CdL Scienza dei Materiali - Fisica delle Nanotecnologie - a.a. 2003/4

Appunti & trasparenze - Parte 4

Versione 2, Ottobre 2003
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Sostanze organiche conduttrici, polimeri conduttori, esempi di elettronica intramolecolare, dispositivi molecolari, autoassemblaggio, SAM.

21/10/2003 - 9.30+1 ITI G
27/10/2003 - 9.30+3 ITI I, L

Elettronica molecolare (*molectronics*)

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.

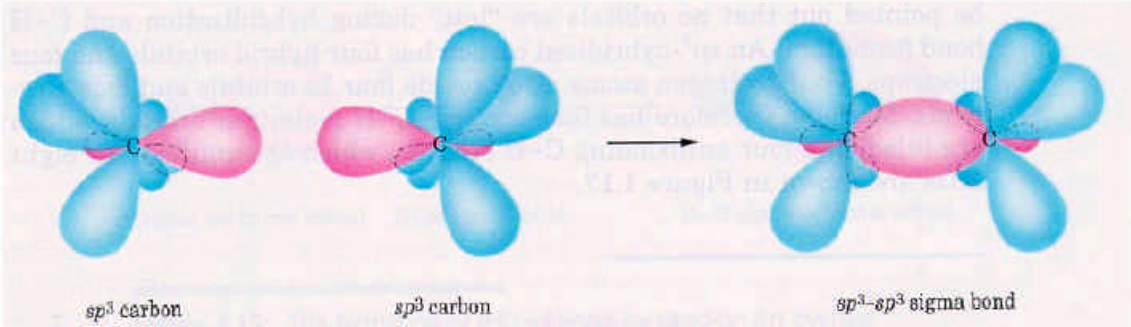
Problematiche elettroniche (ed opto-elettroniche) affrontate con metodi di chimica molecolare e sopramolecolare

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

Approcci all'eletrronica molecolare:
- Conducibilità nel **bulk** (ad esempio, drogaggio di polimeri coniugati)
- Elettronica **intramolecolare** (la funzionalità richiesta dipende dalle "caratteristiche proprie" di *poche* unità molecolari (al limite, singole molecole)

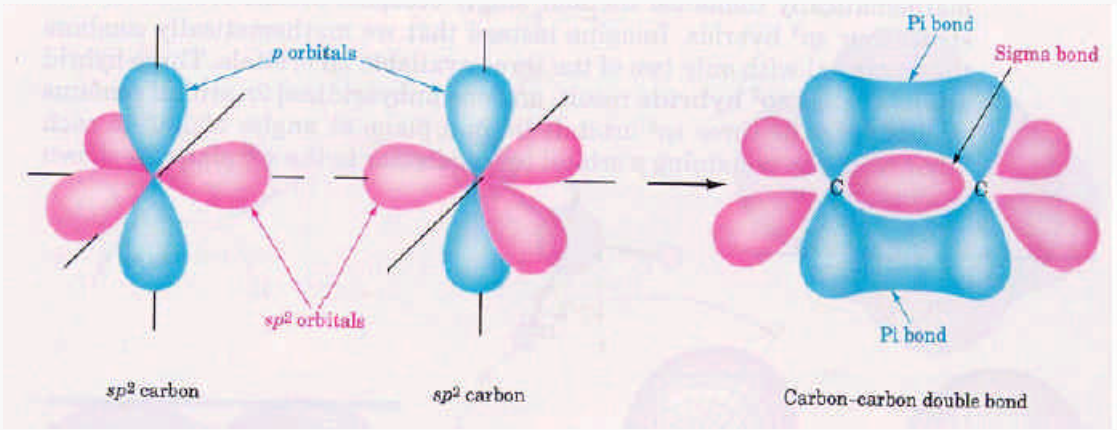
Proprietà di trasporto in molecole organiche

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



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

MA...

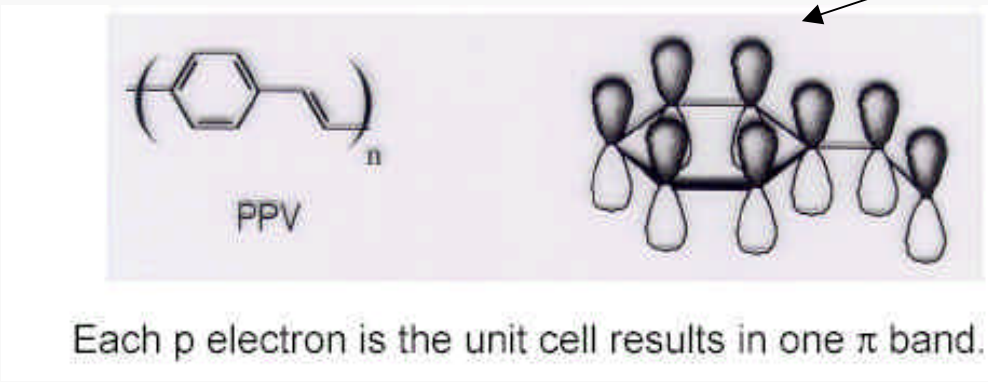


Legami π tra
orbitali ibridizzati sp^2
⇩
"delocalizzazione" elettroni
⇩
carattere **semiconduttore**

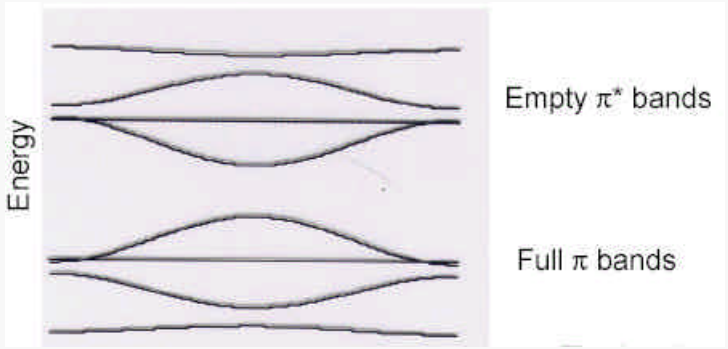
Materiale organico *può essere semiconduttore*

Proprietà di trasporto in polimeri coniugati

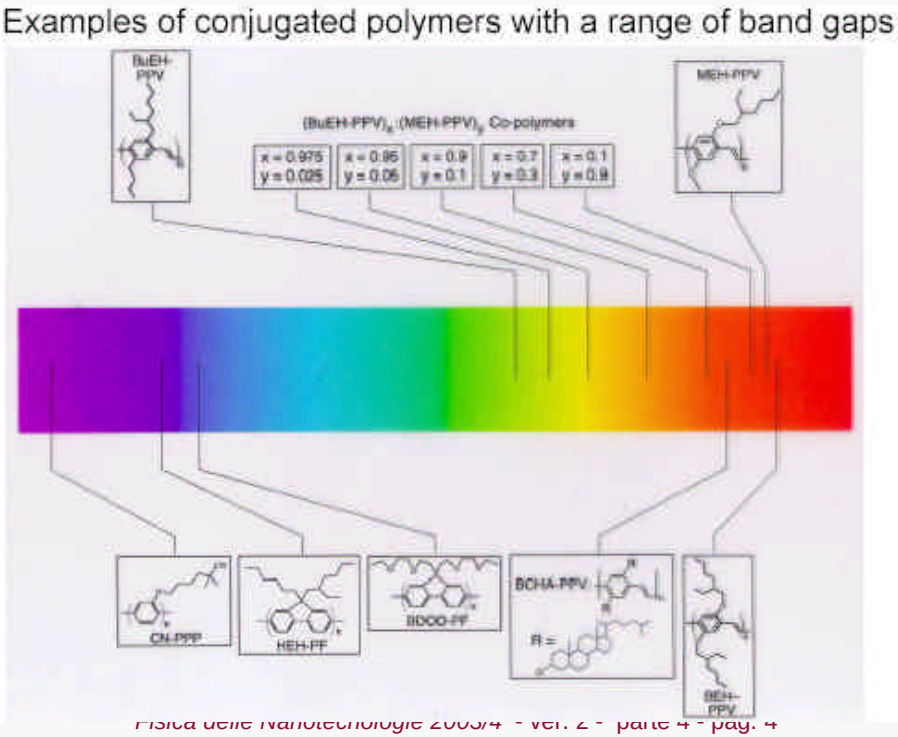
Esempi: polianiline, pirroli, tiofeni, polifenilenvinilene,...



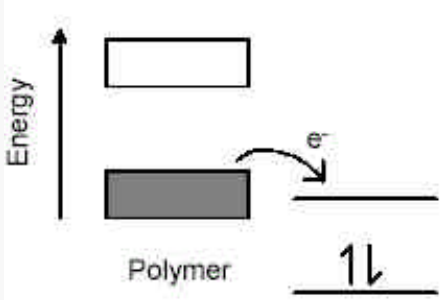
Struttura “a bande” generata da elettroni π



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

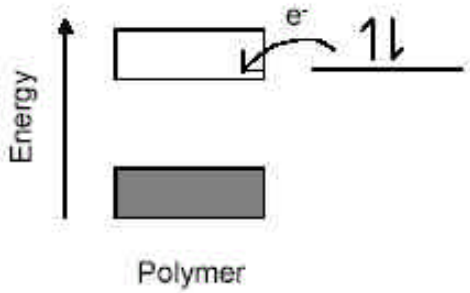


Effetti di drogaggio di polimeri coniugati

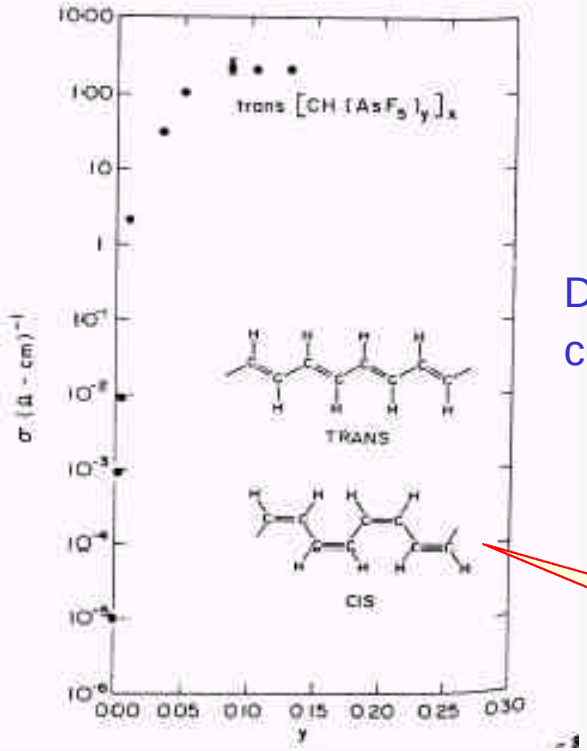


Oxidizing agent (e.g. I_2, Br_2, AsF_5)

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



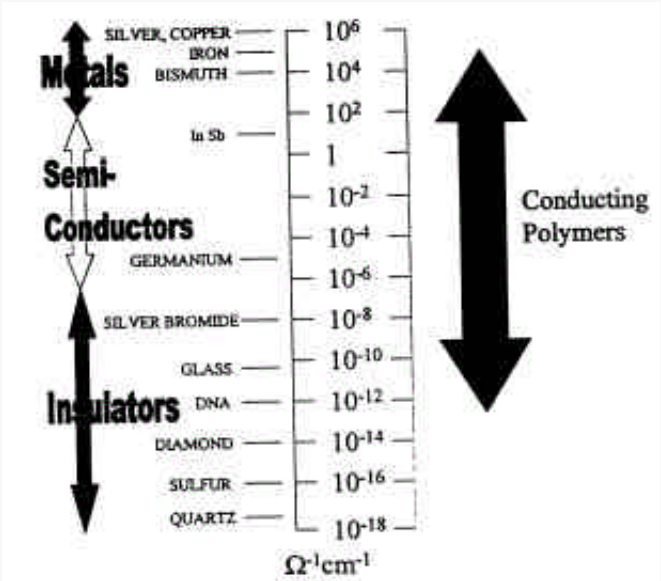
Reducing agents such as calcium and lithium can introduce electrons into the conduction band of a conjugated polymer.



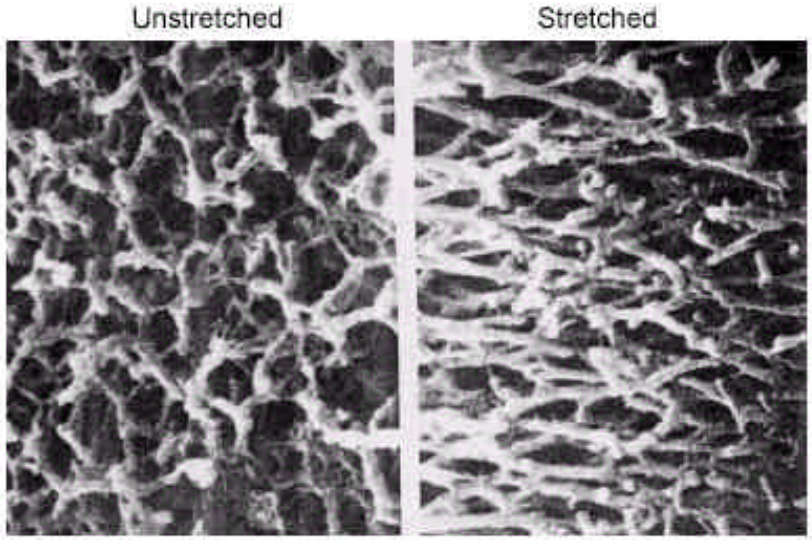
Drogaggio crea buche o elettroni *relativamente* liberi

Drogaggio di trans-acetilene con AsF_5

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



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!!)

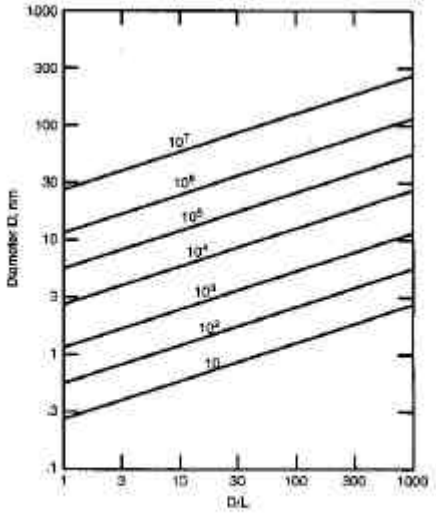


Figure 11.2. Dependence of the diameter D of a cylindrical polymer on its diameter : length ratio D/L for molecular weights from 10 to 10^7 Da, as indicated on the curves. A density $\rho = 1$ g/cm^3 was assumed in Eq. (11.13) for plotting these curves.

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

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

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

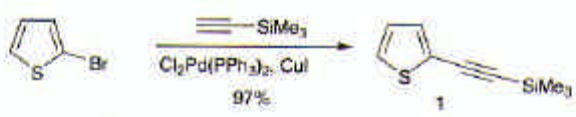
where D and L have the units of nanometers. These expressions are plotted in Figs. 11.2 and 11.3 for $D > L$ and $L > D$, respectively. The figures can be employed to estimate the size parameter for an axially shaped, flat or elongated, polymer if its molecular weight, density, and length : diameter 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.

Requisiti metodi di sintesi per elettronica molecolare

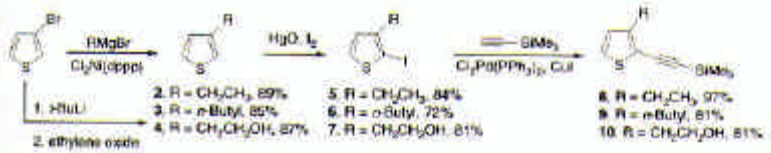
J.M. Tour, Molecular Electronics
(World Scientific, 2003)

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

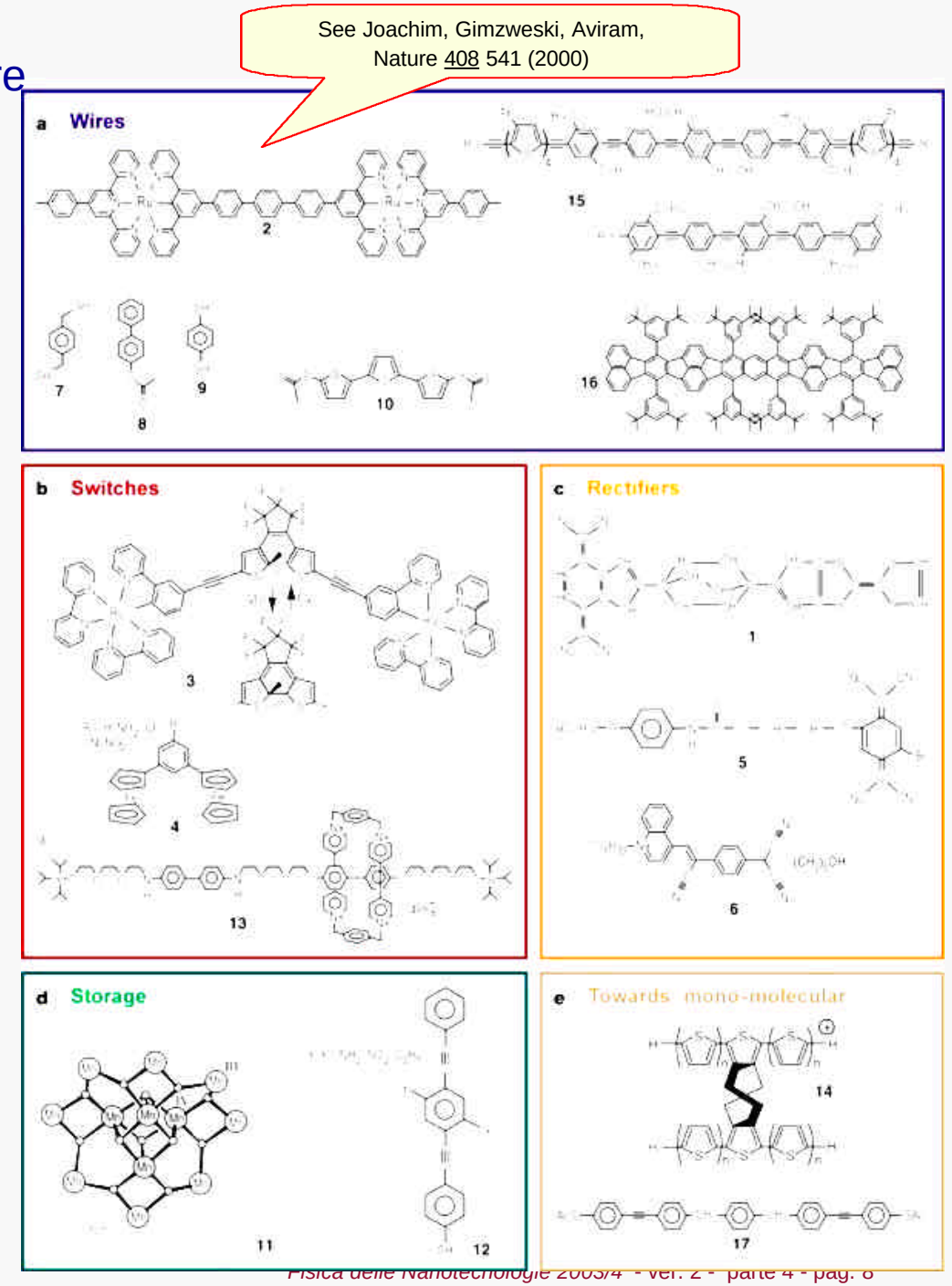
Alcuni vantaggi:

- 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

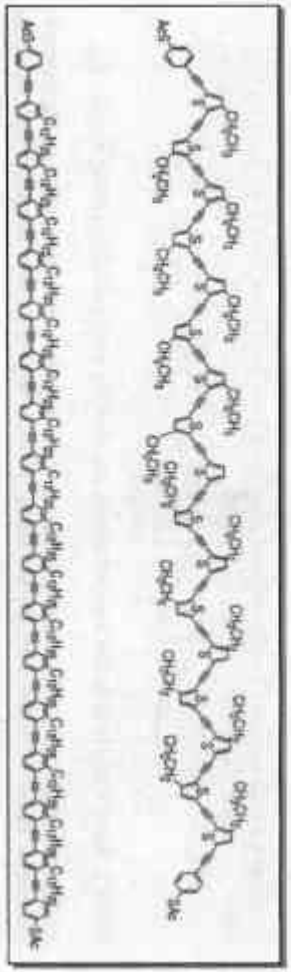


Cavi molecolari (“di Tour”)

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

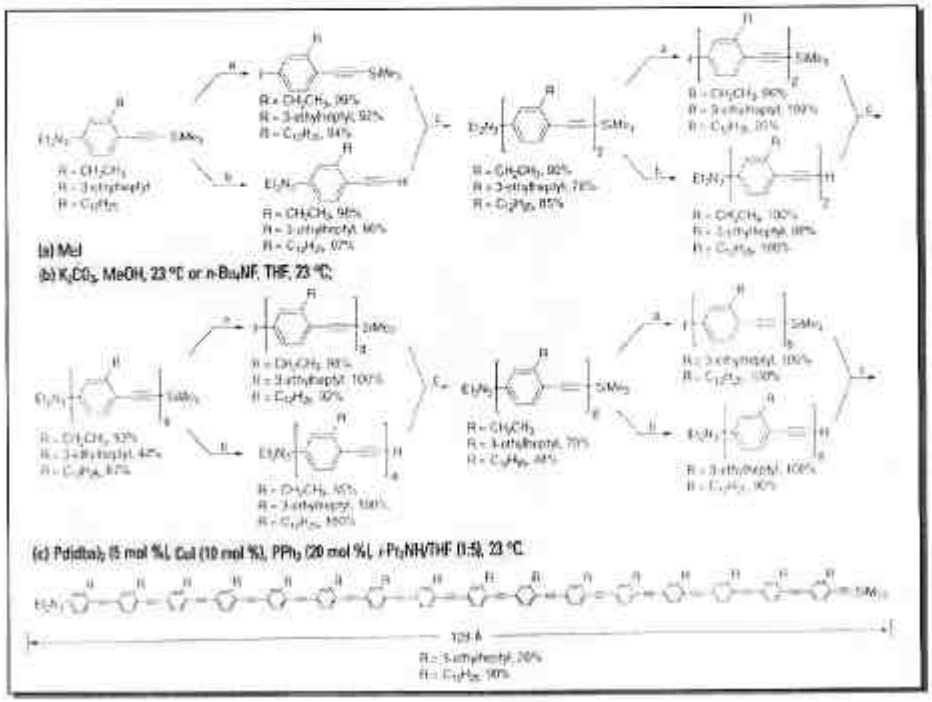
Cavi molecolari: molecole coniugate

- 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



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

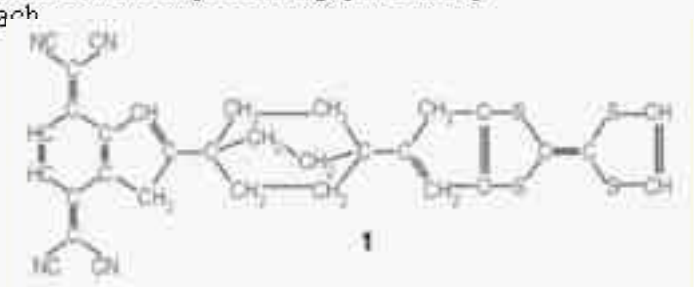
Materiale tratto dal seminario di Oliviero Andreussi, Feb. 2002

Elementi di base di dispositivi intramolecolari

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

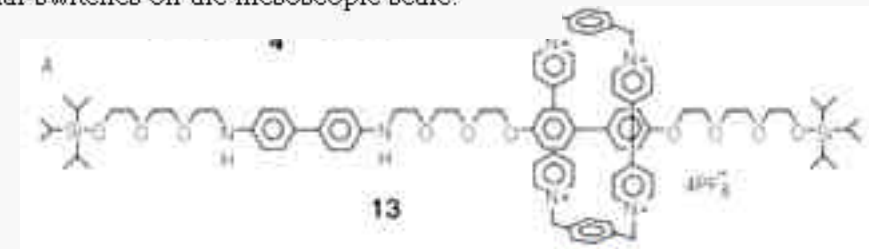
Tunneling intramolecolare controlla la corrente fra due elettrodi creando un elemento rettificante



Suggestions[55-58] for single-molecule molecular switches have been put forward for some time, but relatively few have been synthesized[6, 59]. In an electronic circuit, switching is based on an intrinsic molecular property involving a bistable change of internal structure (such as a conformation change[57] or a unimolecular reaction[6, 59]), which induces a modification of *T*. For example, the photochromic switching of molecule **3** (Fig. 1b) is possible because a photo-induced molecular orbital "up-shift" in the "on" state[6] favours efficient electron transfer through **3**, making this phenomenon an intramolecular analogue of the solid state "valve" effect. Rotaxanes **13** (Fig. 1b) have also been proposed as mechanical molecular switches[60]: the macromolecular ring can move along the molecule's central 'axle' and occupy one of two or more metastable positions or 'stations' along the axle, where one position provides a high-*T* and the other a low-*T* state. The gating used for these two switches has a macroscopic origin (light for the photochromic effect, pH and light control for the rotaxane), but the development of near-field integrated optics[61] may provide a more controlled means to optically gate molecular switches on the mesoscopic scale.

Rotaxane switch

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

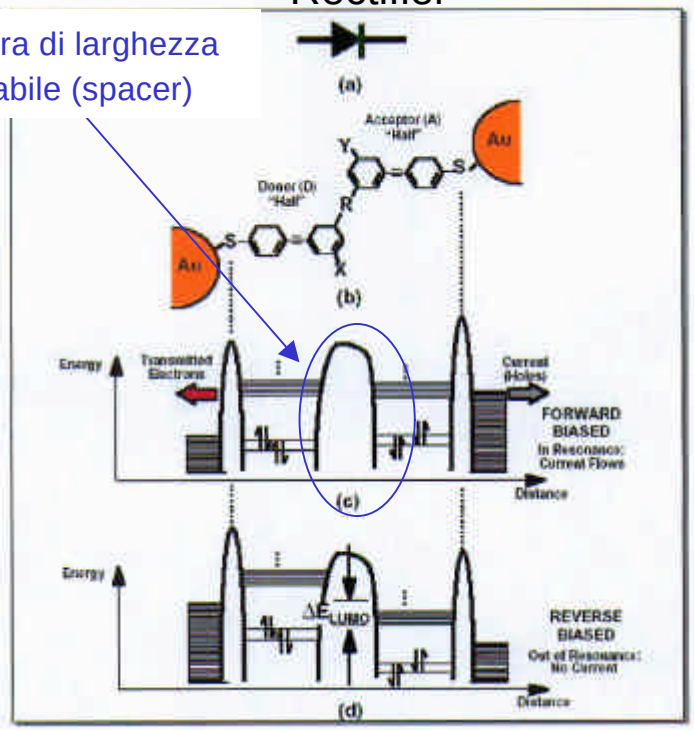


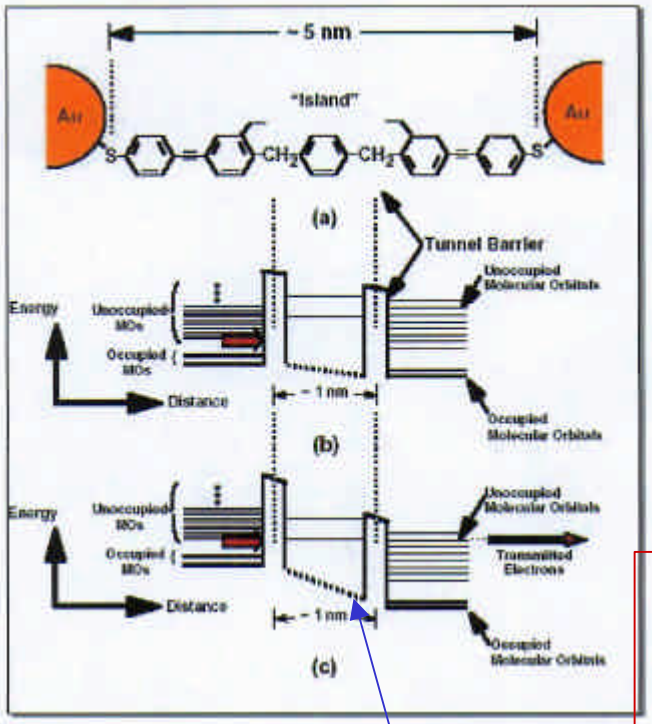
Esempi di dispositivi complessi e innovativ a singola molecola

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

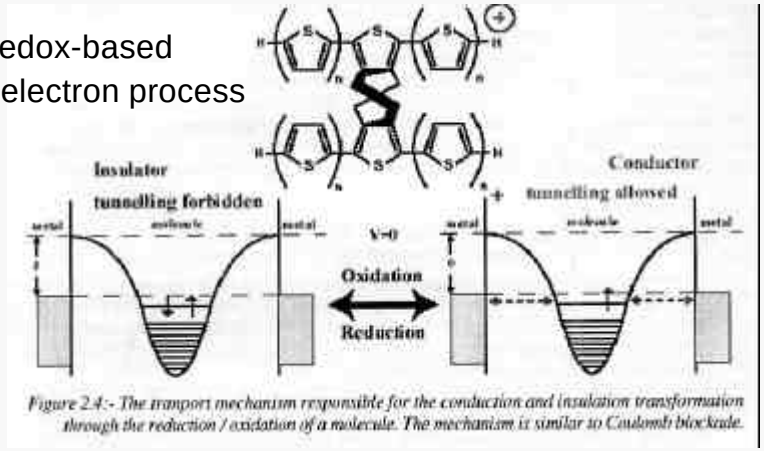


Figure 2.4:- The transport mechanism responsible for the conduction and insulation transformation through the reduction / oxidation of a molecule. The mechanism is similar to Coulomb blockade.

Singole cariche sono generalmente coinvolte nei processi intramol.

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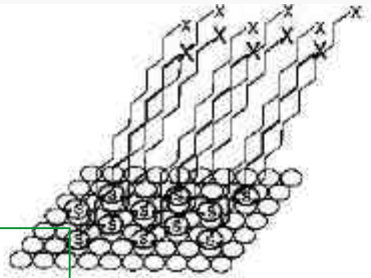
Comportamento di singolo elettrone

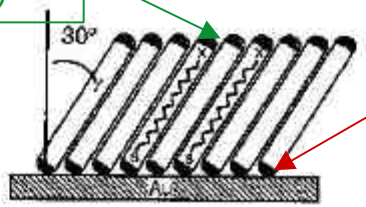
Self-Assembling Monolayers (SAM)

(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

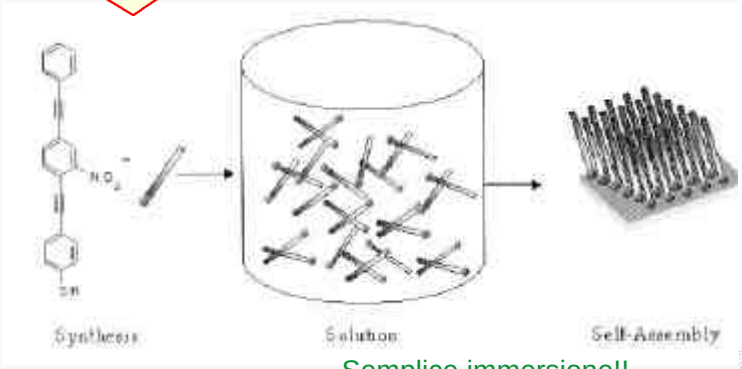
⇩

(uso come resist)

uso come "base" per nanodispositivi

Uso di SAM come “template” molecolare

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



Semplice immersione!!

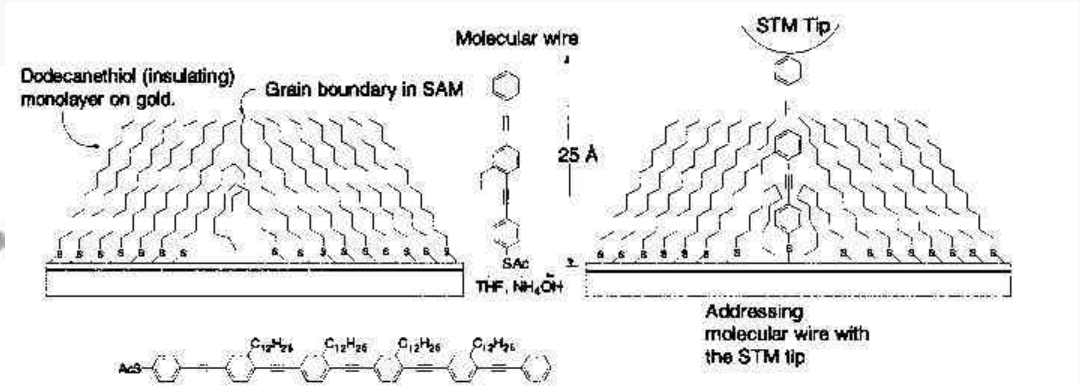


Figure 4.3 Protocol for inserting molecular wires into dodecanethiolate SAMs at grain boundaries and step edges. Relative conductance recording was done with a STM tip. The molecule at the bottom has also been used in this study.

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

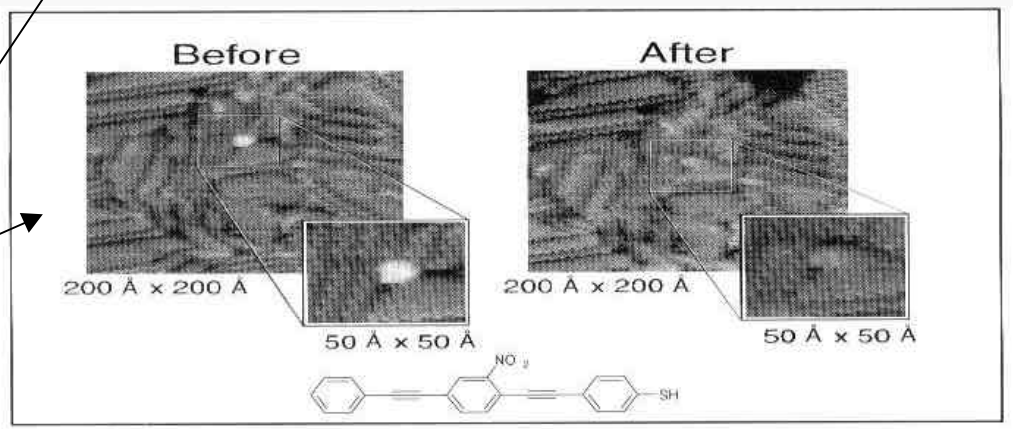


Figure 4.4 A single molecule (nitro OPE structure at bottom) in an alkanethiolate matrix SAM on gold. The dark spheres are the terminal methyl groups of the alkanethiolates. “Before” shows the OPE in an “on” state, and after a voltage pulse from the tip, the OPE is in an “off” state shown under “After”.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

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

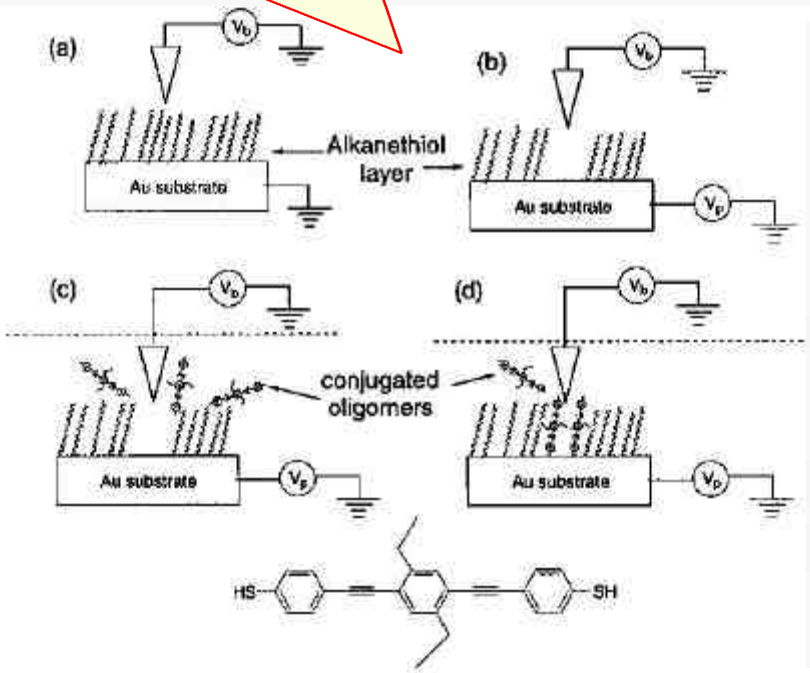


Figure 4.6 Schematic representation of the lithographic patterning and replacement of conjugated molecules in an alkanethiolate matrix. (a) Normal STM imaging of an alkanethiolate SAM with tip bias V_b. (b) SAM removal by applying a voltage pulse V_p to the substrate. (c) Carrying out the same voltage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

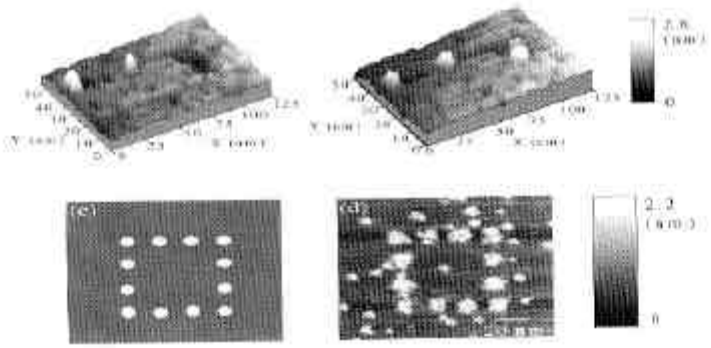


Figure 4.7 (a) A dodecanethiolate SAM surface after three consecutive voltage pulsing events. The first two pulsed locations have molecular wires inserted while the third location remains to be filled. (b) The image taken a few minutes later shows that wire insertion at the third pulse location is now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

SAM usato anche per modificare l'aggregazione di nanoclusters metallici (ancorati)

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

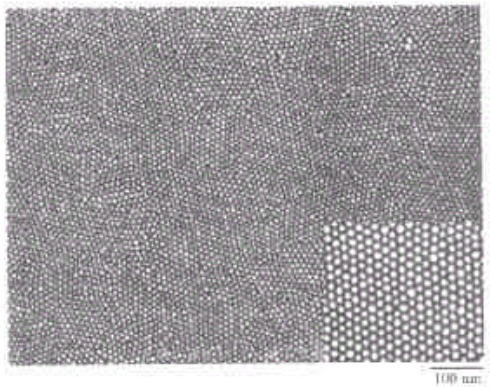


Figure 1. Scanning electron micrograph of a LB monolayer consisting of dodecanethiol-encapsulated gold nanoparticles of 8.3 nm in diameter, displaying long range order [18]. The inset shows higher magnification which reveals hexagonal close-packed structure.

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

Esempi di autoassemblaggio complesso

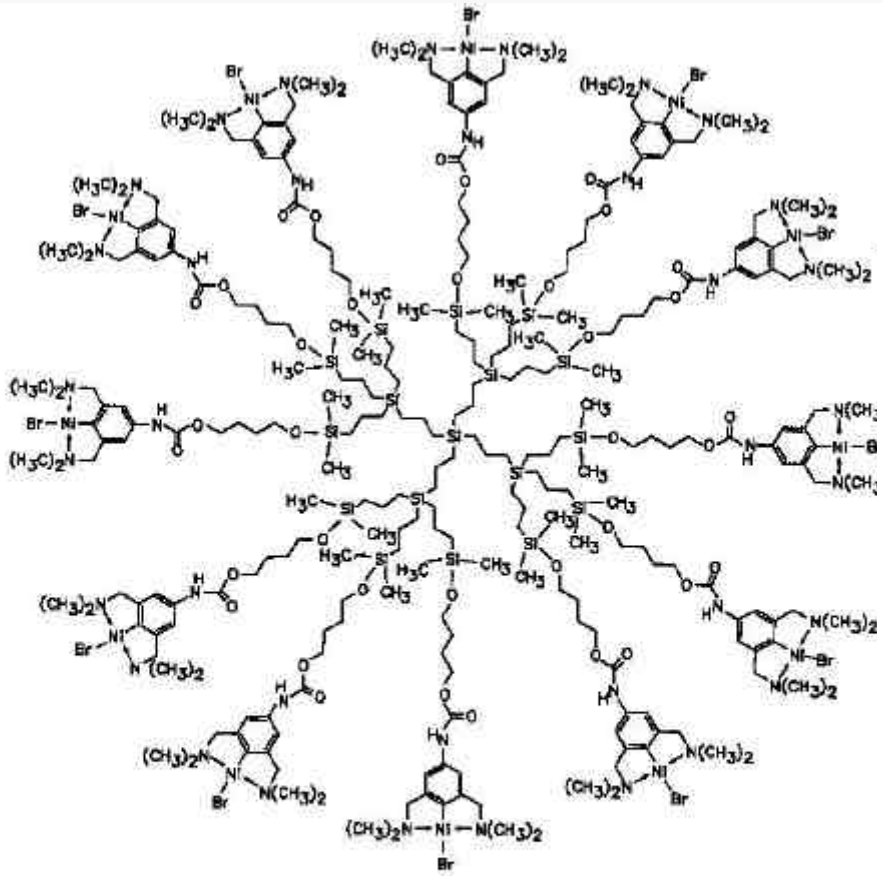


Figure 11.19. Dendrimer catalyst (dendralyst) with an Si core, and terminal group ar nickel complexes as the catalytically active functional groups. [From J. W. J. Knape A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwenn, P. Wijkens, D. M. Gro and G. van Koten, *Nature* **372**, 659 (1994).]

Struttura supramolecolari
(dendriti)

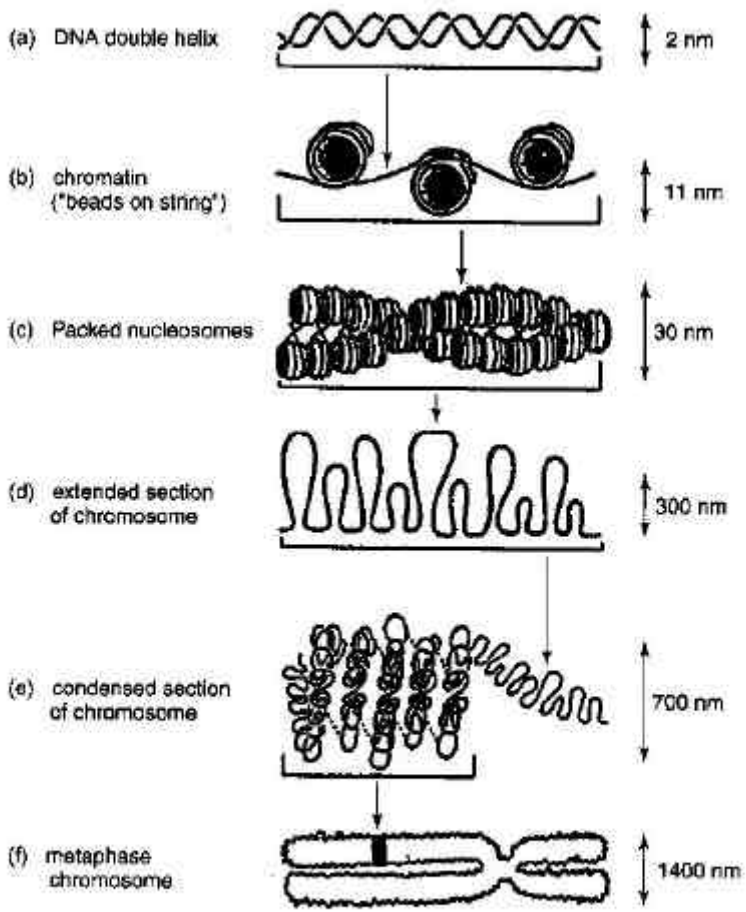


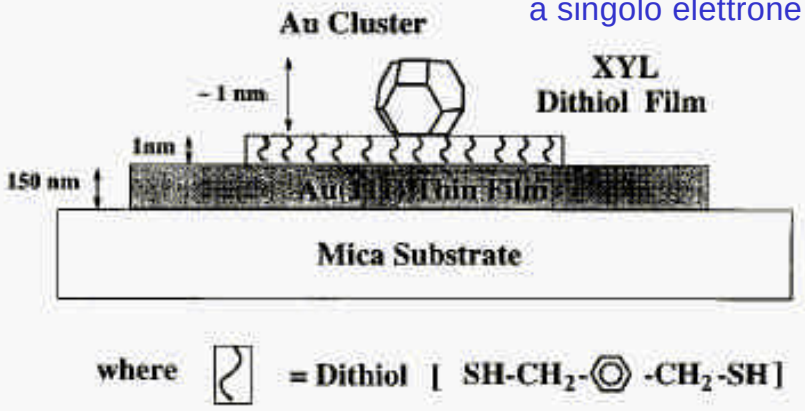
Figure 12.11. Successive twistings and foldings during the packing of DNA into mammalian chromosomes, with the sizes at successive stages given in nanometers. [From R. J. Nossal and H. Lecar, *Molecular and Cell Biophysics*, Addison-Wesley, Boston, 1991, Fig. 4.9 (p. 118).]

Arrangiamento del DNA

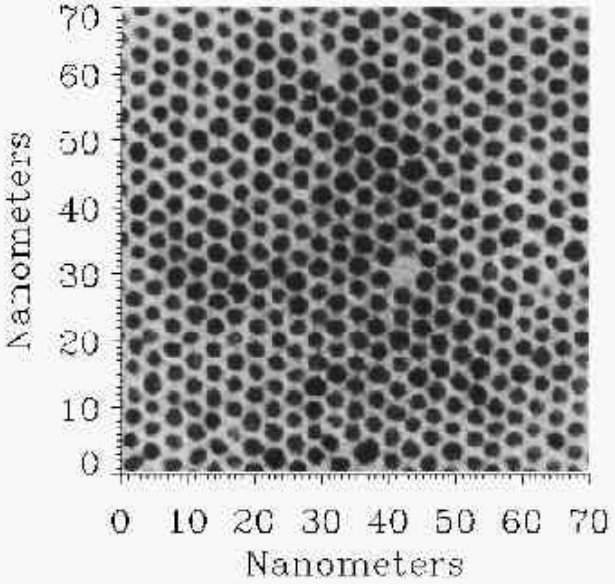
Tunneling attraverso SAM

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

Semplice dispositivo
a singolo elettrone



XYL: p-xylene-α,α'



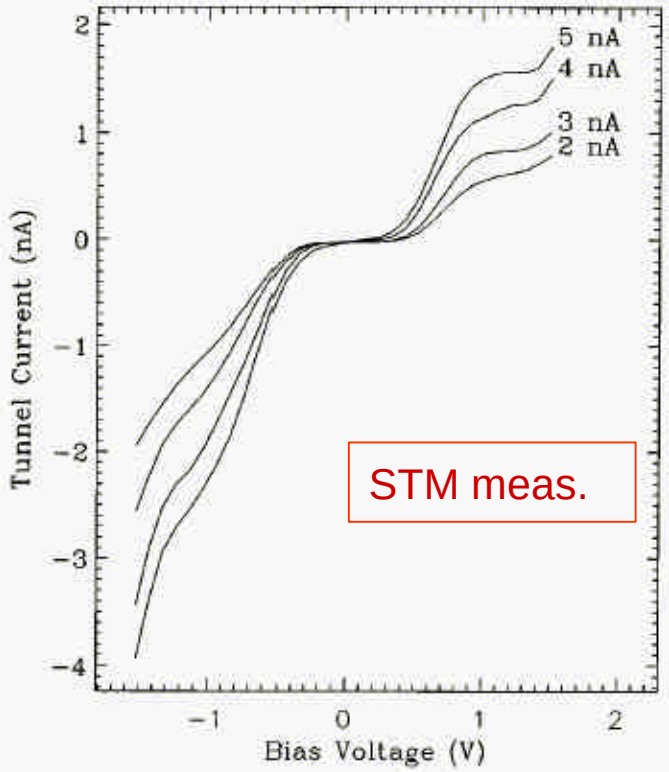


FIG. 6. $I(V,z)$ data obtained at room temperature with the tip positioned over a ~1.8 nm high Au cluster resting on a SAM of XYL dithiol. Each curve is the sum of 100 separate $I(V)$ sweeps. The different data sets illustrate how the $I(V,z)$ characteristics change as the specified set point tunneling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

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

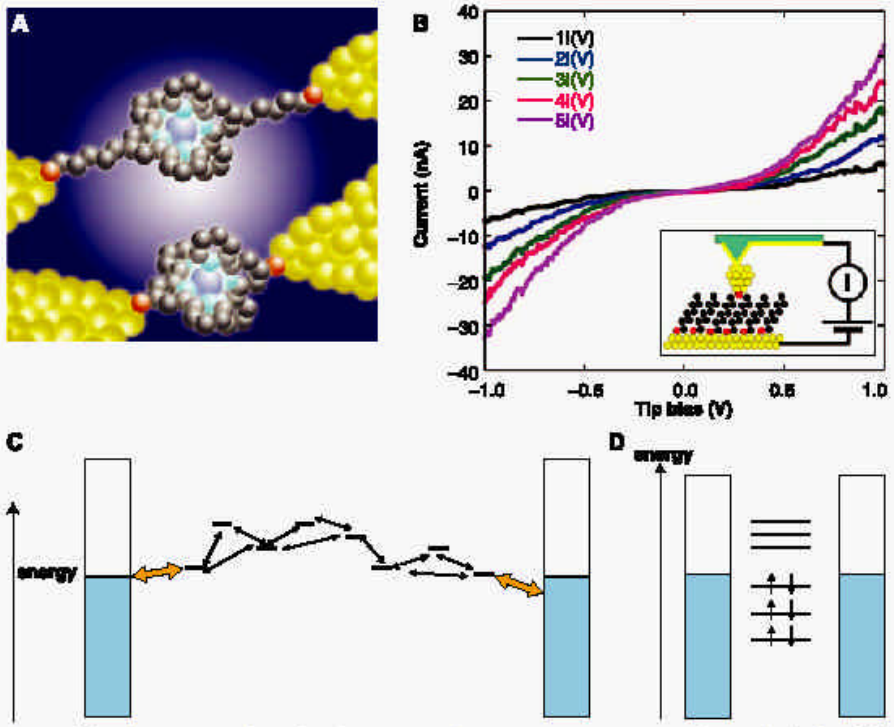


Fig. 1. (**A**) Schematic single molecule junction between two continuous electrodes [after (*5*)] (**B**) Schematic (inset) of an alkane thiol adlayer with gold dot current collector, measured using AFM. Actual data is also shown, corresponding to (suggested) transport through 1, 2, 3, 4, and 5 molecular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