CdL Scienza dei Materiali - Fisica delle Nanotecnologie - a.a. 2004/5

Appunti & trasparenze - Parte 4

Versione 3, Ottobre 2004
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Trasporto elettronico nel mondo organico, polimeri conduttori, drogaggio; film molecolari Langmuir-Blodgett e SAM; esempi di elettronica intramolecolare, esempi di dispositivi molecolari, problematiche principali.

28/10/04 10.30+1 ITI M
3/11/04 15.30+2 fis

Introduzione

Enorme interesse (da oltre dieci anni) attribuito ad ”elettronica molecolare”:
- economicità, semplicità processi, scalabilità, biocompatibilità, etc.

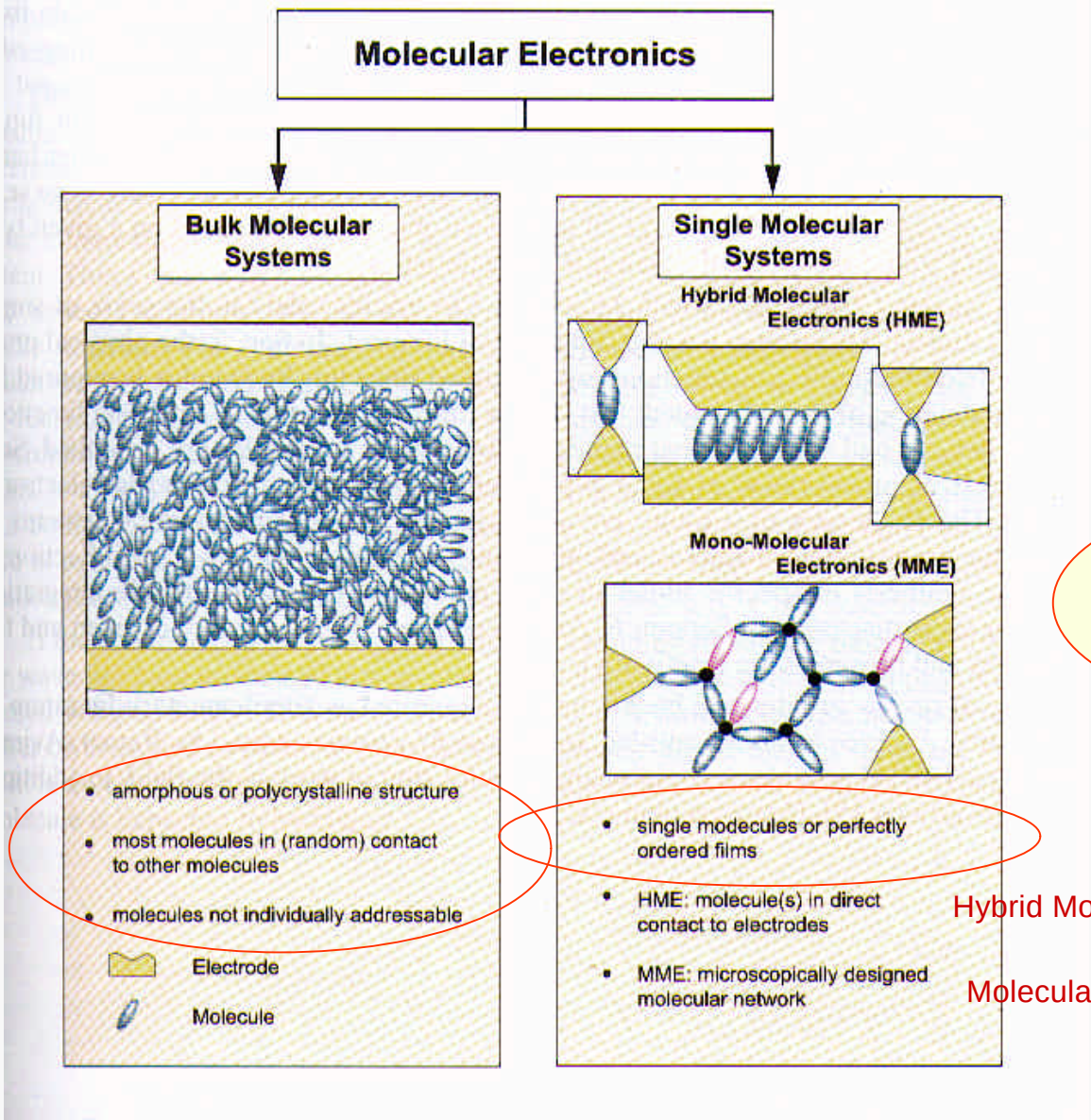
Aspetto maggiormente critico: interfaccia con mondo inorganico

Due “approcci”:
-Film sottili (LB e SAM);
-Singole molecole (*elettronica intramolecolare*)

Problemi associati:
-Proprietà spesso mascherate da disordine, interfaccia, instabilità;
-Enorme flessibilità, ma difficoltà di “indirizzare” singole molecole

(uso di “templates” autoassemblati)

Elettronica molecolare (*molectronics*)



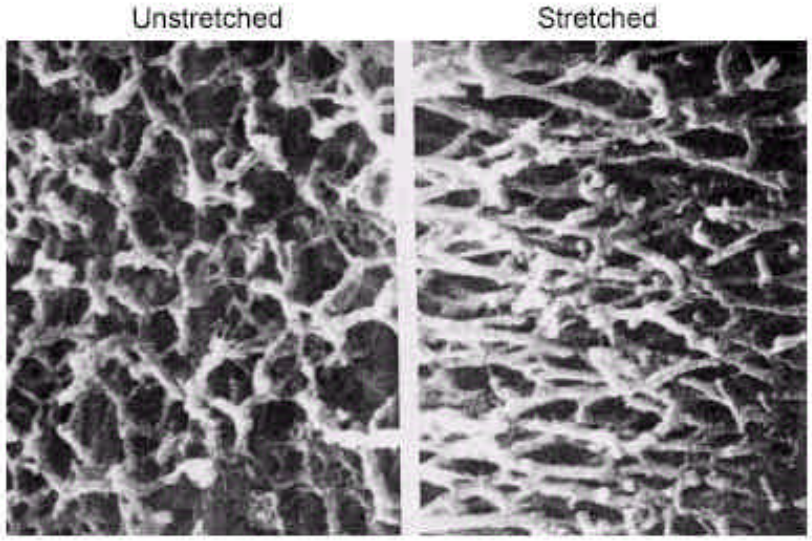
Problematiche elettroniche (ed opto-elettroniche) affrontate con metodi di chimica molecolare e sopramolecolare

economia
very large scale integration
crescita **bottoms-up**

Hybrid Molecular

Molecular-Molecular

Miniaturizzazione e polimeri



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)

Polimeri: sistemi *intrinsecamente* nanotecnologici (vero per singola molecola!!)

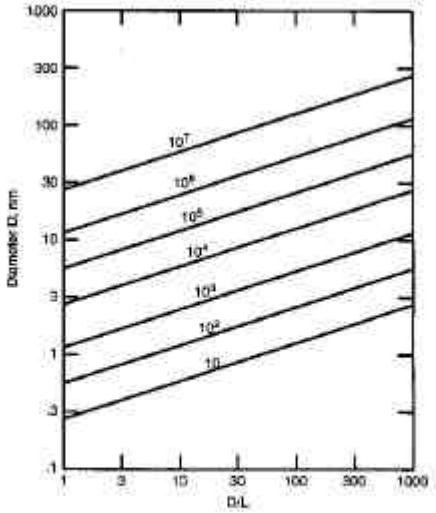


Figure 11.2. Dependence of the diameter D of a cylindrical polymer on its diameter : length ratio D/L for molecular weights from 10 to 10^7 Da, as indicated on the curves. A density $\rho = 1$ g/cm^3 was assumed in Eq. (11.13) for plotting these curves.

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 (nm^3) of a substance of molecular weight M_w and density ρ is given by

$$V = 0.001661 \frac{M_w}{\rho} \tag{11.10}$$

where M_w has the unit dalton or g/mol (grams per mole) and ρ has the conventional units 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:

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

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 $d_{SPH} = D_0 = 0.1469\,(M_w/\rho)^{1/3}$ 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

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

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

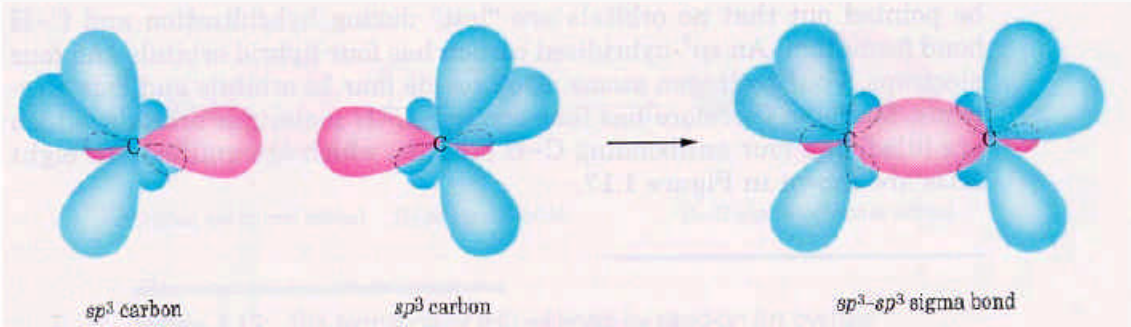
$$D = 0.128\left(\frac{M_w}{\rho}\right)^{1/3}\left(\frac{D}{L}\right)^{1/3} \tag{11.13}$$

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

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 $\rho = 1$ 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.

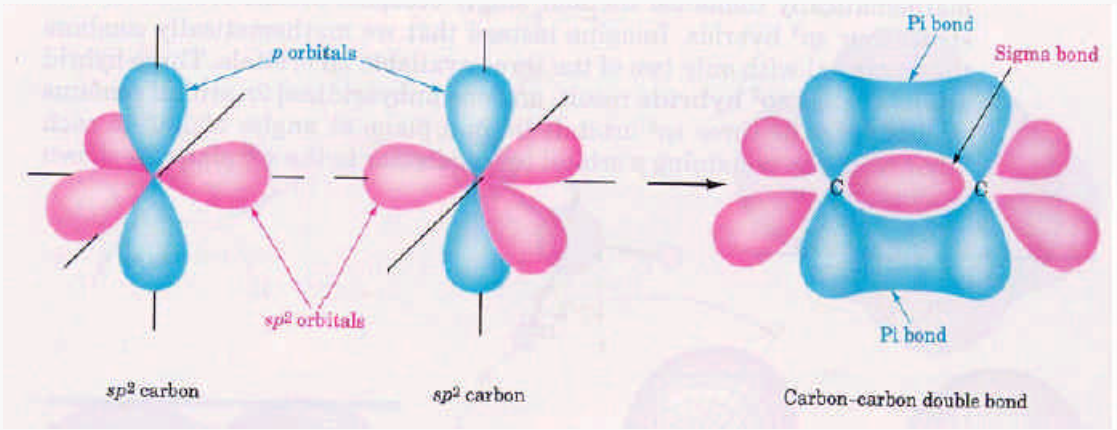
Basi delle proprietà di trasporto in molecole organiche

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



Legami σ tra
orbitali ibridizzati sp^3
⇩
localizzazione elettroni
⇩
carattere **isolante**

MA...

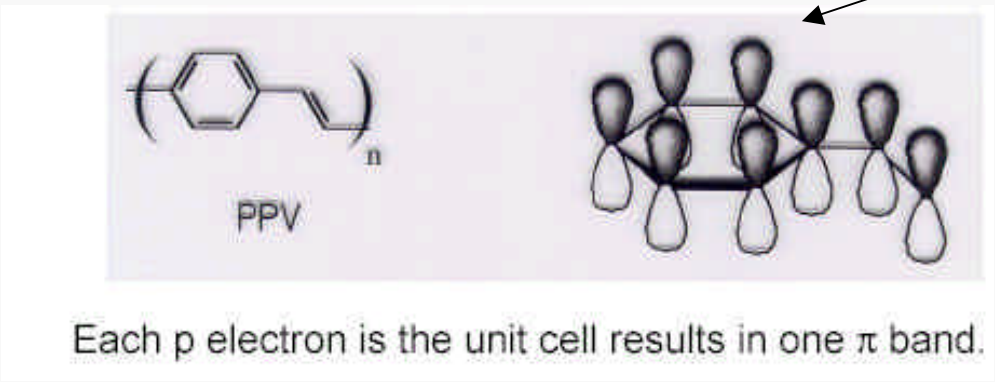


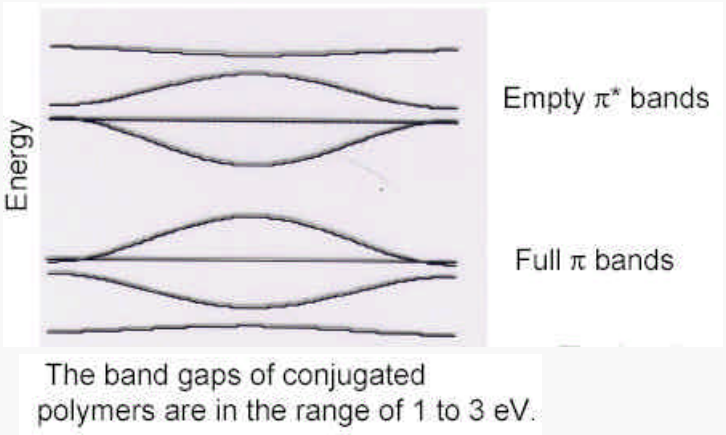
Legami π tra
orbitali ibridizzati sp^2
⇩
"delocalizzazione" elettroni
⇩
carattere **semiconduttore**

Materiale organico *può essere semiconduttore*

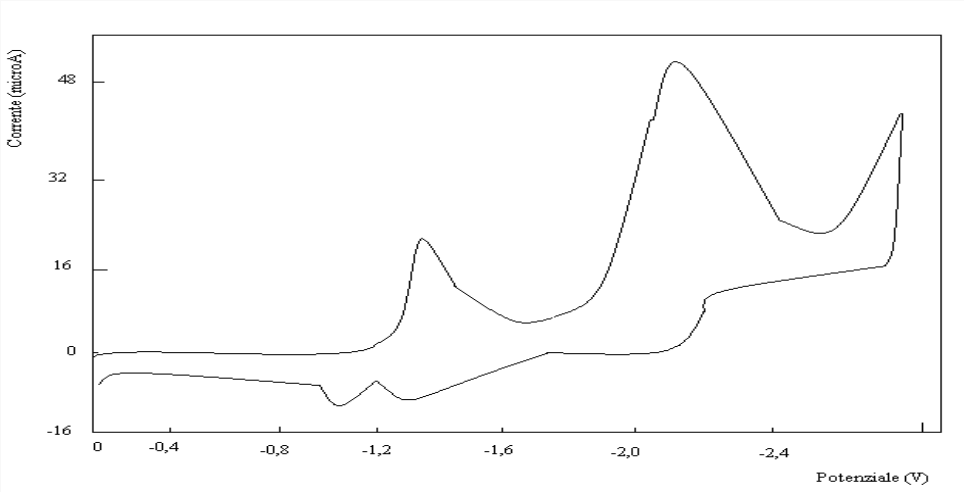
Proprietà di trasporto in polimeri coniugati

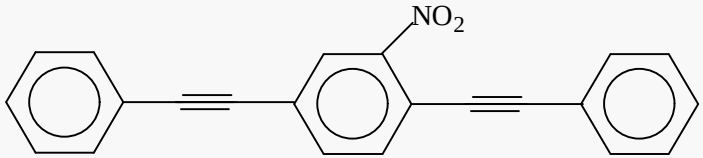
Esempi: polianiline, pirroli, tiofeni, polifenilenvinilene,...





Struttura “a bande” generata da elettroni π



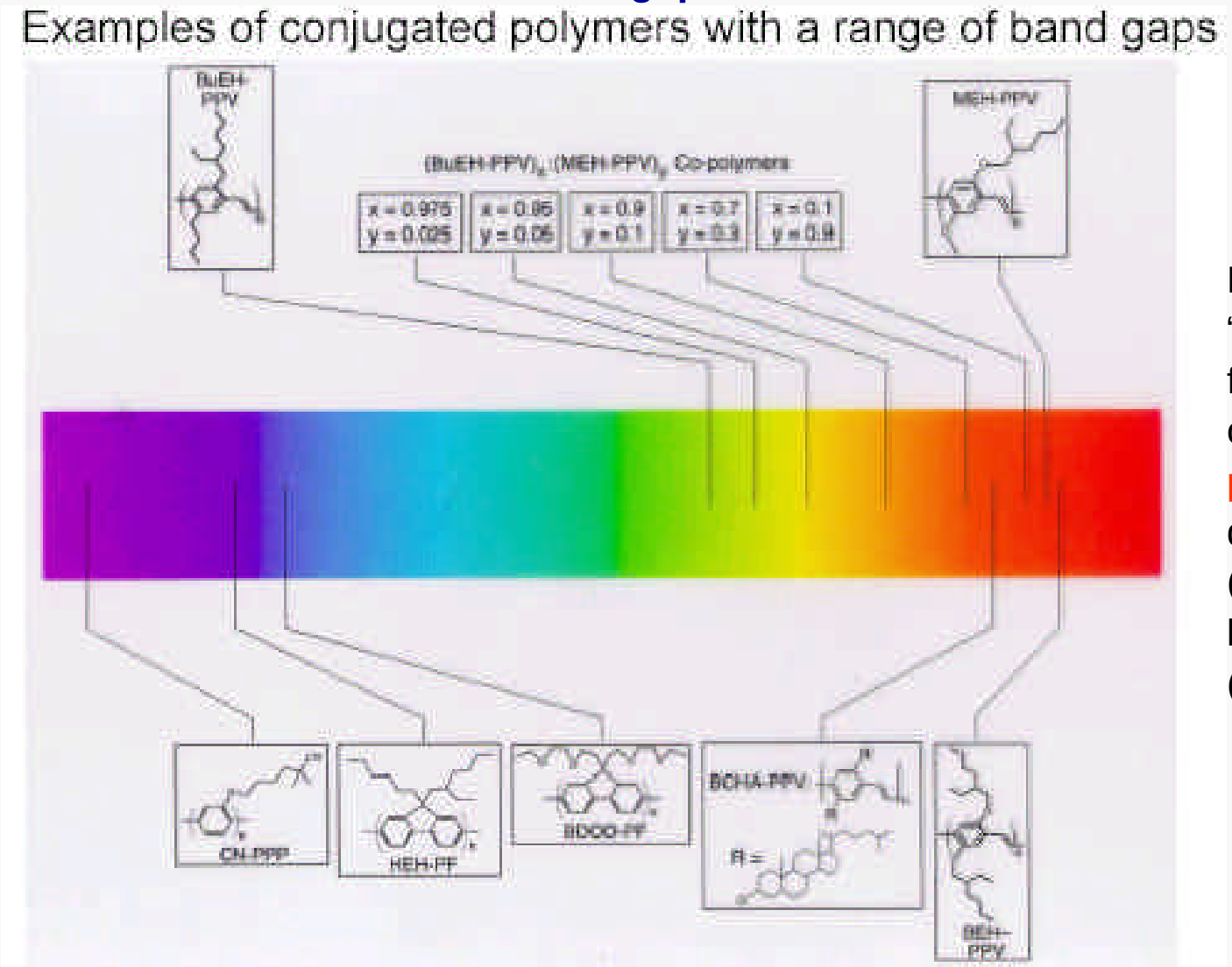


Voltametria del 2-nitro-1,4feniletinil-benzene

In soluzione!!

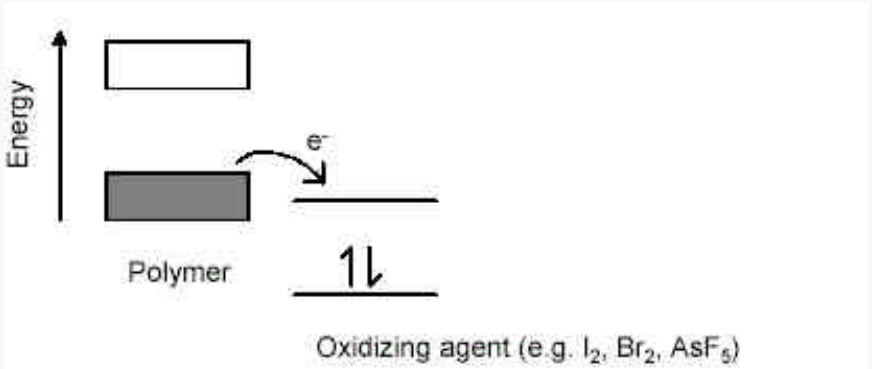
Materiale tratto dal seminario di Marco Donato, Apr. 2004

Band-gap “tunabile”

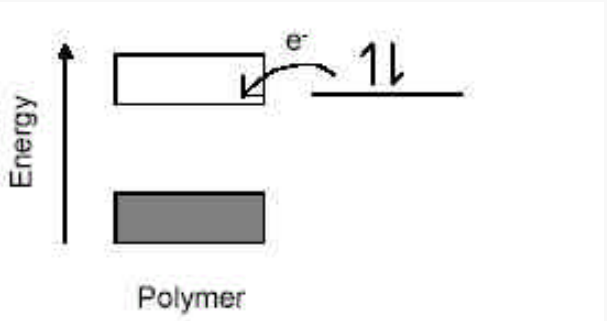


Band-gap “tunabile” in funzione della composizione (co-polimeri), utile in dispositivi (elettro)-luminescenti (OLED)

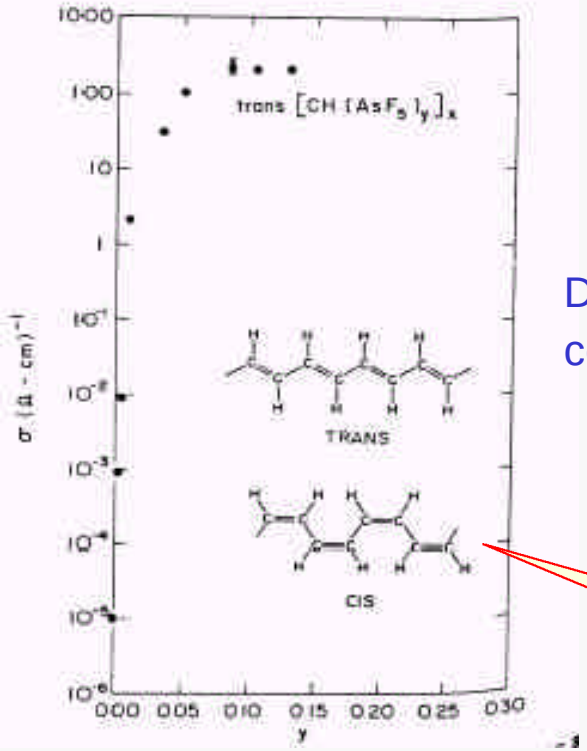
Effetti di drogaggio di polimeri coniugati



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



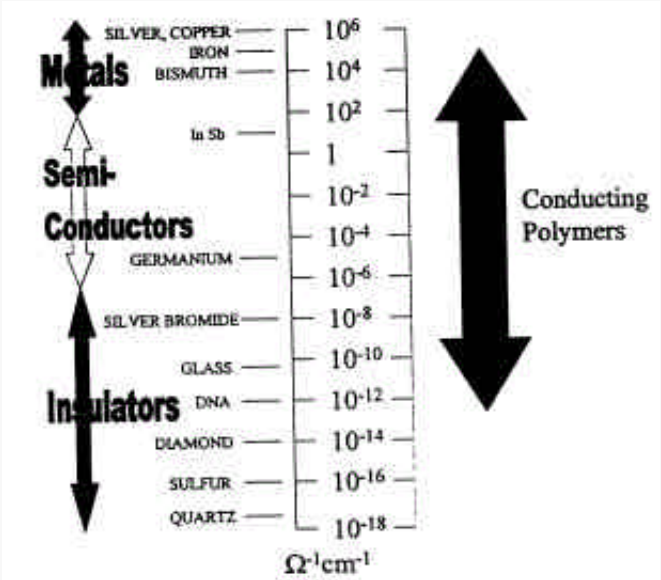
Reducing agents such as calcium and lithium can introduce electrons into the conduction band of a conjugated polymer.



Drogaggio crea buche o elettroni *relativamente* liberi

Drogaggio di trans-acetilene con AsF_5

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



Chemical bonds vs Van der Waals *(elettrodi)*

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 continously 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_2 and TiO_2 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-Blodget (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* π-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 π-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.

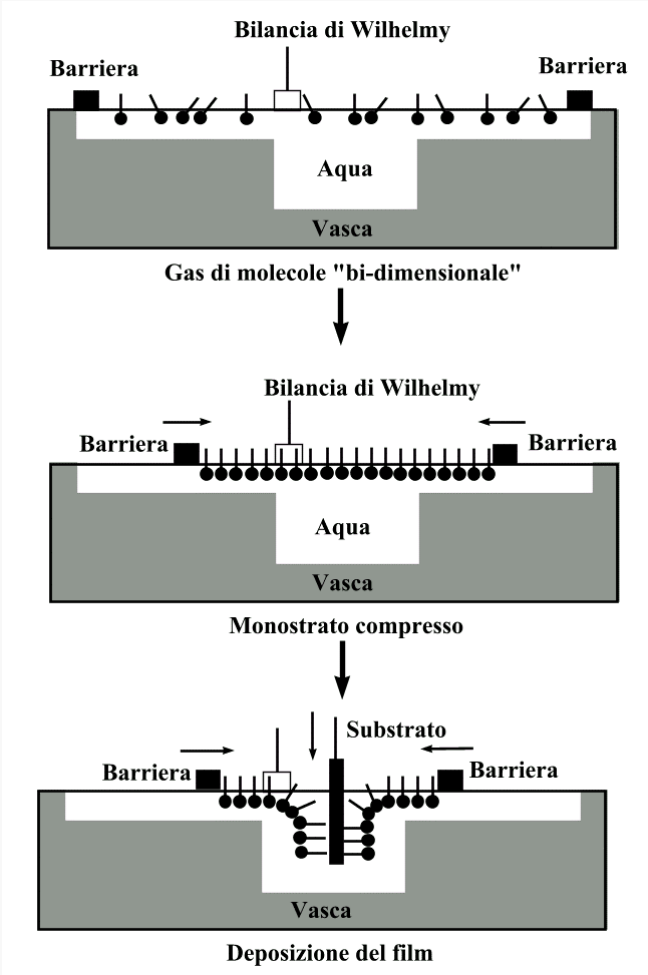
If the distance chosen is larger or badly-conducting molecular units are in between, the wave function inside and outside do not overlap and can with good approximation be treated independently. This case corresponds to LB films. Electron transport can then better be imagined as particles tunneling from 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.

Interfaccia con mondo inorganico (elettrodi) fortemente critica

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° 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° 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

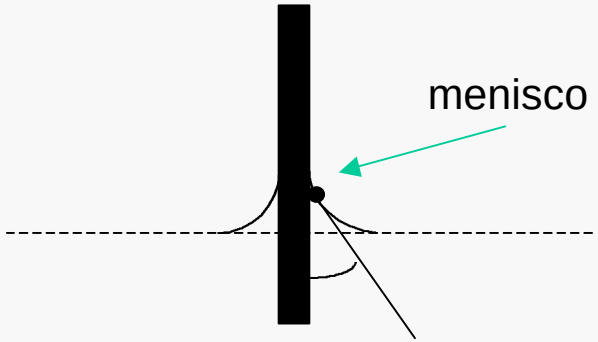
materiali solubili in acqua idrofilici
materiali solubili in solventi apolari idrofobici

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 .

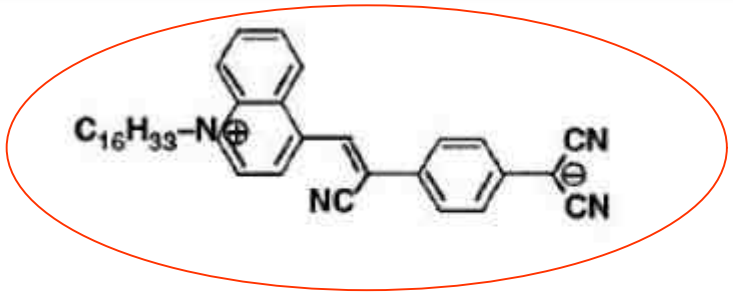
La solubilità di una molecola anfifilica in acqua dipende dal bilanciamento tra la lunghezza della catena alchilica e la forza della testa idrofilica . Nella tab. seguente è riportato l'effetto di diversi gruppi funzionali sulla formazione di film da composti del $-C_{16}$:

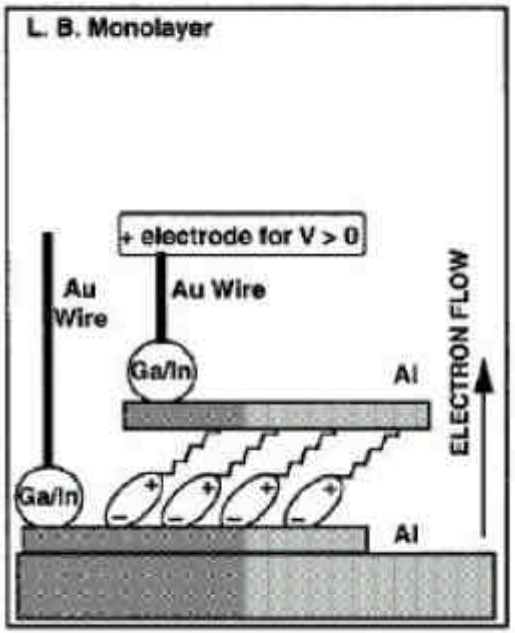


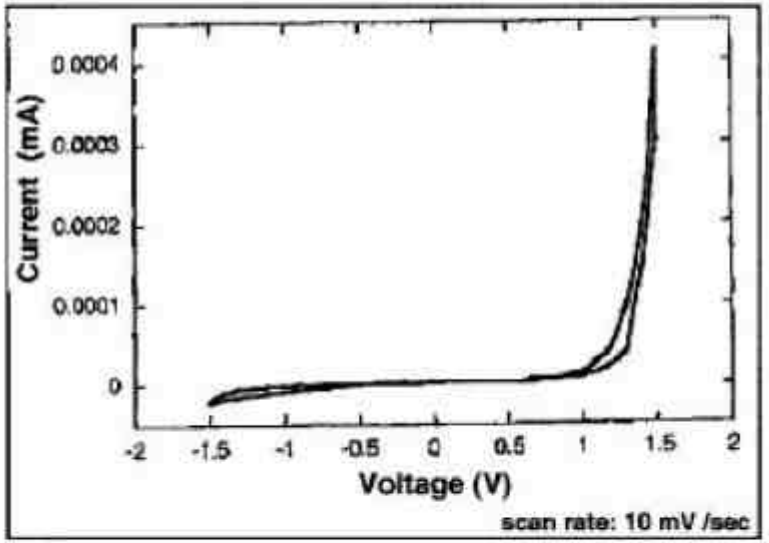
molto debole (no film)	Debole (film instabile)	Forte (film stabile)	molto forte (C_{16} si dissolve)
$-CH_2I$	$-CH_2OCH_3$	$-CH_2OH$	$-SO_3^-$
$-CH_2Br$	$-C_6H_4OCH_3$	$-COOH$	$-OSO_3^-$
$-CH_2Cl$	$-COOCH_3$	$-CN$	$-C_6H_4SO_4^-$
$-NO_2$		$-CONH_2$	$-NR_4^+$
		$-CH=NOH$	
		C_6H_4OH	
		$CH_2\ COCH_3$	
		$-NHCONH_2$	
		$-NHCOCH_3$	

Esempio di diodo costruito con film LB

Molecola anfifilica



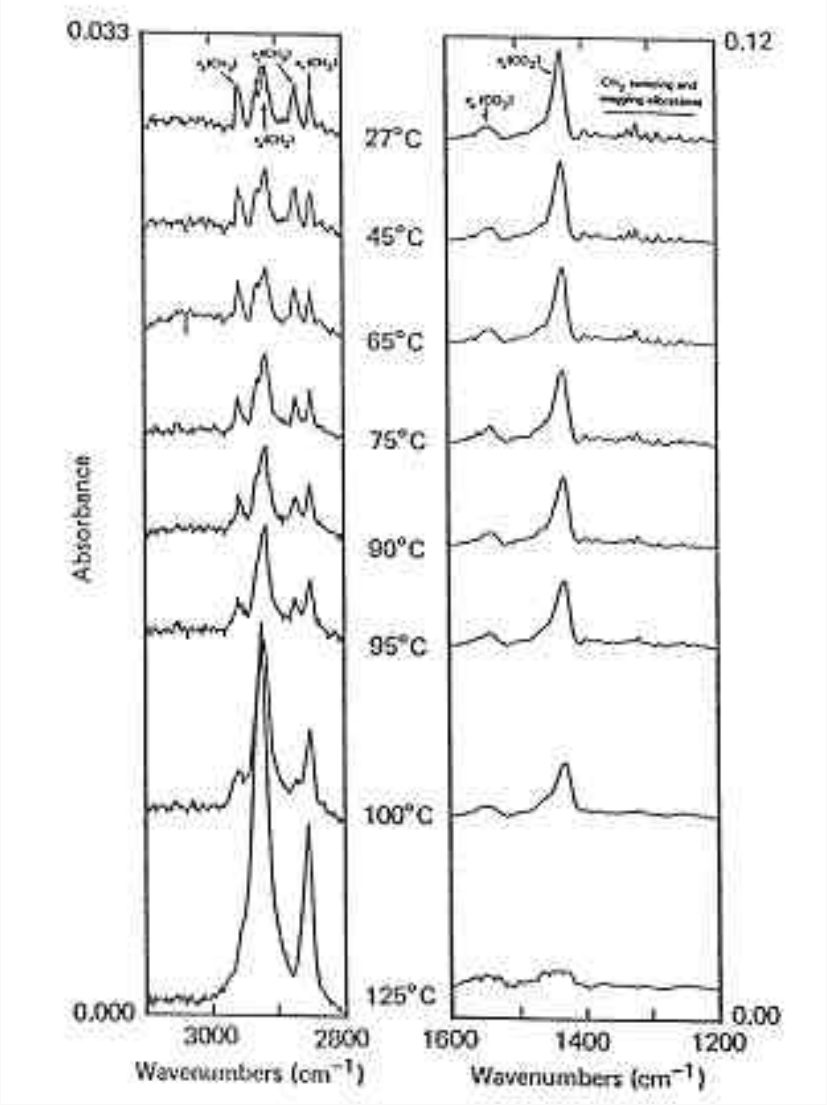




Schema di un diodo rettificante fatto con film LB. A destra, la caratteristica corrente-tensione del diodo.

Stabilità termica film LB

Spettri IR di film LB a diverse T



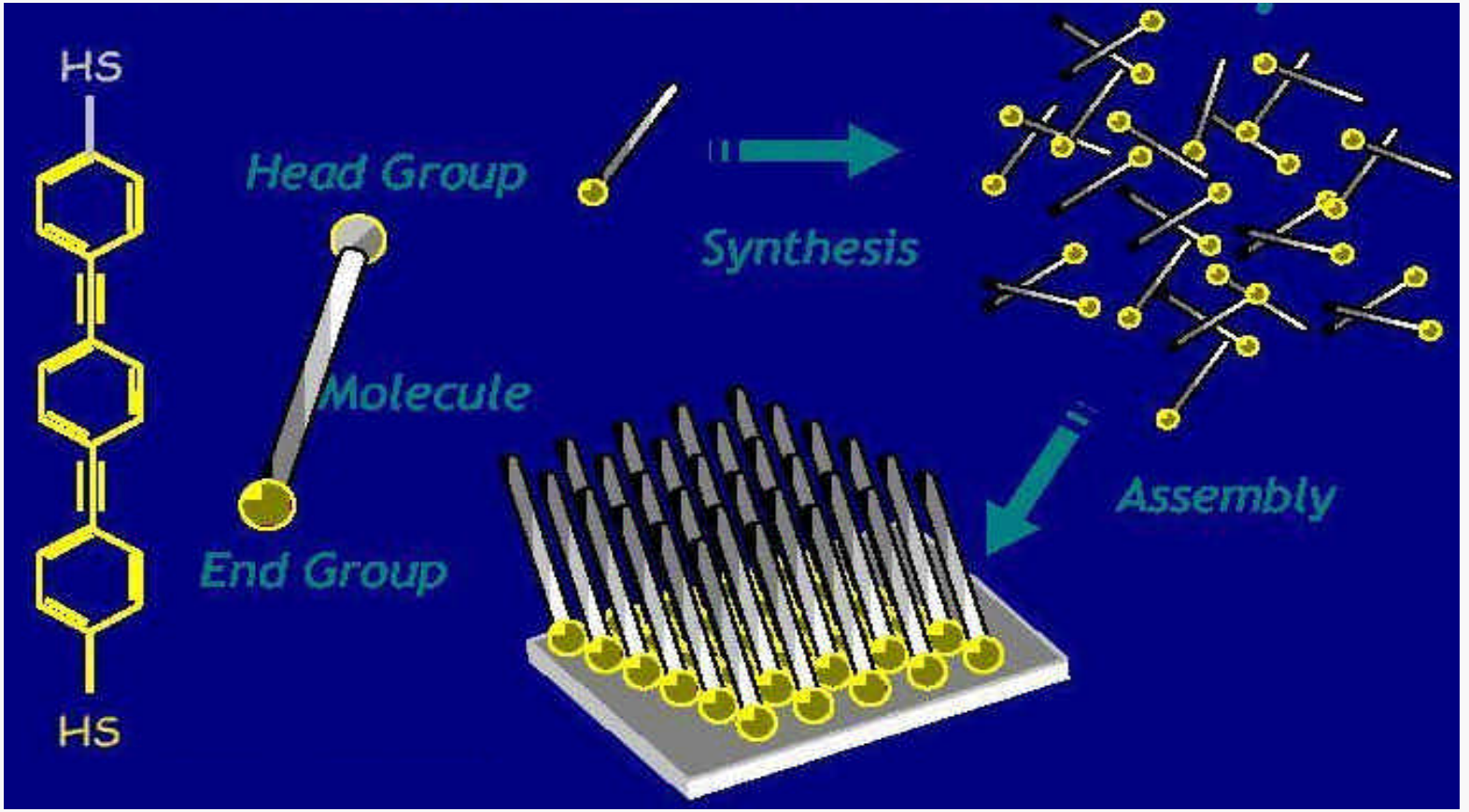
LB: tecnica estremamente semplice ed economica

Limiti principali:

- Applicabilità a *pochi* sistemi;
- Debolezza legame Van der Waals
- Stabilità termica

Tecnica di impiego pratico limitato in applicazioni nanotecnologiche

Autoassemblaggio molecolare (SAM) I



Molecole lineari dotate di un gruppo “legante” e altro gruppo “funzionalizzabile”

Materiale tratto dal seminario di
Marco Donato, Apr. 2004

Autoassemblaggio molecolare (SAM) II

(Semplice) esempio delle capacità auto-organizzative dei materiali organici

Alkanethiols
on Au

forze di Van der Waals
determinano autoorganizz.
(energia ~10 kcal/mol)

gruppo S
attaccato ad Au
(energia ~30 kcal/mol)

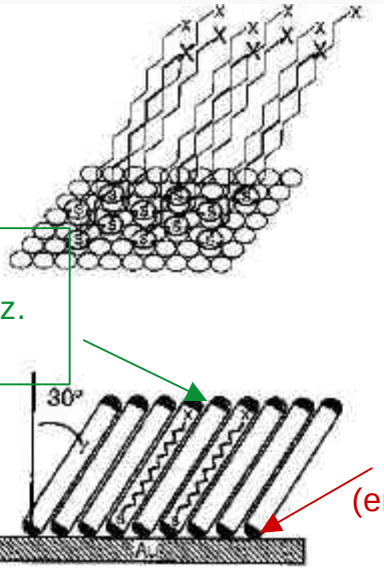


FIGURE 1. Schematic illustration of the molecular-level structure of a self-assembled monolayer of n-alkanethiolates on gold. Figure is not drawn to scale.

MONOLAYERS

SURFACE	LIGAND	BINDING
Au	RSH, ArSH (thiols)	RS–Au
Au	RSSR' (disufides)	RS–Au
Au	RSR' (sulfides)	RS–Au
SiO_2, glass	$RSiCl_3$, $RSiOR_3$	siloxane network
Si	$[RCOO]_2$ (neat)	R–Si
Si	$RCH{=}CH_2$, $[RCOO]_2$	$R–CH_2CH_2–Si$
GaAs	RSH	RS–GaAs
Ag	RSH, ArSH	RS–Ag
Cu	RSH, ArSH	RS–Cu
metal oxides	RCOOH	$RCO_2–\cdots MO_n$
metal oxides	RCONHOH	$RCONHOH\cdots MO_n$, $RCONHO–\cdots MO_n$
Pt	RSH, ArSH	RS–Pt
Pt	RNC	RNC–Pt

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

$$X\text{-}R\text{-}SH + Au \rightarrow X\text{-}R\text{-}S^{-}Au(I)\cdot Au(0)_n + \tfrac{1}{2}H_2 \qquad (1)$$
$$\tfrac{1}{2}(X\text{-}R\text{-}S)_2 + Au \rightarrow X\text{-}R\text{-}S^{-}Au(I)\cdot Au(0)_n.$$

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

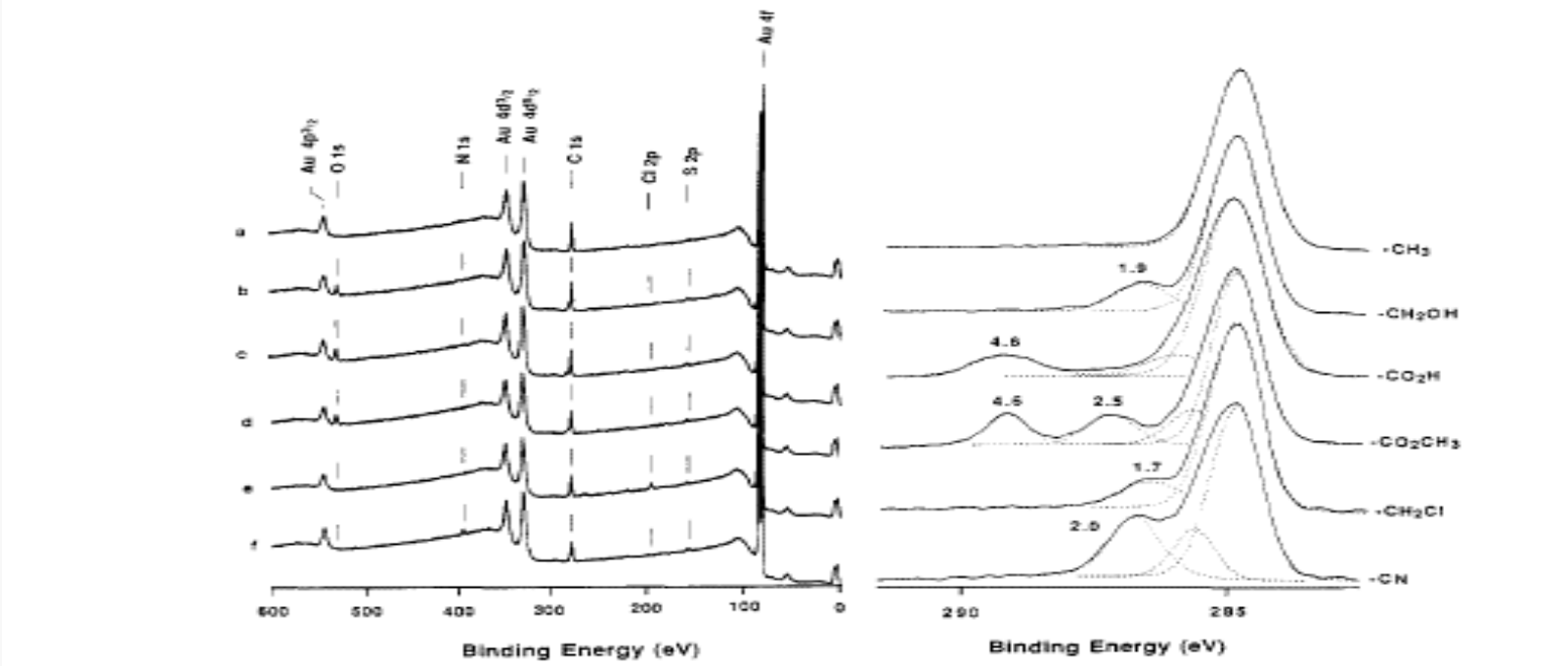
Processo semplice, veloce, economico per produrre monostrati

⇩

(uso come resist)

uso come "base" per nanodispositivi

Analisi XPS di SAM su oro



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) $HS(CH_2)_{10}CH_3$, (b) $HS(CH_2)_{10}CH_2OH$, (c) $HS(CH_2)_{10}CO_2H$, (d) $HS(CH_2)_{10}CO_2CH_3$, (e) $HS(CH_2)_{10}CH_2Cl$, and (f) $HS(CH_2)_{10}CN$

Natura chimica del legame tiolo-oro confermata da XPS

SAM usato anche per
"inibire" aggregazione
di nanoclusters metallici

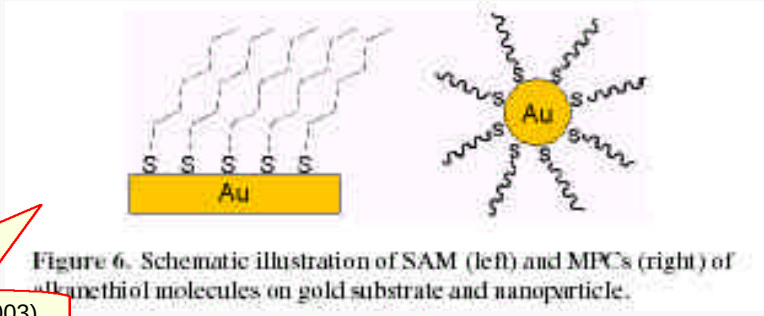
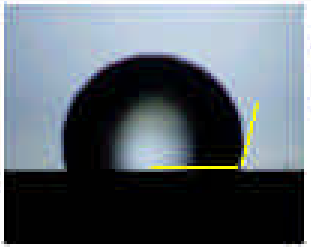


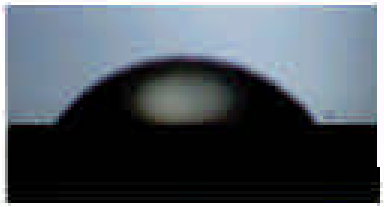
Figure 6. Schematic illustration of SAM (left) and MPCs (right) of alkanethiol molecules on gold substrate and nanoparticle.

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

Dipendenza proprietà SAM da substrato

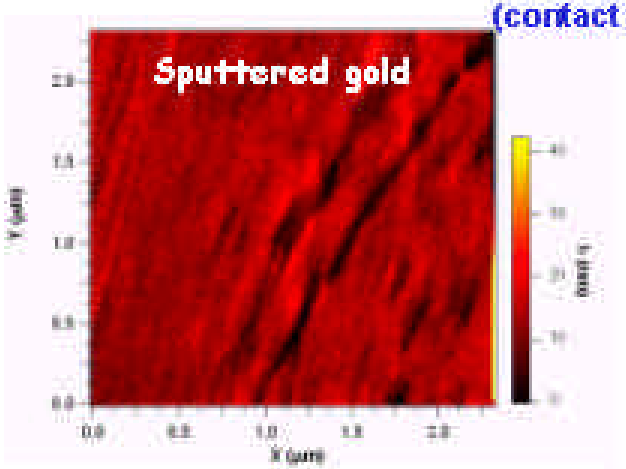


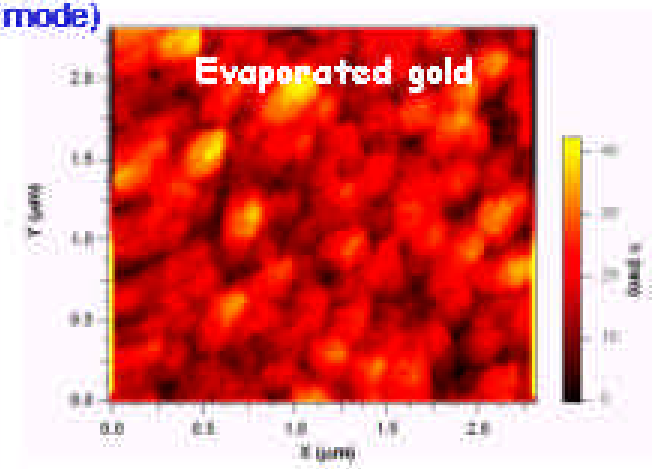
Contact angle Measurement *(hydrofobic character)*



- Particle sensitive resist:
  - Self Assembled Monolayer of nonanethiol [$CH_3(CH_2)_8SH$] onto gold

AFM images (contact mode)





Strong dependence of the resist quality on the underlying gold layer

Proprietà “macroscopica”: idrofobia (dovuta a gruppo terminale metilico) *(uso come resist)*

Misura “macroscopica” idrofobia: angolo di contatto

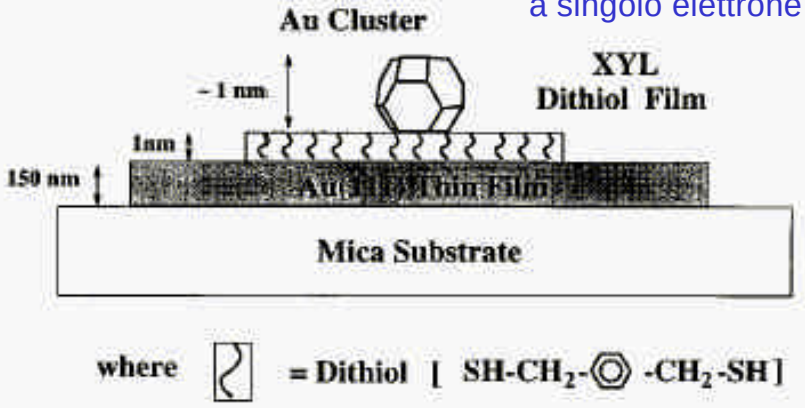
Idrofobia dipende da qualità “microscopica” del susbtrato di Au

Limiti della tecnica SAM:
-Applicabilità a *pochi* sistemi
-Dipendenza dalle proprietà del substrato

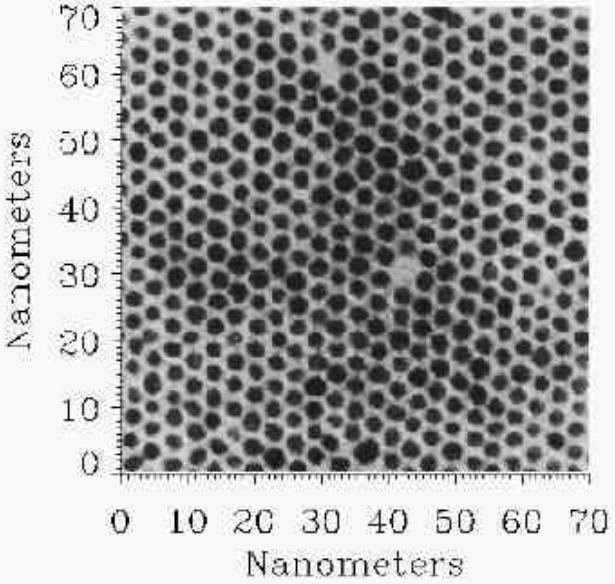
Tunneling attraverso SAM

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

Semplice dispositivo
a singolo elettrone



XYL: p-xylene-α,α'



Nanoclusters di oro depositati su SAM

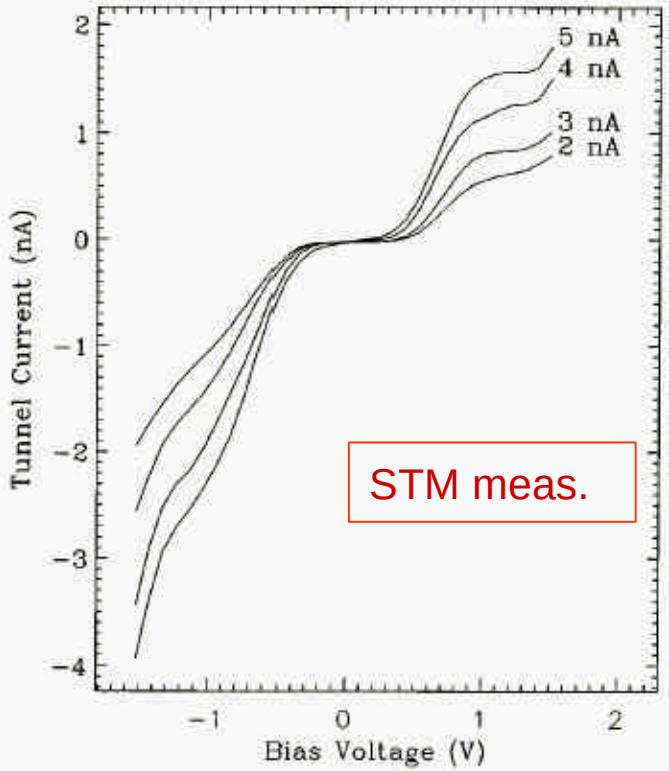


FIG. 6. $I(V,z)$ data obtained at room temperature with the tip positioned over a ~1.8 nm high Au cluster resting on a SAM of XYL dithiol. Each curve is the sum of 100 separate $I(V)$ sweeps. The different data sets illustrate how the $I(V,z)$ characteristics change as the specified set point tunneling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

Effetti di Coulomb blockade
e singolo elettrone a temp. amb.
(dovuti a nanocluster Au)

Esempi di autoassemblaggio complesso

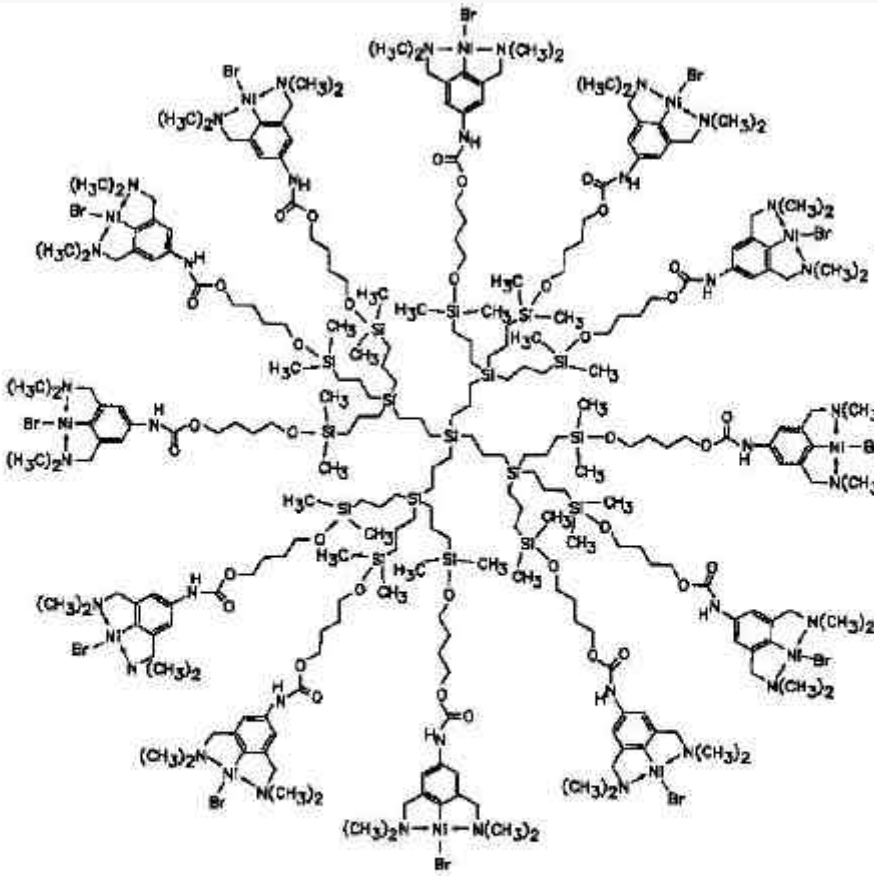


Figure 11.19. Dendrimer catalyst (dendralyst) with an Si core, and terminal group ar nickel complexes as the catalytically active functional groups. [From J. W. J. Knape A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwenn, P. Wijkens, D. M. Gro and G. van Koten, *Nature* **372**, 659 (1994).]

Struttura supramolecolari
(dendriti)

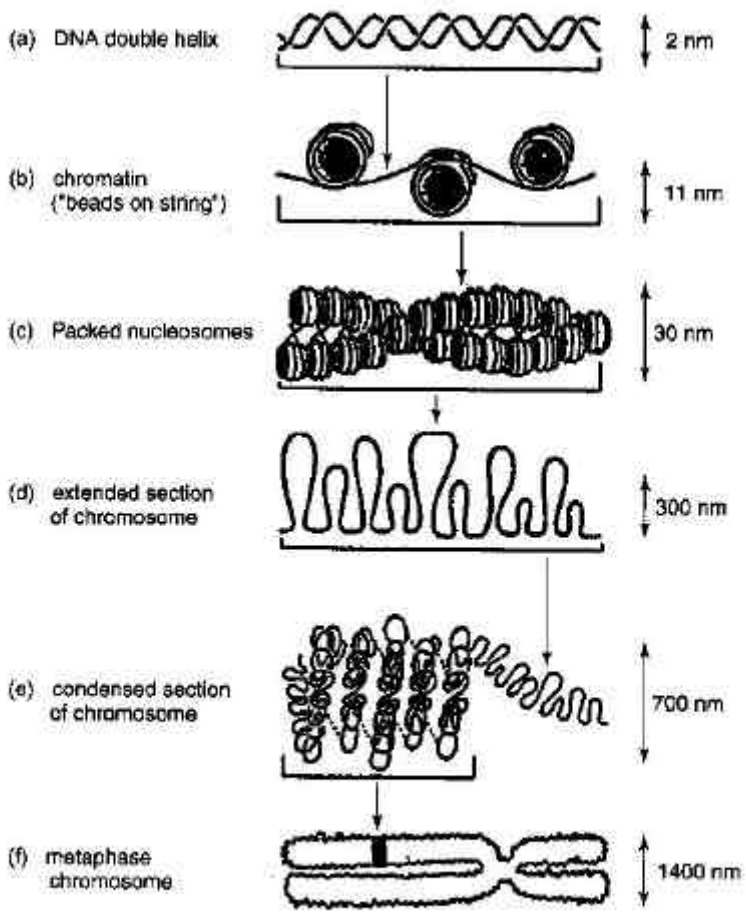


Figure 12.11. Successive twistings and foldings during the packing of DNA into mammalian chromosomes, with the sizes at successive stages given in nanometers. [From R. J. Nossal and H. Lecar, *Molecular and Cell Biophysics*, Addison-Wesley, Boston, 1991, Fig. 4.9 (p. 118).]

Arrangiamento del DNA
(replicazione)

Elettronica nella *singola molecola*

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.[5] Molecular electronics is an area of research that is firing the imagination of scientists as few research topics have ever done in the past.[6] For instance, *Science* magazine labeled the hook-up of molecules into functional circuits as the breakthrough of the year for 2001,[7] 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.

Elettronica **intramolecolare** (la funzionalità richiesta dipende dalle "caratteristiche proprie" di *poche* unità molecolari (al limite, singole molecole)

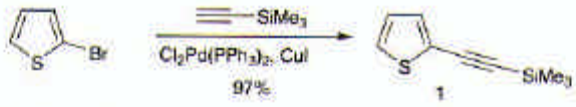
Approccio inerentemente nanotecnologico (bottoms-up)
Possibilità di "molecular engineering" per funzionalità specifiche (es., fili, diodi, switch, memorie, etc.)

Requisiti metodi di sintesi per elettronica molecolare

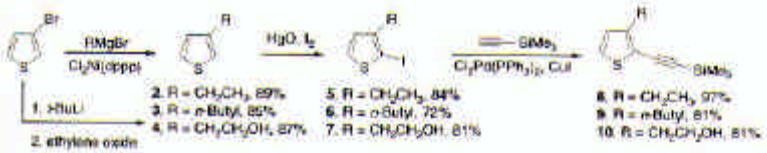
J.M. Tour, Molecular Electronics
(World Scientific, 2003)

There has been considerable recent effort to prepare large conjugated molecules of precise length and constitution.[27] 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 π-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.

Necessità metodi di sintesi "raffinati" per produrre **unità elementari** di dimensioni **~ 10 nm** (dimensione tipica delle sonde, cioè interfaccia con "mondo inorganico") replicabili a volontà in catene più lunghe

Esempi di elettronica intramolecolare

See Joachim, Gimzweski, Aviram, Nature 408 541 (2000)

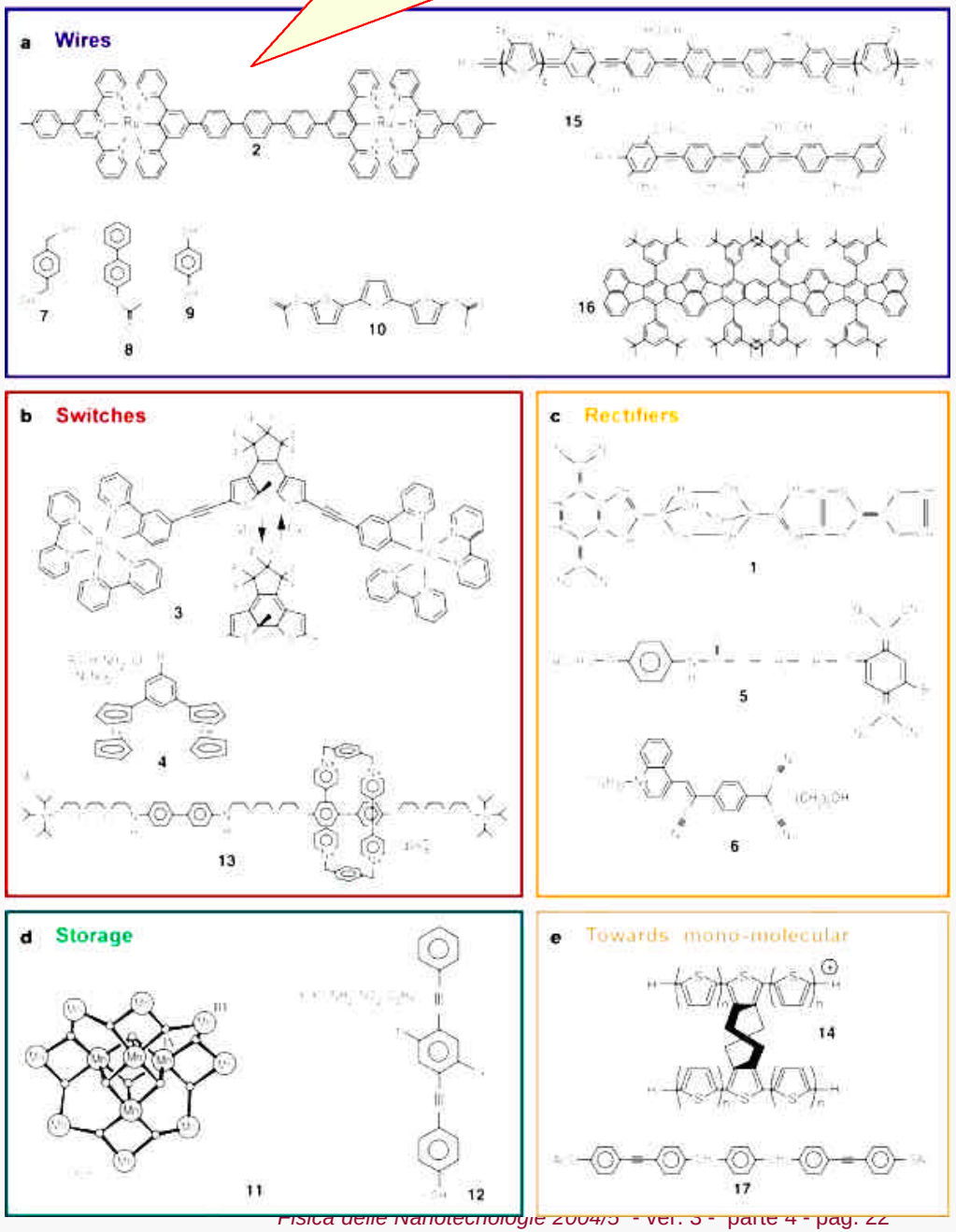
Alcuni vantaggi:

- economicità e semplicità di sintesi su larga scala
- miniaturizzazione “automatica” a livello nm o sub-nm
- possibilità di autoassemblaggio e replicazione (tecniche bottoms-up)

Alcuni svantaggi:

- controllo, ripetibilità dei processi, …
- integrazione con mondo inorganico e con relative tecnologie
- stabilità chimica, durata, proprietà meccaniche, …
- difficoltà di “indirizzare” la singola molecola per probe o dispositivi

Enorme varietà di sistemi possibili con diverse funzionalità

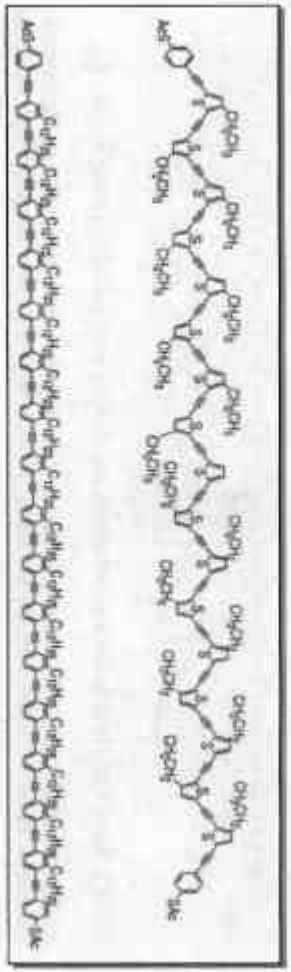


Cavi molecolari ("di Tour")

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

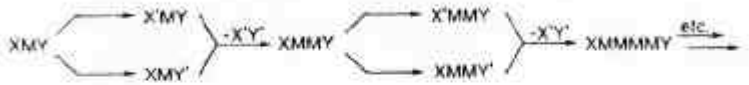
Cavi molecolari: molecole coniugate

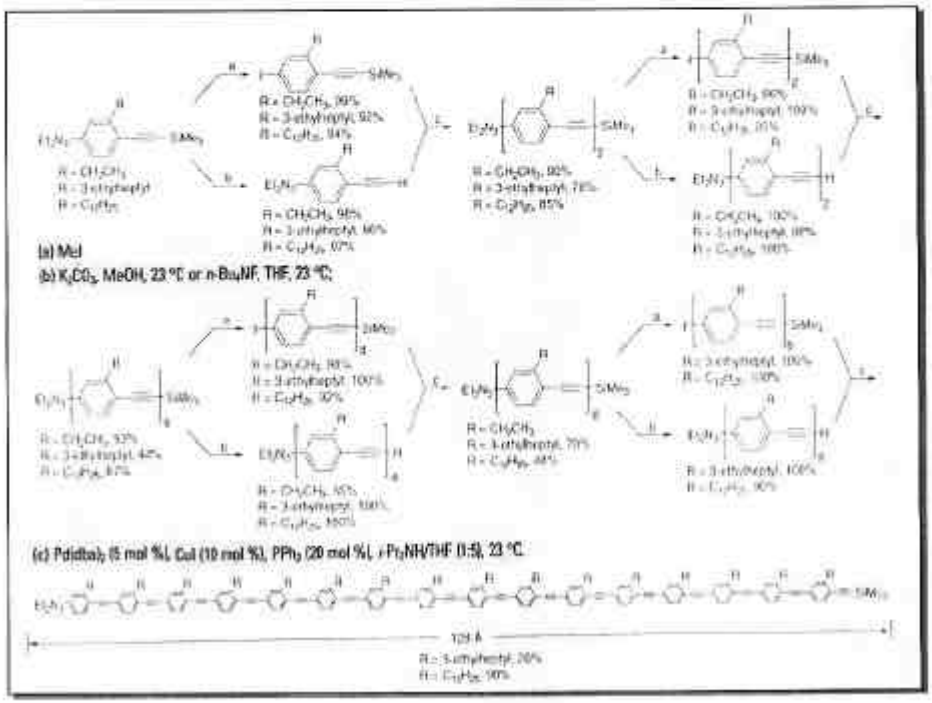
- Sistemi con omogeneità di segnali in ingresso ed in uscita
- Sfruttano la conduzione elettrica
- Possono trasmettere un segnale anche solo attraverso il riarrangiamento della nuvola elettronica
- Sono stati messi a punto diversi metodi di sintesi efficaci
- Esistono metodi già sperimentati per il controllo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

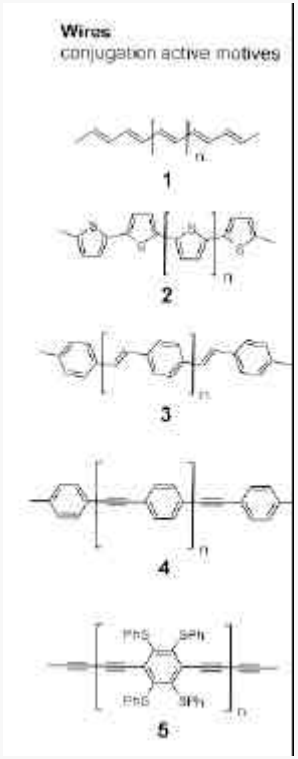




Materiali tratti dai seminari di
Oliviero Andreussi, Feb. 2002
Marco Donato, Apr. 2004

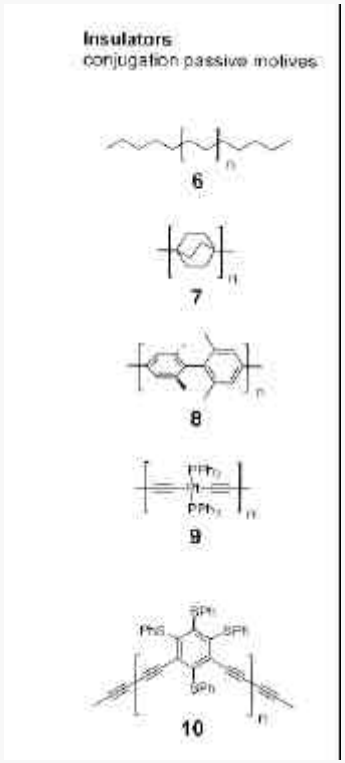
Comportamento atteso simile a guide d'onda elettroniche (trasp. balistico)

“Molecular engineering” per conduttori/isolanti molecolari



The most basic electronic function is a wire, a one-dimensional object that allows the 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 these should be the closest to the Fermi levels of the electrodes (see Sec. 5.1). In general, with increasing size of the π-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 π-systems. Structural motives that allowed the design of chains with delocalized π-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 π-system over the whole length [10]. Many other examples consisting 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 π-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 π-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 π-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 π-system linked together by a spacer [2]. They suggested a rigid adamantyl cage **7** as a non-conjugating linker between both π 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 π 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 π-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. π-Systems meet the rigidity conditions but have already discussed as good conductors. However, the delocalisation of the π-system depends strongly on the torsion angles between the subunits. Two neighboring subunits with perpendicular π-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].

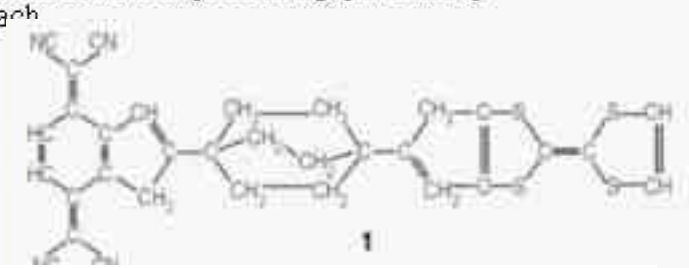


Da R. Waser Ed., Nanoelectronics and information technology (Wiley-VCH, 2003)

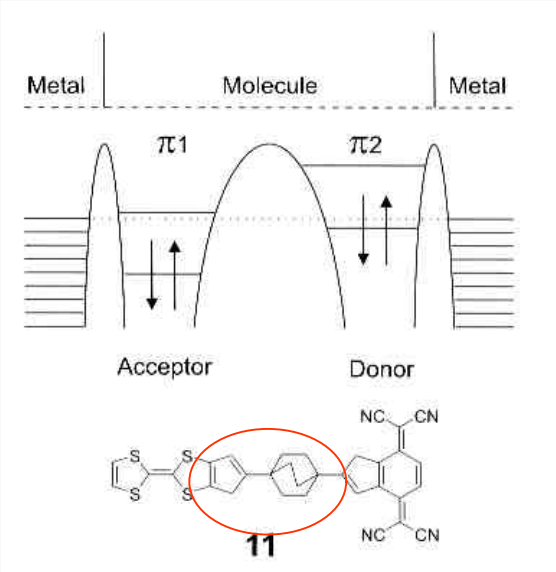
Comportamento rettificante (diodi)

Aviram and Ratner[1] 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[2], 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

Diodo



Tunneling intramolecolare controlla la corrente fra due elettrodi creando un elemento rettificante



Spacer crea barriera

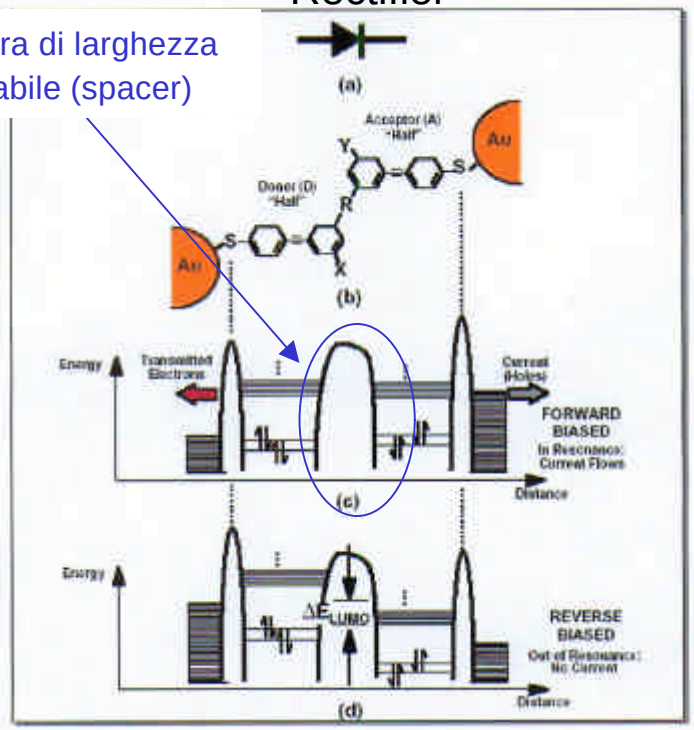
Figure 3: The first approach to molecular electronics [2]. Molecules with a donor and an acceptor group, separated by an insulating spacer, are predicted to behave as diodes. The upper panel displays the electron energies in the system, when no bias voltage is applied: In the metallic electrodes outside, electrons are filled up to the Fermi energy. The π-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.

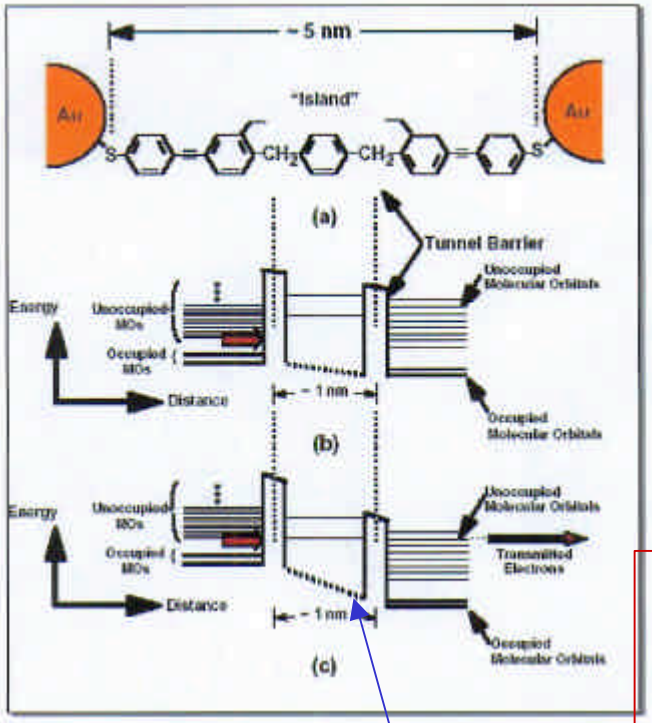
Esempi di dispositivi rettificanti

Rectifier

RTD

Barriera di larghezza variabile (spacer)





Buca di potenziale con livelli discreti

Osservazione di Marco Donato 2003: la buca è poco pronunciata e stretta e il tunneling non è difficile

Redox-based single-electron process

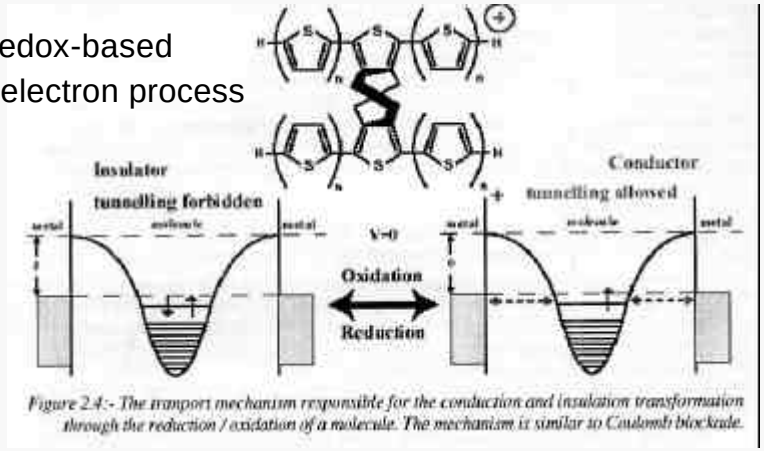


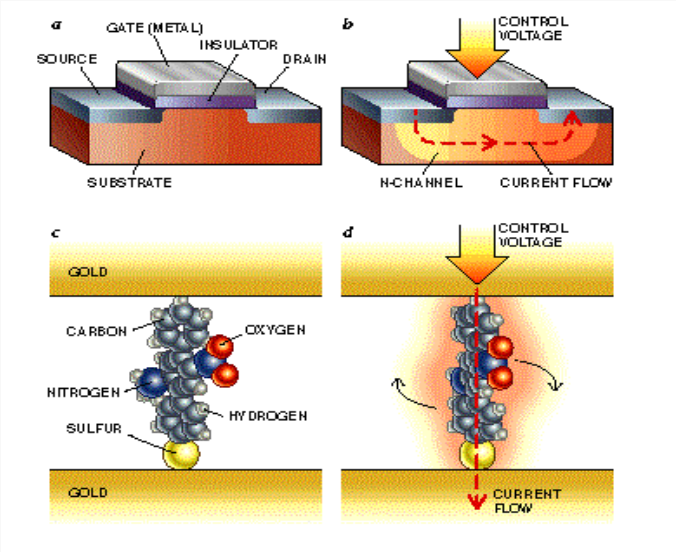
Figure 2.4:- The transport mechanism responsible for the conduction and insulation transformation through the reduction / oxidation of a molecule. The mechanism is similar to Coulomb blockade.

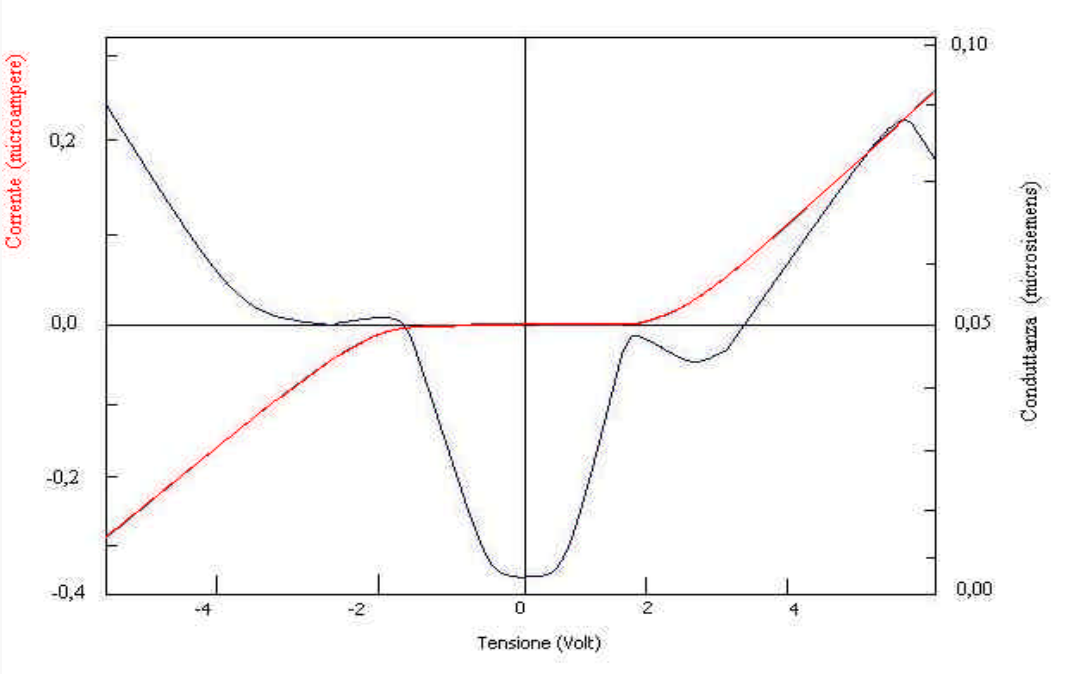
Singole cariche sono generalmente coinvolte nei processi intramol.

⇩

Comportamento di singolo elettrone

Esempi di funzionalità complesse (stile MOS-FET…)

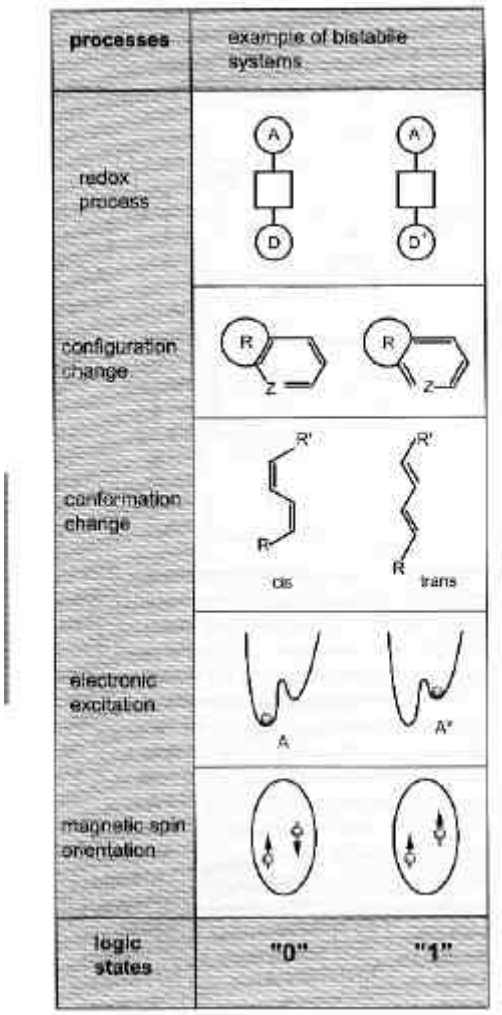




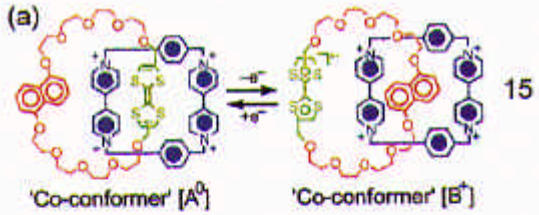
All'anello centrale sono fissati gruppi asimmetrici: quando è applicata una specifica tensione (d), il campo elettrico torce la molecola permettendo alla corrente di fluire

Ampia varietà di possibili metodi di controllo della conducibilità

Esempi di dispositivi con funzionalità di switch



Rotaxane



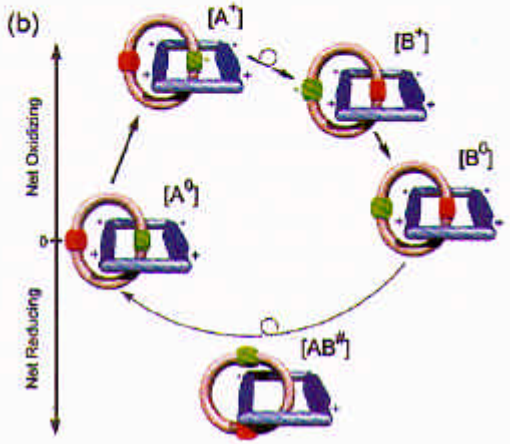


Figure 8: Hysteretic redox-triggered rearrangement of the catenane **15**. At zero bias the molecule is in the ground-state [A^0] with the TTF unit between the two doubly charged viologenes. Biasing the system into the net oxidizing direction by +2V leads to an ionization of the TTF unit into state [A^+]. 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^{3+}] 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).

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Molti metodi di switching richiedono un controllo di natura non elettrica

Switching meccanico "assistito" da *controllo esterno* (luce, pH, …)

"Indirizzamento" e probe di singole molecole

Singola molecola fra elettrodi inorganici

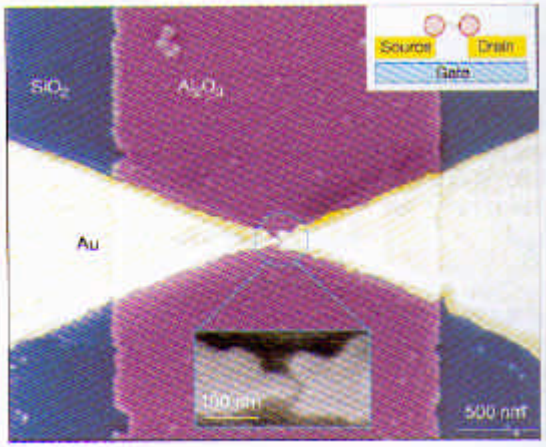


Figure 9: SEM picture of a Au electrode pair on top of an Al gate electrode, which is covered by an Al_2O_3 insulator. Such a setup was used as a molecular field effect transistor [47].

Metodi con microscopi a scansione (utili per testare, non per dispositivi!)

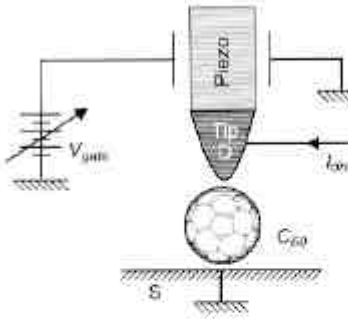


Figure 11: A nanomechanical three device [41]. The C_{60} molecule is co metallic substrate on one side, and h from the opposite side. The steering which replaces the third electrode is which acts on the STM tip. By pushi molecule, the conductance varies by magnitude per nano-newton.

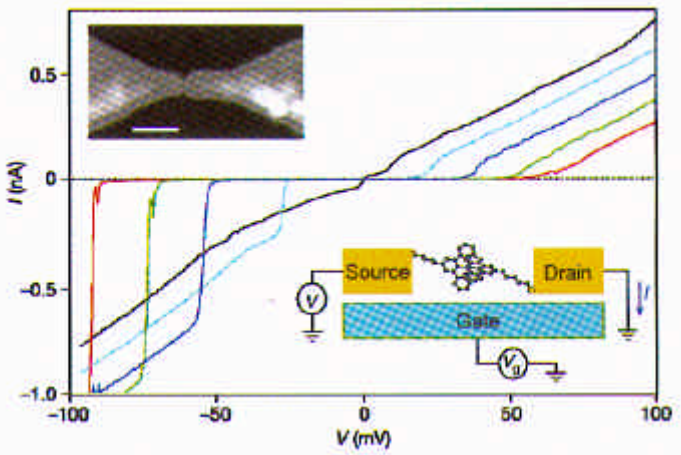
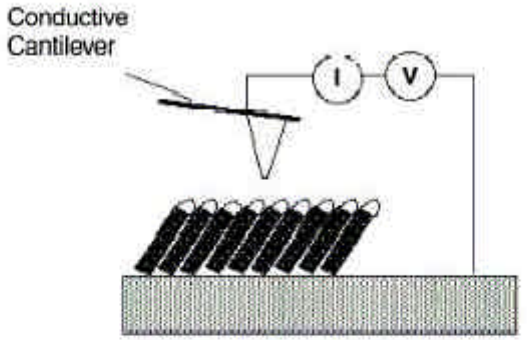
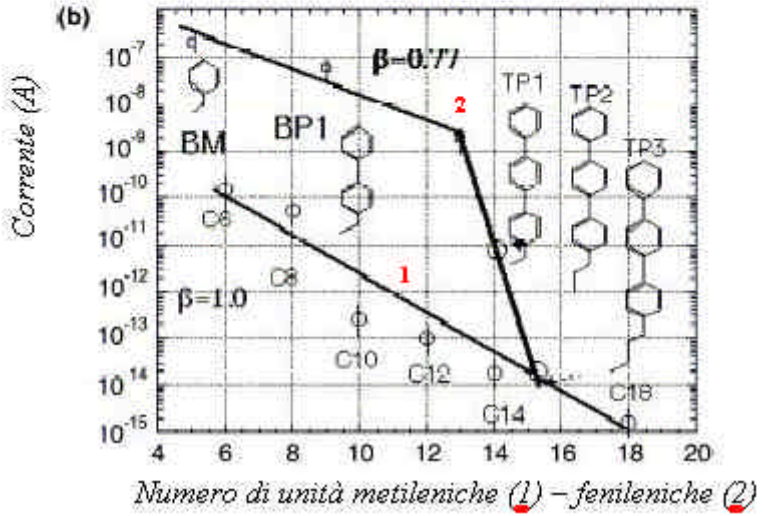


Figure 22: A single molecule transistor with an organometallic molecule [45]. The electrode pair with ~ 2 nm spacing has been manufactured by the electromigration technique (see SEM picture in the inset). The Si substrate served as gate electrode, separated by a SiO_2 insulating layer. If the charge of the central Co ion is fixed to either Co^{2+} or Co^{3+}, no current can flow at small bias voltage due to Coulomb blockade (colored lines). If the gate is tuned such that Co^{2+} or Co^{3+} have the same energy, the ion can be continuously charged or uncharged: current can flow even at small bias voltages (black line).

(a)

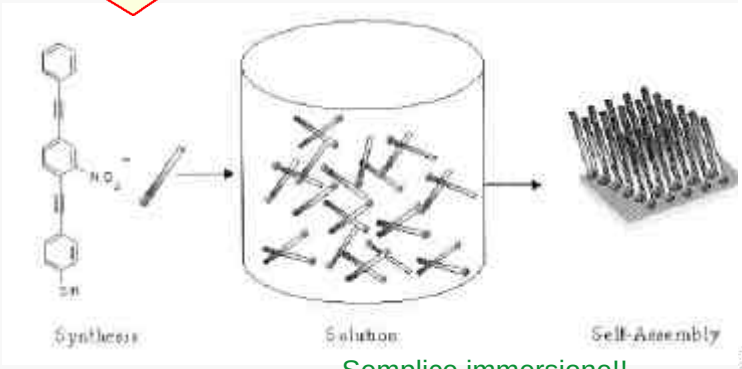


(b)



Uso di SAM come “template” molecolare I

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



Semplice immersione!!

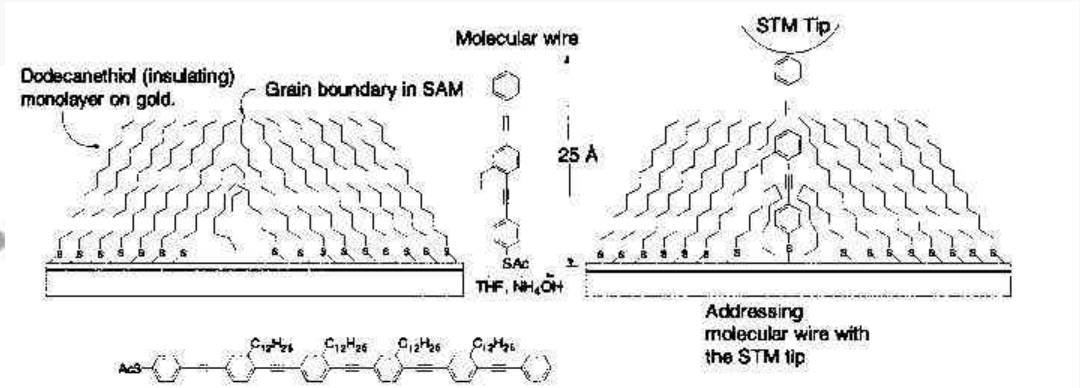


Figure 4.3 Protocol for inserting molecular wires into dodecanethiolate SAMs at grain boundaries and step edges. Relative conductance recording was done with a STM tip. The molecule at the bottom has also been used in this study.

SAM impiegato per “sostenere” singola molecola di OPE (oligophenylene ethynylene) permettendone *direct addressing* con STM

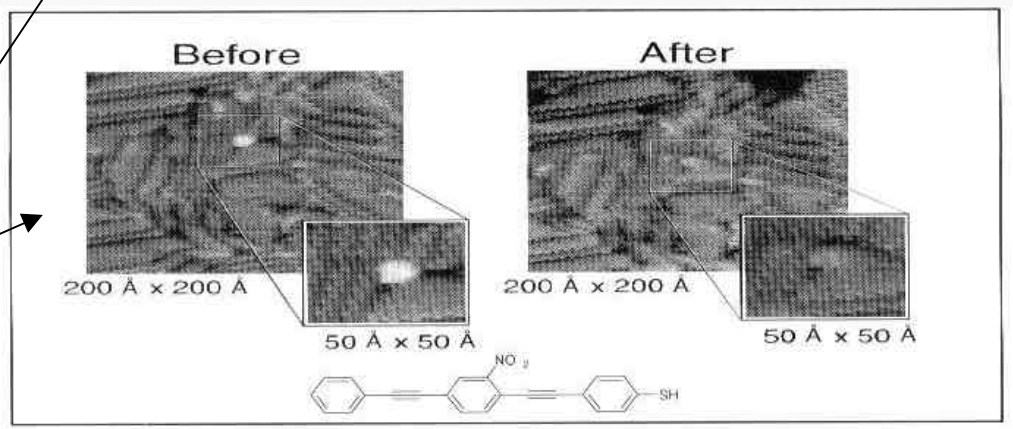
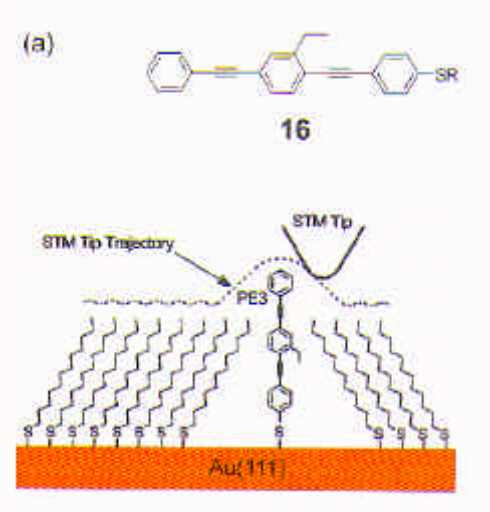


Figure 4.4 A single molecule (nitro OPE structure at bottom) in an alkanethiolate matrix SAM on gold. The dark spheres are the terminal methyl groups of the alkanethiolates. “Before” shows the OPE in an “on” state, and after a voltage pulse from the tip, the OPE is in an “off” state shown under “After”. 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.

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

Uso di SAM come “template” molecolare I I



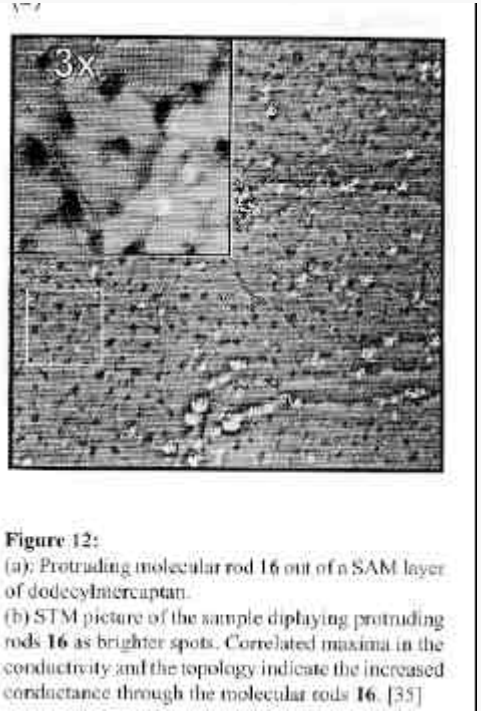
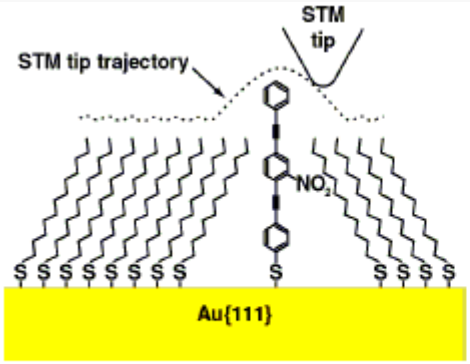
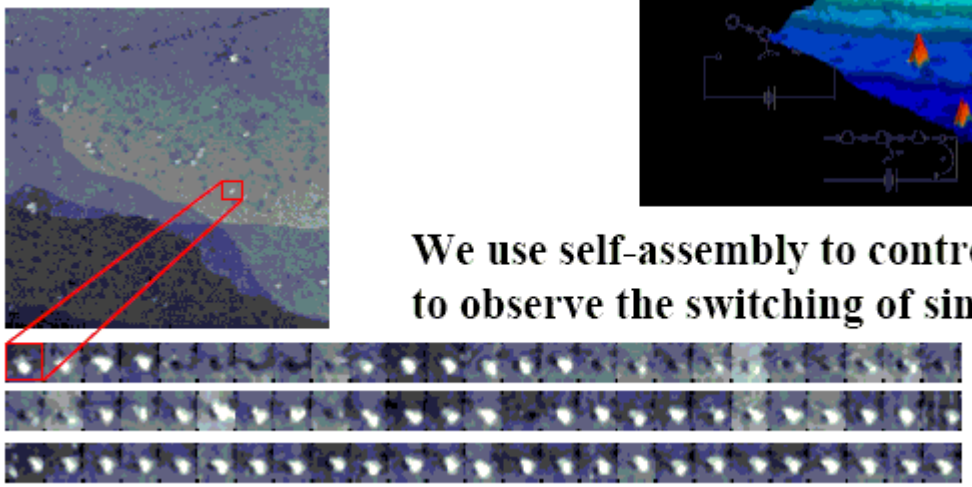
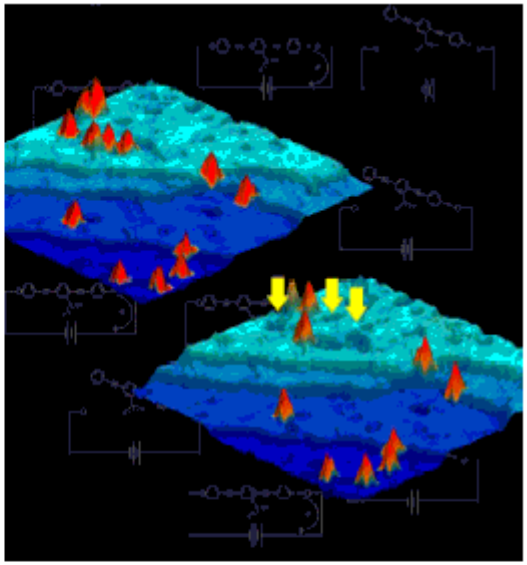


Figure 12:
(a): Protruding molecular rod 16 out of a SAM layer of dodecylmercaptan.
(b) STM picture of the sample diplaying protruding rods **16** as brighter spots. Correlated maxima in the conductivity and the topology indicate the increased conductance through the molecular rods **16**. [35]







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

Uso di SAM come resist (in SPM-imprinting)

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

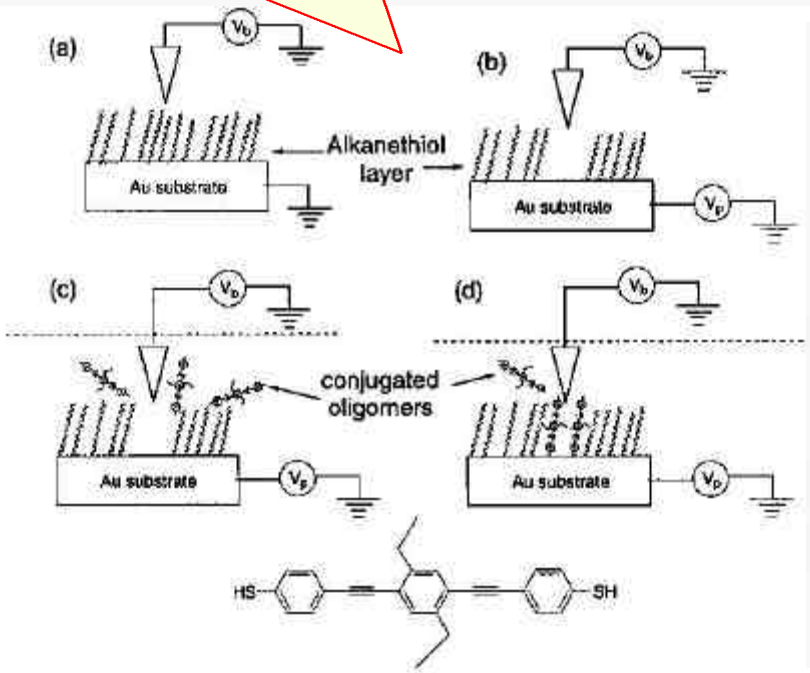


Figure 4.6 Schematic representation of the lithographic patterning and replacement of conjugated molecules in an alkanethiolate matrix. (a) Normal STM imaging of an alkanethiolate SAM with tip bias V_b. (b) SAM removal by applying a voltage pulse V_p to the substrate. (c) Carrying out the same voltage 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.

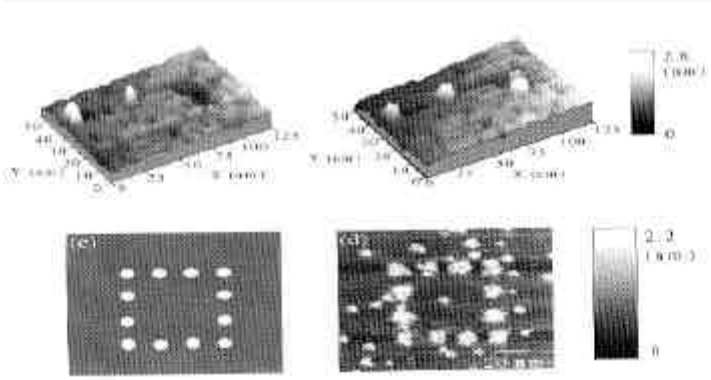


Figure 4.7 (a) A dodecanethiolate SAM surface after three consecutive voltage pulsing events. The first two pulsed locations have molecular wires inserted while the third location remains to be filled. (b) The image taken a few minutes later shows that wire insertion at the third pulse location is now 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.

Switching di un oligomero OPE mediante impulso elettrico da STM

SPM patterning del SAM
(attraverso “scarica” elettrica locale)

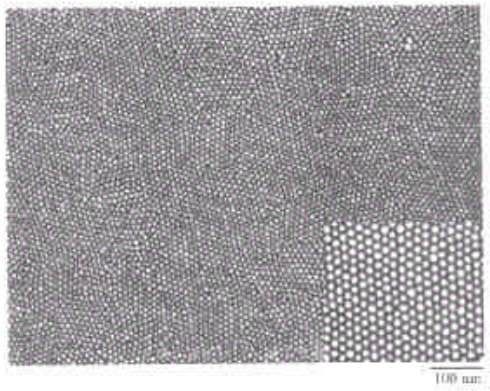


Figure 1. Scanning electron micrograph of a LB monolayer consisting of dodecanethiol-encapsulated gold nanoparticles of 8.3 nm in diameter, displaying long range order [18]. The inset shows higher magnification which reveals hexagonal close-packed structure.

Principali problematiche nel trasporto intramolecolare

Necessità di “interfacciarsi” con “mondo esterno” (es., elettrodi *metallici*)

Le proprietà elettroniche della molecola sono modificate da presenza di elettrodi metallici, principalmente perché:

- modifica orbitali vicinali (legame *quasi-chimico)*;
- effetto delle *immagini* dei dipoli mol.;
- geometria degli elettrodi

⇩

Scattering (anelastico) degli elettroni all’interfaccia ed effetti diffusivi nel trasporto nel sistema “complessivo” molecola + conduttore metallico

Fenomeni “quantistici” (EW, Coulomb blockade, etc.) spesso mascherati da effetti di interfaccia anche in sistemi nanodimensionati

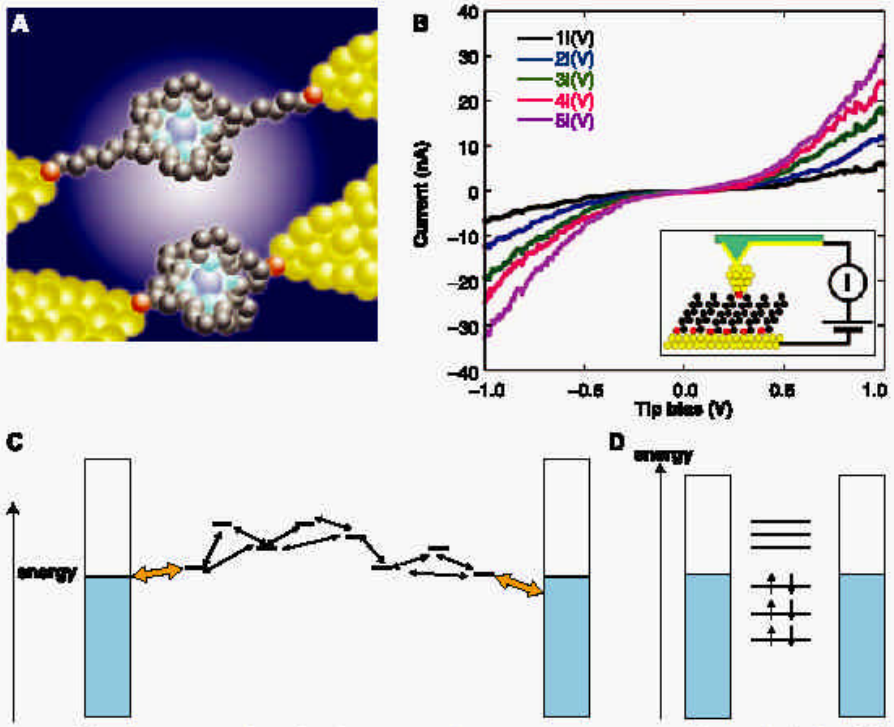


Fig. 1. (**A**) Schematic single molecule junction between two continuous electrodes [after (*5*)] (**B**) Schematic (inset) of an alkane thiol adlayer with gold dot current collector, measured using AFM. Actual data is also shown, corresponding to (suggested) transport through 1, 2, 3, 4, and 5 molecular 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.

Livello di Fermi si colloca tra HOMO e LUMO

See Nitzan and Ratner Science 300 1384 (2003))