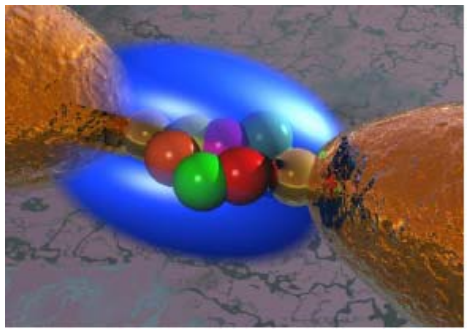
Molecular Electronics and Charge Transfer on the Nanoscale

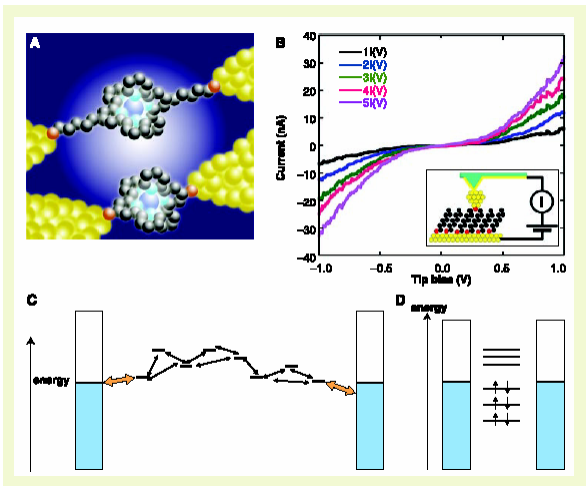
- Molecular electronics
  - definition, motivations, issues
- Charge transfer on the nanoscale
  - introduction, classical and quantum transports
  - electrode-molecule-electrode structure
  - SPM studies
  - other issues
- Miscellaneous
  - molecular vehicle, architecture, interconnection, fabrication

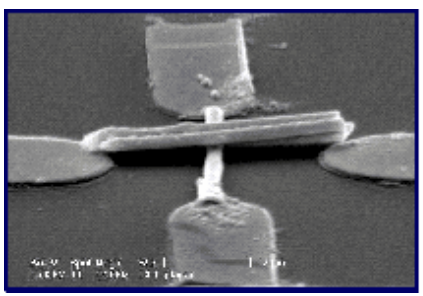
- **Molecular Electronics (ME)**

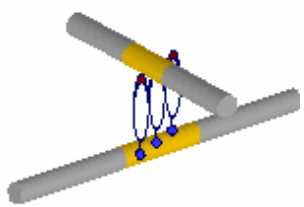
Molecular Electronic Device (MED)

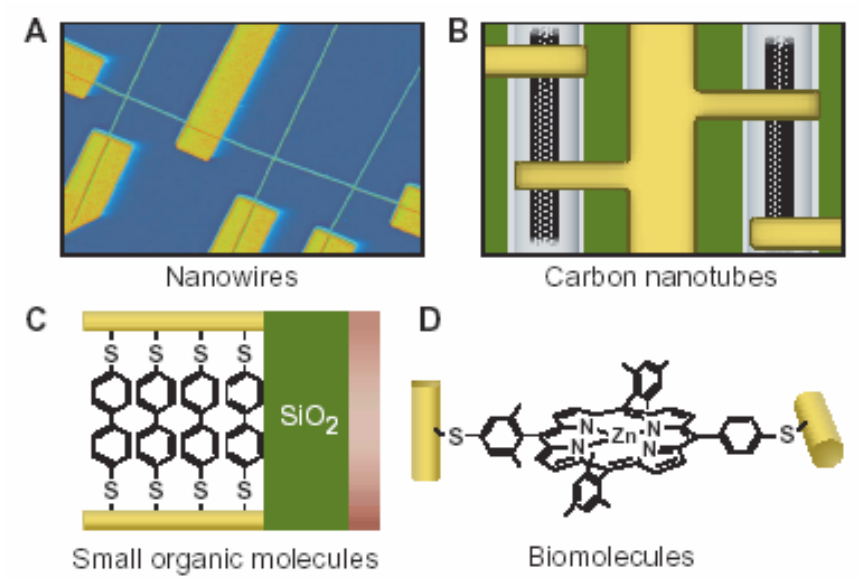


- Utilization of single or a few molecules for electronic device functions, such as diode, transistor, switch, and memory.
- Types of molecule
  - nano-structured materials: nanowire, nanotube, nanoparticle
  - small organic molecules: Tour wire, alkyl chain, …
  - biomolecules: DNA, ferrocene, …

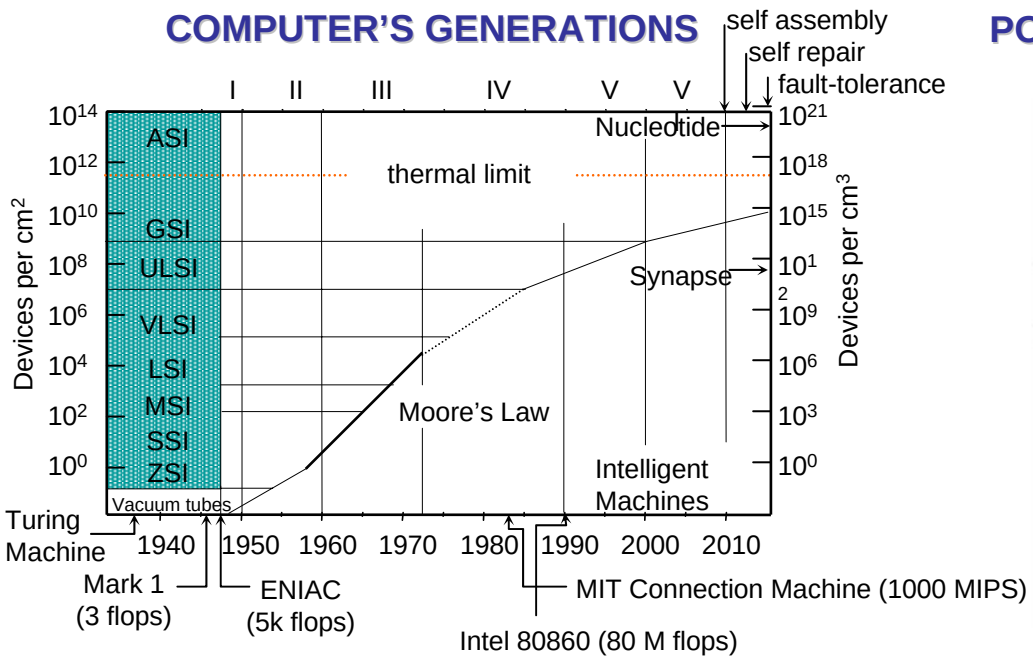


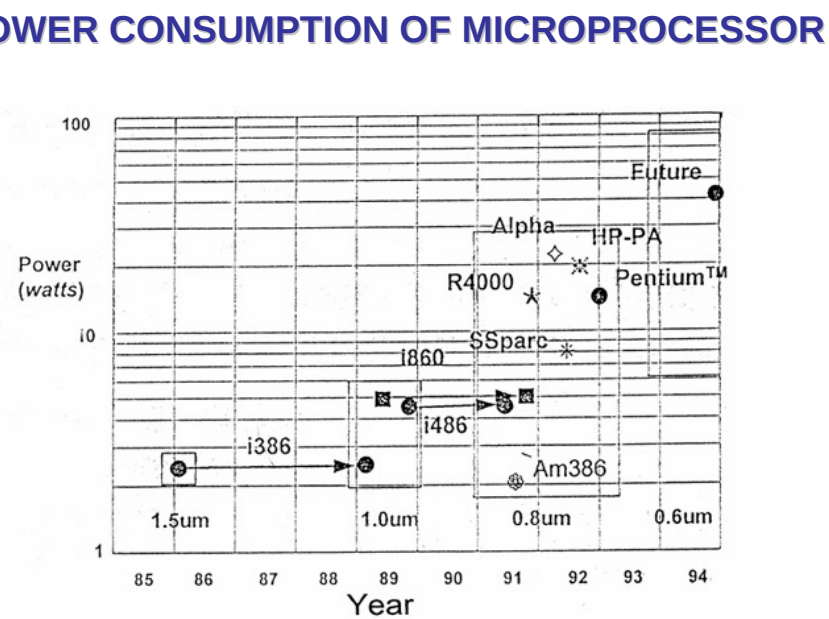






Motivation – Moore's law





Scientific American June 2000, 86

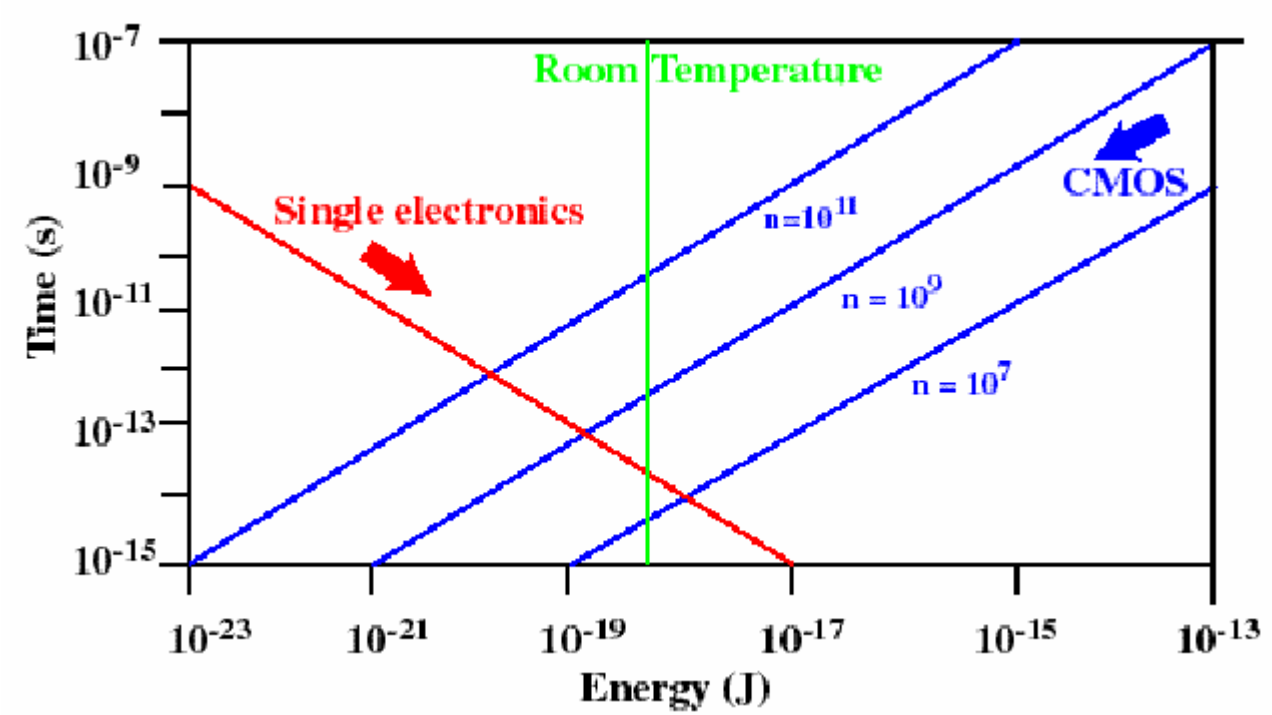
Motivation – size and cost

- **Size**: we will eventually reach the molecular scale (~ nm), probably in this century.
  - fabrication process: top-down, bottom-up, combined
  - materials: Si, C, other materials
  - device structure: nano-CMOS, SET, MRAM, PRAM, Qubit, spin-FET, ….
- **Cost**: as the feature size continues to scale down,

  exponential increase of manufacturing cost is expected.

  → cheaper and easier way of fabrication is required.
- Other factors
  - **speed**: good if fast enough (> 10 GHz).
  - **power consumption**: should be low enough for room temperature operation.
  - **biological considerations**: bio-compatible?

Theoretical limits



- Thermal limit: 2 eV ~ 4 x 10^{-19} J ~ 100 times of kT
- Quantum limit: $\Delta E \Delta t = \Delta E / f \sim 100\ h$
- Dissipation limit: $p = EfnP < 100$ W/cm^2

ME - components and issues

- device units
  - two-terminal devices: diode, capacitor, resistor, capacitor, …
  - three-terminal devices: bipolar Tr., Field Effect Tr., Single-Electron Tr, …
  - memory: 1C1T
- interconnection: nanotube, nanowire, …
- fabrication process: e-beam lithography, self assembly, nano imprint, …
- software: defect-tolerant architecture, quantum cellular automata, …

- issues
  - charge transfer inside the molecule: tunneling, hopping, ballistic, …
  - molecule-electrode junction: Schottky barrier, tunneling, thermionic emission, …
  - molecular conformation: oxidation and reduction, bending, twisting, vibration, …
  - theoretical models
  - electric field, thermal stability, power consumption, power gain, gating, …

Technology roadmap for DRAM

Year of first DRAM shipment	1997	1999	2001	2003	2006	2009	2012
Bits / chip - DRAM	256M	1G	-	4G	16G	64G	256G
Transistors / chip - MPU	11M	21M	40M	76M	200M	520M	1.4G
Minimum feature size DRAM (nm)	250	180	150	130	100	70	50
Minimum feature size MPU (nm)	200	140	120	100	70	50	35
Local clock (GHz)	0.75	1.25	1.5	2.1	3.5	6.0	10.0
Across chip clock (GHz)	0.75	1.2	1.4	1.6	2.0	2.5	3.0
Wafer size (mm)	200	300	300	300	300	450	450
No. levels of interconnect	6	6-7	7	7	7-8	8-9	9
Chip size - DRAM (mm^2)	280	400	445	560	790	1120	1580
Chip size - MPU (mm^2)	300	340	385	430	520	620	750
Power dissipation (W)	70	90	110	130	160	170	175
Power dissipation - hand-held / portable (W)	1.2	1.4	1.7	2	2.4	2.8	3.2
Cost / bit packaged DRAM (µcent)	120	60	30	15	5.3	1.9	0.66
"Afforable" cost/transistor MPU- packaged (µcent)	3000	1735	1000	580	255	110	50
Cost of fab	1.5B$				>5B$		

- Feature size: 30 nm or smaller
- Density: $10^{10}/cm^2$
- Cost: less than 0.7 µcent/bit
- Frequency: 10 GHz operation
- Power: less than 170 W (1.4 billion Tr.)

SIA NTRS (1997)

Memory devices - comparison

Consumer	Military	Space	Attribute	SRAM	DRAM	RTD	SET	MRAM
✔	✔	✔	Low power		✔	✔	✔	✔
✔	✔	✔	Non-volatile					✔
✔	✔	✔	Fast write	✔	✔	✔		
	✔	✔	Radiation hard	✔				✔
		✔	Unlimited R/W	✔	✔	✔	✔	✔
✔	✔	✔	High density	✔	✔	✔	✔	✔
✔	✔	✔	Highly reliable	✔	✔	✔		✔
✔	✔	✔	Random access	✔	✔	✔	✔	✔
		✔	Fast access	✔	✔	✔	✔	✔
✔	✔	✔	Fast read	✔	✔			✔
✔	✔	✔	Low write power	✔	✔			✔
		✔	Long term storage	✔	✔			✔
✔	✔	✔	Noise					
✔	✔	✔	Testing	✔	✔			✔
	✔		High power					

Table 1.2:- Comparison of memory applications and technologies

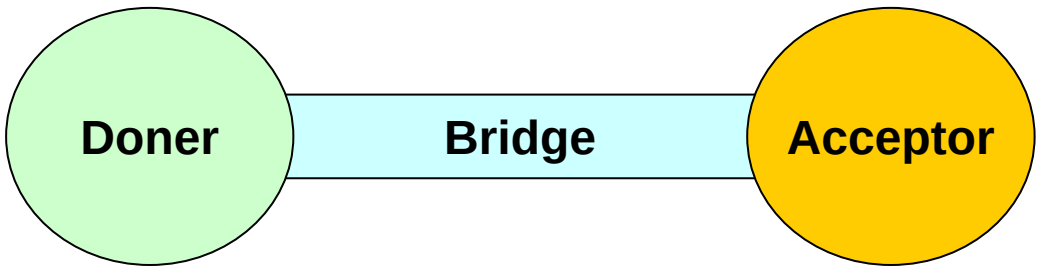
Can we solve all (or most of) the problems related to the attributes cited above?

- **Charge transfer on the nanoscale:**

  introduction

Charge transfer on the nanoscale

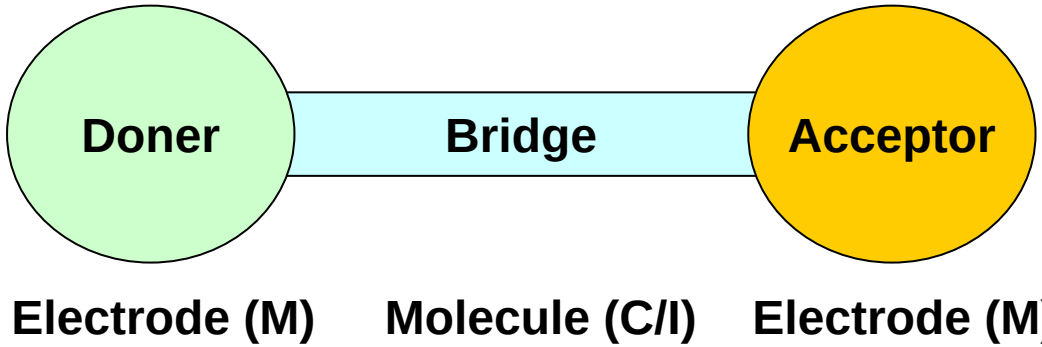
A simplified but general model of charge transfer: D-B-A model



1	**molecule**	**solution**	**molecule**	**electrical/kinetics**
2	**molecule**		**electrode**	**kinetics**
3	**electrode**	**molecule**	**electrode**	**electrical (MED)**
4	**SPM tip**	**molecule**	**electrode**	**STS**
5	**nano particle**	**molecule**	**electrode**	**electrical/kinetics**
6	**nano particle**		**molecule**	**kinetics**

Ratner and Jortner (1997)

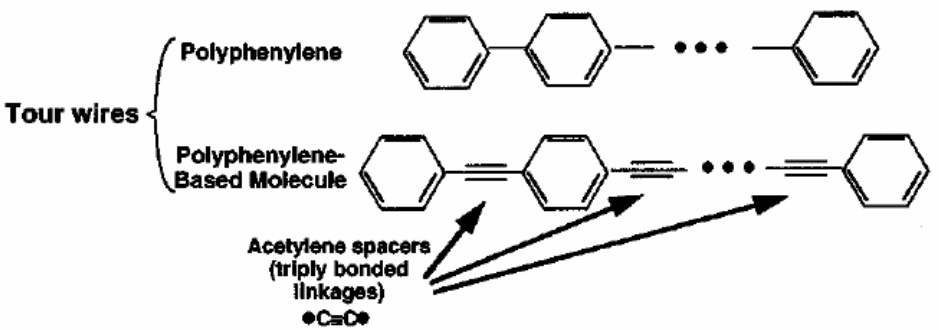
Ingredients and issues

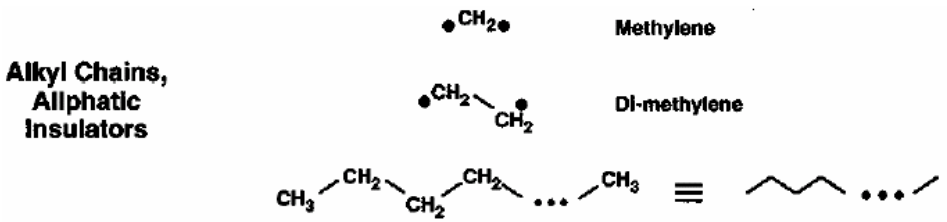


- 2 interfaces, one molecular bridge, two electrodes
- **Electrodes**: let's assume we are dealing with well known material, like Au.
- **Interface** (a few nms)
  - linker: self-assembled monolayer of thiolates
  - wave function mixing: hybridization << eV
  - Fermi level alignment: electric dipole ~ eV ~ Schottky barrier
  - in many case, interface dominates device characteristics.
- **Bridge** (1 - 100 nm)
  - discrete energy levels (HOMO and LUMO)
  - charge transfer: ballistic or diffusive? tunneling? hopping?
  - conformation change: bending, tilting, twisting, …
  - tunnel barrier? quantum dot formation?

- **Ingredients of D-B-A systems: molecule**

Molecule





- **Two of the most thoroughly studied molecules:**

  (1) Oligo (Phenylene-Ethynylene) (OPE) - based molecules: conductors

  → "Tour Wires"

  (2) Alkyl chains : insulators

- **Linear molecules**

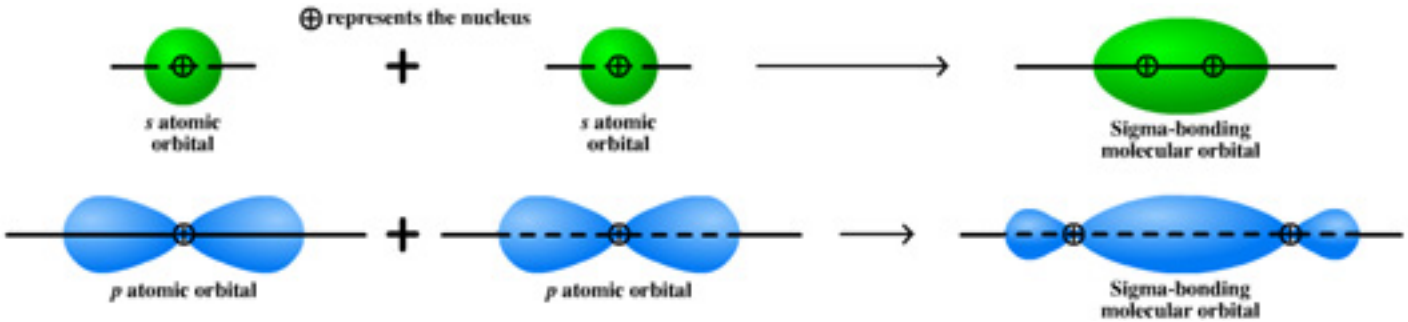
- **Thiol-terminated:**

  → "Molecular Alligator Clips"

Sigma and Pi bonds

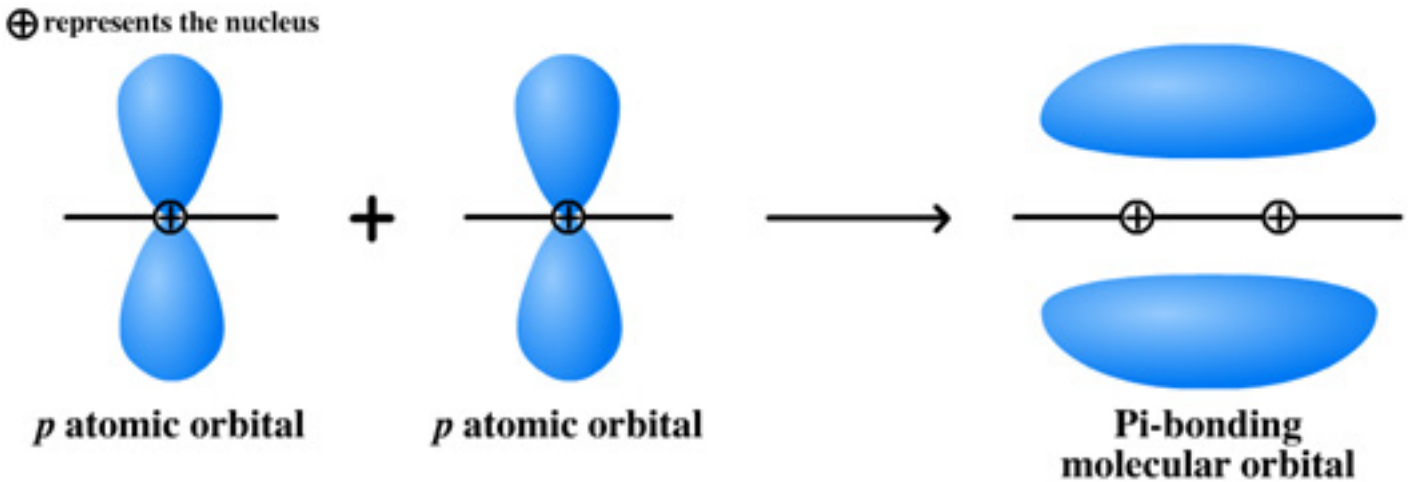
σ bond

A molecular orbital that is symmetrical along the axis connecting two atomic nuclei is called a sigma bond. Sigma bonds formed from overlapping s and overlapping p orbitals are shown below:

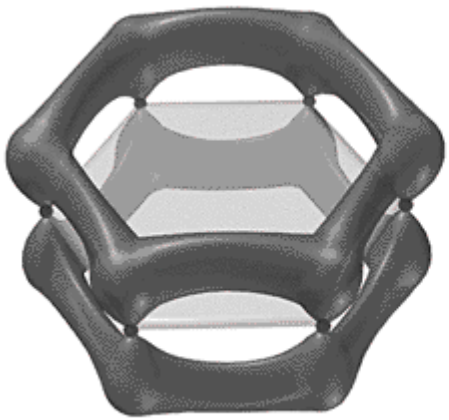


π bond

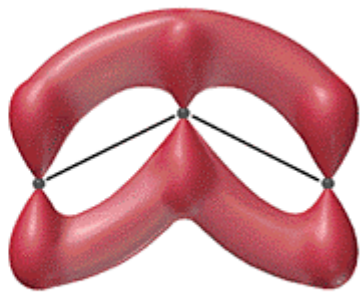
Pi bonds are formed when p orbitals overlap side-by-side. The electron density is concentrated in regions above and below the bonding axis. A pi bond is shown below:



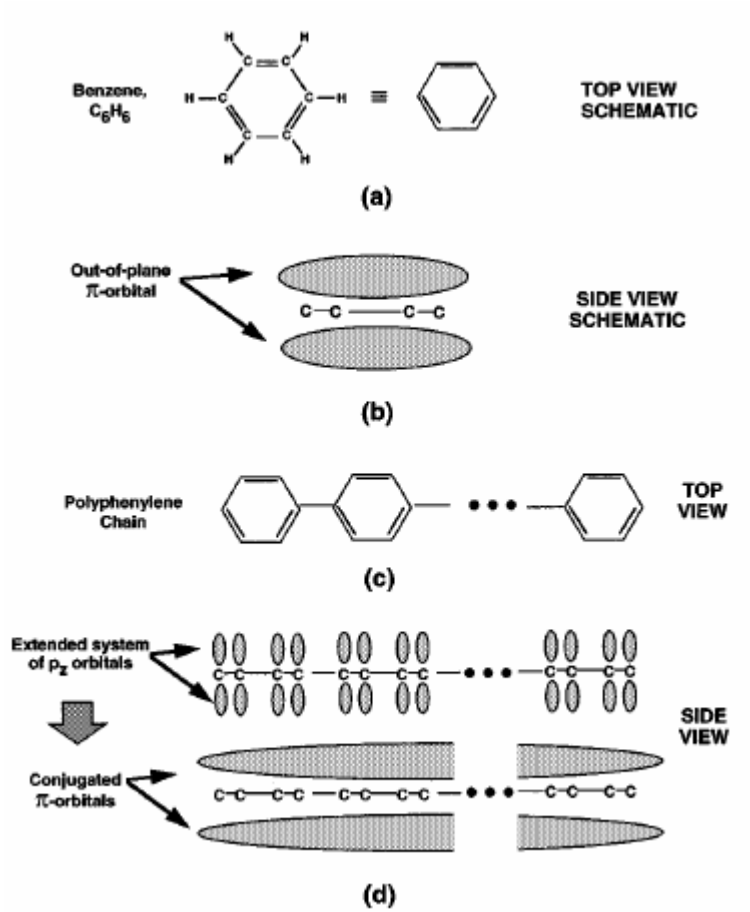
Electron delocalization in π bond



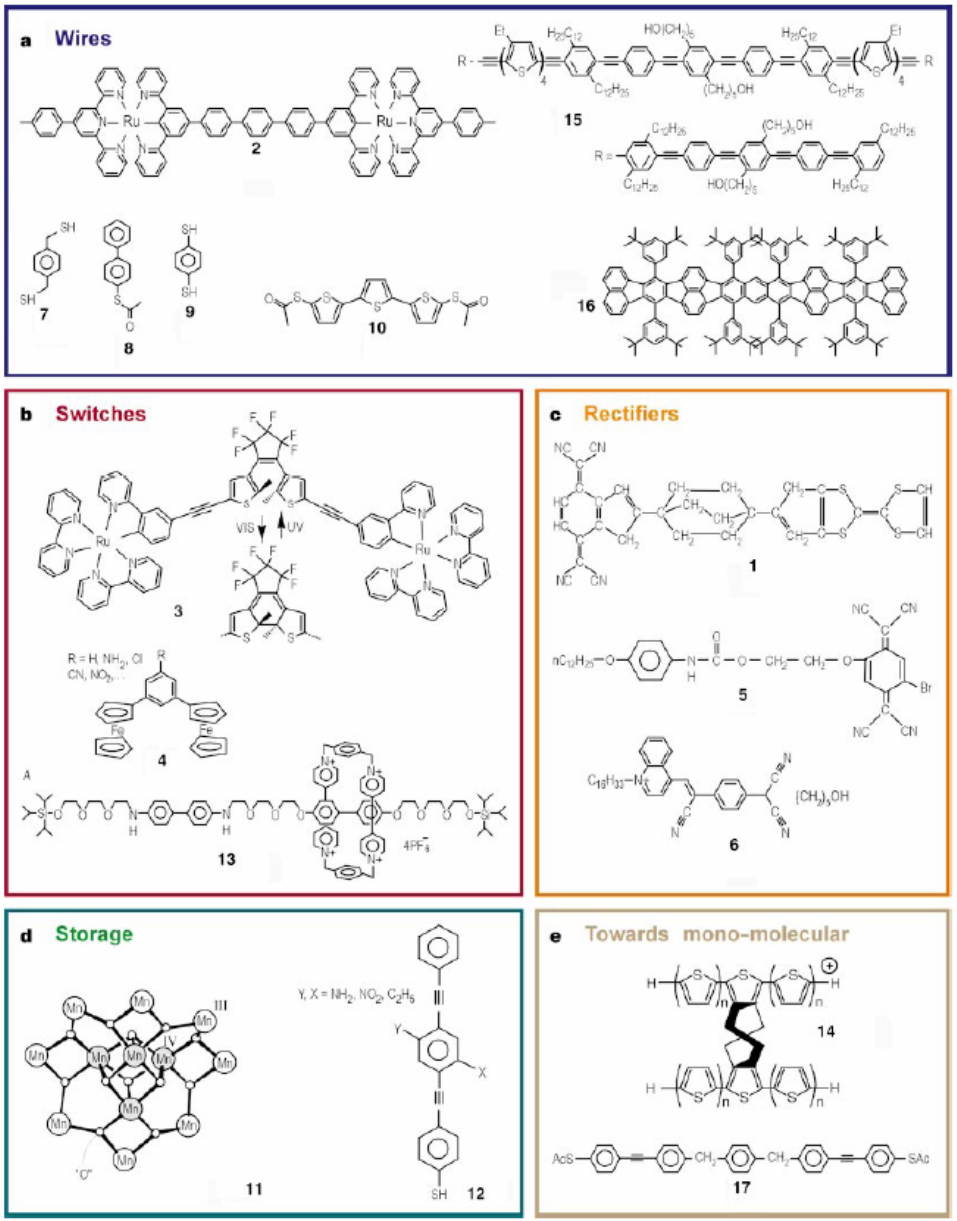
A Benzene, C_6H_6



B Ozone, O_3



Molecules for ME components



- Wire: symmetric, highly conductive
- Switch: bistability (on-off)
- Rectifier: asymmetric
- Storage: charge storing site

Self assembly

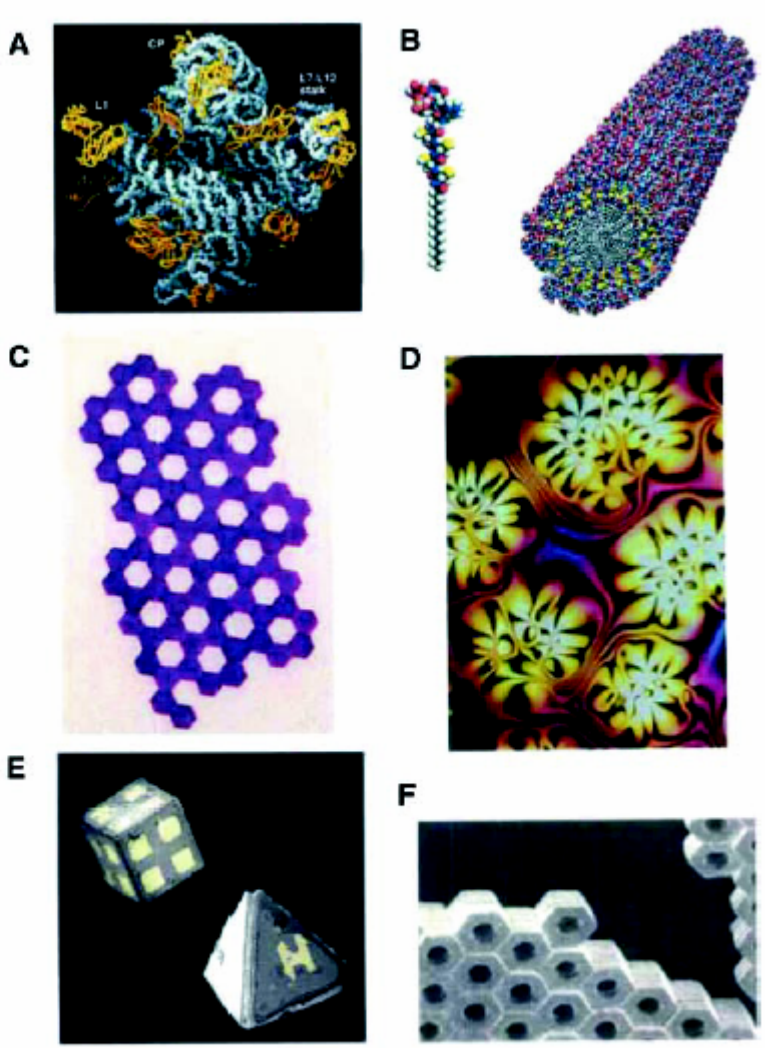
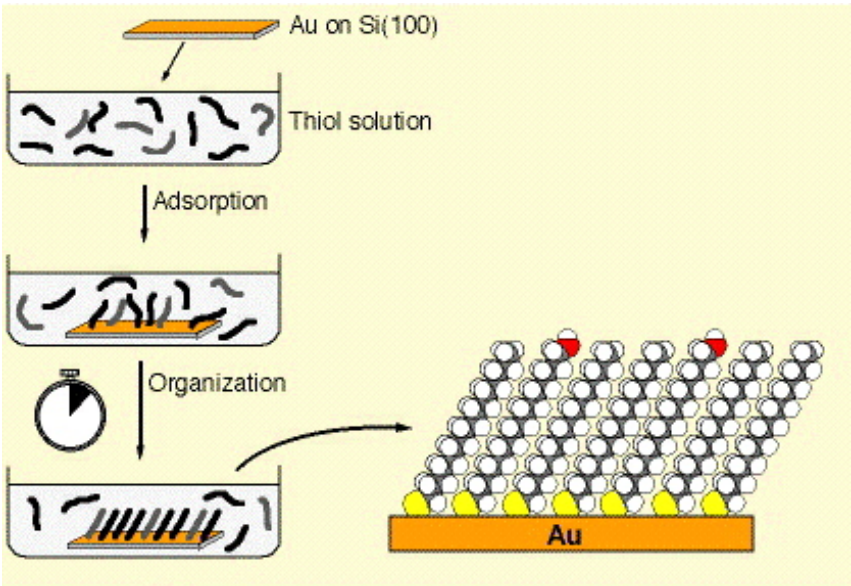


Fig. 1. Examples of static self-assembly. (**A**) Crystal structure of a ribosome. (**B**) Self-assembled peptide-amphiphile nanofibers. (**C**) An array of millimeter-sized polymeric plates assembled at a water/perfluorodecalin interface by capillary interactions. (**D**) Thin film of a nematic liquid crystal on an isotropic substrate. (**E**) Micrometer-sized metallic polyhedra folded from planar substrates. (**F**) A three-dimensional aggregate of micrometer plates assembled by capillary forces. [Image credits: (A) from (*24*); (B) from (*25*); (C) from (*26*); (D) from (*27*); (E) from (*28*); (F) from (29)]

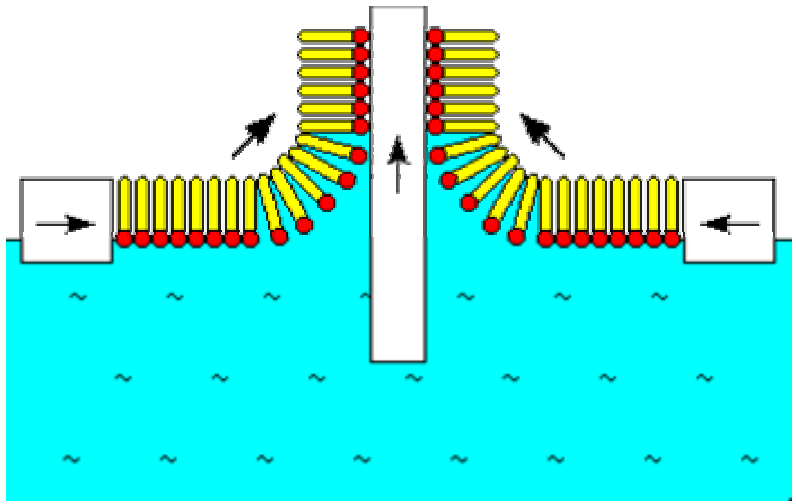
Science **295**, 2418 (2002)

Table 1. Examples of self-assembly (S, static, D, dynamic, T, templated, B, biological).

SAM and LB film



Self-Assembled Monolayer



Langmuir-Blodgett film

SAMs on Au(111): mechanism

- Proposed mechanism (still controversial): oxidative addition of the S-H bond to the gold surface, followed by a reductive elimination of the hydrogen

$$R\text{-}S\text{-}H + Au^{o}_{n} \rightarrow R\text{-}S^{-}Au^{+}\bullet Au^{o}_{n} + 1/2H_2$$

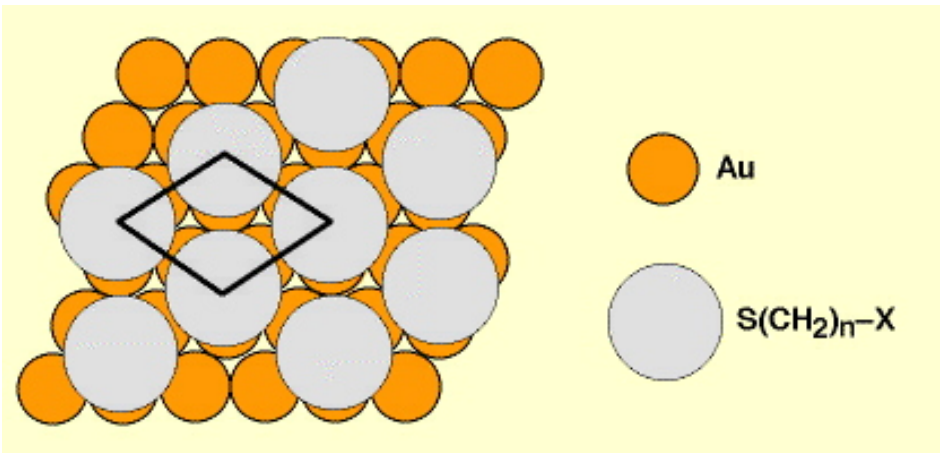
- On the basis of the bond energies of RS-H, H-H, and RS-Au (87, 104, and 40 kcal/mol, respectively), the net energy for adsorption of alkanethiolates on gold would be ca. –5 kcal/mol, which is exothermic.

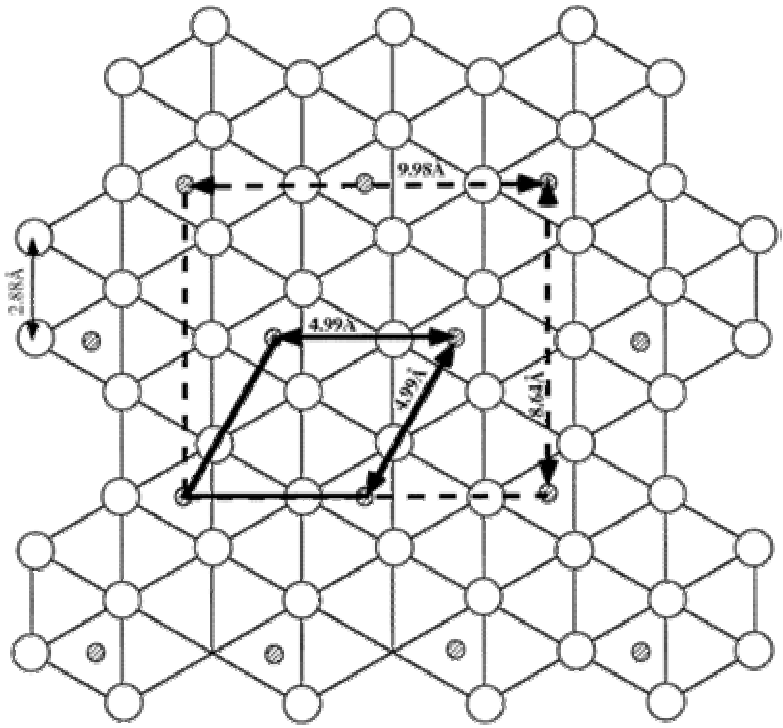
JACS **124**, 1132 (2002)

SAMs on Au(111): structure

- Sulfur atoms occupy 3-fold hollow sites of the Au(111) lattice
- *ab initio* calculations: a mixed σ- and π-bonding character with a dominating contribution of the latter.

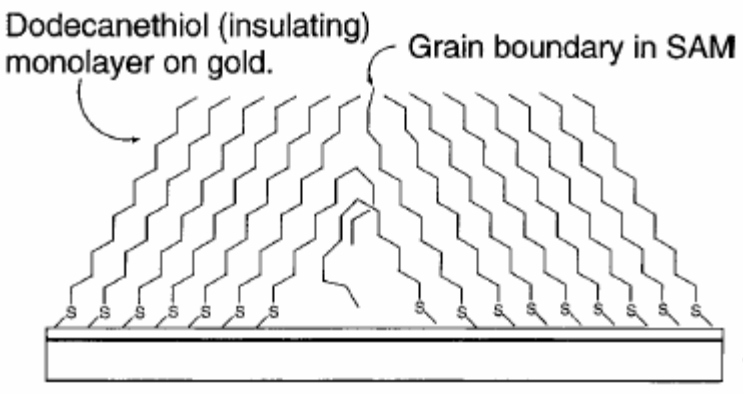
JACS **115**, 9389 (1993)





Langmuir **14**, 7203 (1998)

Defects in SAM



- Grain boundary ~ a few tens of nms
- Substate defects:
  vacancy, dislocation, terrace, …

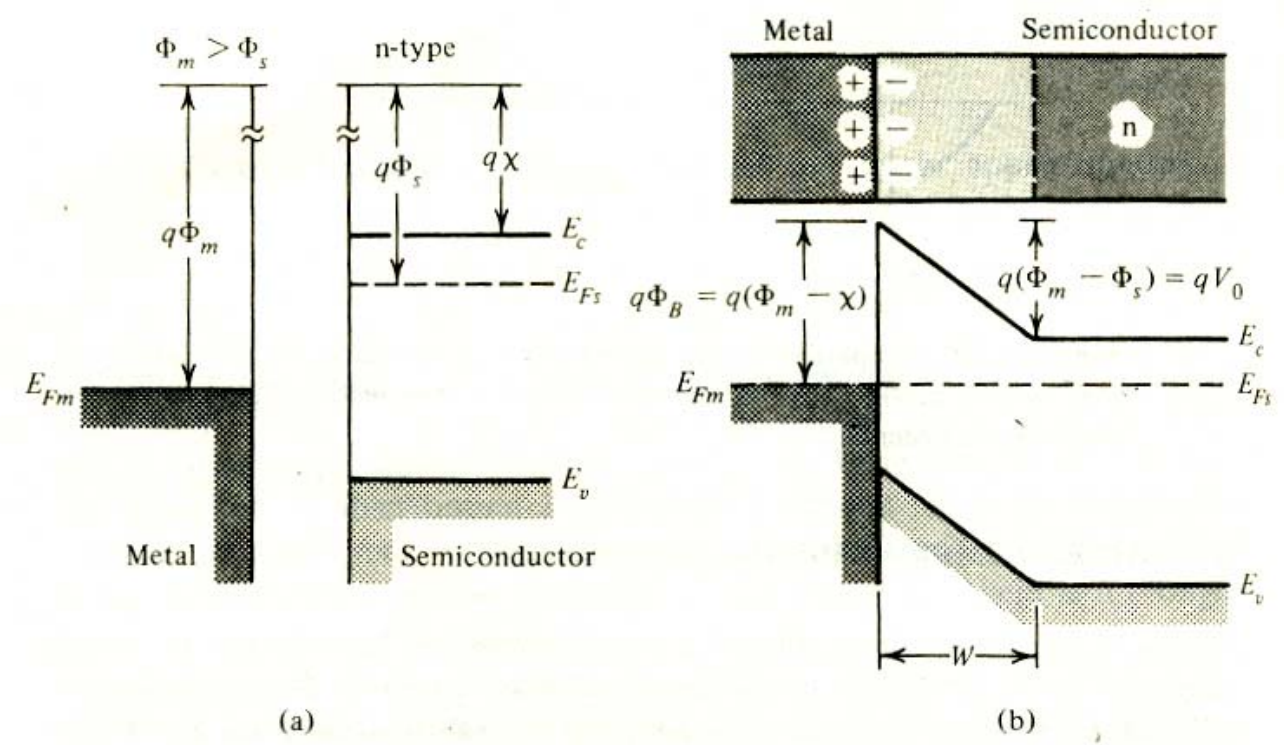
- Nomenclature
  - octane : 8
  - decane : 10
  - dodecane : 12
  - dodecanethiol : 12 carbon chain + thiol
  - dodecanedithiol: thiol + 12 carbon chain + thiol

- **Ingredients of D-B-A systems: junction**

  Fermi-level alignment, Schottky barrier,

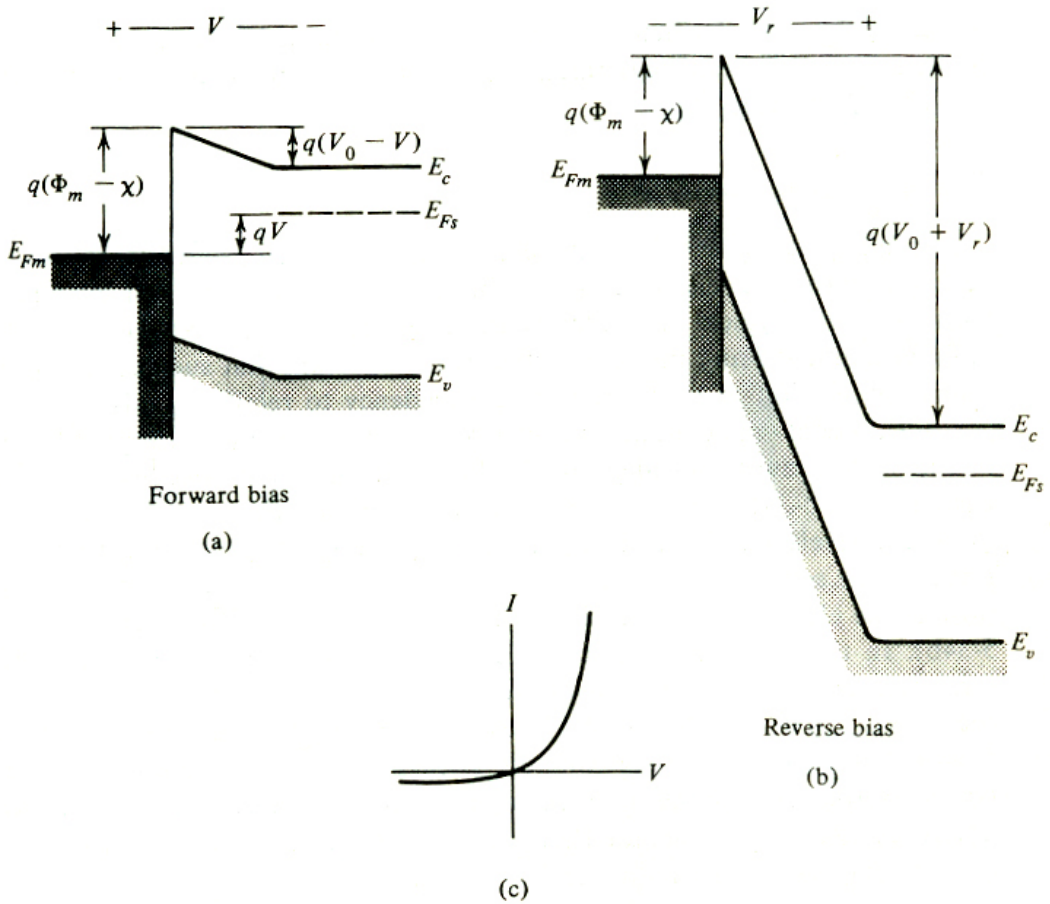
  classical transport in M-Sm systems, …

Schottky barrier at M-Sm interface



- Fermi-level alignment
- Electric dipole formation in the M-Sm interface
- Energy barrier ‘Schottky barrier’ formation

Rectifying behavior



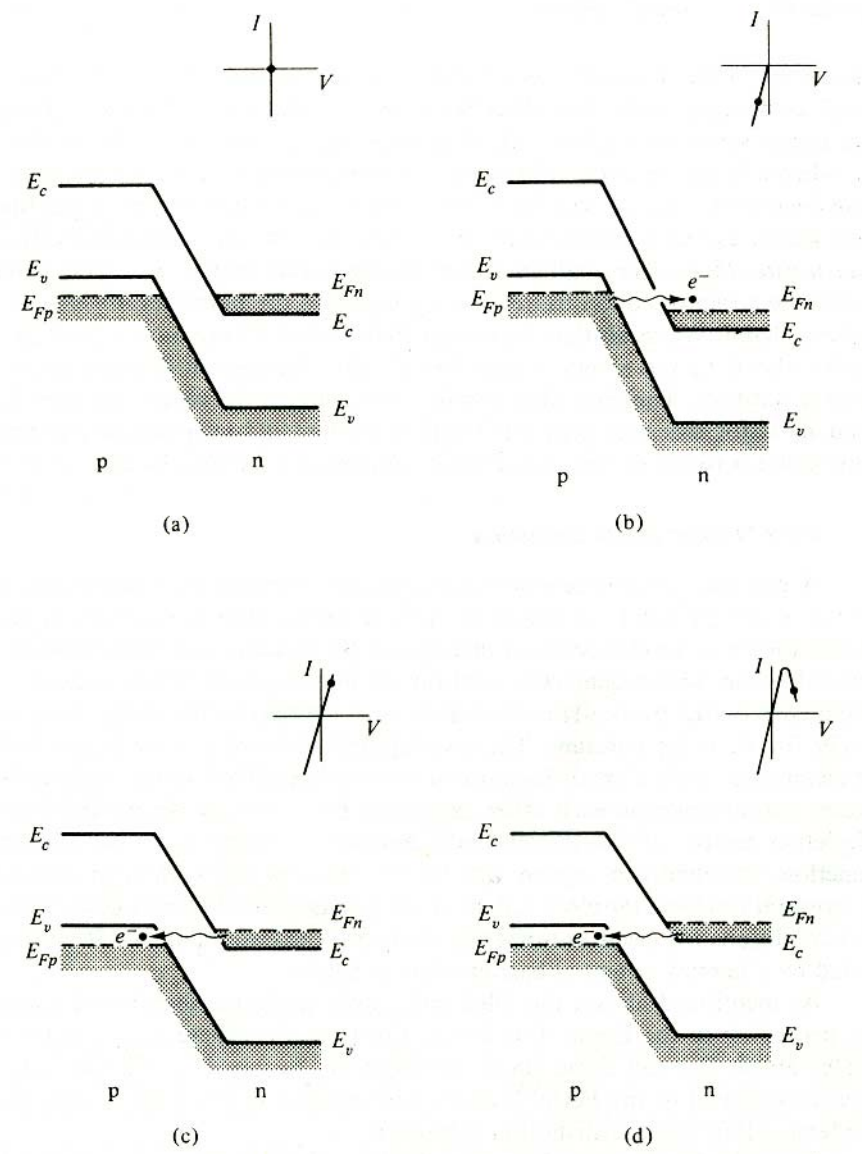
$$I = I_0(e^{\frac{eV}{kT}} - 1)$$

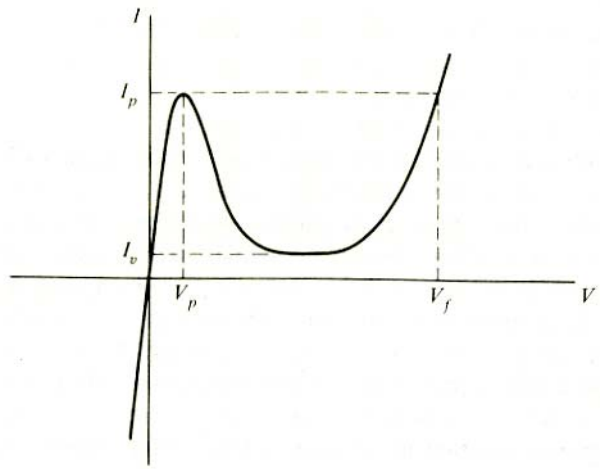
$$I_0 \propto e^{\frac{e\Phi_0}{kT}}$$

Conduction mechanisms with energy barrier

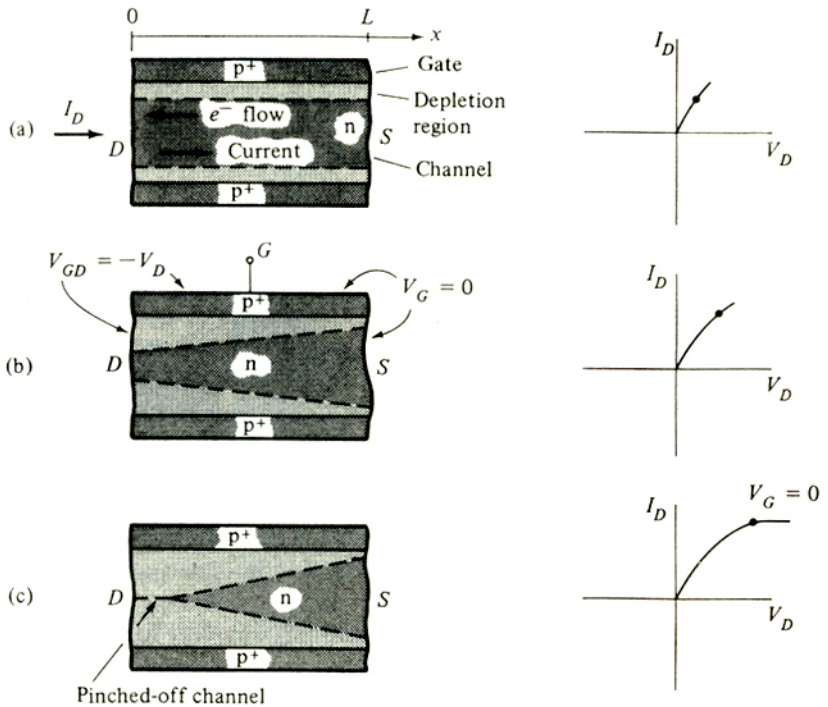
Conduction Mechanism	Characteristic Behavior	Temperature Dependence	Voltage Dependence	Schematic Band Diagram
Schottky Emission	$I \sim T^2 Exp(-q\frac{F-\sqrt{\frac{qV}{4\pi\varepsilon d}}}{kT})$	$\ln(\frac{I}{T^2}) \sim \frac{1}{T}$	$\ln(I) \sim V^{\frac{1}{2}}$	
Frankel - Pool Conduction	$I \sim VT^2 Exp(-q\frac{F-2\sqrt{\frac{qV}{\pi\varepsilon d}}}{2kT})$	$\ln(\frac{I}{T^2}) \sim \frac{1}{T}$	$\ln(\frac{I}{V}) \sim V^{\frac{1}{2}}$	
Hopping Conduction	$I \sim VExp(-\frac{\Delta E}{kT})$	$\ln(\frac{I}{V}) \sim \frac{1}{T}$	$I \sim V$	
Fowler-Nordheim Tunneling	$I \sim V^2 Exp(-\frac{4d\sqrt{2m}}{3q\hbar V}(qF)^{1.5})$	——	$\ln(\frac{I}{V^2}) \sim \frac{1}{V}$	
Direct Tunneling	$I \sim VExp(-\frac{4\pi d}{h}\sqrt{2mF})$	——	$I \sim V$	

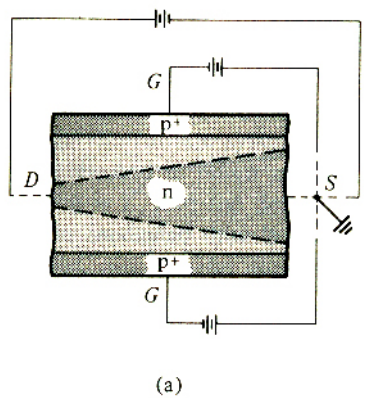
Tunnel diode

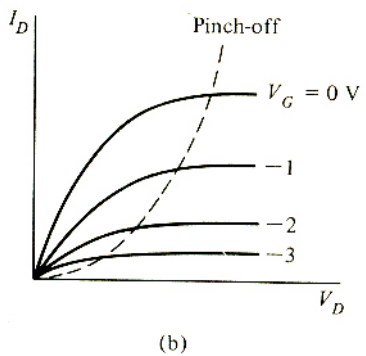




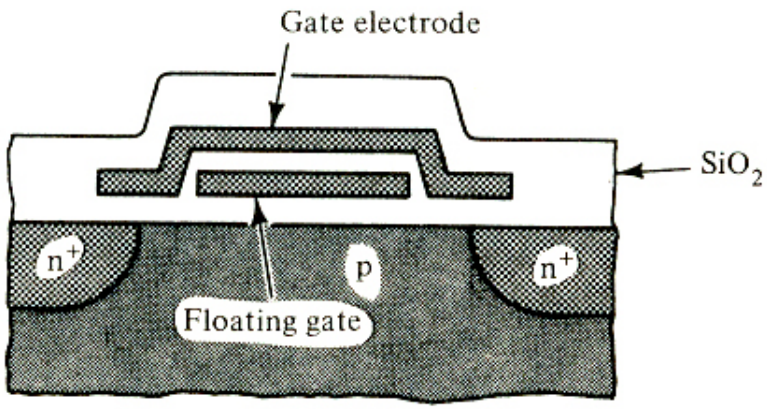
Field Effect Transistor (FET)

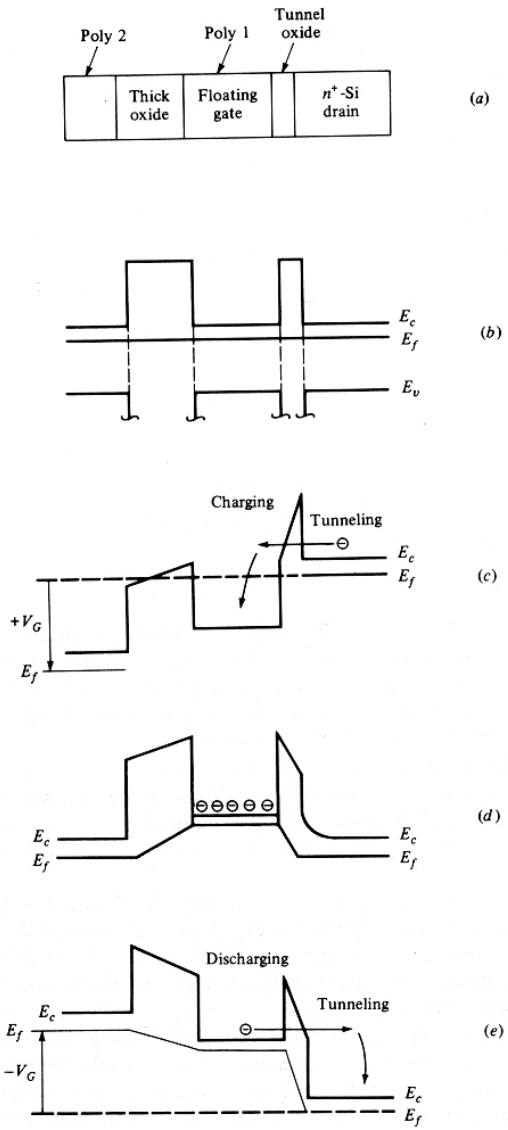




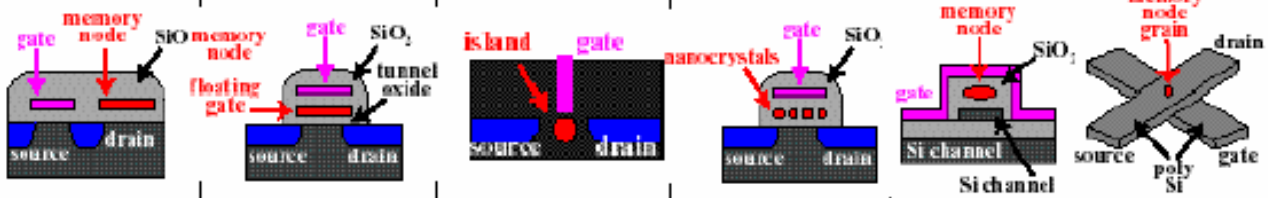


Non-volatile memory





Comparison of the potential nanoscale memories

	Conventional Memory		Quantum Dot Memory			
	DRAM	Flash	SET	Nano-flash		Yano-type
				Multidot	Single dot	
device structure						
read time	~10 ns	~10 ns	1 ns	~10 ns	~10ns	~20 μs
write time	~10 ns	~1 ms	1 ns	~100 ns	<1 μs	~10 μs
erase time	< 1nm	~1ms	< 1nm	~1 ms	<1 ms	~10 μs
retention time	~1 s	~10 years	~ 1s	~1 week	~5 s	~1 day
endurance cycles	infinite	10^6	infinite	10^9	10^9	10^7
operating voltage	3 V	15 V	1 V	5 V	10 V	15 V
voltage for state inversion	0.2 V	~5 V	< 0.1 V	0.65 V	0.1 V	0.5 V
electron number to write bit	10^5	10^3	1 (excluding no to change gate potential)	10^3	1 (excluding no to change gate potential)	2 (excluding no to change gate potential)
cell size	~12 F^2/bit	~9F^2/bit	9-12 F^2/bit	9F^2/bit	9F^2/bit	2F^2/bit

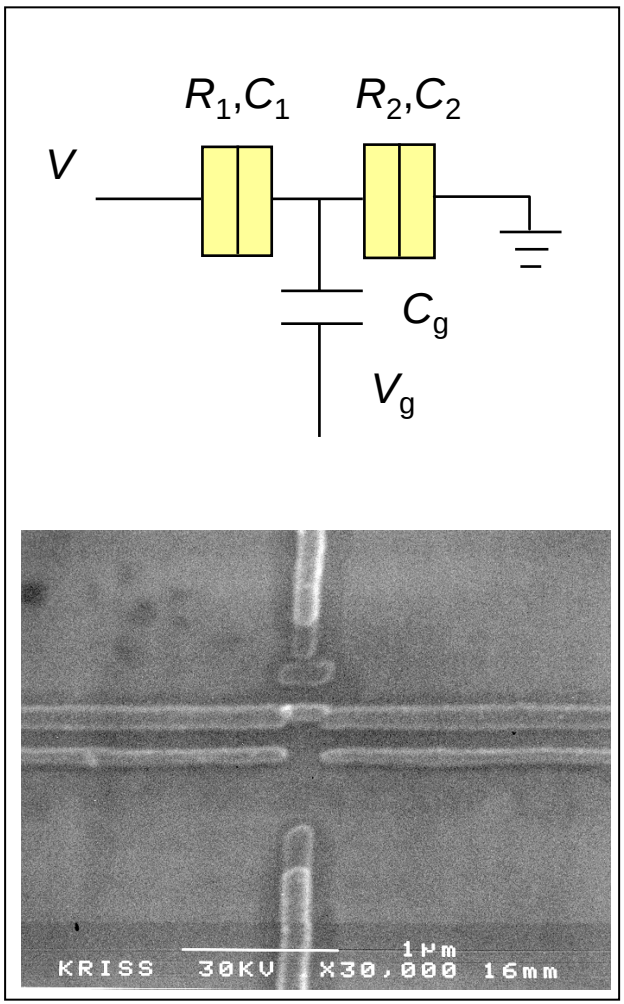
- **Quantum transport on the nanoscale:**

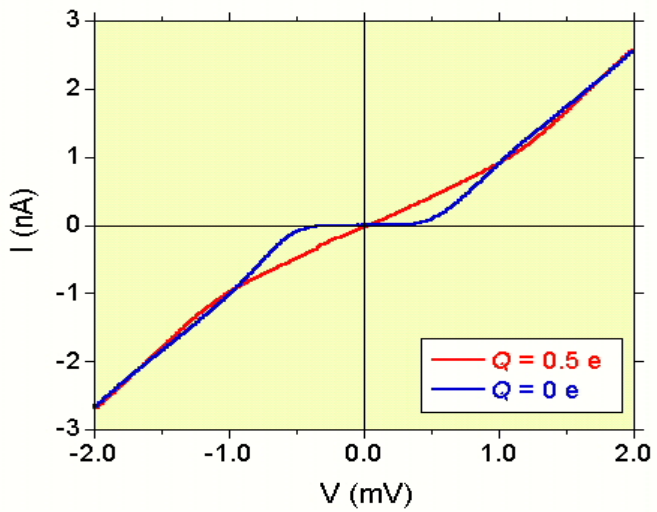
  single-electron tunneling, Kondo resonance,

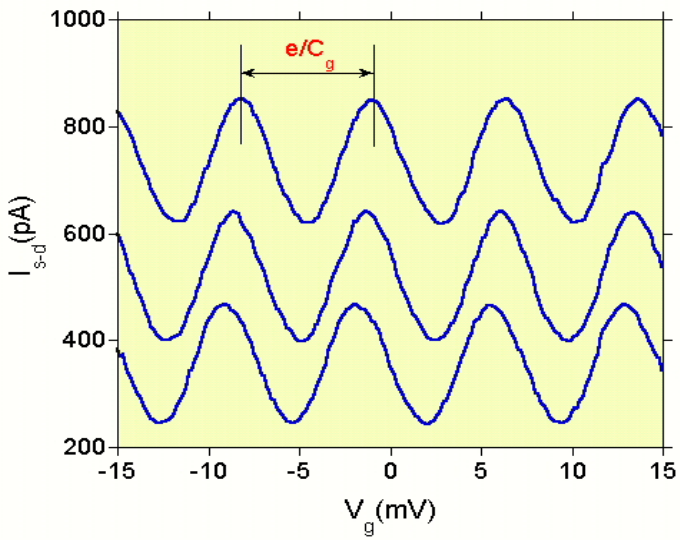
  ballistic transport, conductance quantization

Coulomb blockade of single-electron tunneling

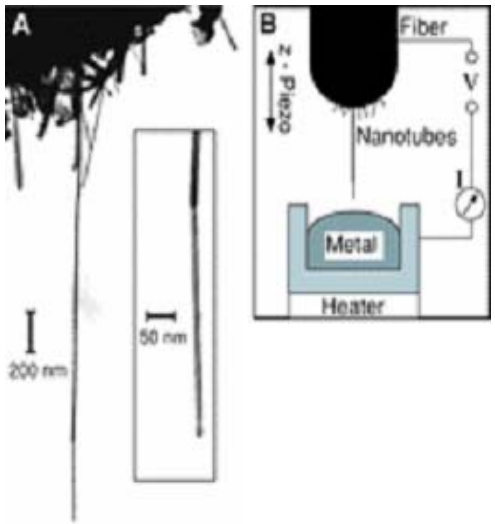
Single-Electron Transistor (SET)

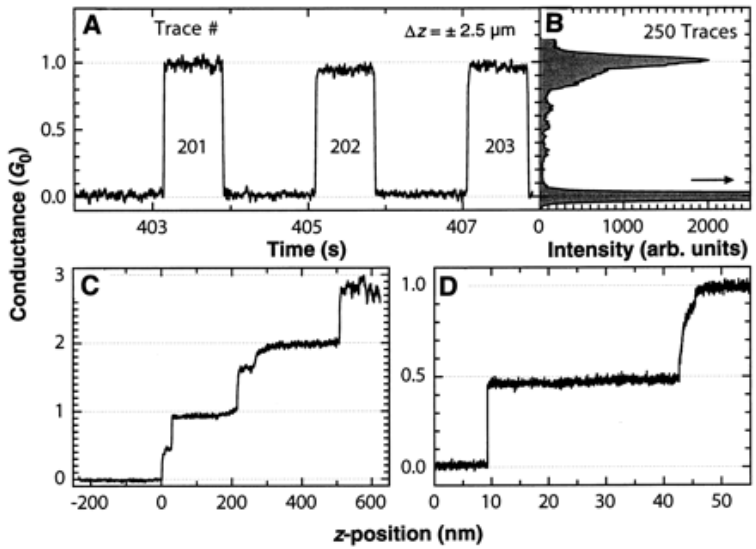




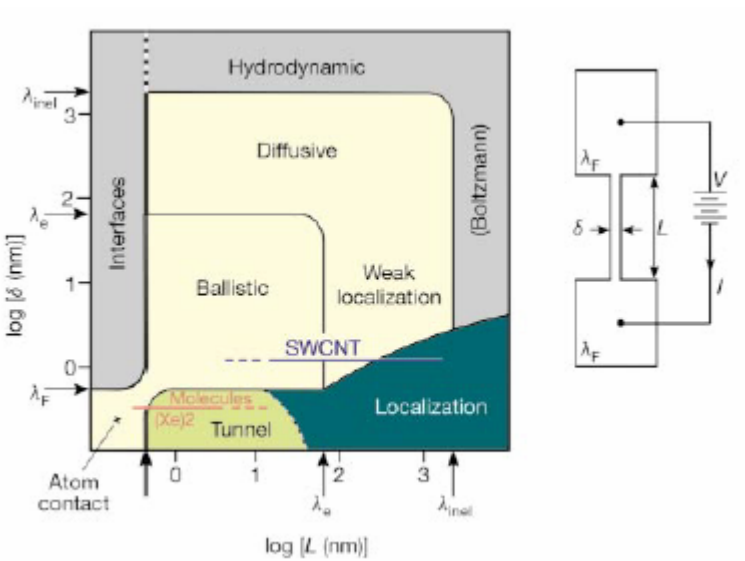


Ballistic transport (in carbon nanotube)





Science **280**, 1744 (1998)



- Ballistic: elastic scattering length > system size
- Conductance quantization
- $\Delta G = 2G_0 = (12.9\ k\Omega)^{-1}$ theory : $4G_0 = (6.5\ k\Omega)^{-1}$

Kondo resonance (in quantum dot)

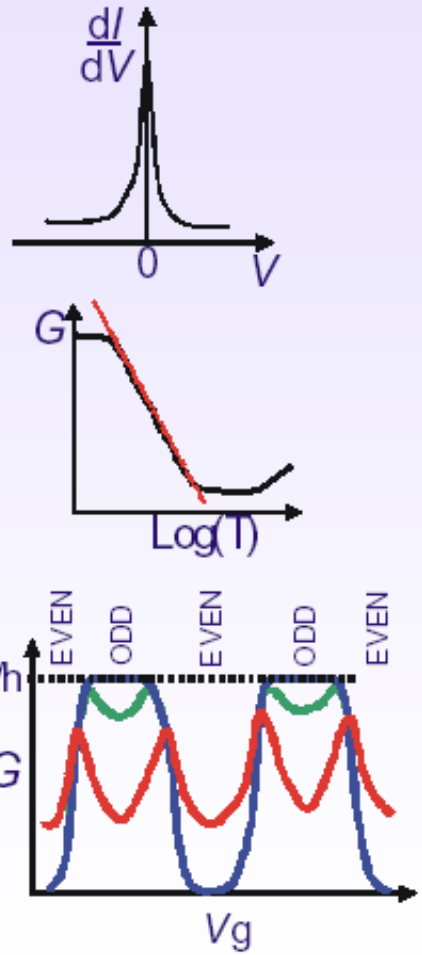
Basic features

- Peak in the density of states at E_F

→ Enhanced conductance at zero bias
$G \rightarrow 2\, e^2/h$ (for symmetric barriers)

- G follows Log(T) dependence near T_K

- Even-odd asymmetry

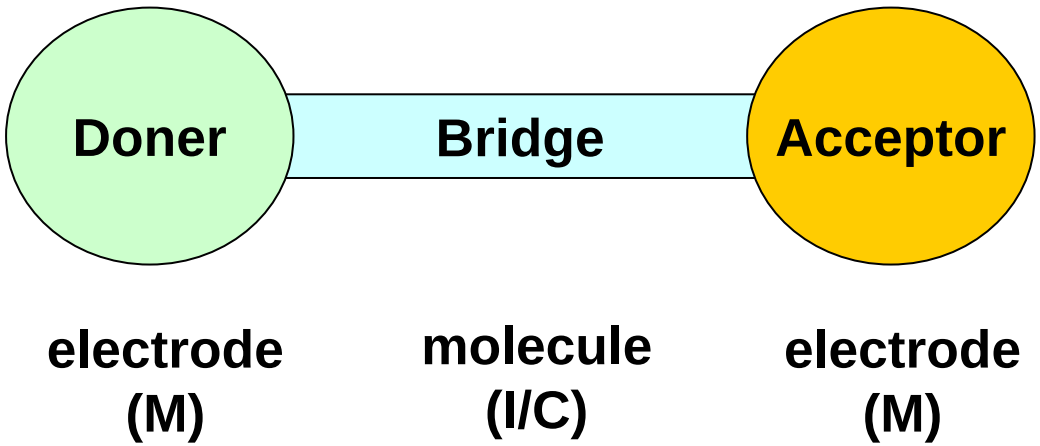


Van der Wiel

- **Charge transfer on the nanoscale:**

  Electrode – Molecule – Electrode systems

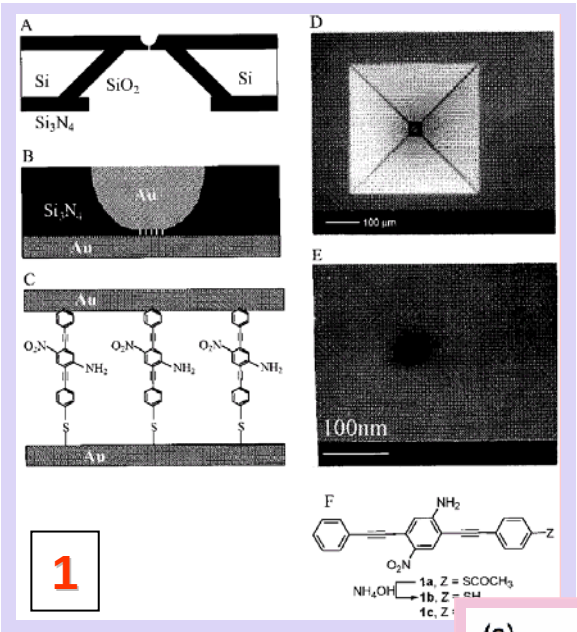
Charge transfer in MED

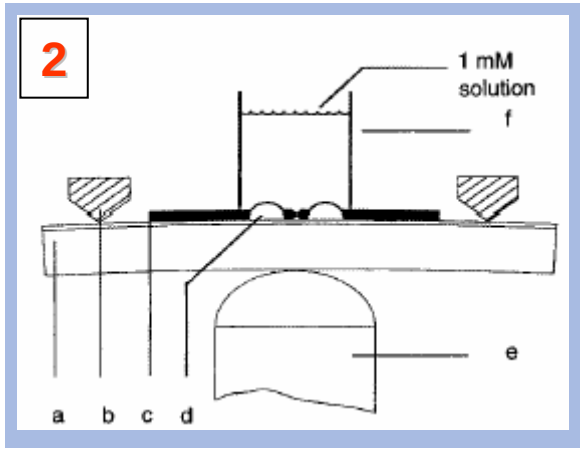


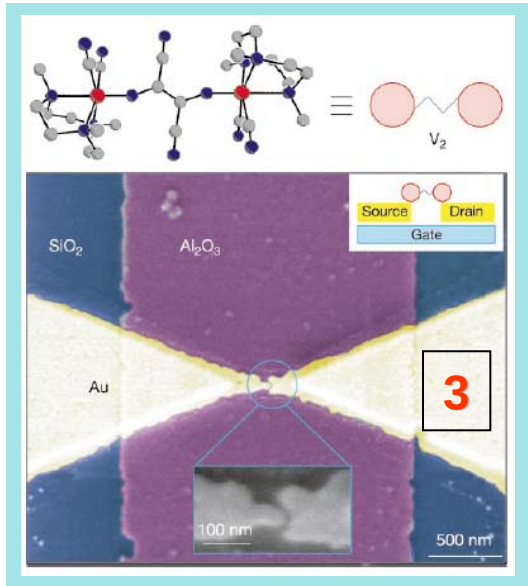
"A prototype of molecular electronic device"

Key technology: to attach macroscopic electrodes to few-nanometer-sized molecules.

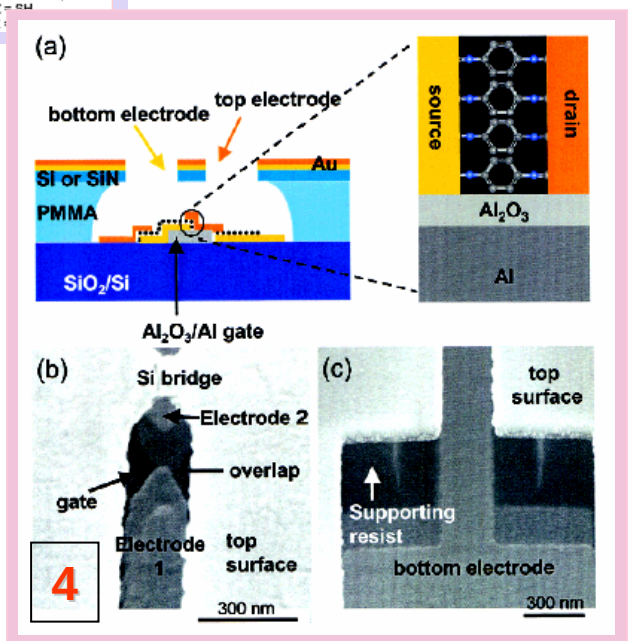
E-M-E systems

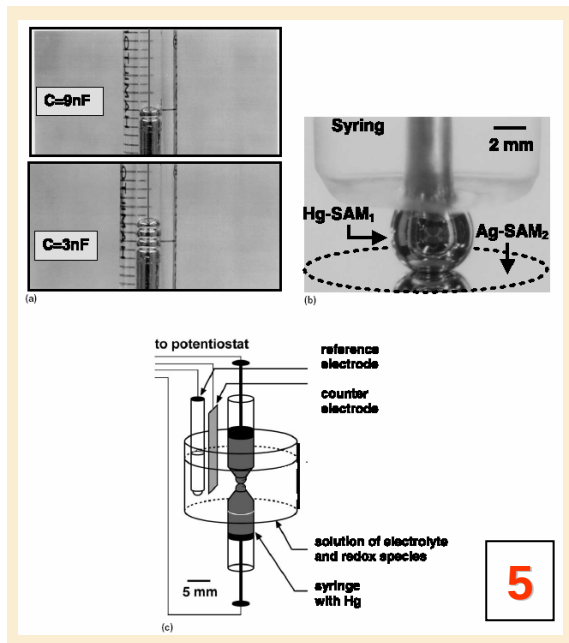




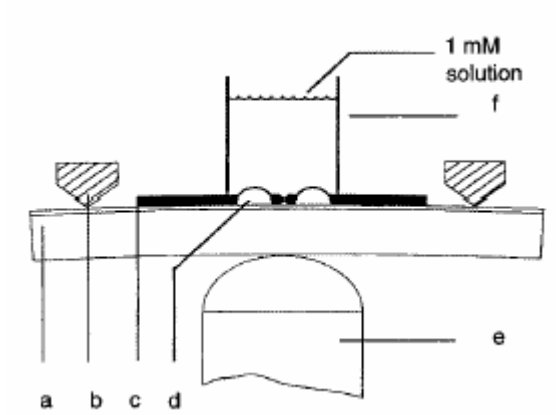


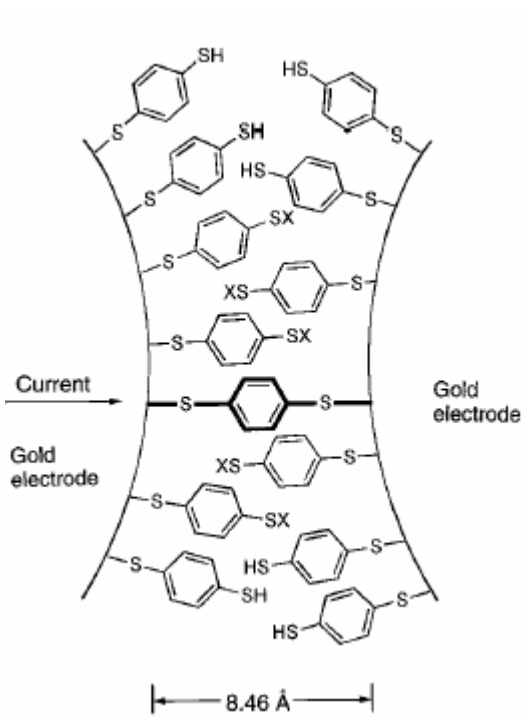
1. Nanopore
2. Break junction I
3. Break junction II
4. Nano gap
5. Mercury drop

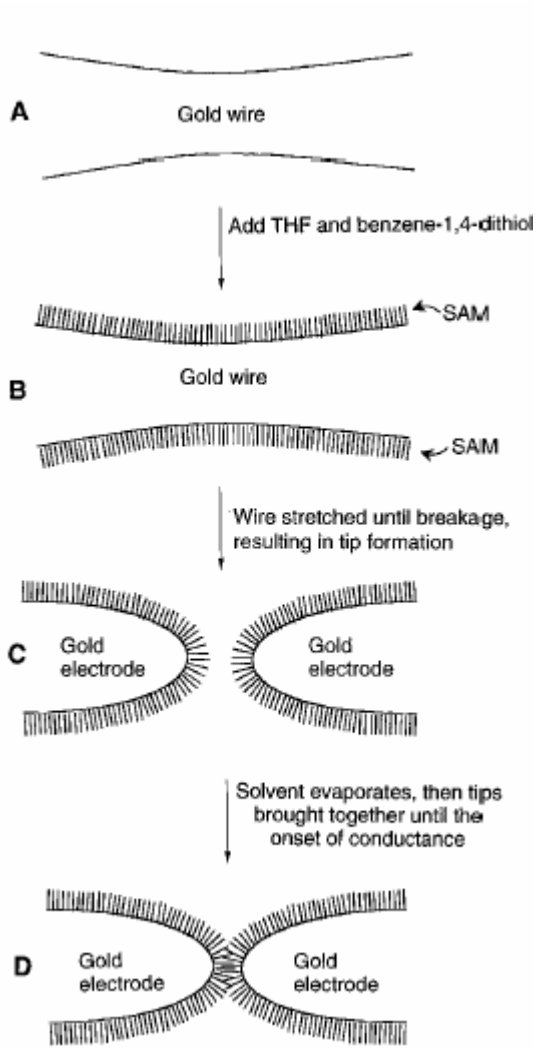


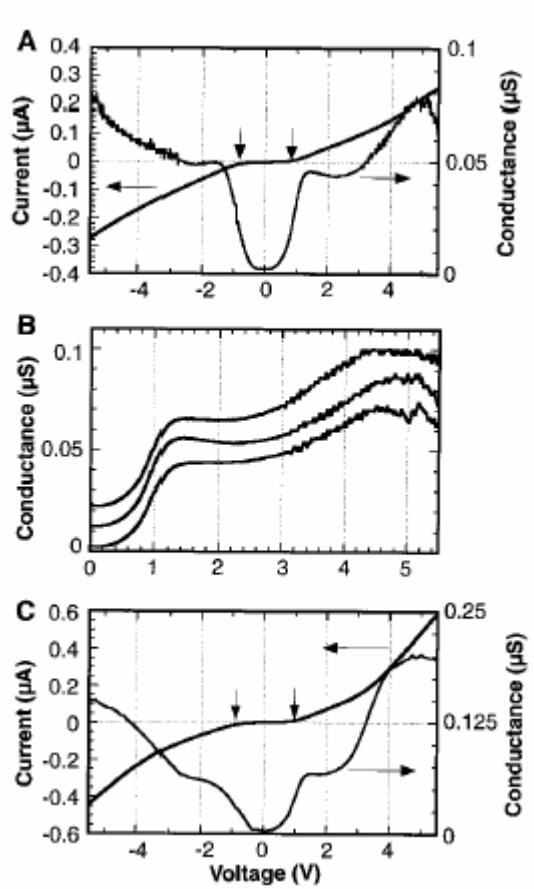


Break-junction method



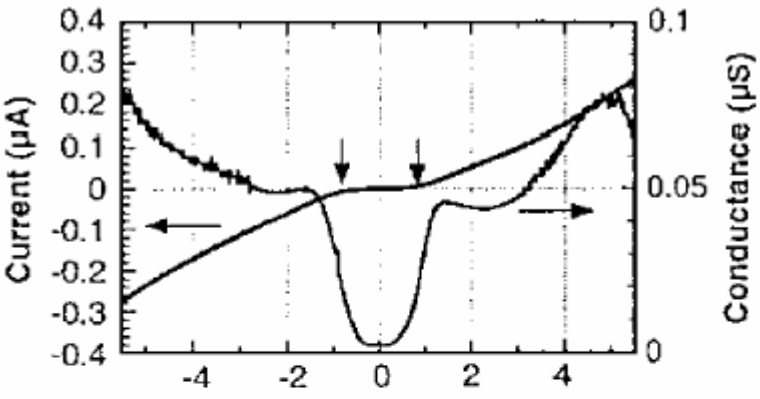


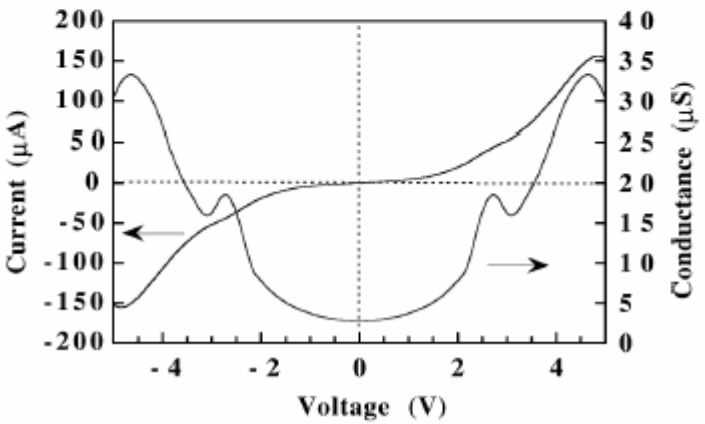


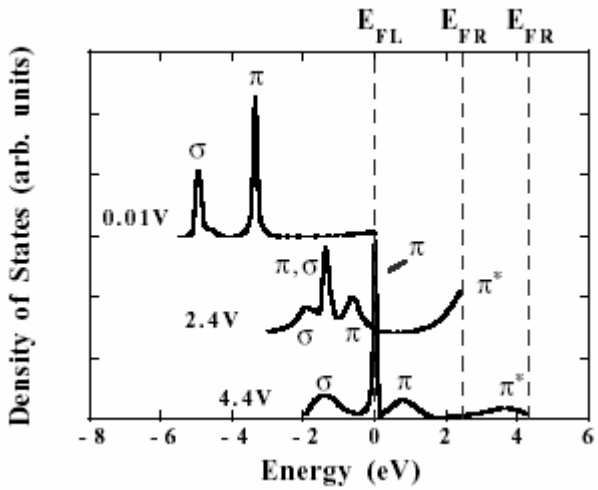


Science **278**, 252 (1997)

Model calculation

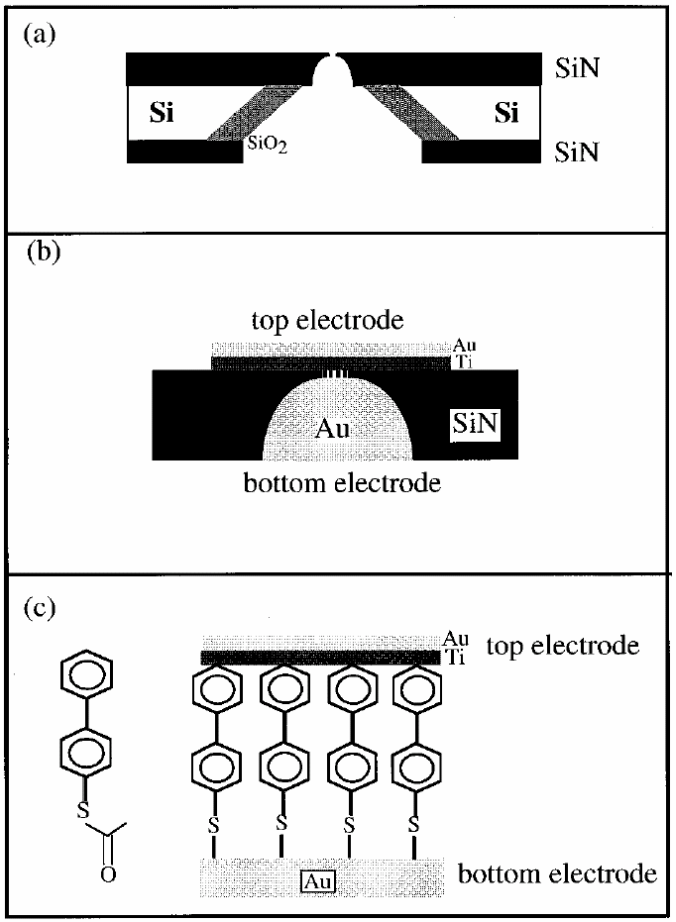




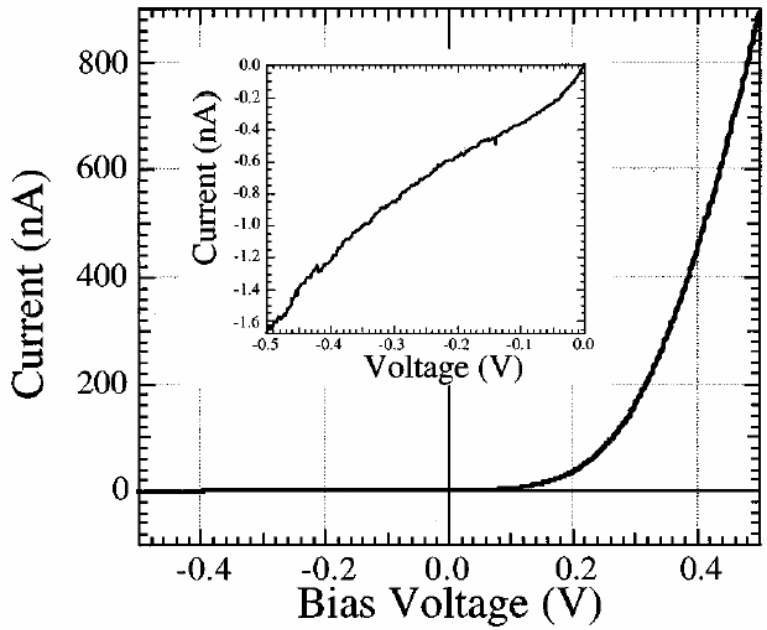


PRL **84**, 979 (2000)

Nanopore and molecular rectifying diode



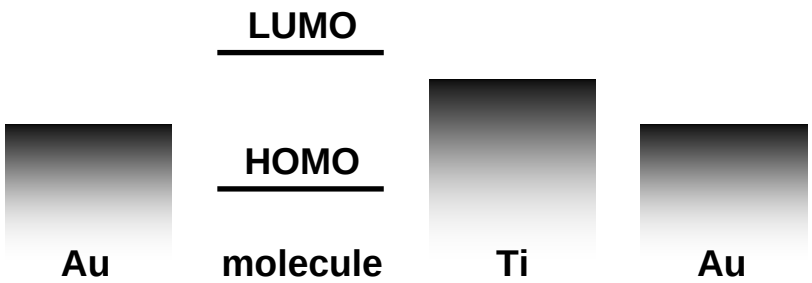
APL **71**, 611 (1997)



- **Sample fabrication: nanopore (~30 nm) in SiN membrane (by EBL, plasma etching) → bottom Au evaporation → SAM formation → top Au/Ti evaporation**
- **Bias direction: bottom Au: (+) / top Ti: (-)**
- **Au-thiol: chemisorbed, Ti-benzene ring: physiorbed**
- **Work function: Au > Ti (Schottky-type junction between Ti & SAM)**

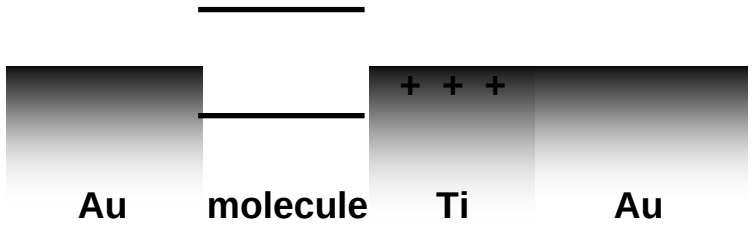
Rectification mechanism - pinning

1. Electronic levels of individual materials



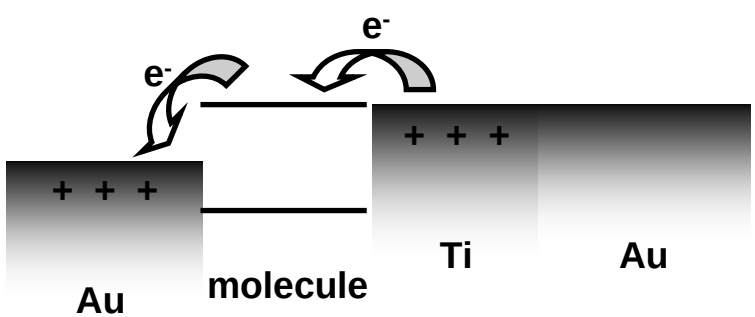
2. On assembly, at zero bias

(the Fermi levels are aligned)



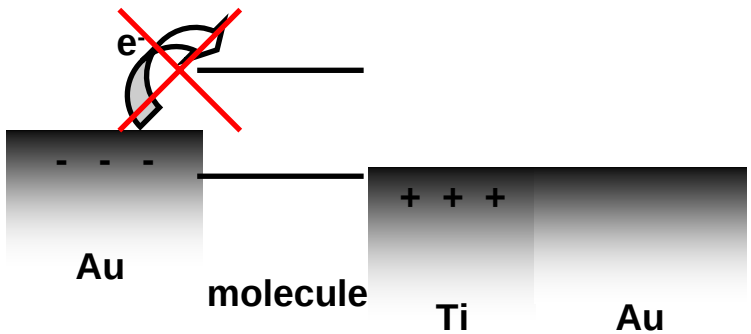
3. Positive biasing

(Tunneling occurs easily through the SAM-Ti barrier for the level matching due to biasing)



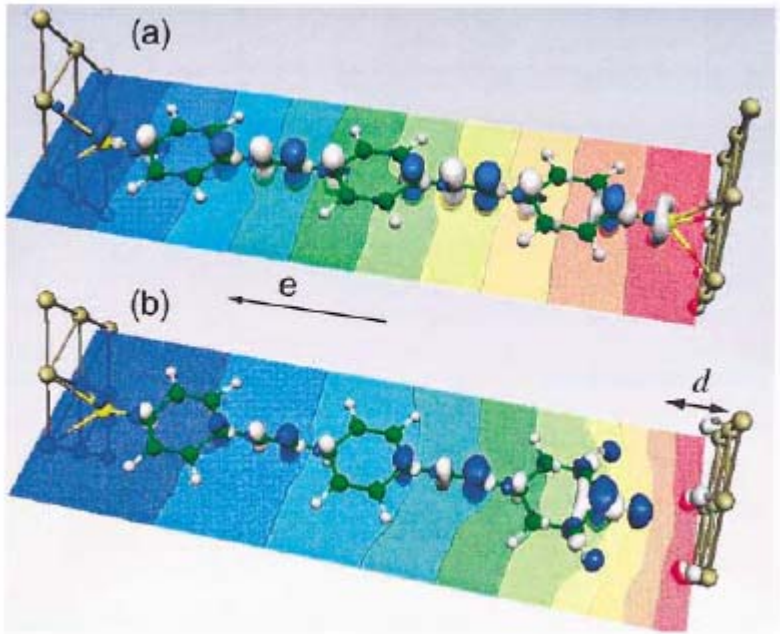
4. Negative biasing

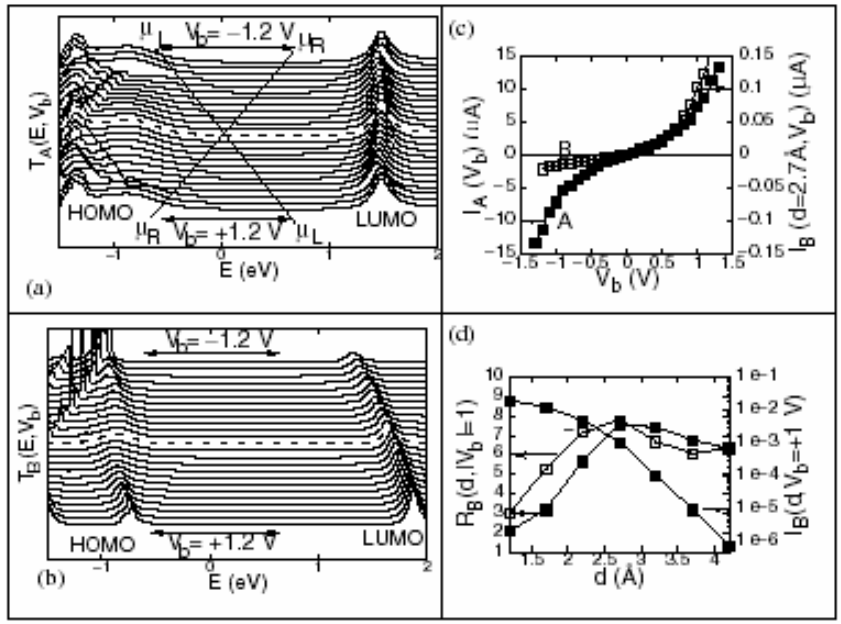
(Molecular level moves with the Au electrode potential due to the higher transparency of the Au-SAM barrier)



Rectification mechanism - asymmetric potential drop

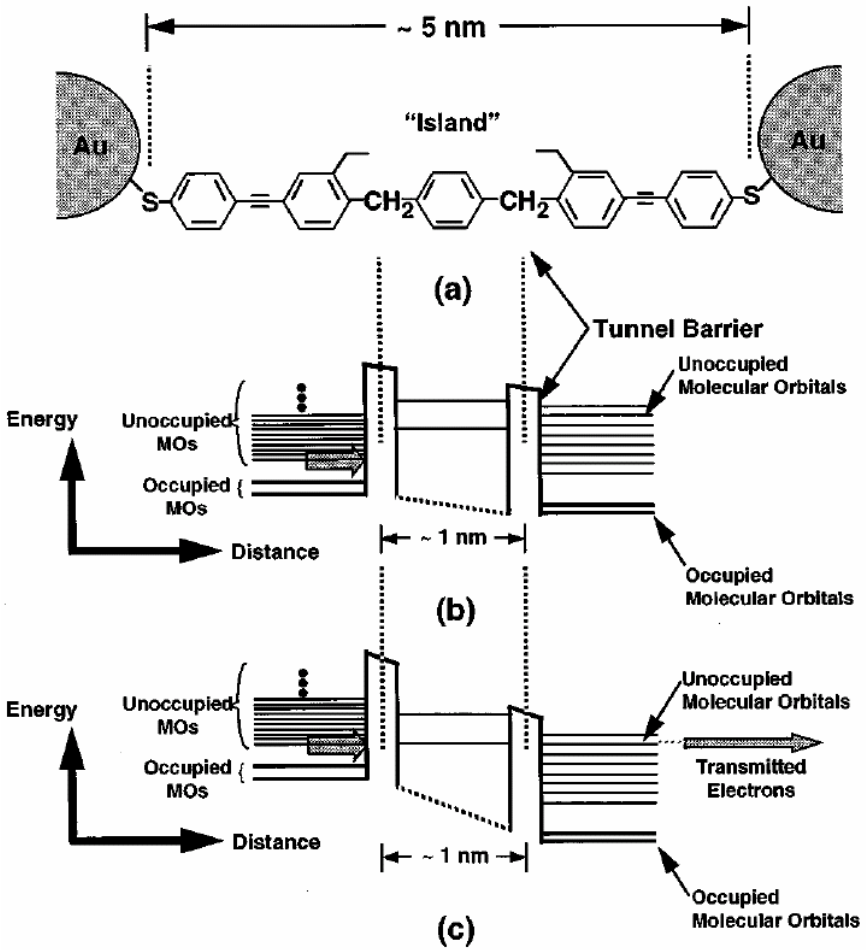
PRL **89**, 138301 (2002)

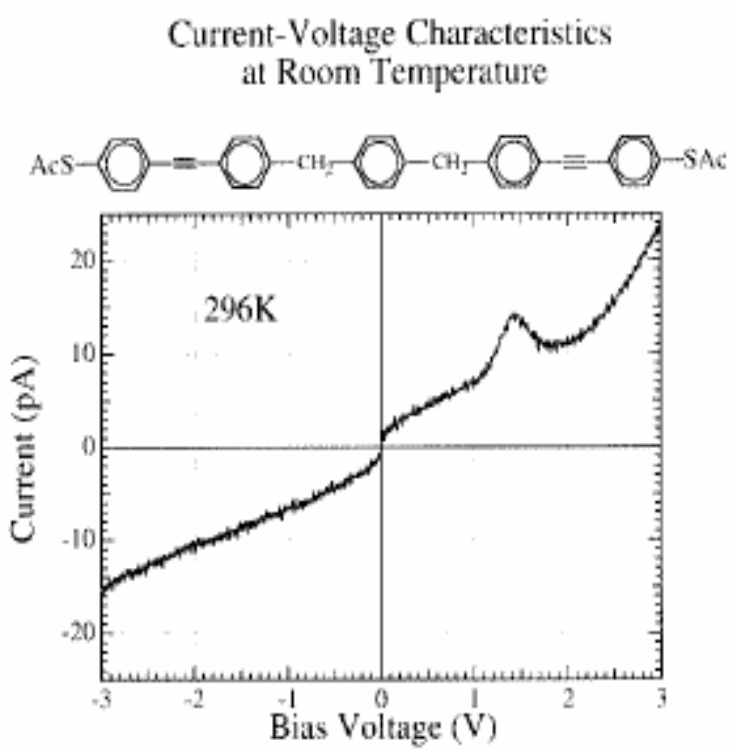




- Symmetric molecule and asymmetric junction
- Asymmetric voltage drop at the junctions → rectification
- First principles nonequilibrium Green's function based package, TRANSIESTA.

Molecular Resonant Tunnel Diode (RTD)

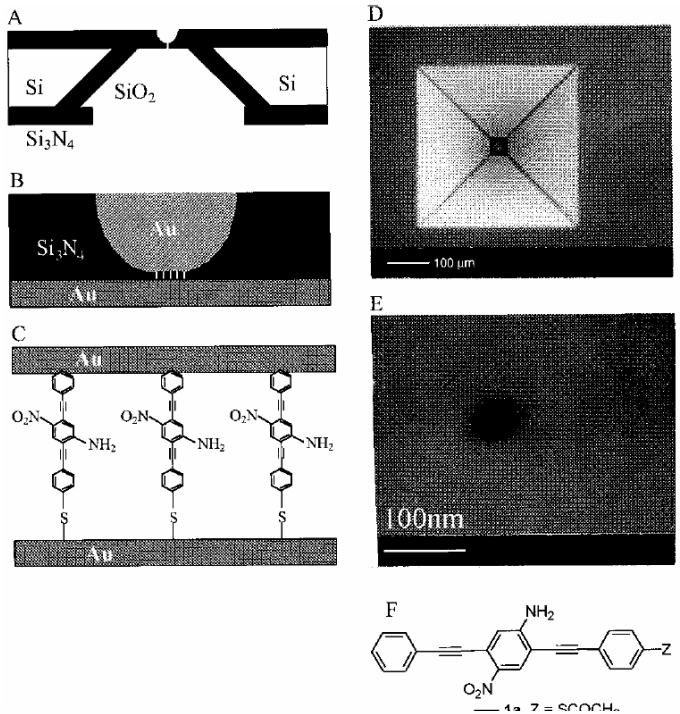


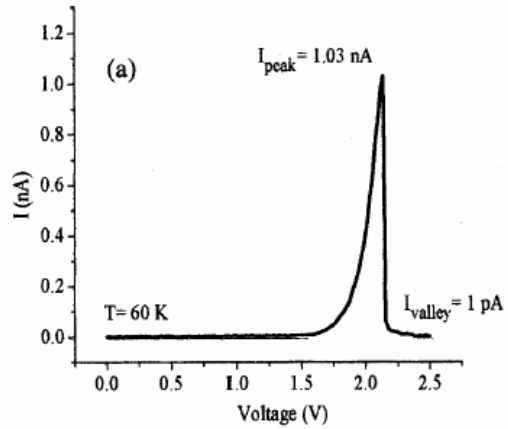


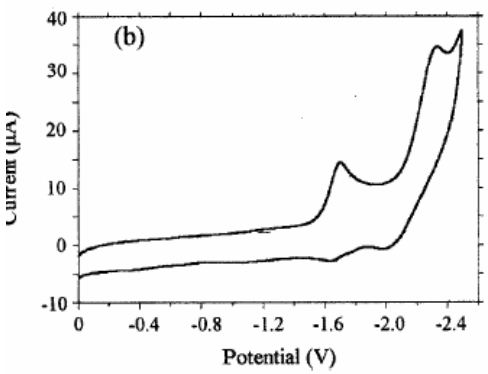
- **Break-junction method (or nanopore ?)**
- **To go from rectifying diode to RTD, we need:**
  - **definite tunnel barriers**
  - **island and electrodes with discrete energy levels**

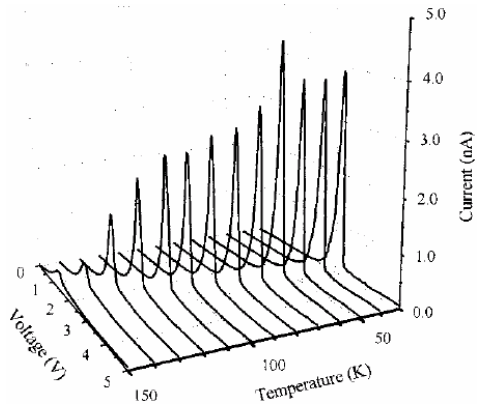
Proceedings of the IEEE **88**, 386 (2000)

Oligo (Phenylene-Ethynylene) - based RTD

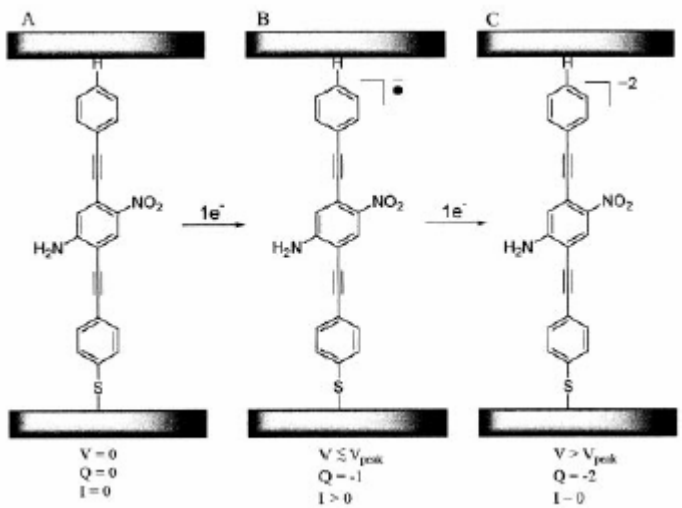






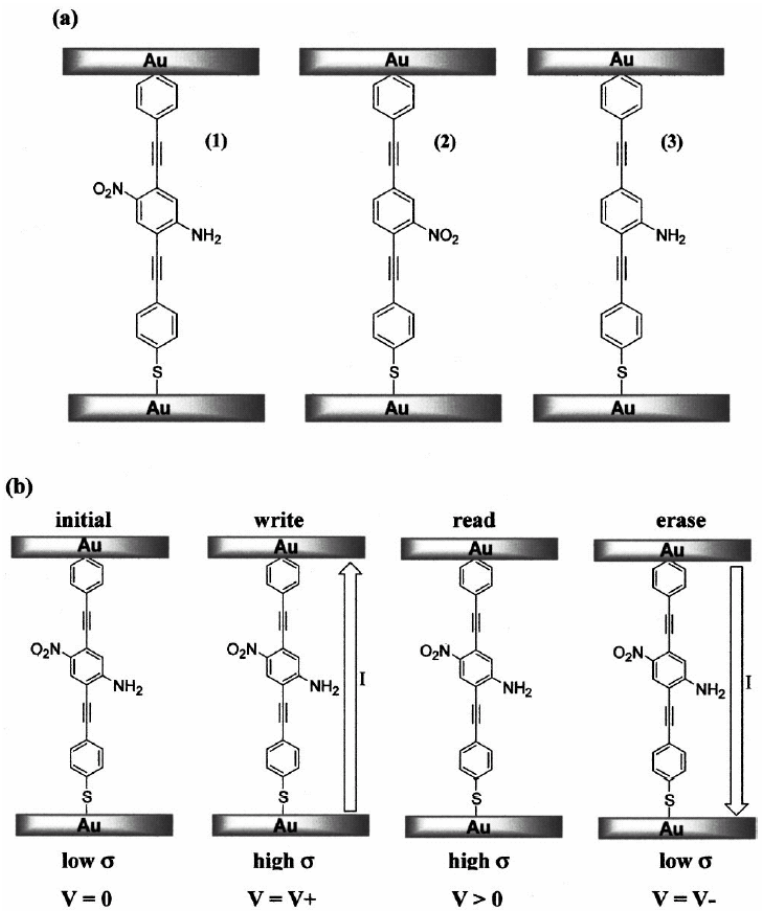


Science **286**, 1550 (1999)
APL **77**, 1224 (2000)

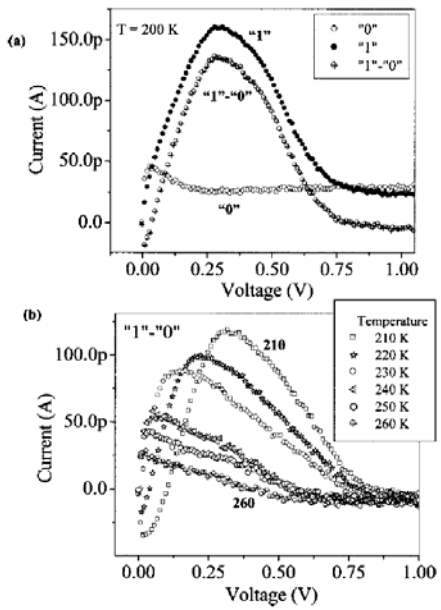


- **Nanopore structure (pore size: 30 - 50 nm)**
- **Molecule: Tour wire with NH_2 and NO_2**
- **Bias direction: bottom thiol (+) / top contact (-)**
- **On-off ratio= 1030:1 at 60 K**
- **Two-step reduction ?**

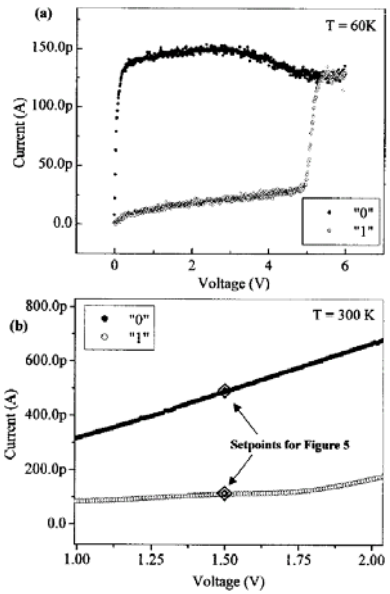
Memory effect on OPE

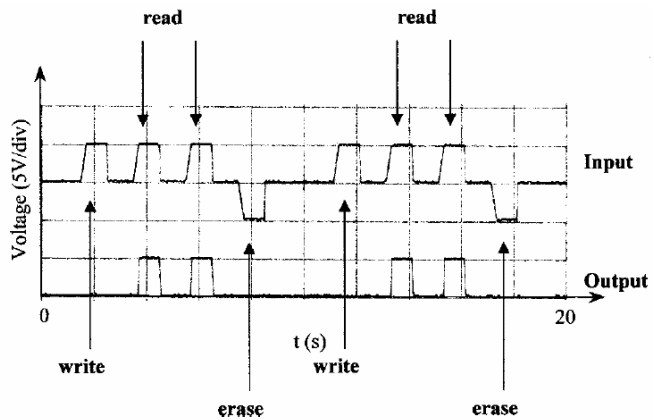


Molecule (1)



Molecule (2)

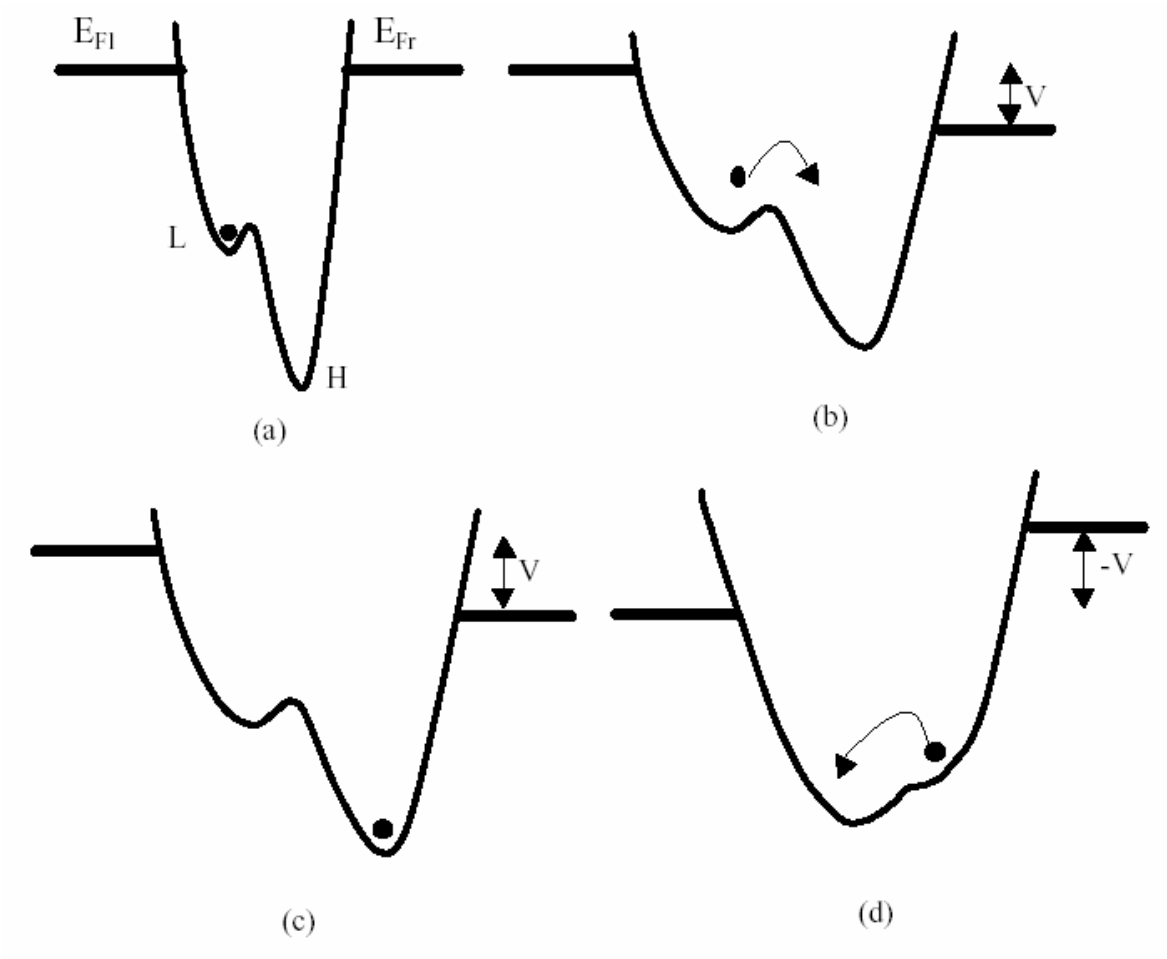




- **Nanopore structure**
- **Molecule: Tour wires**
- **Hysteretic I-V curves**
- **Bias direction: bottom thiol (+) / top contact (-)**

APL **78**, 3735 (2000)

Proposed bi-stability of the OPE derivative



Issues on the OPE derivatives

- **Negative Differential Resistance (NDR) effect in OPE with NO_2:**

  Intrinsic or extrinsic to the molecule ? Junction effect ?

  - NDR effect is intrinsic to single molecules containing an nitro moiety.

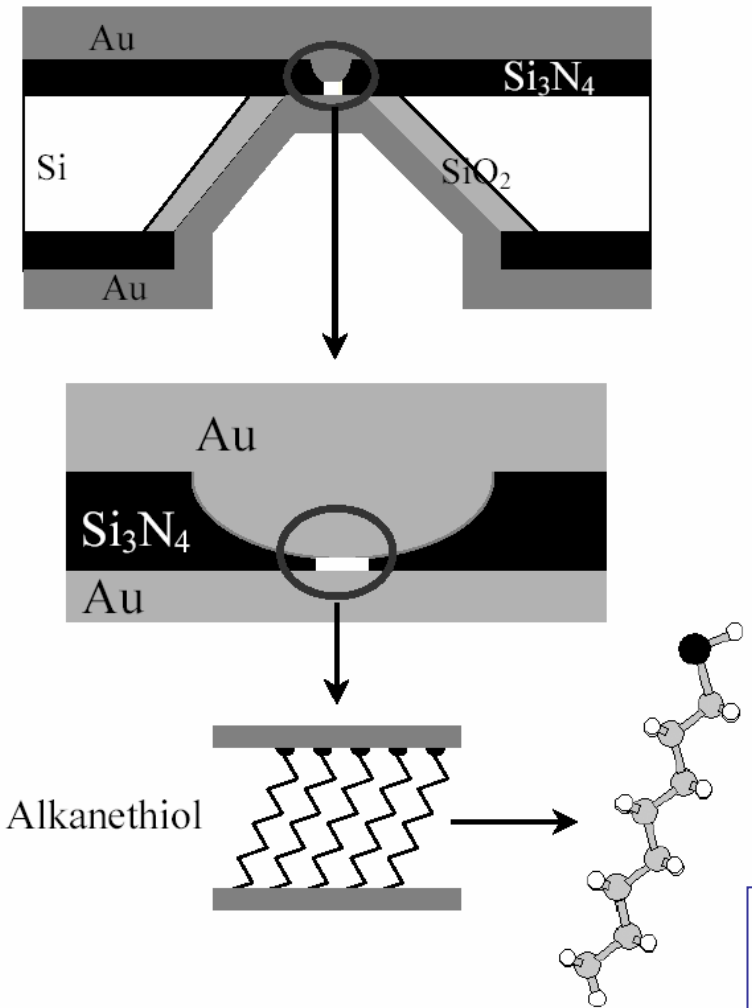
- **Conductance switching and memory effect:**

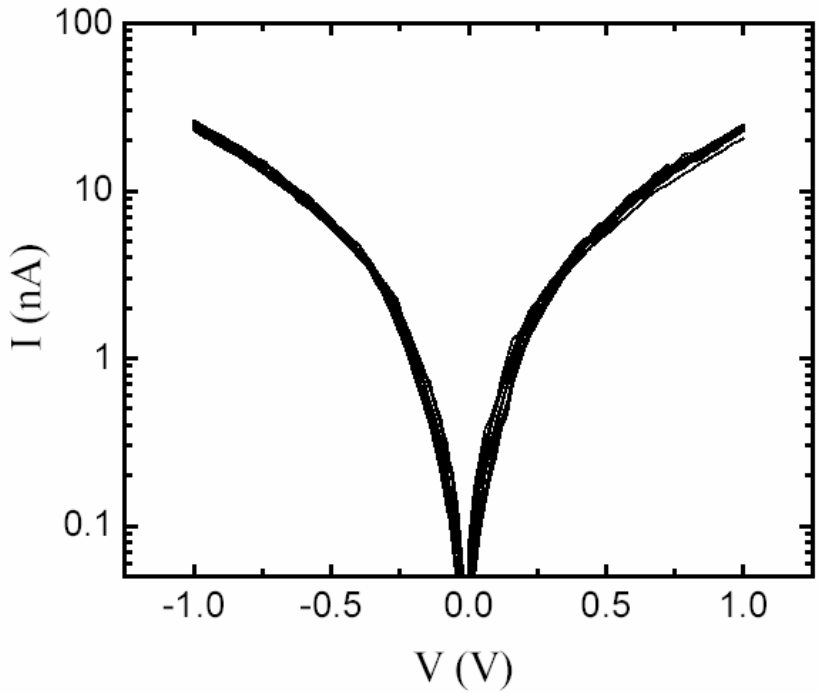
  Conformation change ? Charge trap site ?

  - The switching may be originating from tilting of the molecule.

By SPM study to be shown.

Charge transfer in alkyl chain





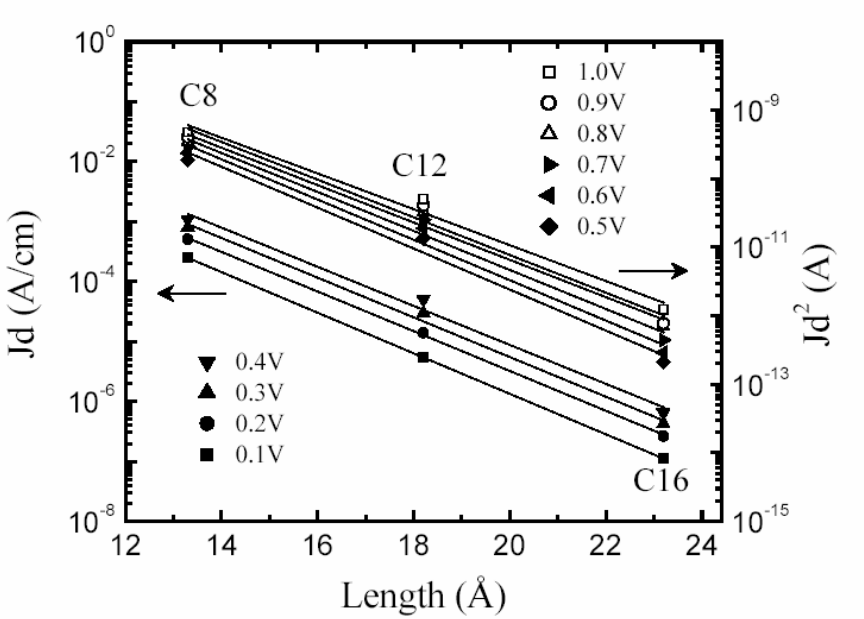
$$R \propto \exp(\beta L)$$

- Aliphatic insulator
- Resistance: exponential length dependence expected
- Temperature-independent *I-V* characteristics.

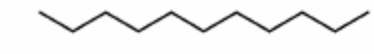
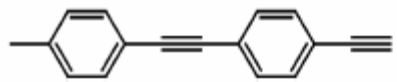
Conduction mechanisms with energy barrier

Conduction Mechanism	Characteristic Behavior	Temperature Dependence	Voltage Dependence	Schematic Band Diagram
Schottky Emission	$I \sim T^2 Exp\left(-q\frac{F-\sqrt{\frac{qV}{4\pi\varepsilon d}}}{kT}\right)$	$\ln\left(\frac{I}{T^2}\right)\sim\frac{1}{T}$	$\ln(I)\sim V^{\frac{1}{2}}$	
Frankel - Pool Conduction	$I \sim VT^2 Exp\left(-q\frac{F-2\sqrt{\frac{qV}{\pi\varepsilon d}}}{2kT}\right)$	$\ln\left(\frac{I}{T^2}\right)\sim\frac{1}{T}$	$\ln\left(\frac{I}{V}\right)\sim V^{\frac{1}{2}}$	
Hopping Conduction	$I \sim VExp\left(-\frac{\Delta E}{kT}\right)$	$\ln\left(\frac{I}{V}\right)\sim\frac{1}{T}$	$I \sim V$	
Fowler-Nordheim Tunneling	$I \sim V^2 Exp\left(-\frac{4d\sqrt{2m}}{3q\hbar V}(qF)^{1.5}\right)$	——	$\ln\left(\frac{I}{V^2}\right)\sim\frac{1}{V}$	
Direct Tunneling	$I \sim VExp\left(-\frac{4\pi d}{h}\sqrt{2mF}\right)$	——	$I \sim V$	

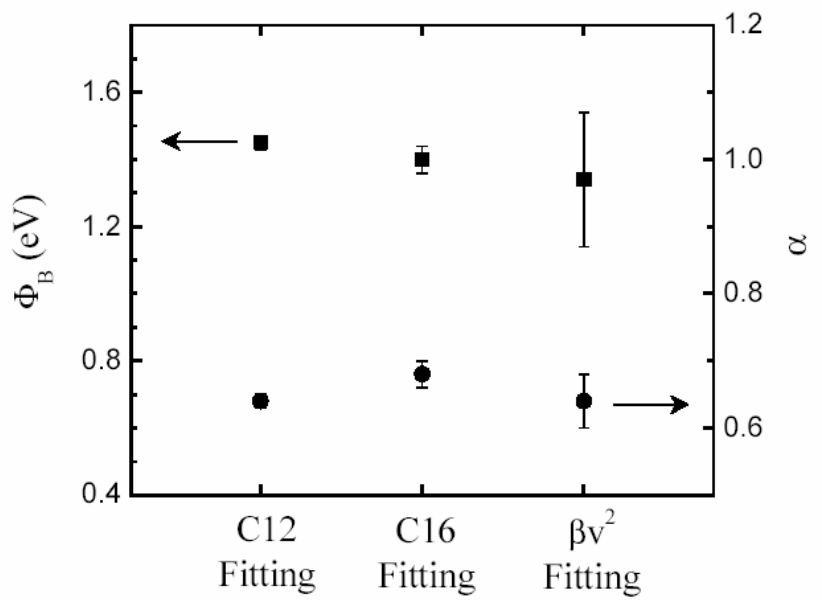
Comparison with theory

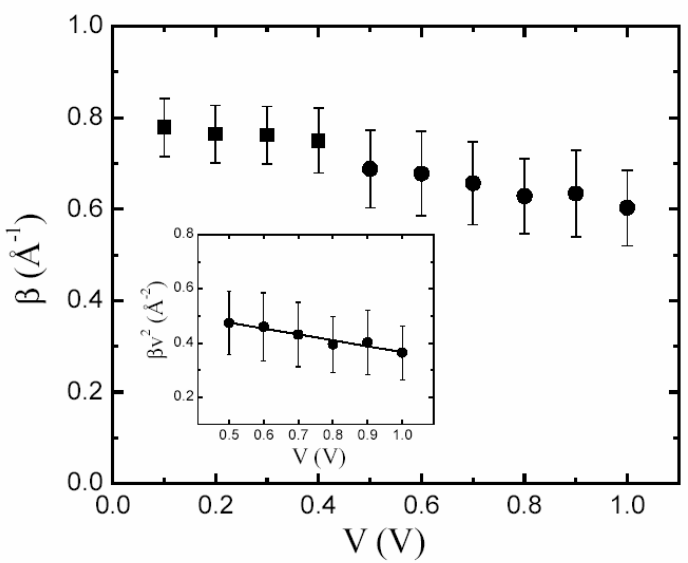


$$R \propto \exp(\beta L)$$

	β, A^{-1}	β, per C
	0.79	~1
	0.27	0.34
	0.27	

ab-initio calculation





A critical question

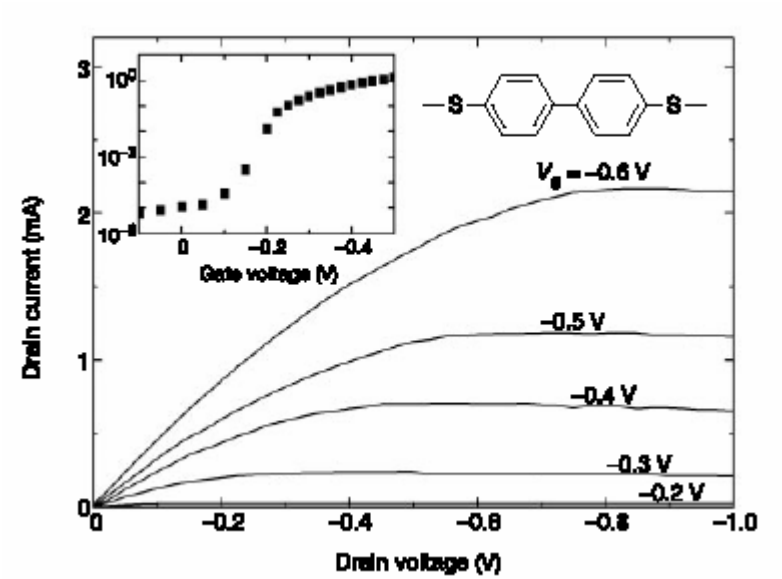
Still, two-terminal devices (diode) only !

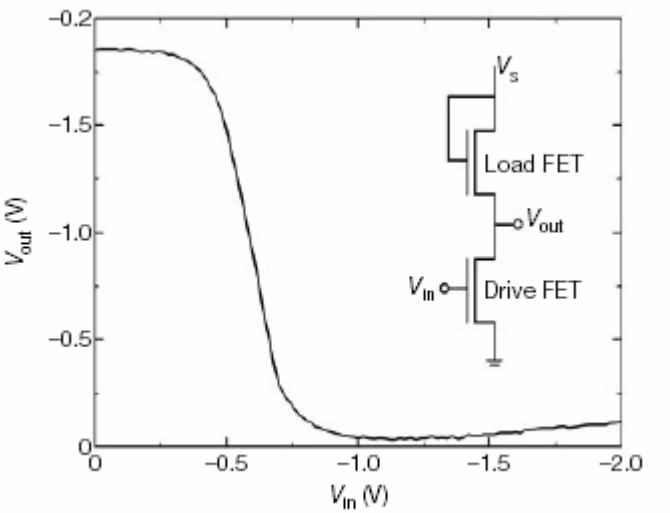
Is three-terminal device (transistor) probable ?

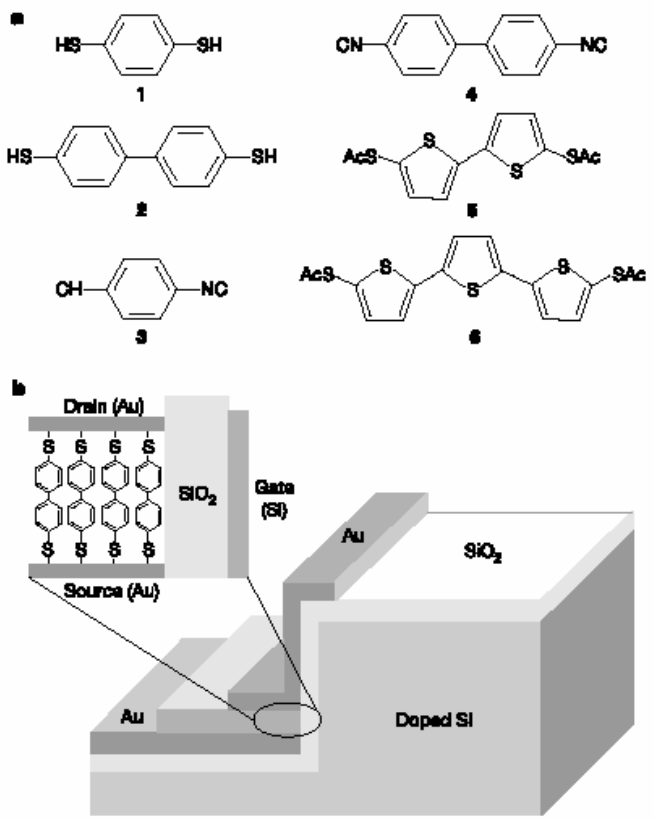
Furthermore, power gain greater than 1 ?

Yes !, ..., Really ?

SAMFET (Self-Assemble Monolayer Field Effect Transistor)





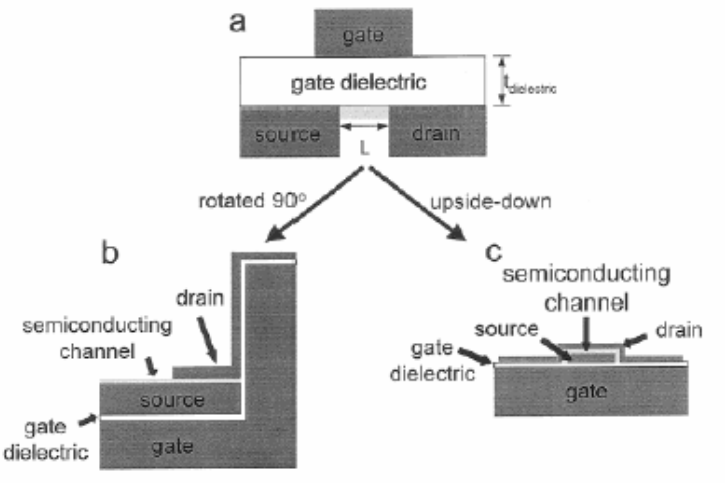


- Field effect even at t_d ~ 23 L ?

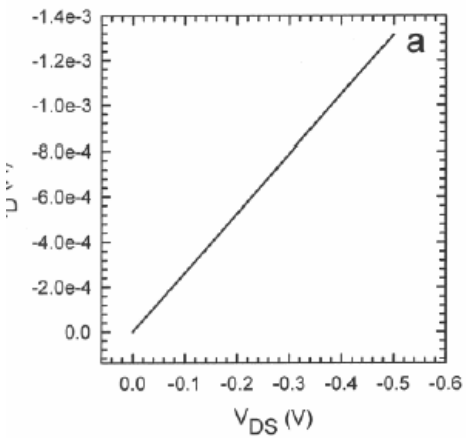
  cf) design rule: L > 1.5 t_d

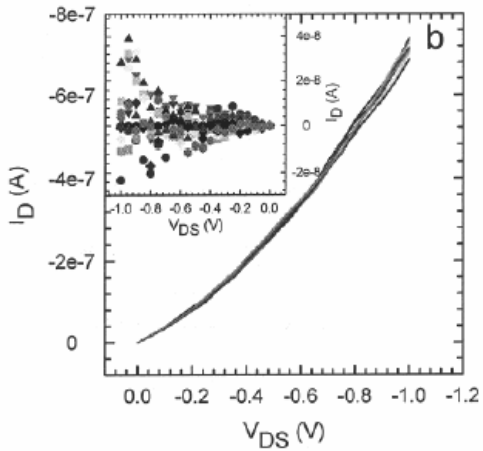
Nature **413**, 713 (2001)

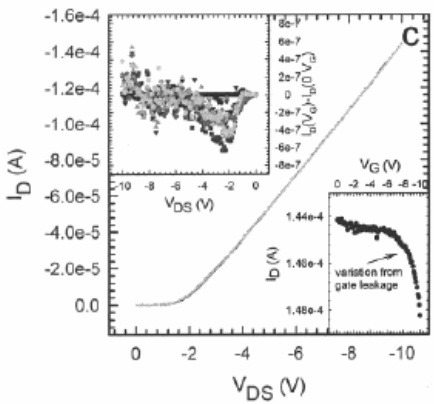
No, in such structure or with such molecules !

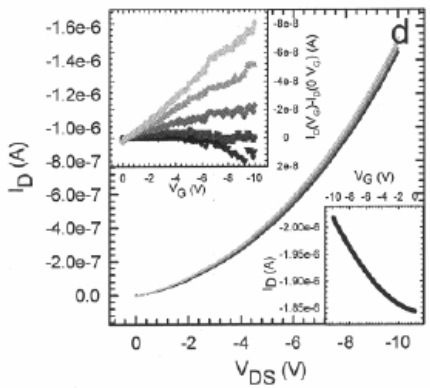


- No difference in the thickness of dielectrics at the trench and the top surface (30 nm)
- No field effect with small *L*.
- Design rule still holds in nano device !







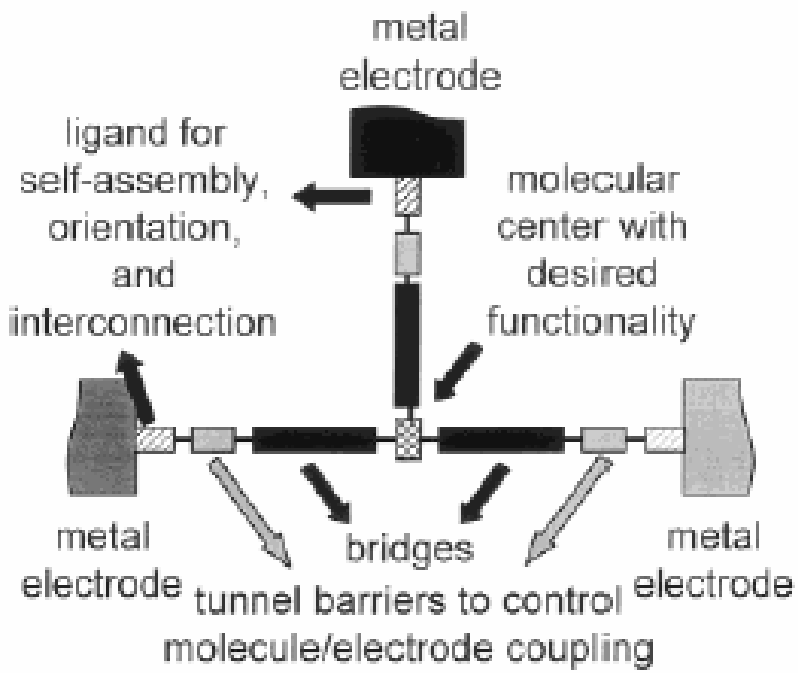


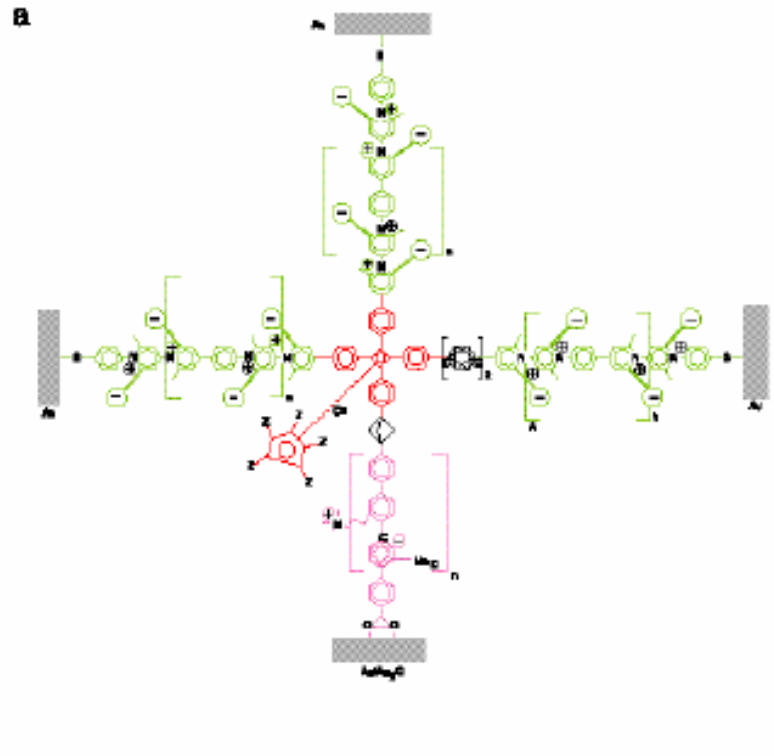
L = 40 nm

L = 400 nm

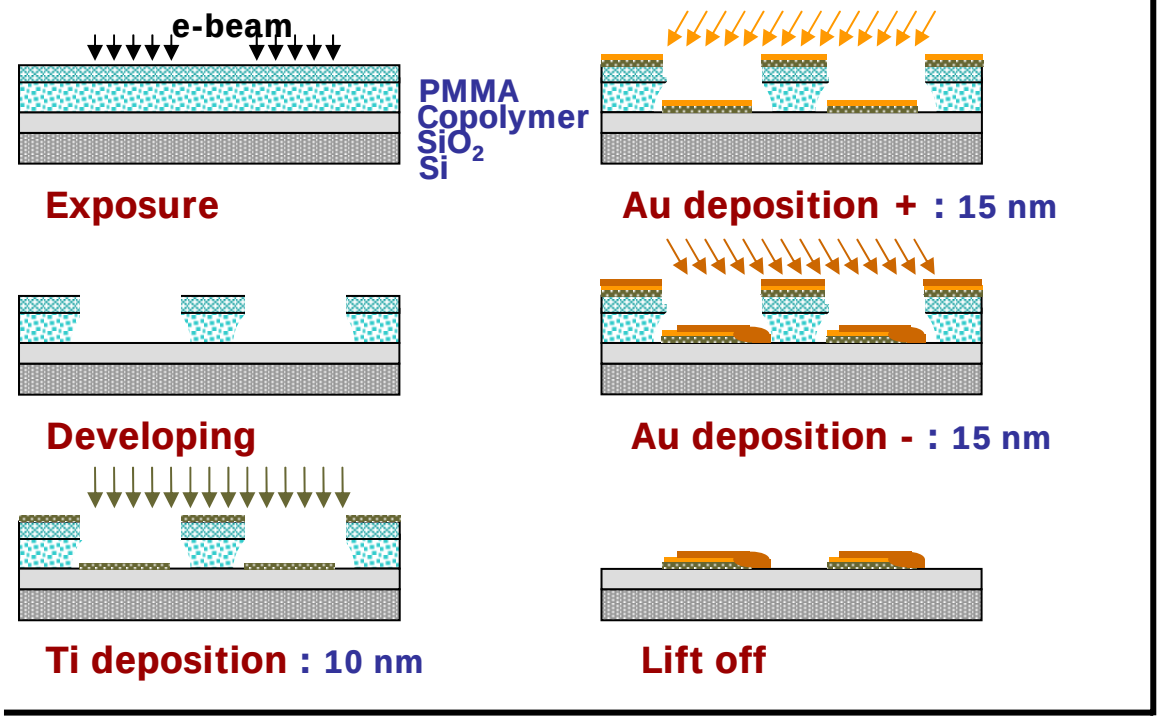
Nano Letters **3**, 119 (2003)

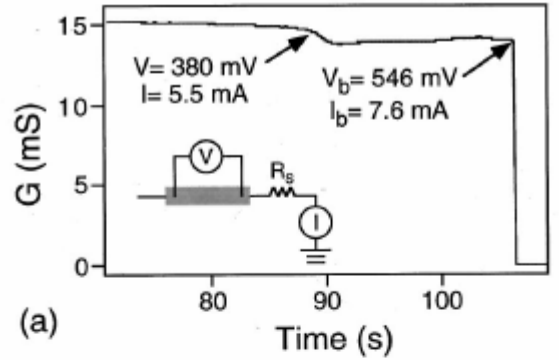
Another approach: gating with molecule

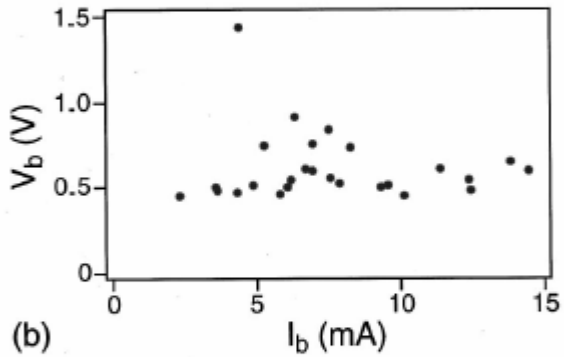




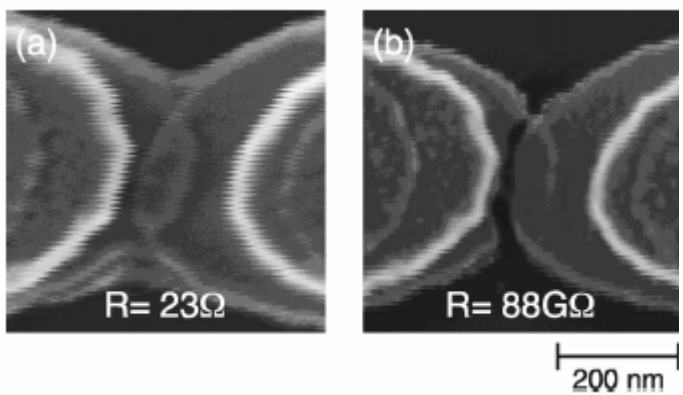
Double angle evaporation and nano-gap by electromigration

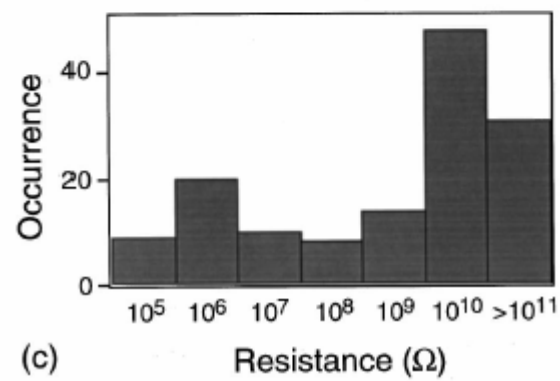






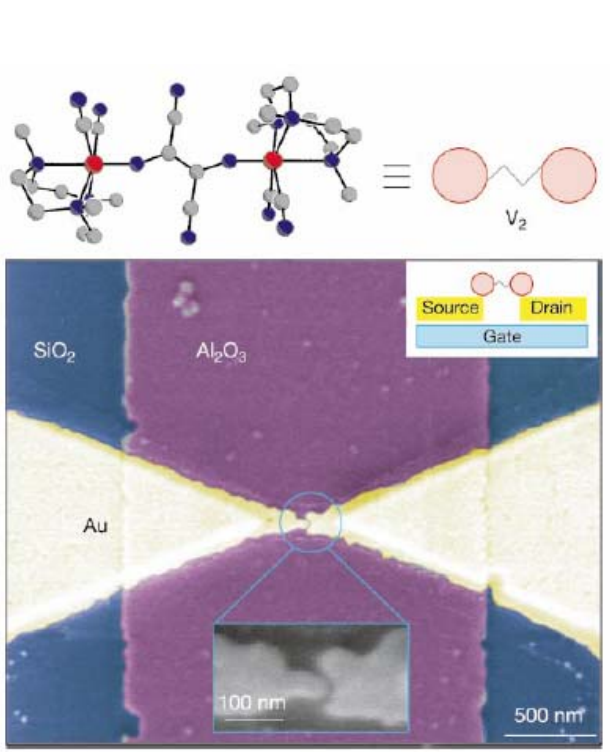
- **Nanowire formation**
- **In-situ monitoring of current**
- **No heating effect**
- **Electromigration of Au**

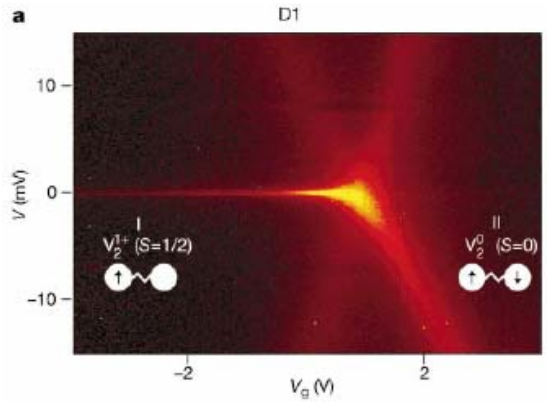


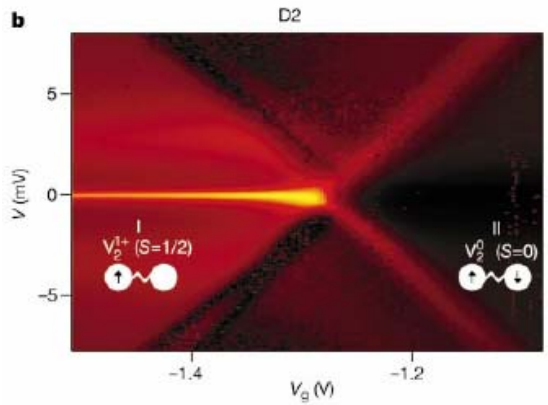


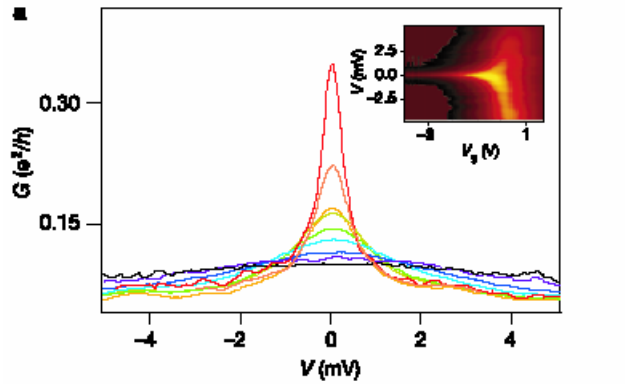
APL **75**, 301(1999)

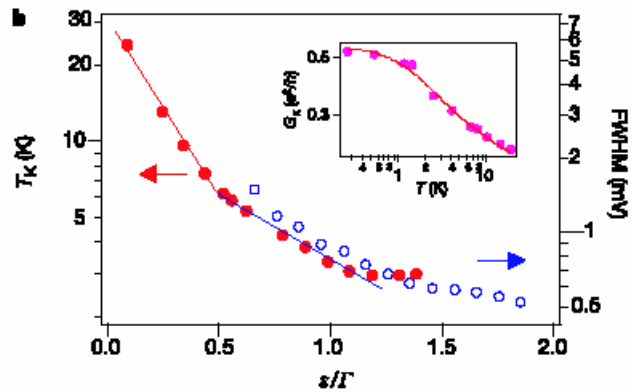
Kondo resonance in MED - I







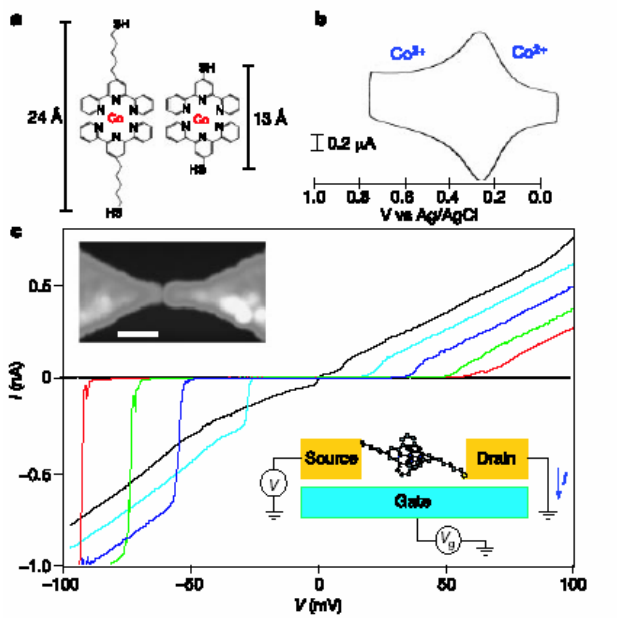


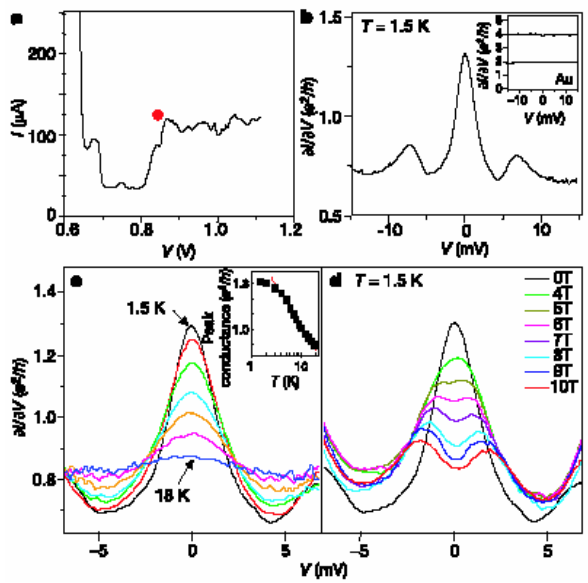


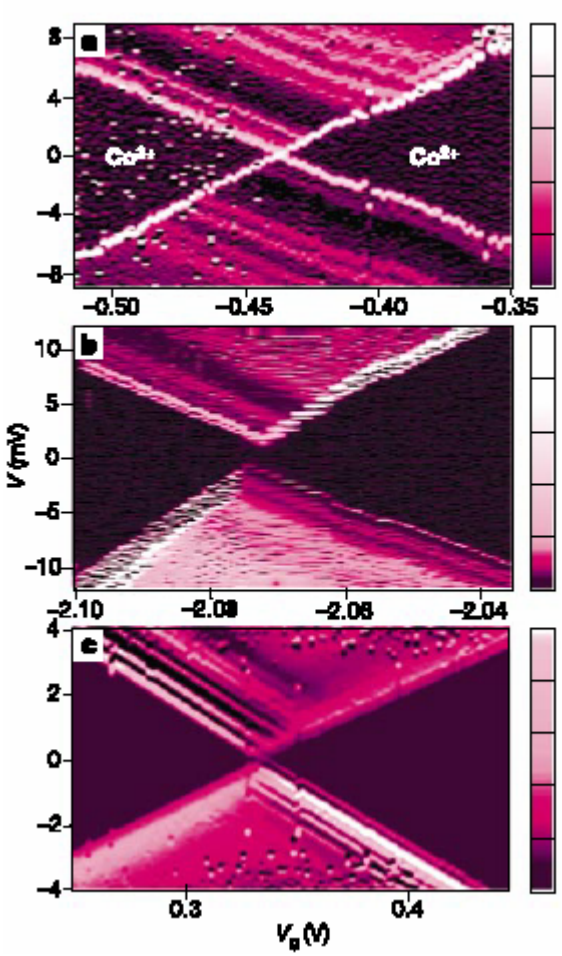
- Break-junction method (electro-migration)
- Molecule: (N,N'0,N'' -trimethyl-1,4,7-triazacyclononane)$_2$-$V_2(CN)_4(\mu\text{-}C_4N_4)$
- Bottom AlOx gate
- Kondo resonance observed: T_K ~ 30 K

Nature **417**, 725 (2003)

Kondo resonance in MED - II



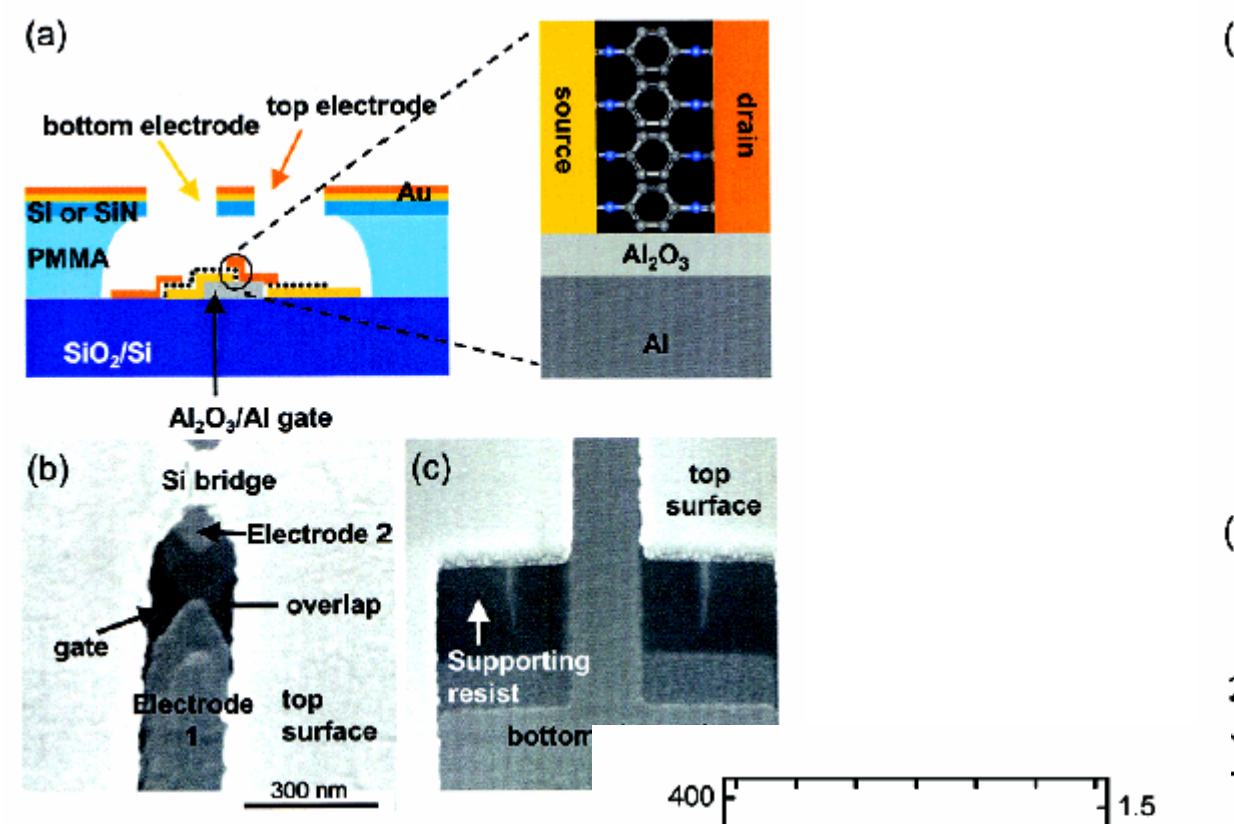


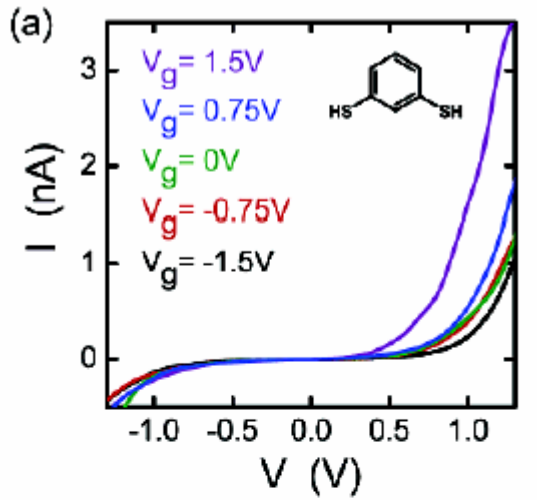


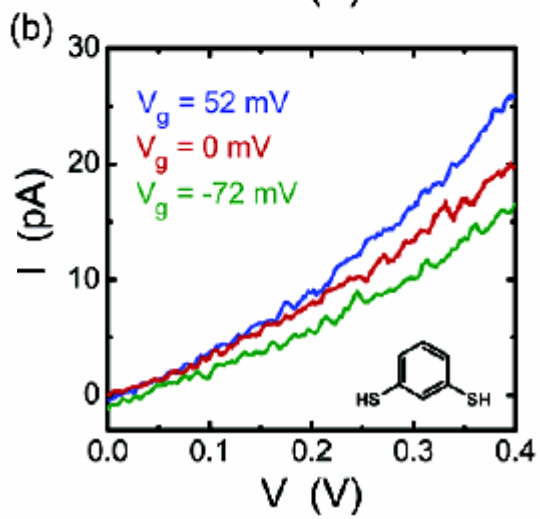
- Two kinds of molecule
- Kondo resonance in small molecule
- Co site behaves as a quantum dot

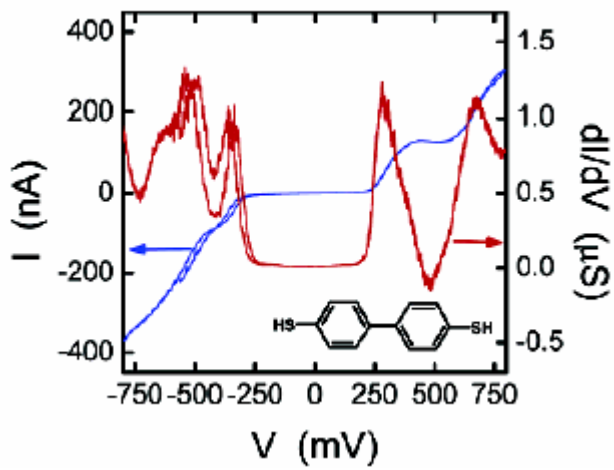
Nature **417**, 722 (2003)

Gate dependence and *I-V* curve asymmetry



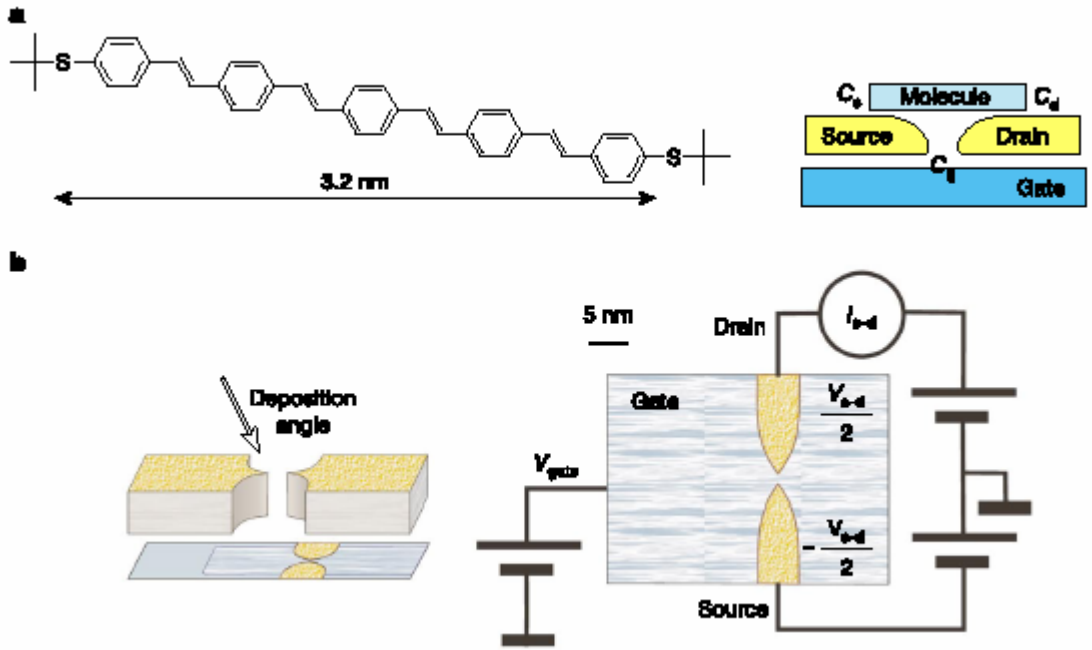


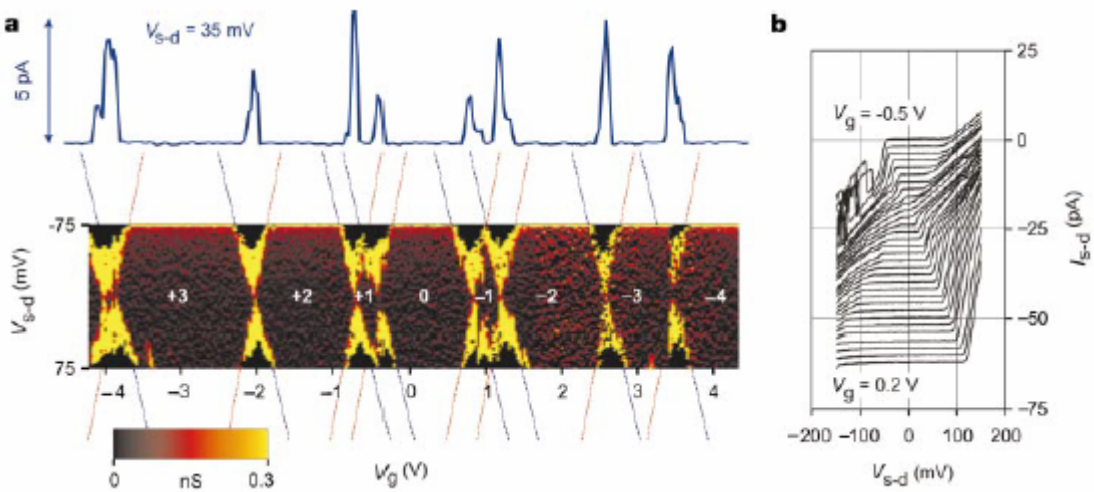


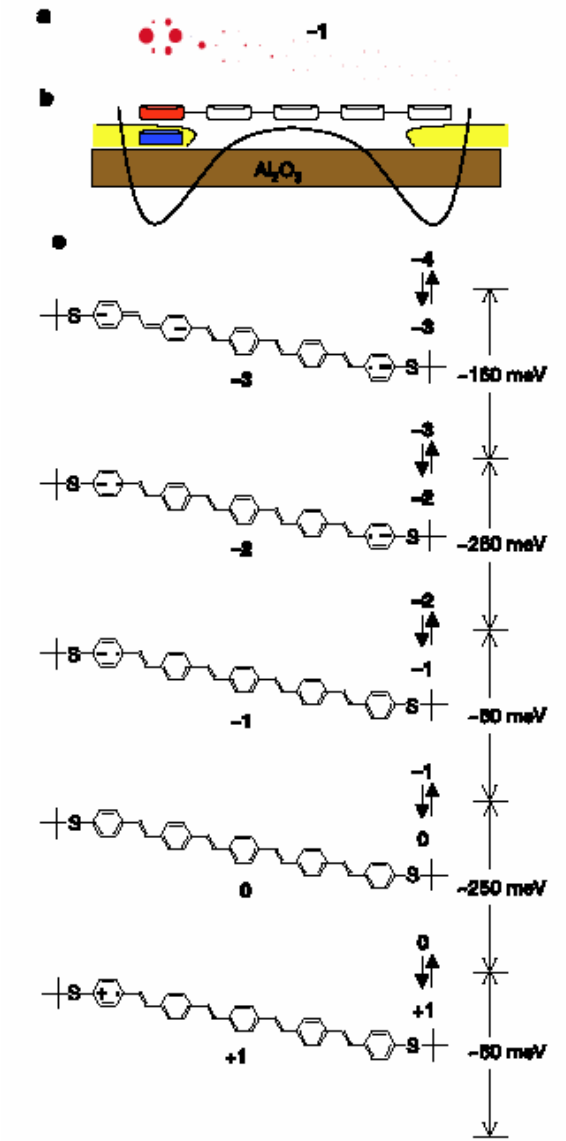


Nanoletters **3**, 113 (2003)

Single-electron tunneling behavior

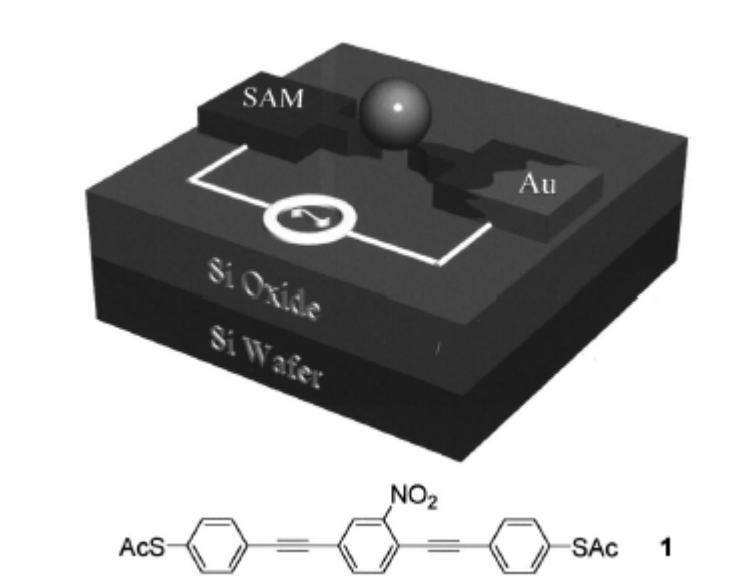


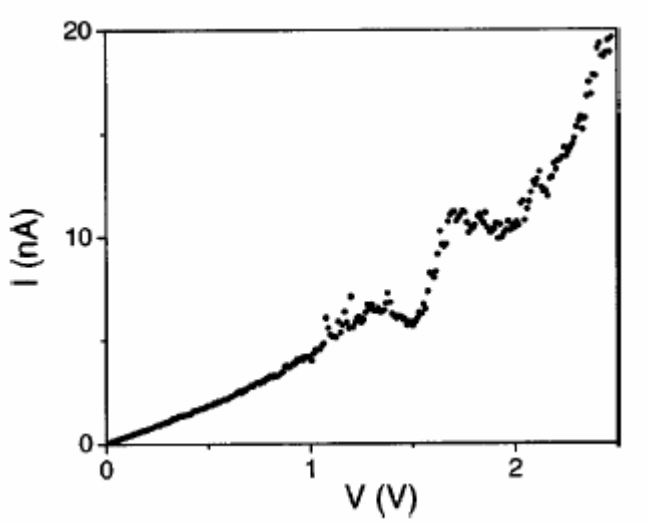


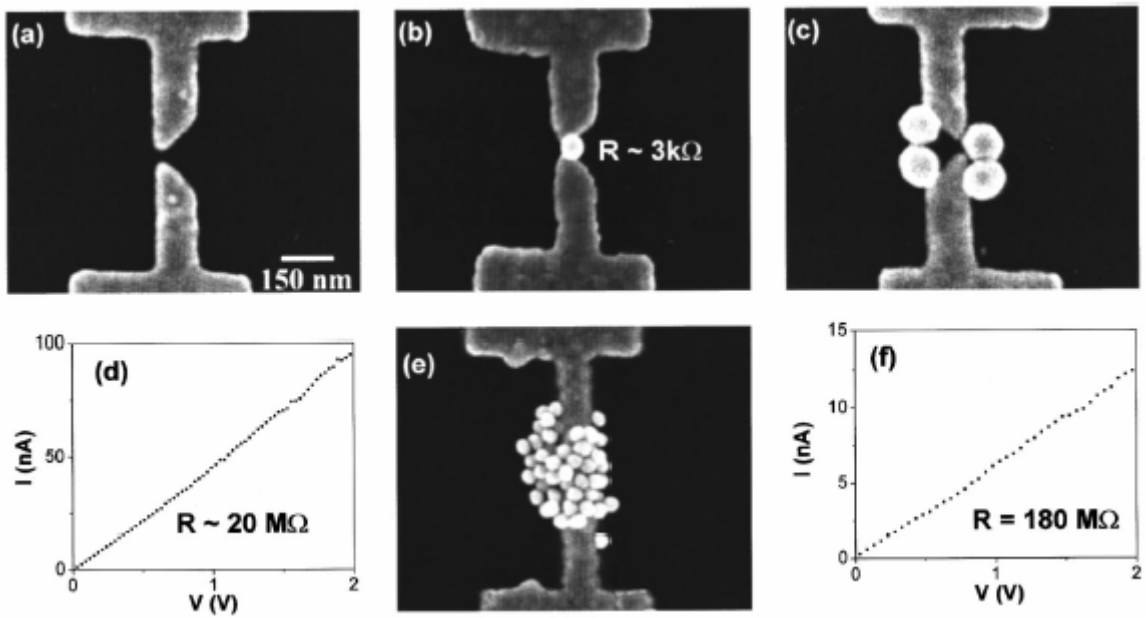


Nature **425**, 698 (2003)

Nano-gap electrodes and nanoparticle for MED



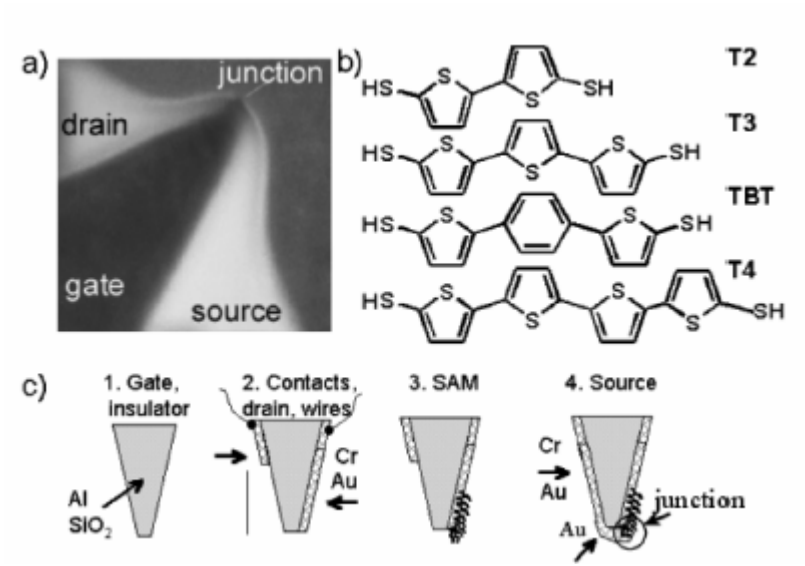


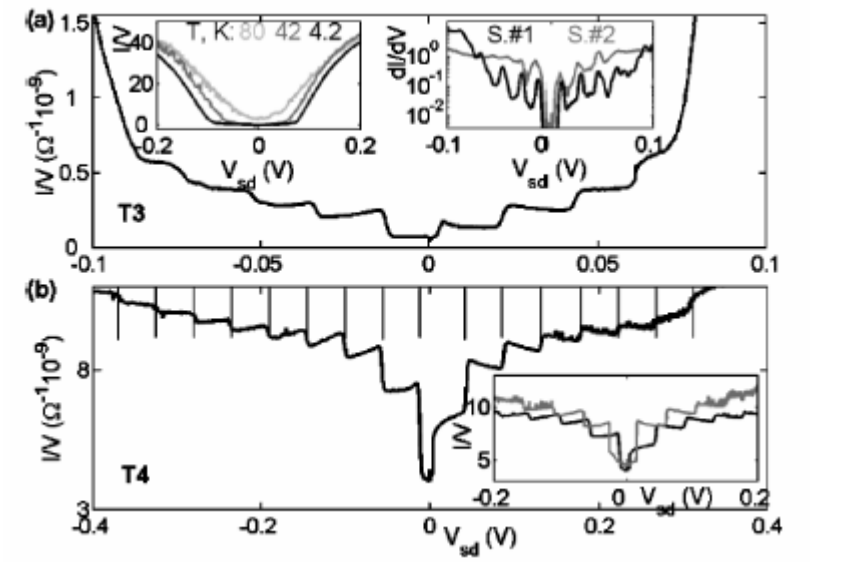


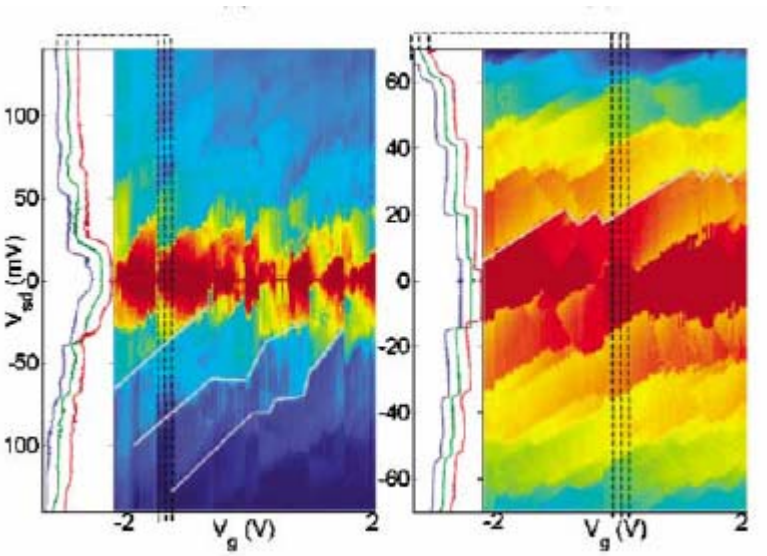
- Nano-gap(~ 50 nm) formation
- Au nanoparticle trapping by electrostatic method
- NDR observed for OPE

APL **80**, 2761 (2002)

Conductance steps in MED



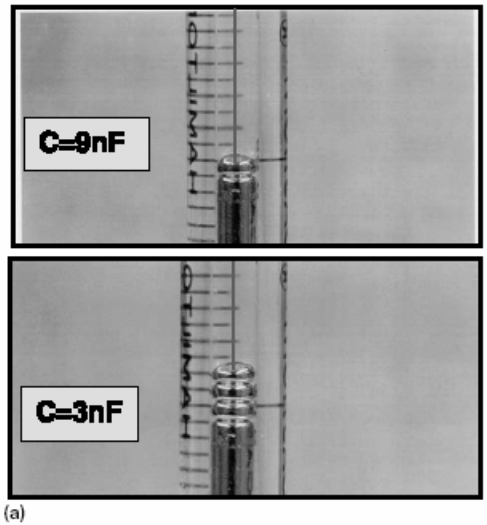


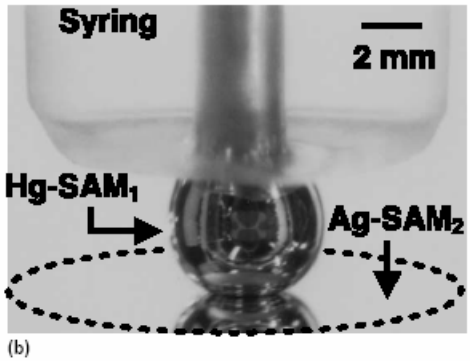


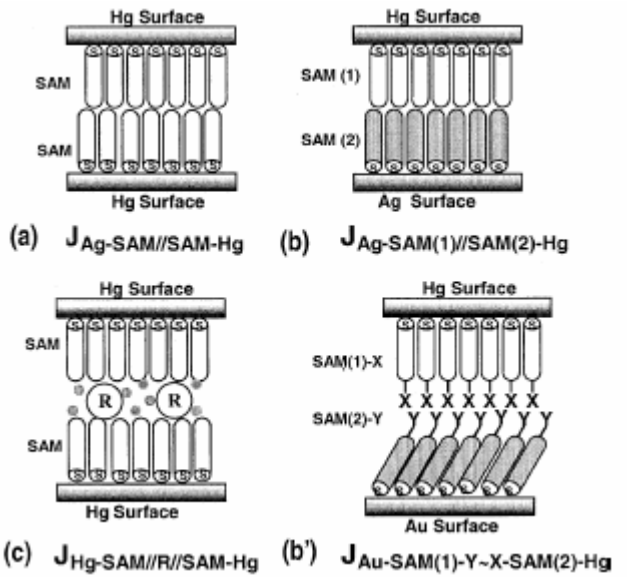
- **Fabrication procedure:**
  - **quarz rod pulled to square tip of size 20-30 nm**
  - **angle evaporation with shadow mask**
  - **in-situ monitoring of the junction resistance**
- **Many steps in conductance curve were shown**
- **Mechanism:**
  - **Coulomb blockade: too small voltage period**
  - **Molecular vibration can be a probable explanation.**

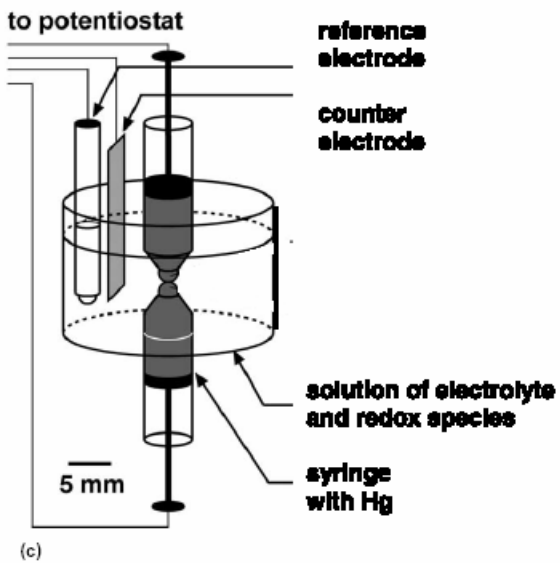
PRL **88**, 226801 (2002)

Mercury droplet method









- **Hg-SAM$_1$//SAM$_2$-Ag (Hg)**
- **Easy to assemble**
- **Stable and reproducible: 80% work well**
- **Versatile: can host a large variety of molecules**

Chem. Phys. **281**, 373 (2002)

Comparison of MEDs

		<——— Molecular Electronic Device ———>				
Quantity	**Units**	**1,4-Dithiol Benzene**	**3-Ring Poly-phenylene Wire**	**Poly-phenylene RTD (5 rings)**	**Carbon Nanotube**	**Copper Wire**
Applied Voltage	Volts	1	1	1.4 (peak)	1	2×10^{-3} (10 cm wire)
Current Measured in Experiment	Amperes	2×10^{-8}	3.2×10^{-5}	1.4×10^{-11}	1×10^{-7}	1 (approx.)
Current Inferred per Molecule	Amperes Electrons per Sec	2×10^{-8} 1.2×10^{11}	3.2×10^{-8} 2.0×10^{11}	1.4×10^{-14} 8.7×10^{4}	1×10^{-7} 6.2×10^{11}	– –
Estimated Cross-Sectional Area per Molecule	nm^2	~0.05	~0.05	~0.05	~3.1 (Radius ≈ 1 nm)	$\sim 3.1 \times 10^{12}$ (Radius ≈ 1 mm)
Current Density	Electrons per Sec-nm^2	$\sim 2 \times 10^{12}$	$\sim 4 \times 10^{12}$	$\sim 2 \times 10^{6}$	$\sim 2 \times 10^{11}$	$\sim 2 \times 10^{6}$
Reference		[7]	[8]	[5,6]	[4]	

Proceedings of the IEEE **88**, 386 (2000)

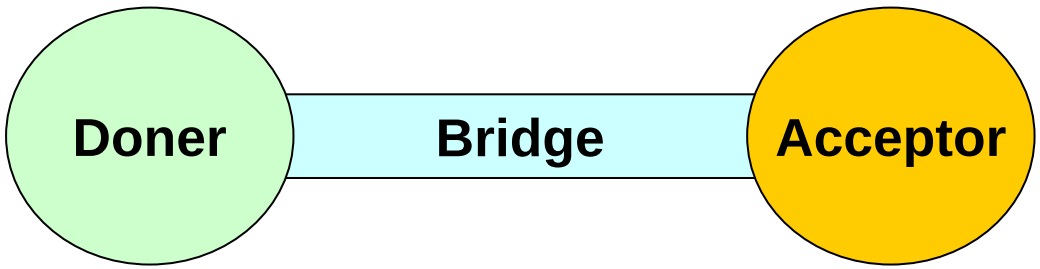
Summary

- A variety of electrode-molecule-electrode structures for MED were shown.
- Molecular electronic device components (rectifying diode, resonant tunneling diode, random access memory, and single electron transistor) were demonstrated.
- Current rectification can be realized by making an asymmetric electronic configuration with any molecule with a small energy gap.
- Resonant tunneling diode can be made in similar ways with rectifying diodes. Factors needed additionally are:
  - definite tunneling barriers and
  - more than two moieties with discrete electronic energy levels.
- Some OPE derivatives show interesting features like NDR (due to resonant tunneling) and conductivity switching (memory) effects.
- The mechanisms of NDR and memory effect have not been clearly understood yet.
- Molecular FET has still to be demonstrated.

- **Charge transfer on the nanoscale:**

  Scanning Probe Microscope studies

SPM study on charge transfer

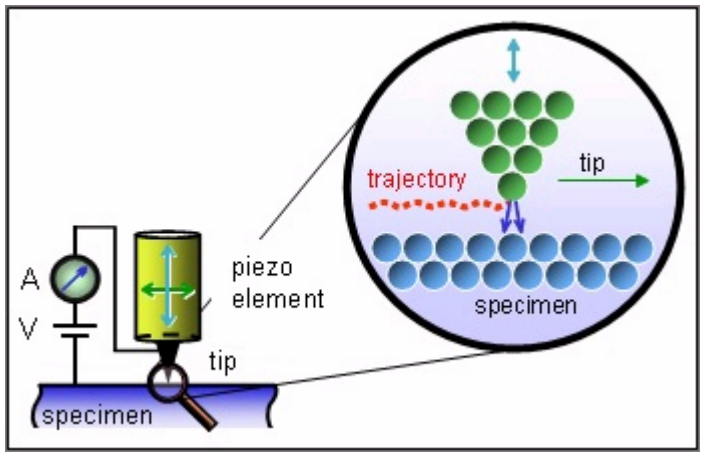


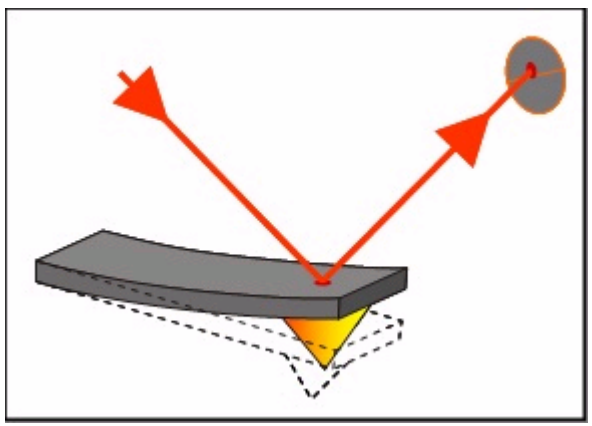
SPM tip (M) **molecule (I/C)** **electrode (M)**

"A powerful tool to study charge transfer on the nanoscale"

Key technology: to make electrical contact between SPM tip and the molecules.

Scanning Probe Microscopy / Spectroscopy





- **Scanning Tunneling Microscope (STM):**
  - **tunneling current between the sample & the tip**
  - **the morphology of the local electronic states**
  - **atomic resolution**
  - **conductive samples only**
- **Atomic Force Microscope (AFM):**
  - **deflection of the cantilever by vdW force**
  - **resolution lower than STM in general**
  - **more versatile**
  - **electron spectroscopy can be made possible using conductively coated cantilever and tip**

Pictures copied from
http://www.physics.leidenuniv.nl/sections/cm/ip/group/Principle_of_SPM.htm

Issues on the MED prone to SPM study

- **Conductance of single molecule?**

  - Conducting molecule: how much conducting?

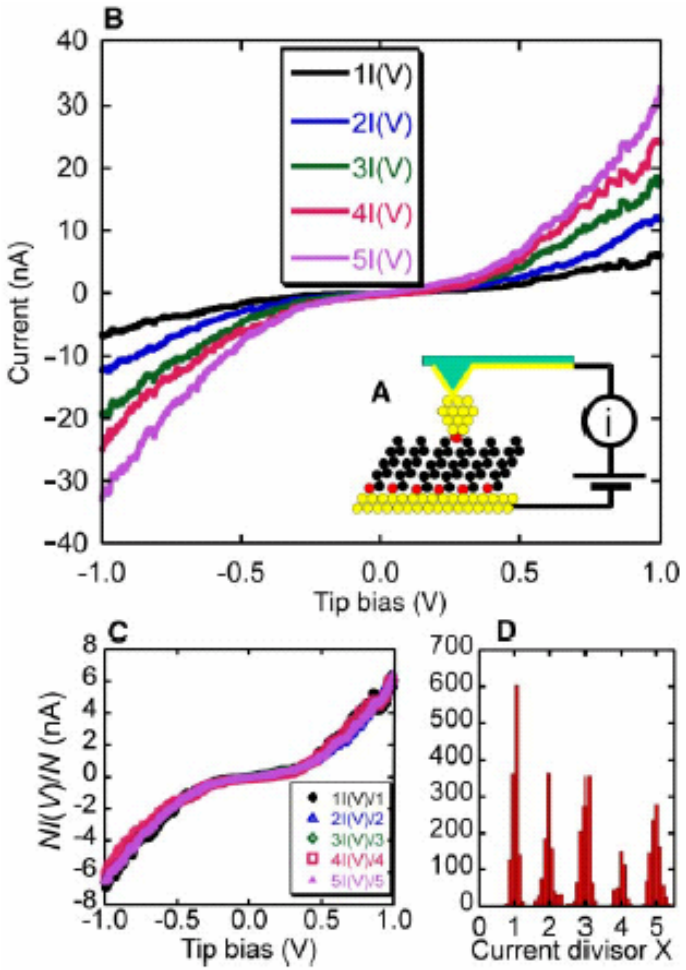
  - Insulating: inverse decay length β

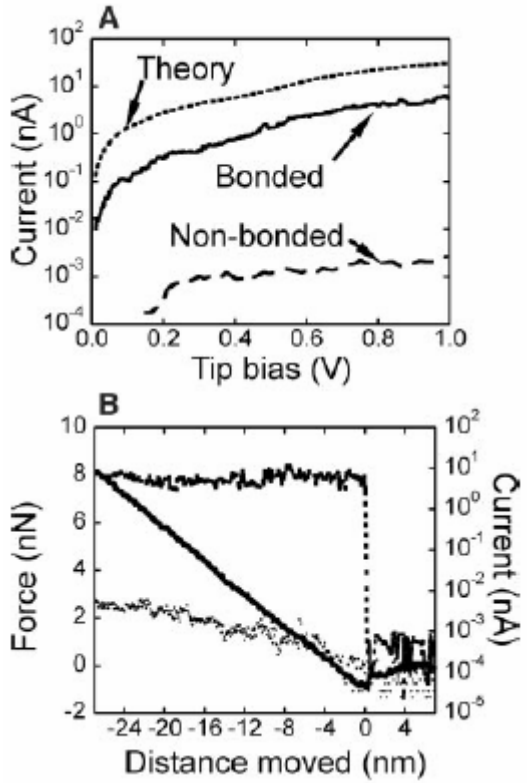
- **Issues on OPE derivatives**

  - Negative Differential Resistance effect in OPE with NO_2

  - Conductance switching and memory effect

Measurement of single alkanedithiol *I-V*

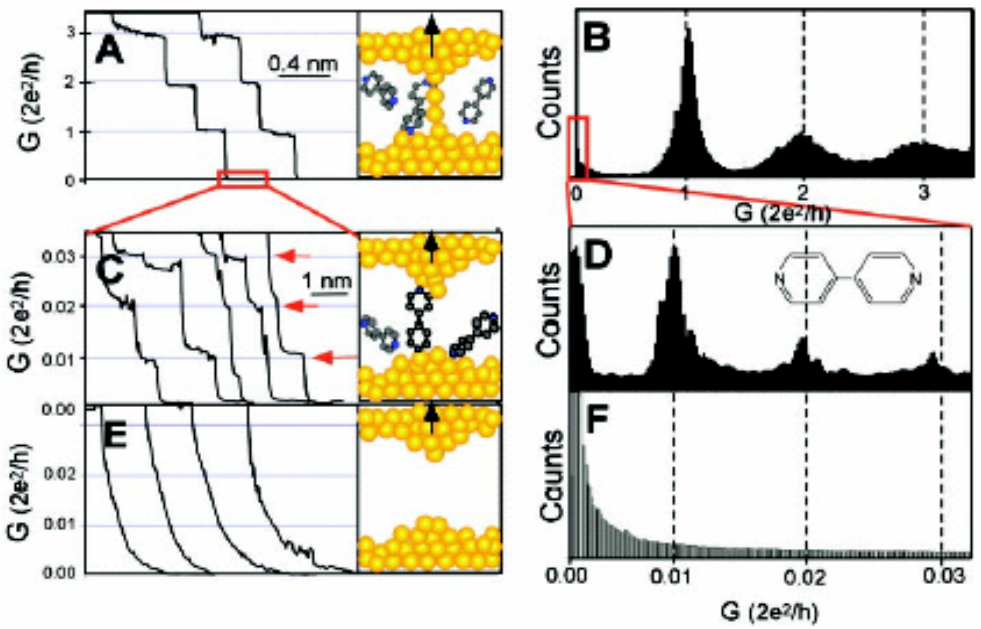


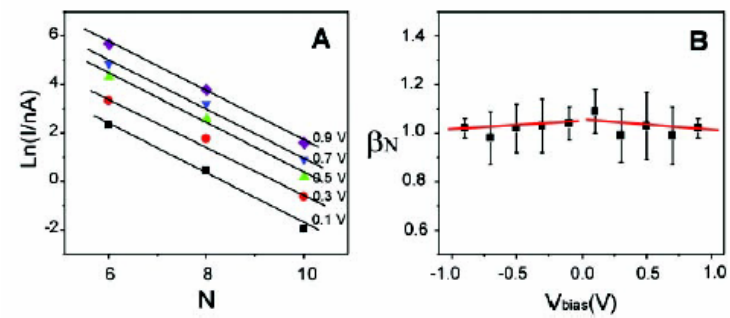


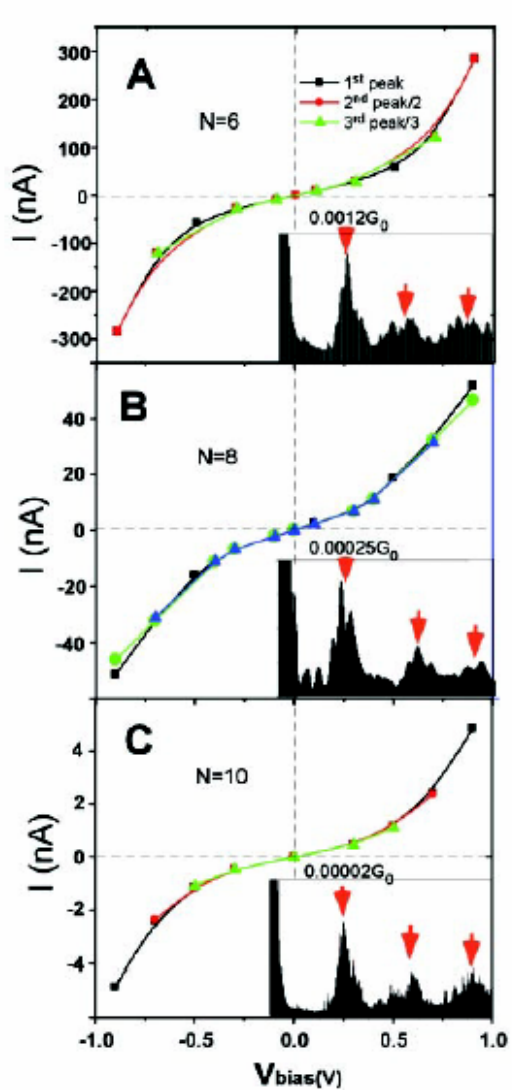
- **Sample fabrication: SAM of octanethiol on Au**
  → partial replacement by octanedithiol
  → Au nanoparticle attachment
- **Contact force dependence was negligible.**
  (For nonbonded contacts, the *I-V* characteristics are dominated by the contact.)

Science **294,** 571 (2001)

Measurement of n-molecule resistance







Science **301,** 1221 (2003)

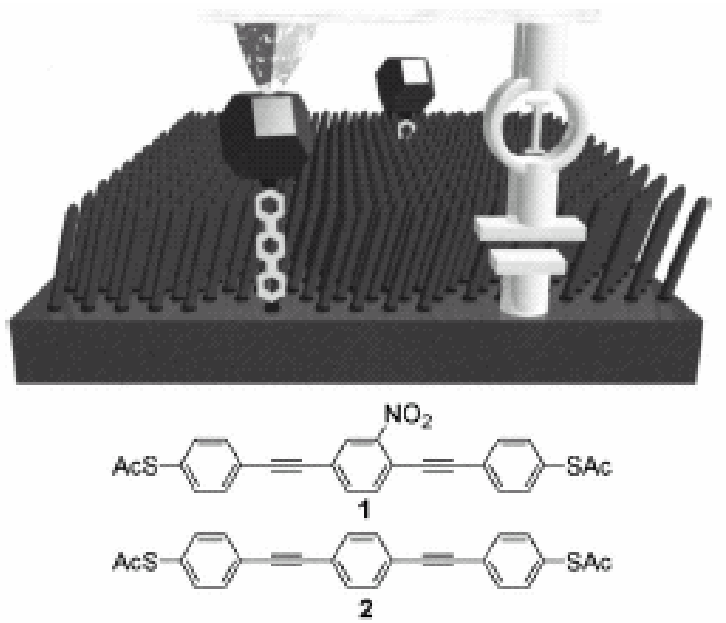
- **STM measurement on a solution contaning molecules.**
- **Current measured at fixed voltage values while retracting the tip.**
- **Molecules: 4,4' bipyridine, alkanedithioles.**

Issues on OPE derivatives

- **Proposed mechanisms for the NDR effect**
  - electric field-induced twist of the central ring (× no hysteresis observed)
  - delocalized orbital of LUMO in the singly reduced state
    (localized LUMO in the neutral & doubly reduced state)
  - resonant tunneling with the twisted central ring acting as a tunnel barrier
- **Conductance switching effect**
  - formation of metal nanofilaments through molecular SAM between electrodes
  - the absence of well-defined chemical bond between the SAM and top electrode
  - electric field-induced twist of the central ring
    (accompanied by the reduction of the central moiety)
  - change of the bonding angle between Au bottom electrode and molecular axis
  - fluctuations in the Au-S linkage (between surface chemisorption sites)

"None of the mechanisms proposed has been accepted as being definitive."

Investigation of NDR effect in single OPE molecules

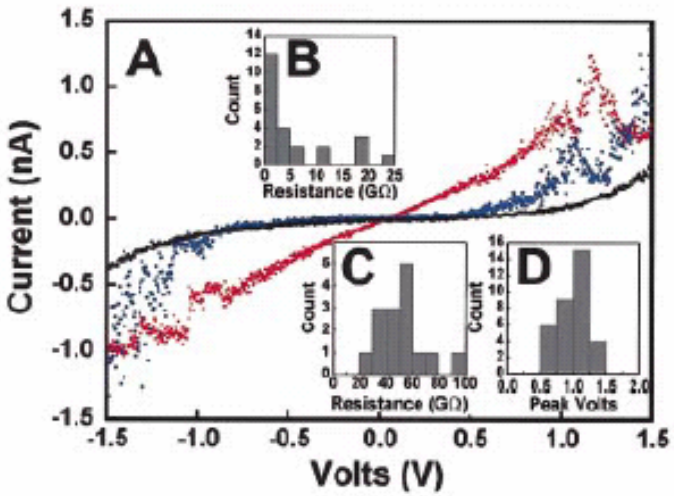


Sample preparation: dodecanethiol SAM on Au

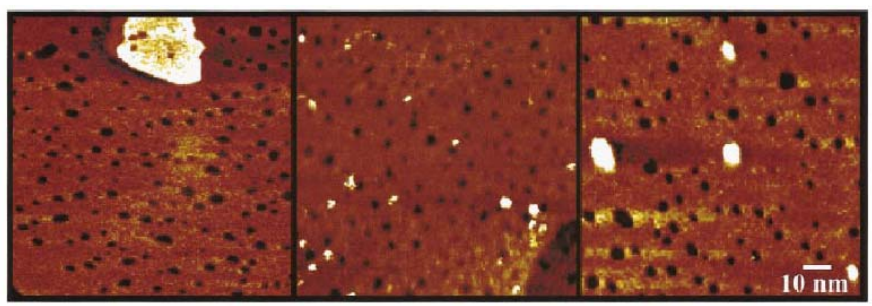
→ insertion of single OPEs (1, 2)

→ attachment of Au-NPs (~ 2nm)

APL **81**, 3043 (2002)

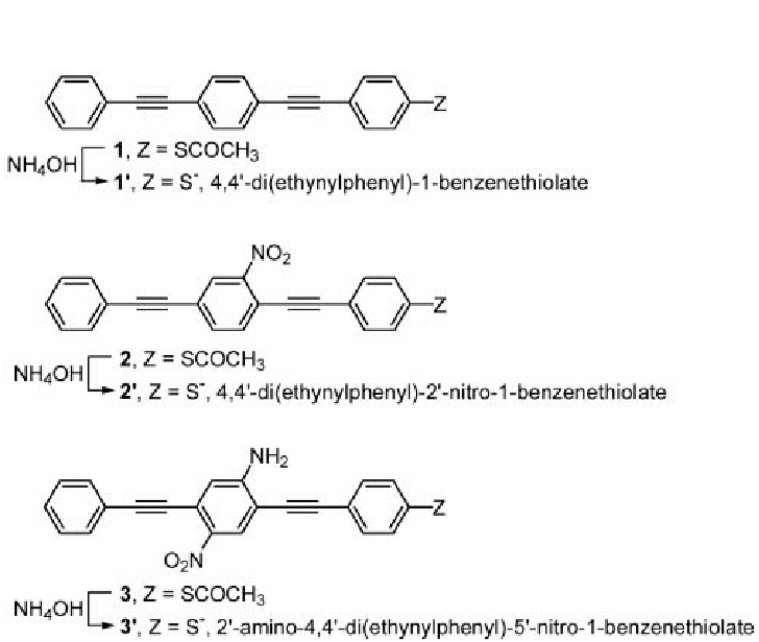


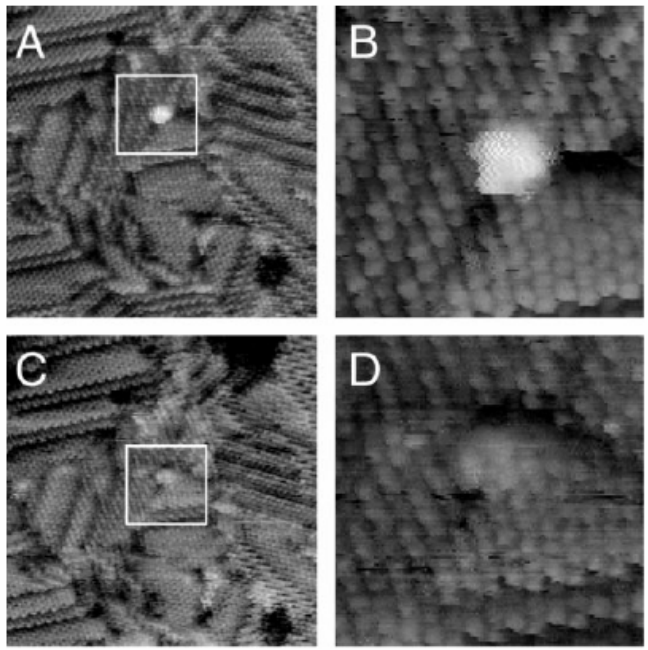
[A] **red**/**blue**: molecule 1, **black**: molecule 2
For molecule 1, NDR features are clearly seen.
[B] Resistance distribution for molecule 1
[C] Resistance distribution for molecule 2
[D] NDR peak voltage distribution

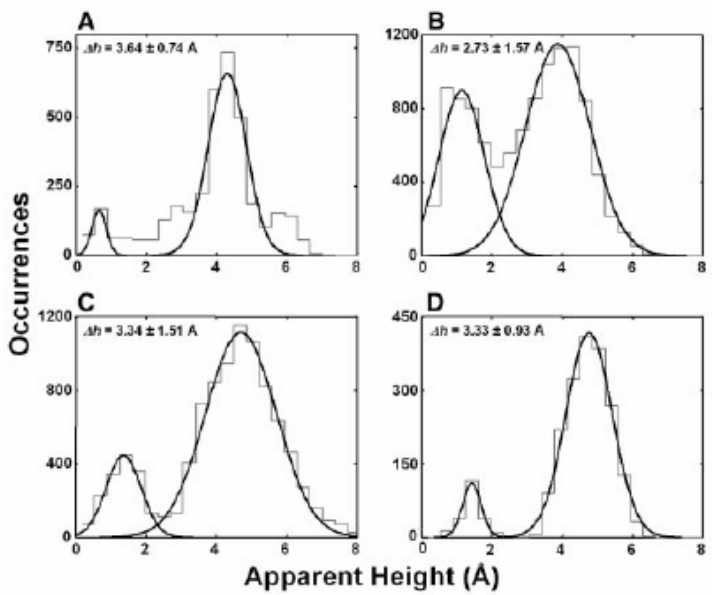


- **cAFM tip/Au nanoparticle/dithiolated molecule**
- **NDR peaks for molecule 1: NDR effect is intrinsic to single molecules with nitro moiety.**

Origin of the conductance switching of OPE - I





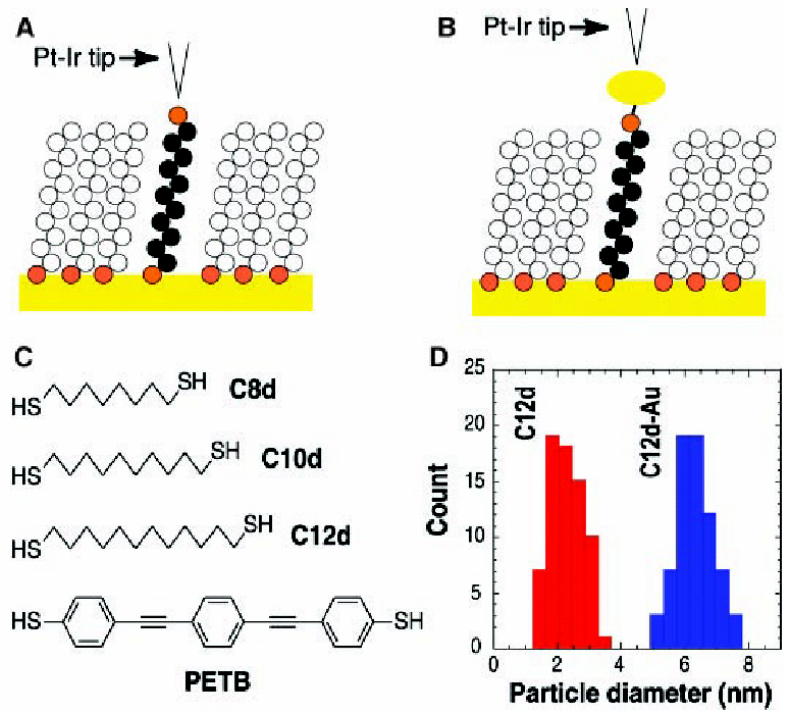


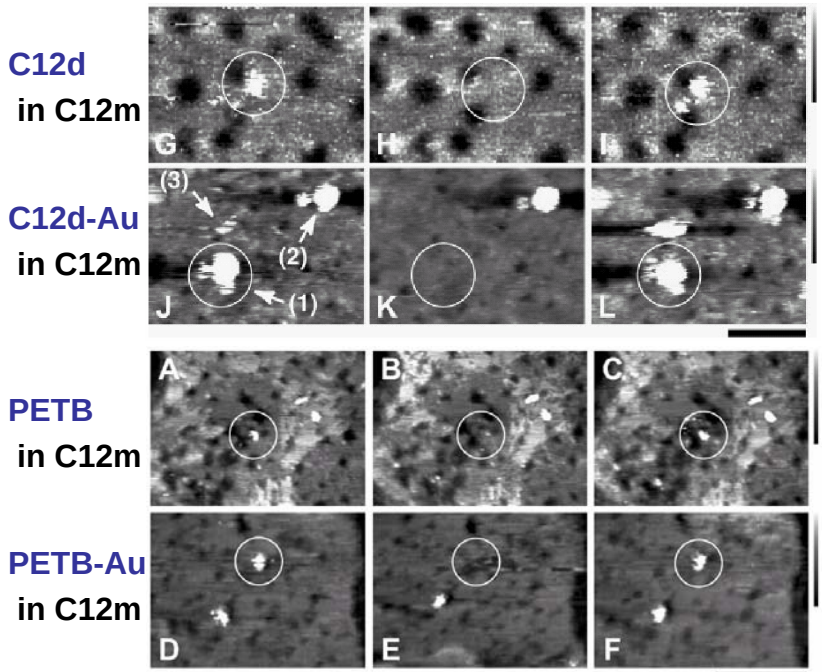
Science **292**, 2303 (2001)

- **Sample preparation:**
  dodecanethiol SAM on Au
  → insertion of single OPEs
  (mainly in defect sites of SAM and Au step edges)
- **Conductance switching observed for all three OPE derivatives**

Origin of the conductance switching of OPE - II

Science **300**, 1413 (2003)

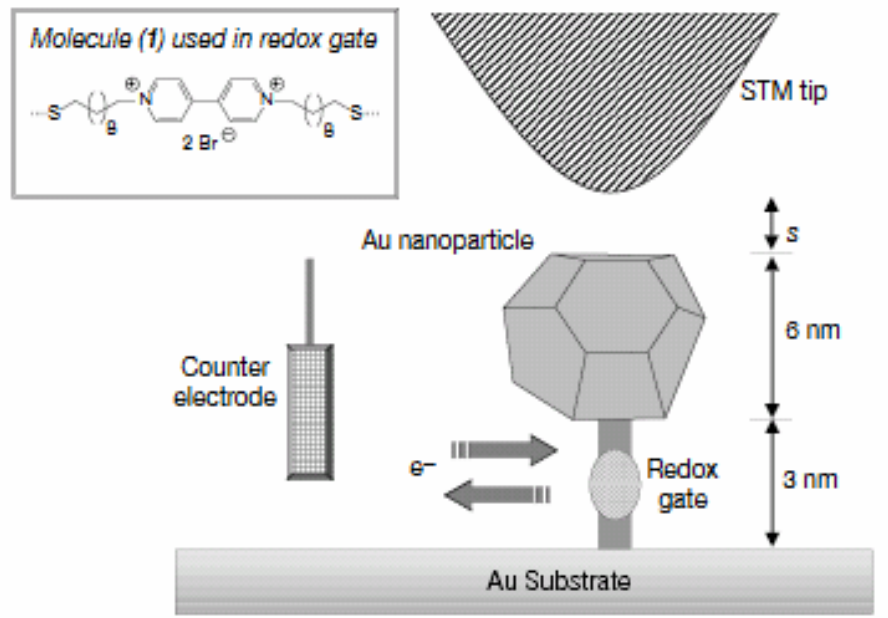


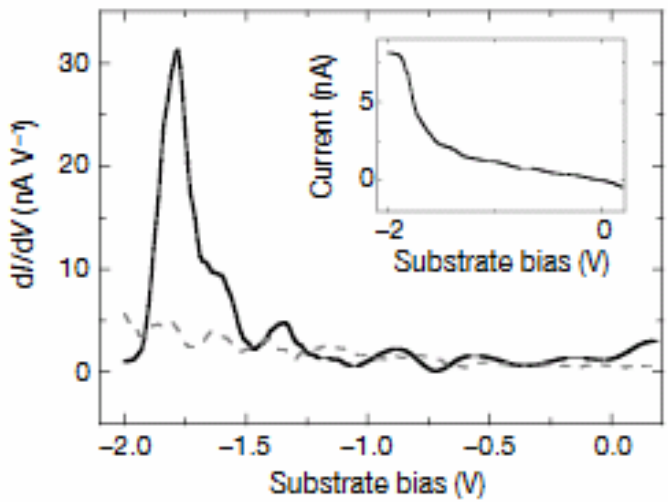


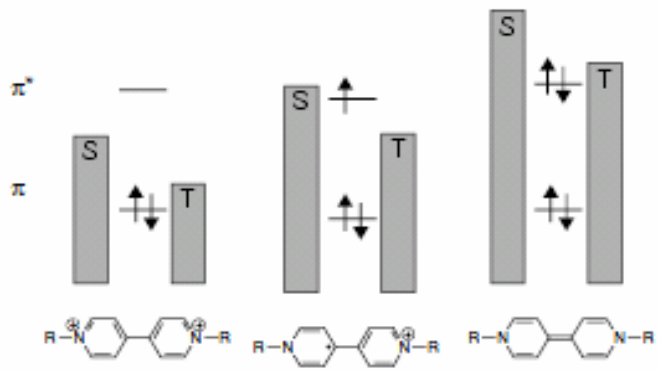
(Au-NP ~ 1.5 nm / STM in toluene / scale: 10 nm)

- **Attaching Au-nanoparticle to the end of the molecule:**
  - **enhance reliability of molecule-tip contacts**
  - **switching off by "tilting burial" can be effectively prevented.**
- **Conductance switching occurred for all the molecules, including alkanedithiols.**
- **Conductance switching is not related to any intramolecular structure.**

Molecular redox transistor (?)







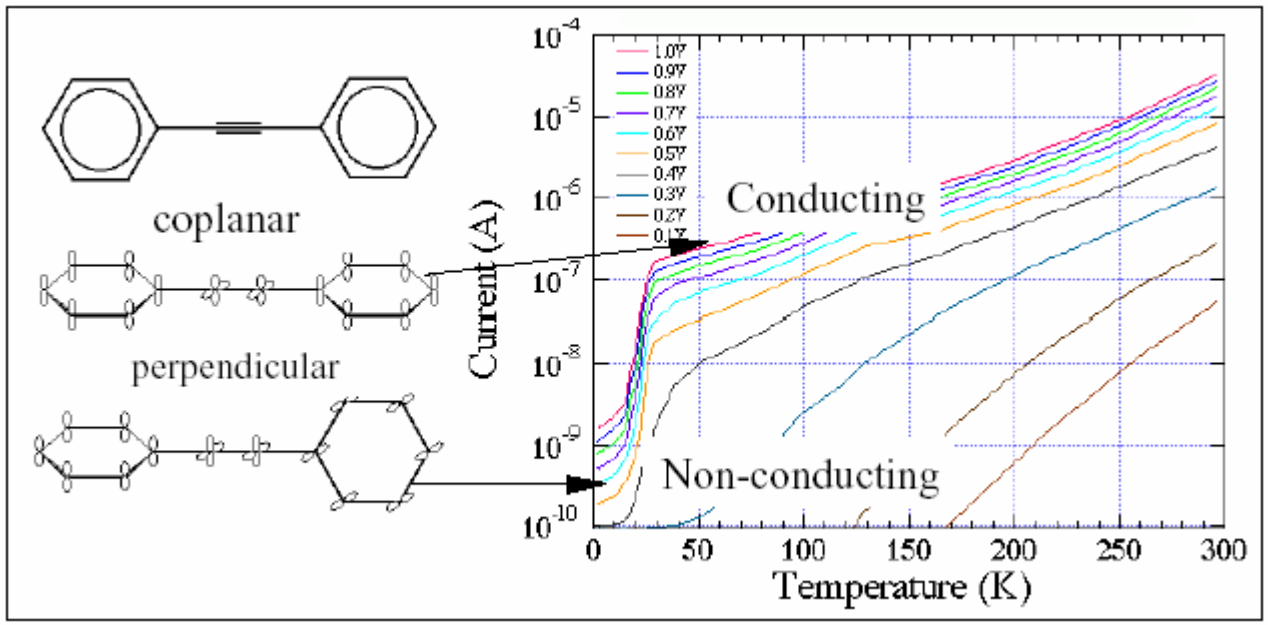
- **Molecule: bipyridium at the center of chains of 20 methylene**
- **Redox process: $bipy^{2+} + e^- \rightarrow\leftarrow bipy^{\cdot+}$**
- **Dashed curve: experiment with hexanedithiol monolayer.**
- **Reduction of the gate moiety enhances the conduction.**
- **Conductance dependence on counter electrode potential (?)**

Nature **408**, 67 (2000)

- **another issues:**

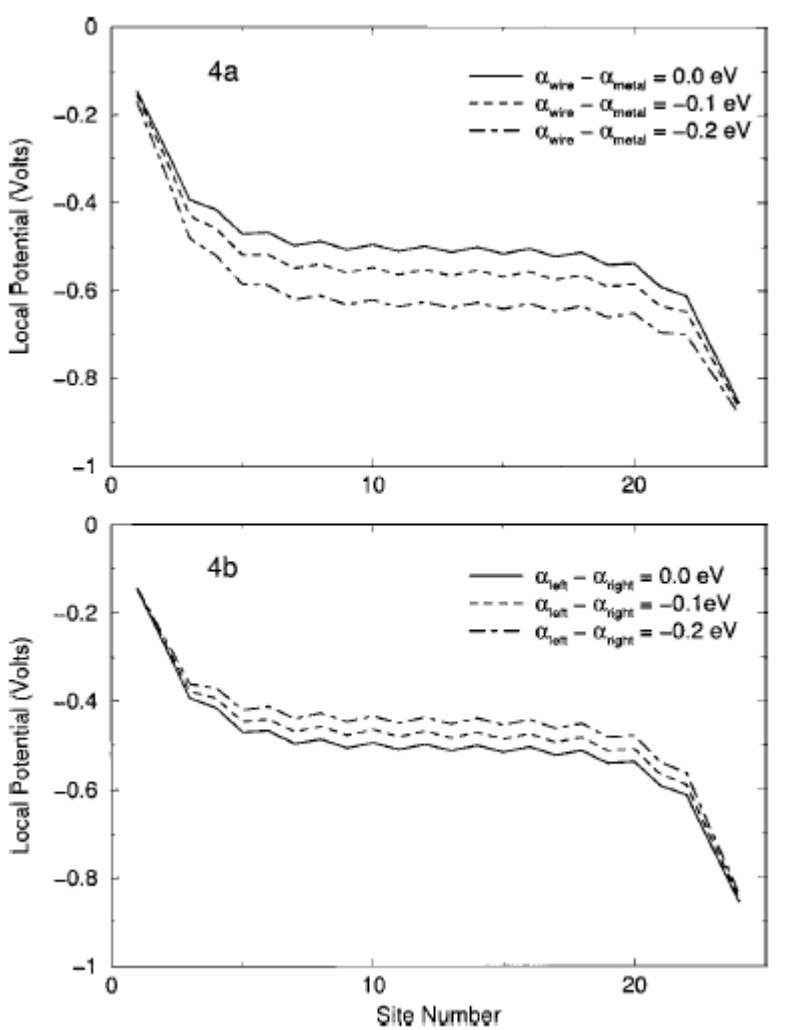
  molecular conformation, electric field

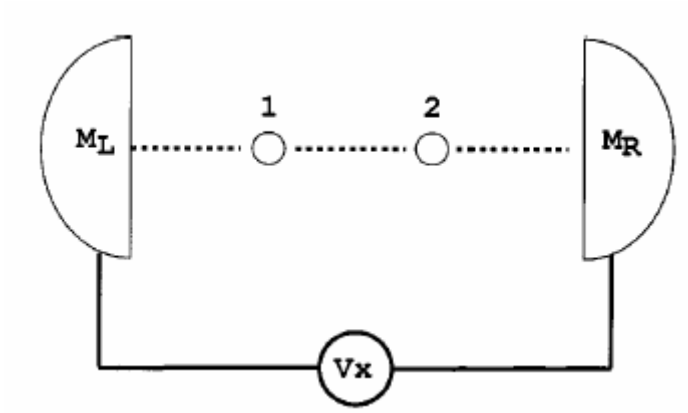
Molecular conformation and electrical properties



Conductor-Insulator transition with the conformation change !!

Potential profile in molecule





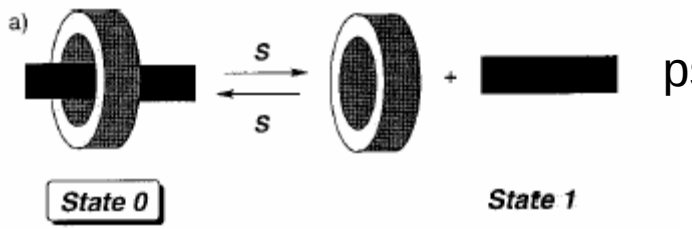
- Large potential drop near the junctions.
- May depend on the conductance of molecule.

JCP **112**, 6834 (2000)

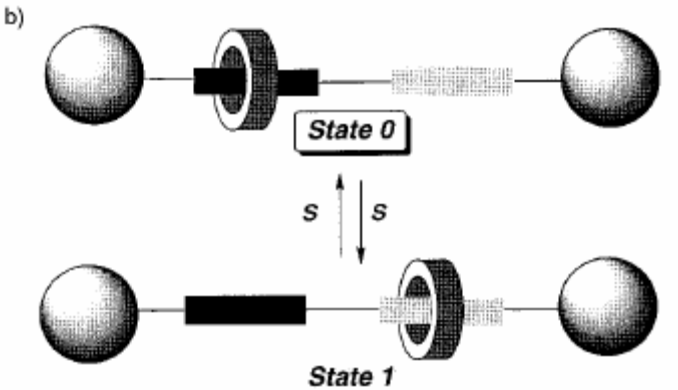
- **Miscellaneous:**

  molecular vehicle, interconnection, fabrication, architecture

Molecular machine

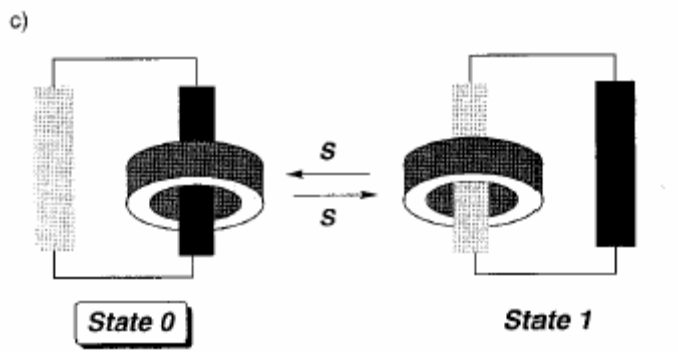


pseudorotaxanes



rotaxanes

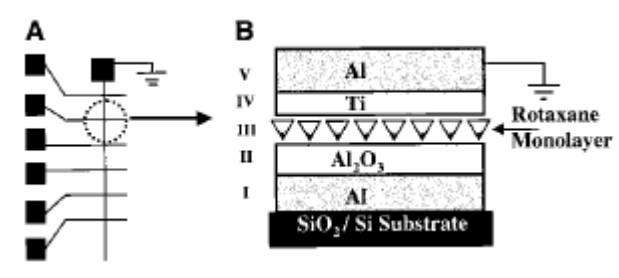
- Macro molecules
- Two (or more) well-defined states.
- Movement of molecule accompanied by change of electrical properties.
- Slow operation

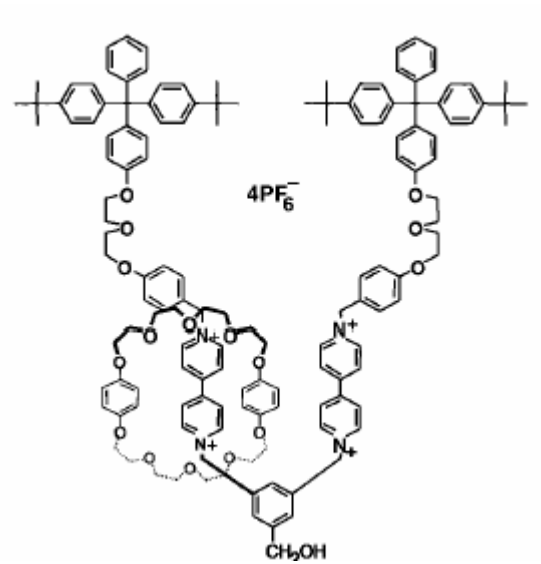


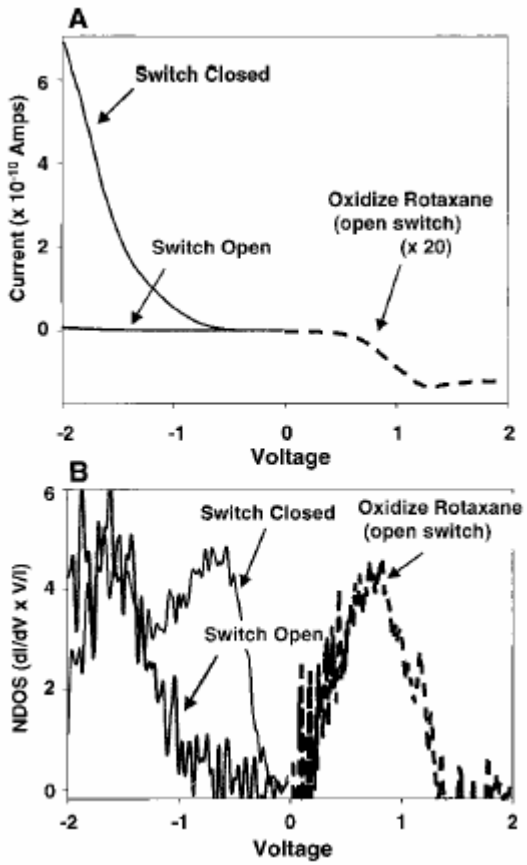
catenanes

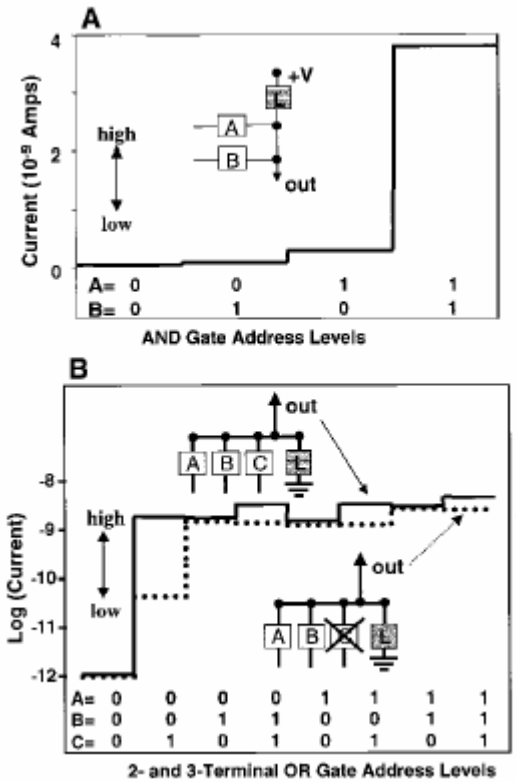
Acc. Chem. Res. **31**, 405 (1998)

Rotaxane



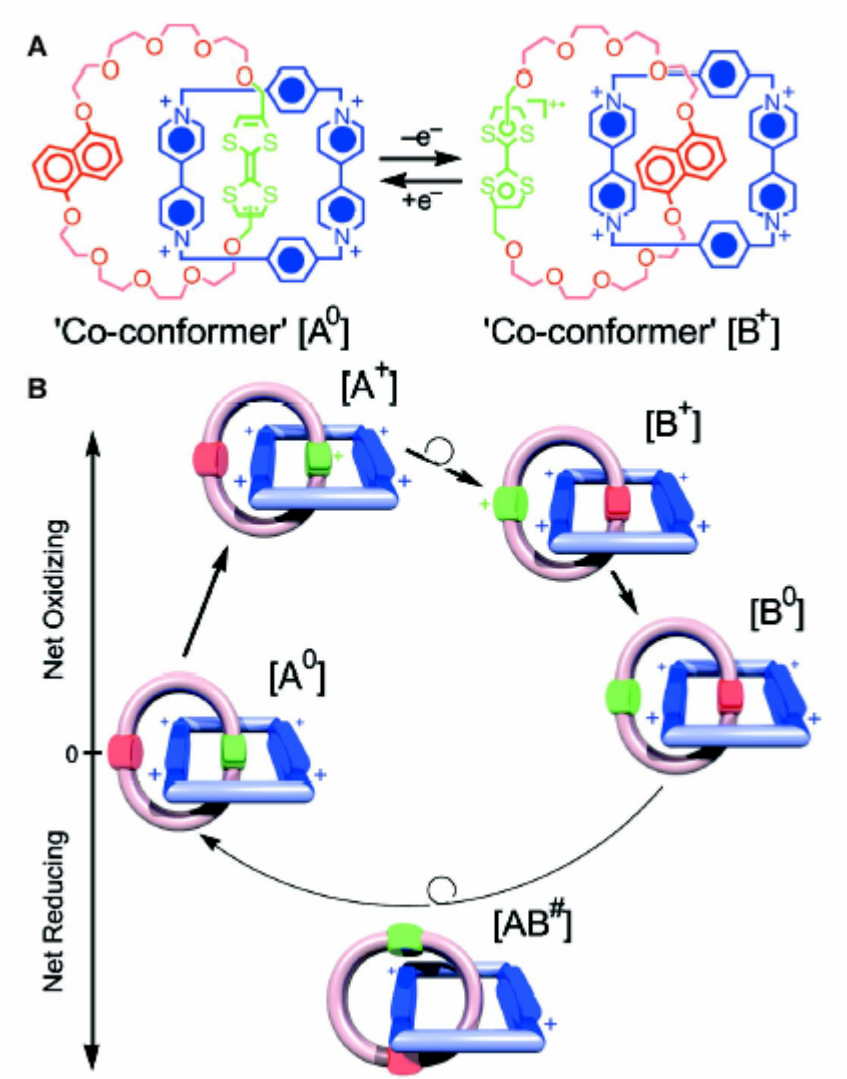


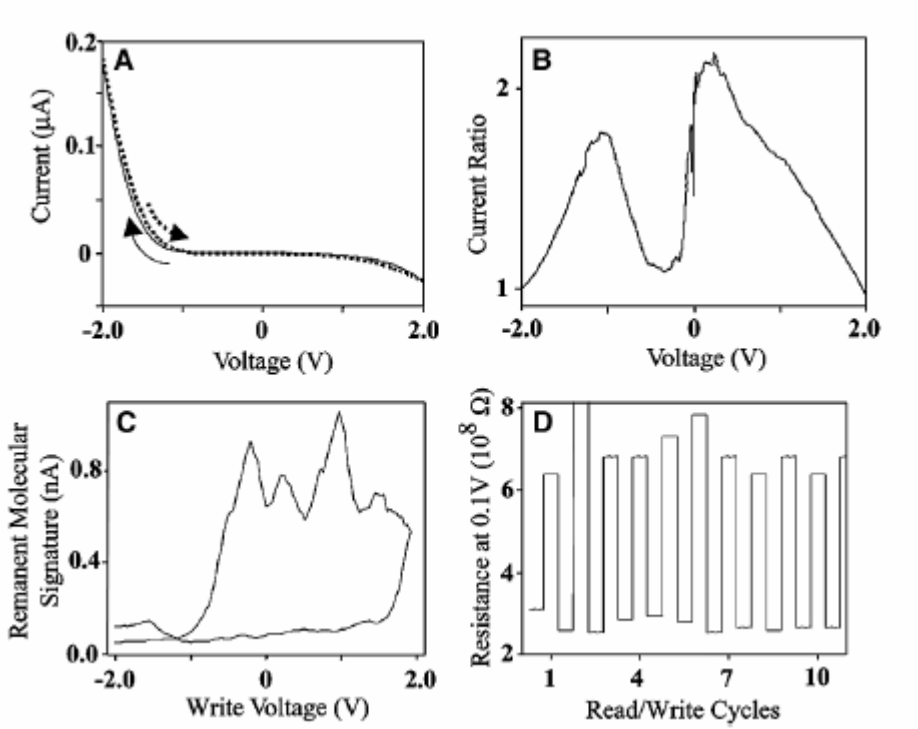




Science **285**, 391 (1999)

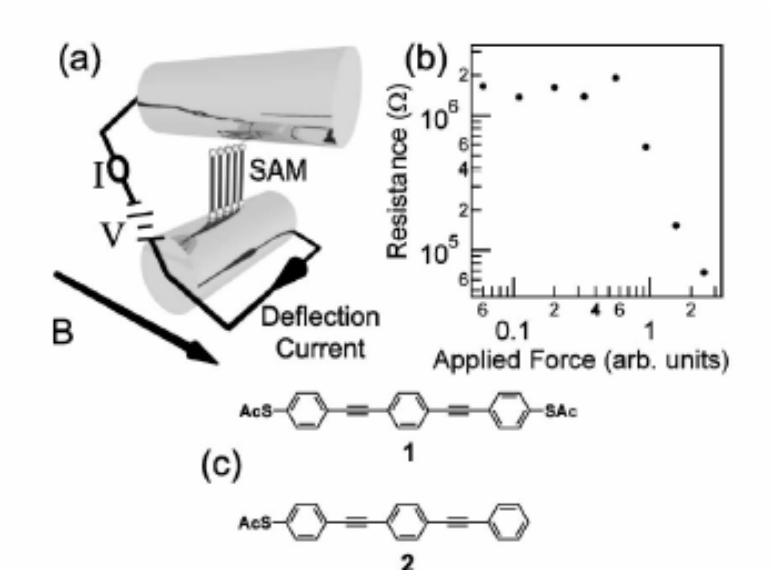
Catenane

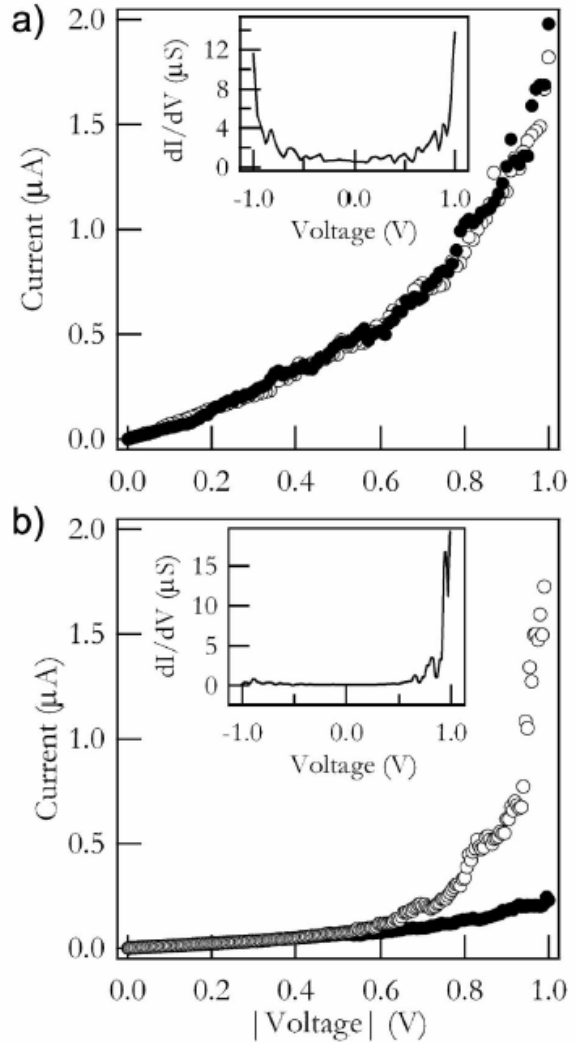




Acc. Chem. Res. **34**, 433 (2001)

MED with crossed wires



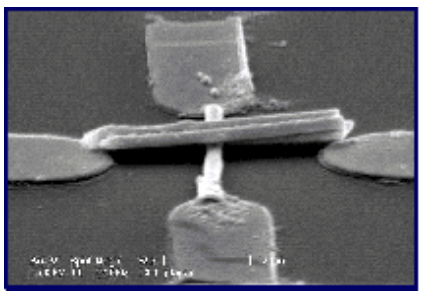


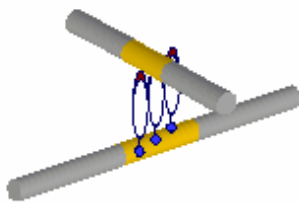
- 10 μm diameter metal wires crossed by Lorenz force.
- OPE molecule inserted between wires.
- Two types of junctions: diode and wire

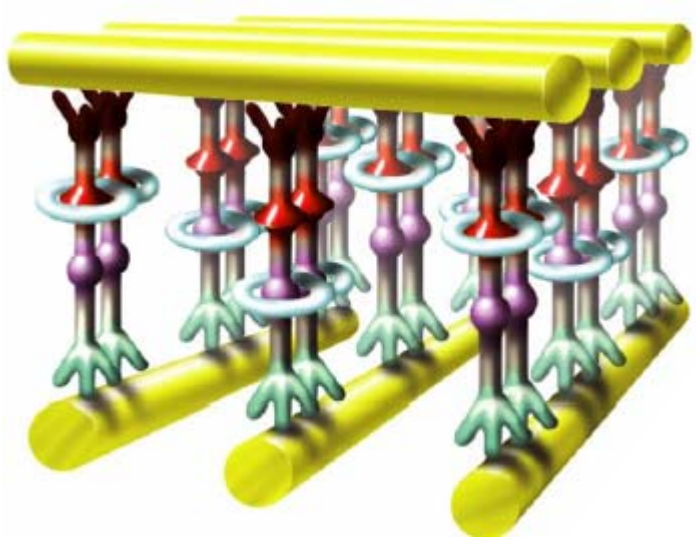
PRL **89**, 086802 (2002)

open: positive bias
solid: negative bias

Interconnection with nanowire

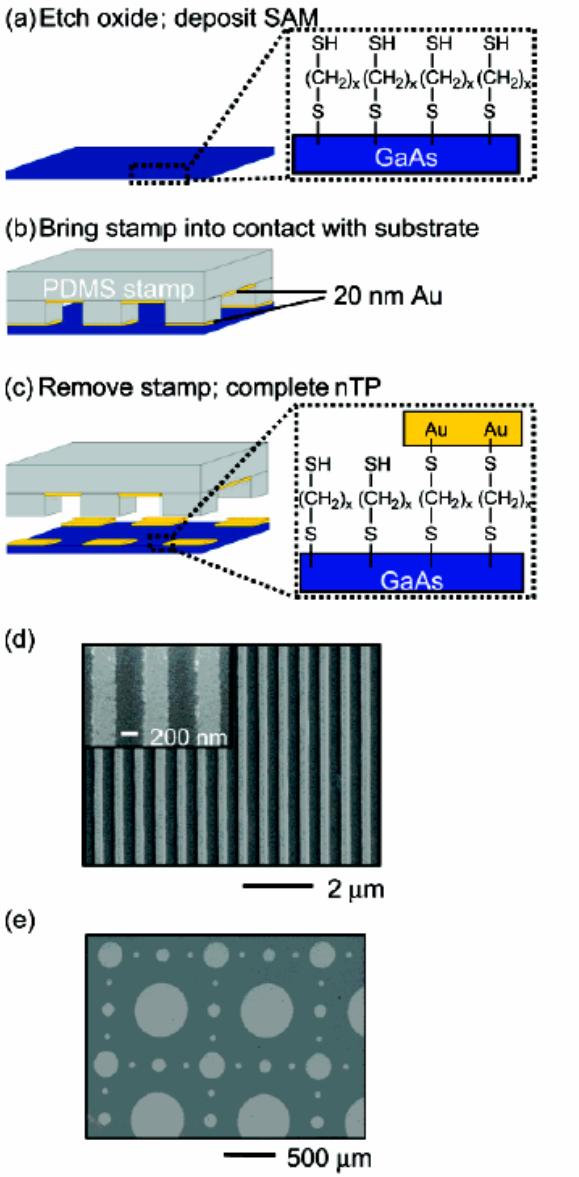


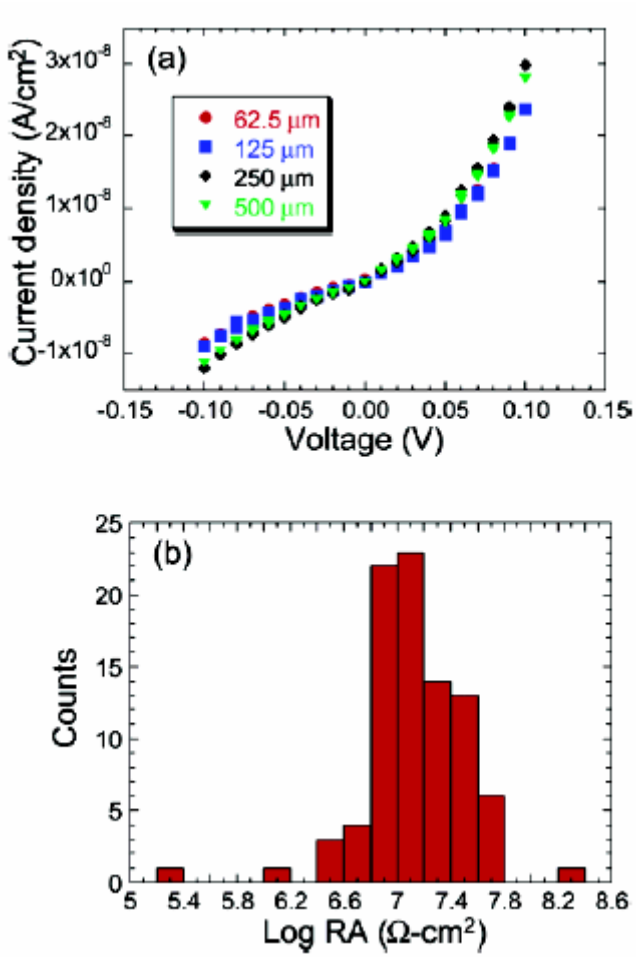




Science **294**, 2442 (2001)

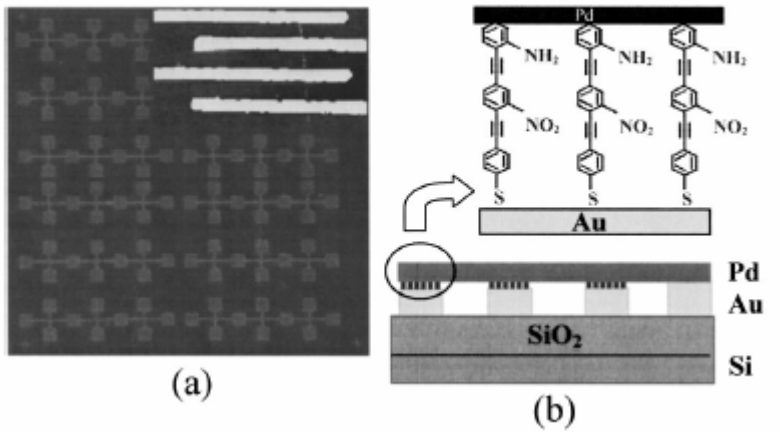
Pattern transfer by nano imprint

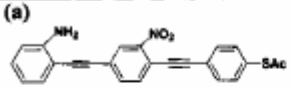
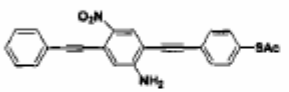
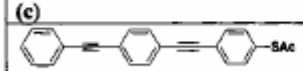
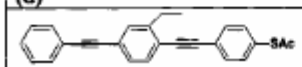


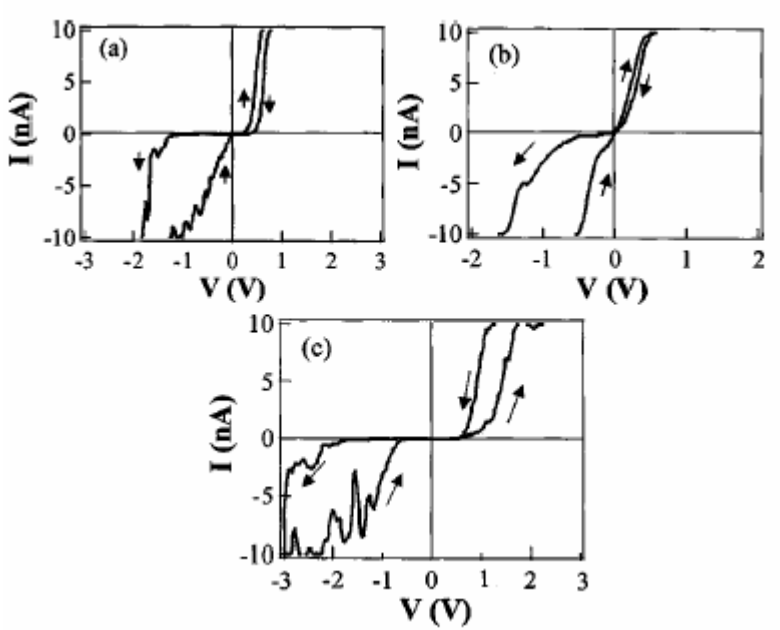


Nanoletters **3**, 913 (2003)

Integrated circuit with MED

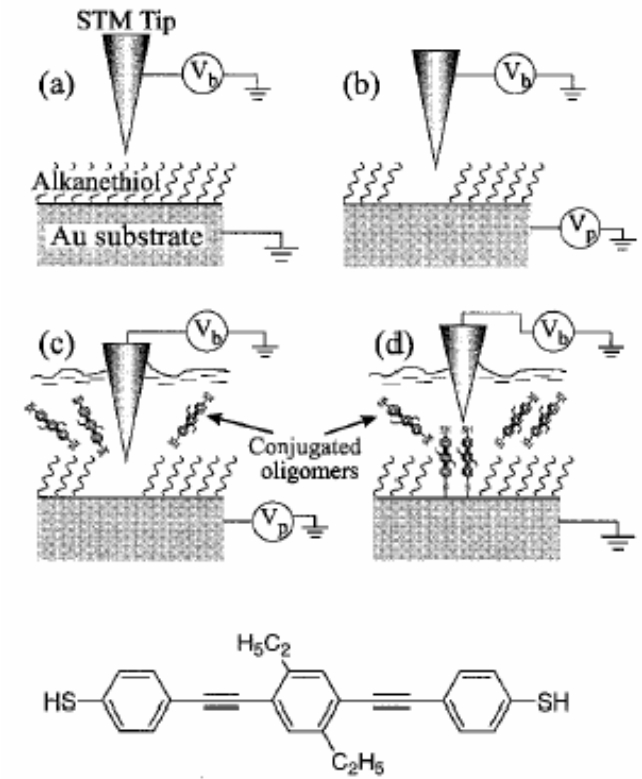


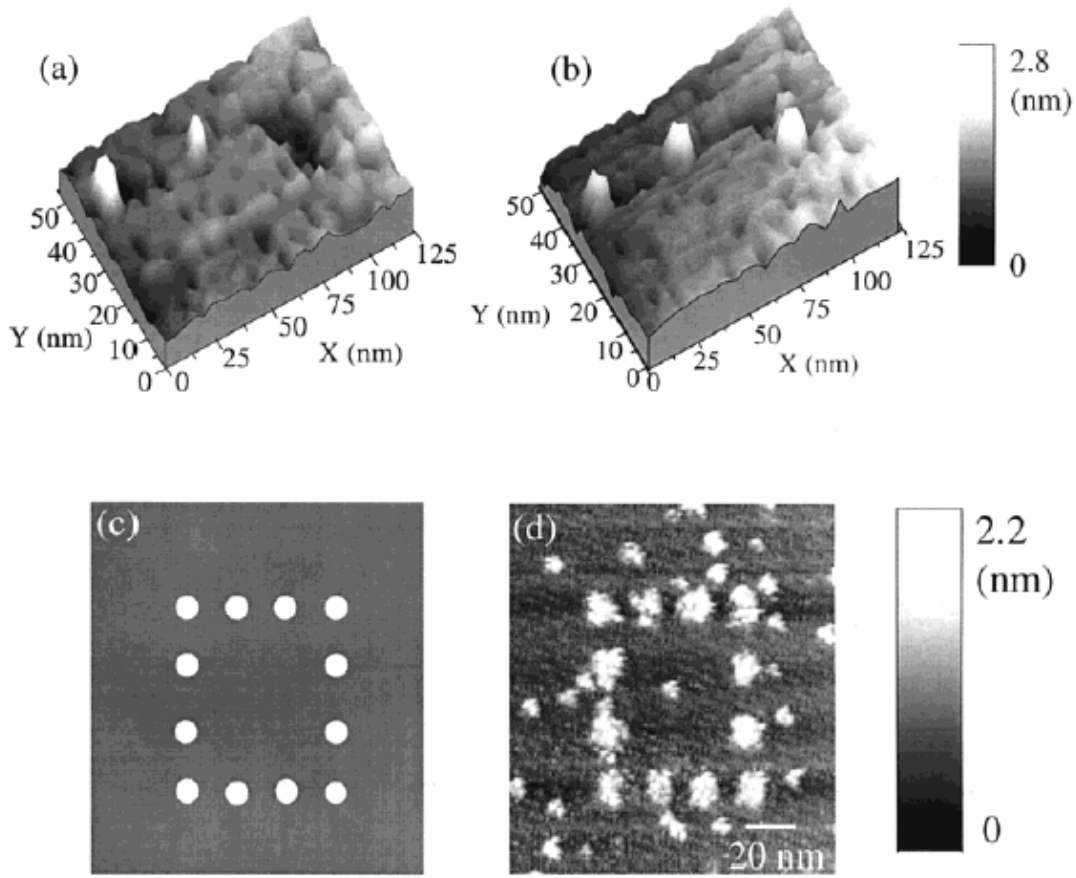
Molecular wires	Hysteresis	Retention time	On/Off ratio
(a) 	Yes	69 s	370 (-1 V)
(b) 	Yes	440 s	30 (-0.5 V)
(c) 	Yes		260 (-1.2 V)
(d) 	No		
(e) 	No		



APL **82**, 645 (2003)

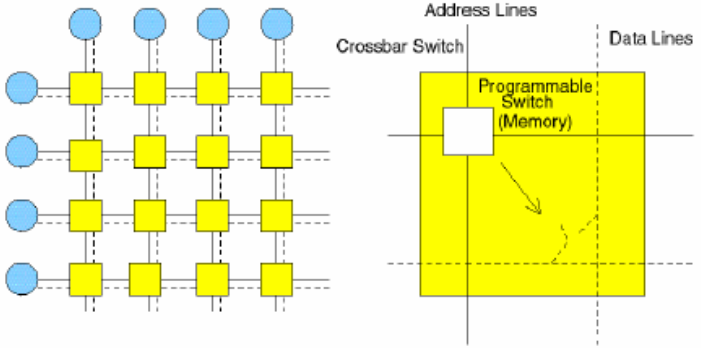
STM lithography with OPE derivatives

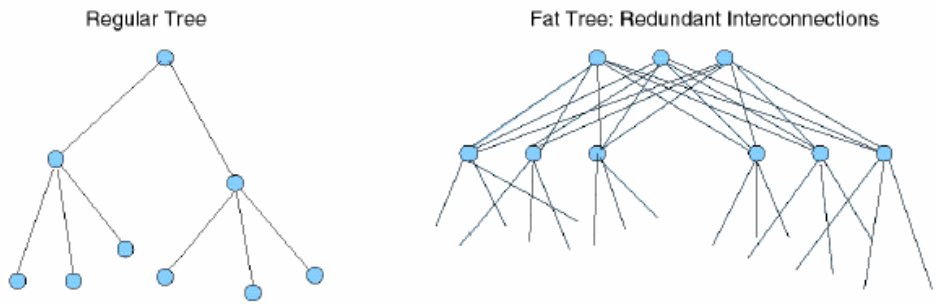




Acc. Chem. Res. **33**, 791 (2000)

Defect-tolerant architecture



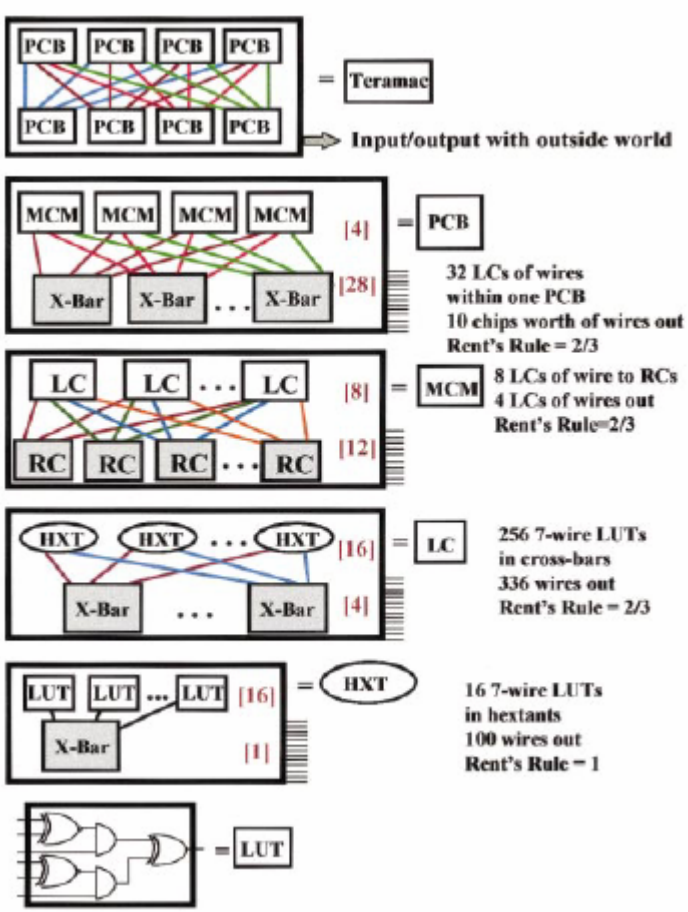


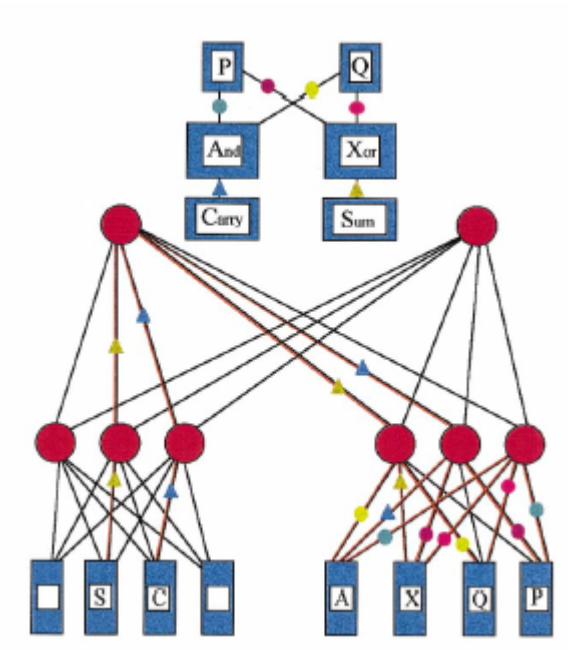
- Reconfigurable architecture
- Look-up table (use memory for logic operation)

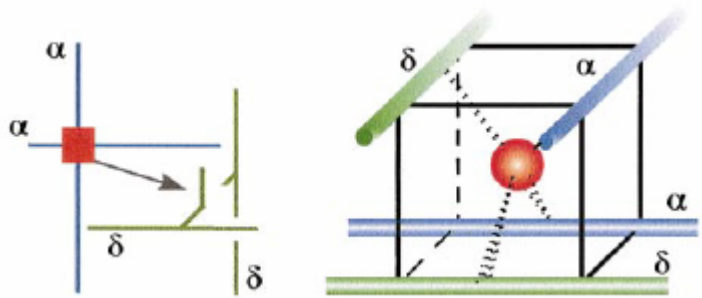
1. Build cheap and imperfect computer
2. Find the defects
3. Configure the resources with software
4. Compile the program
5. Run the computer

Solve hardware problems by software !

Defect-tolerant architecture







Science **280**, 1716 (1998)

MED: limiting factors and the current status

- **Electron tunneling**
  - gating speed limit: $2\pi kT(=300\ \mathrm{K})/h = (25\ \mathrm{fs})^{-1} \sim 1$ Thz
  - crosstalk between neighboring devices should be avoided.
- **Energy dissipation**
  - ballistic junction can be a solution.
  - current level up to μA with a few molecules was demonstrated.
- **Long-term degradation**
  - contamination, electrical shock, oxidation and reduction, …
- **Fabrication Yield**: less than 1% at the present time
- **FET** and transistor with gain greater than 1 should be demonstrated.
- **Ohmic contact**: is it probable without seriously affecting molecule's electronic states?
- **Electric field effect**: field intensity in MED ~ 2×10^9 V/m
  - the breakdown field in dry air: 3×10^6 V/m , STM experiment: 5×10^8 V/m
  - Stark effect: 10^7- 10^8 V/m

Thank you for your attention !