

LS Scienza dei Materiali - a.a. 2006/07

## Fisica delle Nanotecnologie – part 9

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Francesco Fuso, tel 0502214305, 0502214293 - fuso@df.unipi.it

<http://www.df.unipi.it/~fuso/dida>

# **Nanotecnologie su base molecolare: monolayers molecolari, elettronica intramolecolare, dispositivi optoelettronici a base organica (OLED)**

# Introduction to the topics I

(Organic) molecules are inherently related to nanotechnology, even though topics are strongly shared with chemistry and chemical physics

**Huge interest** for organics in nanotechnological applications driven in the last decade(s) by the huge *flexibility, scalability, compatibility, and cheapness* of molecular systems: we will focus mostly (only) on **electronics and optoelectronics** applications, which are among the most advanced and demanding areas

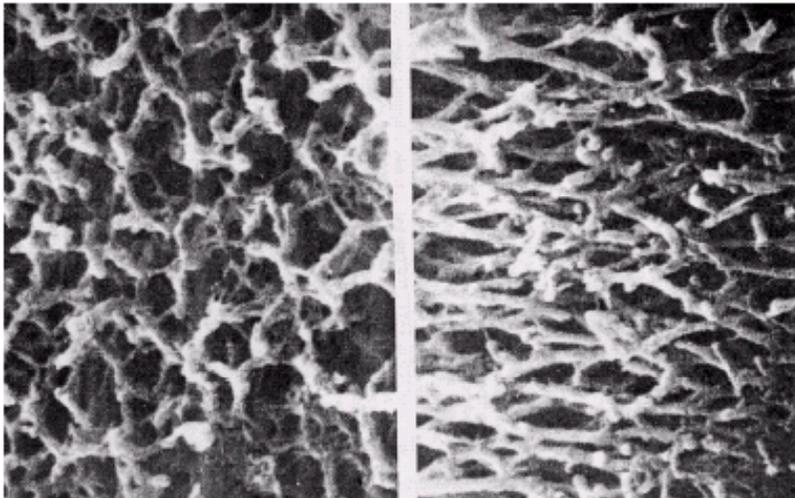
*Potential advantages* in the nanotechnological context include:

- Molecules are “obviously” **nano (or sub-nano) sized** objects (and “perfect”)
- A very **broad range** of molecules can be engineered and produced by well established methods
- A very **broad range** of transport properties can be achieved
- Bottoms-up** techniques can be used, contrary to conventional approaches where a top-down rule is followed (i.e., material is produced at the elemental level, and not removed to obtain a nanostructure)
- Mutual organization of molecular entities may take advantage of specific processes like **self-assembly** and, perhaps, replication

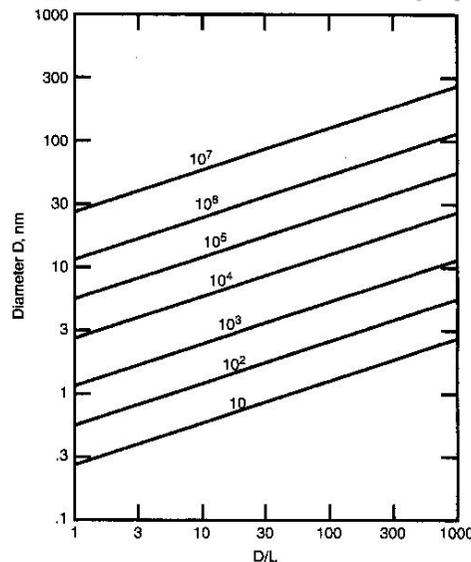
# Miniaturization and polymers

Unstretched

Stretched



Stretching polyacetylene aligns the chains and improves conductivity. Each fiber shown here consists of about 1,500 polymer chains. A goal of molecular electronics is to use individual polymer chains.



Poole, Owens,  
Introduction to Nanotechnol  
(Wiley, 2003)

Figure 11.2. Dependence of the diameter  $D$  of a cylindrical polymer on its diameter: length ratio  $D/L$  for molecular weights from 10 to  $10^7$  Da, as indicated on the curves. A density  $\rho = 1 \text{ g/cm}^3$  was assumed in Eq. (11.13) for plotting these curves.

## 11.2.2. Sizes of Polymers

Polymers are generally classified by their molecular weight, and to discuss them from the nanoparticle aspect, we need a convenient way to convert molecular weight to a measure of the polymer size  $d$ . The volume  $V$  in the units cubic nanometers ( $\text{nm}^3$ ) of a substance of molecular weight  $M_w$  and density  $\rho$  is given by

$$V = 0.001661 \frac{M_w}{\rho} \quad (11.10)$$

where  $M_w$  has the unit dalton or  $\text{g/mol}$  (grams per mole) and  $\rho$  has the conventional units  $\text{g/cm}^3$ . If the shape of the nanoparticle is fairly uniform, with very little stretching or flattening in any direction, then a rough measure of its size is the cube root of the volume (11.10), which we call the size parameter  $d$ :

$$d = 0.1184 \left( \frac{M_w}{\rho} \right)^{1/3} \text{ nm} \quad (11.11)$$

This expression is exact for the shape of a cube, but it can be used to estimate average diameters of polymers of various shapes. If the molecule is a sphere of diameter  $D_0$ , then we know from solid geometry that its volume is given by  $V = \pi D_0^3/6$ , and inserting this in Eq. (11.10) provides the expression  $d_{\text{SPH}} = D_0 = 0.1469 (M_w/\rho)^{1/3} \text{ nm}$  for a spherical molecule. For a molecule shaped like a cylinder of diameter  $D$  and length (or height)  $L$  with the same volume as a sphere of diameter  $D_0$ , we have the expression  $\pi D_0^3/6 = \pi D^2 L/4$ , which gives

$$D_0 = \left( \frac{3}{2} \right)^{1/3} (D^2 L)^{1/3} = \left( \frac{3}{2} \right)^{1/3} D \left( \frac{L}{D} \right)^{1/3} = \left( \frac{3}{2} \right)^{1/3} L \left( \frac{D}{L} \right)^{2/3} \quad (11.12)$$

These equivalent relationships permit us to write expressions for the diameter and the length of the cylinder in terms of its length: diameter ratio, and the molecular weight of the molecule

$$D = 0.128 \left( \frac{M_w}{\rho} \right)^{1/3} \left( \frac{D}{L} \right)^{1/3} \quad (11.13)$$

$$L = 0.128 \left( \frac{M_w}{\rho} \right)^{1/3} \left( \frac{L}{D} \right)^{2/3} \quad (11.14)$$

where  $D$  and  $L$  have the units of nanometers. These expressions are plotted in Figs. 11.2 and 11.3 for  $D > L$  and  $L > D$ , respectively. The figures can be employed to estimate the size parameter for an axially shaped, flat or elongated, polymer if its molecular weight, density, and length: diameter ratio are known. The curves in these figures were drawn for the density  $\rho = 1 \text{ g/cm}^3$ , but the correction for the density is easily made since most polymer densities are close to 1. Typical polymers have molecular weights in the range from  $10^4$  to  $10^7$  Da.

## Introduction to the topics II

Many families of organics compounds may have a technological role: we will focus mostly on **polymers**, especially **conjugated polymers** <http://www.pslc.ws>

*Polymer: skeleton (chain, ring, or other geometries) comprised of unit entities (monomers) organized in a typically long sequence*

*Copolymers: polymers made of sequence of unit entities (either random or block-organized)*

*Conjugation: alternate double/single C-C bonds*

**Crucial issues** (besides technological problems, as durability, process):

- Interface** with the outer (inorganic) world: structural and transport problems
- Addressing** and control of the single molecule: for applications a functional device should be designed and realized (not just demonstration in solutions!)

Main topics (for this presentation):

- Polymer films on inorganic substrates for **hybrid molecular electronics**
- Examples of **intramolecular electronics** for fully molecular electronics
- Optoelectronics devices (**OLED**)

## Outlook

1. Langmuir-Blodgett vs Self-Assembling Monolayers: fabrication and a few features
2. Basic mechanisms for transport in polymers: bands, effects of doping
3. Examples of intramolecular electronics and a short discussion on their practical exploitation
4. Efforts to address single molecules (so far, mostly test devices)
5. A few words on the potential exploitation of DNA-based systems in the nanoelectronic realm
6. Organic Light-Emitting Devices (they already exist!): techniques, materials and problems

# 1. Interface between inorganics and organics

A basic requirement for molecular electronics is the connection of the molecule to the outside world. If we want to drive a current through individual molecules, we need an electrode pair with nanometer-sized spacing to contact them. If we are interested in molecular films, again we need contact electrodes which must be controlled on the scale of atomic length scales. The usual way is to use metallic or semiconducting electrodes, which yield hybrid (HME) devices. In the future, the replacement of metallic electrodes by molecular wires might be investigated (MME).

It turns out that the nature of the electrodes is also of importance for the electronic properties of the device. A molecule which is closely connected to an electrode has very different properties from a molecule in solution. Two main groups of links between molecules and solids can be distinguished: **covalent bonds** and **van der Waals interaction**.

A frequently used and up to now probably the best investigated covalent link is the bond between a thiol (sulfur) group on the molecule and a Au substrate. Au is favorable due to its proper and non-oxidizing surface. The thiol endgroup is one of the rather rare functionalities which form covalent bonds with the noble metal gold. Further requirements are good stability of the bond at room temperature, which must be, however, loose enough to allow for self-assembly (i.e. to rearrange continuously until finally a completely ordered monolayer of molecules is formed). Other combinations like Se-Au or S-Ag have already been investigated as members of this family. Molecules with hydroxy groups are used on SiO<sub>2</sub> and TiO<sub>2</sub> substrates. Such couplings are of particular interest due to the use of these materials in traditional microelectronics and hence may form a bridge between the fields. However, they lack the advantage of subsequent self-organization of the molecules, due to the large stability of the covalent bond formed. Covalent bonds lead to a mechanically fairly stable and resistant connection between the molecule and the substrate.

Da R. Waser Ed., Nanoelectronics and information technology (Wiley-VCH, 2003)

Van der Waals interaction acts in particular between Langmuir-Blodgett (LB) films of organic lipophiles and planar substrates. This technique results in very well organized films with the advantage of substrate diversity: the only requirement is a planar surface with appropriate wetting properties, i.e. a designated lipophilic or hydrophilic characteristic (depending on the type of molecules and the desired orientation). While for some types of molecules LB films might be suitable, in other cases they suffer from poor long-term stability due to the weakness of the Van-der-Waals interactions. A successful example will be discussed in Section 4.2: an LB-film sandwiched between two electrodes displays the characteristics of a (reconfigurable) switch. In other cases, electronic components with molecular building blocks require the stability of covalent linkages rather than the weak van der Waals bound interfaces.

These different contacts types also correspond to different electron transport mechanisms. Imagine a molecule with a *conductive* inner part (this can be realized with extended, *delocalized*  $\pi$ -electron systems, see Chapter 5) connected to a gold electrode. If the distance to the metallic surface is very short (of the order of bond lengths), the inner conducting orbitals and the outer metallic electronic states overlap to a certain extent. This yields a hybridisation of the inner and the outer extended wave functions and hence a common delocalized electronic wave function which extends over the whole junction. The junction then can be imagined as a waveguide for the electrons which are transmitted in a similar way to light passing through an optical fiber. This case is, for example, realized when thiol endgroups are attached to benzene rings: the  $\pi$ -orbitals of the benzene and the conduction band of the metal overlap at the sulfur atom. It should be noted that the sulfur is nevertheless an imperfect transmitter and acts as a bottleneck for the extended wave function. The influence of the bond on the molecule is complicated and is not fully understood. In the theory Section 5.1 some of the challenges of this question will be addressed.

If the distance chosen is larger or badly-conducting molecular units are in between, the wave function inside and outside do not overlap and can with good approximation be treated independently. This case corresponds to LB films. Electron transport can then better be imagined as particles tunneling from one electrode onto the molecule and, after a short dwell time, tunneling to the opposite electrode. In this case, the resistance per molecule is expected to be higher.

Chemical vs van der Waals bonds,  
i.e.,  
Self-Assembly vs Langmuir-Blodgett films

# Langmuir-Blodgett films I

**Def :** mono, multi strato trasferiti dall'interfaccia aria-acqua su un substrato solido

La tecnica Langmuir-Blodgett è stata la prima tecnica chimica per costruire strutture ordinate di molecole.

## 3. Il substrato

La maggior parte delle deposizioni coinvolge substrati idrofilici tuttavia la tecnica LB è unica proprio perché consente il trasferimento dei monostrati su diversi tipi di materiali :

Substrati trasparenti come il vetro permettono lo studio dello spettro in trasmissione ma hanno bisogno di un trattamento di pulitura con  $H_2SO_4$  / $H_2O_2$  4 :1 a  $120^\circ$  per 20 min seguita da sciacquatura con acqua, etanolo e acetone più un asciugatura nella porzione non ossidante della fiamma di un Bunsen per 10 sec circa .

Altri substrati idrofilici sono l'alluminio, il cromo e lo stagno in tutti i loro stati di ossidazione .

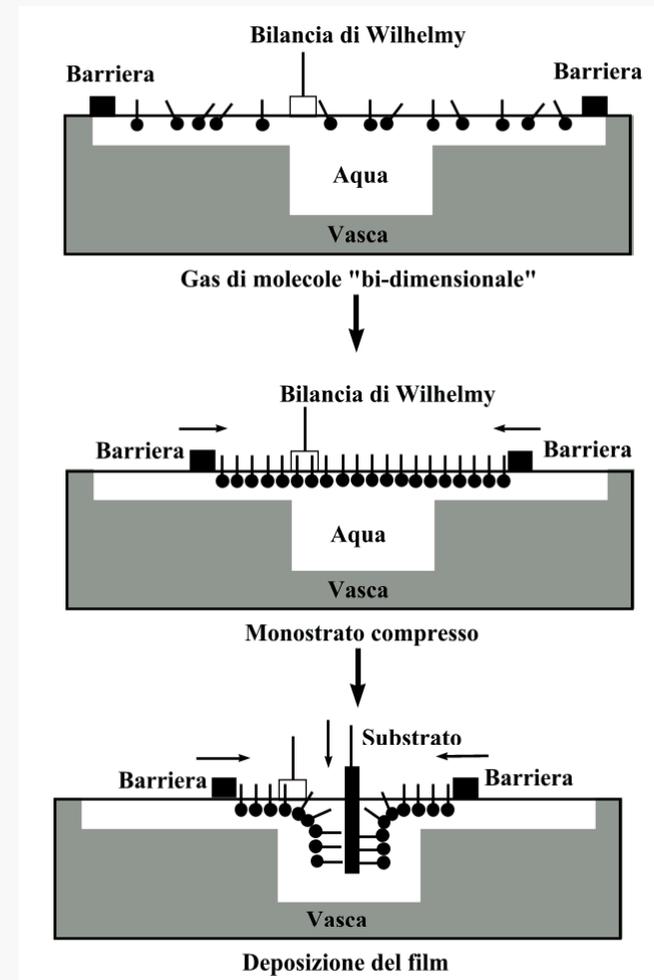
L'argento, previa pulitura con  $CCl_3CH_3$  o plasma di argon.

L'oro, essendo privo di ossido, è il migliore per studi di spettroscopia in riflessione.

Oggi tuttavia uno dei più usati è un wafer di silicio pulito tramite riscaldamento a  $90^\circ$  in una miscela di  $H_2O_2$  e  $H_2SO_4$  concentrato ( 30:70 v/v ) per 30 min ( *soluzione piragna* ) .

Anche wafer di arseniuro di gallio o miche spaccate di fresco possono essere rese idrofiliche e utilizzate come substrati

Materiale tratto dal seminario di  
Fabia Galantini, Apr. 2004



## Langmuir-Blodgett films II

materiali solubili in acqua

idrofilici

materiali solubili in solventi apolari

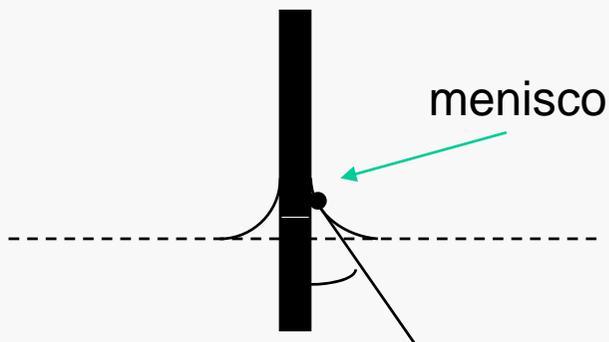
idrofobici

una molecola anfifilica è per metà idrofilica e per metà idrofobica :

es. Acido stearico  $C_{17}H_{35}CO_2H$  idrofilico  
idrofobico

Data la loro duplice reattività, le molecole anfifiliche sono portate a collocarsi alle interfacce come aria-acqua o olio-acqua .

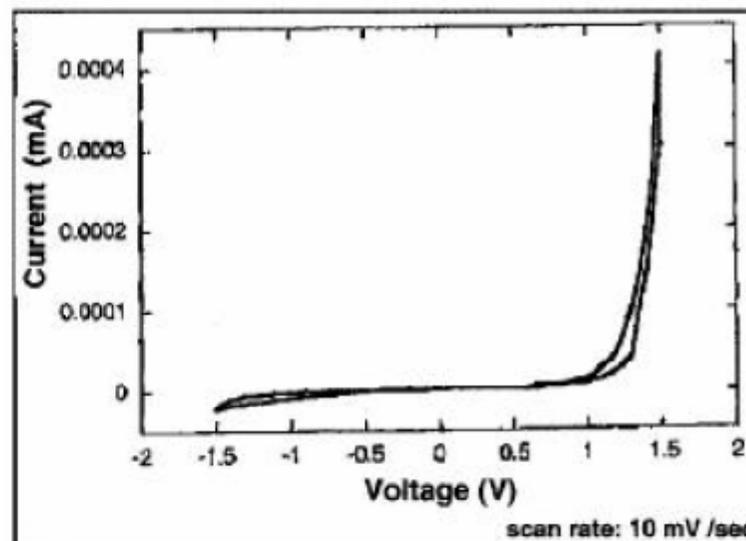
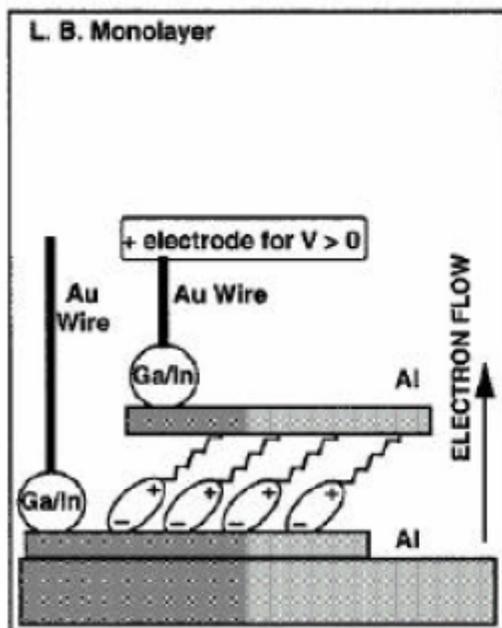
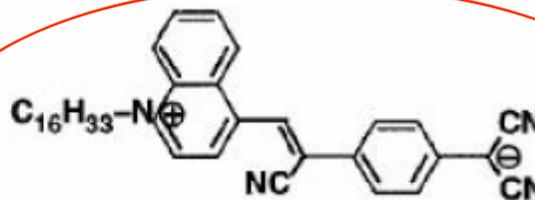
La solubilità di una molecola anfifilica in acqua dipende dal bilanciamento tra la lunghezza della catena alchilica e la forza della testa idrofilica . Nella tab. seguente è riportato l'effetto di diversi gruppi funzionali sulla formazione di film da composti del  $-C_{16}$  :



molto debole ( no film )	Debole ( film instabile )	Forte ( film stabile )	molto forte ( $C_{16}$ si dissolve )
$-CH_2I$	$-CH_2OCH_3$	$-CH_2OH$	$-SO_3^-$
$-CH_2Br$	$-C_6H_4OCH_3$	$-COOH$	$-OSO_3^-$
$-CH_2Cl$	$-COOCH_3$	$-CN$	$-C_6H_4SO_4^-$
$-NO_2$		$-CONH_2$	$-NR_4^+$
		$-CH=NOH$	
		$C_6H_4OH$	
		$CH_2COCH_3$	
		$-NHCONH_2$	
		$-NHCOCH_3$	

## Example of rectifying behavior in a LB film

Amphiphilic molecule

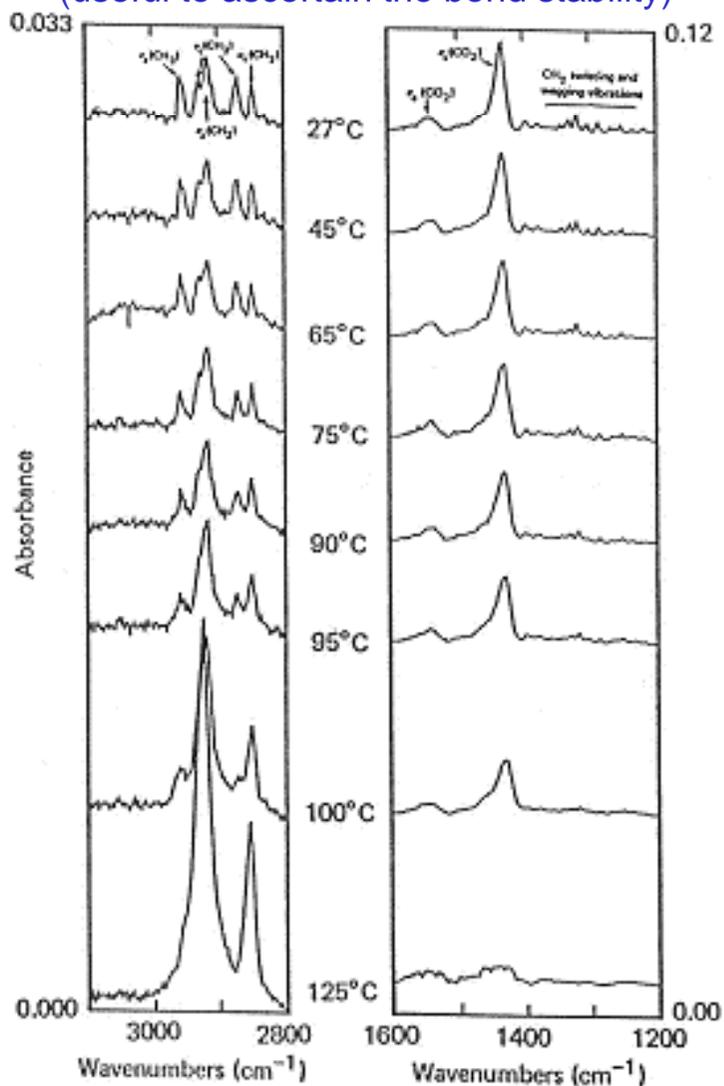


Schema di un diodo rettificante fatto con film LB. A destra, la caratteristica corrente-tensione del diodo.

*The operating principle of the molecule will be explained later on!!*

## Thermal stability of LB films

IR spectra of LB films at different temperatures  
(useful to ascertain the bond stability)



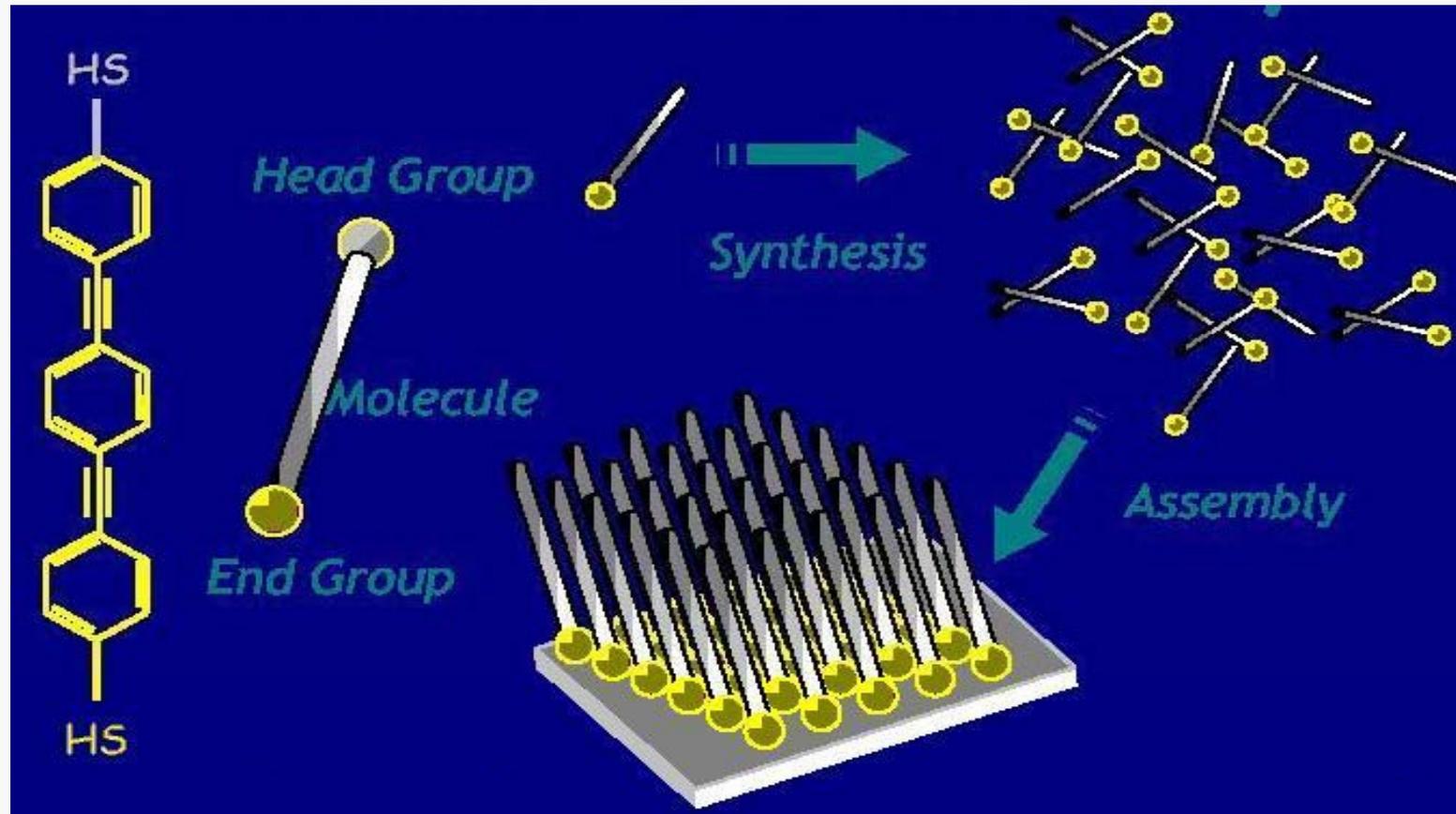
LB: cheap technique, useful to build monolayers of *specific* molecules on inorganic substrates, so to provide an interface between inorganic/organic worlds

Main limitations:

- Few molecular systems can be grown;
- Van der Waals bond not very strong;
- Thermal and chemical stability can be an issue

**With its simplicity, LB technique demonstrates the ability to produce an organic layer over an inorganic substrate**

# Self-Assembled Monolayers (SAM) I



**Specific molecules which grow up spontaneously in an ordered monolayer over an inorganic substrate**

Materiale tratto in parte dal seminario di Marco Donato, Apr. 2004, e dall'Elaborato di Tesi in Fisica dei Materiali di Federico Prescimone, 2005

# Self-Assembled Monolayers (SAM) II

The simplest SAM are *linear* molecules with an head group able to undergo strong binding with an inorganic surface (but non linear molecules can be envisioned as well)

## Energies involved in SAM

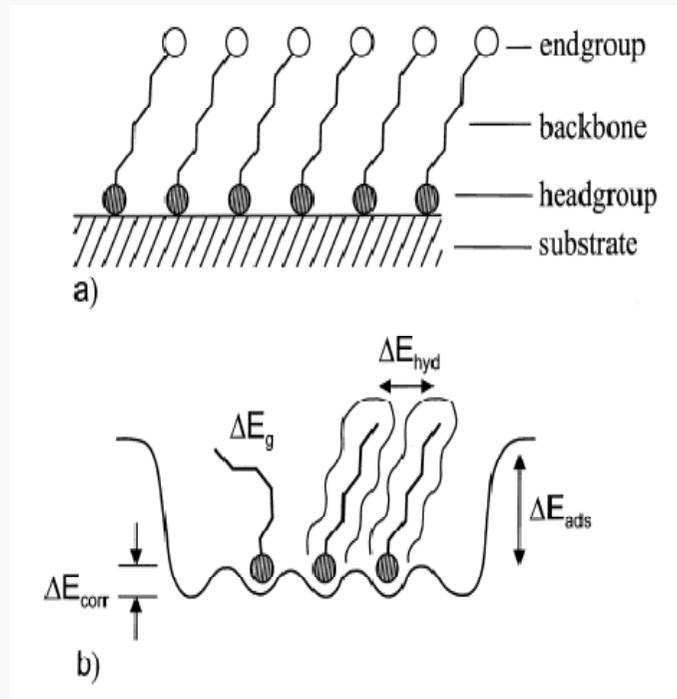


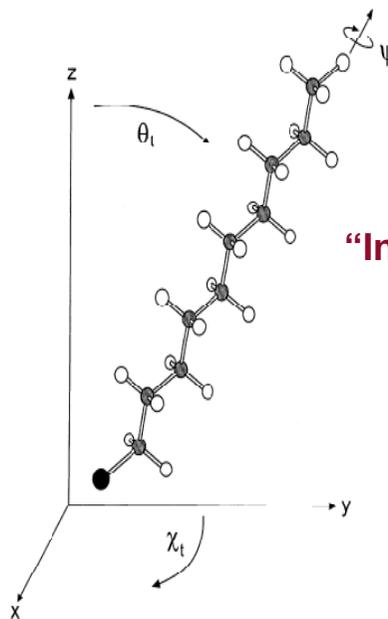
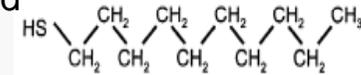
Fig. 2. (a) Schematic of SAM. Shaded circle indicates chemisorbing headgroup and open circle endgroup, which can be chosen from variety of chemical functionalities. (b) Schematic of different energies.  $\Delta E_{\text{ads}}$  stands for adsorption energy,  $\Delta E_{\text{corr}}$  corrugation of substrate potential experienced by molecule,  $\Delta E_{\text{hyd}}$  van der Waals interaction of (hydrocarbon) tails, and  $\Delta E_{\text{g}}$  energy of gauche defect (or, generally, deviation from fully stretched backbone).

## Examples of SAM/substrate choices

MONOLAYERS		
SURFACE	LIGAND	BINDING
Au	RSH, ArSH (thiols)	RS-Au
Au	RSSR' (disulfides)	RS-Au
Au	RSR' (sulfides)	RS-Au
SiO <sub>2</sub> , glass	RSiCl <sub>3</sub> , RSiOR <sub>3</sub>	siloxane network
Si	[RCOO] <sub>2</sub> (neat)	R-Si
Si	RCH=CH <sub>2</sub> , [RCOO] <sub>2</sub>	R-CH <sub>2</sub> CH <sub>2</sub> -Si
GaAs	RSH	RS-GaAs
Ag	RSH, ArSH	RS-Ag
Cu	RSH, ArSH	RS-Cu
metal oxides	RCOOH	RCO <sub>2</sub> -... MO <sub>n</sub>
metal oxides	RCONHOH	RCONHOH ... MO <sub>n</sub> RCONHO ... MO <sub>n</sub>
Pt	RSH, ArSH	RS-Pt
Pt	RNC	RNC-Pt

# Alkanethiols on Au I

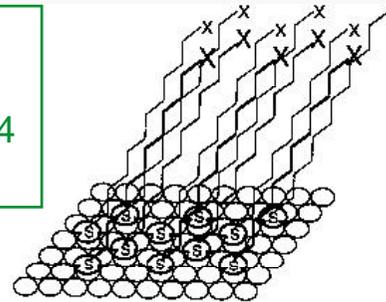
Linear molecule with alkyl  $(CH_2)_n$  chain (typ  $n = 3-15$ ), a thiol (HS) head group and an end group which can be “functionalized” (most frequently an hydrofobic methyl group,  $CH_3$ )



Van der Waals forces rule mutual organization (max energy  $\sim 10$  kcal/mol  $\sim 0.4$  eV/molecule)

“Inclined” growth

Thiol/Au bonding (energy  $\sim 30$  kcal/mol  $\sim 1.2$  eV/molecule)



Da G. Timp, Nanotechnology (Springer-Verlag, 1999)

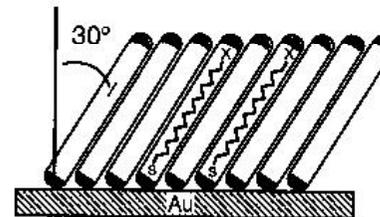


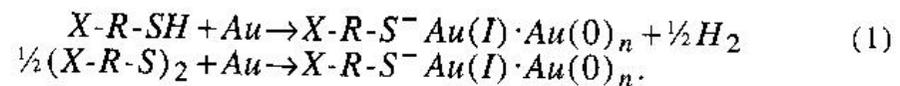
FIGURE 1. Schematic illustration of the molecular-level structure of a self-assembled monolayer of  $n$ -alkanethiolates on gold. Figure is not drawn to scale.

Strong chemical affinity between thiol and gold surfaces

Fabrication from the liquid state (simple 24 hrs dipping in a mM SAM solution in methanol)

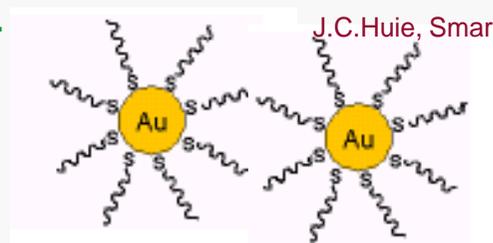
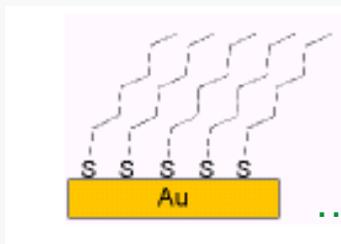
**Simple and efficient fabrication**

SAMs of alkanethiolates on gold[29,30] form by spontaneous adsorption of alkanethiols  $(X(CH_2)_nSH)$  [27,30,36-42] and dialkyldisulfides  $(X(CH_2)_nS-(CH_2)_mY)$ [41,43] (from the liquid or vapor phase) onto a clean gold surface according to:



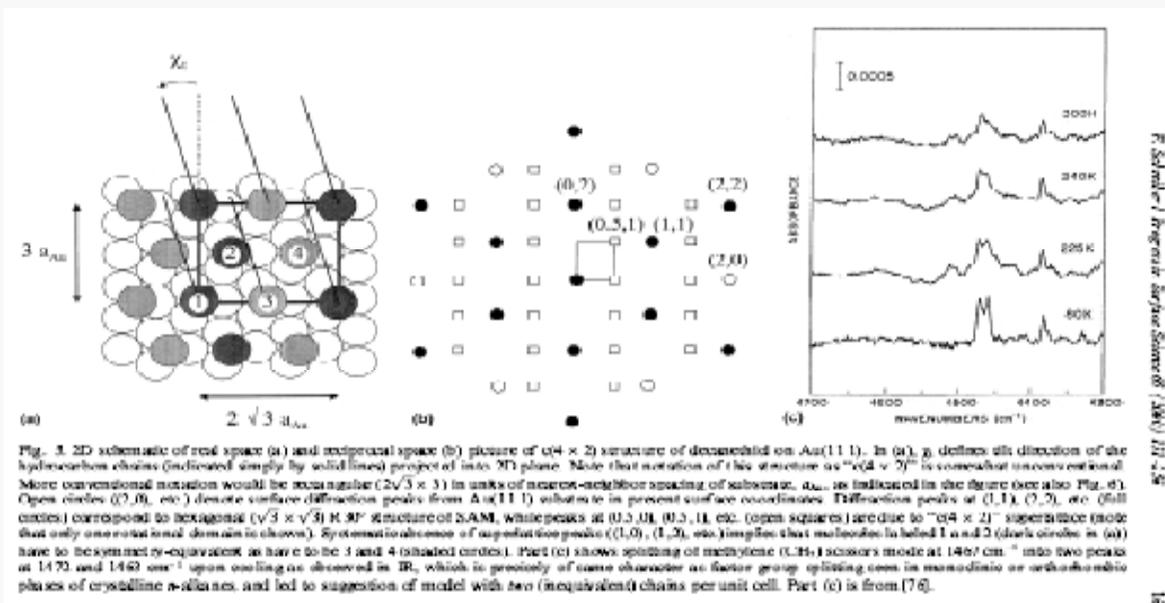
# Alkanethiols on Au II

Chemical bond possible with *any* Au surface (e.g., SAM useful as a spacer to prevent Au nanoparticle coalescence in the liquid phase).



J.C.Huie, Smart Mater. Struct. 12 264 (2003)

... but , but crystalline (111) Au is preferred because of dense molecule packing



**Dense (virtually defect-free) mutual organization of molecules bound to Au (111) surfaces**

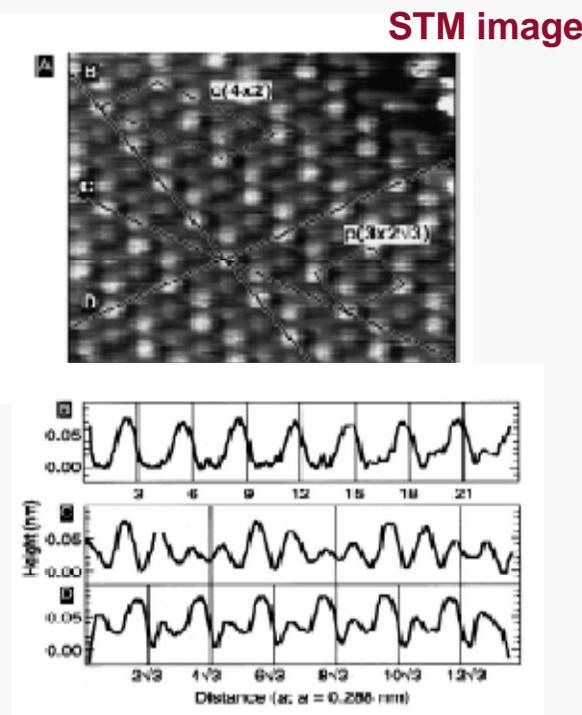
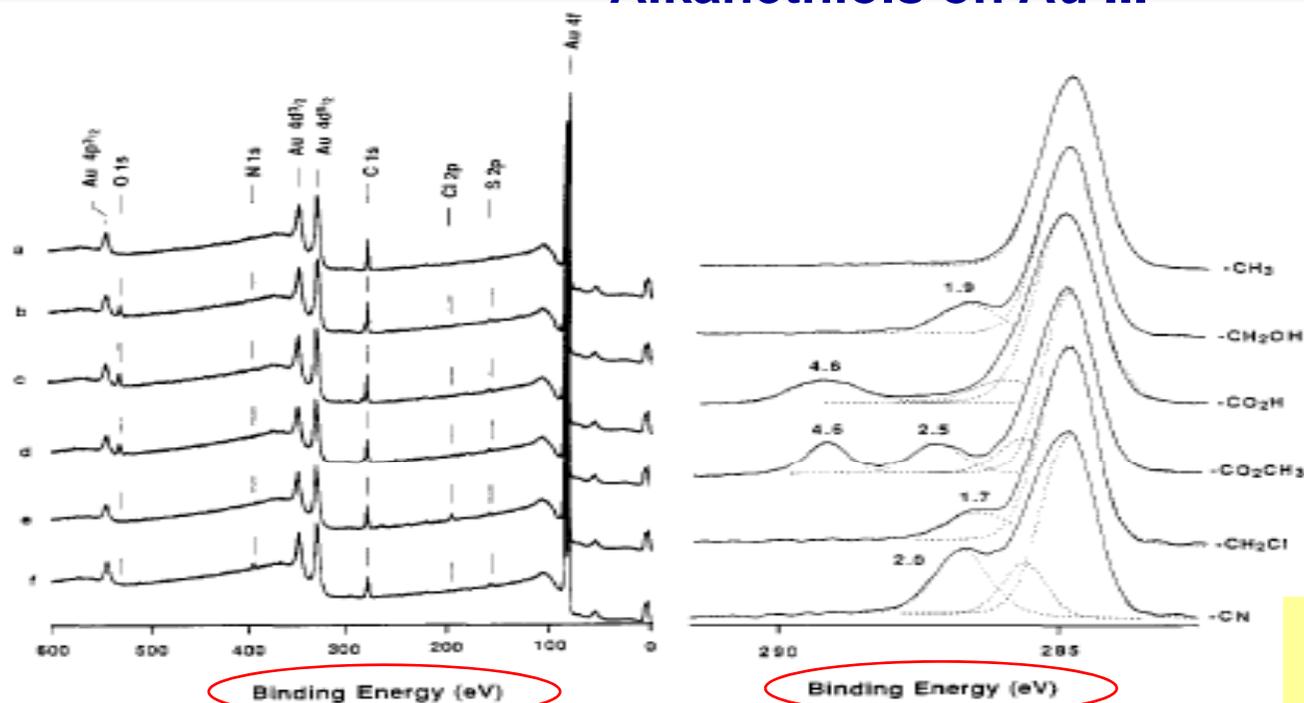


Fig. 5. (A) Constant-current STM image ( $60 \text{ \AA} \times 60 \text{ \AA}$ ) of octanethiol on Au(111) in standing-up phase. The  $(2\sqrt{3} \times 3)$  unit mesh and of  $4 \times 2$  superlattice unit cell are outlined. (B) Plot of cross-section B in (A) running in the Au nearest-neighbor direction. (C and D) Cross-sectional plots running in two of Au 3DIN directions. From [9].

## Alkanethiols on Au III

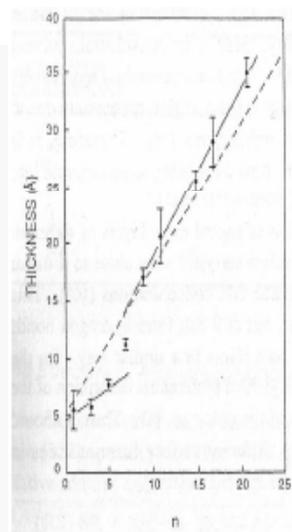


X-ray photoelectron spectroscopy (XPS)

Chemical nature of the thiol/Au bond

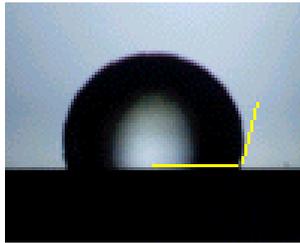
XPS of thiol monolayers on gold: survey spectra (left) and high-resolution spectra of the carbon 1s region (right). Dotted lines represent computer-generated peak fits using 90% Gaussian/10% Lorentzian peak shapes. Numbers above the peaks indicate shifts in binding energy from the principal methylene peak. The following thiols were used: (a) HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>, (b) HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH, (c) HS(CH<sub>2</sub>)<sub>10</sub>CO<sub>2</sub>H, (d) HS(CH<sub>2</sub>)<sub>10</sub>CO<sub>2</sub>CH<sub>3</sub>, (e) HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>Cl, and (f) HS(CH<sub>2</sub>)<sub>4</sub>CN.

Ellipsometric measurement of the SAM thickness for different lengths of the alkyl chain (n)



Homogeneous monolayers are formed, with thickness in the nm range (depending on the length of the alkyl chain)

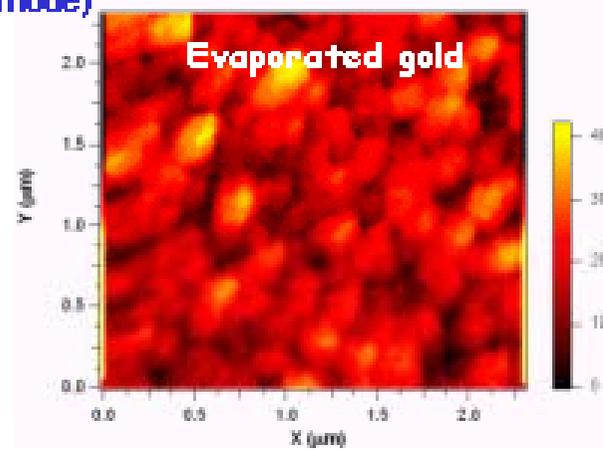
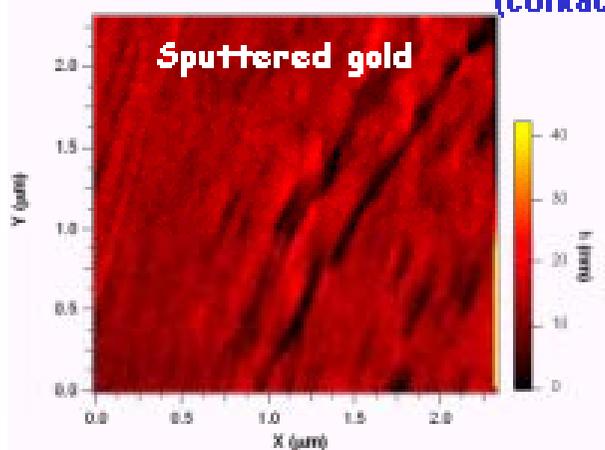
## Dependence of the SAM quality on the Au substrate



Contact angle Measurement  
(hydrophobic character)



AFM images  
(contact mode)



Strong dependence of the resist quality on the underlying gold layer

Dense SAM organization clearly fails at Au grain boundaries

- Particle sensitive resist:
  - Self Assembled Monolayer of nonanethiol [ $\text{CH}_3(\text{CH}_2)_9\text{SH}$ ] onto gold

Hydrophobic character of the exposed metal surface (in case of methyl-terminated SAMs) can be investigated with macroscopic **contact angle** measurements

Results depend on the quality of the underlying Au layer (here available as grown by two different methods, evaporation and sputtering – we will see more on that!)

# SAM exploitation in nanotechnology I

The availability of a dense and homogeneous organic monolayer grown with simple and self-assembling method can be useful for a variety of purposes, e.g.:

- Particle-sensitive resist for atom lithography (*already seen*)
- Molecular templates for single molecule or nanoparticle holding (*we will see more on that!*)
- Local modification by functionalization of inorganic surfaces
- Inorganic/organic interface for single nanoparticle addressing (*see next slide!*)

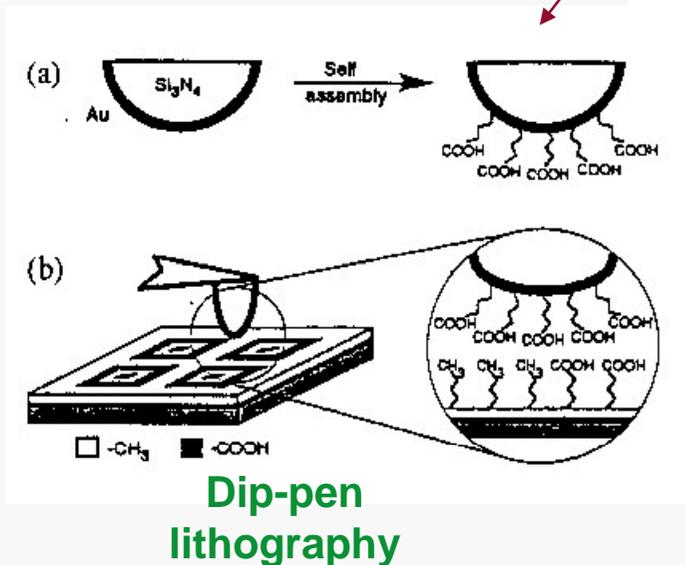
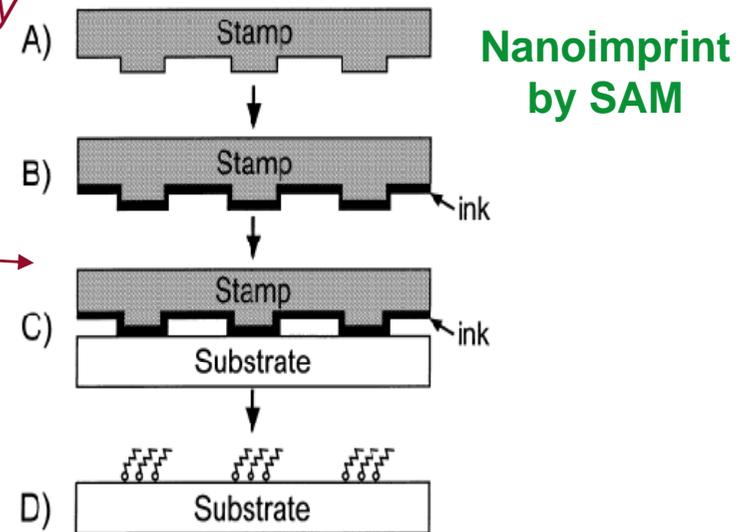


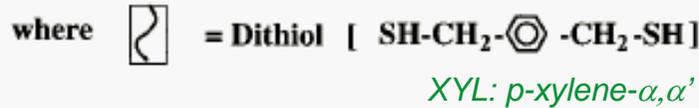
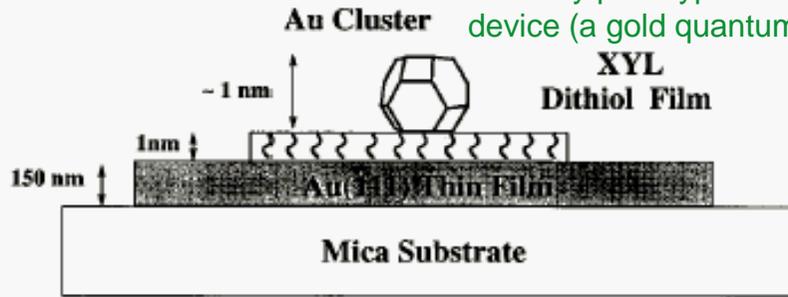
Fig. 19. Schematic of microcontact printing ( $\mu$ CP) technique for lateral structuring. Laterally structured elastomeric replica (stamp) (A), is “inked” with self-assembling molecules (B) and then printed to substrate (C). After release of stamp (D), laterally structured SAM is obtained on substrate. Applications can make use of either structured SAM itself or use SAM as etching mask to obtain structured substrate.

SAM can be used as “ink” to locally modify (functionalize) surfaces

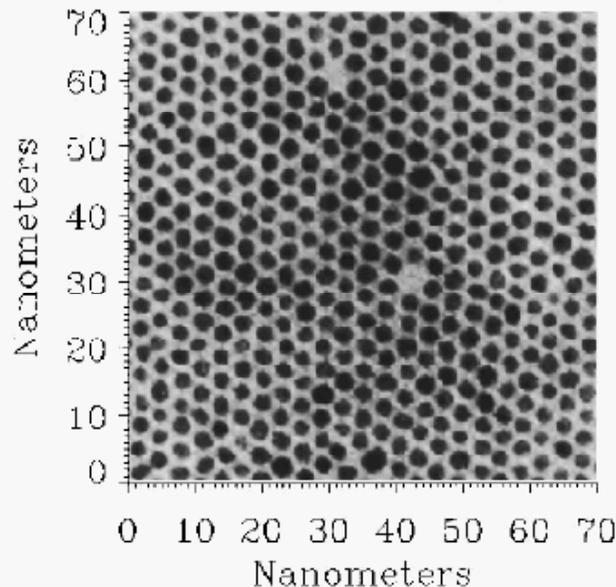
# SAM exploitation in nanotechnology II

See Andres et al.,  
JVSTA 14 1180 (1996);  
Science 272 1323 (1996)

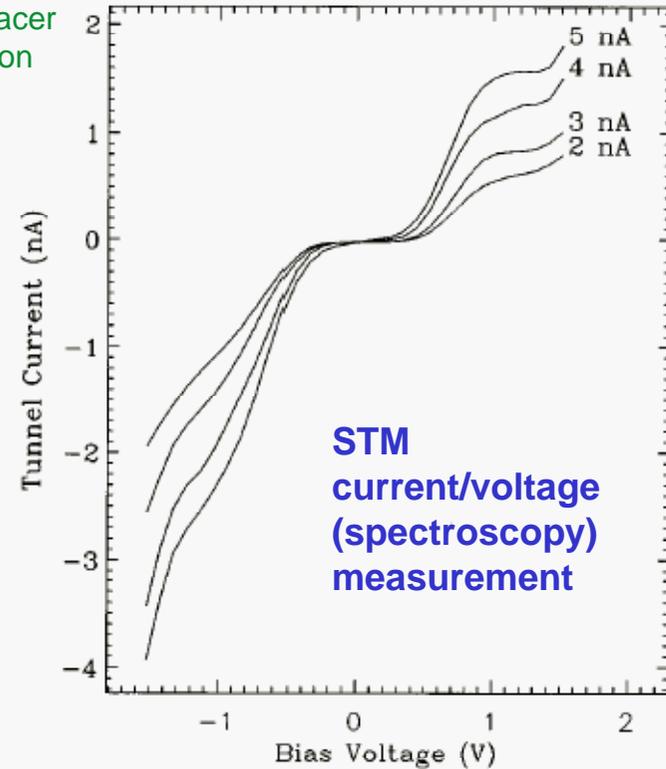
SAM Dithiol (bond on both sides with Au) used as a dielectric nanospacer in a very prototypal single electron device (a gold quantum box)



Gold nanoparticles deposited on Dithiol SAM on gold



AFM image



STM current/voltage (spectroscopy) measurement

FIG. 6.  $I(V,z)$  data obtained at room temperature with the tip positioned over a  $\sim 1.8$  nm high Au cluster resting on a SAM of XYL dithiol. Each curve is the sum of 100 separate  $I(V)$  sweeps. The different data sets illustrate how the  $I(V,z)$  characteristics change as the specified set point tunneling current is varied. The reproducible non-linearities in the  $I(V)$  data indicate a Coulomb staircase behavior at room temperature.

**SAM acts as a spacer/holder for single gold nanoparticles (on gold)**

## 2. Molecular electronics

Major question:

“once we have solved the problem of interfacing the two worlds (which means, we can potentially hold and electrically access an organic entity using inorganic substrates), what can we do with such molecules of interest for nanotechnology?”

Keeping in mind the most striking features of nanotechnology in the (restricted but important) field of nanoelectronics, the above question can be rephrased as:

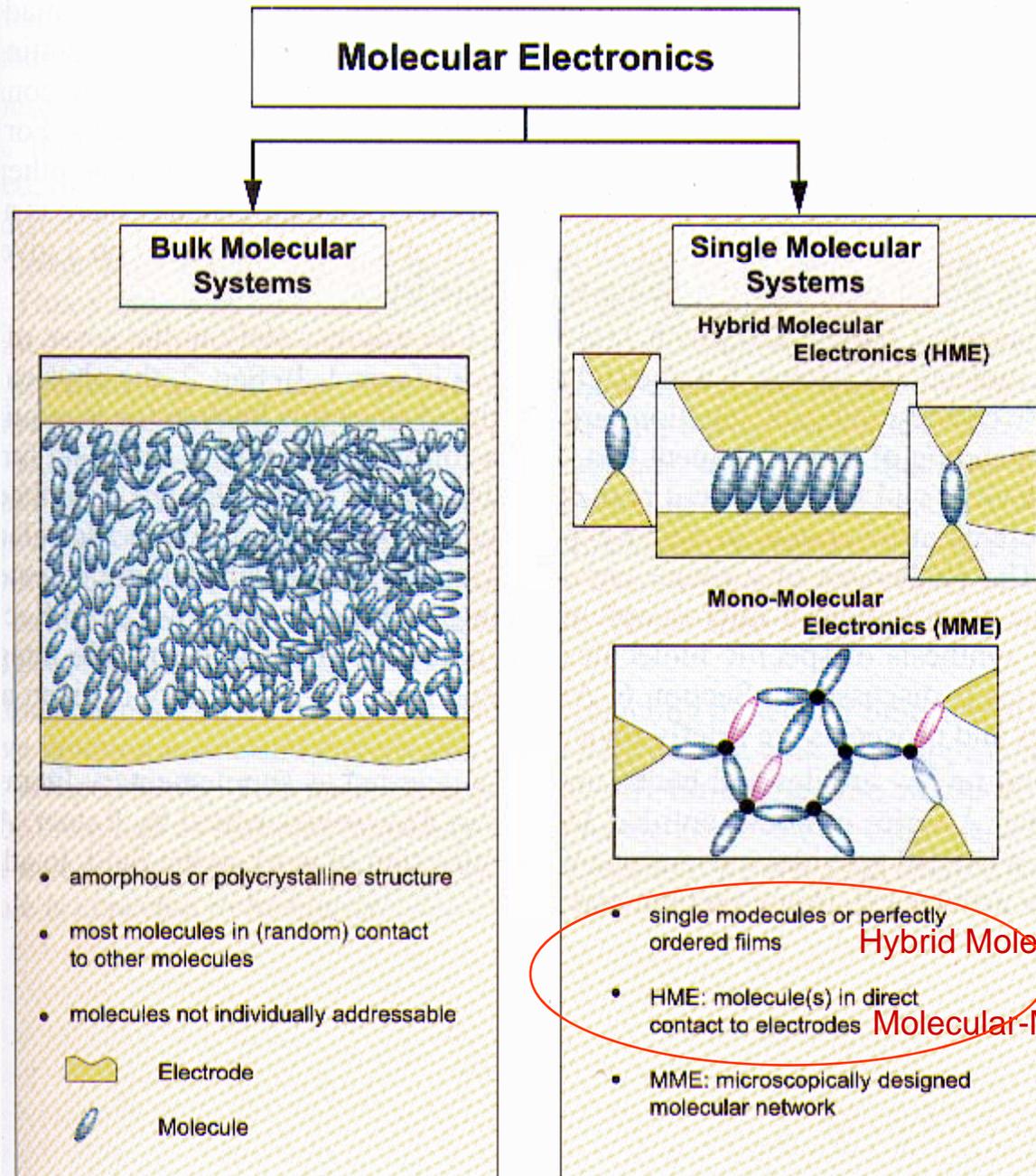
“what kind of functional device can we envision exploiting organic entities?”

More generally:

“what kind of electronic functions can we associate to organic compounds and how can we exploit them in potential advanced applications?”

*Note: we will restrict ourselves to electronic-driven applications, neglecting a wide range of other goals which can, at least potentially, be met with nanotechnologies*

# Molelectronics scenarios



Two approaches, aimed at using transport properties in bulk systems, or at addressing specific systems

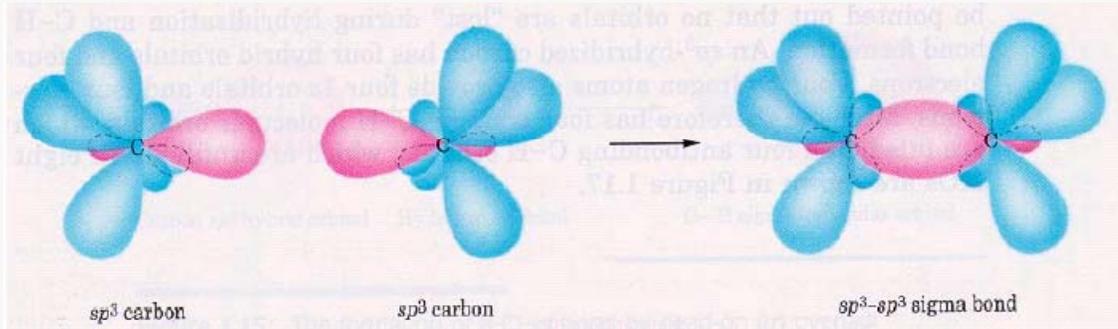
Hybrid Molecular

Molecular-Molecular

We are mostly concerned with those

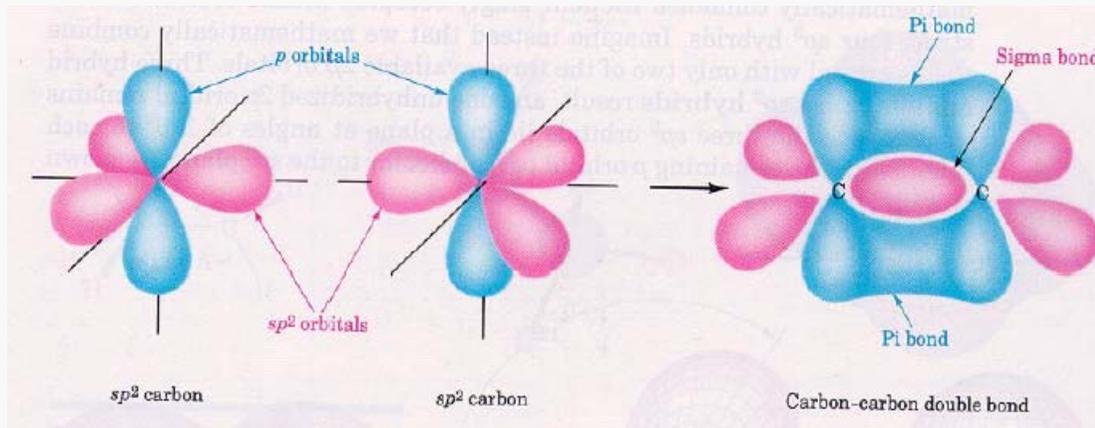
# Basics of electron transport in carbon-based molecules

See M. McGehee,  
www2.latech.edu (Louisiana Tech, 2002))



$\sigma$  bonds involving  $sp^3$   
orbitals  
↓  
localized electrons  
↓  
**dielectric behavior**

**...BUT...**



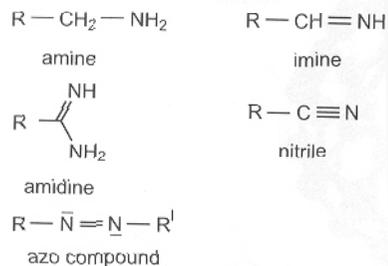
$\pi$  bonds involving  $sp^2$   
orbitals  
↓  
de-localized electrons  
↓  
**(semi)conducting behavior**

**Some transport can be supported by (or within) an organic molecule**

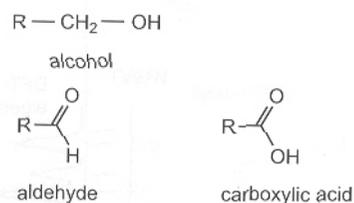
# A little bit on nomenclature

Huge range of possibilities offered in engineering and building up conjugate systems

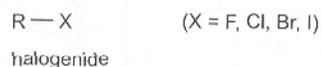
## Groups involving nitrogen



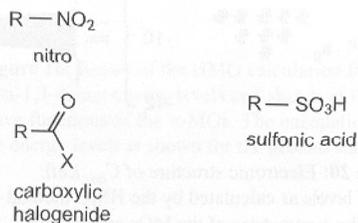
## Groups involving oxygen



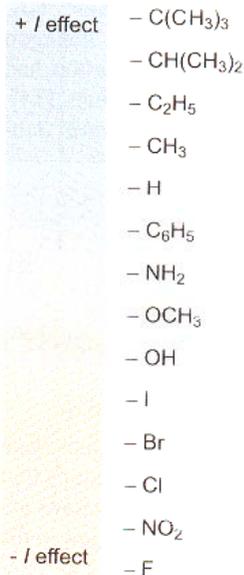
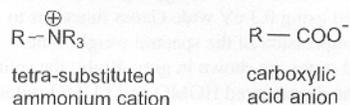
## Groups involving halogenes



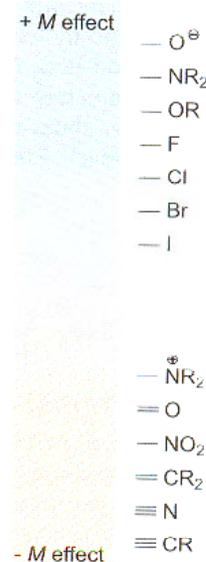
## Groups involving different atoms



## Charged groups



**Figure 22:** Inductive effect of substituents: the ability to attract electrons along  $\sigma$ -bonds increases from top to bottom. In a comparison to hydrogen, substituents on top are said to show a +I effect ( $\sigma$ -donors), those at the bottom show a -I effect ( $\sigma$ -acceptors).



Da R. Waser Ed., Nanoelectronics and information technology (Wiley-VCH, 2003)

**Figure 23:** Substituents showing mesomeric effects.

“Substitution” of groups may affect the electron density acting like **donors or acceptors**

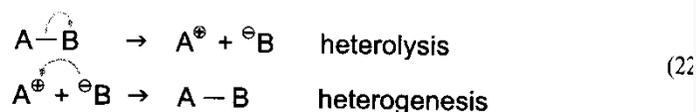
**Enormous flexibility, unknown to the inorganic realm**

## A little bit on synthesis

A chemical reaction is controlled by thermodynamics, specifically the tendency of the system to attain lower Gibbs (free) energy, and by kinetics, the rate of the process is determined by the ability to overcome the intermediate energy barriers along the reaction path. Because organic molecules are covalently bonded, all chemical reaction entails *bond forming*, *bond breaking*, or both. Depending on what happens to the electron, these basic processes can be classified into one of the following categories:

### Polar reaction

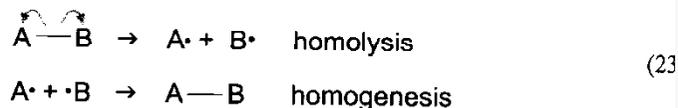
If the bond forming or breaking does not separate the electron pair involved and hence, involves ions as intermediates or – at least – in the transition state, the reaction is called a polar reaction:



A positively charged C ion is called **carbocation**, a negative C ion is called a **carbanion**.

### Radical reaction

If the reaction does involve the separation of the electrons of a bonding pair, the reaction is classified as a radical reaction:



### Pericyclic reaction

Electron movements may occur in a concerted manner, without intermediate radicals, carbanions, or carbocations.

Most reactions used for the synthesis of organic compounds used in the context of this book, e.g. for liquid crystals displays, organic light-emitting or optically active systems for studies on molecular electronics, and for molecular biology, are based on polar reactions. Polar reactions rely on electrostatic interactions, such as **nucleophiles**, species that seek centres of positive charge, interacting with at least partially positively charged regions of the target molecule and **electrophiles**, species that seek centres of negative charge, interacting with regions of high electron density. A nucleophile must have at least one lone pair of electrons that it can donate to the target molecule. Species with high nucleophilicity are often negatively charged or possess a high negative partial charge: they can be regarded as Lewis bases, electron-pair donors, that react with the target molecule behaving as a Lewis acid, an electron-pair acceptor. Electrophiles are either positively charged or have low-lying unoccupied orbitals.

Figure 30 shows some common nucleophiles and electrophiles. Some reagents are ambivalent: for example, water can act as a nucleophile through its oxygen atom (which carries a negative partial charge), whereas the protons of water are electrophilic. The

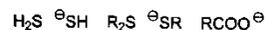
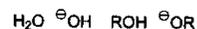
strength of the nucleophilicity and electrophilicity is determined by the local electron density at the active region of the reagent, by geometrical aspects (how exposed this region is), and by the polarizability of the species.

The overall chemical reaction, which is used in a synthesis strategy, typically is classified according to the type of change it brings to the constitution of the target molecules:

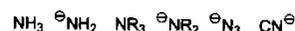
- **Substitution**, in which one substituent of the target molecule is exchanged for another,
- **Addition**, in which a  $\pi$ -bond of a multiple bond is opened and two substituents are added,
- **Elimination**, in which two substituents on neighboring atoms are removed and an additional  $\pi$ -bond is formed,
- **Rearrangement** of the skeleton of the molecule.

### Nucleophiles

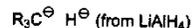
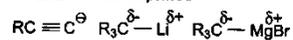
#### O- and S- Nucleophiles



#### N- Nucleophiles



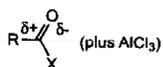
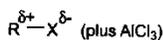
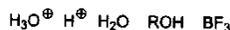
#### C- and H- Nucleophiles



#### Halogenide Nucleophiles



### Electrophiles



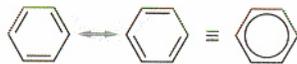
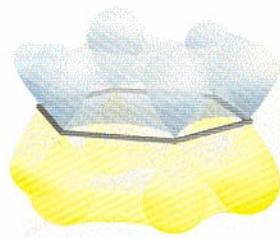
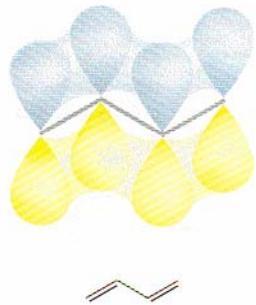
**Simple, relatively well-controlled and highly scalable methods exist for synthesis of organics (typically, based on liquid phase manipulations)**

Da R. Waser Ed., Nanoelectronics and information technology (Wiley-VCH, 2003)

Figure 30: Examples of common nucleophiles and electrophiles.

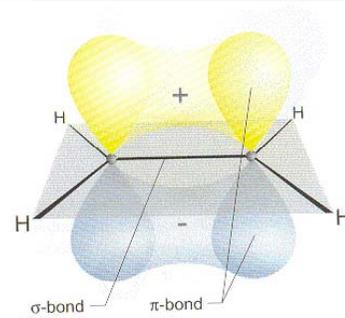
# Transport in conjugated polymers I

benzene



**Figure 9:** Structure and illustration of the electron density of the  $\pi$ -conjugated system of benzene. The two mesomeric Kekulé formulas according to the valence-bond theory as well as the frequently used Robinson ring symbol are shown.

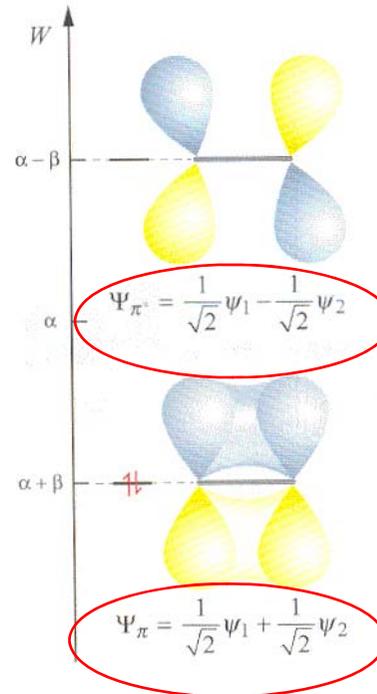
ethene



**Figure 4:** Illustration of the  $\pi$ -bond of ethene,  $C_2H_4$ , resulting from the co-planar p-AOs of the  $sp^2$  hybridized C atoms. For clarity of the picture the  $\sigma$ -bonds are not shown in their full shape.

Examples of simple conjugated species

ethene



**Figure 15:** Result of the HMO calculation for ethene: energy levels and sketch of the wave functions of the  $\pi$ -MOs. The occupation of the energy levels is shown for the ground state.

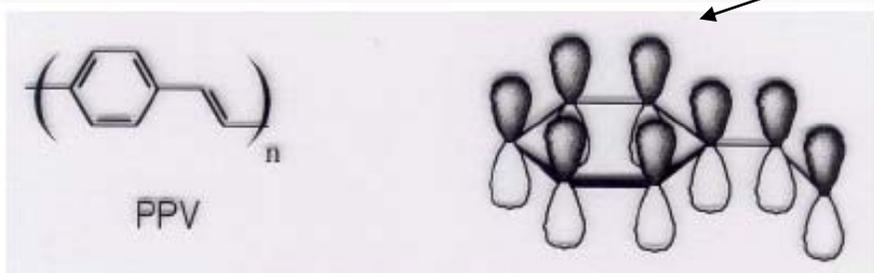
Energy level calculation made by LCAO (linear combination of atomic orbitals) and/or HMO (Hueckel molecular orbitals) approaches

Superposition of  $\pi$  mol. orbitals leads to  $\pi^*$  and  $\pi$  bands ( $\sigma$  orbitals do not strongly overlap)

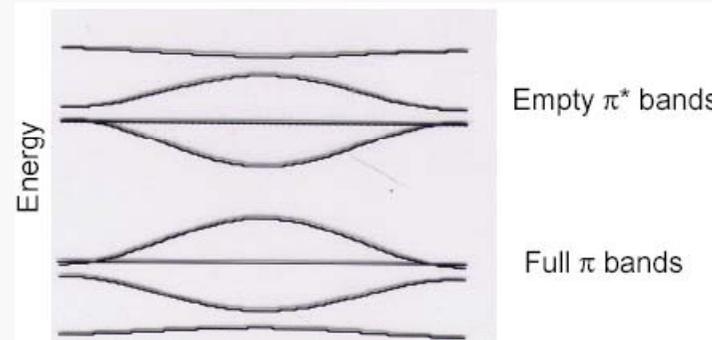
**“As usual”, when (atomic) orbitals overlap each other, energy bands are formed**

## Transport in conjugated polymers II

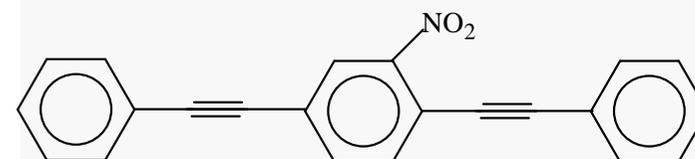
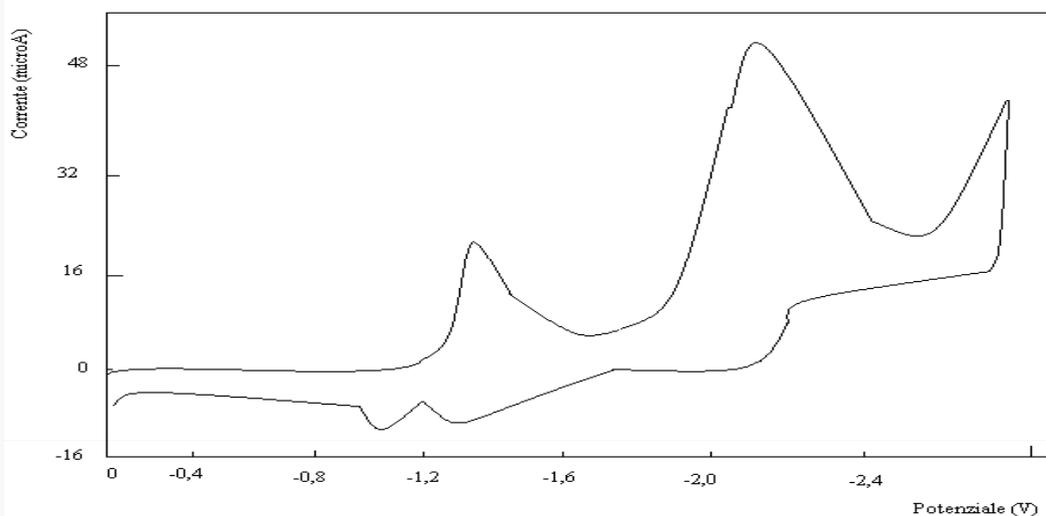
Examples: polyaniline, pyrrols, thiophens, polyphenylenvinylene,...



Each p electron is the unit cell results in one  $\pi$  band.



The band gaps of conjugated polymers are in the range of 1 to 3 eV.



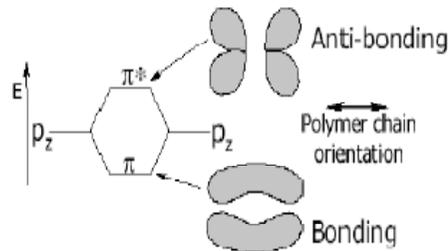
Current-voltage plot on 2-nitro-1,4phenylethynyl-benzene

**In the liquid phase!!  
(many molecules  
addressed at one  
time!!)**

Materiale tratto dal seminario di  
Marco Donato, Apr. 2004

# Orbitals (molecules) and bands (solids)

## $\pi$ -orbitals



Bonding/anti-bonding levels and associated molecular orbitals\*

- The bonding and anti-bonding components of the molecular orbital are the in-phase (+) and out-of-phase (-) combinations of the constituent  $p_z$  orbitals respectively.
- Electrons from  $p_z$  orbitals (most energetic)  $\rightarrow$  in the bonding molecular orbital (molecule in ground state).
- The bonding,  $\pi$ -orbital is therefore the highest occupied molecular orbital or **HOMO**, the equivalent of the *Top of the Valence Band* in inorganic semiconductors
- ... and the anti-bonding,  $\pi^*$ -orbital the lowest unoccupied molecular orbital or **LUMO**, the equivalent of the *Bottom of the Conduction Band* in inorganic semiconductors.
- As more  $p_z$  orbitals along the chain are combined, the discrete  $\pi$  and  $\pi^*$  orbitals form quasi-continuous bands.

\* From V. Cleave PhD thesis, Cambridge 1999 23

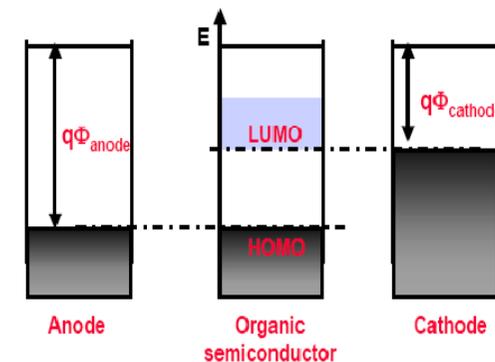
## Charge Injection in Semiconductors

### Energy levels relevant for charge injection and conduction

- CB  $\rightarrow$  LUMO = Lowest Unoccupied Molecular Orbital
- VB  $\rightarrow$  HOMO = Highest Occupied Molecular Orbital

### Ideal injection

Match cathode (anode) work function with the LUMO (HOMO)



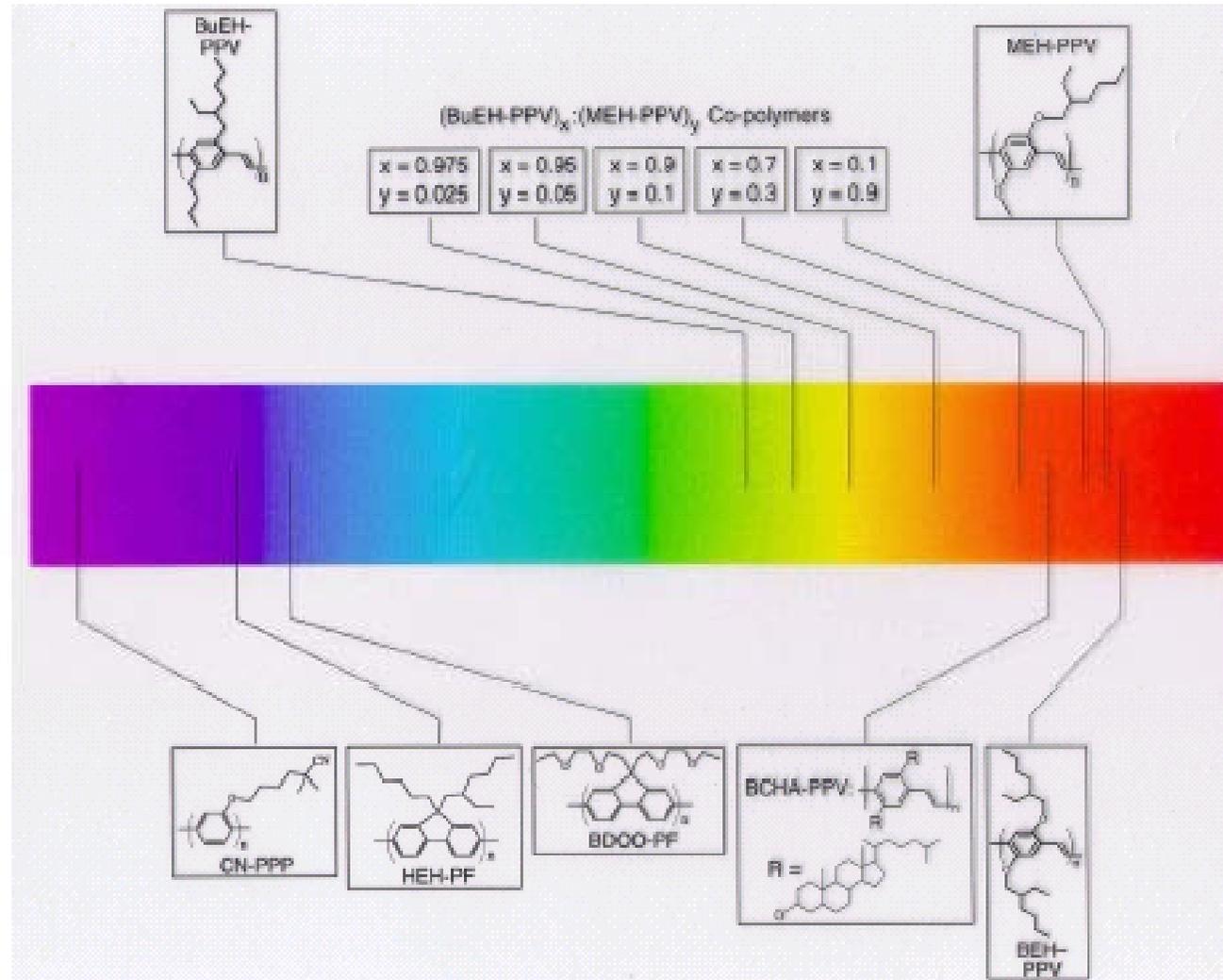
Franco Cacialli, Course on "Plastic Electronics",  
PhD School "Galileo Galilei", 2006

$\pi$  orbitals play the role of valence/cond bands

Semiconductor features ideally recovered!

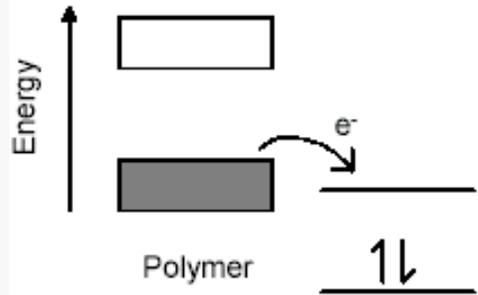
## “Tunable” band gap

Examples of conjugated polymers with a range of band gaps



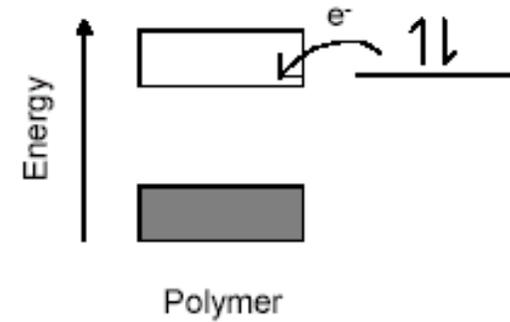
Co-polymers can be fabricated exhibiting band gaps corresponding to photon energies in a wide spectral range (useful in light emitting devices)

# Doping the conjugate polymers



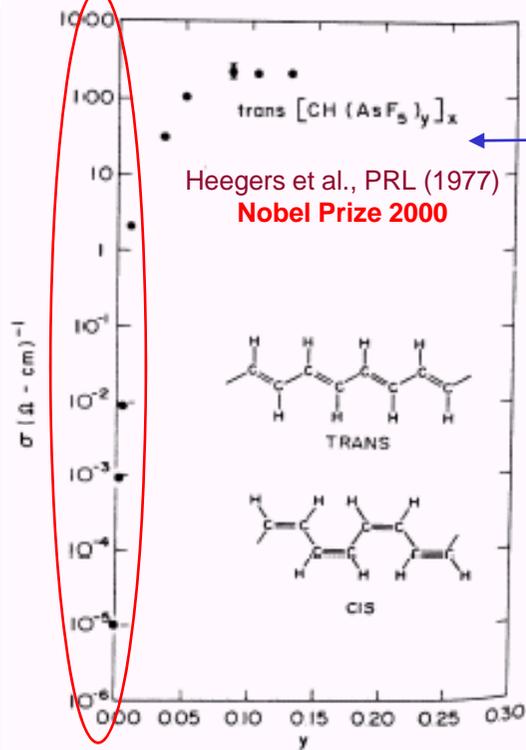
Oxidizing agent (e.g. I<sub>2</sub>, Br<sub>2</sub>, AsF<sub>5</sub>)

“As usual” (i.e., as with inorganic semicond), material can be doped to enhance electron or “hole” conductivity



Oxidizing agents act as p-type dopants, i.e. they generate holes in the polymer.

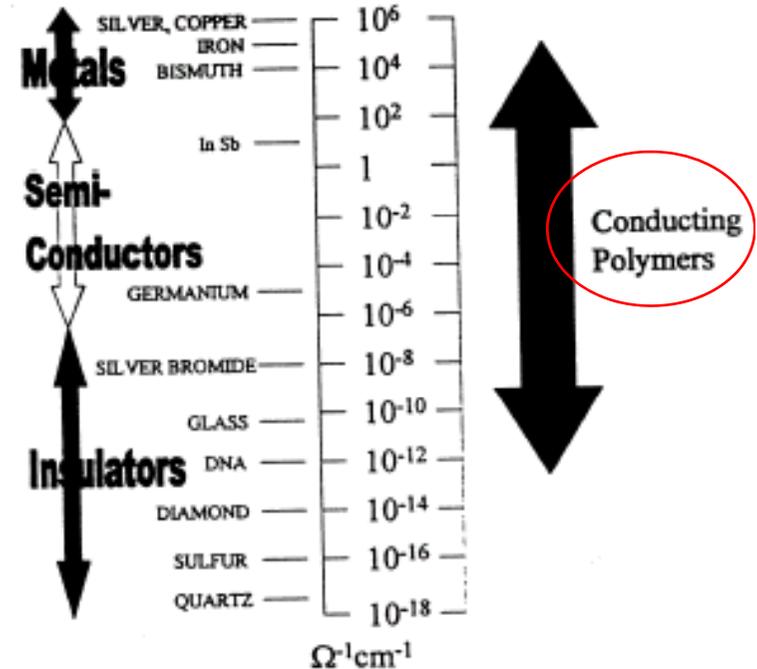
Reducing agents such as calcium and lithium can introduce electrons into the conduction band of a conjugated polymer.



Doping trans-acetylene with AsF<sub>5</sub>

Heegers et al., PRL (1977)  
Nobel Prize 2000

Conductivity can be varied in a very wide range



### 3. Electronics at the single molecule level

J.M. Tour, Molecular Electronics  
(World Scientific, 2003)

Molecular electronics, sometimes called moletronics, involves the use of single or small groups of molecules in device-based structures, that can be used as the fundamental units for electronic components such as wires, switches, memory and gain elements.<sup>5</sup> Molecular electronics is an area of research that is firing the imagination of scientists as few research topics have ever done in the past.<sup>6</sup> For instance, *Science* magazine labeled the hook-up of molecules into functional circuits as the breakthrough of the year for 2001,<sup>7</sup> and teams of chemists, engineers, materials scientists, physicists and computer scientists are learning each other's languages to hopefully turn this interdisciplinary new field into a worldwide product-bearing reality.

**Intramolecular electronics:** the operation depends on the specific features (by design) of a **single** (or few) molecules

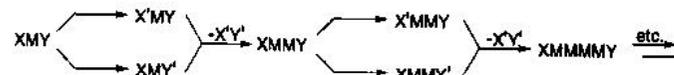
Interface issues are “restricted” at the borderline of the (molecular) device

- ✓ Inherently nanotechnological approach with bottoms-up fabrication
- ✓ Inherent “single electron” and “ballistic transport” capabilities
- ✓ Possibility of “molecular engineering” to tailor specific functions (e.g., wires, diodes, switches, memories, or any combination of them)

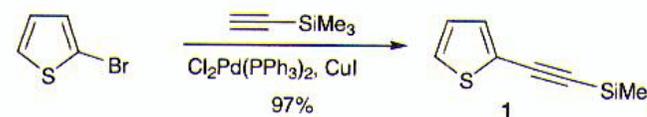
# Requirements for synthesis methods in molectronics

J.M. Tour, Molecular Electronics  
(World Scientific, 2003)

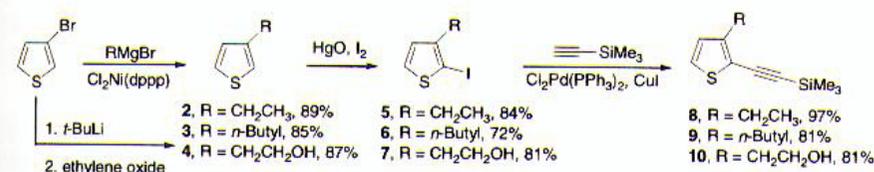
There has been considerable recent effort to prepare large conjugated molecules of precise length and constitution.<sup>27</sup> Our approach to these compounds maintains several key features that make it well suited for the requisite large molecular architectures for molecular scale electronics studies. Specifically, the route involves (1) a rapid construction method that permits doubling molecular length at each coupling stage to afford an unbranched 100 Å oligomer, the approximate size of present nanopatterned probe gaps, (2) an iterative approach so that the same high yielding reactions can be used throughout the sequence, (3) the syntheses of conjugated compounds that are semiconducting in the bulk, (4) products that are stable to light and air so that subsequent engineering manipulations will not be impeded, (5) products that could easily permit independent functionalization of the ends to serve as molecular alligator clips that are required for surface contacts to metal probes, (6) products that are rigid in their frameworks so as to minimize conformational flexibility yet containing substituents for maintaining solubility and processability, (7) alkynyl units (cylindrically symmetric) separating the aryl units so that ground state contiguous  $\pi$ -overlap will be minimally affected by rotational variations, (8) molecular systems that do not have degenerate ground state resonance forms and are thus not subject to Peierls distortions, and finally, (9) products that serve as useful models for the understanding of bulk polymeric materials



Scheme 3.1 Schematic presentation of the iterative divergent/convergent approach to molecular length doubling.



Scheme 3.2 Synthesis of monomers.



Scheme 3.3 Synthesis of functionalized monomers.

**Need for synthesis methods able to produce elemental units (sized below 10 nm, the dimension typical of nanoscopy probes, i.e., the bridge to the macroscopic world) which can be replicated at will in order to produce longer chains**

# Examples of molectronics

See Joachim, Gimzewski, Aviram,  
Nature [408 541](#) (2000)

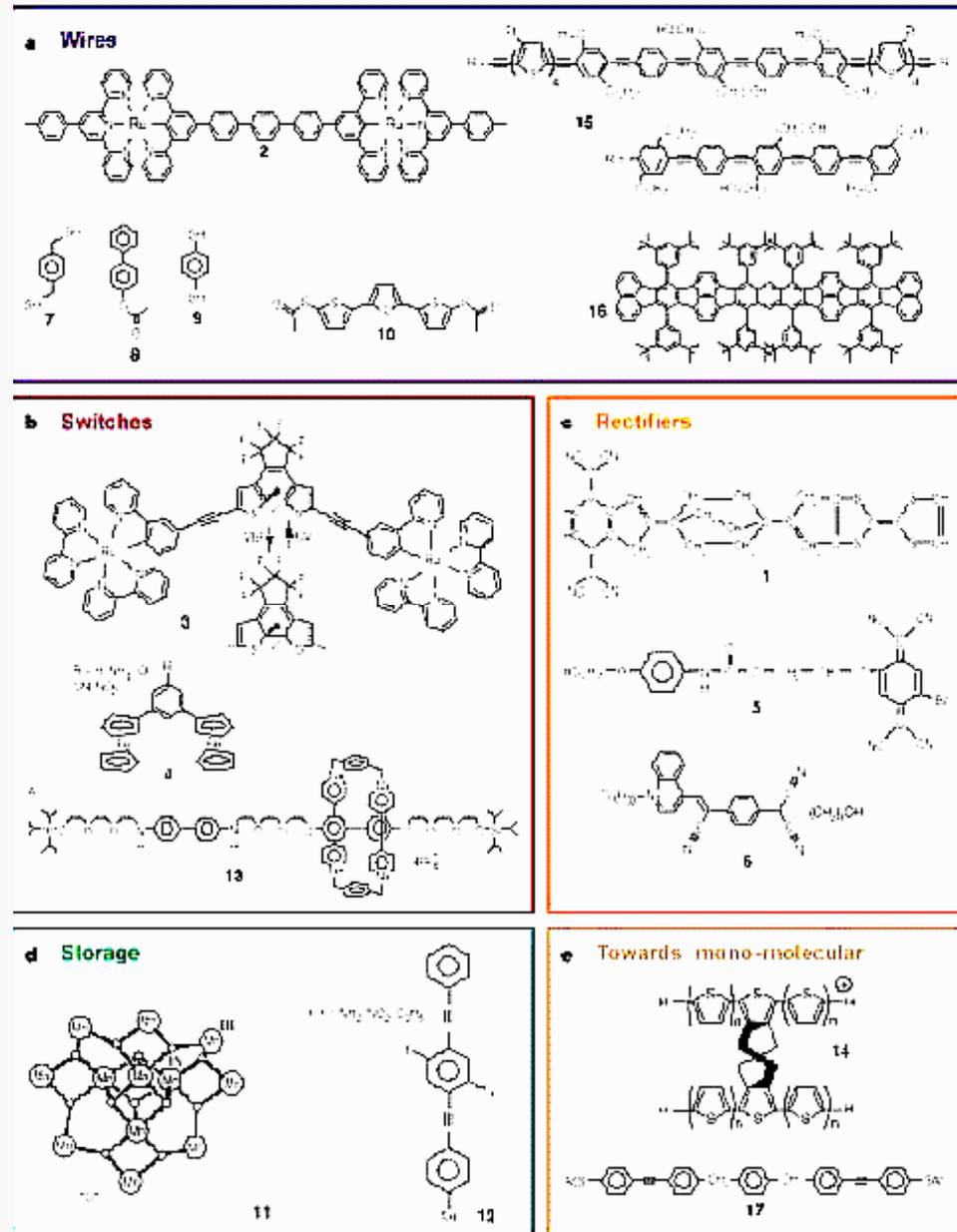
Some advantages:

- cheap and simple large scale production;
- nanosized (or even sub-nanosized) units readily produced;
- possibility to exploit self-assembly

Some disadvantages:

- fabrication process control;
- cumbersome integration with inorganics technologies;
- stability (chemical, temperature, light) and durability;
- how to address the single element?

**Continuously growing enormous variety of “electronic” molecules**

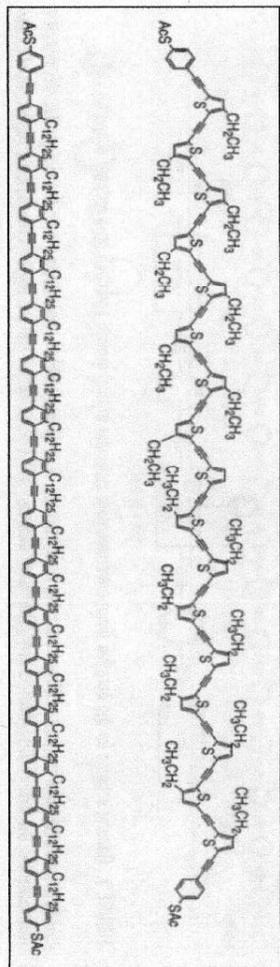


# Molecular wires (Tour)

See Tour et al.,  
Acc. Chem. Res. **33** 791 (2000);  
J. Am. Chem. Soc. **120** 8486 (1998)

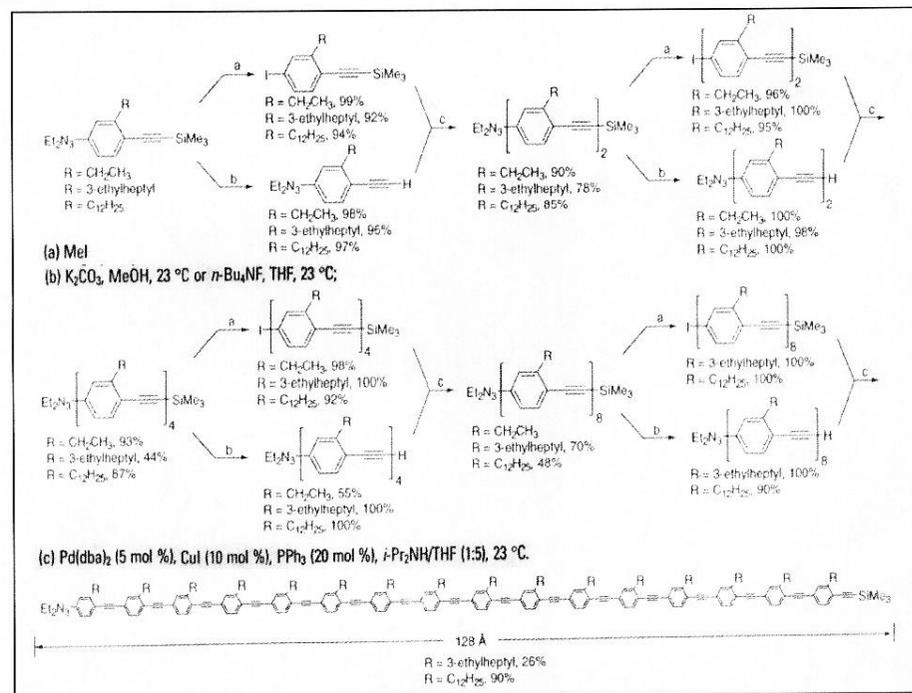
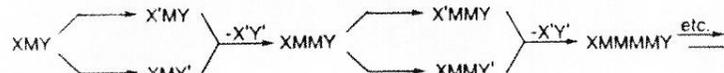
## Cavi molecolari: molecole coniugate

- Sistemi con omogeneità di segnali in ingresso ed in uscita
- Sfruttano la conduzione elettrica
- Possono trasmettere un segnale anche solo attraverso il riarrangiamento della nuvola elettronica
- Sono stati messi a punto diversi metodi di sintesi efficaci
- Esistono metodi già sperimentati per il controllo delle proprietà di dispositivi a due terminali



## Esempi di cavi molecolari e sintesi

- La sintesi, messa a punto da J. Tour, è di tipo iterativo divergente/convergente e può essere realizzata sia in soluzione che su supporto solido

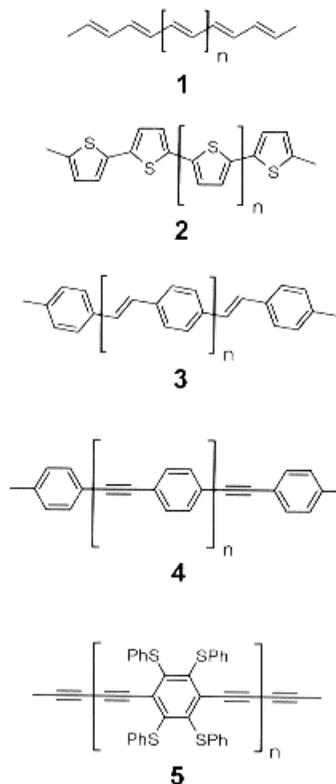


**Expected behavior similar to electron waveguides (ballistic)**

Materiali tratti dai seminari di  
Oliviero Andreussi, Feb. 2002  
Marco Donato, Apr. 2004

# “Molecular engineering” for molecular conductors/dielectrics

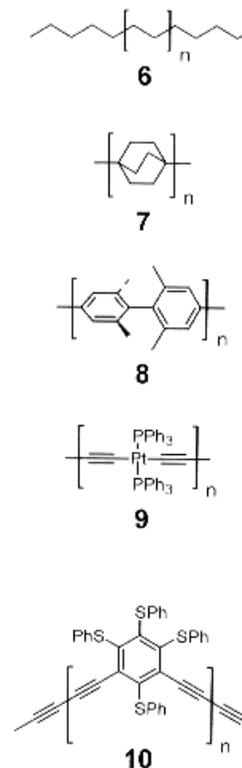
**Wires:**  
conjugation active motives



The most basic electronic function is a wire, a one-dimensional object that allows transport of electric charge [7]. Transferred to a molecular scale, of particular interest are rod-like structures that transport electrons from one end to the other [8]. Electron transport is expected to take part through the frontier orbitals of a molecule, as they should be the closest to the Fermi levels of the electrodes (see Sec. 5.1). In general, with increasing size of the  $\pi$ -system the energy difference between the frontier orbitals decreases and hence the energy difference to the Fermi level of the electrode. Promising candidates as molecular wires are therefore large delocalized  $\pi$ -systems. Structural motives that allowed the design of chains with delocalized  $\pi$ -systems were studied extensively in solution [9]. The simplest example of such a chain is a polyene **1** (for the following molecules, cf. Figure 2) consisting of an alternating sequence of single and double bonds leading to a  $\pi$ -system over the whole length [10]. Many other examples consist of aromatic building blocks like polybenzene [11], polythiophene **2** [12], polypyrrole and combinations of aromatic building blocks with conjugated double or triple bonds like polyphenylenevinylene **3** [13] or polyphenyleneethynylene **4** [14] were extensively studied. The enormous developments in nanoscale manipulations down to the single atom level, made it possible to investigate the electric current through selected  $\pi$ -systems, on surfaces or between electrodes, as will be discussed in detail in sections of this chapter. An experiment that illustrates the concept nicely is the incorporation of protruding rigid  $\pi$ -systems as molecular rods out of a self-assembled monolayer (SAM) of an thioalkane in Ref. [15] (Sec. 4.3). This first conductance investigations of single molecules demonstrated substantial differences in electron transport properties between the rod and the thioalkane SAM emphasizing the concept of delocalized  $\pi$ -systems as molecular wires.

Conductance is not always the property which has to be optimized. The opposite property, a rather insulating molecular structure, is of similar importance for particular applications. The very first HME-device considered, the rectifier by Aviram and Ratner, is based on a donor and an acceptor  $\pi$ -system linked together by a spacer [2]. They suggested a rigid adamantyl cage **7** as a non-conjugating linker between both  $\pi$  systems which was expected to behave as an insulating molecular unit. The choice of the spacer will be very important, as it has to be sufficiently insulating to preserve the energy differences between the  $\pi$  systems, but still allows to some extent electron transport. In this particular case, the authors suggested electron transport by tunneling through the insulating structure. Structural motives not consisting of delocalized  $\pi$ -systems are in general poor conductors but reasonably good insulators. However, on a molecular scale the rigidity of the structure is of similar importance to prevent short circuiting of the separated units through space. Rigid molecular structures restricted to non-conjugating systems are rather limited. The above-mentioned adamantyl structure meets the conditions but is synthetically quite demanding. Alkanes **6** are known for their insulating properties, but lack the required rigidity.  $\pi$ -Systems meet the rigidity conditions but have already discussed as good conductors. However, the delocalisation of the  $\pi$ -system depends strongly on the torsion angles between the subunits. Two neighboring subunits with perpendicular  $\pi$ -systems reduce their electronic communication and hence the connecting single bond between them becomes a rigid and insulating connection on a molecular scale, as is the case for the tetramethylsubstituted biphenyl building block **8**. The transparency for electrons through a benzene core also depends on the relative positions of the linkages. While *ortho*- and *para*-connections are conjugation-active linkers, the *meta*-position is conjugation-passive [16]. This has been shown, for example, in the comparison of *para*-diacetylene connected thiophenyl-substituted benzenes **5** and the corresponding *meta*-connected building block **10** [17]. Another approach to meet the required rigidity and electronic passivity is the use of metalorganic complexes as linkers. The potential of this approach has already been demonstrated on a single-molecule level by the investigation of a *trans*-acetylene platinum(II) molecule **9**, which turned out to display the characteristics of a single molecule insulator, as will be discussed below (Section 4.2) in detail [18]. An additional motivation for using metal centers as connectors is the adaptability of the electronic transparency by the choice of the linking metal center, raising hopes of a rich future construction kit consisting of tailor-made linkages based on metal ions. An overview of molecular building blocks for rigid rods is given by Schwab, Levin and Michl [19].

**Insulators:**  
conjugation passive motives



**Chains, donors, acceptors, spacers as building blocks**

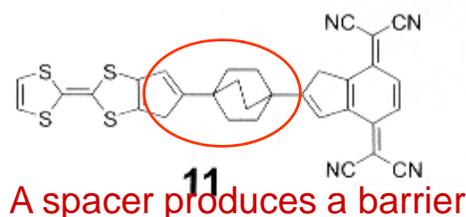
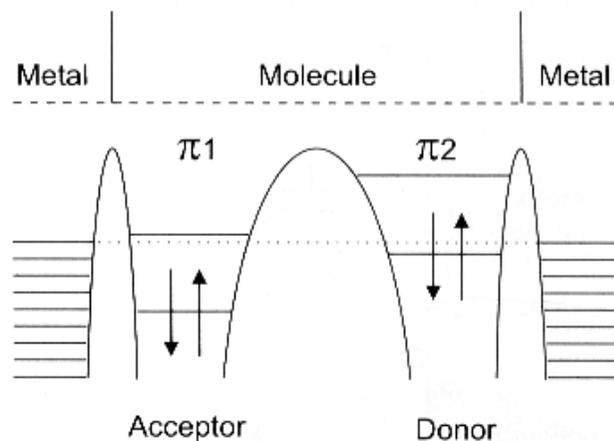
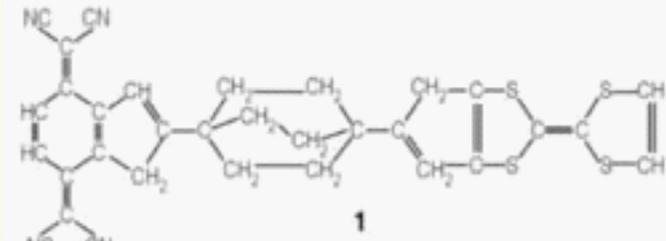
Da R. Waser Ed., Nanoelectronics and information technology (Wiley-VCH, 2003)

# Rectifying behavior (diodes) I

Aviram and Ratner<sup>1</sup> suggested that a single molecule with a donor–spacer–acceptor (d–s–a) structure (see **1** in Fig. 1c) would behave as a diode when placed between two electrodes: electrons can easily flow from the cathode to the acceptor, and electrons from the donor are then transferred to the anode. The working principle of this device is analogous to that underlying the "valve" effect introduced by Schockley 60 years ago<sup>2</sup>, but involves manipulating the electronic wavefunction of the metallic electrodes extending through the d–s–a molecule, rather than the carrier density in a semiconductor material. Such hybrid molecular electronic (HME) devices, comprising molecules embedded between several electrodes, thus differ radically from bulk-material-based molecular electronic technologies found in applications such as dye lasers, light-emitting diodes, liquid-crystal displays, and soft plastic transistors. However, the design of functional devices and machines based on the molecular electronics concept poses the challenge of integrating the functions required for advanced processing, particularly computing, within the same molecule in a mono-molecular electronics (MME) approach<sup>h</sup>

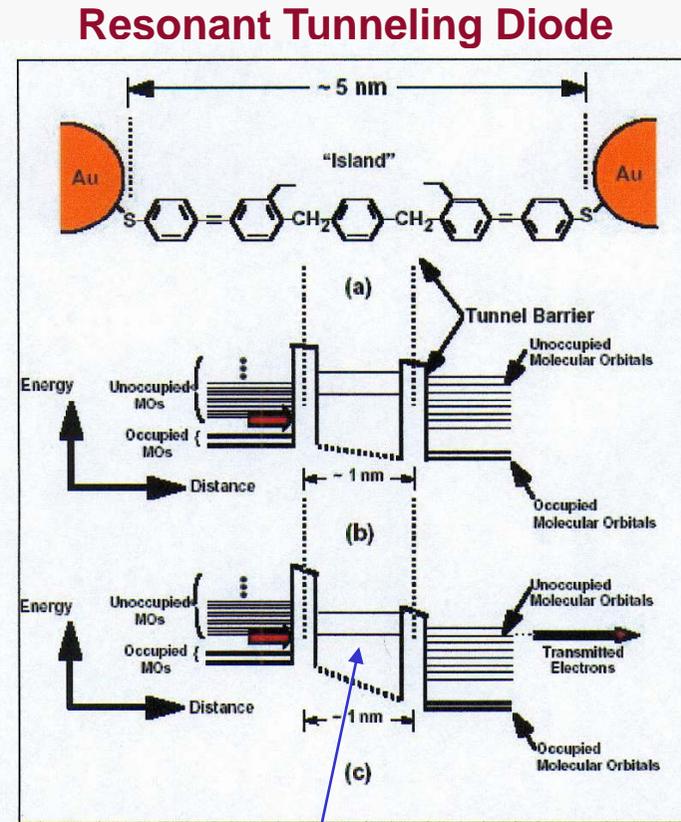
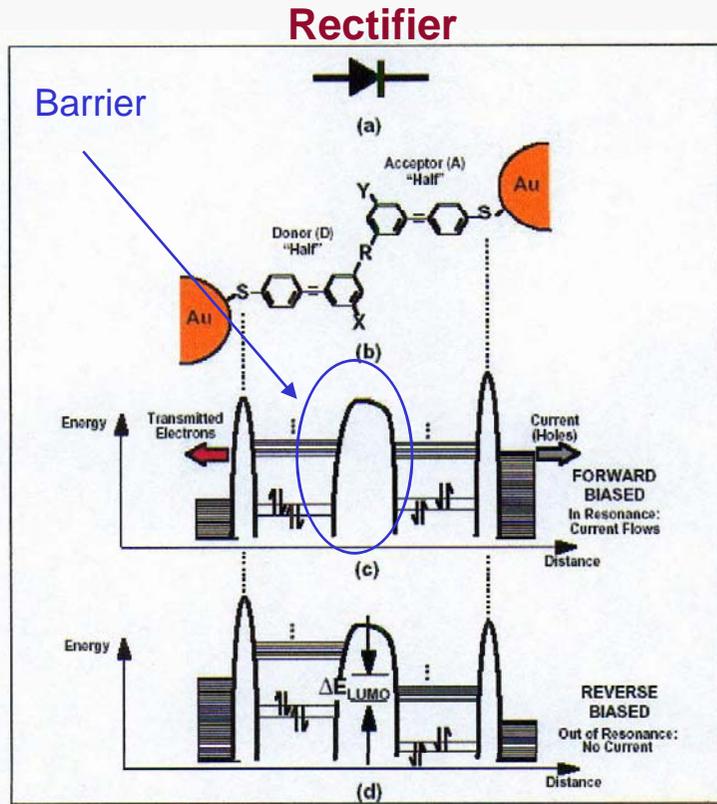
Diode

**Intramolecular tunneling rules the transport and leads to a rectifying behavior**



**Figure 3:** The first approach to molecular electronics [2]. Molecules with a donor and an acceptor group, separated by an insulating spacer, are predicted to behave as diodes. The upper panel displays the electron energies in the system, when no bias voltage is applied: In the metallic electrodes outside, electrons are filled up to the Fermi energy. The  $\pi$ -systems of the donor and acceptor units are confined in two potential wells. If a positive voltage is applied, the potential of the left lead is slightly increased and the potential of the right lead is correspondingly lowered; current can flow from the left to LUMO1, then to HOMO2 and further to the right electrode, going towards lower energies at each step. If the opposite voltage is applied, conduction take place only at much higher voltages. This is the behavior of a diode with the favourable current direction from the acceptor to the donor.

# Rectifying behavior (diodes) II



Potential well with discrete energy levels

**Redox-based single-electron process**

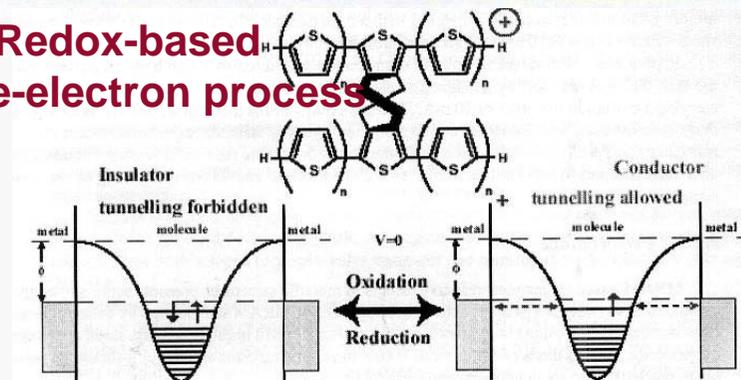
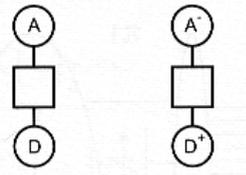
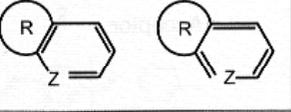
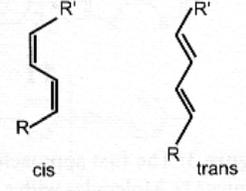
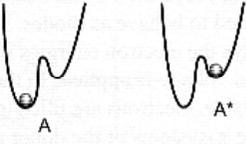
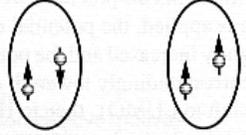


Figure 2.4:- The transport mechanism responsible for the conduction and insulation transformation through the reduction / oxidation of a molecule. The mechanism is similar to Coulomb blockade.

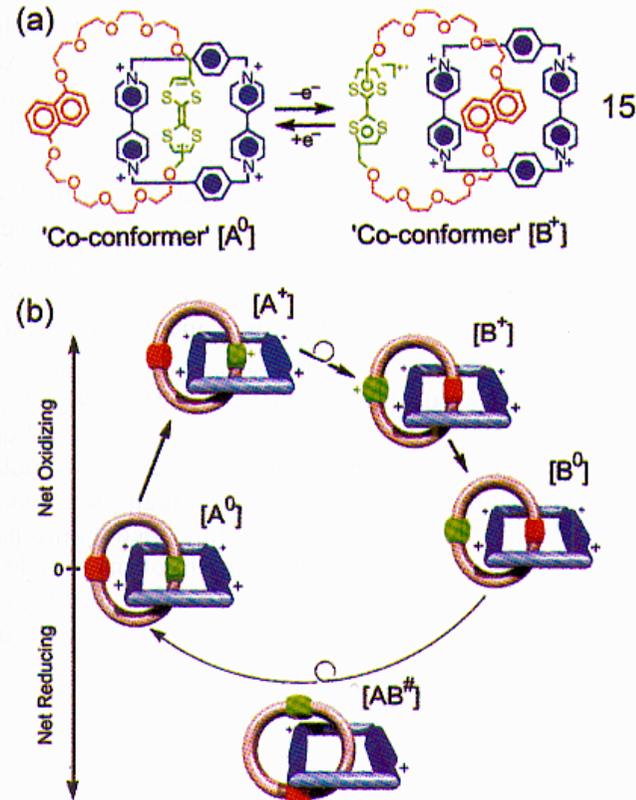
**Single charges are typically involved**

**Single electron behavior achievable**

# Molecules with switch (and storage) functions

processes	example of bistabile systems
redox process	
configuration change	
conformation change	
electronic excitation	
magnetic spin orientation	
logic states	"0"      "1"

## Rotaxane



**Figure 8:** Hysteretic redox-triggered rearrangement of the catenane **15**. At zero bias the molecule is in the ground-state  $[A^0]$  with the TTF unit between the two doubly charged viologenes. Biasing the system into the net oxidizing direction by +2V leads to an ionization of the TTF unit into state  $[A^+]$ . Because of electrostatic repulsion, the ring will mechanically rotate into state  $[B^+]$ . Reducing the bias back to zero will remove the ionization and, hence, the ground-state  $[B^0]$  with the dioxynaphthalene between the two doubly charged viologenes is established. A bias pulse into the net reducing direction with an amplitude of -1.5 V reduces the two viologenes into the monocharged state  $[AB^{\#}]$  which causes a preference for the TTF unit between the viologenes. Resetting the bias to zero results again in the state  $[A^0]$  with the two positively charged viologenes surrounding the neutral TTF unit. (Reproduced from Collier et al. [28] with permission; copyright © 2000 by the American Association for the Advancement of Science).

**Bistable molecular systems can be engineered with potential exploitations as switches/memories (but control is typically non electric, e.g., light, pH, etc.!)**

## 4. Addressing a single molecule (test measurements)

Examples of intramolecular electronics are typically thought to operate in liquid, i.e., involving a multitude of molecules

As mentioned before, organic films can be produced (LB, SAMs) interfacing with the outer world and simple functions (e.g., diodes) involving the molecular film can be realized

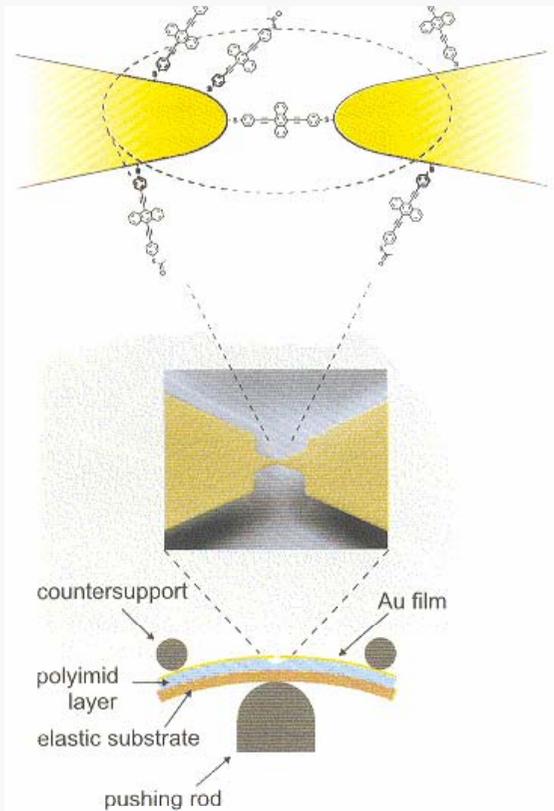
Practical exploitations, especially for more advanced functions (e.g., three terminal devices) do require the ability to integrate the molecule with inorganics and to address single molecules

**So far, no universal method has been discovered  
(great efforts are being devoted to this aim)**

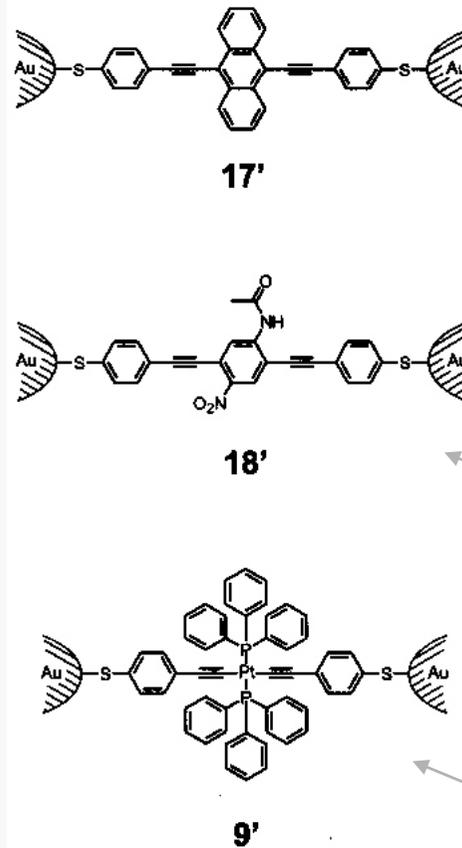
However, in particular for test purposes, procedures have been developed:

- Metal templates (electrodes with a gap in between, where the molecule can be located **at chance**) worked out by lithographies of inorganics (e.g., metals);
- SAM based templates as single molecule holder, for further addressing by Scanning Probe Microscopy (STM, in particular);
- Scaffolding techniques with biological entities (yet very rudimental)

# Test devices for single molecule electronics I

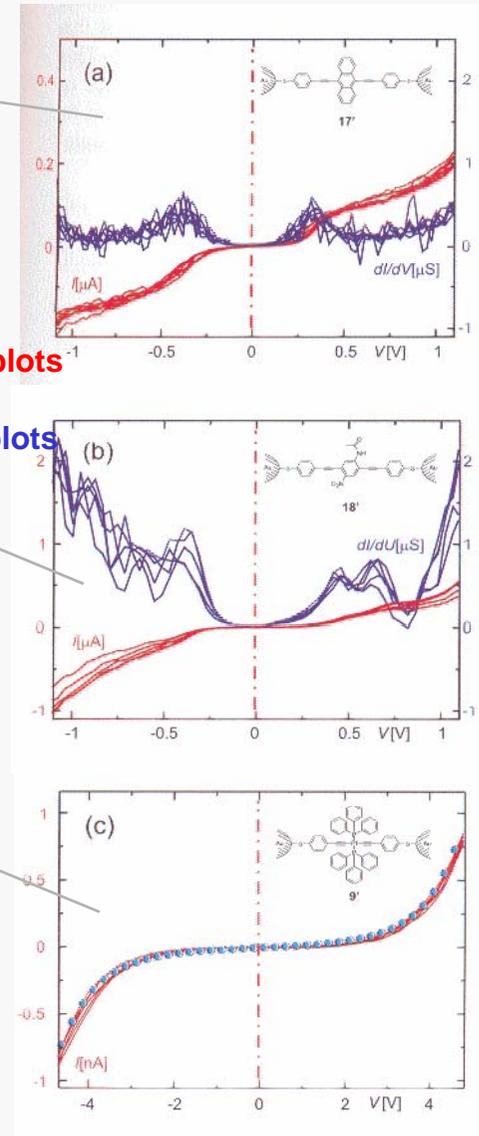


**Figure 19:** Scheme of a mechanically controlled break junction. On top of a bendable substrate a Au film is patterned with a freely suspended bridge in the center (see SEM micrograph in the middle panel). By bending the substrate in a three point support (lower panel: the pushing rod is driven by a motor), the Au bridge can be broken into two electrodes. By bending the substrate back and forth, the gap between the electrodes can be tuned with a distance resolution much better than Angstroms. This setup can be used to match the electrode gap precisely to the length of a molecule and finally to contact a molecule from two sides via well defined chemical S-Au bonds.



**Figure 20:** Rigid molecular rods **17'**, **18'** and **9'** immobilized between two gold electrodes with terminal sulfur groups.

Since the molecule length is below the maximum space resolution offered by lithography, a special “mechanical” break method is used to produce interelectrode (Au) gaps compatible with the molecule length, allowing single molecule addressing



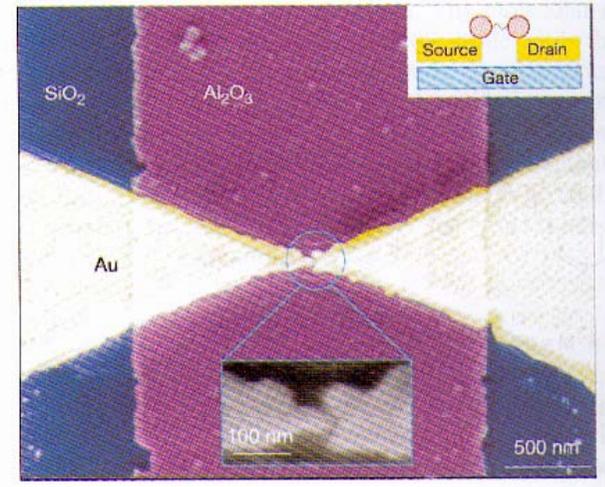
**Figure 21:**  $I$ - $V$  curves (red) and differential conductance  $dI/dV$  (blue) for a) Au-**17'**-Au and b) Au-**18'**-Au. c)  $I$ - $V$  curve (red) for Au-**9'**-Au and simulated current with a barrier height of 2.5 eV (blue circles) are shown.

# Test devices for single molecule electronics II

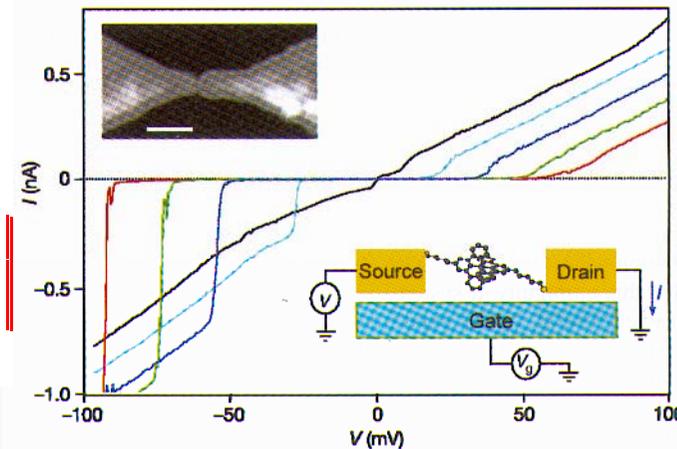
## 3.4 Three-Terminal Devices

While the implementation of two-terminal devices like diodes or resistive memory switches can be made on a very small scale of few nanometers or even with single molecules, it is much more difficult to obtain three-terminal devices, simply because three independent leads have to be structured on a few-nm scale. However, if one wants to build up integrated circuits (ICs) performing logic operations with traditional architectures, transistor-type devices are important because they are able to provide power amplification to the signal.

There are two possible approaches to solving the problem. One is to make a molecule with three branches, which are independently contacted by three leads. This would fit into the MME concept. However, it is an enormous challenge for lithography and will certainly involve physical phenomena much more complex than for a two-terminal molecular device. So far, no meaningful concept has been developed for this case. An HME-type approach is to place the third lead relatively far away (for example, buried in the substrate, see Figure 9), not in contact with the molecule, but able to modify the electrostatic potential inside the molecule by field effects. This has already been demonstrated [45], [47] in low-temperature experiments. The conductivity of single organometallic molecules was tuned by electrostatic gate electrodes and the properties of a Single Electron Transistor (cf. Chapter 16) were observed (Figure 22). The junction was switched from the Coulomb blockade regime with a strong suppression of the current to a conducting mode (which has still a high resistance:  $R \sim 100 \text{ M}\Omega$ ). The gate voltage dependence demonstrates that indeed a single molecule could be selected in a few cases. A key issue is to make this third gate electrode sufficiently close to the molecule to enable operation at small voltages. One of the emerging problems which can be seen in Figure 10 is then the reproducibility of the transistor, as the exact distance of the molecule with respect to the gate will affect the voltage necessary to switch the molecule's conductance. If, however, the molecular junction comprises of a large number of molecules, the tuning by electrostatic gating will be complicated by screening effects. The polarizability of the external molecules will weaken the field which acts on the inner molecules and the gate effect will be smeared out. This problem might be overcome by molecules which react to external stimuli with changes in the conformation, which might allow a cooperative switch of all molecules as soon as the external field reaches a certain threshold. This, however, would involve nucleation statistics as an uncertainty.

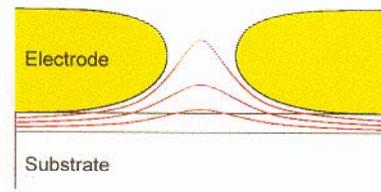


**Figure 9:** SEM picture of a Au electrode pair on top of an Al gate electrode, which is covered by an  $\text{Al}_2\text{O}_3$  insulator. Such a setup was used as a molecular field effect transistor [47].



**Figure 22:** A single molecule transistor with an organometallic molecule [45]. The electrode pair with  $\sim 2 \text{ nm}$  spacing has been manufactured by the electromigration technique (see SEM picture in the inset). The Si substrate served as gate electrode, separated by a  $\text{SiO}_2$  insulating layer. If the charge of the central Co ion is fixed to either  $\text{Co}^{2+}$  or  $\text{Co}^{3+}$ , no current can flow at small bias voltage due to Coulomb blockade (colored lines). If the gate is tuned such that  $\text{Co}^{2+}$  or  $\text{Co}^{3+}$  have the same energy, the ion can be continuously charged or uncharged; current can flow even at small bias voltages (black line).

**Figure 10:** Scheme of an electrode gap with a buried gate electrode formed by the substrate (covered by an insulating layer). When a gate voltage is applied, the equipotential lines (red) are not homogeneous in the gap region. If the molecule is far away from the surface, high gate voltages are needed to affect the potential at the molecule's position. If the distance from the gate electrode is not well controlled, this will result in strongly varying switching voltages.



Da R. Waser Ed., Nanoelectronics and information technology (Wiley-VCH, 2003)

**Single-electron transistor behavior may be achieved in organic/inorganic test devices**

# SAM-based molecular templates I

If we wish to study the conduction along a rod-like single molecule on a surface, while the surface acts as one electrode and the STM tip as the opposite electrode, we have to prepare the molecules such that they stand up right on the surface. However, isolated molecules often prefer to lie flat on surfaces due to Van-der-Waals interaction. To force configurations perpendicular to the surface, tripod attachments to the molecules has been proposed such as tetrahedral-shaped molecules in which three of the four legs are terminated by S-groups as 'alligator clips' [34]. Another approach makes use of a carpet of upright standing *insulating* alkanethiols to embed the *conducting* molecules under investigation. A stabilization of the position and the orientation of the sample molecules at angles between 60° and 90° to the surface was thus achieved. It should be noted that most of these experiments are in the tunnel regime, where the tip-molecule contact is not a chemical bond.

As an example, the molecular rod **16** (cf. Figure 12) is a fairly good electronic conductor, due to its conjugated  $\pi$ -system. To investigate its conduction properties it was embedded in a SAM matrix of electrically insulating molecules, such as dodecylmercaptan ( $C_{12}H_{26}S$ ) as a long-chain thioalkane [29], [35]. The film preparation started with the preparation of the pure alkane SAM layer. As observed by STM, the SAM layer is organized in domains, which resemble 2-D crystals. Within one domain, the molecules are perfectly ordered. Subsequently, the SAM layer is treated in a diluted solution of **16**, which leads to a partial exchange at the Au surface. STM studies show that the exchange takes place at domain boundaries and triple points while **16** is not observed within the domains. Since STM is based on the tunneling current, which is determined by both, the thickness of the SAM layer (i.e. the length of the molecules) and the conductance of the molecules, additional physical information is needed to separate the contribution of the two properties. The combination of conventional DC-voltage STM with a microwave AC-STM (alternating current-STM) technique allowed at the same tip the two properties to be distinguished [35]. Based on this method, the topography of the SAM film was separated from the conductance mapping. In many spots (but not always), the topography maxima attributed to molecules **16**, which are approx. 0.7 nm longer than the dodecane molecules, coincide with conductance maxima.

SAM can be used to "hold" a single molecule (e.g., OPE, oligophenylene ethynylene) which is thus precisely located and contacted to the metal layer underlying the SAM

Electrical/topographical addressing can be accomplished by tunneling microscopy (STM)

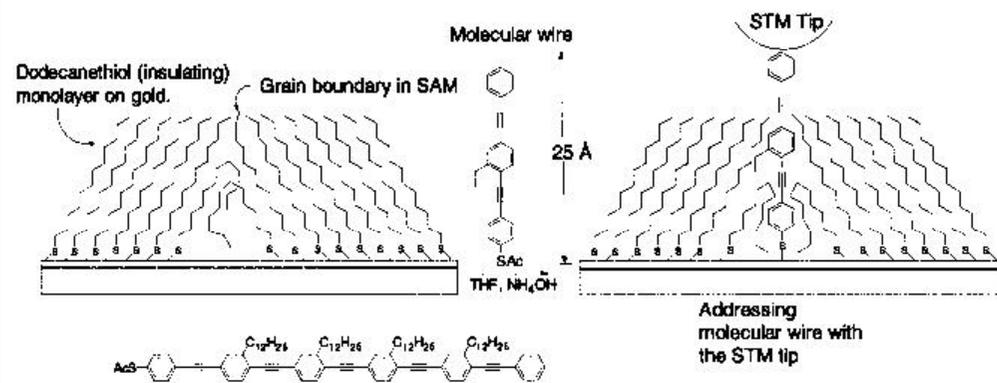


Figure 4.3 Protocol for inserting molecular wires into dodecanethiolate SAMs at grain boundaries and step edges. Relative conductance recording was done with a STM tip. The molecule at the bottom has also been used in this study.

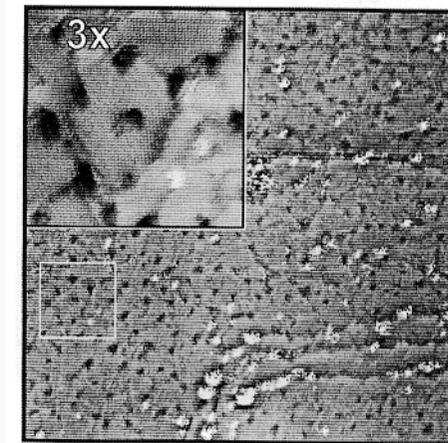
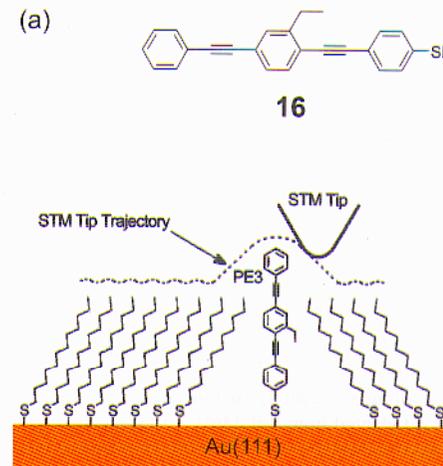
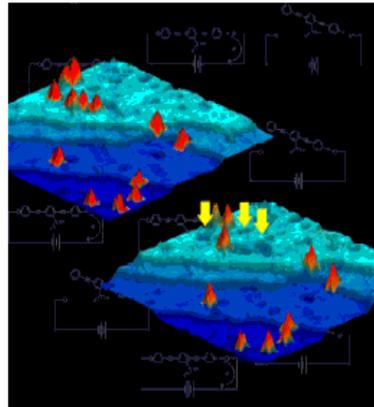
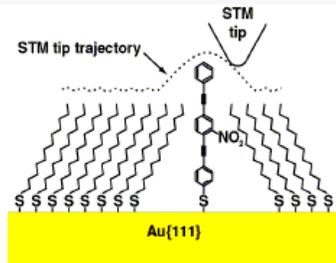


Figure 12: (a): Protruding molecular rod **16** out of a SAM layer of dodecylmercaptan. (b) STM picture of the sample displaying protruding rods **16** as brighter spots. Correlated maxima in the conductivity and the topology indicate the increased conductance through the molecular rods **16**. [35]

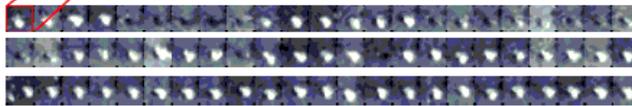
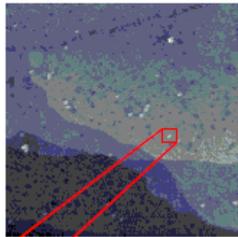
# SAM-based molecular templates II

J.M. Tour, Molecular Electronics  
(World Scientific, 2003)

See also Bumm et al,  
Science 271 1705 (1996)



We use self-assembly to control and STM to observe the switching of single molecules.



The OPE molecule can undergo a (conformational and electrical) switching between two stable states after application of a localized electric field

**STM allows for control and assessment of the single molecule properties (electrical and morphological)**

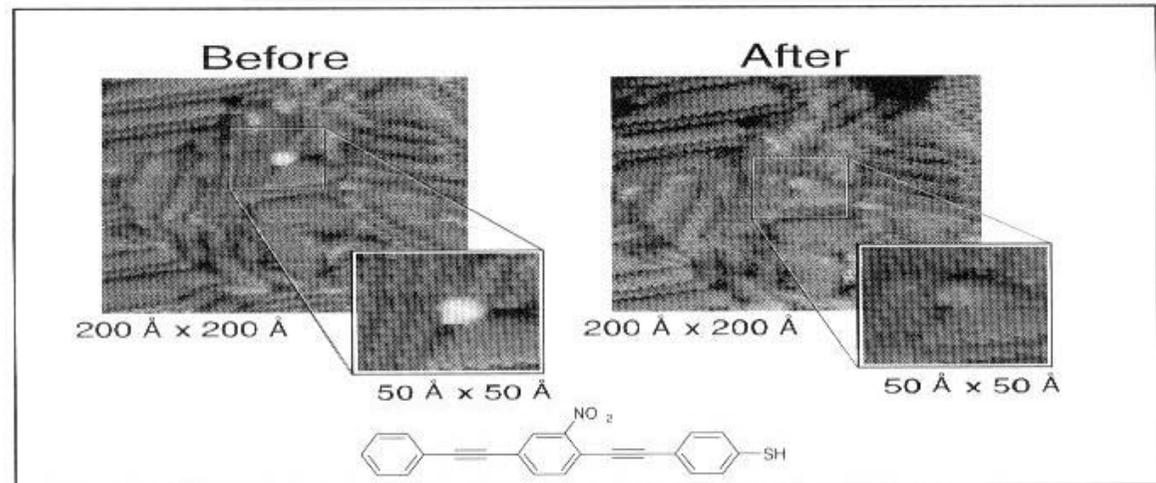


Figure 4.4 A single molecule (nitro OPE structure at bottom) in an alkanethiolate matrix SAM on gold. The dark spheres are the terminal methyl groups of the alkanethiolates. "Before" shows the OPE in an "on" state, and after a voltage pulse from the tip, the OPE is in an "off" state shown under "After". Note that the OPE appears to have too large a diameter; however, when an asperity is sharper than the STM tip, one obtains an image of the tip rather than an image of the asperity.

# SAM patterning with STM

See also Donhauser et al,  
Science 292 2303 (2001)

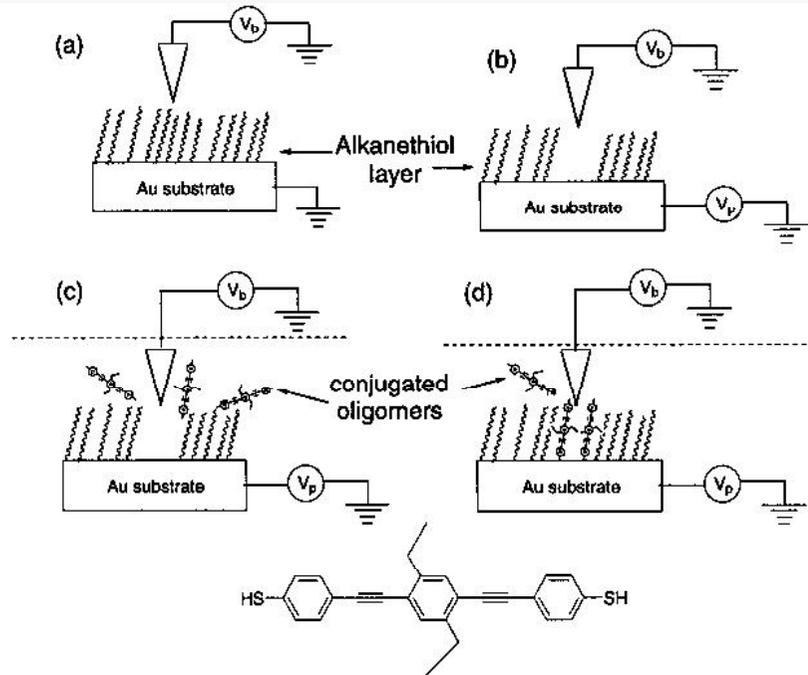


Figure 4.6 Schematic representation of the lithographic patterning and replacement of conjugated molecules in an alkanethiolate matrix. (a) Normal STM imaging of an alkanethiolate SAM with tip bias  $V_b$ . (b) SAM removal by applying a voltage pulse  $V_p$  to the substrate. (c) Carrying out the same voltage pulse as in (b), but under a solution of molecular wires (expanded structure at bottom) causes (d) insertion of the wires into the newly vacated site.

The location where the single molecule will be placed can be controlled by patterning the SAM layer through application of a voltage pulse (again, with STM)

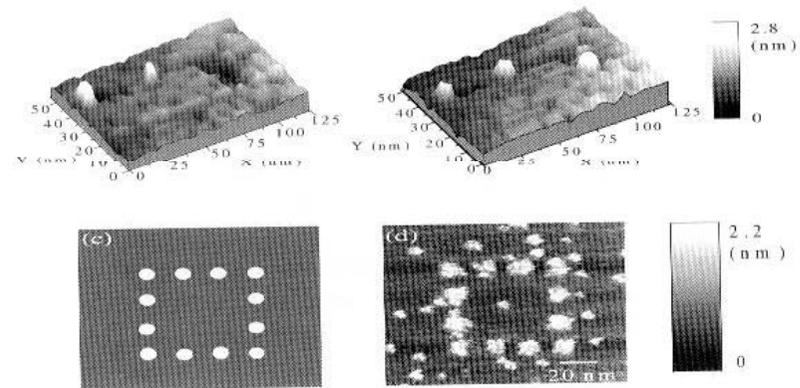


Figure 4.7 (a) A dodecanethiolate SAM surface after three consecutive voltage pulsing events. The first two pulsed locations have molecular wires inserted while the third location remains to be filled. (b) The image taken a few minutes later shows that wire insertion at the third pulse location is now complete. (c) A programmed rectangular pattern for controlled voltage pulses. (d) The image of the patterned SAM after pulsing and molecular wire insertion. Some random insertions at grain boundaries or other defect sites are also evident.

SAM is locally damaged or removed after application of an electric pulse

The damaged (void) SAM molecule is “replaced” by the molecule to be investigated

## “Caveat” about the organic/inorganic interface

The use of electrodes to contact the molecule implies modifications of the designed transport properties of the molecule because of:

- Modifications of the vicinal orbitals (especially in the case of chemical bonds);
- Molecular dipole images due to the presence of the conductive layer;
- Geometries of the electrodes can play a role

Inelastic scattering processes can occur at the interface;  
The quantum-mechanical model of the molecule must account for the presence of the electrodes (but this is a highly demanding task)

**Quantum confinement effects may be masked because of the metal electrodes**

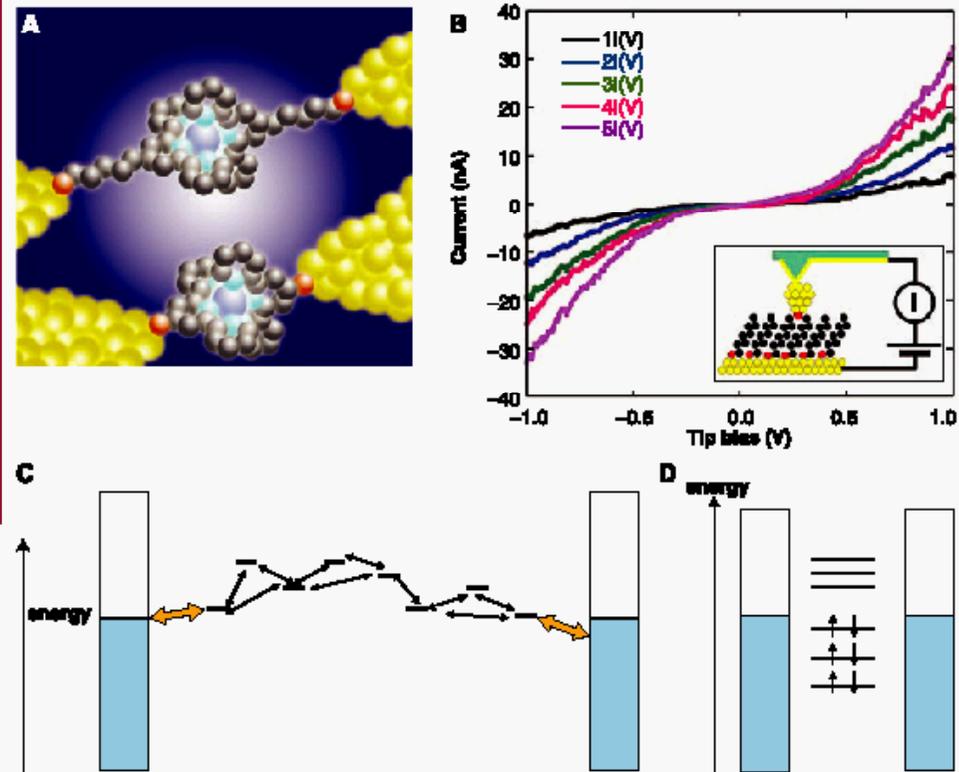


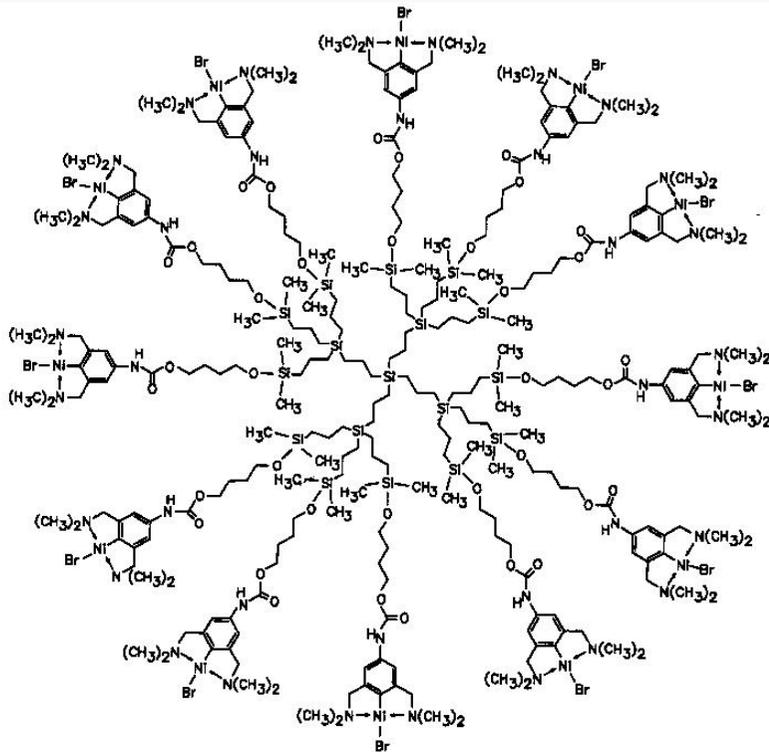
Fig. 1. (A) Schematic single molecule junction between two continuous electrodes [after (5)] (B) Schematic (inset) of an alkane thiol adlayer with gold dot current collector, measured using AFM. Actual data is also shown, corresponding to (suggested) transport through 1, 2, 3, 4, and 5 molecular strands [from (12)]. (C) Many site molecular wire, with striped arrows indicating coupling between molecular levels and electrode and black arrows indicating intersite interactions along the molecular chain. The filled and empty parts of the rectangles represent filled and empty levels of the electrode conduction bands. (D) Molecular orbital equivalent of 1e, including the effects of electrode interaction, such that the electrode Fermi level lies in the HOMO-LUMO gap.

Fermi level is in between HOMO and LUMO

See Nitzan and Ratner  
Science 300 1384 (2003))

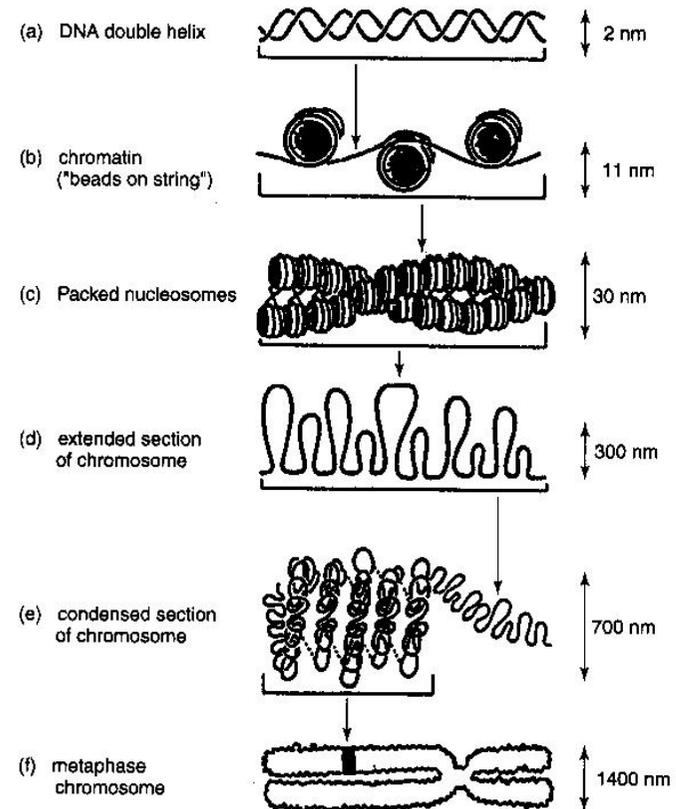
## 5. Suggestions and methods from biophysics

### Example: a self-assembled dendritic macrostructure



**Figure 11.19.** Dendrimer catalyst (dendralyst) with an Si core, and terminal group aryl-nickel complexes as the catalytically active functional groups. [From J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwenn, P. Wijkens, D. M. Grove, and G. van Koten, *Nature* **372**, 659 (1994).]

### Example: DNA self packing (and replication)



**Figure 12.11.** Successive twistings and foldings during the packing of DNA into mammalian chromosomes, with the sizes at successive stages given in nanometers. [From R. J. Nossal and H. Lecar, *Molecular and Cell Biophysics*, Addison-Wesley, Boston, 1991, Fig. 4.9 (p. 118).]

**The organics world is full of possibilities for the self organized of complex structures**

**Can this be exploited, in a perspective view, to realize novel (nanoelectronics) devices?**

# A few words on nanobiotechnology possibilities

One possibility: exploitation of **nanoparticles and organics** to produce complex architectures

Key ingredient: **functionalization** of the organics (macro)molecules, i.e., controlled modifications aimed at enabling an interface with the inorganic (nanoparticle) components

**Templates** (complex structures) can be designed and realized

The unique electronic, optical, and catalytic properties of metal and semiconductor nanoparticles (1–200 nm), together with the different methods available for the preparation of nanoparticles of controlled shape and size, provide exciting building blocks for nanoscale assemblies, structures, and

The chemical functionalities associated with nanoparticles enable the assembly of 2D and 3D NP architectures on surfaces.<sup>[9]</sup> On the basis of the tremendous success in supramolecular chemistry,<sup>[12]</sup> NPs functionalized with various molecular and biomolecular units were assembled into complex hybrid systems. Composite layered or aggregated structures of (macro)molecule-cross-linked NPs on surfaces

The convergence of biotechnology and nanotechnology has led to the development of hybrid nanomaterials that incorporate the highly selective catalytic and recognition properties of biomaterials, such as proteins/enzymes and DNA, with the unique electronic, photonic, and catalytic features of nanoparticles. The conjugation of NPs and other nanoobjects (e.g. nanorods and carbon nanotubes) with biomolecules is an attractive area of research within nanobiotechnology.<sup>[20,21]</sup> Biomolecules are fascinating macromolecular structures in terms of their unique recognition, transport, and catalytic properties. The conjugation of NPs with biomolecules could provide electronic or optical transduction of biological phenomena in the development of novel biosensors.<sup>[22]</sup> Enzymes, antigens and antibodies, and biomolecular receptors have dimensions in the range of 2–20 nm, similar to those of NPs, thus the two classes of materials are structurally compatible.

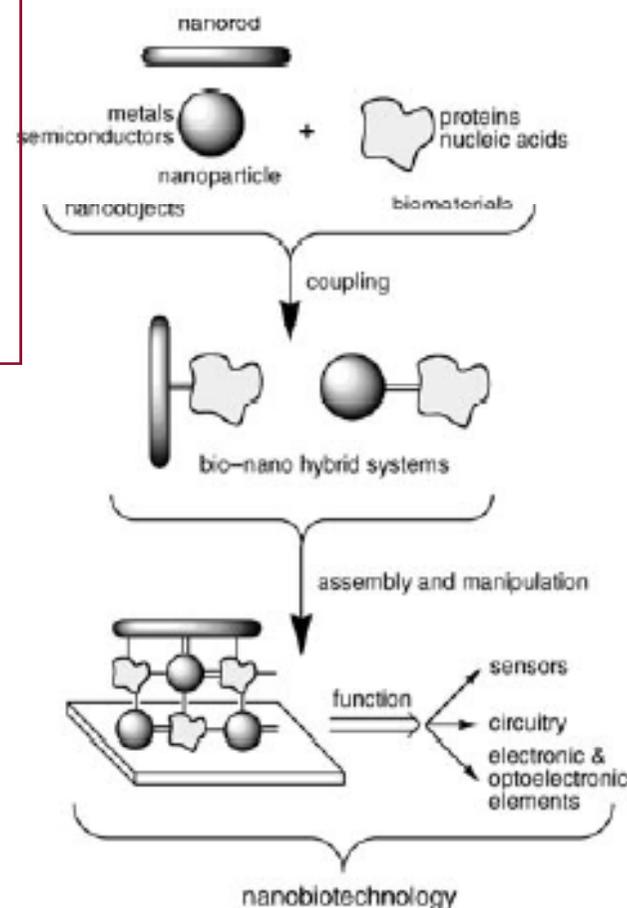


Figure 1. The conceptual generation of biomolecule–nanoparticle/nanorod conjugates to yield functional devices.

Reviews

nd E. Katz

Nanobiotech

Angew. Chem. Int. Ed. 2004, 43, 6042–6108

Integrated Nanoparticle–Biomolecule Hybrid Systems: Synthesis, Properties, and Applications

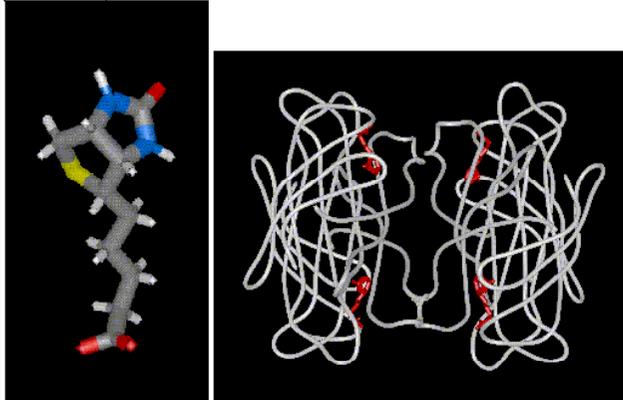
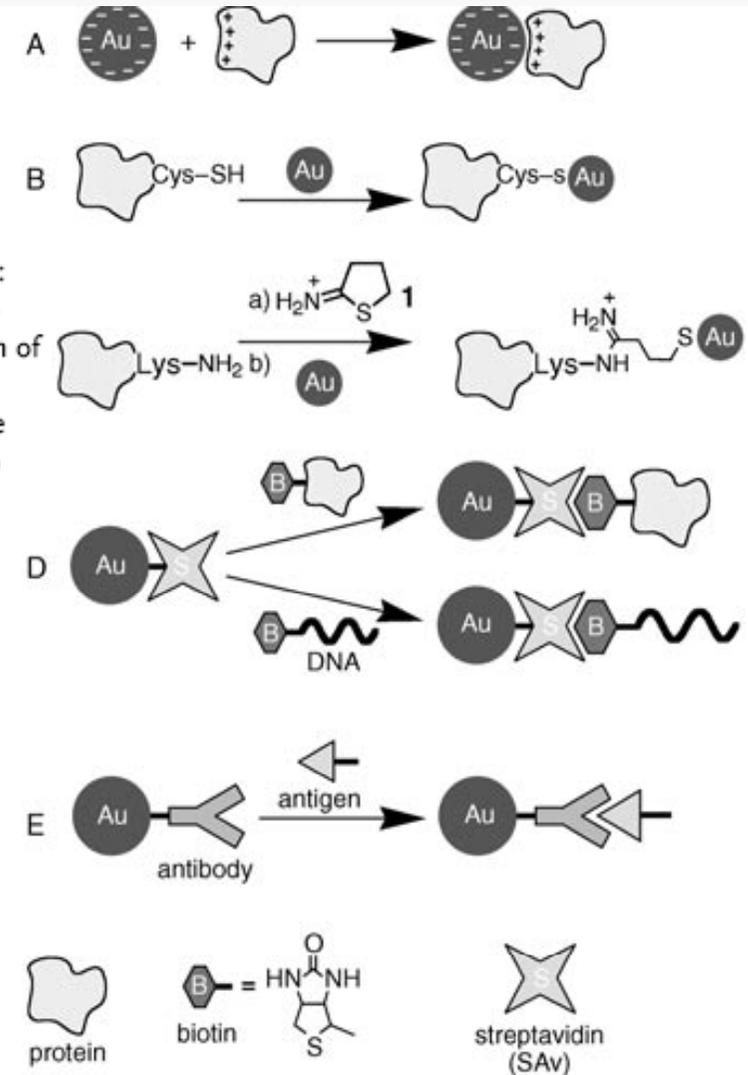
Eugenii Katz and Itamar Willner\*

**Hybrid  
biomolecular/nanoparticle  
systems**

# Examples of nanobiotechnology I

Several steps are involved into the system realization

**Figure 2.** Formation of the biomolecule–nanoparticle (NP) hybrids: A) The assembly of NP–protein conjugates by electrostatic interactions. B), C) The formation of NP–protein conjugates by adsorption of NPs on natural (B) and synthetic (C) thiol groups of the protein. D), E) The assembly of biomolecule–nanoparticle conjugates by the use of bioaffinity interactions upon streptavidin–biotin binding (D) and antibody–antigen associations (E).



## Biotin/Streptavidin Tutorial

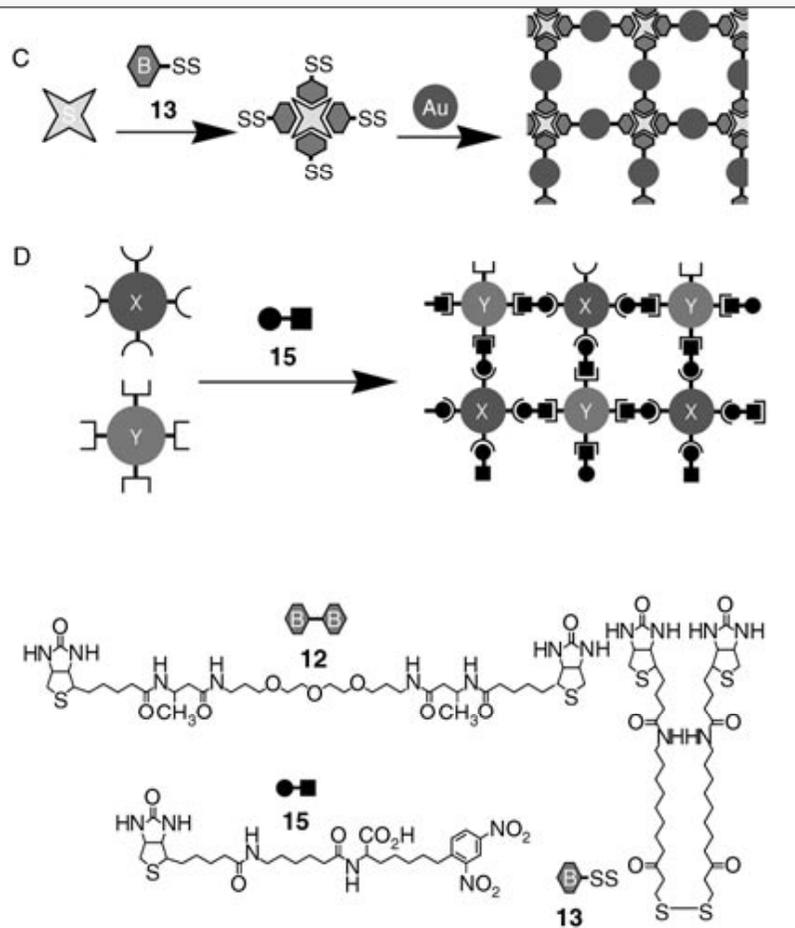
The streptavidin/biotin system is of special interest because it has one of the largest free energies of association of yet observed for noncovalent binding of a protein and small ligand in aqueous solution ( $K_{\text{assoc}} = 10^{14}$ ). The complexes are also extremely stable over a wide range of temperature and pH.

The streptavidin protomer is organized as an 8-stranded beta-barrel. Pairs of the barrels bind together to form symmetric dimers, pairs of which in turn interdigitate with their dyad axes coincident to form the naturally-occurring tetramer.

<http://amber.scripps.edu/tutorial/streptavidin/index.html>

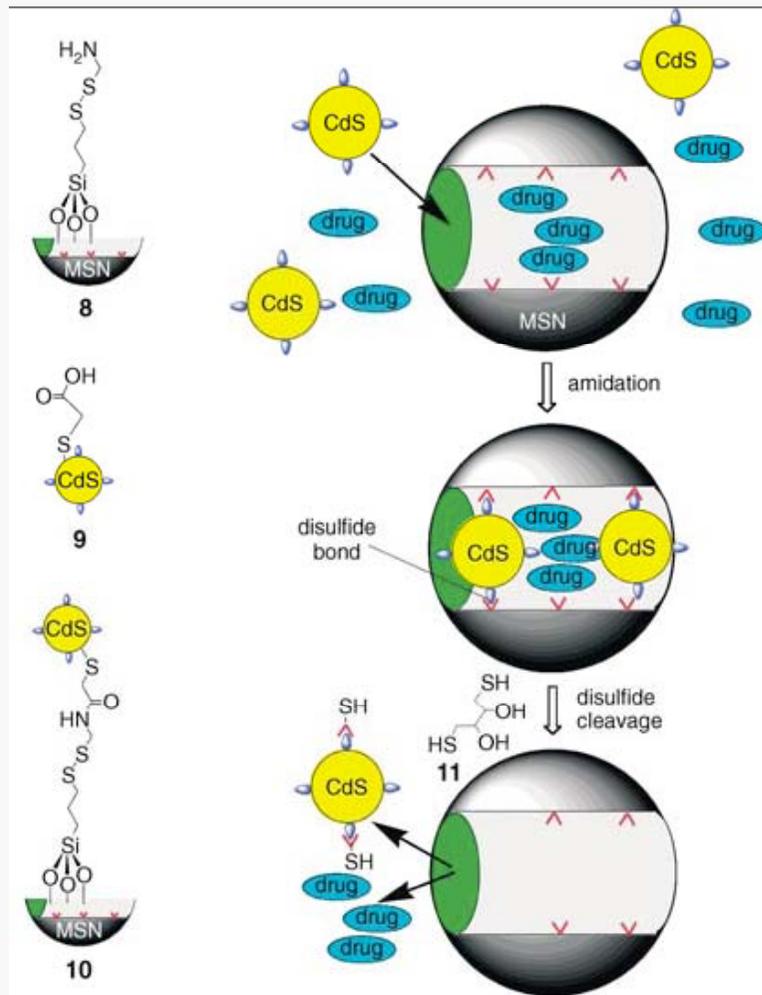
# Examples of nanobiotechnology II

## Au nanoparticle network



**Figure 7.** The use of biotin-streptavidin (SAv) interactions to build nanoparticle networks: A) Streptavidin as a linker between biotin-functionalized Au NPs; B) A biotin dimer used to link streptavidin-functionalized Au NPs; C) Streptavidin-linked thiolated biotin used to build NP networks; D) The formation of a network from two types of NPs that are functionalized with different recognition units and cross-linked with a bifunctional linker, **15**, which is composed of a biotin unit and a dinitrophenyl-antigen unit.

## CdS nanospheres (drug delivery)



**Figure 6.** CdS NP-capped mesoporous silica nanosphere (MSN)-based system for the controlled delivery of drugs and neurotransmitters. (Adapted from Ref. [108], with permission; Copyright American Chemical Society, 2003).

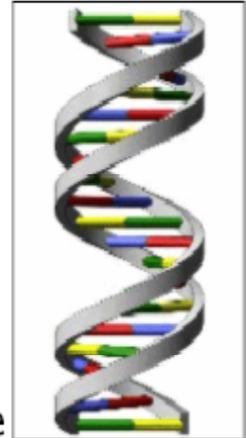
# The marvellous world of DNA (a very very few words!)

Among other molecules, DNA has several specific features, including, e.g.:

Key points:

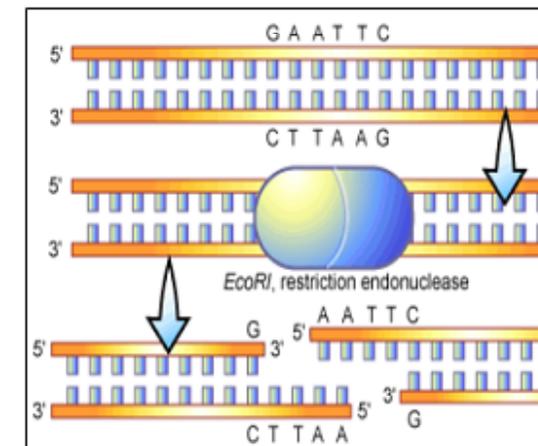
- Great flexibility in tailoring the molecule;
- Complex self-assembling features;
- Compatibility with biological entities

- Molecola rigida (struttura a doppia elica) e relativamente stabile
- Molecola facilmente sintetizzabile
- Possibilità di auto-assemblaggio
- Disponibilità di molti enzimi di controllo
- Tecniche di biochimica sviluppate



## Enzimi per il controllo del DNA

- Enzimi di restrizione: taglia la molecola a sequenze specifiche
- Ligasi: unisce covalentemente due molecole
- Elicasi: svolge l'elica
- DNA polimerasi: fa copie della sequenza
- Topoisomerasi: cambia avvolgimento dell'elica



**DNA (and other biophysical macromolecules) can be of interest also in view of bottoms-up fabrication of systems aimed at electrical transport**

Material e tratto dal seminario di Daniele Tomerini, Lug. 2005

# Unclear electrical properties of DNA strands

## Long (16 $\mu\text{m}$ ) DNA filament between two electrodes

Sono stati effettuati una decina circa di studi (teorici e pratici) sul possibile utilizzo di molecole di DNA per trasmettere segnali elettrici in circuiti, dal 1998 (\*) in poi. Questi evidenziano una conduttività dipendente da diversi parametri

\*, Braun E, Eichen Y, Sivan U, Ben-Yoseph G (1998) Nature 391:775

## DNA filament between a short (8 nm) gap

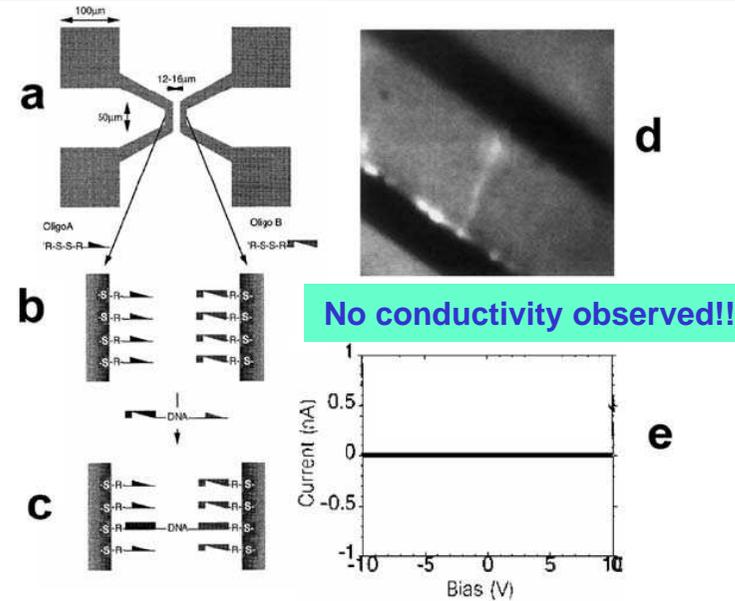
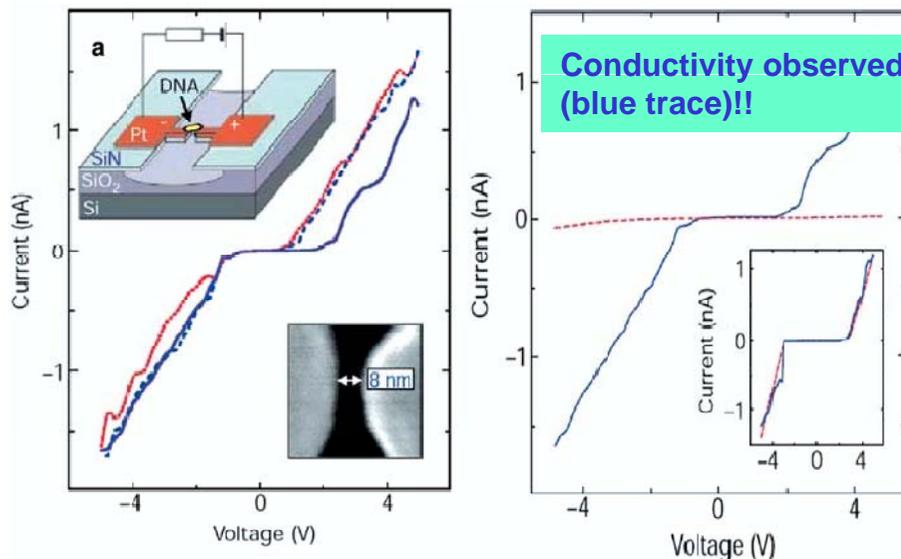


Fig. 1 a-c 16- $\mu\text{m}$ -long  $\lambda$ -DNA was stretched between two metal electrodes using short hang-over single strands complementary to single strands that were preattached to the metal electrodes. d A fluorescent image of the DNA molecule, connecting the metal electrodes. e The flat, insulating current-voltage that was measured. (from [12], with permission; Copyright 1998 by Nature Macmillan Publishers Ltd)

**In specific conditions, DNA can exhibit conductive properties (but the topic is still under debate)**

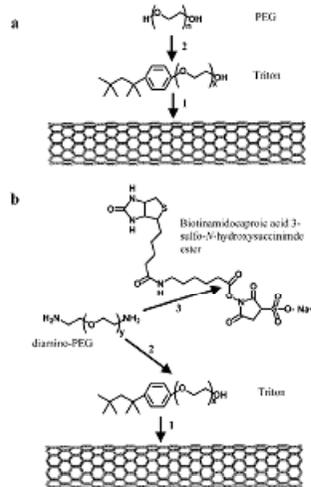
# CNTs as interconnects in DNA-based systems

Specifically functionalized CNTs can be used as interconnects

## Funzionalizzazione dei SWNT

E' necessario agire in 3 stadi, assorbendo TRITON, su questo PEG, per avere una maggiore affinità con la biotina e poi con la proteina di interesse. Alla pagina successiva, immagini AFM dell'assorbimento.

Functionalization of Carbon Nanotubes for Biocompatibility and Biomolecular Recognition, Shim, Kan, Chen, Nanoletters 2002

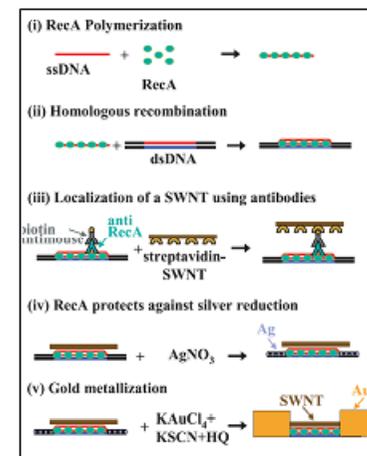


\* A surfactant Triton-X 100 is first adsorbed onto the sidewalls of SWNTs followed by adsorption of PEG. \* Triton-X 405 is adsorbed on SWNTs followed by amine-terminated PEG covalently linked to biotin.

## Autoassemblaggio di DNA con SWNT

A fianco lo schema per l'assemblaggio tra uno strand di DNA e un transistor: quest'ultimo (pre-funzionalizzato) viene autoassemblato ad una doppia elica (anch'essa funzionalizzata) mediante riconoscimento specifico.

DNA-Templated Carbon Nanotube Field-Effect Transistor, Science, 302, 1380



Public release date: 20-Jul-2005

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Contact: Garazi Andonegi  
[garazi@elhuyar.com](mailto:garazi@elhuyar.com)  
34-943-363-040  
[Elhuyar Fundazioa](#)

### DNA-based molecular nano-wires

An international consortium of 7 universities and research centres are seeking an alternative to silicon-based microelectronics in using molecules of DNA, which could enable a reduction in size of the current systems by a thousand times. The University of the Basque Country (UPV/EHU) is participating in this project through the research group led by Professor Angel Rubio Secades of the Department of Materials Physics.

The really innovative nature of this project lies, on the one hand, in the use of all the recognition and self-assembly potential of biological systems, more specifically, using derivatives of DNA such as G4-DNA, M-DNA and PC-DNA with a greater electronic potential than DNA itself (which is by itself an insulator). On the other, it lies in carrying out studies in surface chemistry combined with scanning probe microscopy (SPM) and spectroscopy, the measurement of electrical transport, sophisticated nano-manufacture and theoretical studies of the computational simulation of the stability and properties of synthesised devices and/or motivating new structures that might have a greater potential. In this way the manner of designing nano-wires using these molecular derivatives is being developed. As is the way of controlling the interaction between the molecular electrode and the molecular substrate, seeking a deep understanding of the energy conduction mechanisms of these nano-wires and being able to produce models of nanomolecular devices based on these DNA derivatives.

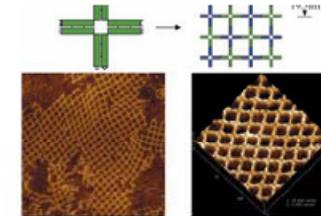
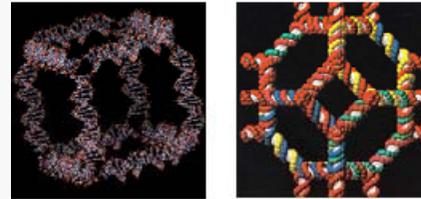
[http://www.eurekalert.org/pub\\_releases/2005-07/ef-dmn072005.php](http://www.eurekalert.org/pub_releases/2005-07/ef-dmn072005.php)

# Supramolecular structures and scaffolding

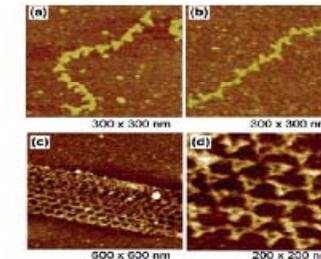
Supramolecular structures can be built based on DNA, including **molecular scaffolds**

**Possibilities seem to exist for producing (in a way similar to self-assembly) complex molecular networks interconnected by nanowires consisting of CNTs**

## Strutture supramolecolari

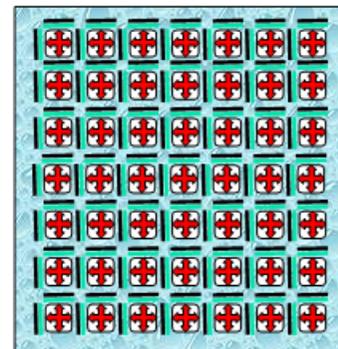


Chen et al. *Nature* 250, 631-633 (1991)  
 Zhang, Y. W. and H. C. Bosman (1994).  
*JACS* 116(5): 1991-1999  
 Yan, H., S. H. Park, et al. (2003).  
*Science* 301(5641): 1882-1884.  
 Liu, D. et al. (2004).  
*JACS* 126(8): 2324-2325



## Impalcature molecolari (I)

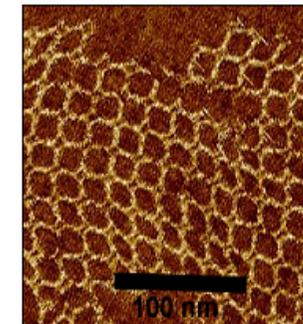
Ogni transistor a nanotubi va funzionalizzato in modo che si possa assemblare alla localizzazione esatta in cui si vuole inserire



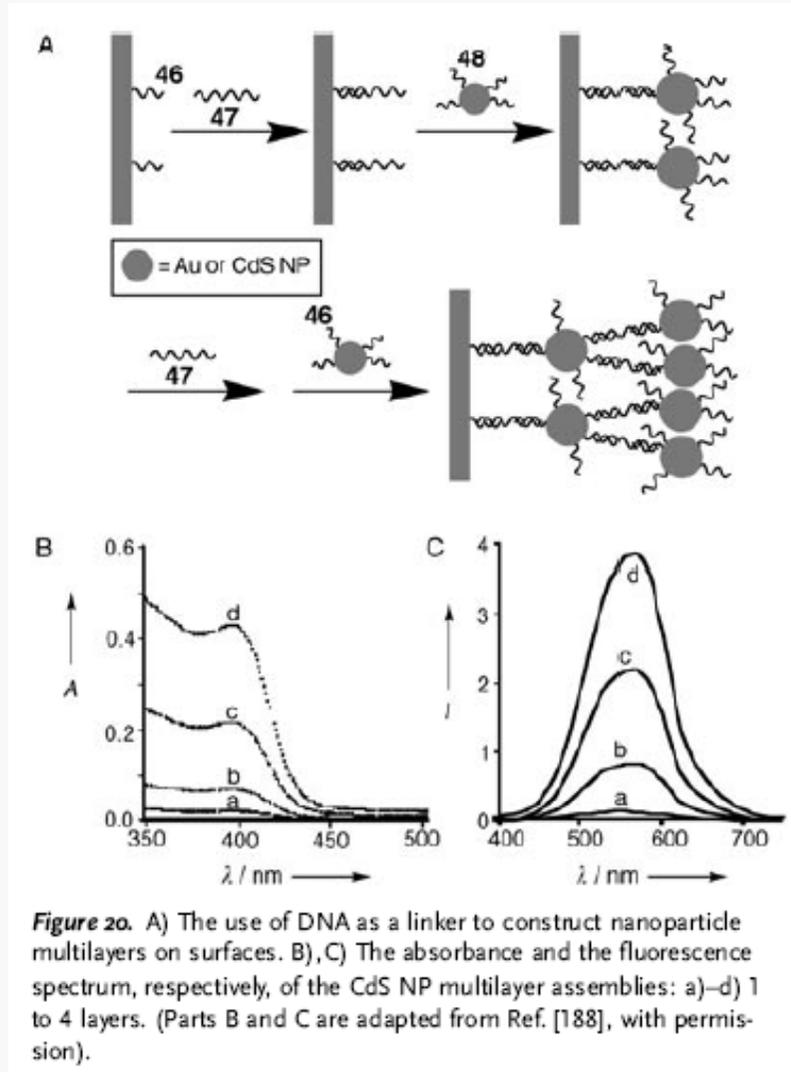
— Nanocavi della struttura (nanotubi)  
 + Transistor a nanotubi  
 ○ Base di DNA

## Autoassemblaggio di impalcature molecolari

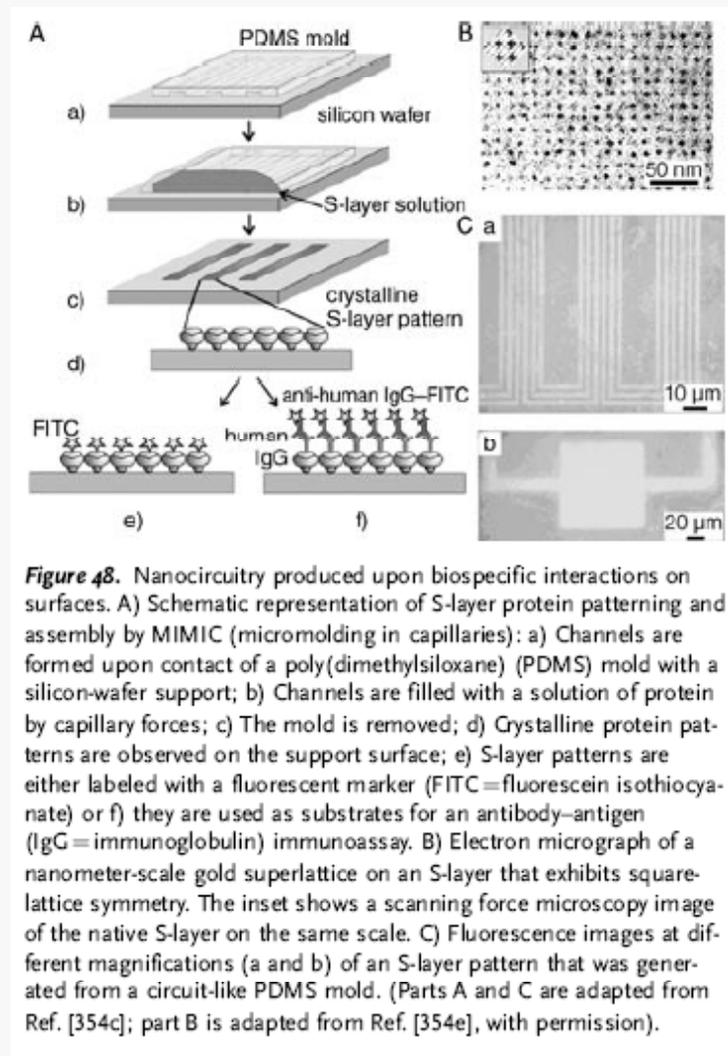
Le molecole di DNA vengono assemblate in strutture ordinate periodiche, a cui associare successivamente i dispositivi. Questi saranno poi interconnessi tra di loro da nanocavi.



## Other examples of DNA exploitations I



### DNA as a linker for nanoparticle multilayers



### “Nanocircuitry” fabrication

## Other examples of DNA exploitations II

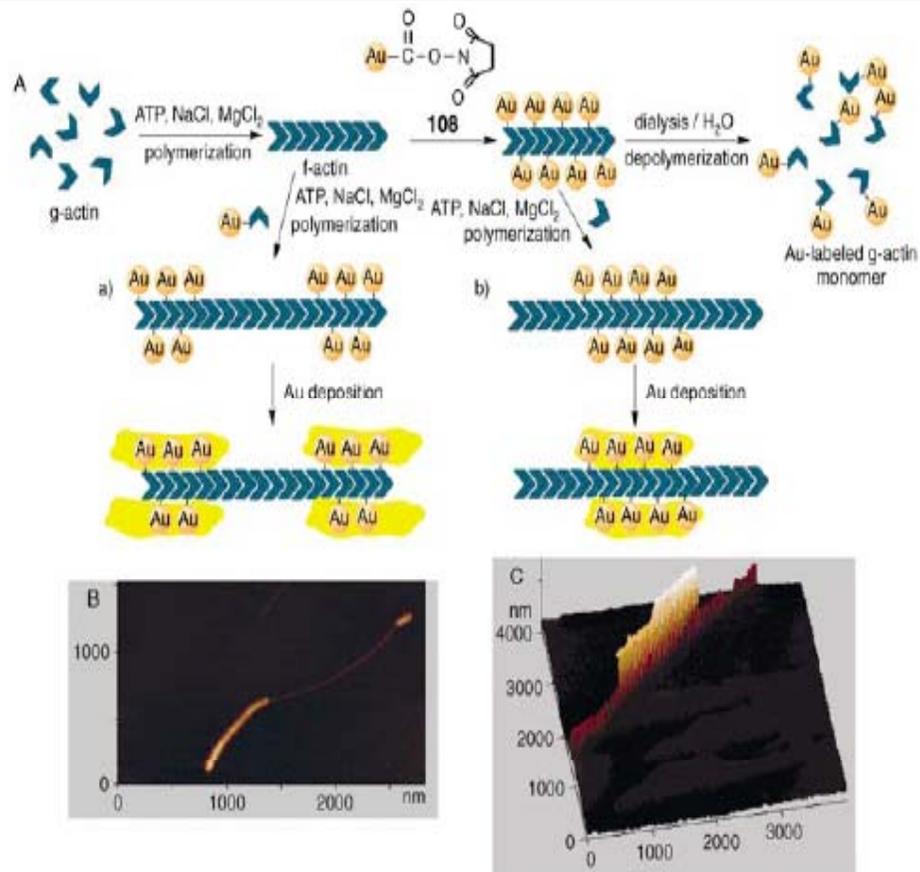


Figure 50. A) The assembly of patterned actin-based Au nanowires: Left: a Au wire/actin/Au wire filament; Right: an actin/Au wire/actin filament  
B) AFM image of the Au wire/actin/Au wire filament. C) AFM image of the actin/Au wire/actin filament.

An enormous world of possibilities is linked to the use of DNA and other bio-organics materials (yet to be understood the applicative potential and to fix several fundamental issues)

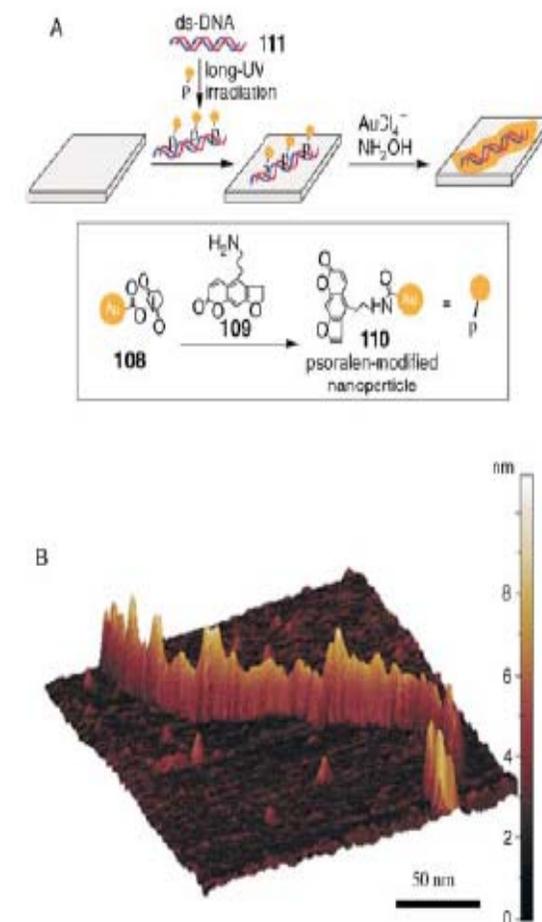


Figure 53. A) Assembly of a Au NP wire in the pA/pT template by using Au NPs that are functionalized with intercalator (psoralen) molecules. B) AFM image of the Au NP wire in the pA/pT template. pA/pT = polyadenylic acid/polythymidylic acid.

## 6. Organics and optoelectronics I

General situation with all proposed electronics applications of organics is that work has still to be done to overcome technical and, maybe, fundamental problems

In particular, contrary to the enormous variety of molecules and approaches, ways to practically exploit single molecule properties are still far from being found

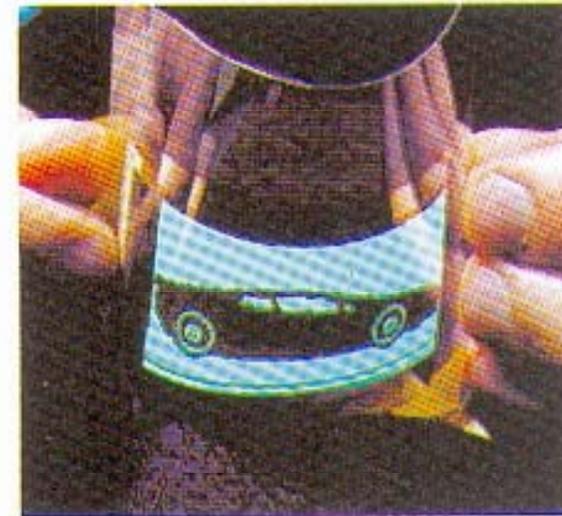
Contrary to “pure” electronics applications, organics-based optoelectronics is gaining practical momentum

**In this case, there is no need for single molecule addressing** (more molecules emit, the better is the device...)

Fabrication of Organic Light Emitting Diodes (OLEDs) is presently in the industrial stage, with advantages respect to conventional inorganic (semiconductor) devices in terms of:

- ✓ Cheapness, simple fabrication and large scale production;
- ✓ Wide spectral range which can be covered (e.g., “white” light achievable);
- ✓ Exploration of new possibilities (e.g., “electronic paper”).

Durability and stability problems are being solved (but lasing effect, mostly due to the high intracavity energy density and the broad emission features, is not yet fully achieved)



**Figure 15:** A flexible 0.18 mm thick passive matrix OLED display fabricated by Universal Display Corporation.

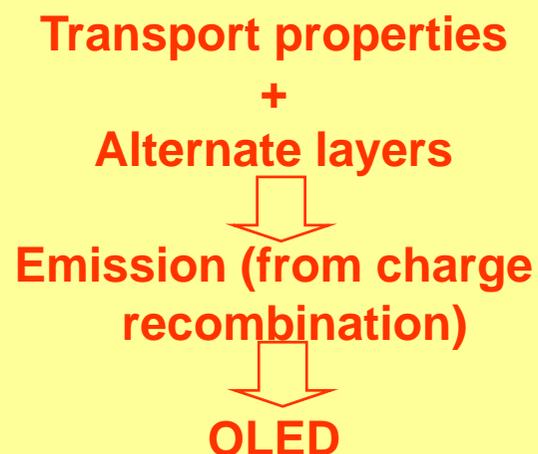
## Organics and optoelectronics II

Organic dyes with conjugated  $\pi$ -electron systems have attracted a large and rapidly increasing interest in the last decade as possible materials for various electronic and optoelectronic devices because of their advantageous semiconductor properties. For application as photoactive materials in photocopiers, they have already reached maturity and replaced inorganic semiconductors on a large scale. Efficient electroluminescence (EL) from an organic solid was first demonstrated in large (50  $\mu\text{m}$  to 1 mm thick) single crystals of anthracene [1], [2]. Although these devices showed a high EL quantum efficiency of up to 8 %, they were impractical due to the large applied voltage (>1000 V) required to inject electrons and holes into the crystal. More recently, practical organic light-emitting devices (OLEDs) consisting of sequentially vacuum-deposited layers of hole- and electron-transporting molecular materials [3], [4], [5], [6] or of spin-coated thin polymer films [7], [8] have been demonstrated with active device thicknesses of only a few hundred Ångströms. Applying about 3 to 5 V, they are already brighter than a conventional TV screen with much higher efficiencies, brilliant colors, large viewing angle, switching times fast enough for video real time image displays and lifetimes well above 10,000 hours. The first displays based on organic semiconductors have become commercially available and companies like Pioneer and Philips and many others are currently developing this promising technology. Small independent firms, such as Universal Display Corporation in the U.S. and Cambridge Display Technology in the U.K., have been created solely to turn these innovations into commercial reality.

The large interest is not only caused by technological aspects such as the low costs, the possibility to prepare flexible large area devices at low process temperatures on polymer foils, and the almost unlimited variety of organic compounds that allow tuning of e.g. energy levels and emission colors. They also have some unique physical properties and advantages compared to inorganic semiconductors [9]. Due to their low dielectric constants, the reflection losses at interfaces are lower than for III-V-semiconductors. The internal fluorescence efficiency is close to unity for some organic dyes with their emission peaks strongly red shifted to the absorption edge thus avoiding re-absorption losses in the devices. For this reason, it is possible to prepare efficient sandwich structures of several OLEDs with different emission wavelengths [10]. The electronic structure of organic semiconductors is largely determined by the individual molecules and only weakly modified by solid state effects. Therefore, interface states play a minor role. Also, amorphous layers grown on cheap, flexible substrates exhibit attractive electrical properties to allow for efficient electroluminescence. The amorphous matrices also enable the incorporation of a wide range of dopants, if necessary in high concentrations, to tune both the conduction type [5], [11] and the emission wavelength [12]. For instance, the admixture of about 7 % of phosphorescent dyes has led to OLEDs that convert 100 % of the electrically excited molecular states into visible light with internal efficiencies close to unity [4], [13], [14].

Thin molecular crystal films or polymers can be used to both **charge transport and emission**

As in semiconductor LEDs, emission involves **charge recombination** (in molecular terms, this can be seen as a vibronic emission)



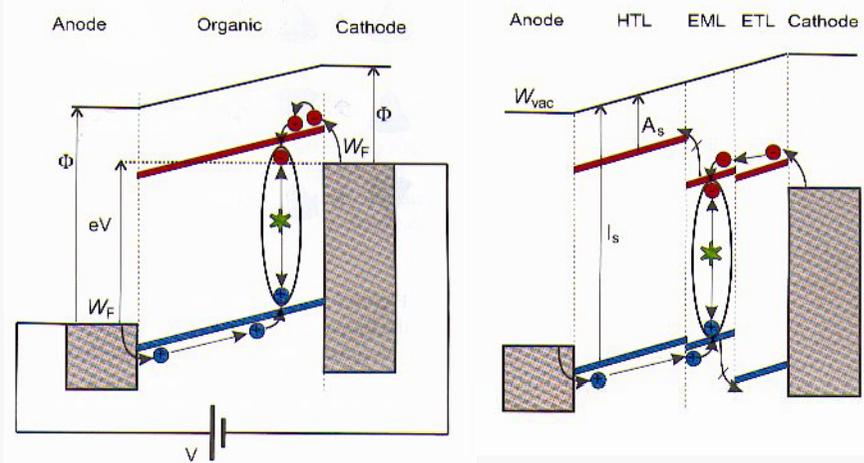
# Double layer OLED

## 3.2 Single and Double Layer OLEDs

The operation principle of a single layer OLED is schematically shown in Figure 5. For such devices, the exciton recombination region is near the middle of the device if injection of holes from the anode and electrons from the cathode into the organic material is equally efficient, and the mobilities for both carrier types are also equal. Otherwise the active region where excitons are formed moves close to one of the electrodes which leads to a reduced efficiency: The type of carrier which is more mobile or more efficiently injected has a higher probability of reaching the opposite electrode without being captured by the opposite charge type (thereby reducing  $\gamma$ ). Moreover, excitons formed close to an electrode may be quenched by defects or diffuse to the electrode where they non-radiatively recombine.

Typical OLEDs therefore consist of at least two or three layers of different organic materials (c.f. Figure 1), i.e. forming single or multi-heterojunction devices. The single heterojunction device of Tang and van Slyke [3] consisting of TPD and Alq<sub>3</sub> sandwiched between ITO and Al, marked a breakthrough in low voltage, high efficiency device performance. In their OLED, the energy levels were chosen such that there was only a small barrier to hole injection from the hole transport layer (HTL) into the light emission layer (EML), while electrons from the EML met a high barrier so they were not able to penetrate into the HTL. Consequently, there are almost no loss by electrons reaching the anode. On the other hand, the hole mobility in the EML was much lower than the electron mobility. Therefore, the active region is close to the heterointerface in the EML, i.e. roughly in the middle of the OLED structure, thus avoiding the problems encountered in single layer devices (see, for example, Ref. [33]).

Even in the double layer OLED, losses by holes reaching the cathode or by quenching at the cathode can be significant, especially if the thickness of the EML is low, i.e. on the order of the exciton diffusion length. However, thin layers of these low mobility (and hence high resistance) layers are desirable to minimize the operating voltage. Consequently, optimized devices comprise a second heterojunction: An electron transport layer (ETL) is inserted between the EML and the cathode. It should have a wider HOMO-LUMO gap and a larger ionization potential than the EML so that neither excitons nor holes from the EML can penetrate into the ETL [34] (c.f. Figure 5). Therefore, this layer is variously referred to as the hole-blocking or exciton blocking layer (HBL or EBL, respectively). Such heterojunction architectures are self-balancing due to their internal barriers, i.e. they guarantee  $\gamma \rightarrow 1$  without requiring either the mobilities or contact injection barriers to be equal.



**Figure 5:** Energy level scheme for a single layer (top) and double heterojunction OLED (bottom) with an applied bias voltage  $V$  showing the vacuum energy level  $W_{vac}$ , the Fermi levels  $W_F$  and workfunctions  $\Phi$  of the metallic contacts and the hole and electron transport levels of the organic layers. The level offsets at the organic heterojunctions are determined by the different ionization energies  $I_s$  and electron affinities  $A_s$  of the adjacent layers.

**Double layer structures lead to emission close to the interface, thus preventing loss of charges reaching the electrodes (which, obviously, do not participate in the recombination process)**

## OLED structure

in OLEDs light-emitting excitons are formed by the recombination of electrically injected electrons and holes. Therefore, the organic layer system is sandwiched between two electrodes, the work function of which matches the molecular orbital energy levels of the adjacent organic layers (Figure 2). Holes are injected from the anode, which is usually the transparent electrode, consisting of indium tin oxide (ITO). The holes proceed via hopping of defect electrons in the HOMO (highest occupied molecular orbital) energy level of the hole-transporting molecules. Similarly, electrons are injected from the low-work-function cathode and proceed via the LUMO (lowest unoccupied molecular orbital) energy level of the electron-transport layer. From an electrochemical point of view, the charge-transport mechanism can be regarded as mutual solid-state redox reactions involving molecular radical cations for hole transport and radical anions for electron transport, respectively. By recombination, singlet and triplet excited states are formed that emit light directly or undergo excitation-energy transfer. In guest-host systems, however, with dopants acting as charge-carrier traps, recombination predominantly takes place at the dopant.<sup>46</sup>

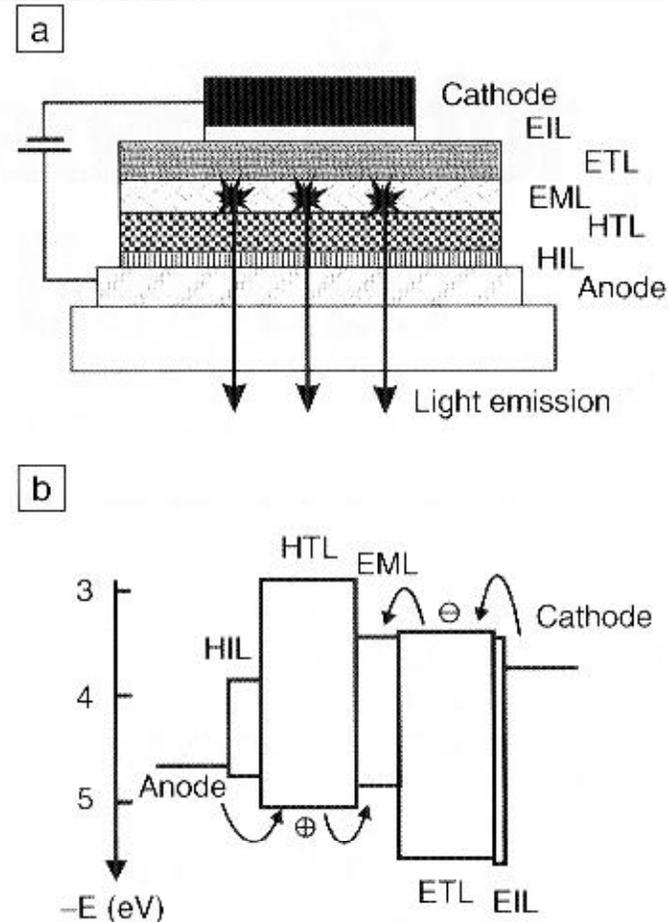
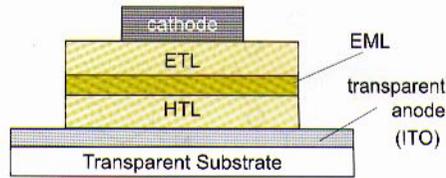


Figure 2. (a) Structure and (b) energy-level diagram of a typical organic light-emitting diode (OLED). EIL = electron-injection layer, ETL = electron-transport layer, EML = emission layer, HTL = hole-transport layer, and HIL = hole-injection layer.

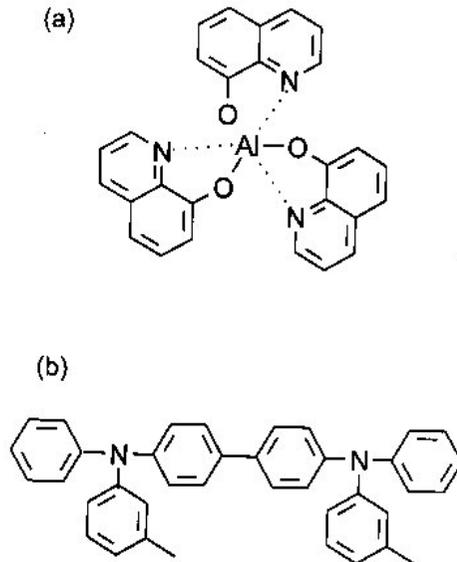
See MRS Bull. 27 (July 2002)

# OLED materials I



**Figure 1:** Schematic cross section of an organic light emitting device (OLED) showing the contacts, the electron transport layer (ETL), the light-emitting layer (EML) and hole transport layer (HTL). The total thickness of the organic layers is typically around 100 nm.

A schematic cross section of a conventional, small molecule based OLED with three organic layers (a double heterostructure) is shown in Figure 1. The top, ohmic, electron-injecting electrode consists of a low work function metal alloy, typically Mg-Ag or Li-Al, deposited by vacuum evaporation. The bottom, hole-injecting electrode is typically a thin film of the transparent semiconductor indium tin oxide (ITO), deposited onto the substrate by sputtering or electron beam evaporation. Light is emitted through this electrode when the device is operated in *forward bias*, i.e., with the ITO biased positive with respect to the top electrode. The next layer deposited is a hole transporting layer (HTL) of a material such as TPD. This is followed by the light emitting (EML) layer consisting of, for example, Alq<sub>3</sub> for green light or a host material doped with fluorescent or phosphorescent dyes and optionally an additional electron transport layer (ETL). The chemical structures of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) and tris (8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) are shown in Figure 2. E



**Figure 2:** Chemical structures of (a) Alq<sub>3</sub>, an electron transport and green fluorescent emitting material and (b) TPD, a hole transport material.

Organic light emitting devices can be prepared either from **small molecules** (c.f. Section 2.1) or from **polymers**. While the basic physics of both classes of materials is similar, the fabrication processes are very different. Small molecules are usually deposited by thermal evaporation in high or ultrahigh vacuum. Alternatively, the molecules can be evaporated into a stream of a **hot inert gas** directed to the substrate [17]. This so-called organic vapor phase deposition (OVPD) may provide a means for inexpensive and large-scale manufacturing. The typical sublimation temperatures are between 200 and 400°C. The molecules often have a thermal decomposition temperature much higher than the sublimation temperature. In this case, materials can be purified by repeated sublimation in vacuum or in an inert gas [18]. To separate components with different sublimation temperatures, long glass tubes inside a furnace with a temperature gradient are used. Such high purity materials are not only needed for good device performance, but are essential for long device operational lifetimes. Thermal deposition in vacuum or in the gas phase also allows for easy fabrication of multilayer devices. With sophisticated multilayer architectures, the distribution of charge carriers and excitons can be tuned (cp. e.g. Section 3.2 and 3.5). Small molecular weight devices with long lifetimes have been demonstrated to emit across the visible spectrum [19]. The highest emission efficiencies have been reported for small-molecular weight devices using phosphorescent emitters [13].

Polymers, on the other hand, cannot be deposited or purified by thermal evaporation because their decomposition temperature is generally lower than their sublimation temperature. Devices are accordingly prepared from solution, e.g. by spin coating. A particular advantage of polymers is their adaptability to potentially low cost large-scale display production by ink jet printing [20]. With optimized chemical synthesis and purification procedures, green and blue polymers with high fluorescence efficiencies have been obtained. Green polymeric OLEDs have also reached operational lifetimes in excess of 10,000 h. Polymer devices also have lower operating voltages than devices made from small molecules. However, using controlled doping, small molecular weight devices can compete here as well [5].

**Polymers (spin coated)  
Vs  
Small molecules (vacuum deposited)**

Da R. Waser Ed.,  
Nanoelectronics and  
information  
technology (Wiley-  
VCH, 2003)

# OLED materials II

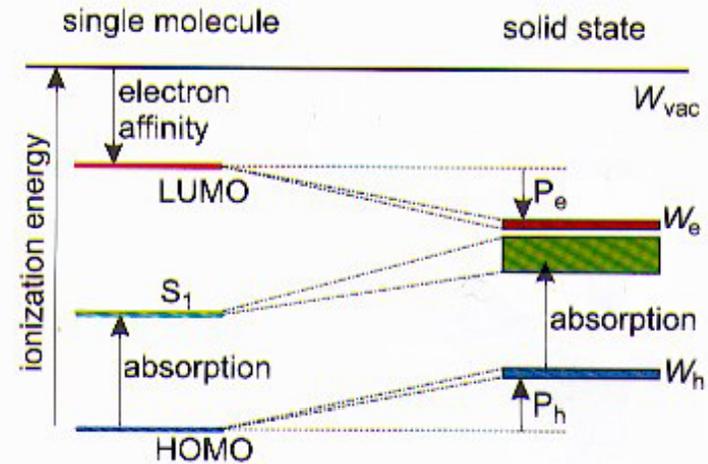
## Molecular (van der Waals) crystals

### 2.1 Isolated Molecules and Molecular van der Waals Crystals

The basic electronic structure of the class of organic molecules typically used for OLEDs is similar to the benzene discussed in Chapter 5. They feature a  $\pi$ -electron system delocalized over the entire molecule and characterized by frontier orbitals known as the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital). As discussed below, these two orbitals largely determine the electrical and optical properties of both the single molecules and the molecular solids. The HOMO is a fully occupied bonding  $\pi$ -orbital, and the LUMO is an antibonding unoccupied  $\pi^*$ -orbital. Thus, the  $\pi$ -electron-system is typically saturated (i.e. fully occupied with no unpaired spins); hence intermolecular covalent bonds cannot form. Consequently, the solids formed of such molecules are only bonded by weak van der Waals forces [9].

The overlap of the  $\pi$ -electron-system of adjacent molecules is small, leading to an energetic splitting of the order of tens to a few hundred meV. Nevertheless, this splitting is sufficiently large for ordered molecular crystals to show band-like charge transport at low temperatures, i.e. the HOMO levels form a narrow hole transport band and the LUMO levels split into a narrow electron transport band. Note that the overlap of the  $\pi$ -orbitals of neighbouring molecules is generally much smaller than the intramolecular overlap of the  $p_z$ -orbitals of neighbouring C-atoms inside the individual molecules, leading to the splitting between the different  $\pi$ -electron-orbitals of the molecule. Accordingly, the narrow bands that arise from each of the molecular  $\pi$ -orbitals exhibit only a small intermolecular overlap. Such systems are often called *small molecular systems* or *low molecular weight systems* even though the total number of atoms forming such small molecules can be on the order of fifty or more.

The situation is somewhat different in polymeric systems where the large number of C-atoms taking part in the  $\pi$ -conjugation leads to broad quasi-continuous energy bands of  $\pi$ -electron states along the molecular chains. However, this does not imply that polymers have larger charge carrier mobilities than small molecular weight solids because the interchain overlap in polymers tends to be small and mobilities are always limited by the most energetically costly hopping steps – in this case a hop between chains. In fact, the highest mobilities are achieved for highly ordered crystals of small, flat molecules that form closely packed stacks with high intermolecular  $\pi$ -electron overlap [21], [22].



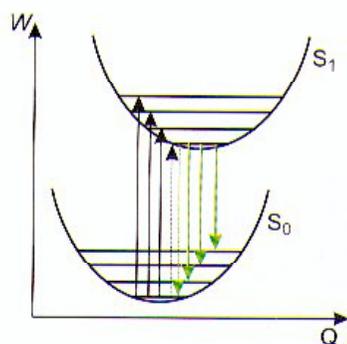
### Discrete levels appear

**Figure 3:** Ionization energy, electron affinity and first optical transition ( $S_0$  to  $S_1$ ) in a single molecule and formation of charge carrier and exciton bands in molecular solids from the respective molecular orbitals. The ionic energy levels are energetically stabilized in the solid state by the polarization energies  $P_e$  and  $P_h$  for electrons and holes, respectively. Note that an energetic stabilization of a hole leads to an upward shift in this electron energy picture.

Energy diagrams with discrete levels appear in systems comprised of small molecules or van der Waals crystals (as well in polymers, as we have already seen)

# “Molecular excitons” and charge transport

In the solid state, the optical gap is 0.5 to 1 eV smaller than the electronic gap [24] due to the Coulomb energy gained when a free electron and hole meet at a molecule to form an excited state or *exciton* [9]. Molecular excitons are different from hydrogenic Wannier-excitons found in inorganic semiconductors. In a molecular *Frenkel exciton*, the electron and the hole are localized on the same molecule, typically on the same ligand. In ordered crystals, bands of Frenkel excitons can be formed by wave-type linear combination of molecular excitations, i.e. the exciton may be delocalized even though the electron and the hole are coulombically bound. For closely packed materials of flat molecules, the energy of these delocalized states may differ from an excitation on an individual, *free* molecule by several hundred meV. This leads to the formation of broad exciton bands, and the absorption of the solid differs significantly from single molecules in solution [9]. Accordingly, the excitons couple strongly the phonon system, which can lead to exciton self-trapping by excimer formation [25]. Here, an excimer is an excited state shared by two, adjacent molecules, causing them to *bind* somewhat more tightly than in their ground state, thus giving rise to a new, lower energy excitation than that afforded by a simple Frenkel state. Excimers provide additional channels for non-radiative decay (e.g. aggregate quenching). Therefore, non-planar molecules that form amorphous, loosely packed solids are typically chosen for OLEDs. In this latter case, the optical absorption spectrum is similar in solution and in the solid state since the Frenkel exciton is localized on a single molecule. This excitation can diffuse around the solid by hopping transport. For Alq<sub>3</sub>, e.g., the exciton lifetime is 16 ns [26], leading to a diffusion length of 10 – 20 nm [26], [27].



**Figure 4:** Potential energy lines and vibronic levels for the ground state  $S_0$  and the first excited state  $S_1$  as a function of a configuration coordinate  $Q$  reflecting the intramolecular atomic distances. The electronic transitions without change in  $Q$  are always most pronounced in the spectra. Clearly, the absorption wavelengths (black) are larger, in general, than the emission wavelengths (green), causing a red shift of the emission spectrum with respect to the absorption spectrum.

## Vibronic transitions involved

## 2.3 Charge Carrier Transport

As in the case of conventional crystalline semiconductors such as Si, perfect molecular crystals show band-like charge carrier transport at low temperatures even though the bands are significantly energetically narrower in organic materials [21]. However, at room temperature, carriers are often localized on individual molecules [21] since the energy bands narrow at higher temperature along with increasing thermally induced molecular vibrations and lattice vibrations (phonons) that reduce the intermolecular  $\pi$ -electron overlap. Eventually, the electron-phonon interaction energies exceed the electronic bandwidth and charge carriers become trapped on individual molecules. In contrast, wider bandwidths exist in conventional semiconductors due to the considerably tighter covalent interatomic bonds. In this case, lattice vibrational energies are much smaller than the electronic bandwidth, significantly reducing the probability of electronic localization (i.e. self trapping) on an individual constituent lattice atom. These effects lead to typical room temperature hopping mobilities of  $\sim 1 \text{ cm}^2/\text{Vs}$  for most organic single crystals, which is two to three orders of magnitude lower than observed for conventional semiconductors. Furthermore, the charge carrier mobility decreases by another four to six orders of magnitude due to structural disorder in amorphous or polycrystalline thin films. Here, a distribution in the trapping energy (the polarization energy) due to the distribution in relative molecular orientations characteristic of disordered solids, leads to a distribution of the energetic density of transport states (DOS) [23]; consequently electron transport can be described by variable-range hopping in the tails of these distributions [28]. In such a situation, the effective mobility increases with the density of injected carriers or the electron donor or acceptor dopant density, respectively: With increasing occupation, the highly localized states deep in the tail of the distribution saturate while states close to the center of the DOS become occupied. Here, the density of states is high, the mean hopping distance is correspondingly reduced, and the hopping rate increases. This leads to a superlinear increase of conductivity with the doping concentration [29] and, for undoped samples, to a current that increases rapidly with the applied voltage [30] (c.f. Section 3.5).

## Vibronic emission Charge hopping-based transport

# Singlet/triplet fluorescence emission

## 3.1 Prerequisites for an Efficient OLED

For an efficient fluorescent OLED, an electron and a hole should form a singlet molecular excited state, this exciton should recombine radiatively and the energetic losses throughout the process should be low. Accordingly, the total external power efficiency  $\eta_P$  of an OLED is given by:

$$\eta_P = \gamma r_{st} \Phi_r \Phi_{out} \frac{\hbar\omega}{eV} \quad (1)$$

Here,  $\gamma$ , also called the charge-balance factor, is the ratio of the number of excitons formed to the number of electrons flowing in the external circuit,  $r_{st}$  is the fraction of excitons which are formed as singlets,  $\Phi_r$  is the efficiency of radiative decay,  $\Phi_{out}$  is the light outcoupling efficiency,  $\hbar\omega$  is the average energy of the emitted photons,  $e$  the elementary charge and  $V$  the applied voltage.

Singlet excitons refer to those states that are spin antisymmetric (with a total spin quantum number  $S=0$ ). Singlet exciton transitions to the ground state (also in a singlet configuration) are quantum mechanically allowed, and hence are fast ( $\sim 1 - 10$  ns) and efficient, giving rise to fluorescence. In contrast, triplets have even symmetry ( $S=1$ ). Their transition to a singlet ground state does not conserve spin angular momentum, and hence are disallowed. For this reason, triplet transitions are slow ( $100 \mu s - 10$  s) and highly inefficient, leading to phosphorescence. From the multiplicity of angular momentum states, there is one  $S=0$  state ( $m_s=0$  is the quantum number for the projection of the spin on the z-axis), and three  $S=1$  states ( $m_s=\pm 1, 0$ ); hence the names singlet and triplet. Due to the random nature of spin production via electron injection in electrically driven devices such as OLEDs, simple statistical arguments suggest that only 25% of the injected charge will combine into emissive fluorescent states. In Section 3.2, we will discuss device architectures that ensure that  $\gamma$  is close to unity, and that by employing heavy metal containing phosphor molecules, all electrically excited molecules can be made efficiently emissive from their triplet state.

**Singlet: antisymmetric (S=0) state**  
**Singlet to singlet (ground state)**  
**transitions allowed**

The efficiency of radiative decay,  $\Phi_r$ , is given by

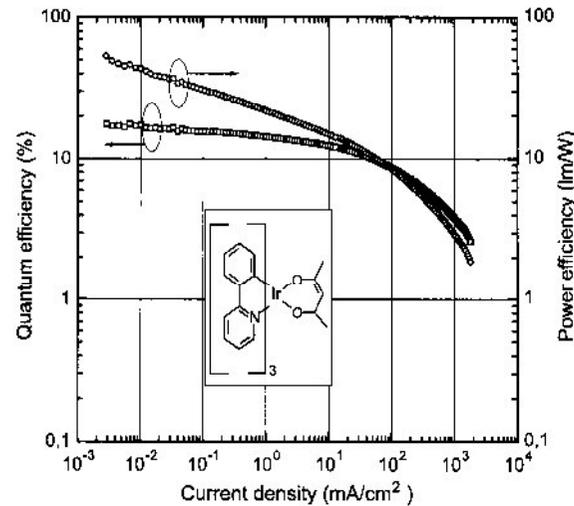
$$\Phi_r = \frac{\kappa_r}{\kappa_r + \kappa_{nr}} \quad (2)$$

where  $\kappa_r$  and  $\kappa_{nr}$  denote the rate constants for radiative and non-radiative decay of an exciton, respectively. The radiative decay constant is largely determined by the strength of the transition dipole moment [25], and is also influenced by the proximity of the radiating molecule to a reflecting surface, such as a metal cathode. Here, the transition dipole moment is proportional to the overlap of the wavefunctions in the molecular excited and ground states: the larger overlap leading to increased probability for the electron to transit from one state to the other, emitting light when this transition releases energy. The rate of non-radiative decay is a function of the coupling of the electronic excitation to intramolecular vibration modes. However, in molecular solids, further effects like traps and aggregate formation can further increase the non-radiative decay rate [31]. These losses can be minimized by using mixed emitter layers as described in Section 3.3. A successful strategy to reduce the driving voltage is by doping the transport layers by electronic acceptor or donor molecules (cp.3.5). Finally, light outcoupling is  $\sim 20\%$  [13] when glass substrates are used due to total reflection at the interface between the substrate and the ambient. To maximize  $\Phi_{out}$ , the emission region should be removed by approximately one quarter of a wavelength from the reflecting top contact to provide constructive interference for emission normal to the substrate. Otherwise, the probability increases that the emitted light is coupled into waveguide modes in the substrate. Furthermore, various techniques have been reported to reduce waveguiding losses by structuring the substrate surface, e.g. by employing an array of microlenses [32] or by using microcavities.

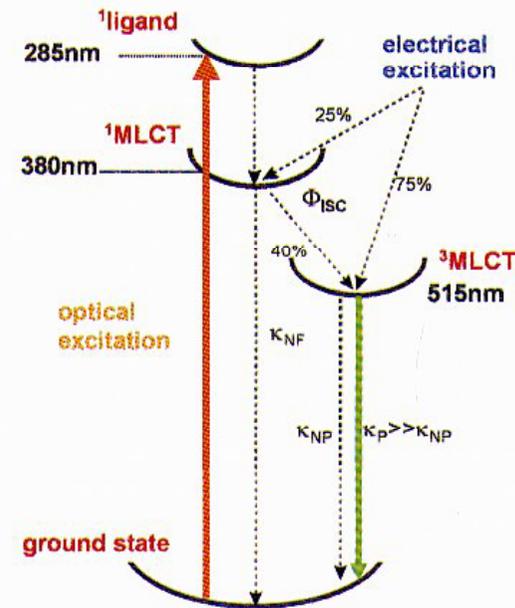
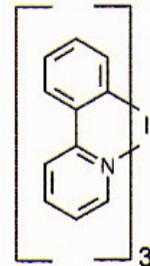
**Triples: symmetric (S=1) state**  
**Triples to singlet (ground state)**  
**transitions disallowed**

**Excitation of triplet states should be avoided in order to increase fluorescence efficiency**

# Dye-doping in OLEDs



**Figure 7:** Chemical structure and energy level scheme for the metalorganic phosphor,  $\text{Ir}(\text{ppy})_3$  (from [38]). The ligand singlet state ( $^1\text{ligand}$ ) and metal-to-ligand charge-transfer singlet state ( $^1\text{MLCT}=\text{S}_1$ ) were determined by the absorption peaks in toluene solution ( $10^{-5}$  M). Also, the triplet MLCT state ( $^3\text{MLCT}=\text{T}_1$ ) was estimated from the phosphorescence peak.  $\kappa_{\text{NF}}$ ,  $\kappa_{\text{P}}$ , and  $\kappa_{\text{NP}}$  are quantum yields for nonemissive transitions from  $^1\text{MLCT}$  intrinsic phosphorescent transitions, and nonemissive transitions from  $^3\text{MLCT}$ , respectively. Also,  $\Phi_{\text{ISC}}$  is the yield for intersystem crossing from  $^1\text{MLCT}$  to  $^3\text{MLCT}$ .

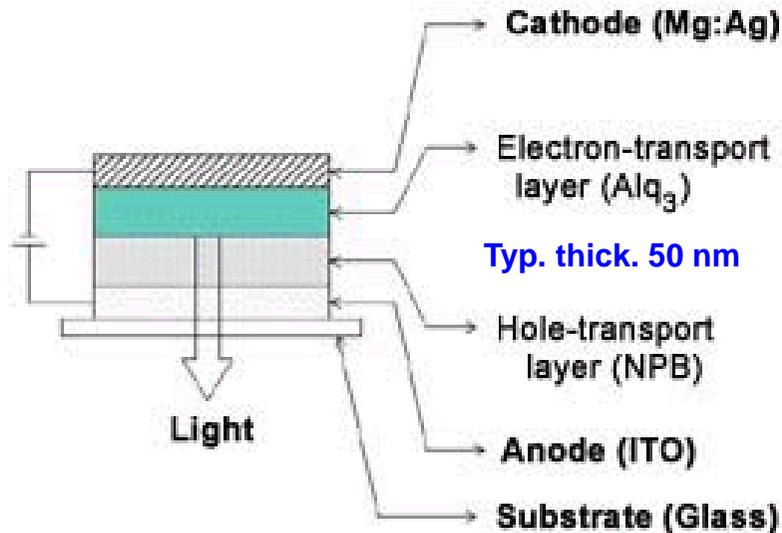


## 3.4 High Efficiency Phosphorescent OLEDs

The internal quantum efficiency of fluorescent OLEDs cannot exceed 25 % because of the singlet-triplet-ratio  $r_{\text{st}}$  discussed above. As shown in Figure 6, there are three ways to form a triplet and only one way to form a singlet. This intrinsic limitation can be overcome by incorporating *phosphorescent guest molecules* into a host matrix material to generate light from both the triplet and the singlet excitons, and achieve internal quantum efficiencies close to unity [13], [14].

**Doping with molecular dyes can enhance efficiency (through phosphorescence) and allow tuning on a larger spectral range**

# Practical choices of materials/techniques for OLEDs



Oemagazine (SPIE, Feb 2001)

## Fabrication

OLED devices can be divided into two classes: small-molecule devices and organic-polymer devices. Small-molecule devices are fabricated using vacuum evaporation techniques, whereas polymer structures can be applied using spin-casting or even ink-jet printing techniques. Originating at Eastman Kodak Co. (Rochester, NY), the small-molecule technology has achieved commercialization.

## Materials

One of the most basic OLED device structures uses an organic material called NPB as the hole-transport layer and tris-8-hydroxyquinoline aluminum (alq<sub>3</sub>) as the electron-transport layer. A typical structure incorporates layers of indium tin oxide/ NPB/alq<sub>3</sub>/magnesium-doped silver (ITO/ NPB/alq<sub>3</sub>/Mg:Ag), where ITO is the transparent anode and Mg:Ag is the cathode. The energy barriers between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels are about 0.4 and 0.9 eV, respectively, which are sufficiently high to localize the holes in the NPB layer and electrons in the alq<sub>3</sub> layer. Recombination of these charges occurs across the barriers, with holes primarily moving into alq<sub>3</sub>. This effect produces excited states or excitons in alq<sub>3</sub> that emit a green fluorescence with its characteristic efficiency. The overall external quantum efficiency is about 1% in photons emitted per charge passing through the OLED device.

## Doping

Altering the basic two-layer structure to include a luminescent layer between the hole-transport layer and the electron-transport layer can yield OLED devices with much improved efficiencies. A well-known scheme is to dope the interface region with molecules of high fluorescence efficiencies, as in the three-layer NPB/alq<sub>3</sub>:C540/alq<sub>3</sub> structure. Here, alq<sub>3</sub> is the host and C540, a coumarin laser dye, is the dopant present at a concentration of about 1%. The luminescent layer is simply a part of the alq<sub>3</sub> electron-transport layer doped with C540. Because of the enhanced fluorescence from the dopant, the electroluminescence efficiency of the doped OLED device can exceed that of the undoped device by a factor of two to three.

## Durability

The reliability of OLED devices has been the major concern for practical applications. It has, however, improved substantially over the years. Using various sets of organic materials, many laboratories have reported achieving luminance life (half decay) on the order of 10,000 hours in devices of all colors using various sets of organic materials. Some of the reliability problems, such as the deterioration of the reactive cathode, have been adequately addressed with engineering solutions. The more basic problem of organic material degradation is now better understood. For instance, it has been shown by Zoran Popovic of Xerox Canada, Inc. (Toronto, Ontario) that it is the hole carrier in Alq<sub>3</sub> that is partially responsible for the OLED degradation, and remedies for such a degradation include deliberate introduction of stabilizing dopants.

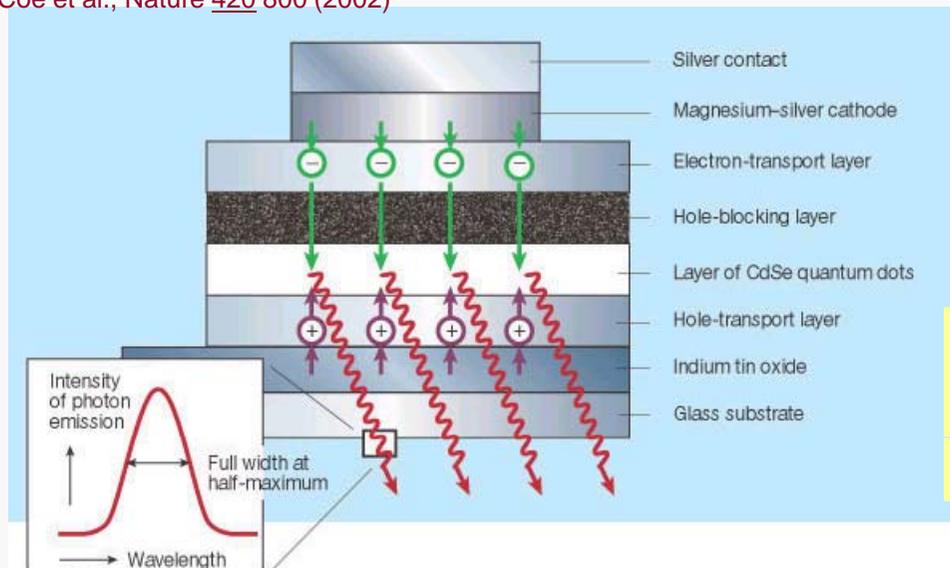
## OLED + QDs as an alternative possibility

Mobile phones with small colour displays using organic LEDs are already commercially available. The images are generated through fluorescence, as electrons make transitions between orbital states of  $\pi$ -conjugated organic molecules (the  $\pi$ -bond arises from the overlap of the  $2p$  orbitals of electrons in carbon atoms). As well as having high quantum efficiency for electron-to-photon conversion,  $\pi$ -conjugated molecules in organic LEDs have the advantage of colour tunability, so that they can be used to build full-colour displays of red–green–blue (RGB) emitters.

But there is also a drawback: the emission spectra of  $\pi$ -conjugated molecules are very broad, typically spanning 50 to 100 nm (the 'full width at half-maximum', or FWHM; Fig. 1, inset). This range of molecular fluorescence is caused by the vibrational and rotational motion of atoms inside the  $\pi$ -conjugated molecules. So with an organic LED, it is difficult to get, for example, pure red light emitted with high quantum efficiency. Nevertheless, sharp RGB emission has been demonstrated from LEDs based on some specific materials, such as europium chelates, aggregated structures of cyanine dyes or layered inorganic–organic perovskite compounds. But these LEDs have not achieved the emission efficiency or device durability needed for practical display applications<sup>2, 3</sup>.

**(Broad) molecular emission sometimes is not desirable (e.g., in lasers)**

Coe et al., Nature [420](#) 800 (2002)



nc-CdSe fabricated by liquid methods

**Doping with CdSe nanocrystals (QDs) can enhance efficiency and narrow the emission band**

## Conclusions

- ✓ Organics do offer huge potential advantages as building blocks for nanoelectronics; DNA-based systems can open even wider perspectives
- ✓ First issue to be solved: interface with inorganics (e.g., molecular films on metal layers)
- ✓ Second issue: addressing the single molecule (so far, mostly test devices have been proposed)
- ✓ Intramolecular electronics provides molecular engineers with strong impulse to design entities showing almost any desired electronic behavior
- ✓ Contrary to electronics, optoelectronics with organics has much progressed and OLEDs are commercially available