create "barriers" along a molecular wire to control transmission of electrons through a quantum well



- Advantages:
  - Molecules much smaller and every one is exactly alike
  - Easily can be made in vast numbers (10^{23} at a time)

Proposed Resonant Tunneling in a Conjugated Molecule



A potential problem is that it could be hard to line up energy levels in the source, island and drain since the source and drain have a limited number of energy levels.

Goldhaber-Gordon, Proc. of IEEE, 85 (1997) p.521

Silicon-Base Molecular Device - Theory

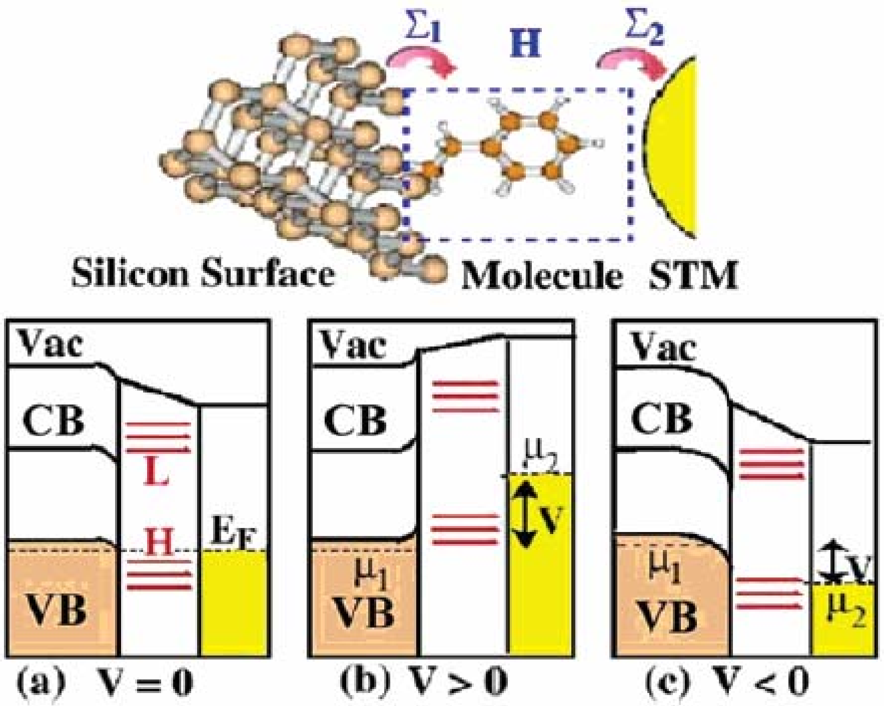


Figure 1. Schematic description of molecular RTD involving a silicon band edge (CB: conduction band, VB: valence band, Vac: vacuum, L: LUMO, H: HOMO) and an STM tip. Bottom: (a) Equilibrium band alignment in p-Si molecule−metal heterostructure corresponds to a flat Fermi energy E_F (dashed line) near the silicon VB edge. (b) For positive substrate bias V, the levels move up until the HOMO levels leave the silicon valence band into the band gap, leading to a sudden drop in transmission (Figure 3) and a corresponding NDR in the $I-V$ (Figure 4). (c) For negative bias, there is no NDR.

T. Rakshit, Nano Letters 2004

Silicon-Base Molecular Device - Theory

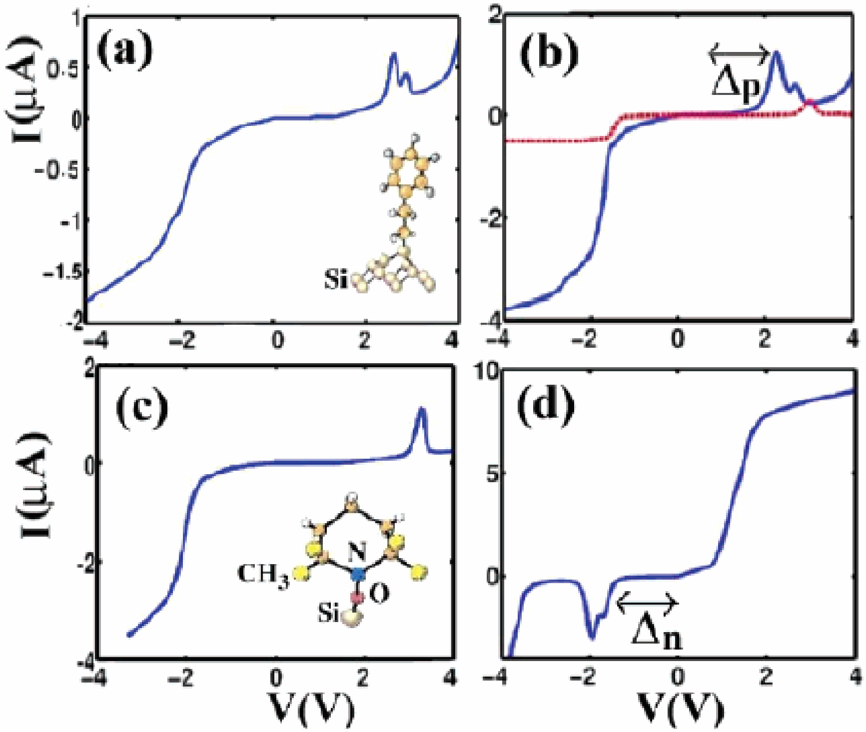
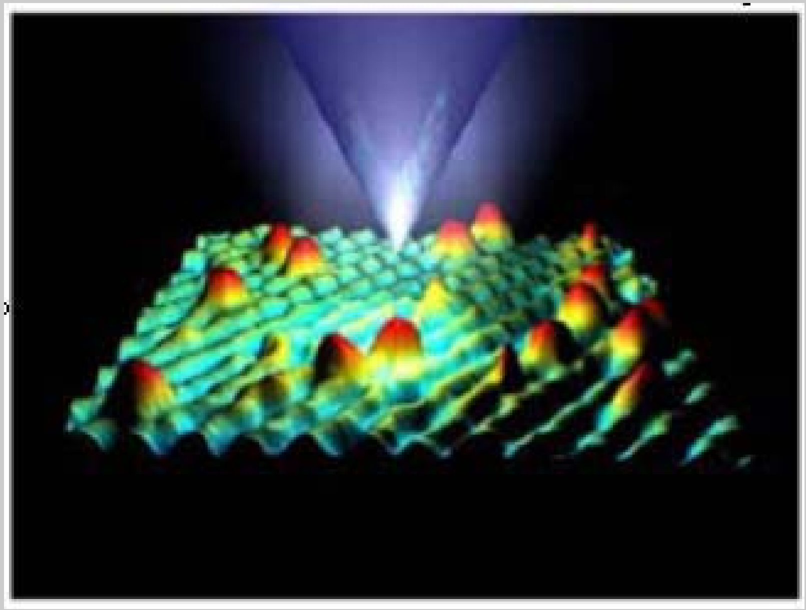
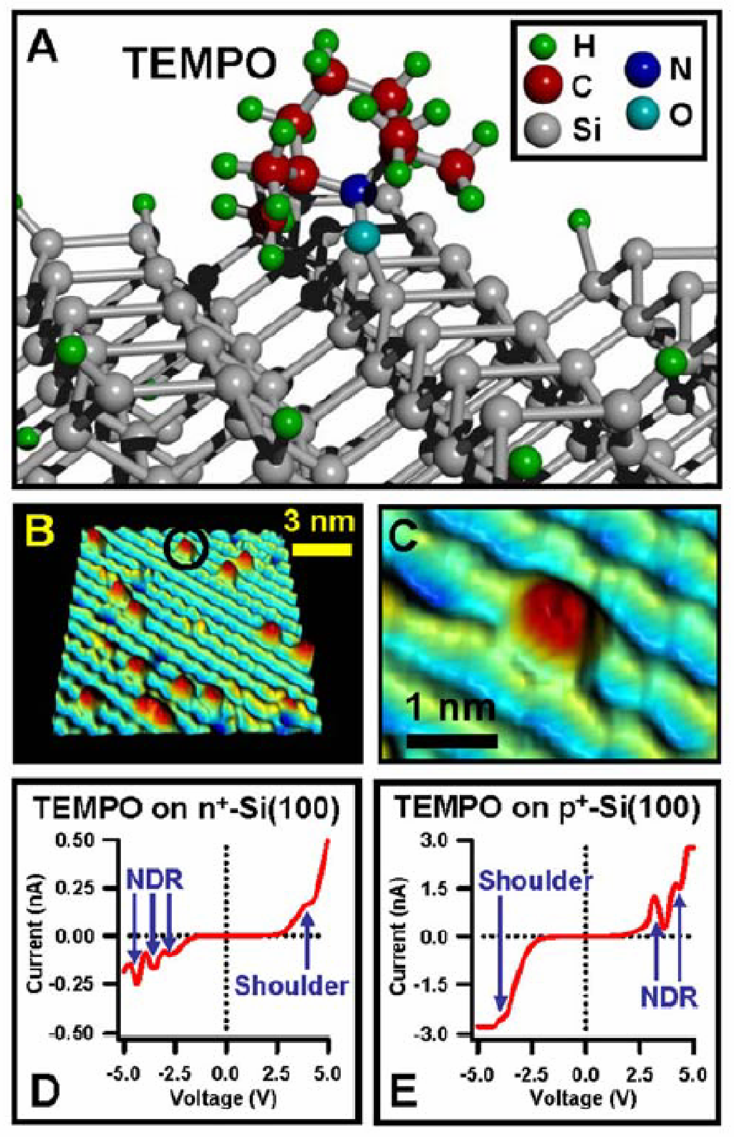


Figure 4. Calculated *I*−*V* curves for styrene on p-doped H:Si-(100) with an STM almost touching the molecule, using (a) EHT and (b) EM basis for Si. The calculations are non self-consistent at this time (ref 29). Increasing the air gap to 2 Å (dashed line) decreases the current and postpones the NDR. (c) *I*−*V* for TEMPO on p-Si(100) (EM) and (d) styrene on n-doped H:Si(100) (EM) (ref 31). The NDR reverses polarity on reversing doping, although in calculations for this specific geometry, we had to lower the LUMO levels artificially to bring the NDR into the bias window.

T. Rakshit, Nano Letters 2004

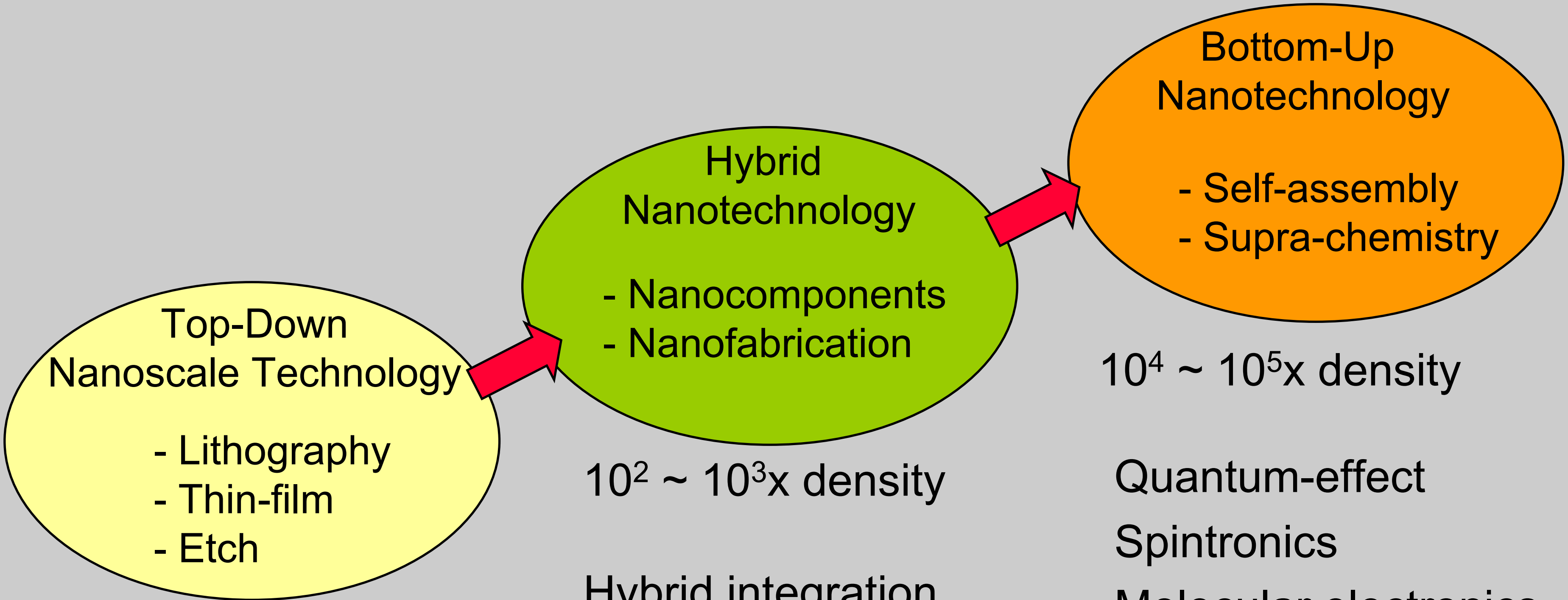
Silicon-Base Molecular Device - Experiment





M. Hersan, 2004

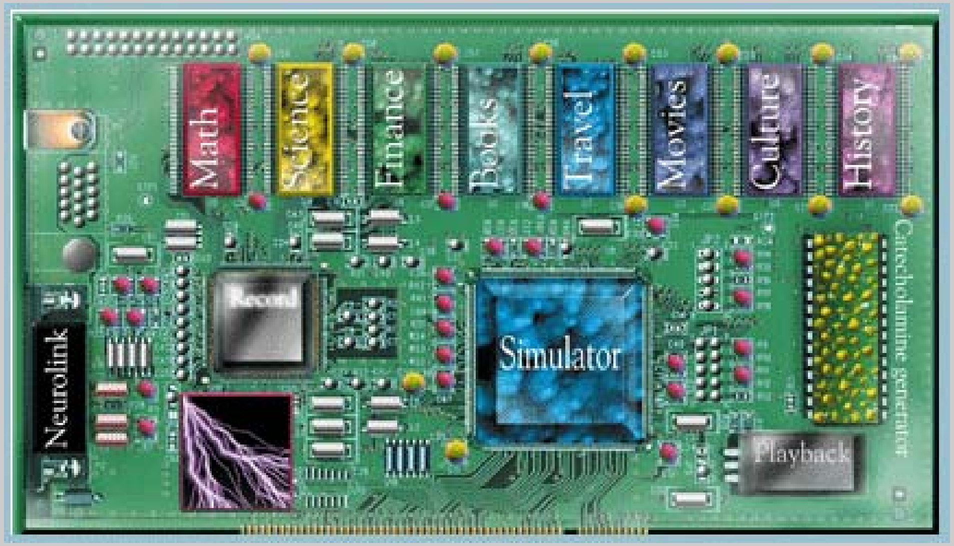
Electronics: Possible Evolution Path



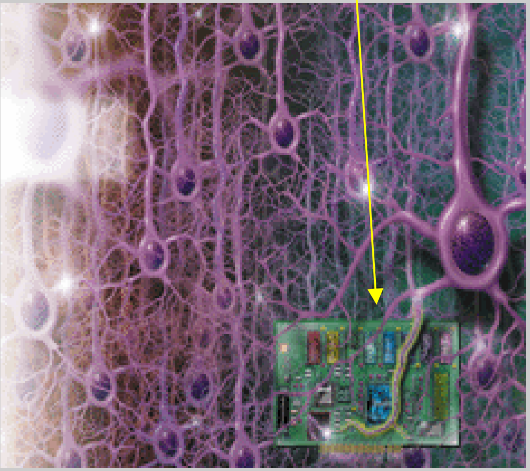
Hybrid integration
quantum-effect/bulk
effect

Microelectronics
Bulk-effect

Merging of Mind and Machine



Neural Implants



our intelligent creations will soon eclipse us

and that their creations will eventually eclipse them.