PLASTRONICS
molecular, organic and biological electronics: an overview

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Outline

- The driving force: optoelectronics
- The future: electronic devices and circuits
- Single molecule electronics
- Carbon nanotubes
- Conclusions

In collaboration with:

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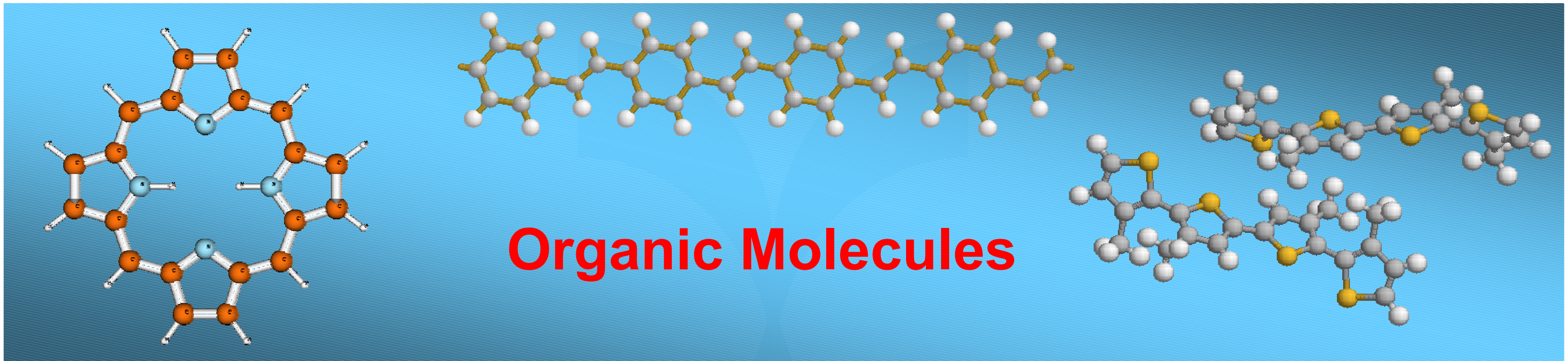
M.L. Terranova, R. Paolesse, C. Lo Sterzo (*Chemistry Dept*)

Molecular electronics



Organic Material for electronics

- Electroluminescent devices
- Organic Transistors
- Organic Lasers
- Organic Solar Cells

Conventional devices with organic semiconductors

Molecular Electronics

- Diodes
- Transistors
- Memories

New devices with nanosize dimension

Why molecular electronics ?

Products: Organic LEDs, displays, Thin Film Transistors, detectors, sensors, solar cells, electronic circuits, memories, antennas

Organic devices and circuits will have worse performance with respect to their inorganic counterparts, but they offer several advantages

Advantages

Integrability

- Large integration: scale up to molecular scale
- Function integration: the same material can perform several functions

Mass Reduction

Low Power Consumption

Cost Reduction

- Material production based on Self-assembling chemical technologies
- Component production: very simple technologies (inkjet printing, inprinting, digital printing)
- Customized components easy to produce

Large Area

- The reduction in weight, cost production and consuption leads to the development of very large area apparata (solar panels, large antennas)

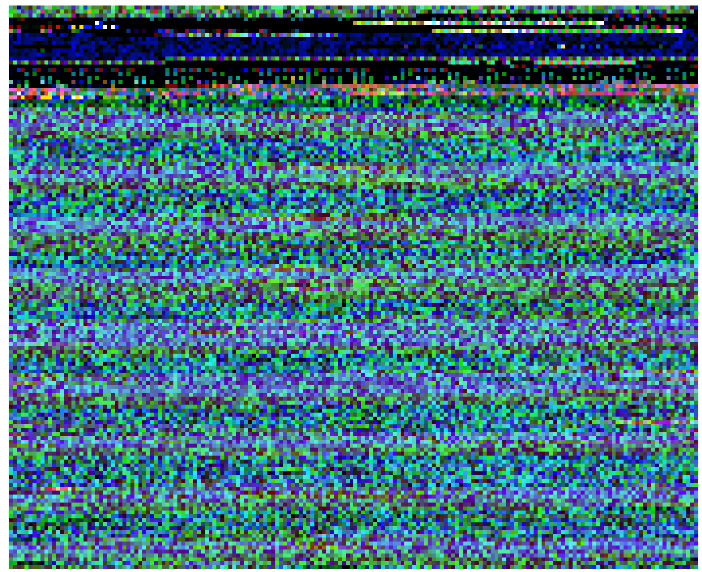
Materials

- A large variety of organic materials available

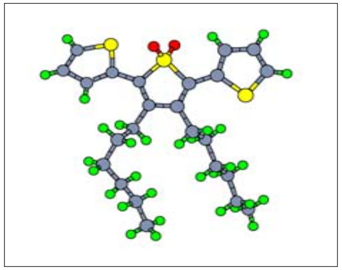
OLED

Since OLED pixels are self-luminous, this display technology **requires no backlighting** – unlike LCD displays. Therefore, OLED displays are flatter and lighter than LCD displays of equal size. They also consume much less energy.

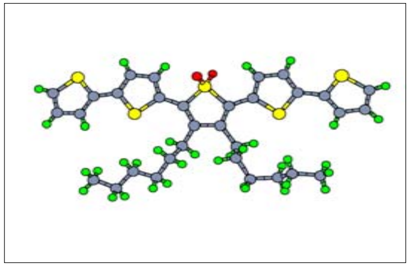
- **Unlimited viewing angle**
- **Faster response (100 to 1000 times faster than LCD)**
- **Brighter display (150cd/m^2)**
- **High-contrast picture (>100:1)**
- **Wide operating-temperature range (-80°C to +80°C)**



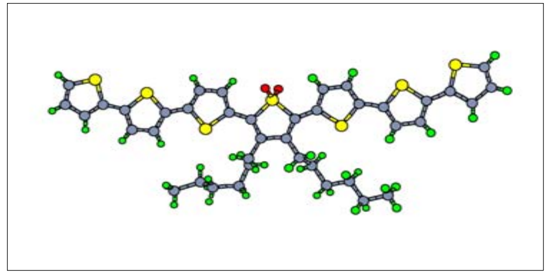
Oligo-thiophen Absorption spectra



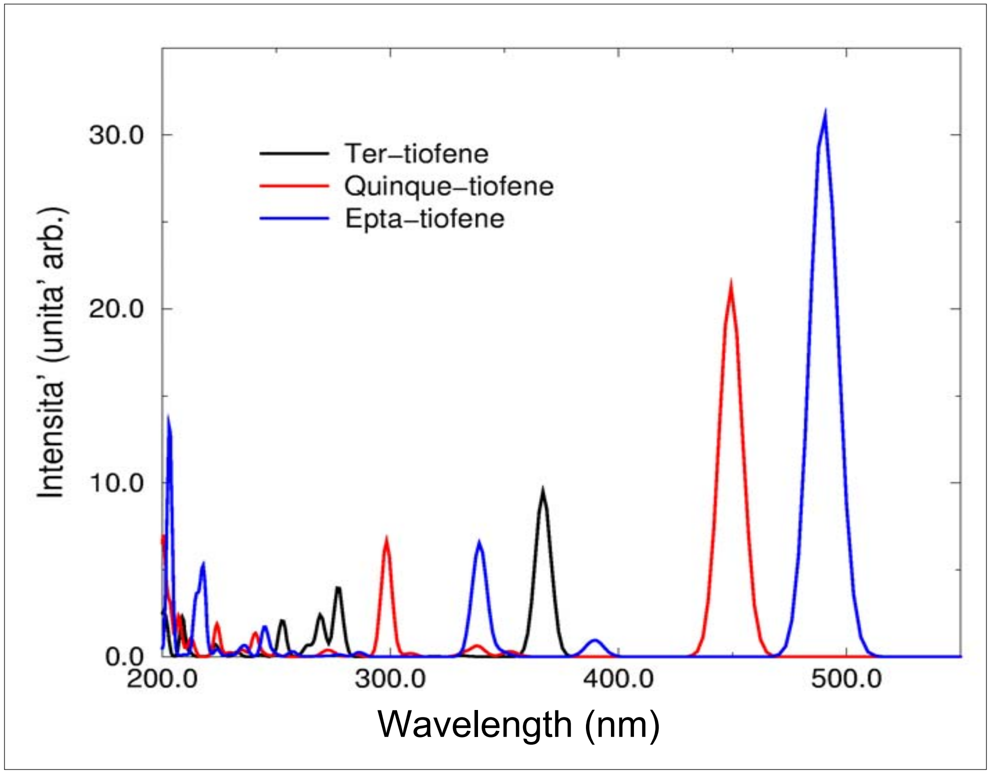
3TO2



5TO2



7TO2



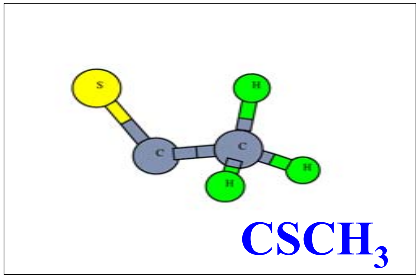
3TO2
370 nm

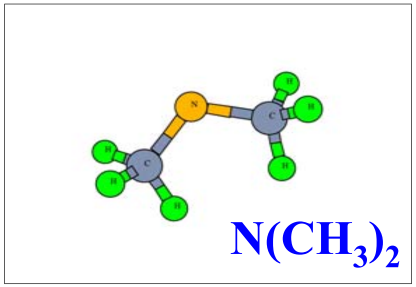
5TO2
450 nm

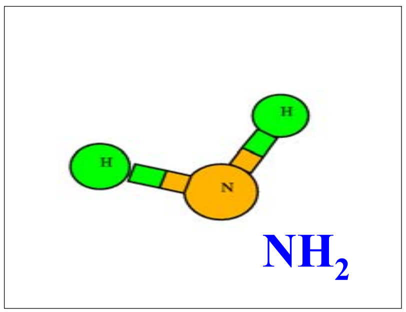
7TO2
495 nm

9TO2
UNSTABLE !!
550 nm

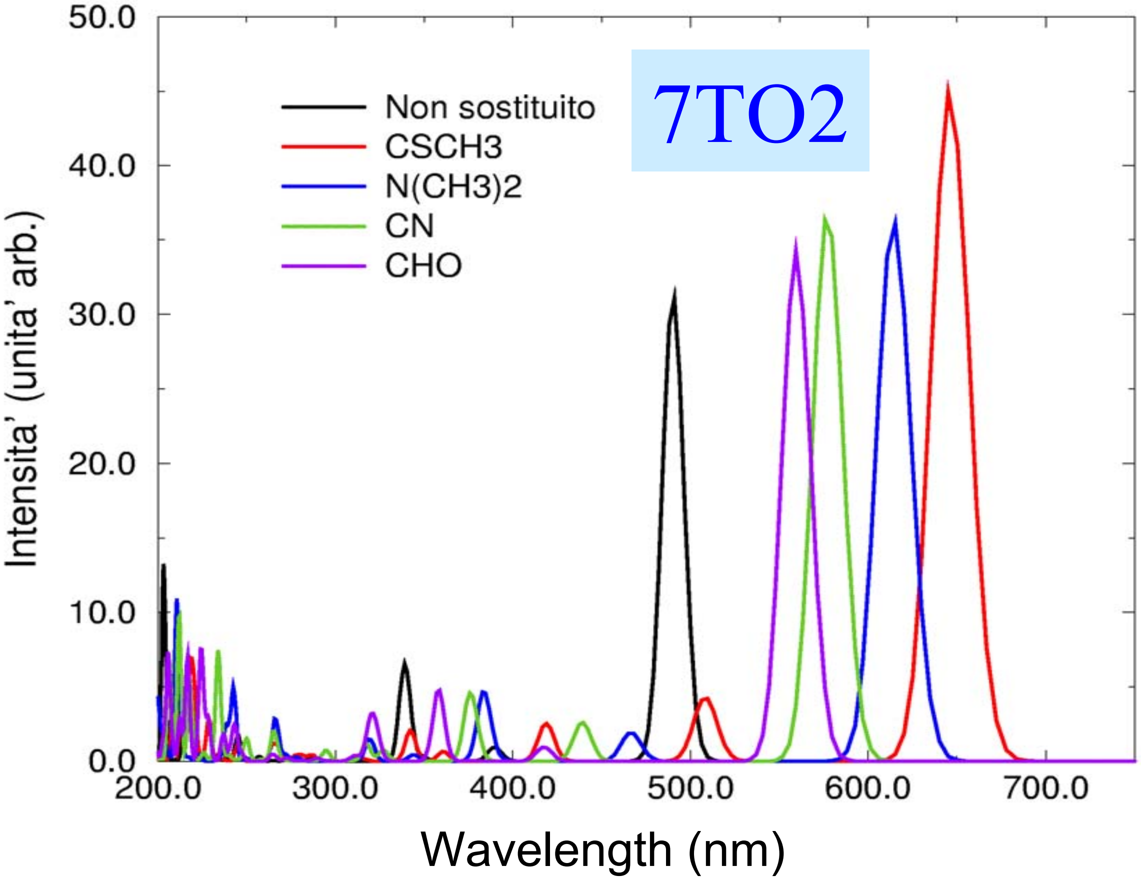
Substituents

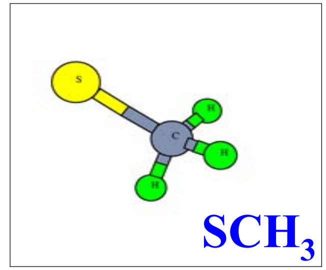


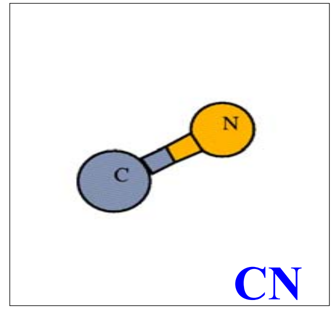


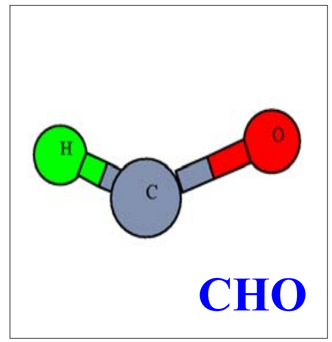


It is possible to attach to the end chain of an oligomer a functional group





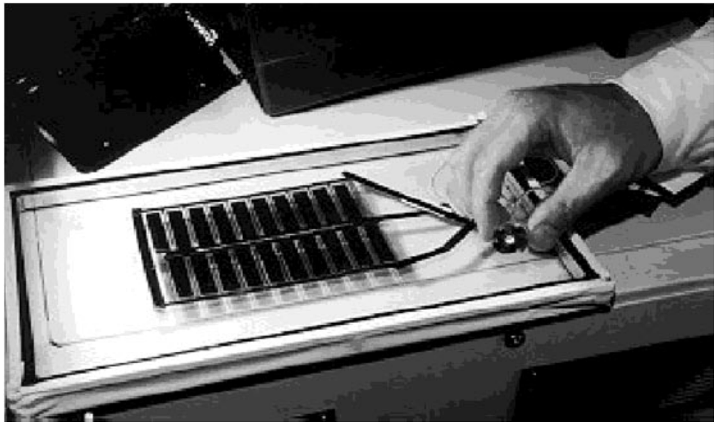




Plastic Solar Cells

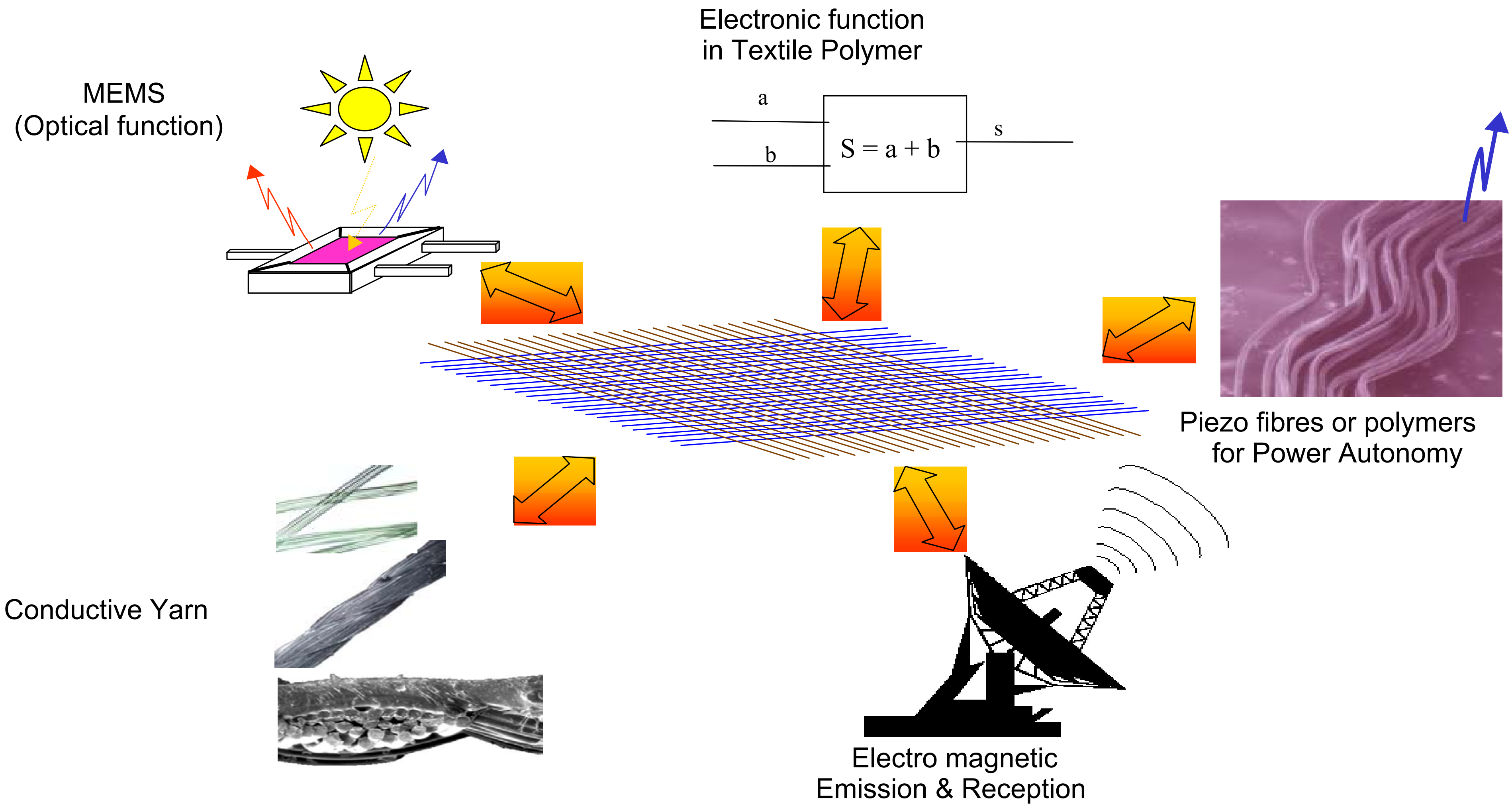
-Solar cells might one day be produced by the roll, as cheaply and easily as wallpaper

-Nowadays people coat the glass with a transparent, electrically conducting material that acts as one of the solar cell's electrodes. On top of this, they lay down a thin film of a polymer, which helps to gather current from the photovoltaic material. Finally, they deposit a blend of two organic compounds that convert light into electricity. One, a carbon-based molecule called fullerene, produces charged particles that carry an electrical current when light shines onto the molecules. The other, a polymer, ferries the current to electrodes on the top and bottom of the cell. <u>Power conversion efficiency=3%</u>

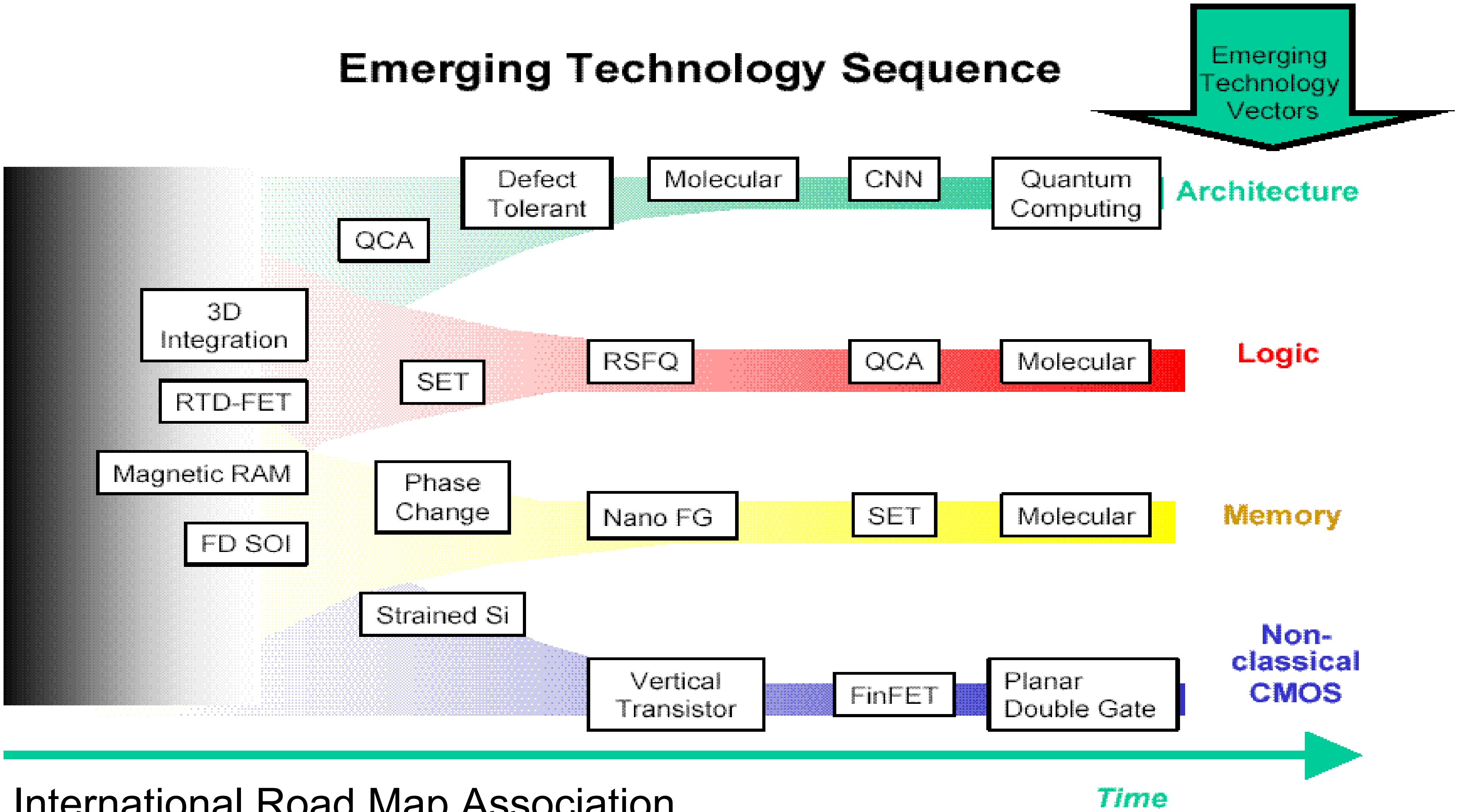


A large area plastic solar cell running a small motor

Smart clothes

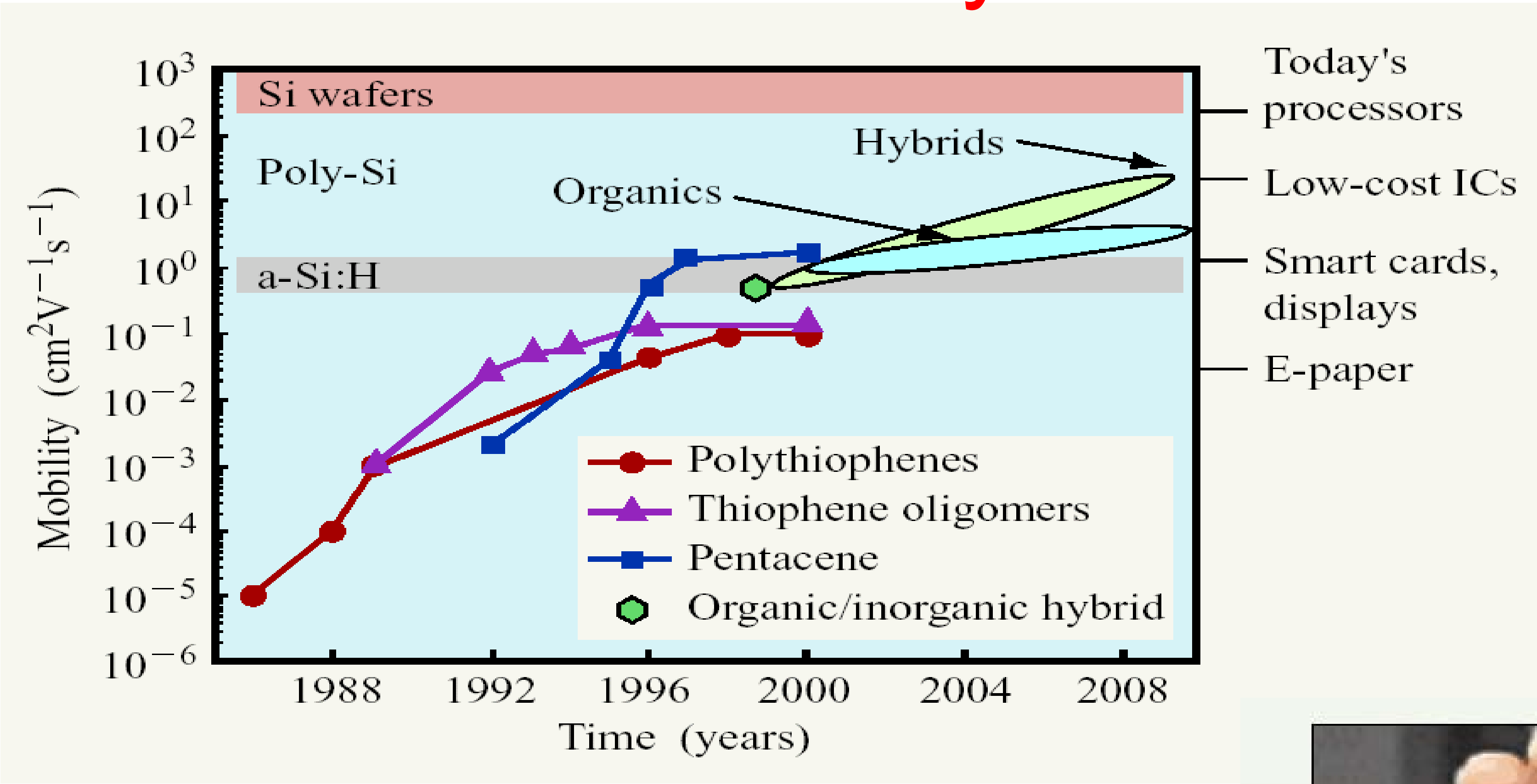


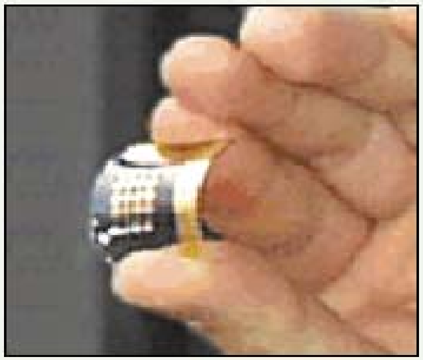
Emerging technologies



International Road Map Association

Mobility

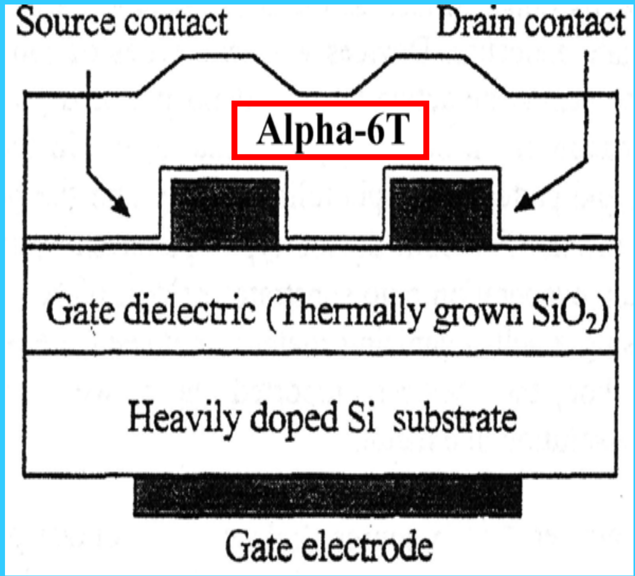




Mobilities of organic semiconductors have improved by five orders of magnitude over the past 15 years. Large research efforts using materials such as these led to some of this increase.

FET implementations

Organic electronics

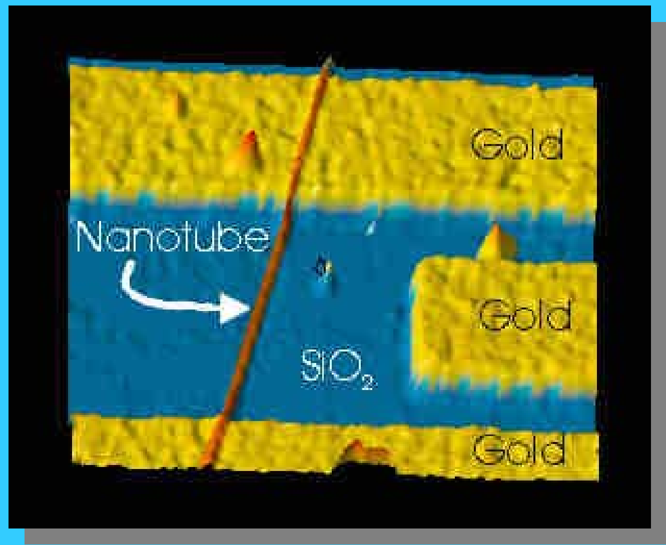


An organic semiconductor is used instead of a standard one

Low cost, flexible substrates or Si, large areas, simple processing

FET

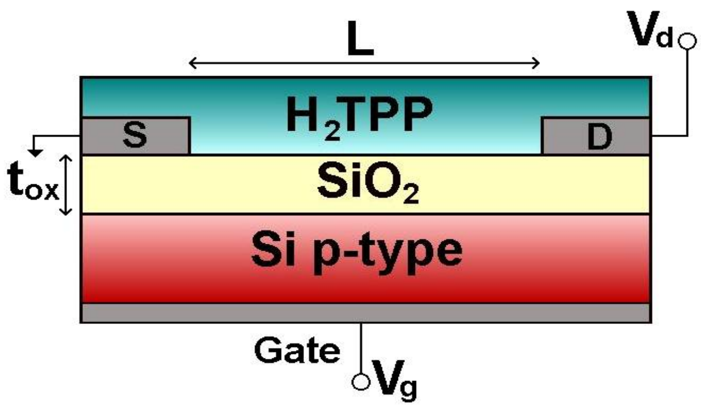
Molecular Electronics



A molecular nanostructure or a single molecule acts active device

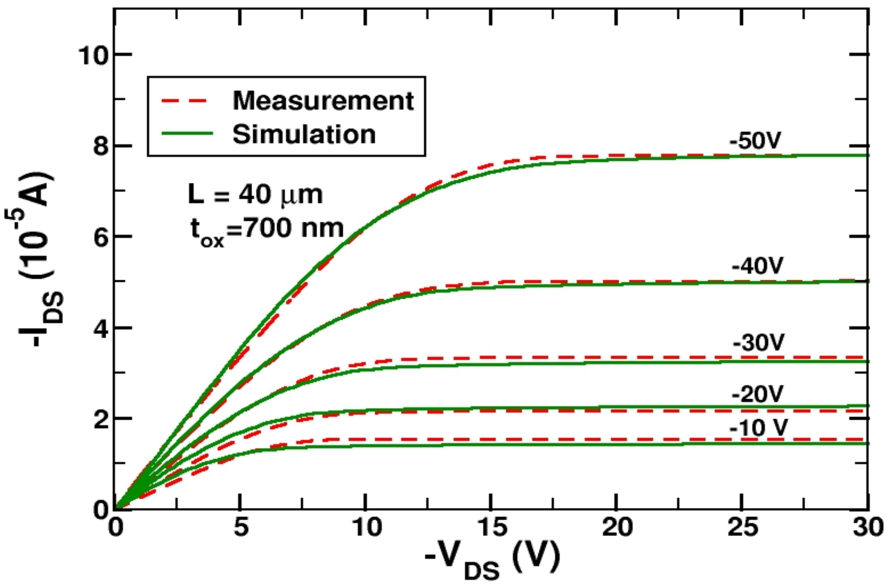
Nanometer dimension, very high current densities

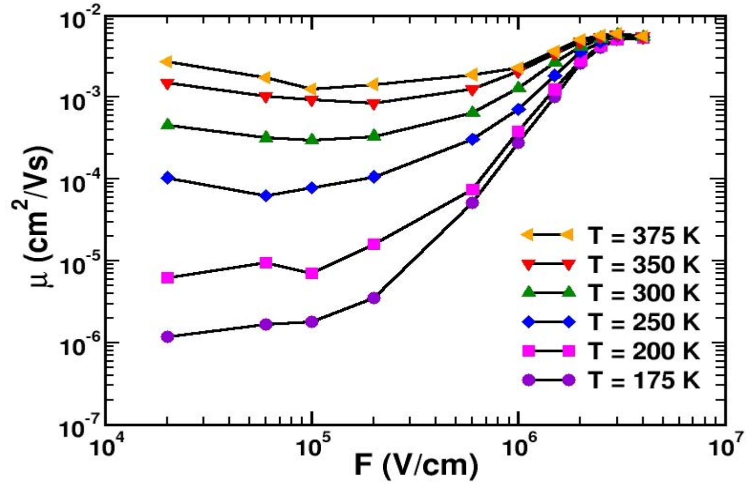
H_2TPP OTFT



Simulation of organic devices with commercial Drift-Diffusion simulator:

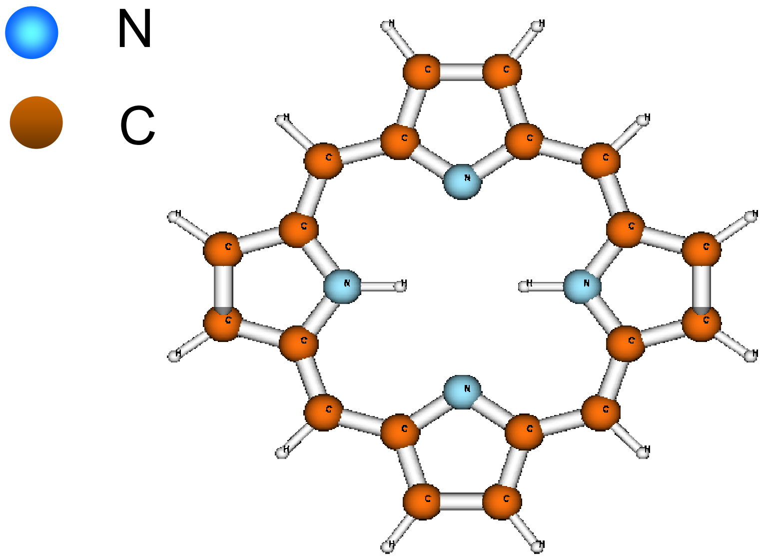
- HOMO-LUMO
- Equivalent doping
- Field-dependent mobility
- Traps



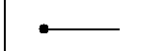
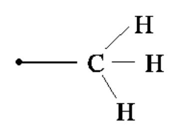
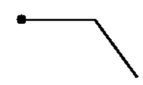
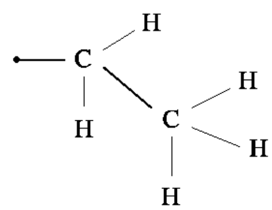
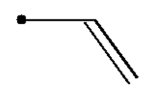
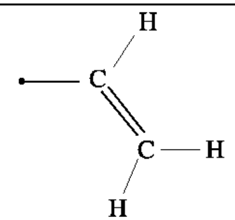


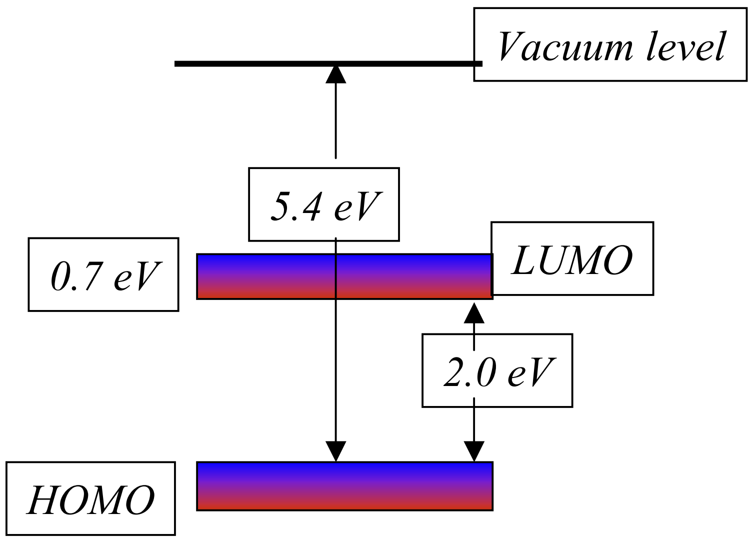
$$\mu = \mu_0(T)\exp\left(\frac{q\beta}{kT}\sqrt{F}\right)$$

Metal-Free Tetra-Phenyl-Porphyrin



Planar molecule. By substituting the external H atoms with a given group, it is possible to modify the molecule properties and planarity

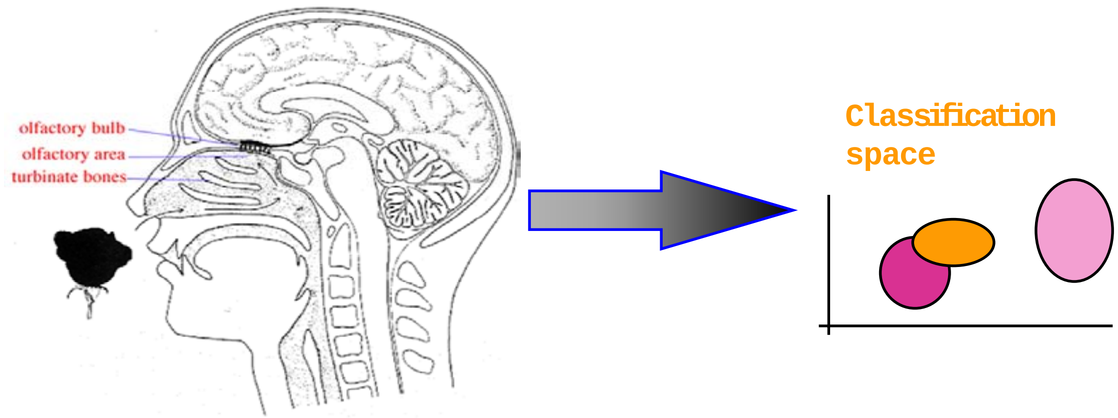
Metile		
Etile		
Vinile		

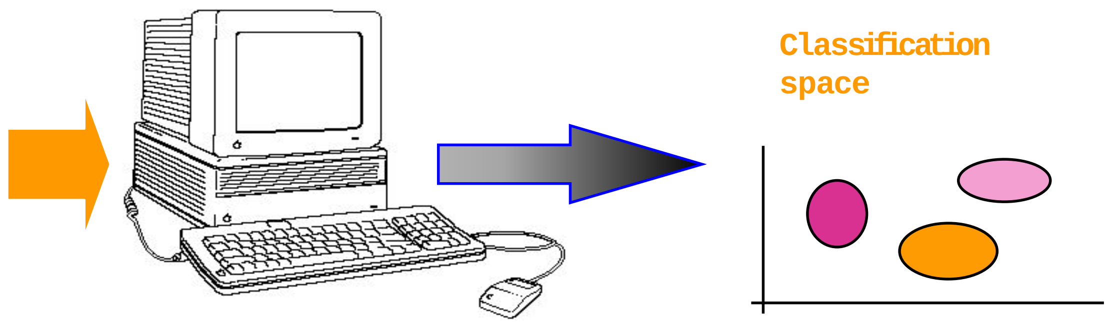


It is also possible to insert a metal in the middle of the ring

Natural and Artificial Olfaction

- ***Olfaction components:***
  - ***Sampling system***
  - ***Measurement chamber***
  - ***Sensors***
  - ***Signal processing***
  - ***Pattern recognition***



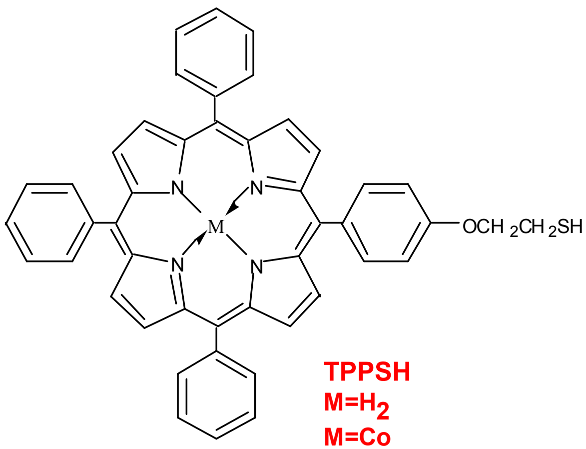


LIBRA Electronic nose – Tor Vergata

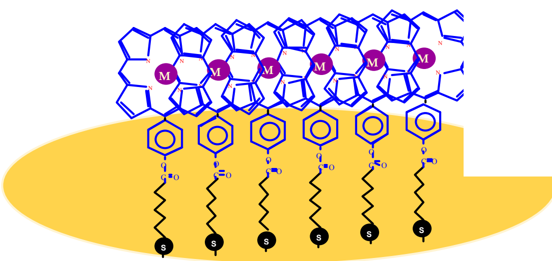
Courtesy of A. D'Amico and C. Di Natale

Self-assembled monolayer

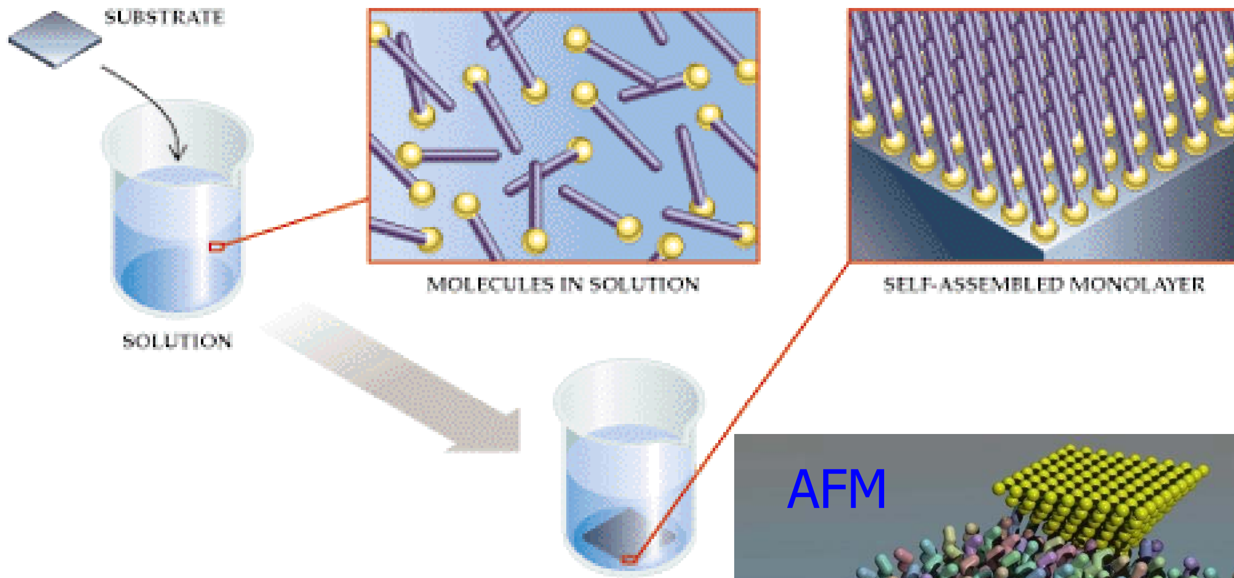
porphyrin molecules can be functionalized with thiol-derivatized chains in order to be covalently bounded onto gold surface

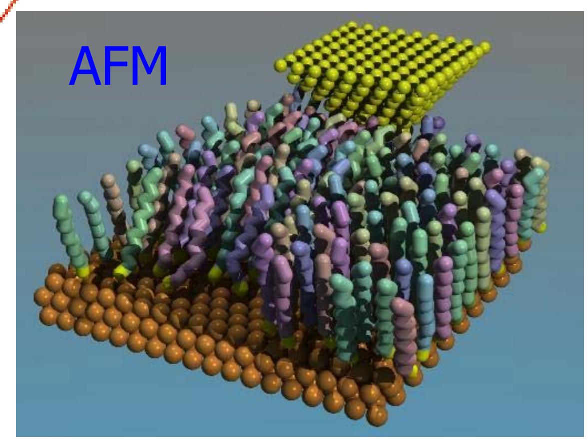


TPPSH
$M=H_2$
M=Co

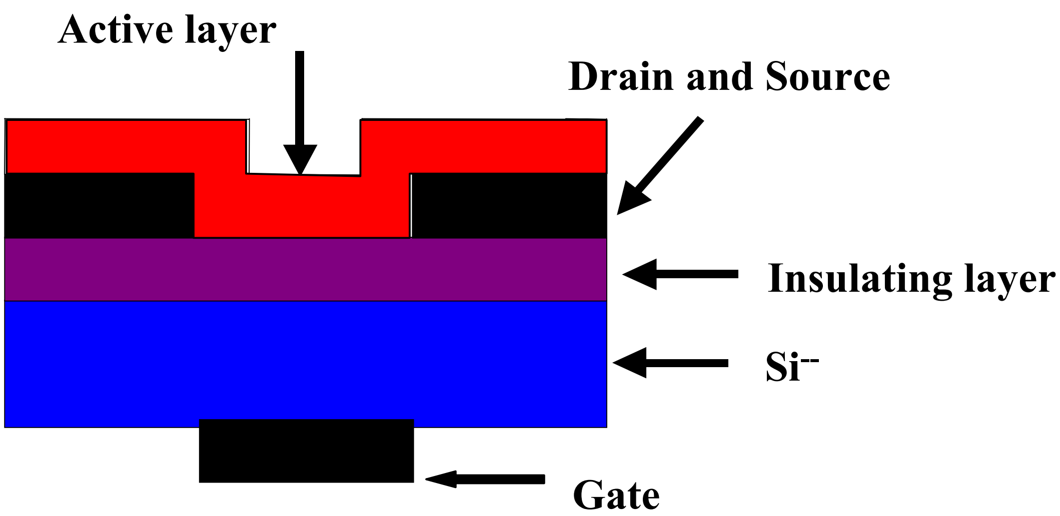


Gold surface

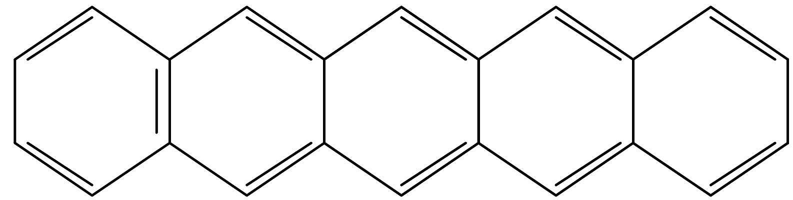




Pentacene OTFT



Pentacene (sublimated active layer)

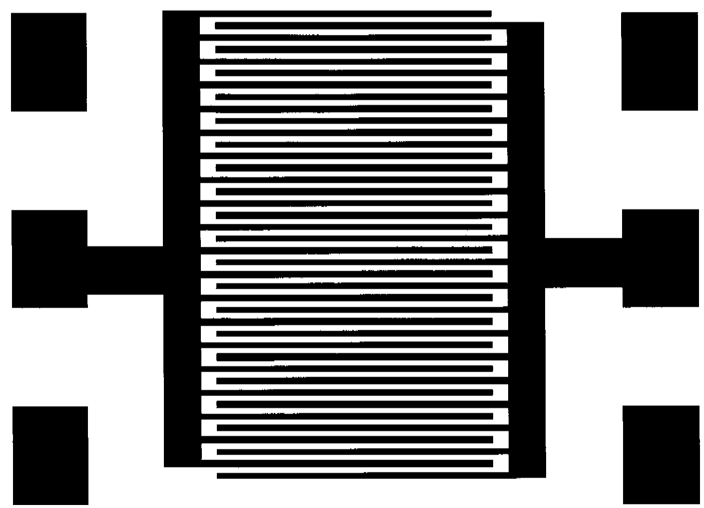


ALDRICH

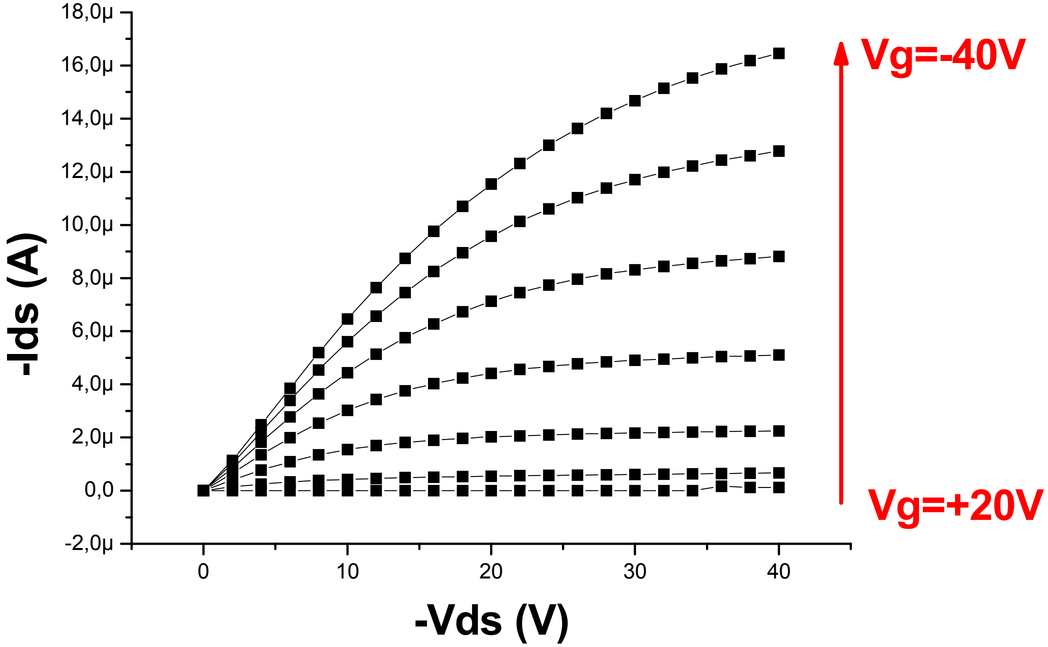
Drain and Source contacts (evaporated):

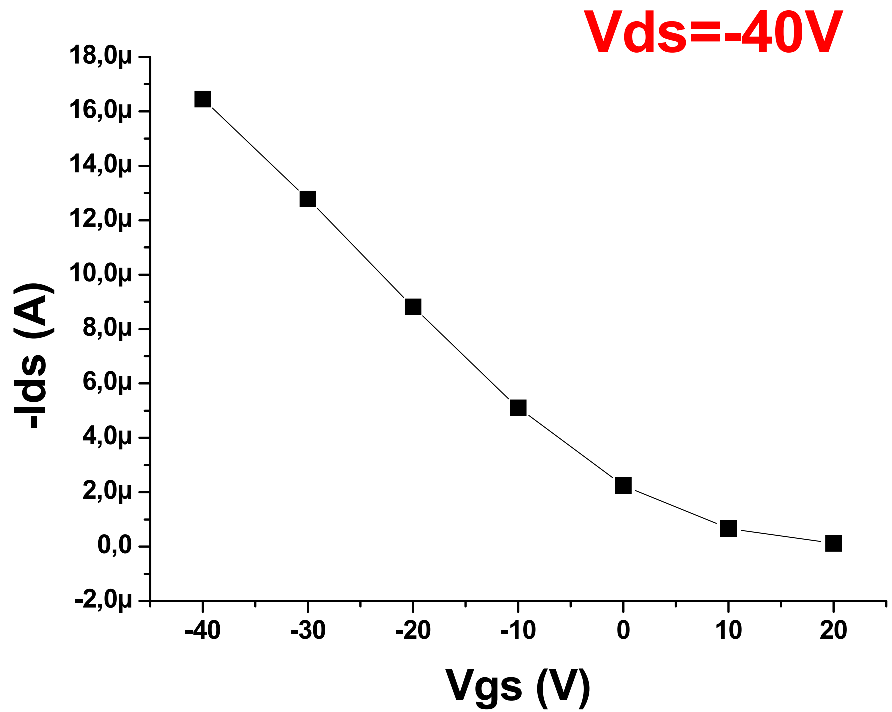
Spacing: 20 µm

Thickness: 50Å Cr / 450Å Au



Pentacene OTFT Characteristics



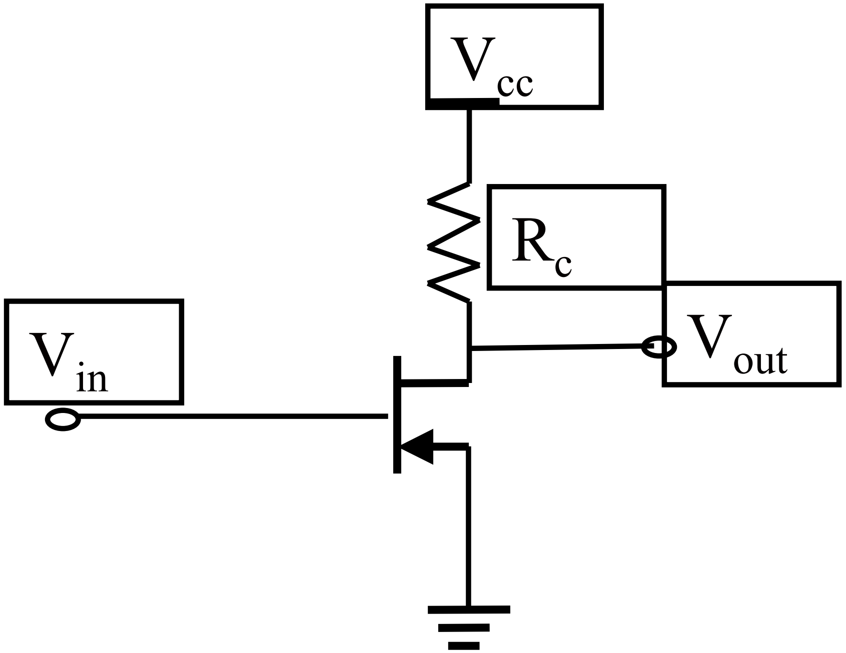


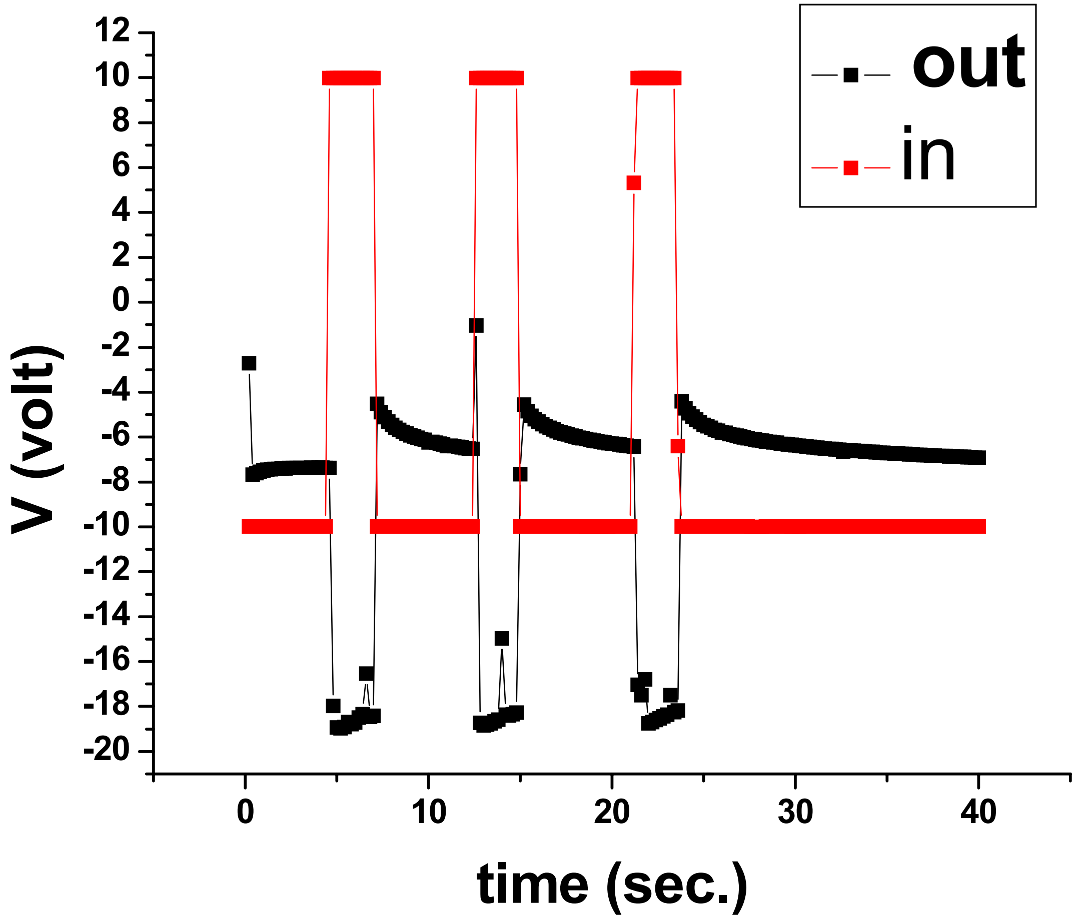
$\mu = 3*10^{-3}\ cm^2/Vs$

W/L=15000

$I_{on}/I_{off} = 10^2$

OTFT-based Inverter





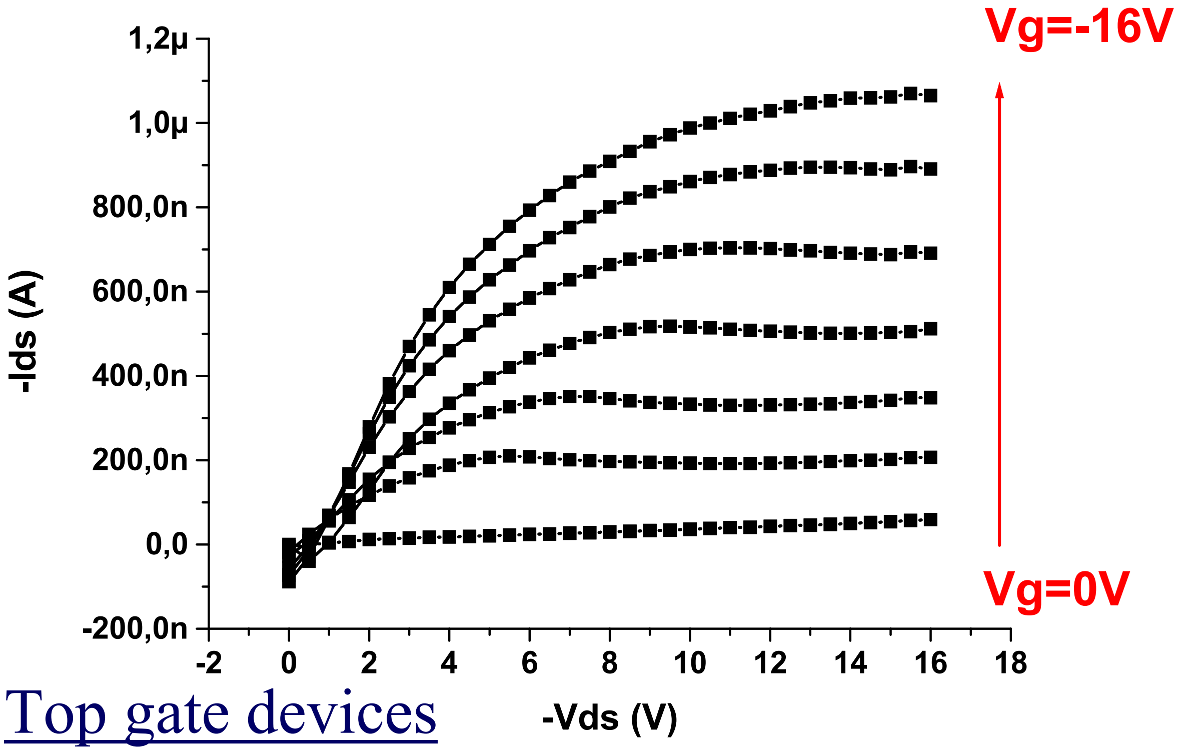
Vin: 200 mHz; Vpp=20 V

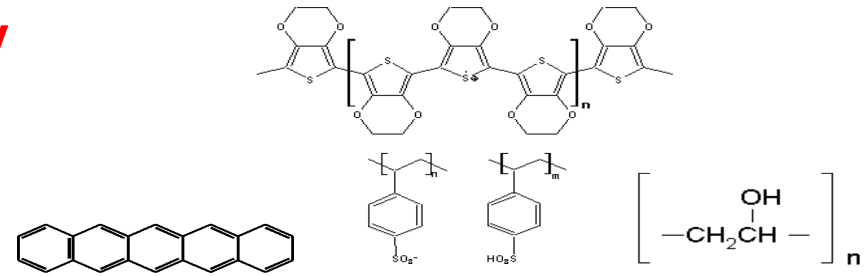
Vcc: -20V

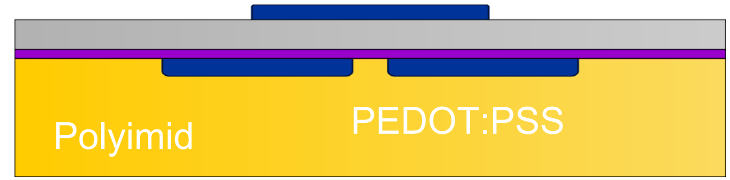
Rc: 10 MΩ

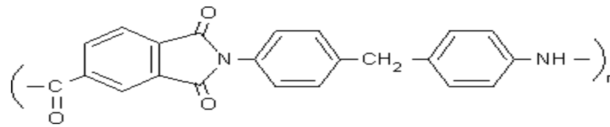
Channel lenght: 20 µm

Plastic TFT



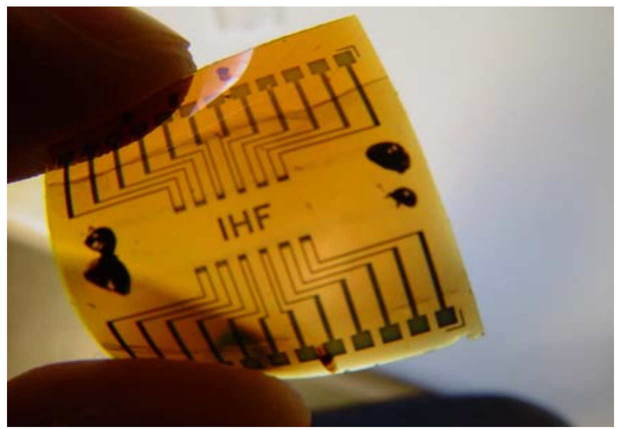






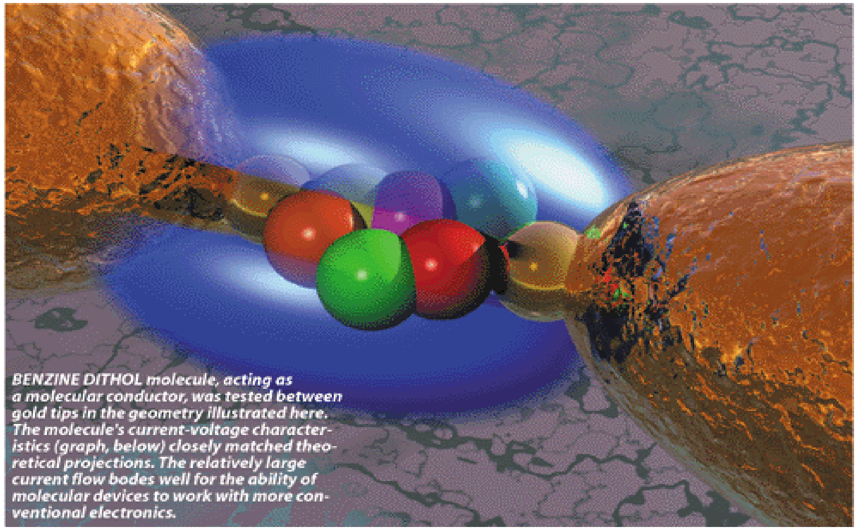
Top gate devices

- Flexible substrate : Polymid depositated by casting and removed by peeilng off
- Drain/Source contact deposited by electropolimerization
- Active layer: pentacene
- Insulating layer: PVA deposited by spin coating
- Pedot Gate contact by ink-jet deposition

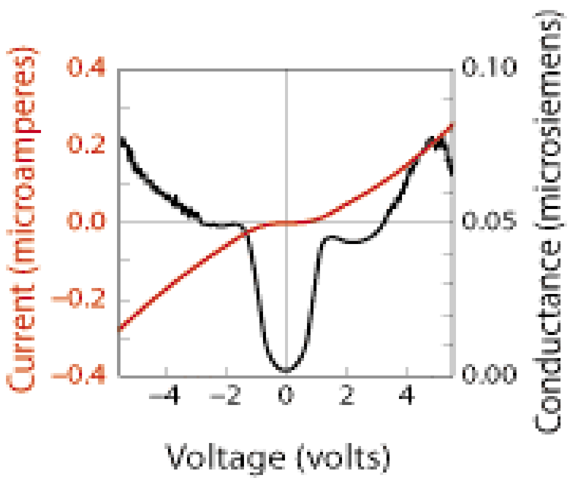


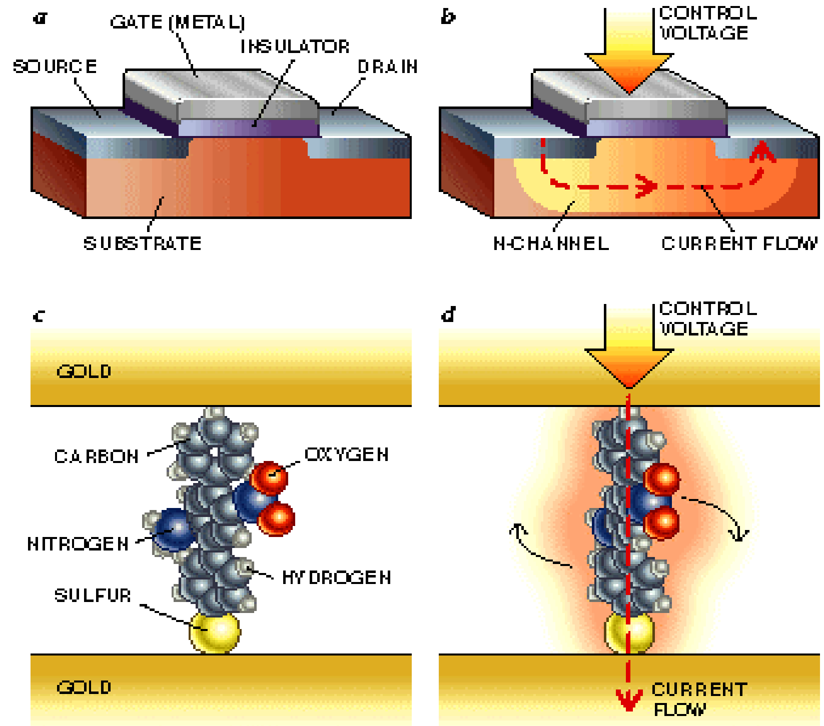
Fabricated at T.U. Braunschweig

Molecular electronics



BENZINE DITHOL molecule, acting as a molecular conductor, was tested between gold tips in the geometry illustrated here. The molecule's current-voltage characteristics (graph, below) closely matched theoretical projections. The relatively large current flow bodes well for the ability of molecular devices to work with more conventional electronics.

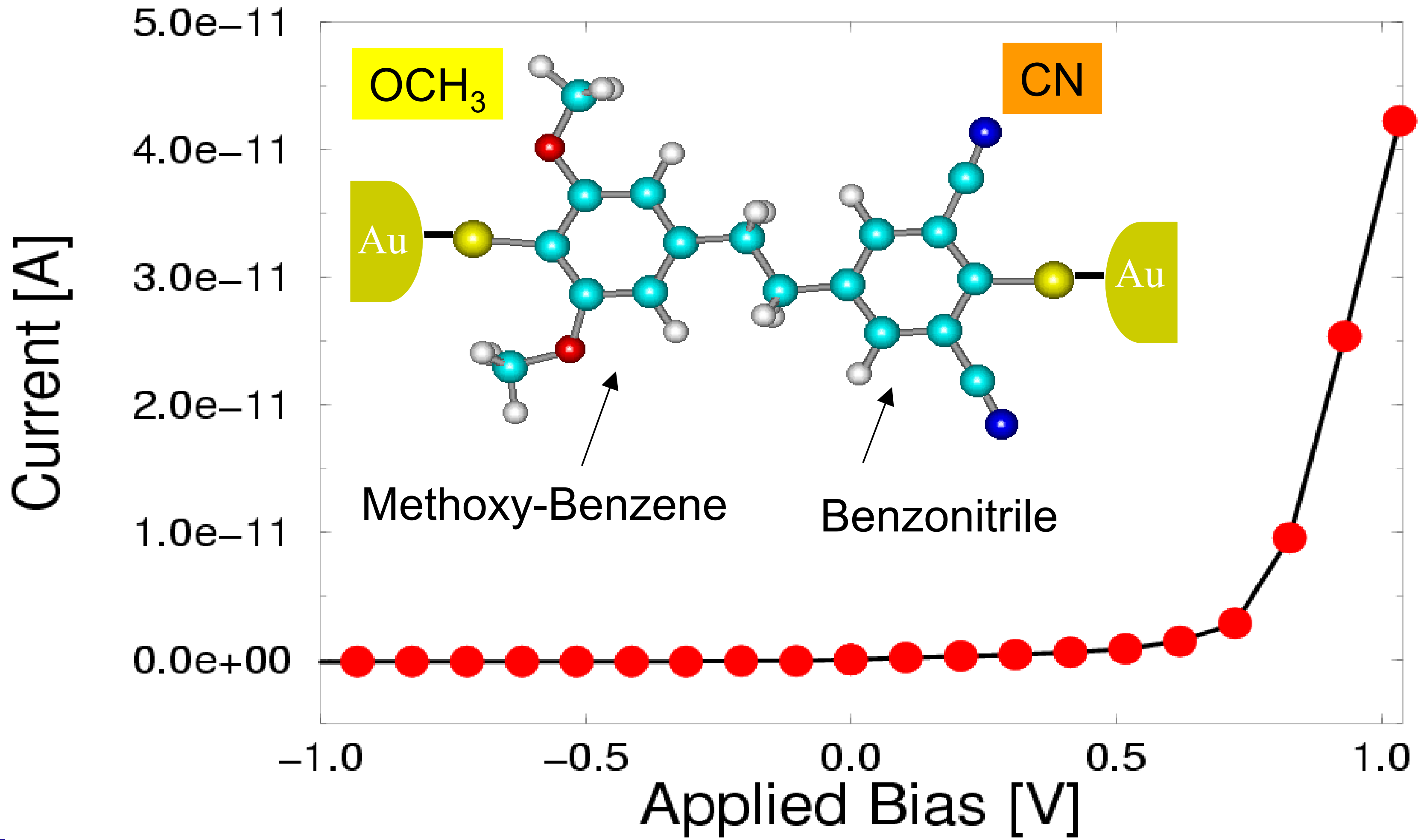




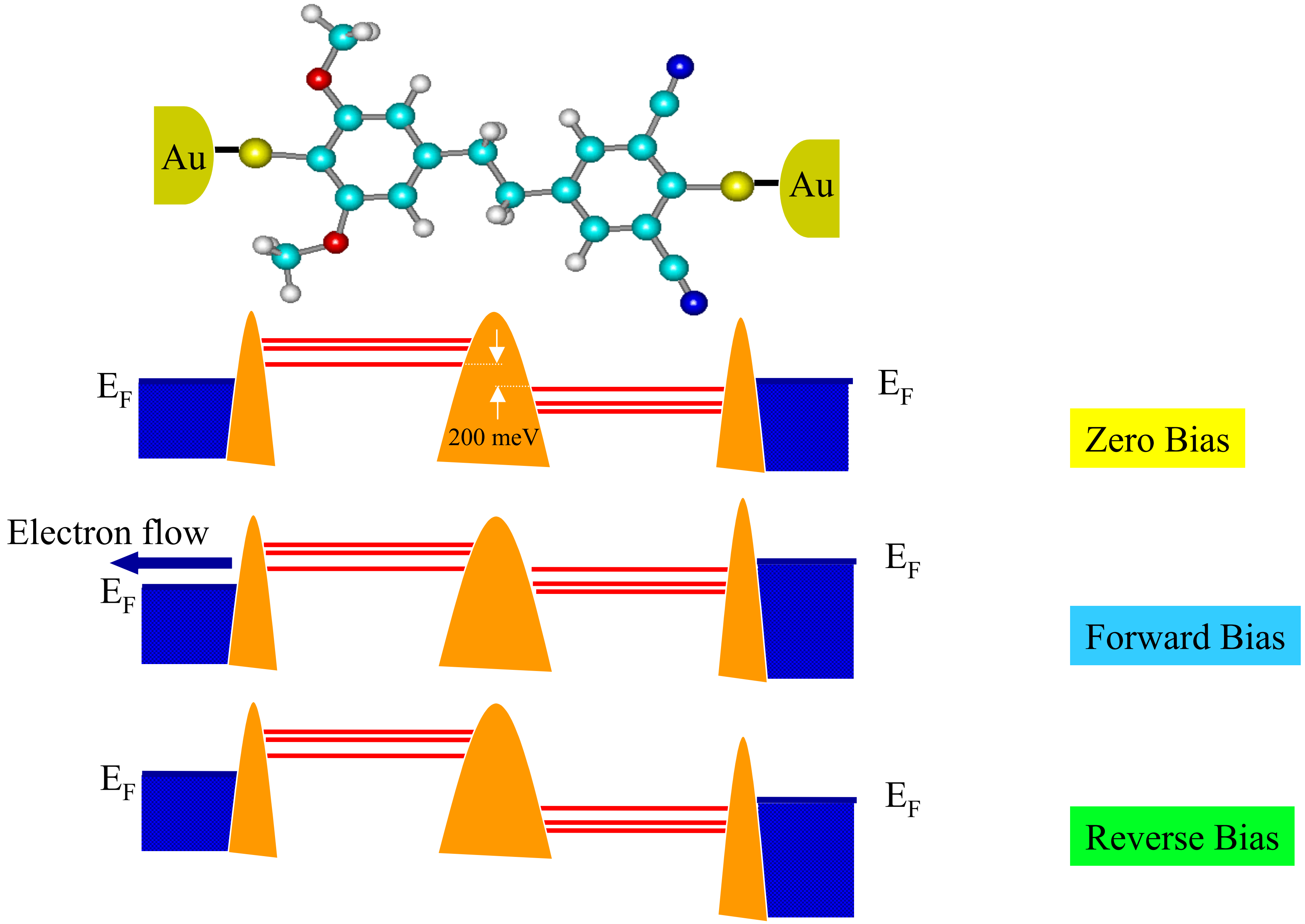
CONVENTIONAL MICROTRANSISTOR (a) has three terminals, known as the source, gate and drain. A positive voltage applied to the gate draws electrons to the insulator (b), enabling current to flow from the source to the drain. A molecule based on three benzene rings (c) was also used to switch an electric current. The center ring had asymmetric fragments, enabling it to be twisted by an electrical field (d). With a specific voltage applied, the electrical field twisted the molecule and permitted current to flow.

Molecular diode

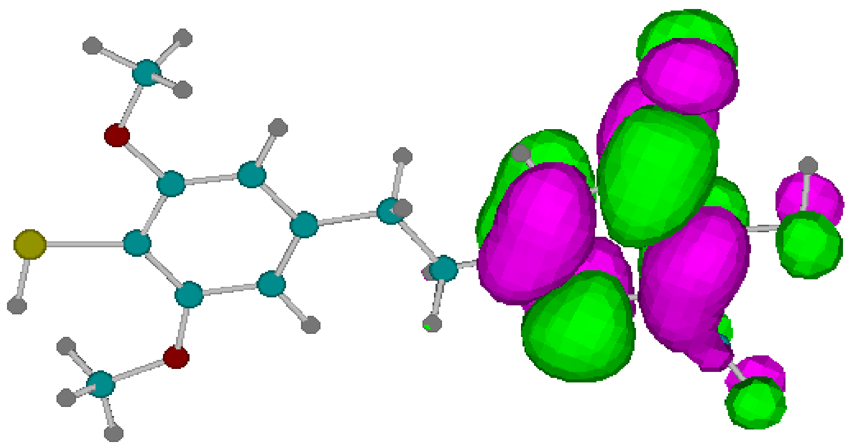
We have developed a quantum mechanical self consistent approach to calculate the current across molecular chains



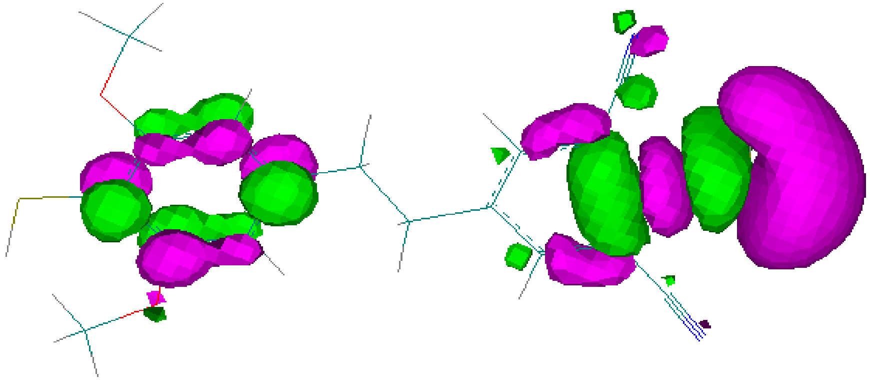
Level structure with bias



Molecular orbitals

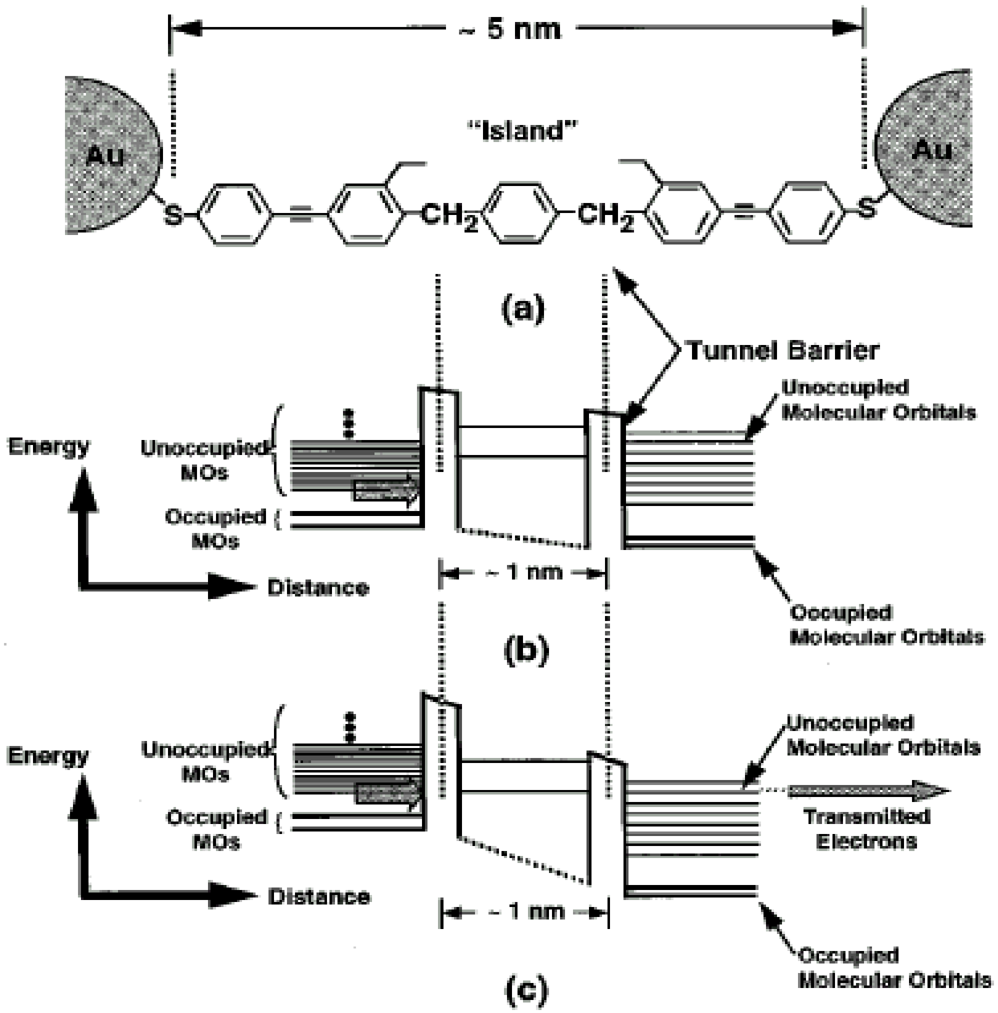


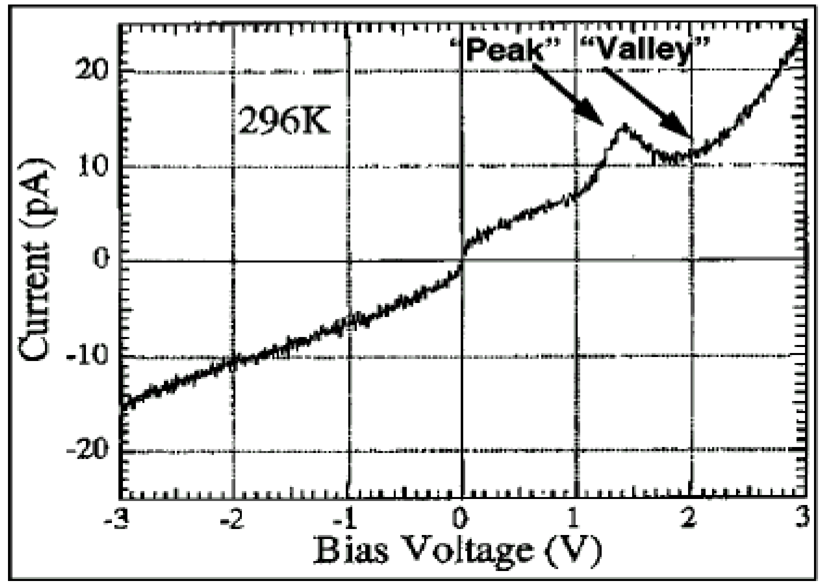
Zero bias: Orbitals are separated and do not communicate



Forward bias: orbital is delocalized over the entire molecule and leads to conduction

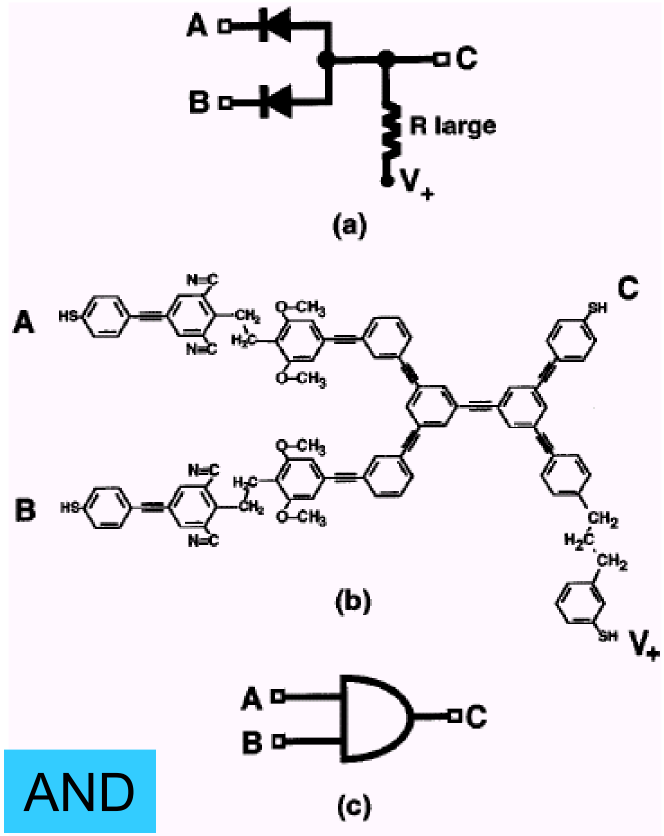
Molecular RTDs (Reed-Tour)





Room temperature NDR operation

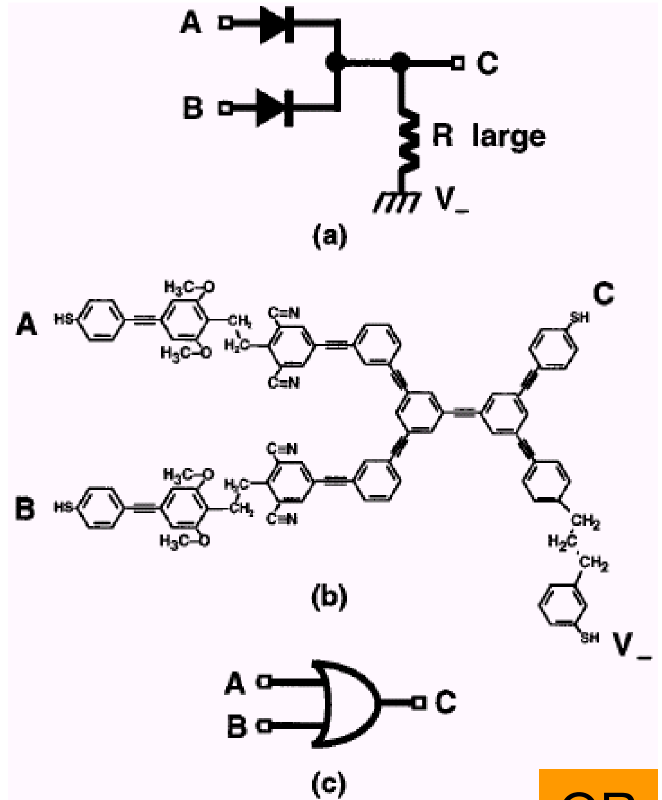
Molecular Digital Electronics



AND

A	B	C
0	0	0
1	0	0
0	1	0
1	1	1

(d)



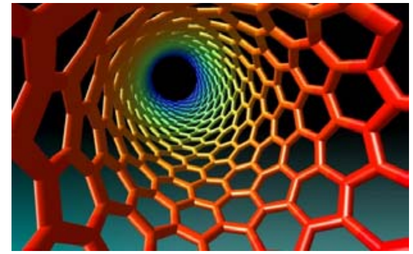
OR

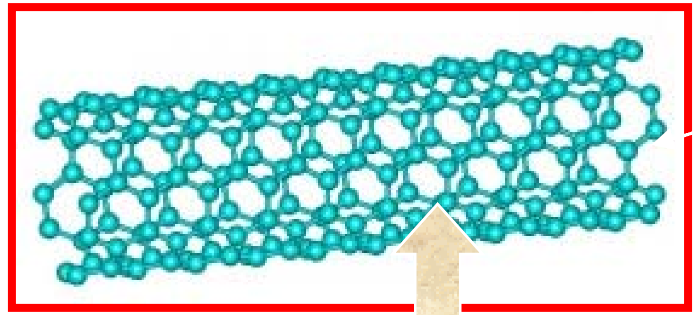
A	B	C
0	0	0
1	0	1
0	1	1
1	1	1

(d)

Ellenbogen and Love PROCEEEDINGS OF THE IEEE, VOL. 88, (2000)

Carbon Nanotubes



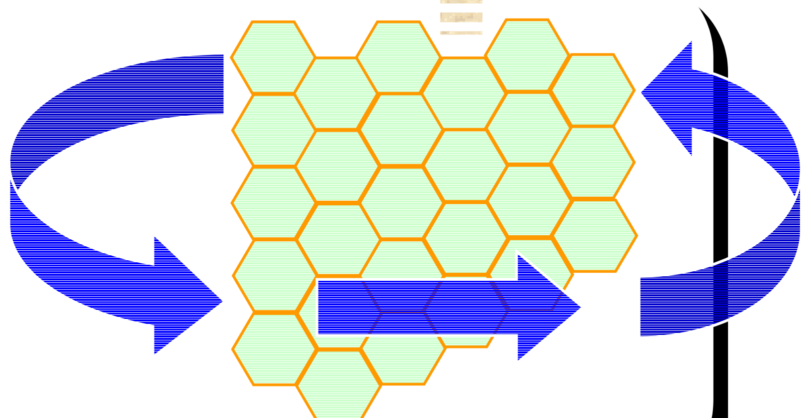


- **Discover in 1991 by Sumio**
- **Fabrication: CVD, Laser Ablation, Arc Discharge**

CARBON NANOTUBE STRUCTURE CAN BE OBTAINED FROM THAT OF GRAPHITE

Elementary cell of graphite

Six atoms of carbon with sp^2 ibridization



CNT: physical properties

- Electronic:
  - Bandgap $\propto$ 1 / diameter (Eg =0.5 eV for a diameter of 1.4 nm)
  - Bandgap ~ 100 meV (IR region)
- Magnetic:
  - Diamagnetic
  - Pronounced anisotropic susceptibility $\chi_{\perp} >> \chi_{||}$
- Mechanical:
  - Young Modulus ~ 1 TPa (SWNT) and 1.25 TPa (MWNT) (Steel: 230 GPa)
  - High Aspect Ratio: 1000 – 10,000
  - Density: 1.3 – 1.4 g/cm^3
  - Maximum Tensile Strength: 30 Gpa
- Thermal:
  - Conductivity: 2000 W/m.K (Copper: 400 W/m.K)

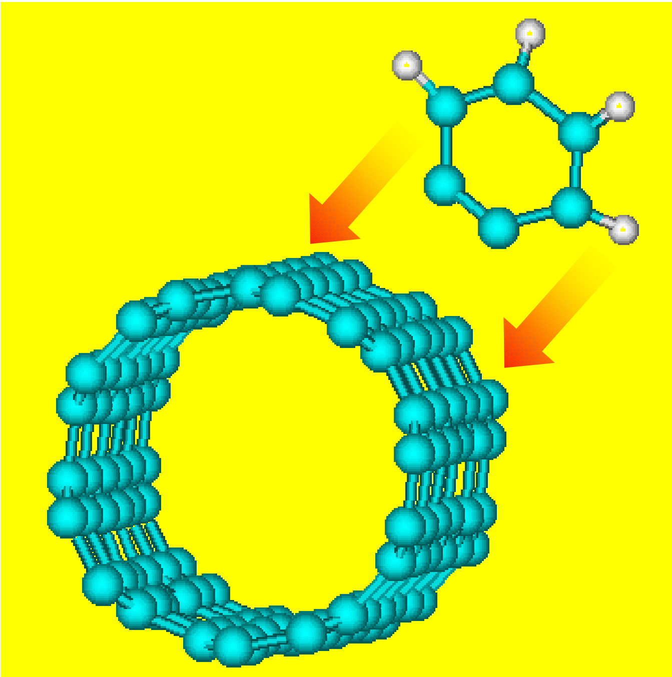
Carbon Nanotube Applications

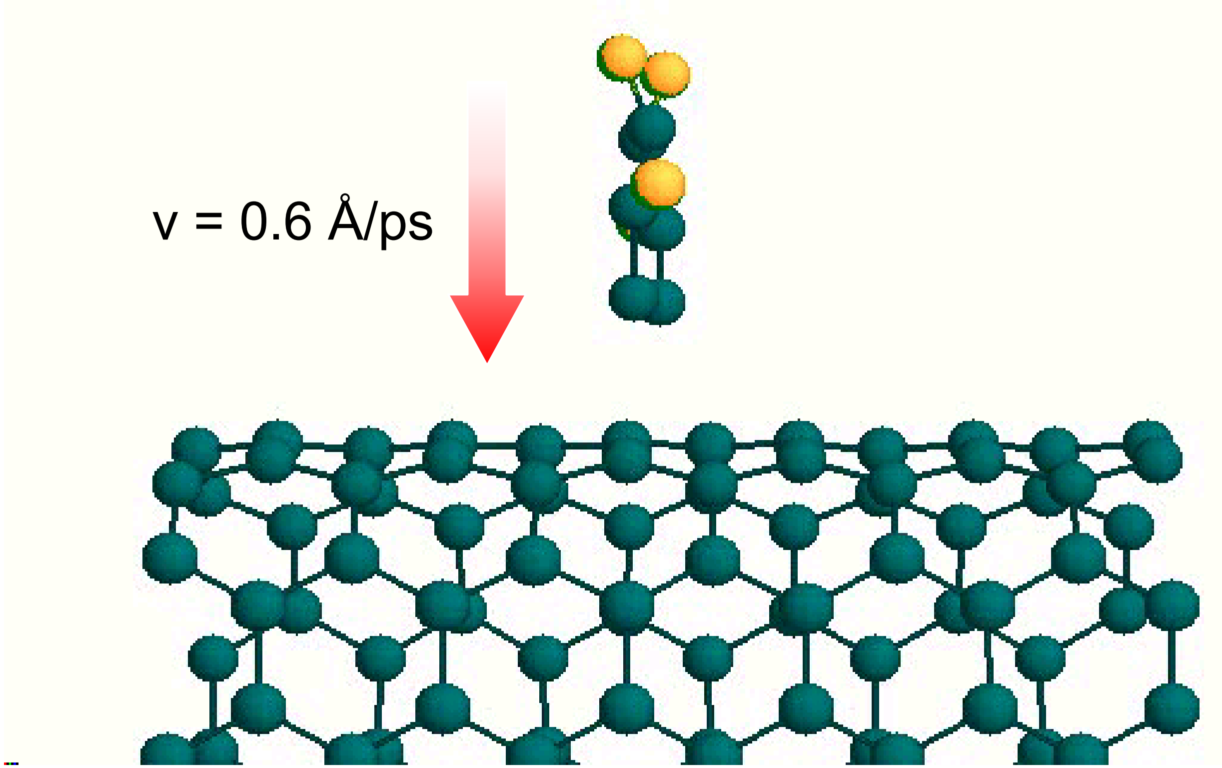
- Quantum wire as interconnects
- CNT-based molecular electronics, computer systems
- AFM-based imaging, nanomanipulation
- Nanotube sensors: force, pressure, chemical…
- Nanotube biosensors, bionic eye, bionic ear
- Molecular motors, Nanoelectromechanical Systems (NEMS)
- Hydrogen storage, lithium storage
- Field emitters for instrumentation
- Flat panel displays
- High strength, light weight composites, cables
- Multifunctional materials

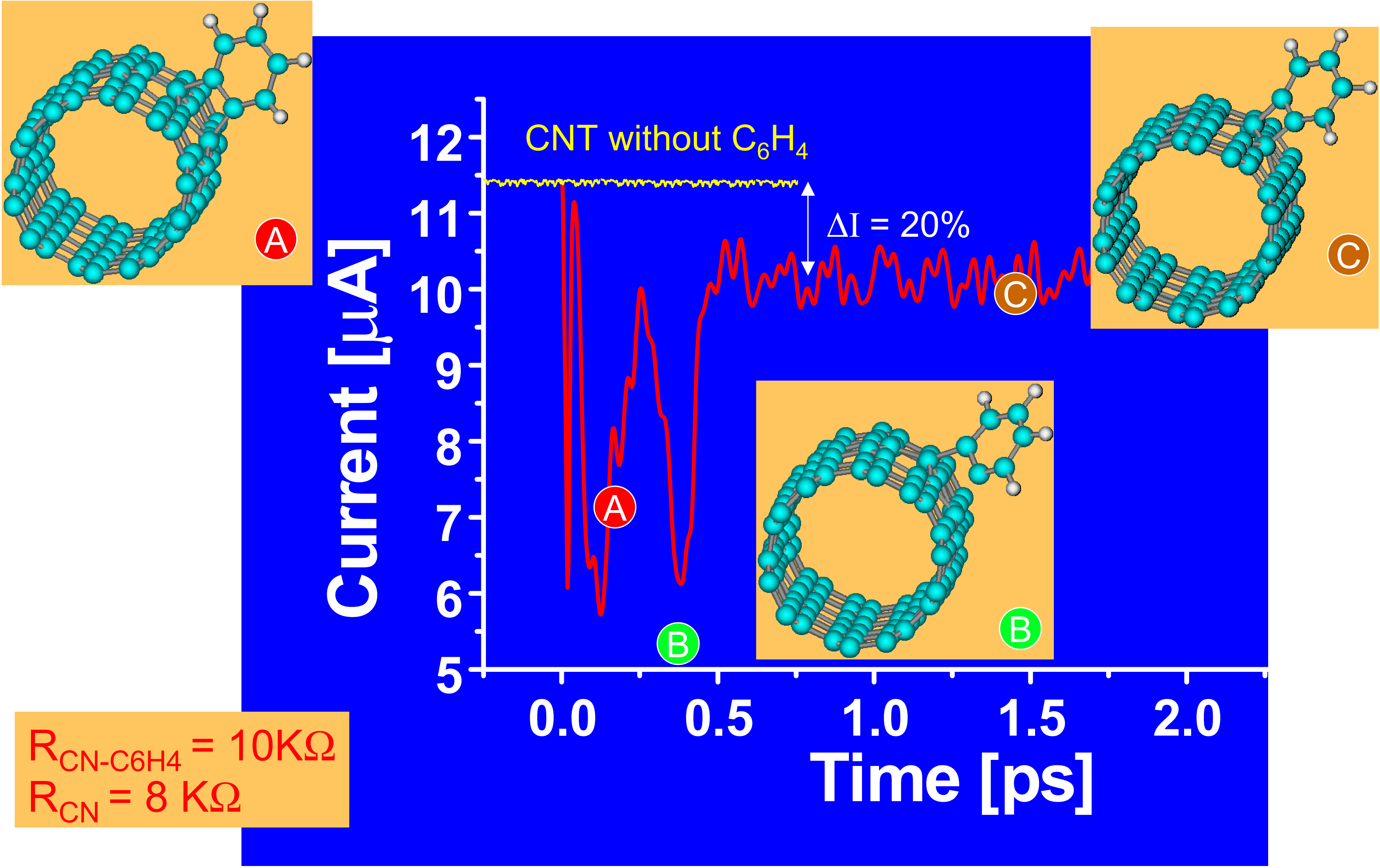
Sensing with Carbon Nanotubes

We have performed Molecular Dynamics simulations of a reactive collision of a biased nanotube (V=100mV) and benzyne and we have calculated the current flowing in the nanotube at each MD step

[Following the NASA MD simulations (J. Han, A. Globus, R. Jaffe, G. Deardorff)]



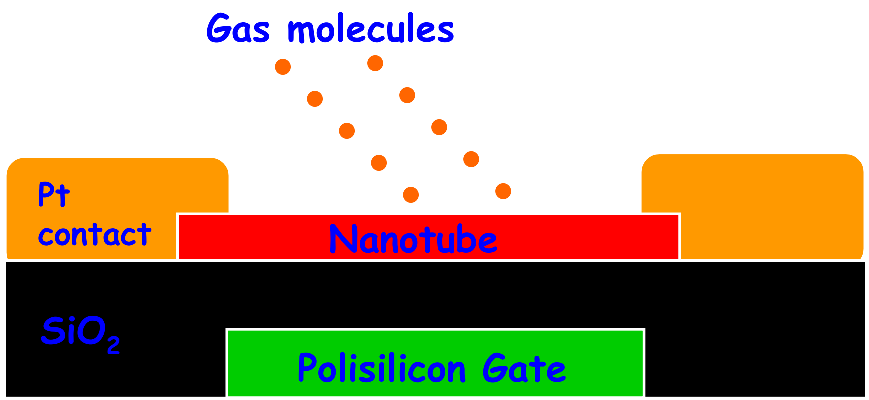




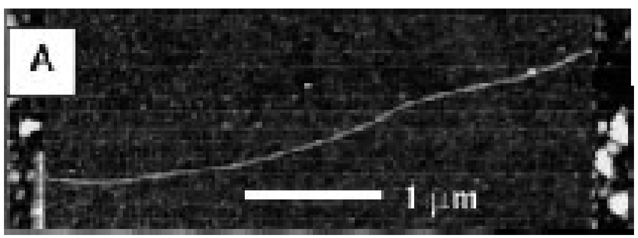
$R_{CN-C6H4}$ = 10KΩ
R_{CN} = 8 KΩ

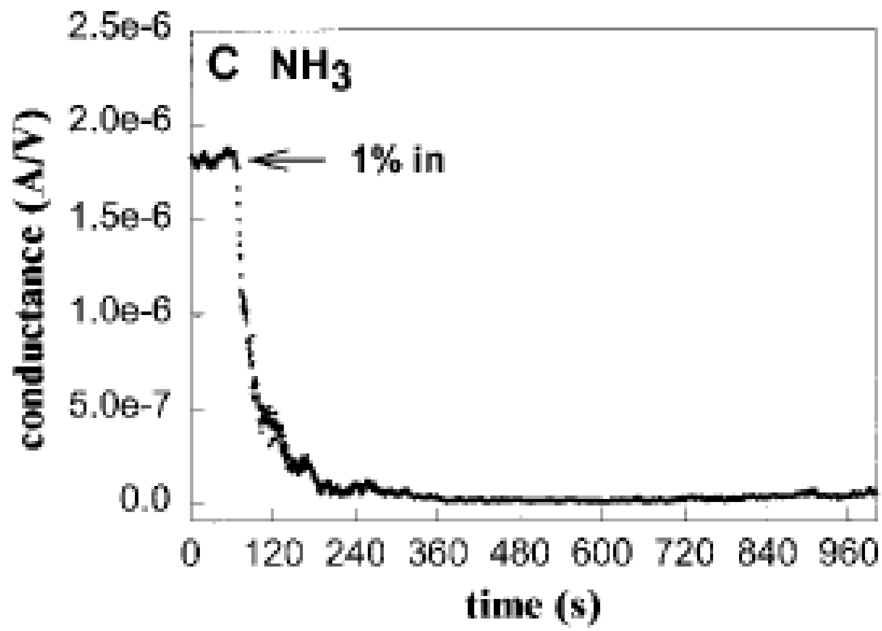
Chemical Sensor *Kong et al., Science (2000)*

Chemical sensors based on individual single-walled carbon nanotubes (SWNTs) are demonstrated. Upon exposure to gaseous molecules such as NO_2 or NH_3 , the electrical resistance of a semiconducting SWNT is found to dramatically increase or decrease. This serves as the basis for nanotube molecular sensors. The nanotube sensors exhibit a fast response and a substantially higher sensitivity than that of existing solid-state sensors at room temperature. Sensor reversibility is achieved by slow recovery under ambient conditions or by heating to high temperatures.

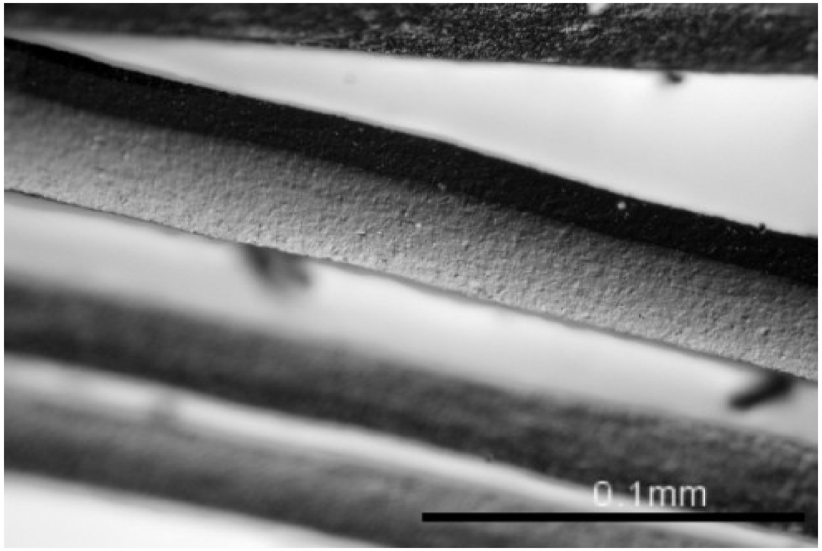


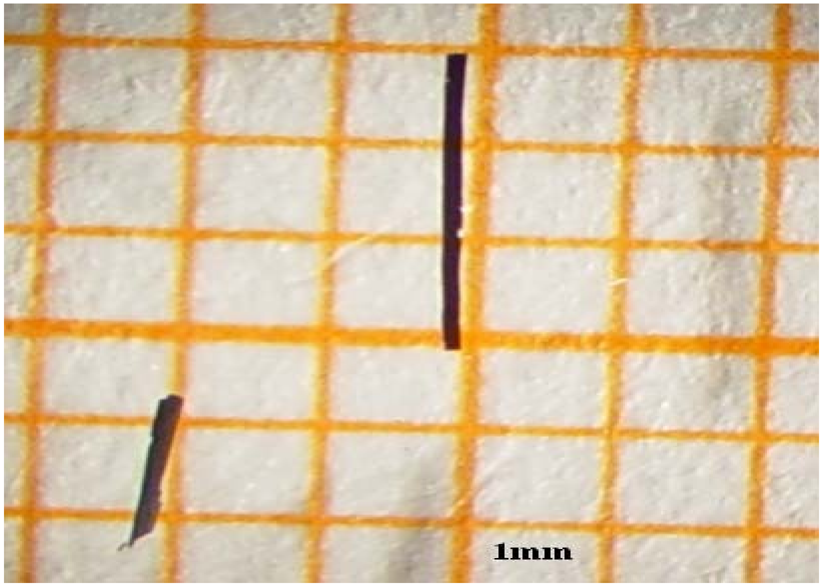
FET structure



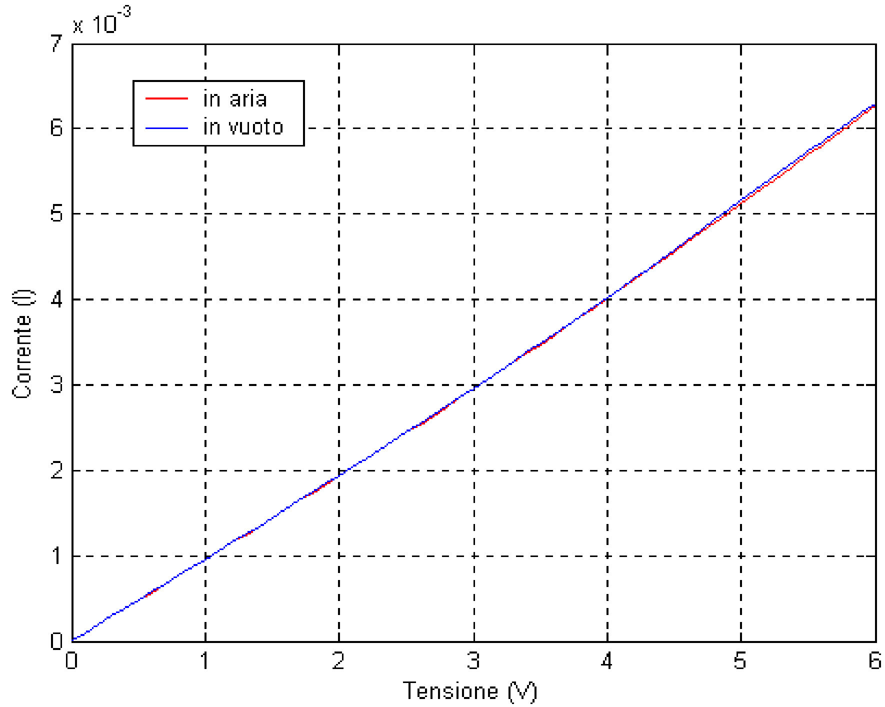


SWNT fibers



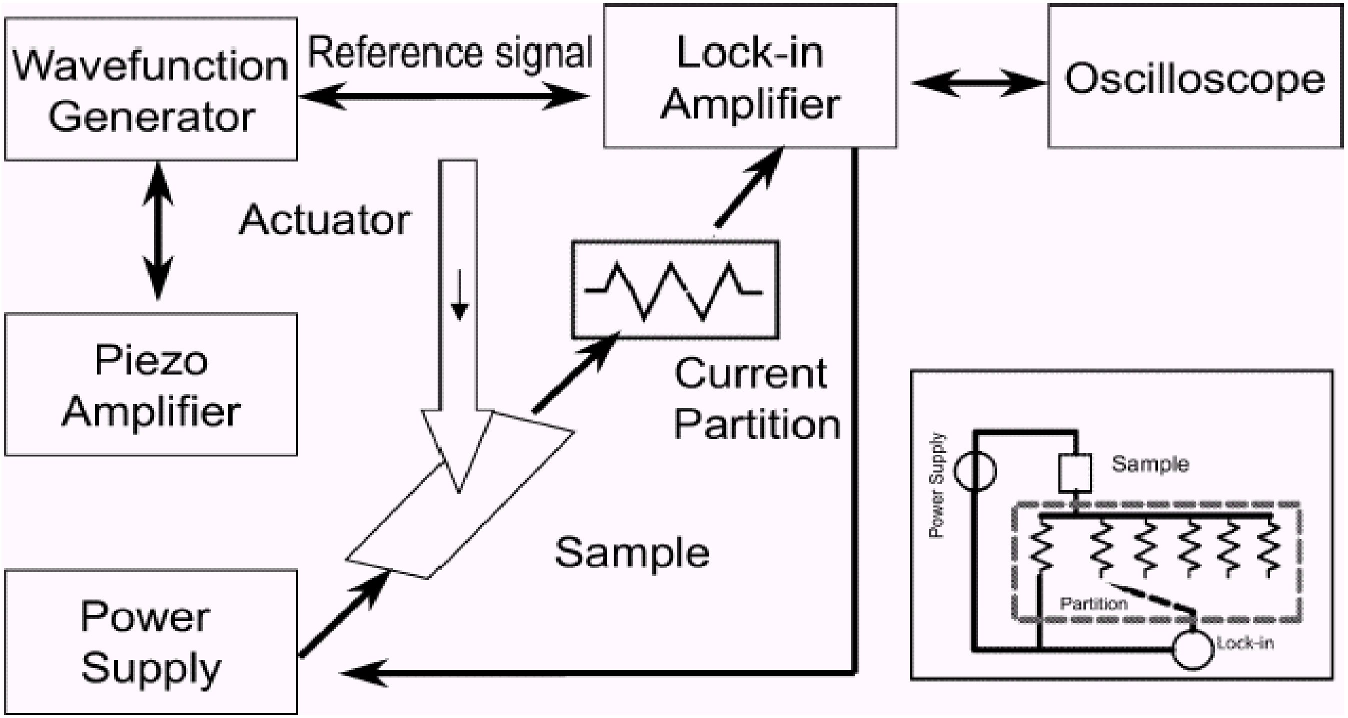


- **DIAMETER : about50nm**
- **LENGHT : few mm**



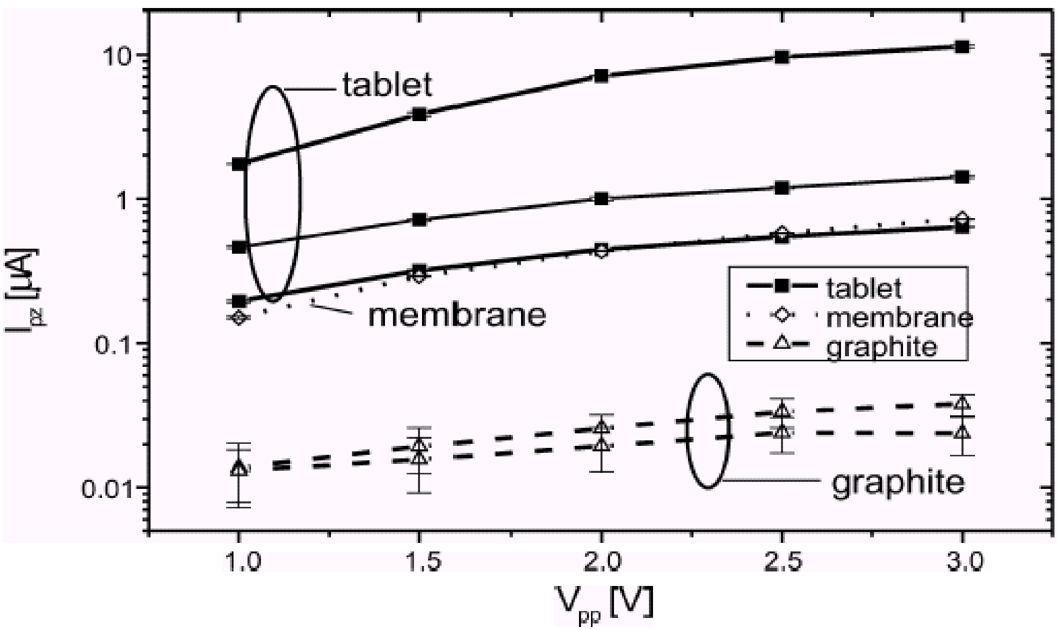
Same current in air and in vacuum !

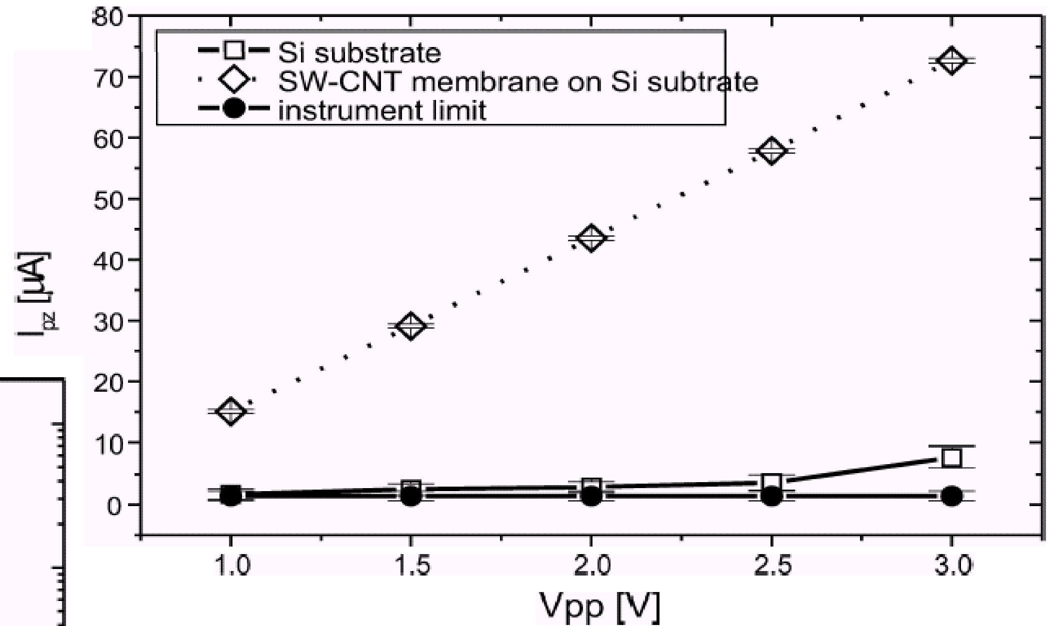
SWNT piezoresistivity set-up



The setup arrangement for the evaluation of conductance modulation in the CNT samples. The inset shows details of the current partitionon used for the optimal choice of the sensitivity of the lock-in amplifier

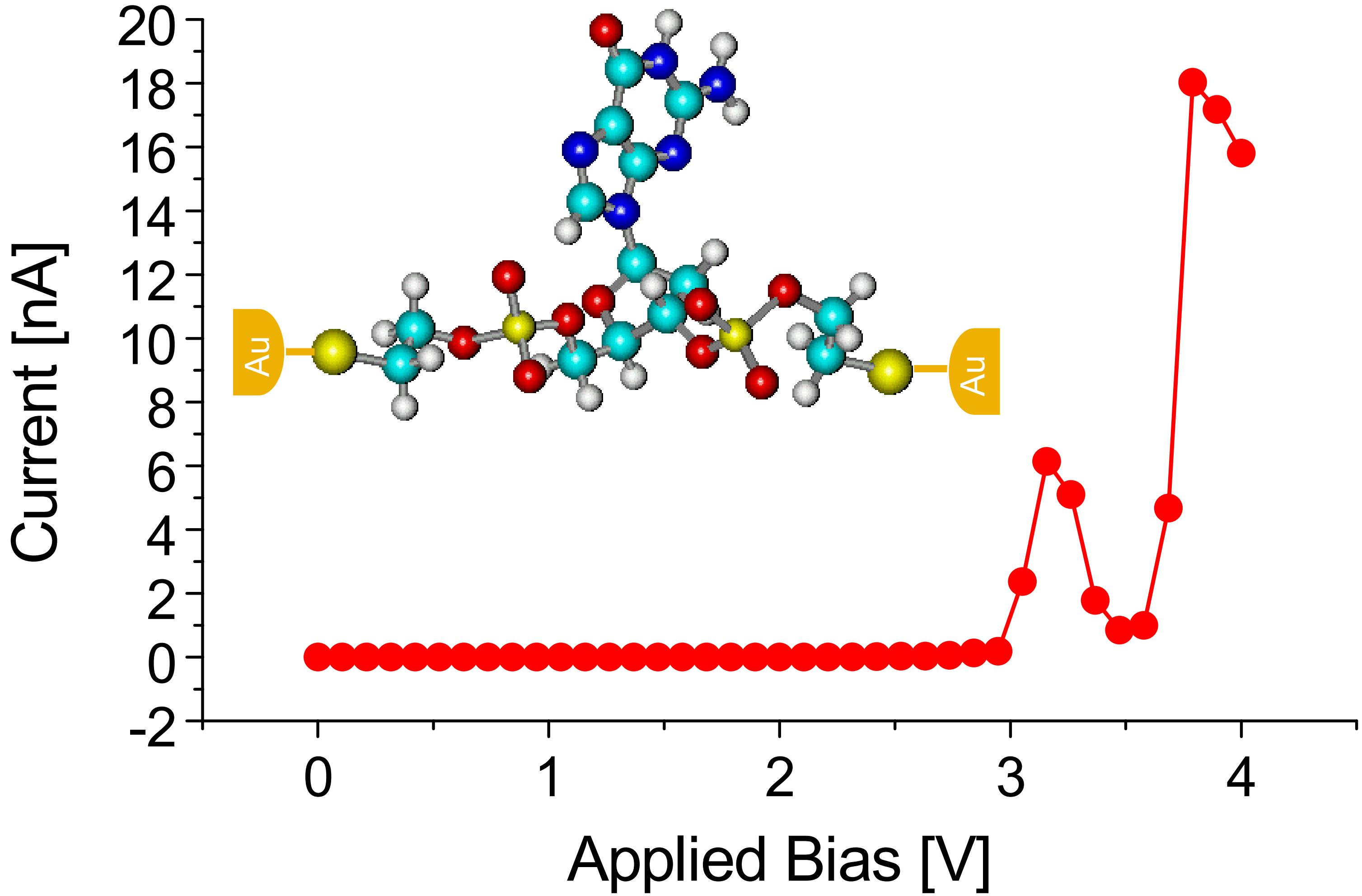
SWNT piezoresistivity





Vpp= voltage signal controlling the mechanical deformation (1V=8μm elongation)

Current in a DNA fragment



DNA is conductive and present non linear characteristics

Conclusions

- ❖ Organic materials offer great opportunities for space applications, offering flexibility, tunability, mass/volume reduction and multifunctionality
- ❖ Stability and reliability are still unsolved problems
- ❖ Carbon nanotubes are emerging as the most interesting molecular system

A unified, coordinated effort on molecular electronics could lead to major advances in the field and prepare the future materials and components for space:

?? SOLAR SAIL ??