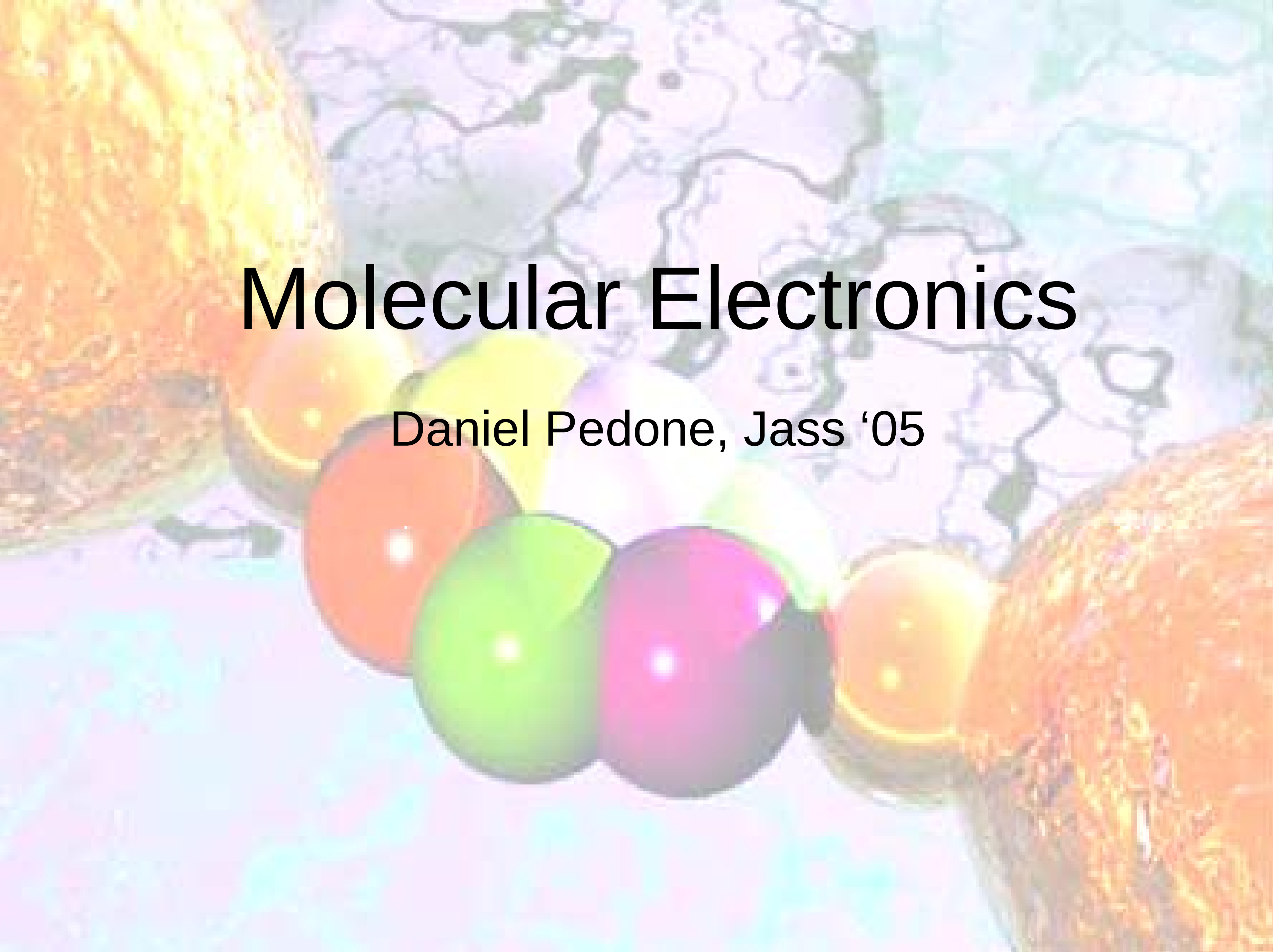
Molecular Electronics

Daniel Pedone, Jass '05



Content

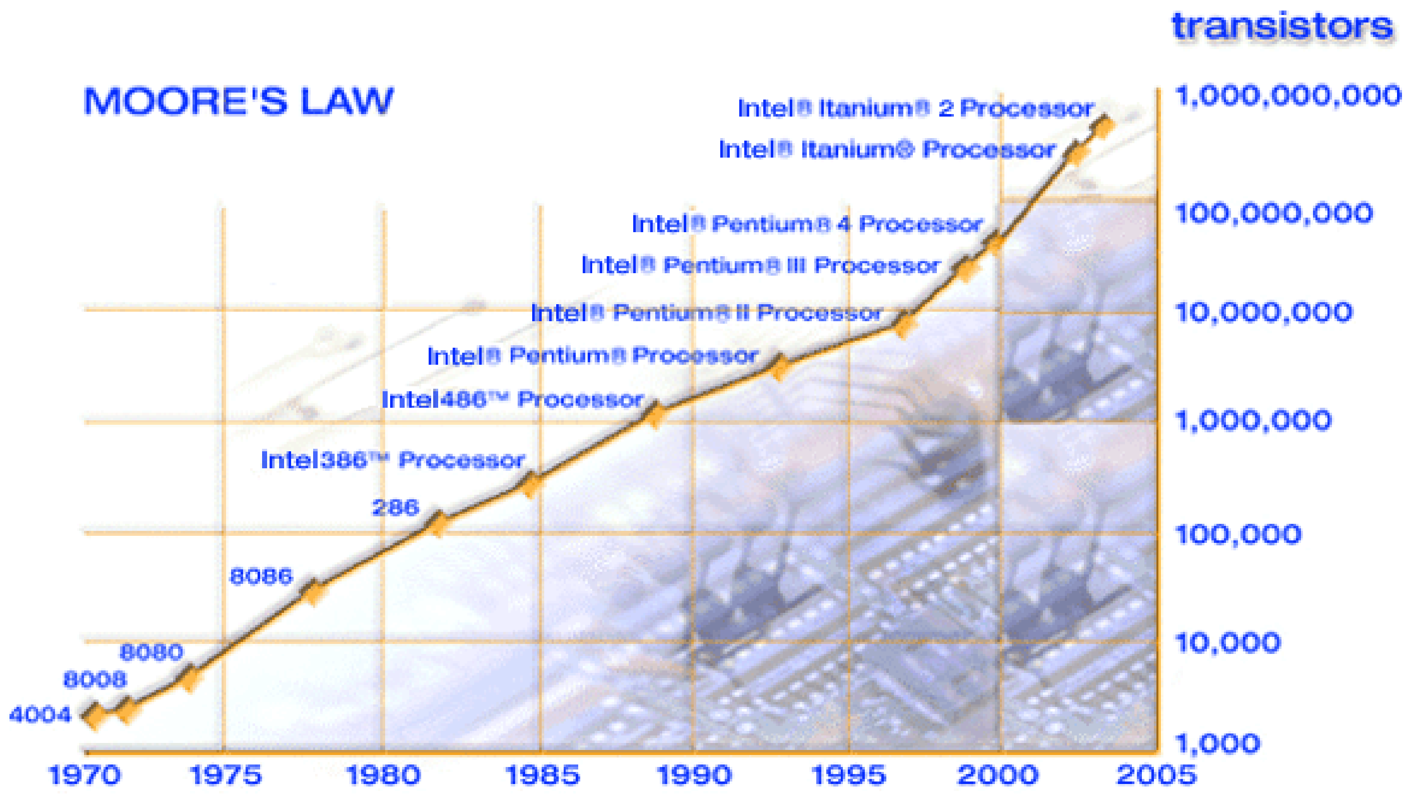
- Introduction
- Electrodes and Contacts
- Functions of Single Molecules
- Molecular Electronic Devices
- Summary and Outlook

Content

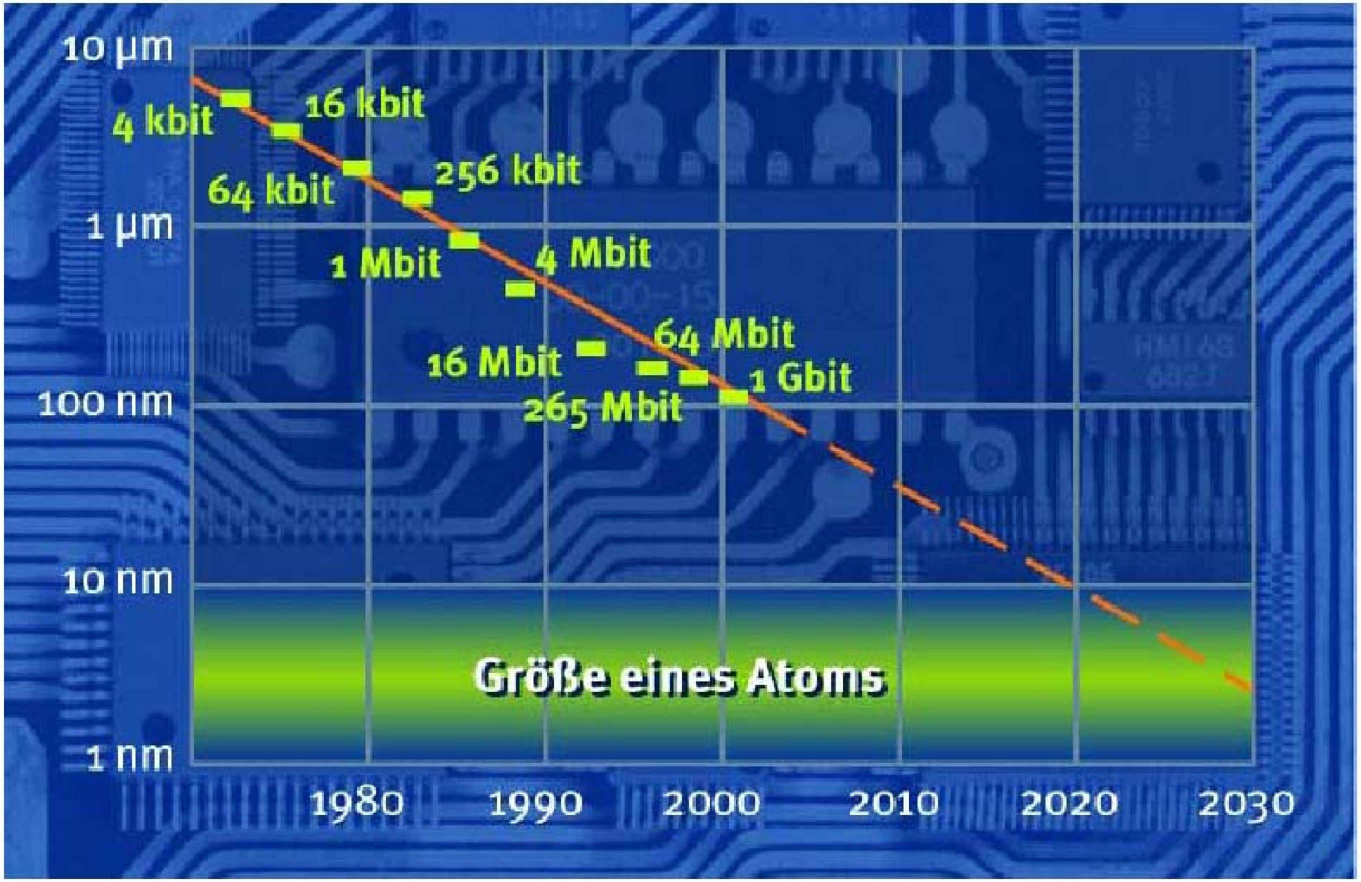
- Introduction
  - Motivation (Top-down approach)
  - Advantages (Bottom-up approach)
- Electrodes and Contacts
- Functions of Single Molecules
- Molecular Electronic Devices
- Summary and Outlook

Moore's Law

Doubling the number of transistors per integrated circuit every 18-24 months. (Electronics, Vol. 38, Number 8, 1965)



Transistor Scaling



Top-down Approach

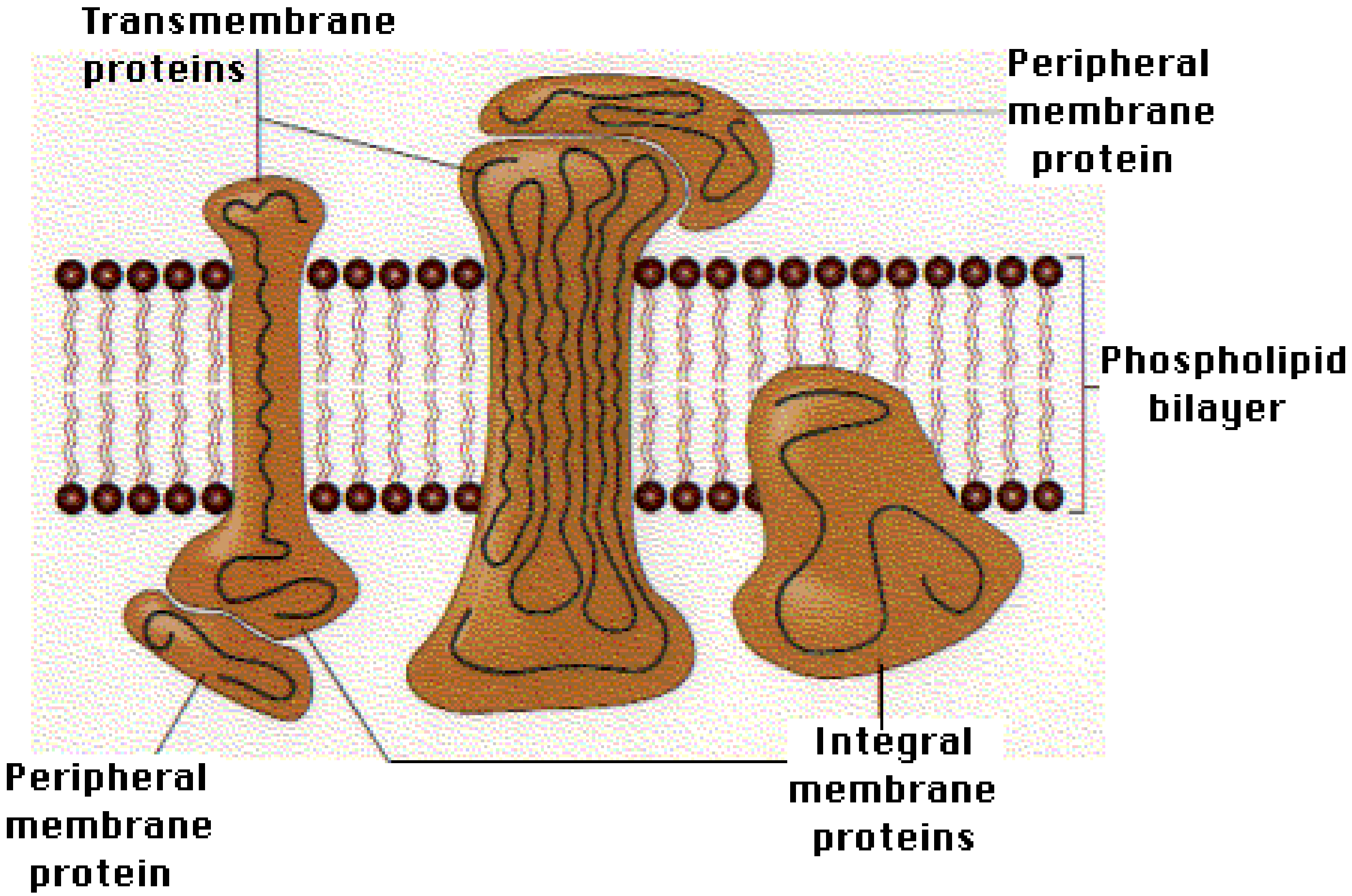
- Any object of few nm in size shows discrete quantum energy levels
- Inorganic clusters will slightly differ in the number of atoms they consist of

Top-down Approach

- Any object of few nm in size shows discrete quantum energy levels
- Inorganic clusters will slightly differ in the number of atoms they consist of

➡ Scatter of quantum energy levels

Bottom-up Approach



Bottom-up Approach

- Mimicking nature’s bottom-up processes results in several advantages:
    - Molecules are several orders of magnitude smaller than present feature size

Bottom-up Approach

- Mimicking nature's bottom-up processes results in several advantages:
  - Molecules are several orders of magnitude smaller than present feature size
  - Organic molecules of a given compound are absolutely identical

Bottom-up Approach

- Mimicking nature's bottom-up processes results in several advantages:
  - Molecules are several orders of magnitude smaller than present feature size
  - Organic molecules of a given compound are absolutely identical
  - Great amount of different materials (i.e. molecules)

Bottom-up Approach

- The goal: electronic properties of a device may be adjusted by the design of the chemical structure

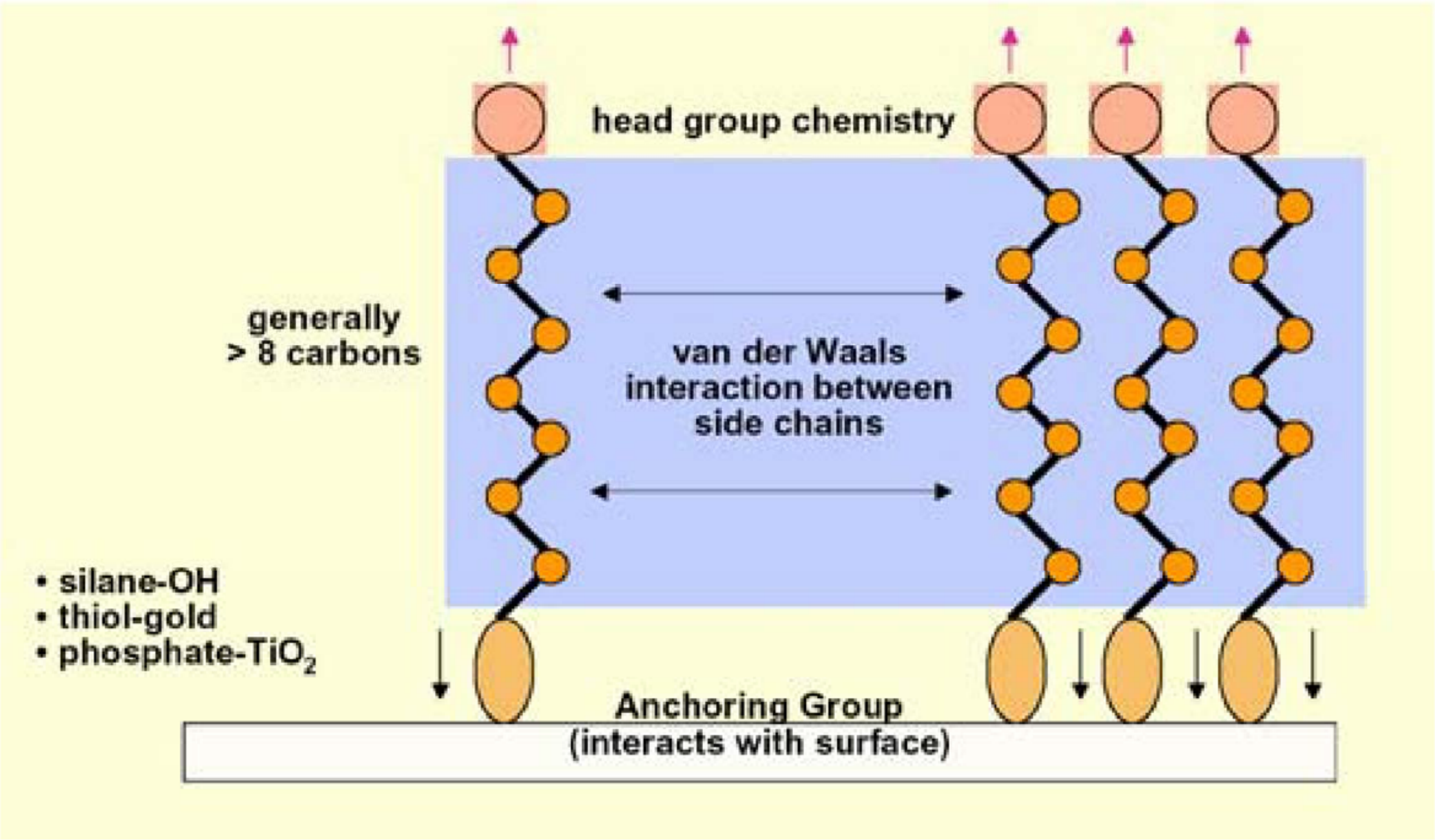
Bottom-up Approach

- The goal: electronic properties of a device may be adjusted by the design of the chemical structure
- Two different approaches, to be distinguished:
  - Single molecular systems
  - Bulk molecular system (OLED, OTFT)

Content

- Introduction
- Electrodes and Contacts
  - “Covalent bond” (SAM, Electromigration)
  - Van-der-Waals interaction (LB-film)
- Functions of Single Molecules
- Molecular Electronic Devices
- Summary and Outlook

SAM – Self Assembled Monolayer



SAM – "Covalent bond"

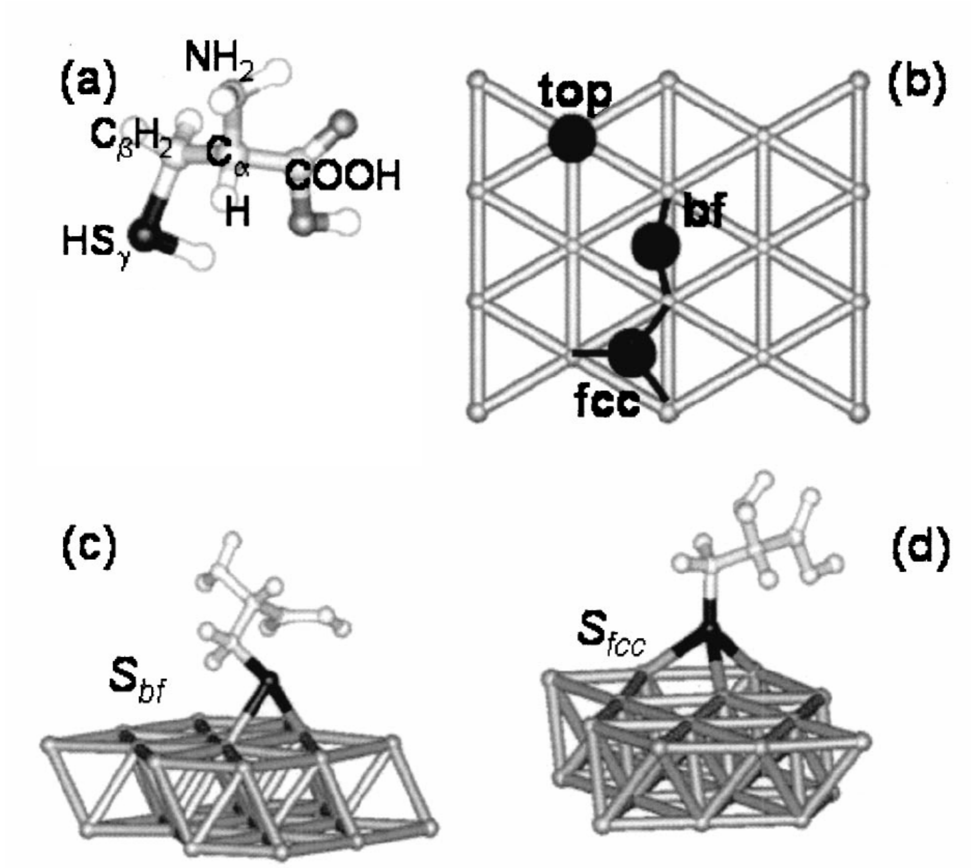
- Required:
  good stability and loose enough

SAM – “Covalent bond”

- Required:
  good stability and loose enough

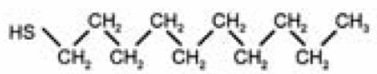
- Best investigated:
  thiol group (S-H group) on the molecule
  +
  Au-Substrate
  (strength of ~1.8 eV)

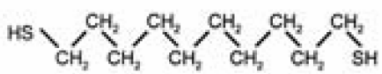
Thiol-Au Interface

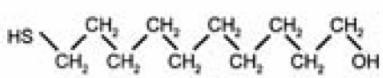


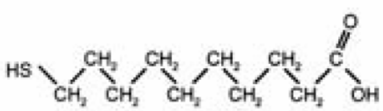
Rosa Di Felice, J. Chem. Phys., Vol. 120, No. 10, 2004

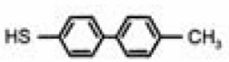
Frequently used molecules for SAMs

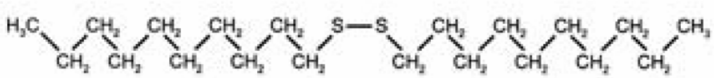

n-alkanethiol (n=10): $HS\text{-}(CH_2)_{n-1}CH_3$

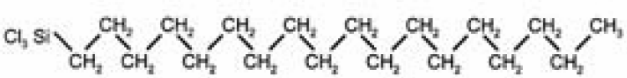

α,ω-alkanethiol : $HS\text{-}(CH_2)_n\text{-}SH$


ω-mercaptoalkanol : $HS\text{-}(CH_2)_n\text{-}OH$

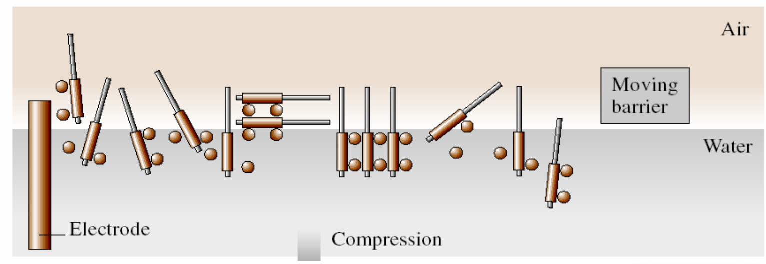

ω-mercaptoalkane carboxylic acid: $HS\text{-}(CH_2)_{n-1}\text{-}COOH$


4-methyl-4’-mercaptobiphenyl (MMB) : $HS\text{-}(C_6H_4)_2\text{-}CH_3$


1,1’-dialkyl-disulfide: $H_3C\text{-}(CH_2)_{n-1}\text{-}S\text{-}S\text{-}(CH_2)_{n-1}\text{-}CH_3$


alkyltrichlorsilane: $Cl_3Si\text{-}(CH_2)_{n-1}\text{-}CH_3$
here: octadecyltrichlorsilane $Cl_3Si\text{-}(CH_2)_{17}\text{-}CH_3$

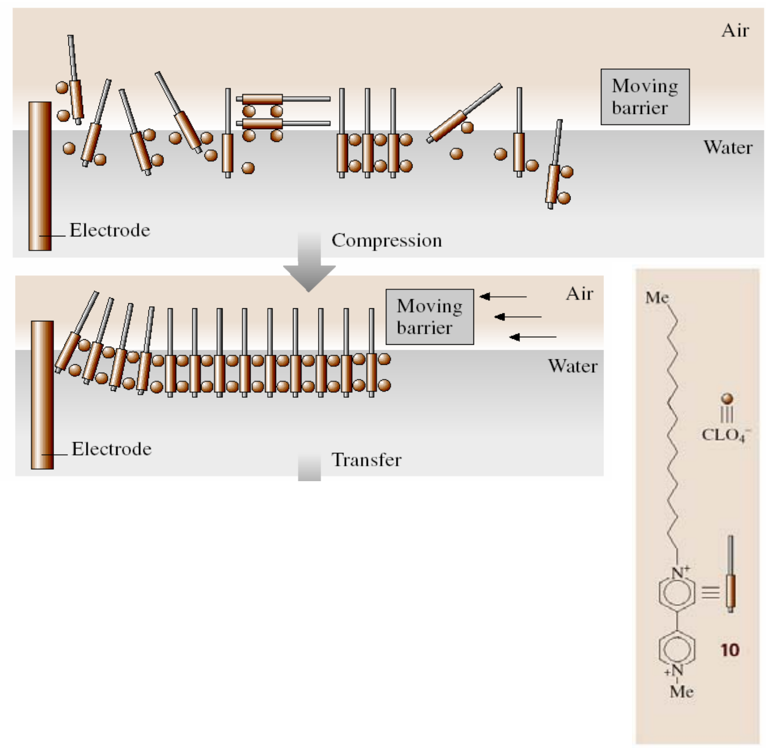
Van - der - Waals Interaction: Langmuir-Blodgett (LB)-films



10

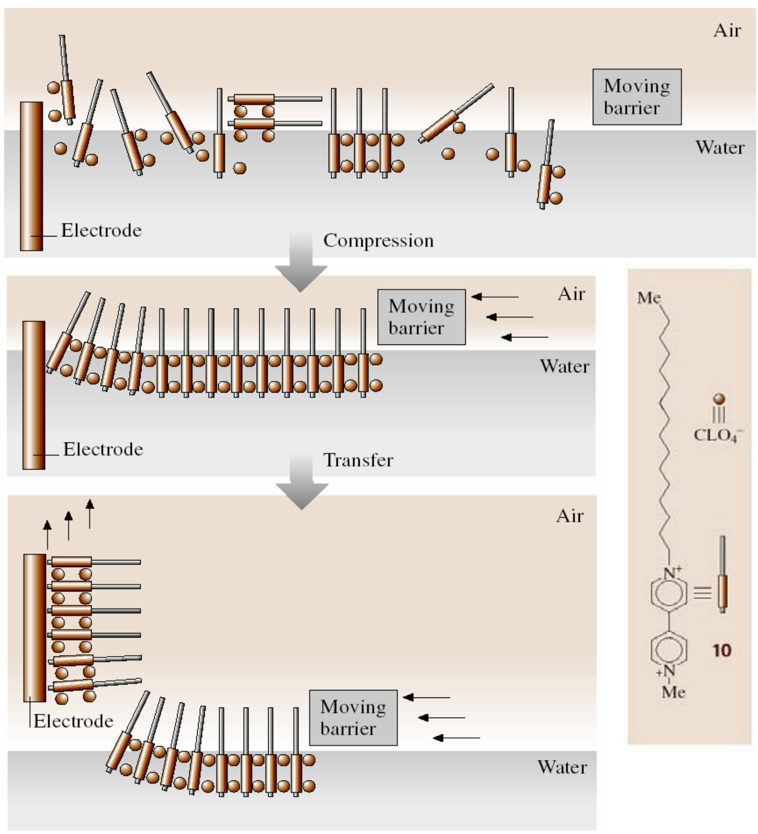
- Spreading of organic solution of the molecule
- Evaporation of organic solvent

Van - der - Waals Interaction: Langmuir-Blodgett (LB)-films



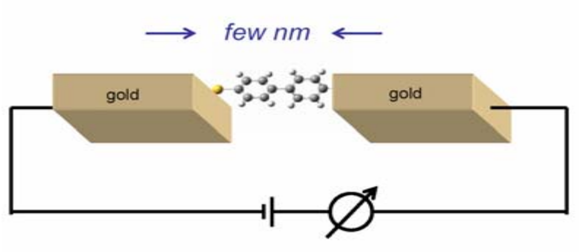
- Spreading of organic solution of the molecule
- Evaporation of organic solvent
- Formation of a packed monolayer by compression

Van - der - Waals Interaction: Langmuir-Blodgett (LB)-films



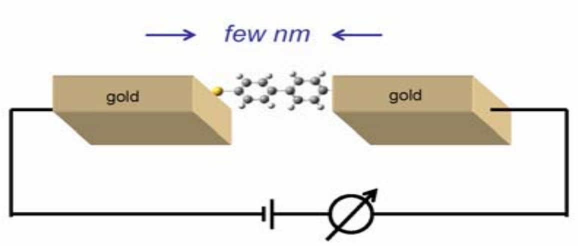
- Spreading of organic solution of the molecule
- Evaporation of organic solvent
- Formation of a packed monolayer by compression
- Lifting of the electrode

Electromigration Technique



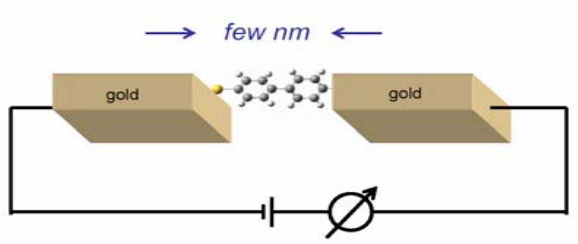
- Addressing a single molecule

Electromigration Technique

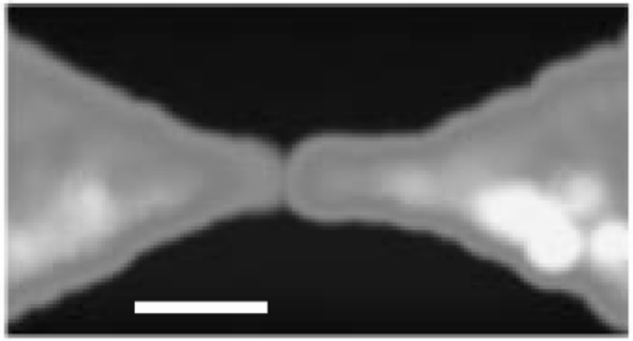


- Addressing a single molecule
- High-resolution lithography is not enough

Electromigration Technique



- Addressing a single molecule
- High-resolution lithography is not enough
- Breaking up a hyphenation point by applying electric current (Electromigration)
- Resulting electrodes with 1 - 3 nm gap

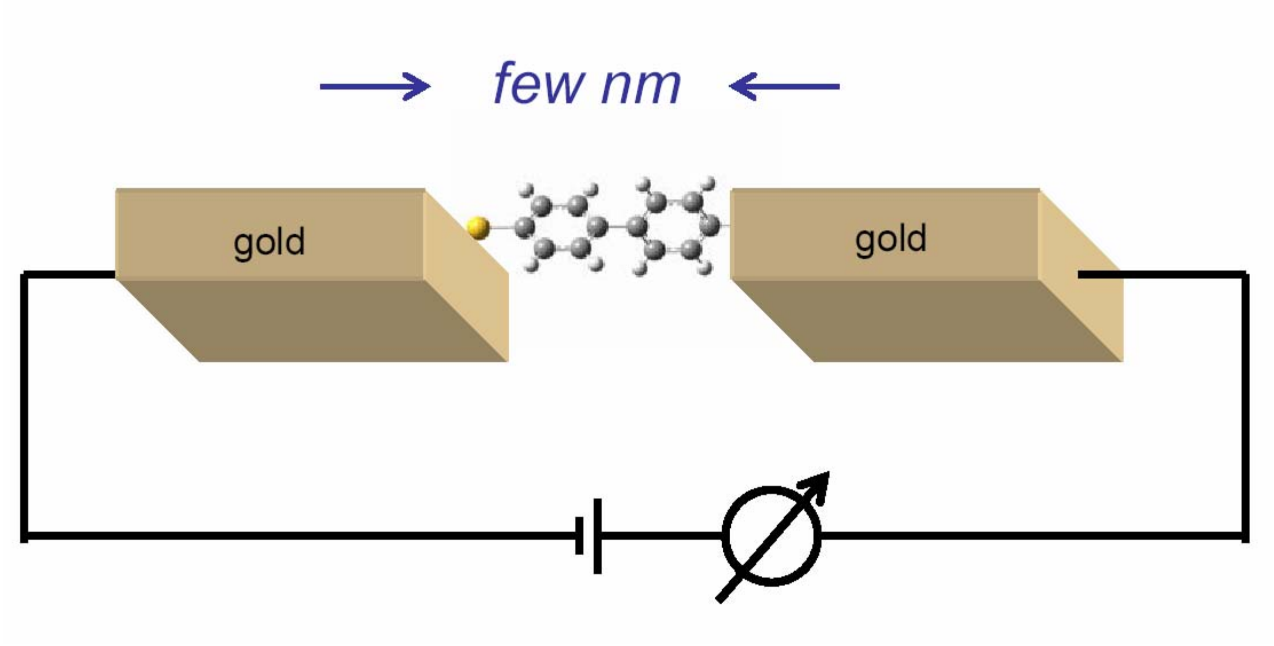


H. Park et al., *Nature* 417, 722 (2002.

Content

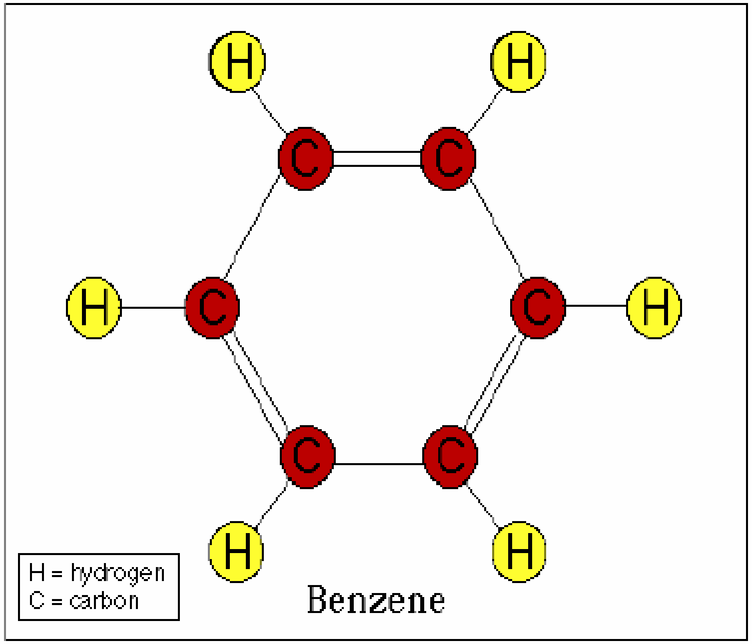
- Introduction
- Electrodes and Contacts
- Functions of Single Molecules
  - Molecular Wires
  - Electron Transport
  - Insulators
  - Diodes
- Molecular Electronic Devices
- Summary and Outlook

Electron Transport Mechanism

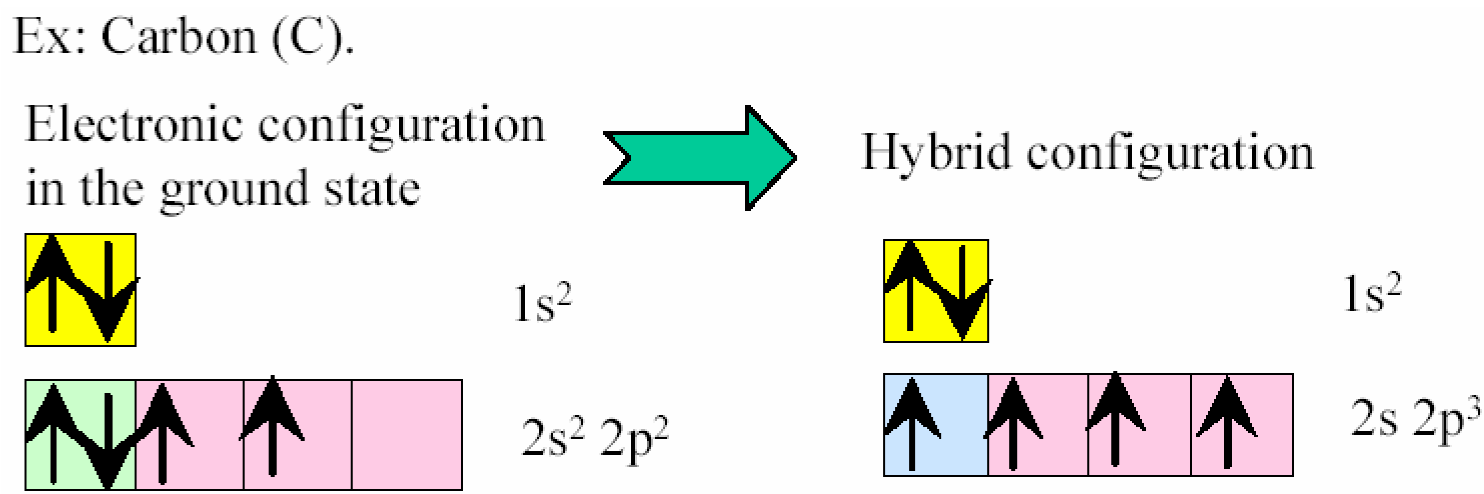


Organic molecules as "electrical wires"

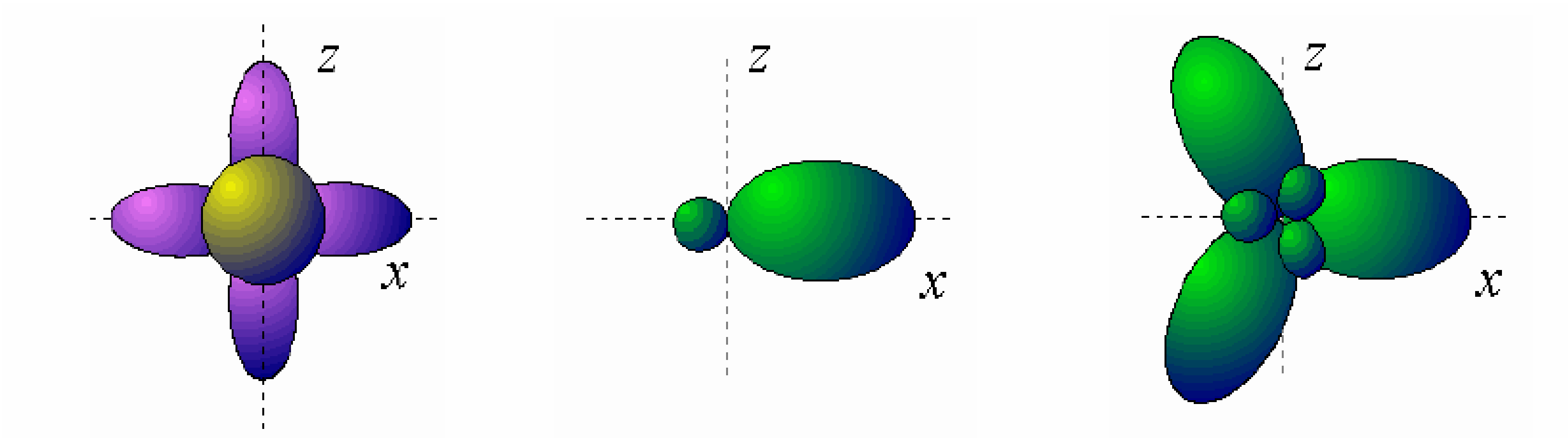
Benzene



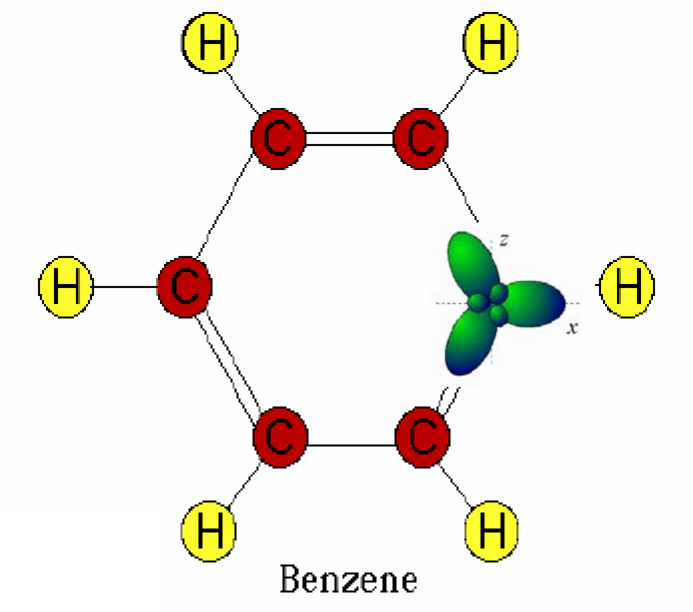
Hybridisation

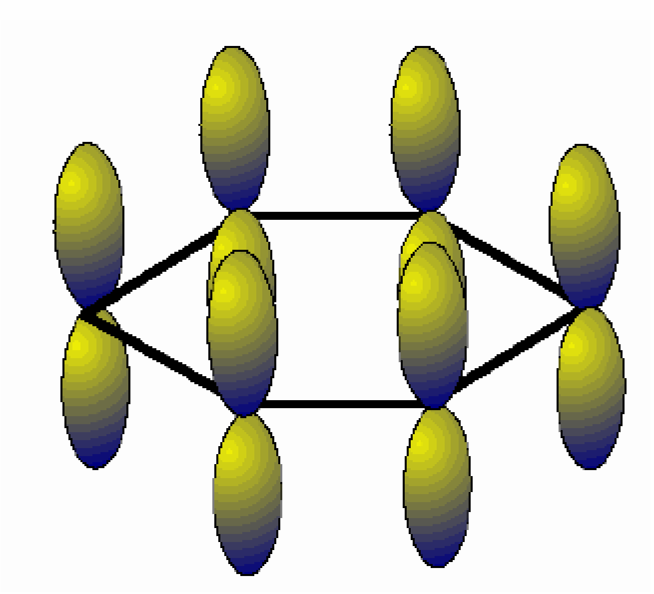


sp^2-Hybridisation

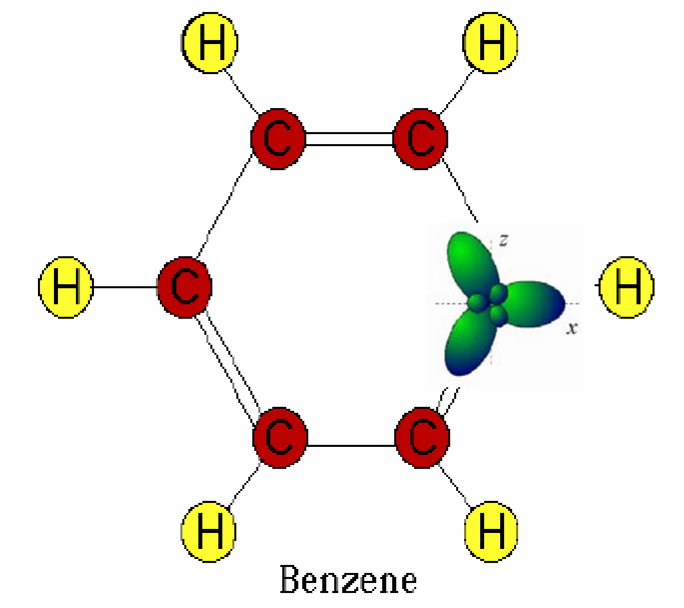


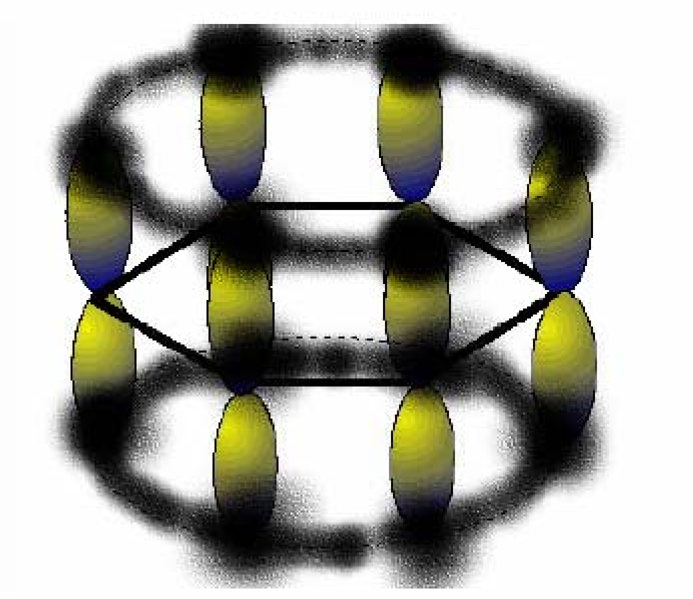
sp^2-Hybridisation



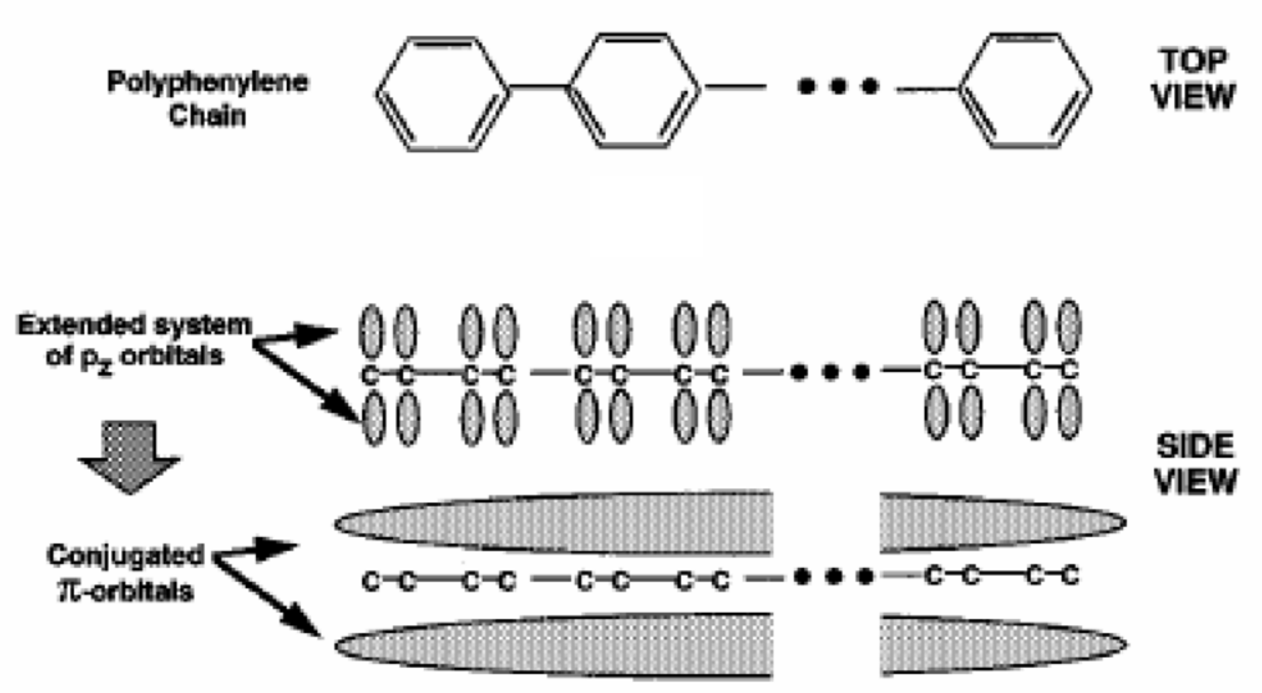


sp^2-Hybridisation



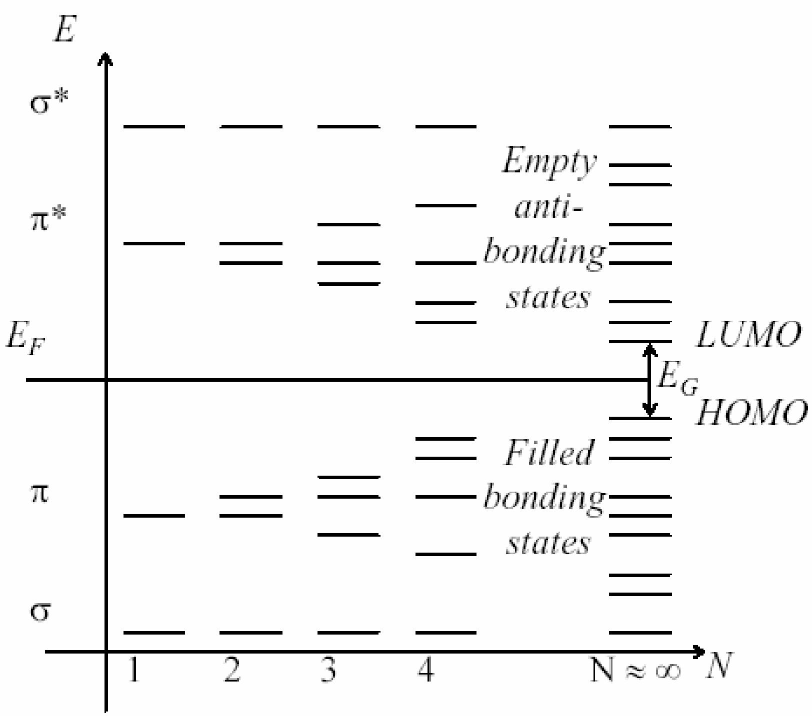


Conjugated Oligomers as Semiconductors



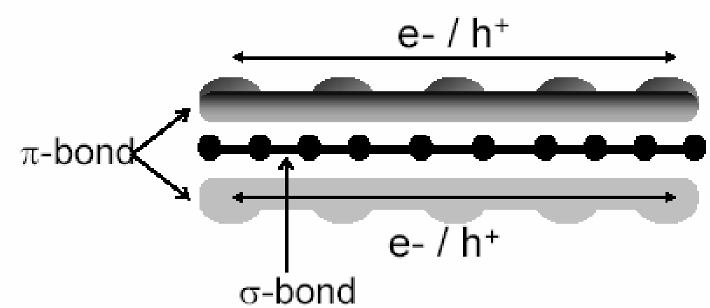
Conjugated Oligomers as Semiconductors

Energy band



N = number of double bonds

As N increases, the π bonding electron wavefunctions will tend to delocalise along the whole length of the chain.



Conjugated polymers are 1-dimensional (in the polymer chain direction) semiconductors.

Electron Transport

- Coherent electron motion – on resonance
  - Coherent: Absence of dissipative Effects (inelastic scattering)
  - Resonance: Metal Fermi level is resonant with an unoccupied molecular orbital

Electron Transport

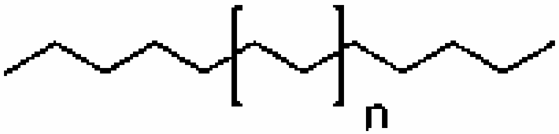
- Coherent electron motion – on resonance
  - Coherent: Absence of dissipative Effects (inelastic scattering)
  - Resonance: Metal Fermi level is resonant with an unoccupied molecular orbital
- Landauer Approach
  - Molecule is considered as a scatterer for the electron

Electron Transport

- Coherent electron motion – on resonance
  - Coherent: Absence of dissipative Effects (inelastic scattering)
  - Resonance: Metal Fermi level is resonant with an unoccupied molecular orbital
- Landauer Approach
  - Molecule is considered as a scatterer for the electron
  - Current is related to the transmission probability
  - Conductance g is given by:

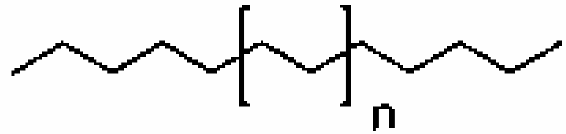
$$g = \frac{e^2}{\pi\hbar} T(E_F); \qquad T(E) = \exp\left[-\frac{4\pi}{\hbar} \int_{s_1}^{s_2} [2m(V_B(x) - E_x)]^{1/2} dx \right]$$

Insulators

- Alkanes:  insulating, but flexible

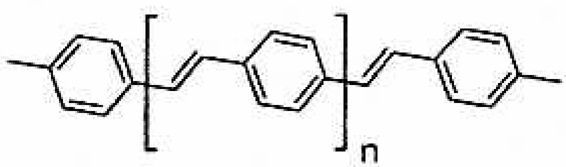
Insulators

- Alkanes:



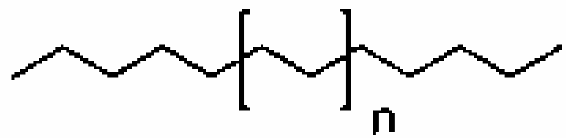
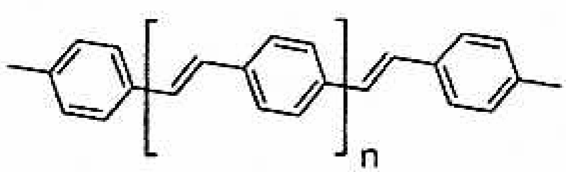
insulating, but flexible

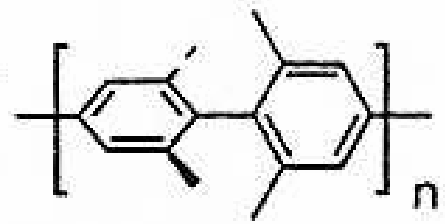
- π -System:



not flexible, but conducting

Insulators

- Alkanes:  insulating, but flexible
- π -System:  not flexible, but conducting
- Perpendicular π-System:



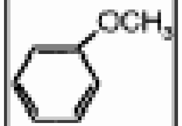
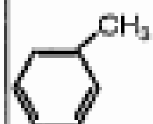
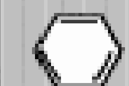
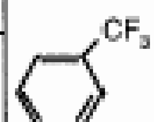
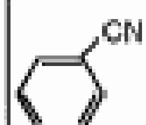
insulating and not flexible

Molecular Doping

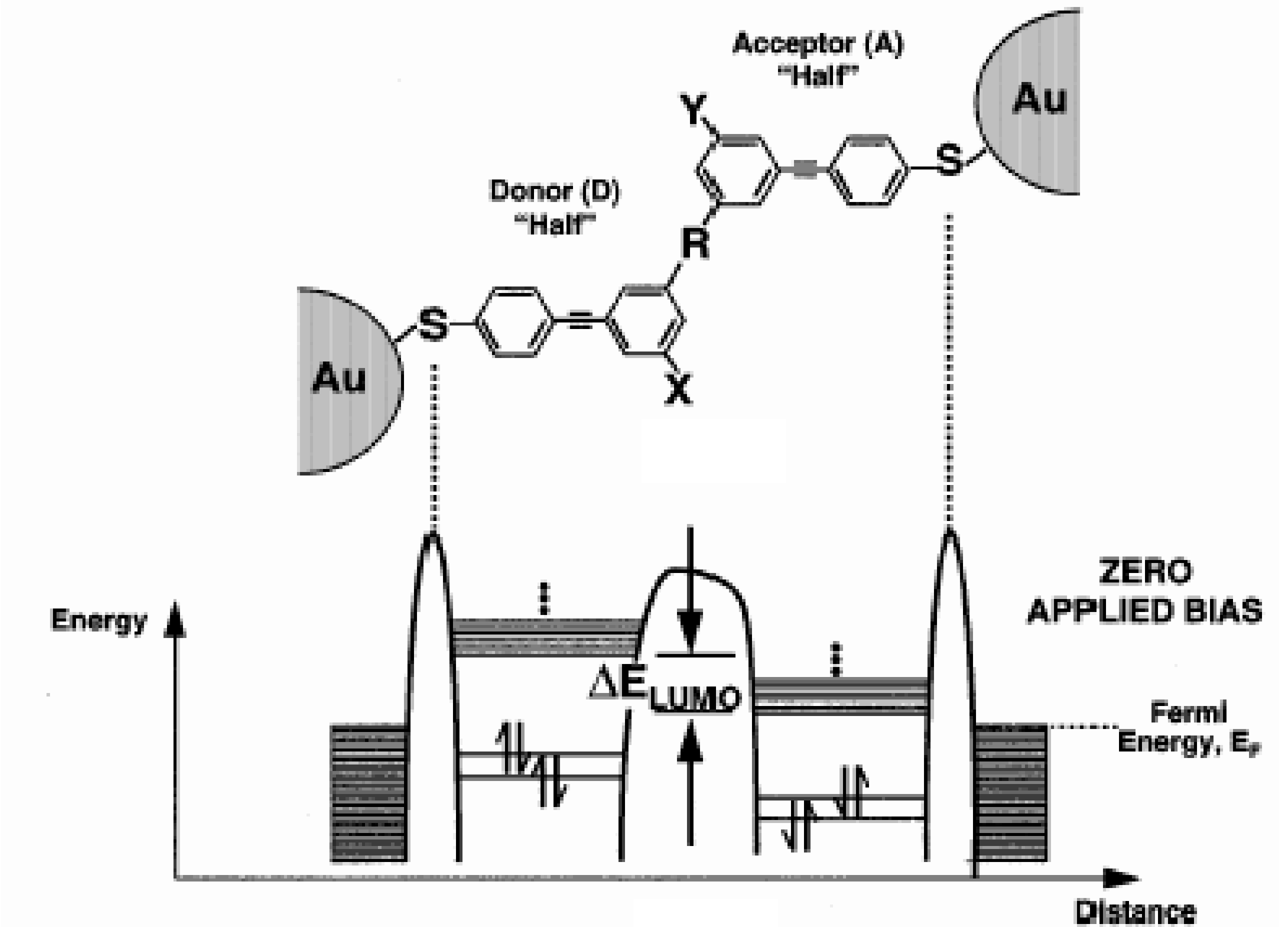
Increasing IP

Donor Substituents (X)

Acceptor Substituents (Y)

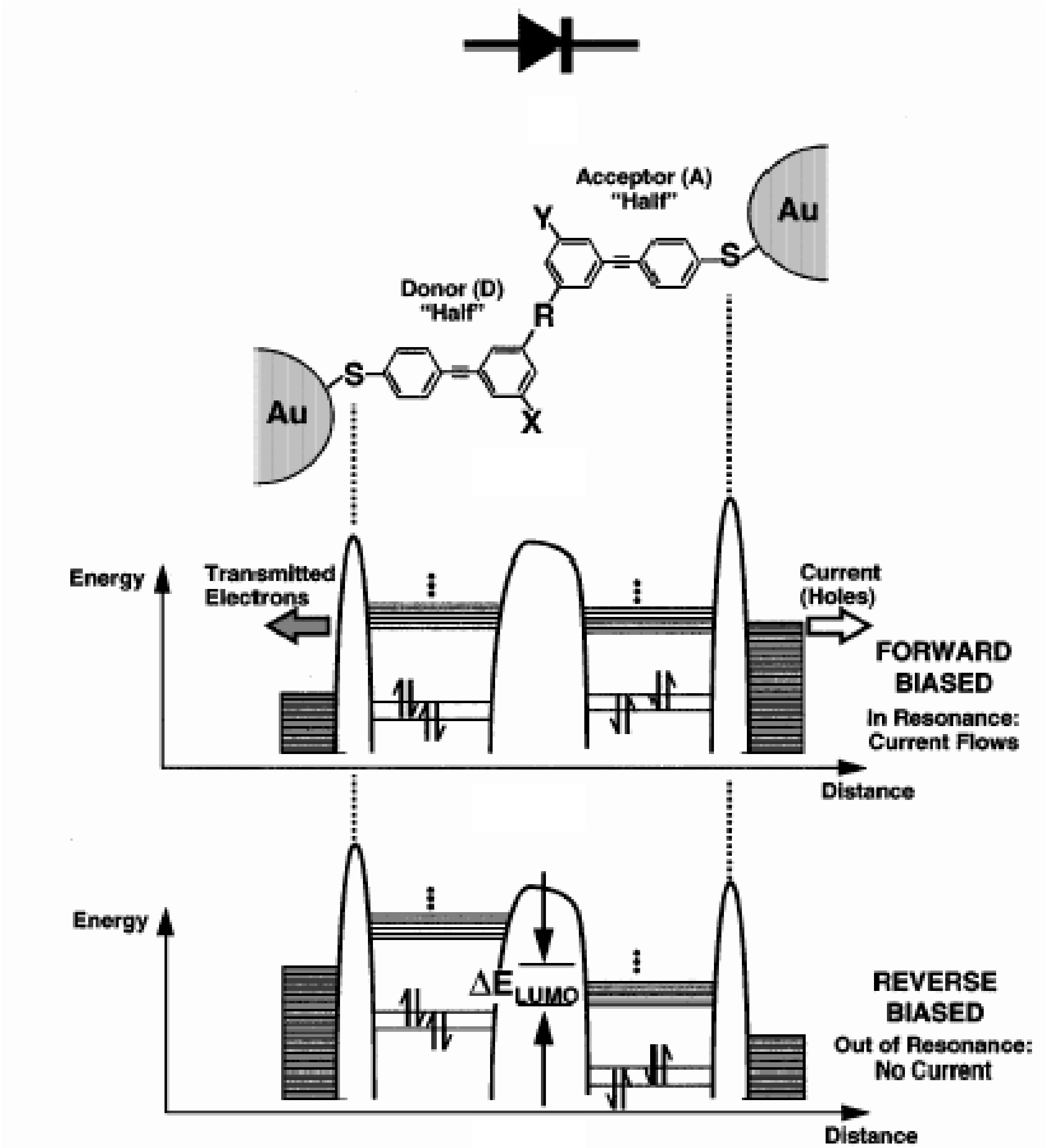
Mono-substituted Benzene	Structure	Experimental Ionization Potential (IP)*	Results of SCF Molec Orb. Calc'ns**			
			STO 3-21G Basis		STO 6-31G Basis†	
			E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}
Methoxy-benzene C_6H_5-OCH_3		8.20 eV	-8.93 eV	3.98 eV	-8.75 eV	3.85 eV
Methyl-benzene C_6H_5-CH_3		8.83 eV	-8.88 eV	4.15 eV	-8.69 eV	4.09 eV
Benzene C_6H_6		9.24 eV	-9.20 eV	4.02 eV	-8.98 eV	4.00 eV
Trifluoromethyl-Benzene C_6H_5-CF_3		9.69 eV	-9.98 eV	2.73 eV	-9.69 eV	2.87 eV
Benzonitrile C_6H_5-CN		9.73 eV	-9.71 eV	2.33 eV	-9.58 eV	2.27 eV

Diodes



Acceptor (A)
"Half"
Au
Y
S
Donor (D)
"Half"
R
Au
S
X
ZERO
APPLIED BIAS
Energy
ΔE
LUMO
Fermi
Energy, E
Distance

Diodes

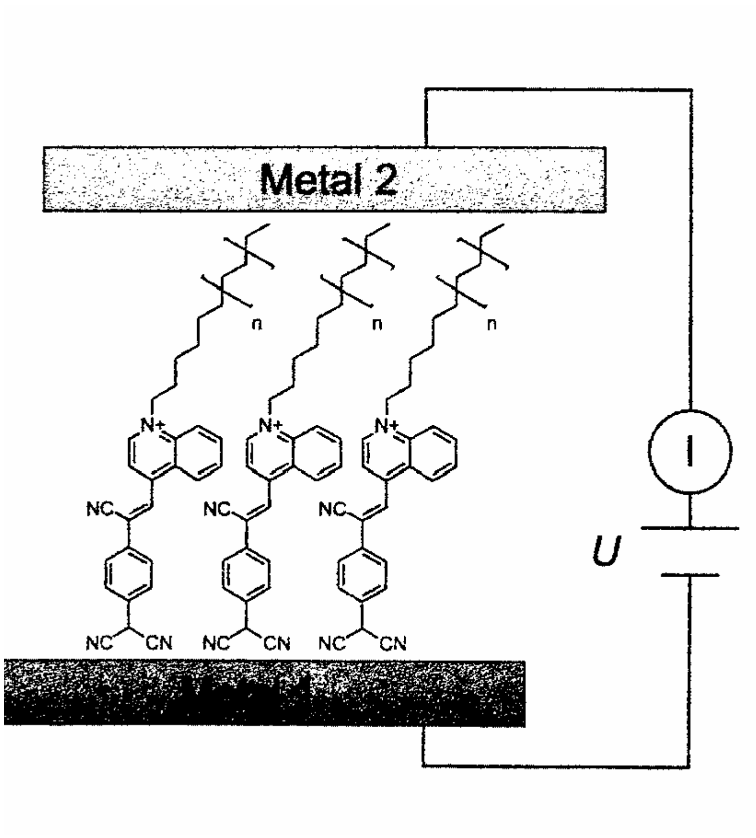


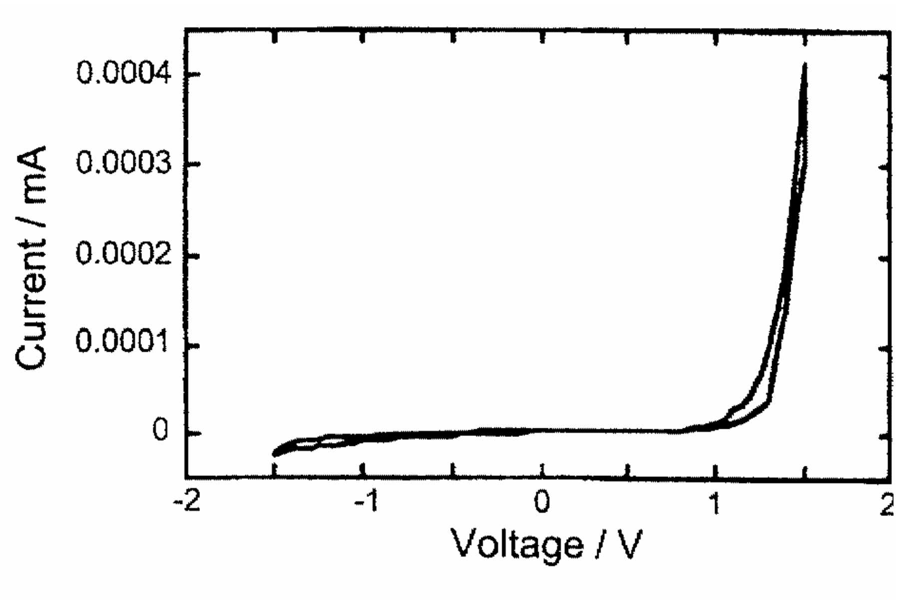
Acceptor (A)
"Half"
Au
Y
S
Donor (D)
"Half"
R
S
Au
X
Energy
Transmitted
Electrons
Current
(Holes)
FORWARD
BIASED
In Resonance:
Current Flows
Distance
Energy
ΔE LUMO
REVERSE
BIASED
Out of Resonance:
No Current
Distance

Content

- Introduction
- Electrodes and Contacts
- Functions of Single Molecules
- Molecular Electronic Devices
  - Monomolecular Film Devices
    (Diodes, Switches, Memories)
  - Single Molecule FET
  - Organic Light Emitting Diode (OLED)
- Summary and Outlook

Diodes - Experiment





Switches and Storage Elements

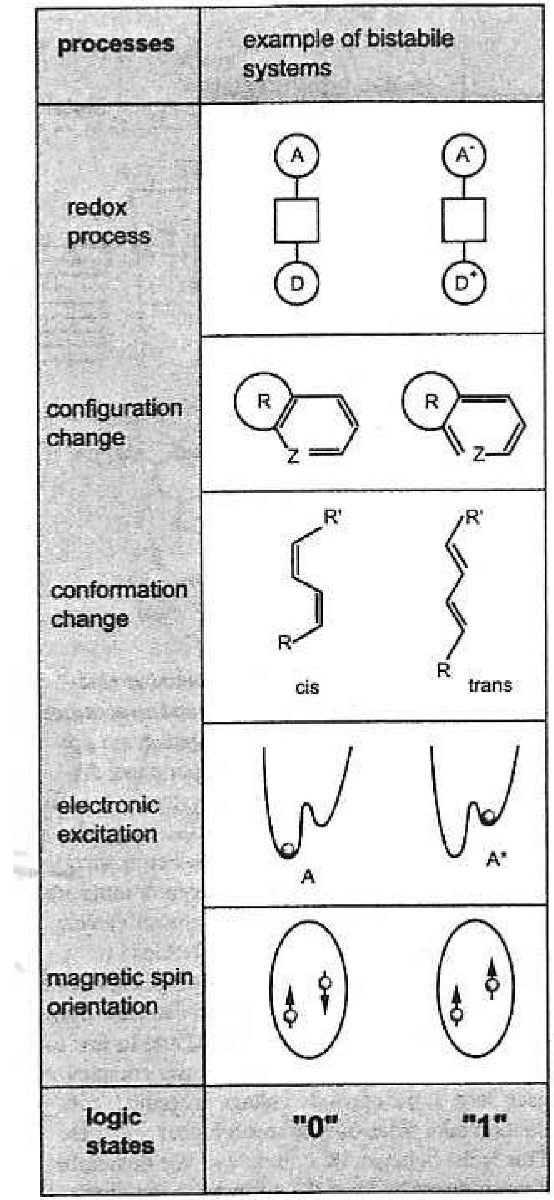
- Classes of molecules, which are stable in two different states (bistable)

Switches and Storage Elements

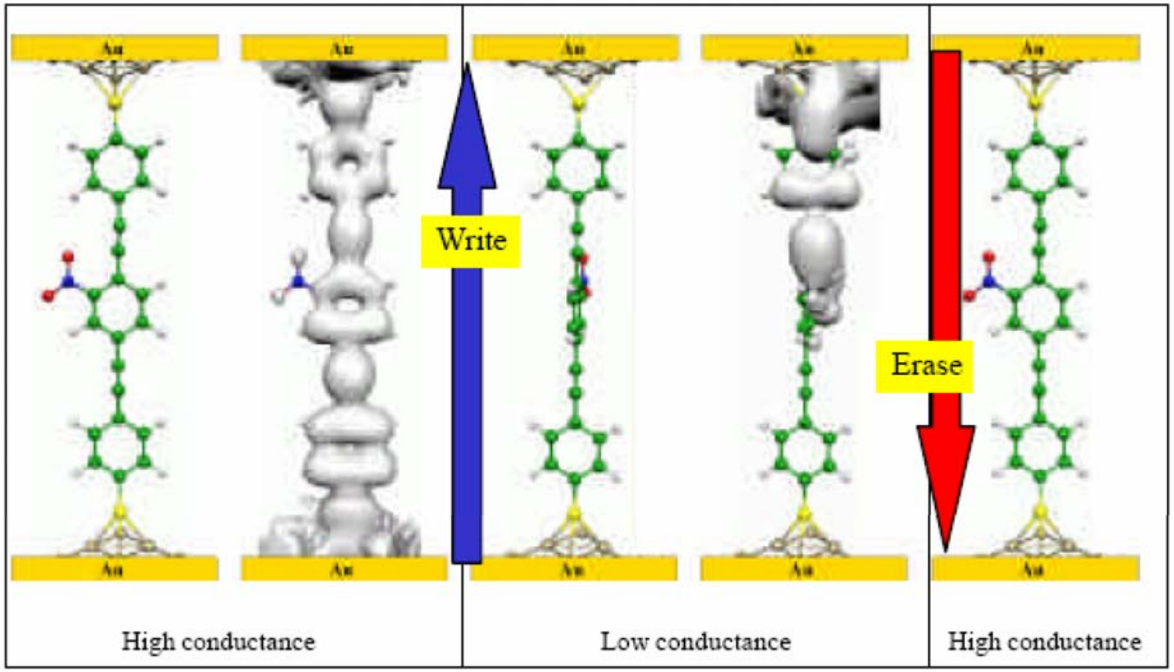
- Classes of molecules, which are stable in two different states (bistable)
- Classified by:
  - stimulus that triggers the switch
    (light, pH value, electrical potential)

Switches and Storage Elements

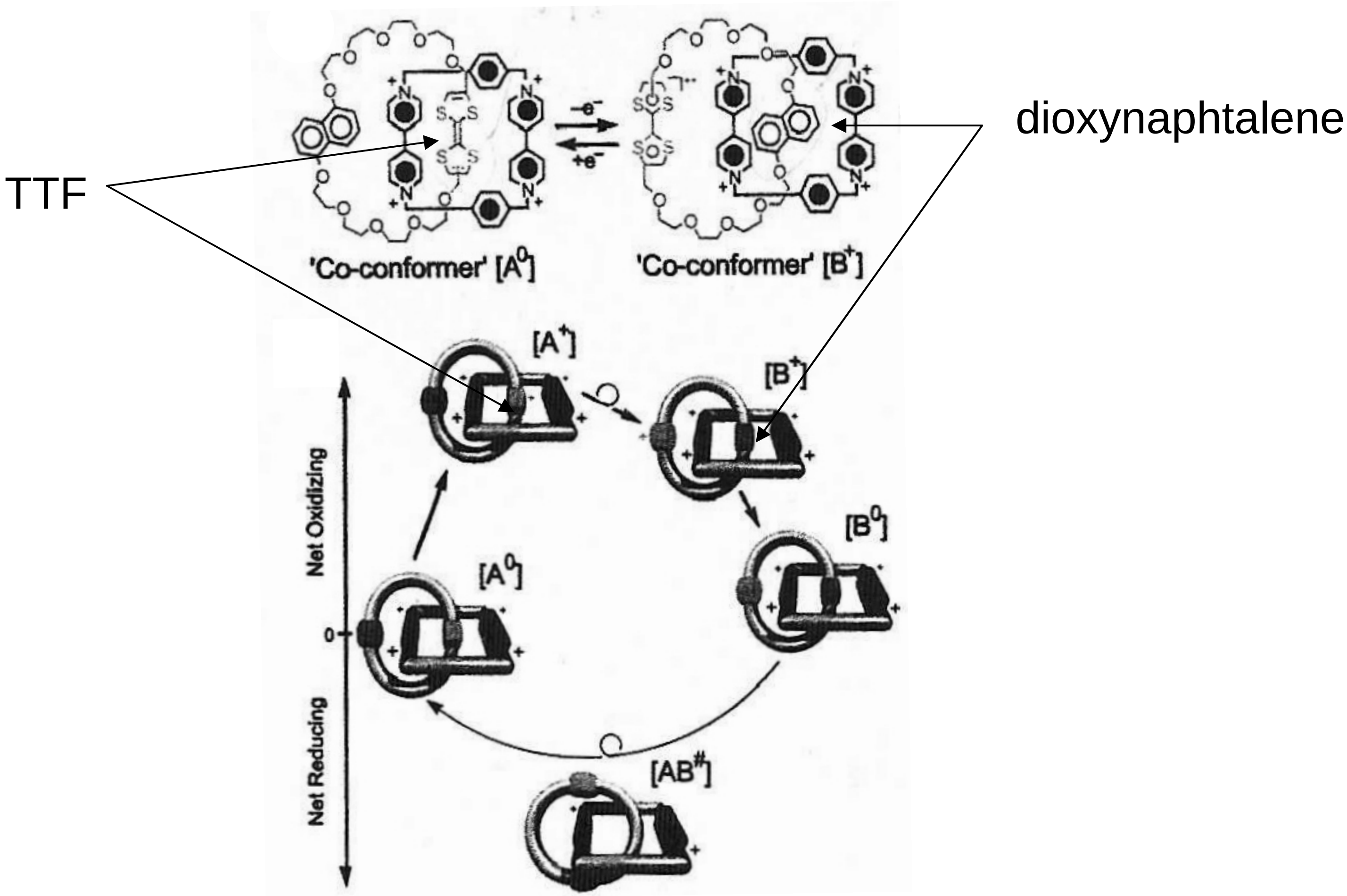
- Classes of molecules, which are stable in two different states (bistable)
- Classified by:
  - stimulus that triggers the switch (light, pH value, electrical potential)
  - property or function that is switched (structural feature, current transport)



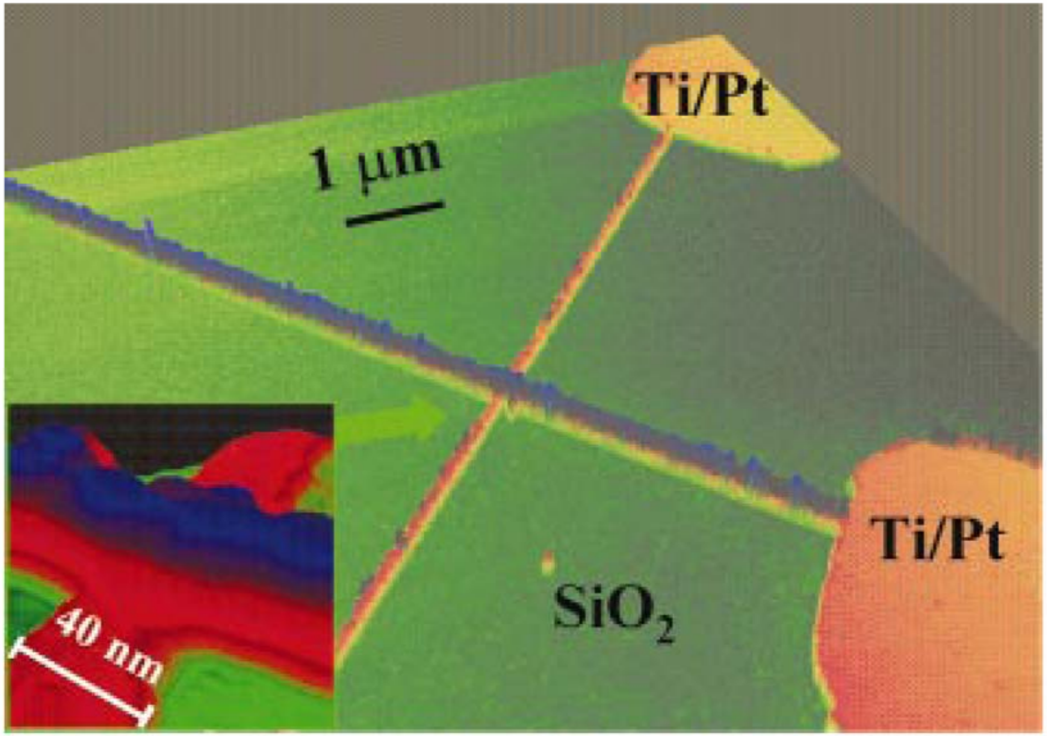
Switches and Storage Elements - Example



Catenane as memory device

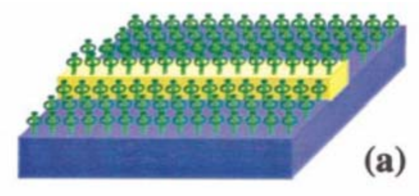


Rotaxane as Crossbar-Memory



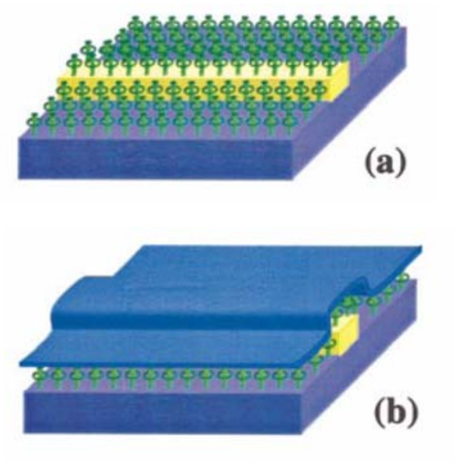
Young Chen et al., Appl. Phys. Lett., Vol. 82, No. 10

Rotaxane as Crossbar-Memory - Fabrication



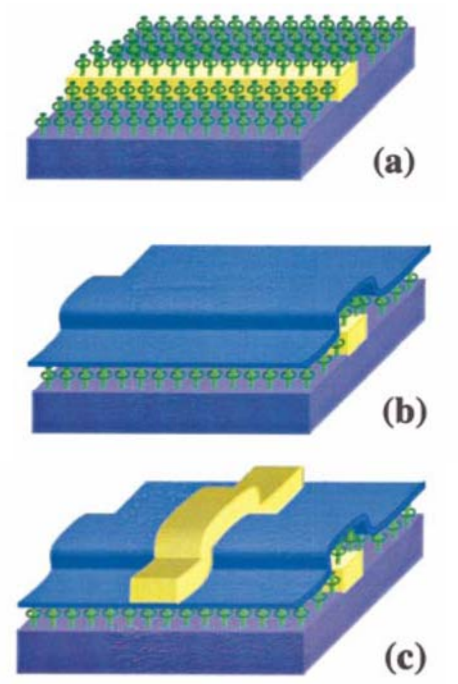
a) Deposition of Rotaxane by LB-technique

Rotaxane as Crossbar-Memory - Fabrication



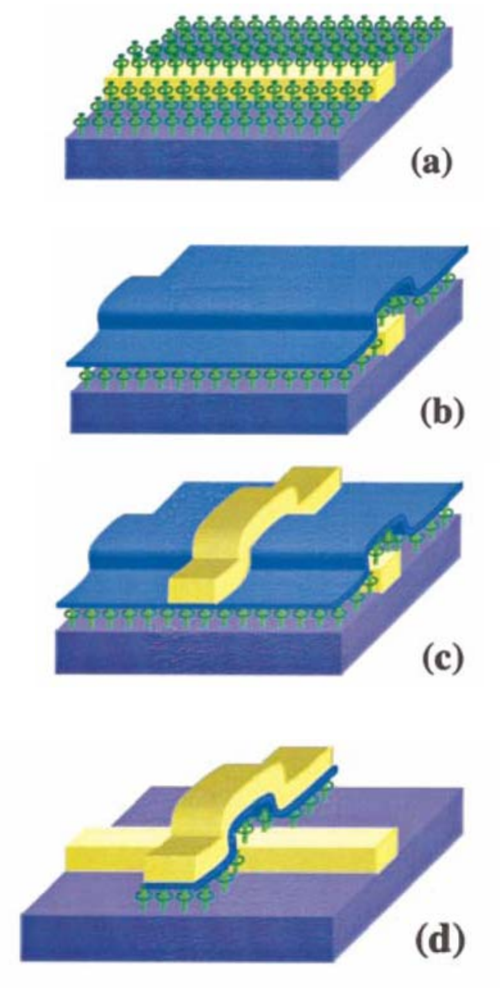
a) Deposition of Rotaxane by LB-technique
b) Evaporation of Ti protective layer

Rotaxane as Crossbar-Memory - Fabrication



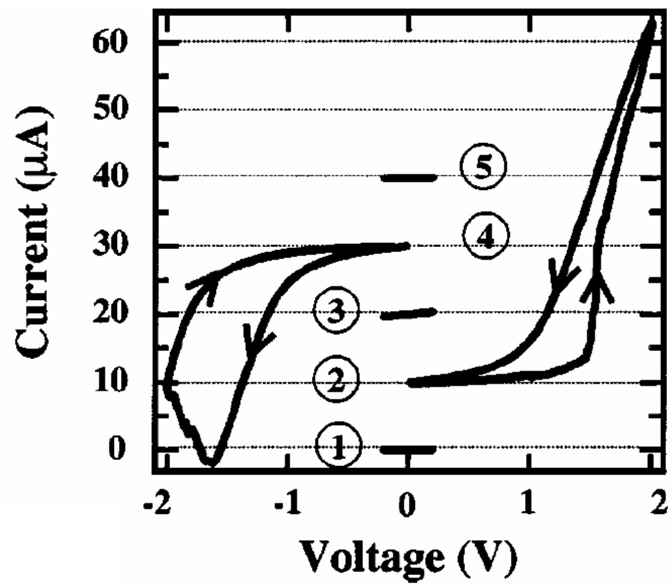
a) Deposition of Rotaxane by LB-technique
b) Evaporation of Ti protective layer
c) Evaporation of top electrode

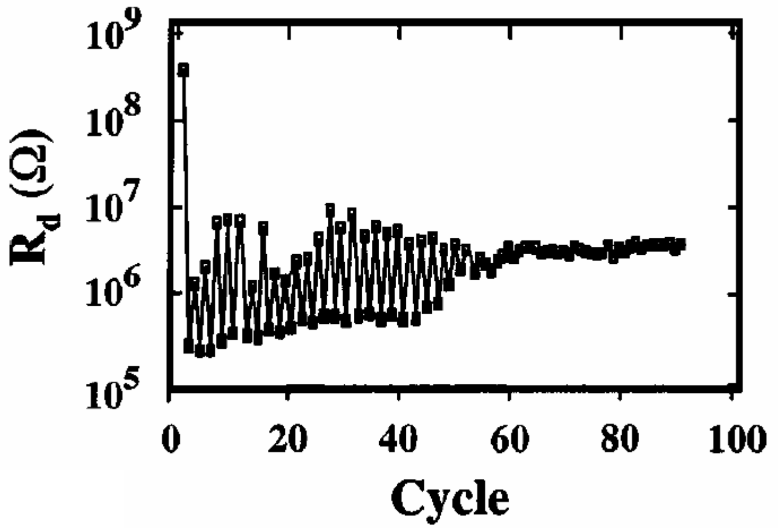
Rotaxane as Crossbar-Memory - Fabrication



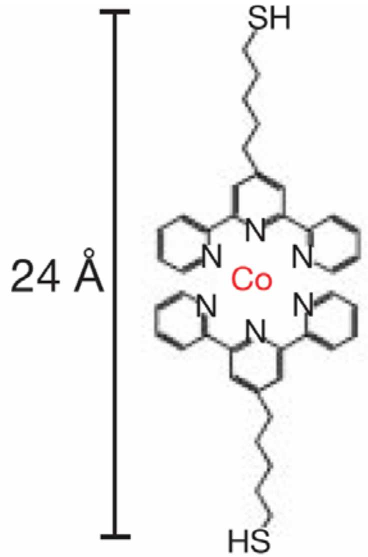
a) Deposition of Rotaxane by LB-technique
b) Evaporation of Ti protective layer
c) Evaporation of top electrode
d) Anisotropic RIE down to the SiO_2

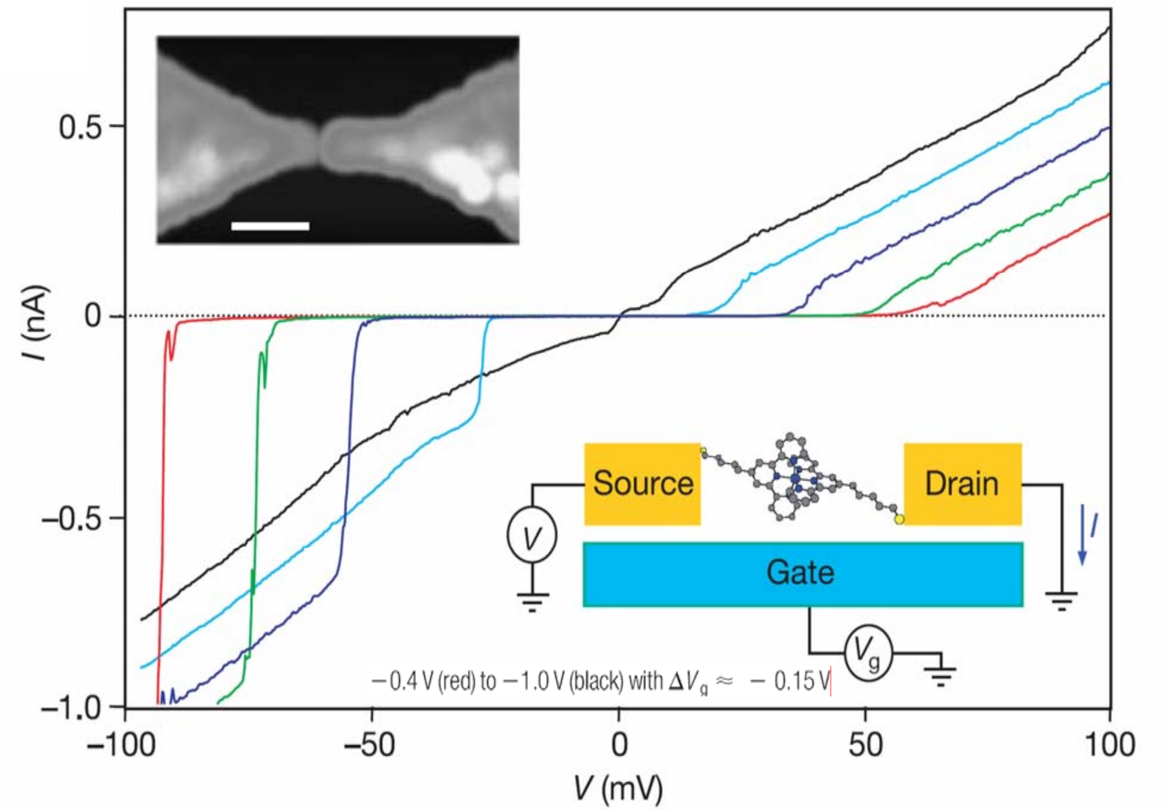
Rotaxane as Crossbar-Memory - Data





Single Molecule FET

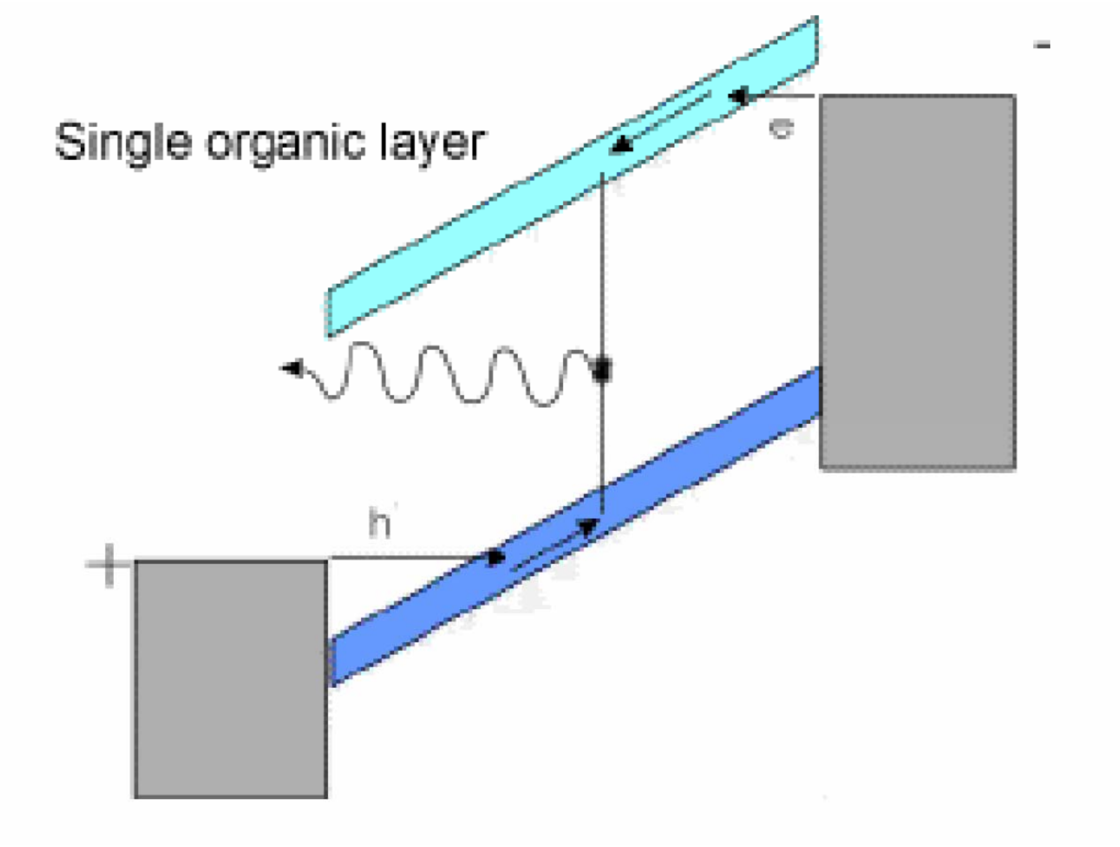




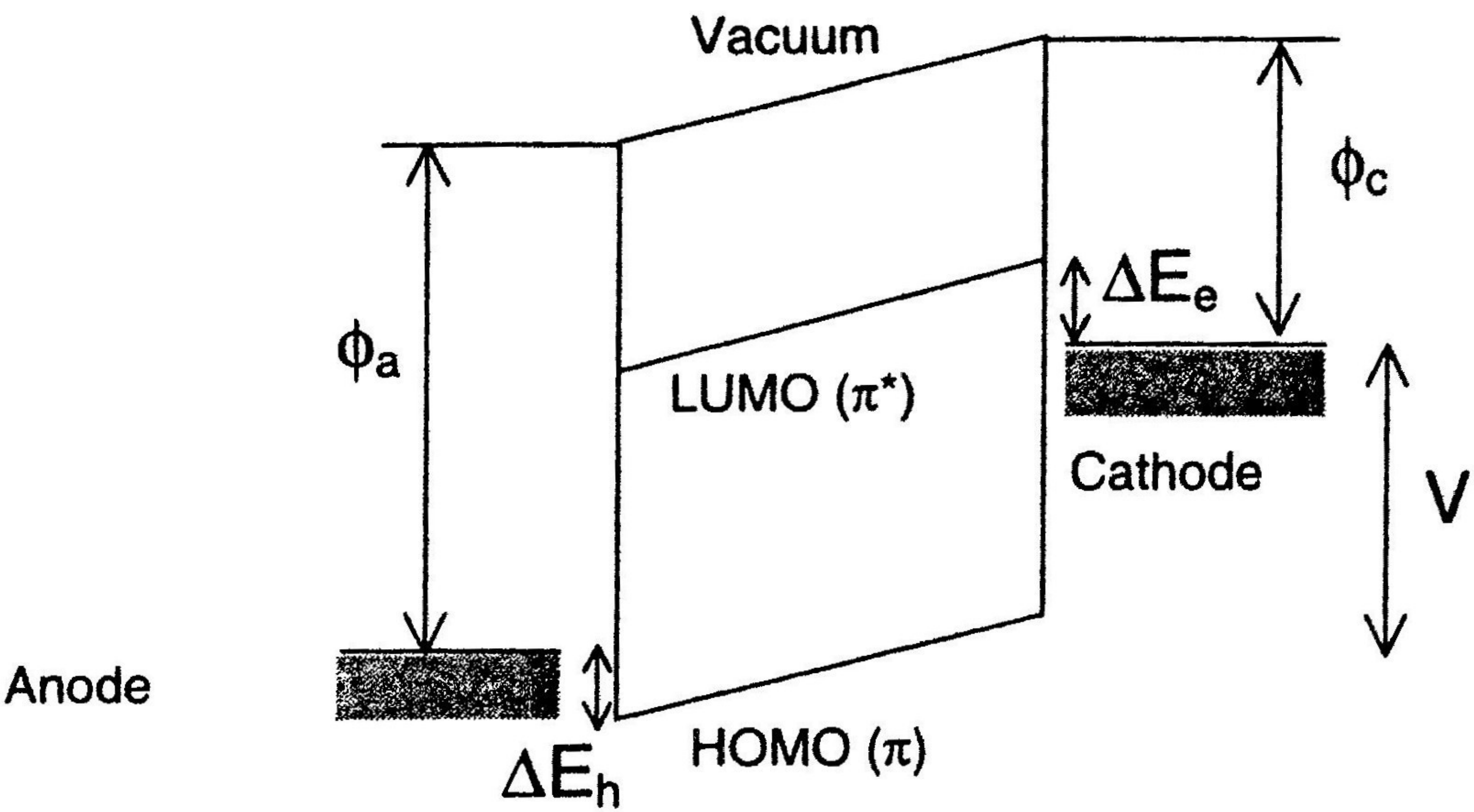
H. Park et al., *Nature* 417, 722 (2002.

Organic Light Emitting Diode

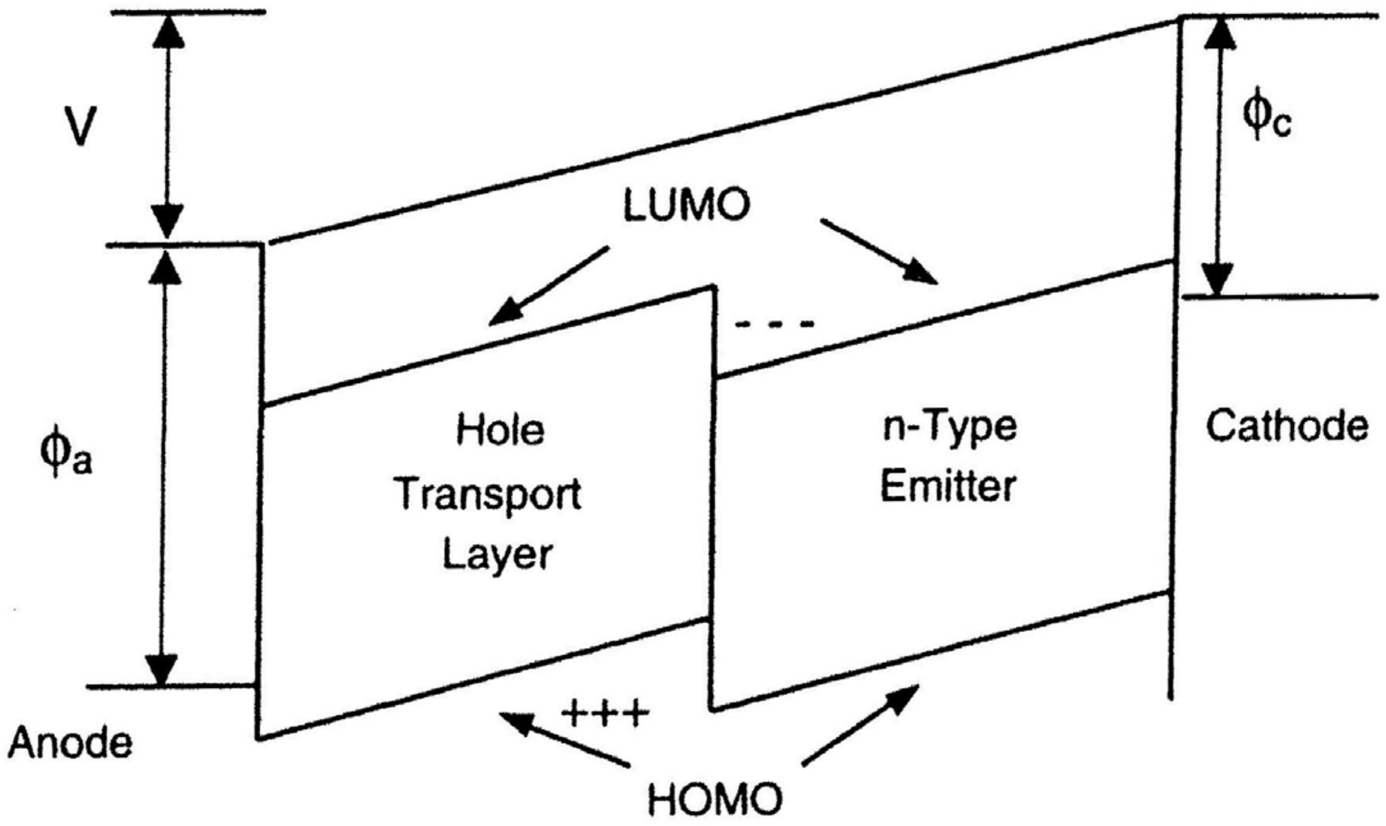
OLED - Principle



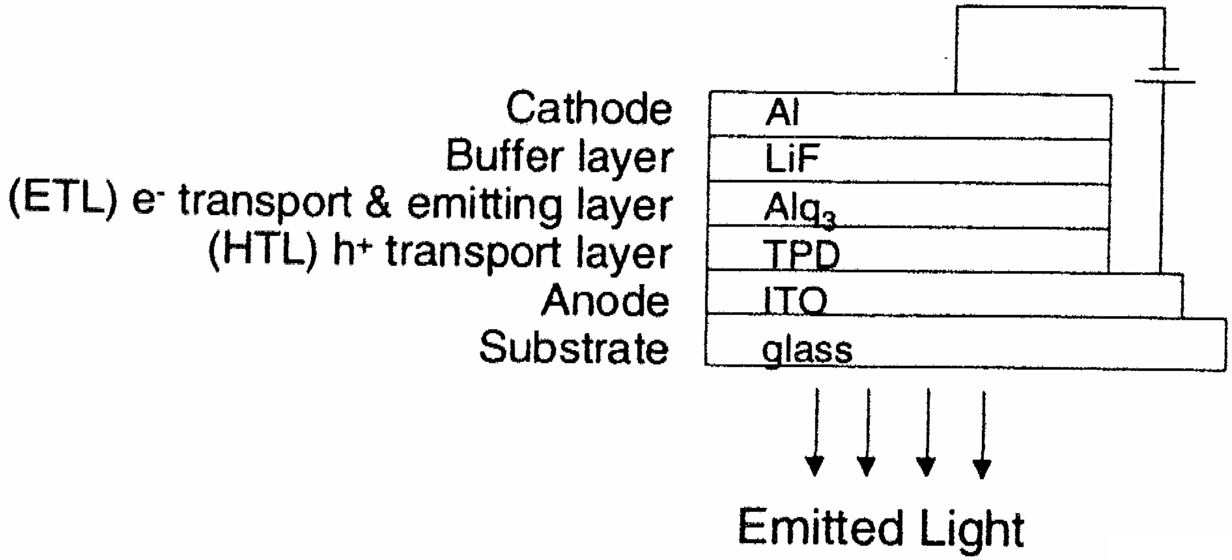
OLED - Principle

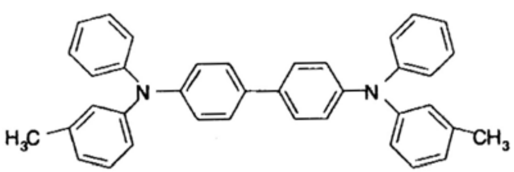


OLED - Principle

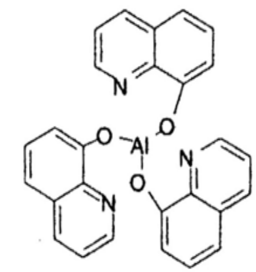


OLED - Structure and Materials



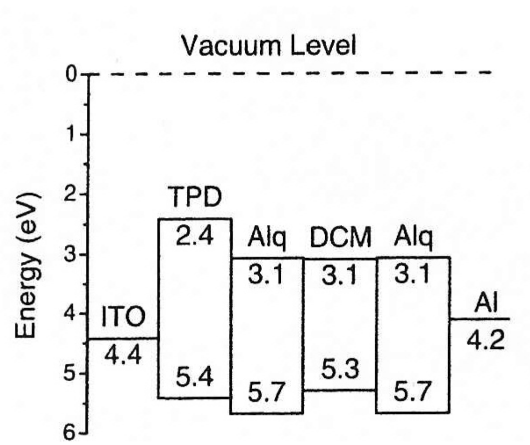


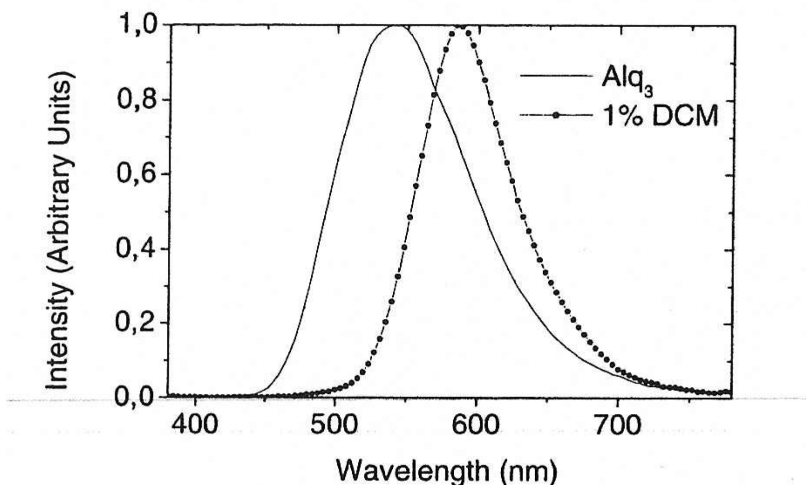
TPD N,N'-diphenyl-N,N'-bis(3-methylphenyl)benzadine

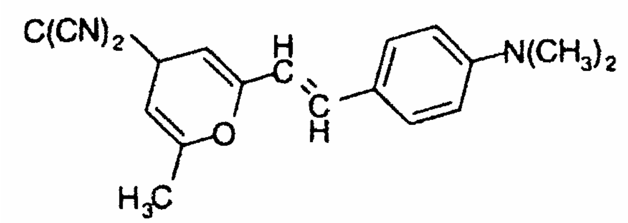


Alq_3 8-hydroxyquinoline aluminum

OLED - Effect of Dopants







Summary and Outlook

- Bottom-up approach in order to overcome the physical limitations of the Top-down approach

Summary and Outlook

- Bottom-up approach in order to overcome the physical limitations of the Top-down approach
- Molecular film devices are already commercialised (OLED)

Summary and Outlook

- Bottom-up approach in order to overcome the physical limitations of the Top-down approach
- Molecular film devices are already commercialised (OLED)
- Single molecule devices are still under investigation

Summary and Outlook

- Bottom-up approach in order to overcome the physical limitations of the Top-down approach
- Molecular film devices are already commercialised (OLED)
- Single molecule devices are still under investigation
- In order to use the ultimate density of logic and memory functions of molecules, problems like their addressability, reproducibility and reliability have to be solved

Literature

- General information:
  Nanoelectronics and Information Technology, Rainer Waser (Ed.), Wiley-VCH
  Handbook of Nanotechnology, Bhushan (Ed.), Springer
  Molecular Nanoelectronics, Mark A. Reed et al., ASP

- Chemisorption:
  Mark H. Dishner et al., Langmuir, Vol. 13, 2318-2322, 1997
  Rosa Di Felice, J. Chem. Phys., Vol. 120, No. 10, 2004

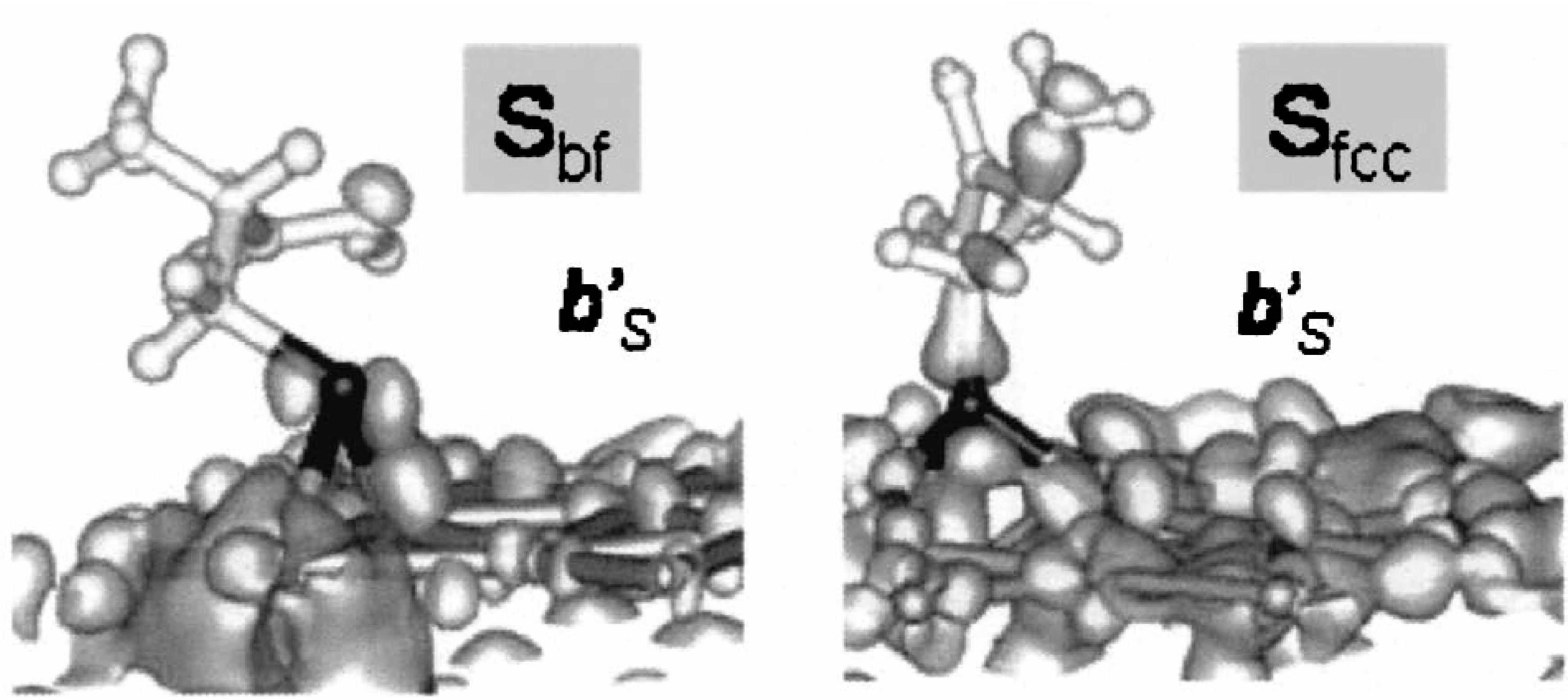
- Electronic Transport:
  Adi Salomon et al., Adv. Mater., Vol. 15, No.22, 2003
  Yoram Selzer et al., Nano Letters, Vol. 5, No.1, 61-65, 2005

- SET:
  Jiwoong Park et al., Nature, Vol. 417, 13 June 2003

- Molecular Switch:
  Yong Chen et al., Appl. Phys. Lett., Vol. 82, No.10, 2003

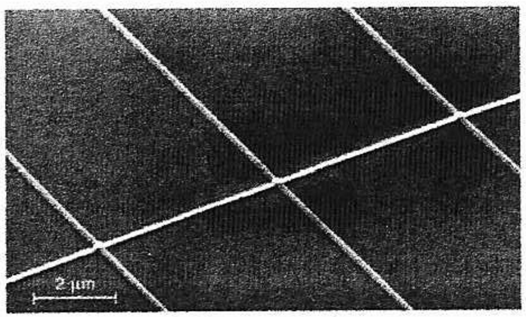
- OLED:
  Molecular Nanoelectronics,Chapter 12, Mark A. Reed et al., ASP

Thiol-Au Interface



Rosa Di Felice, J. Chem. Phys., Vol. 120, No. 10, 2004

Catenane in a crossbar memory



Paper: Yong Chen: