



Dipartimento di Fisica, Università di Modena e Reggio E, Italy



CNR-NANO, Istituto Nanoscienze, S3-Modena, Italy

Polimeri conduttivi



Alice Ruini



Plastica !



Mr. McGuire: I just want to say one word to you - **just one word.**

Ben: Yes sir.

Mr. McGuire: Are you listening?

Ben: Yes I am.

Mr. McGuire: **'Plastics.'**

Ben: Exactly how do you mean?

Mr. McGuire: **There's a great future in plastics.** Think about it. Will you think about it?

Ben: Yes I will.

Mr. McGuire: Shh! Enough said. That's a deal.



Cosa e' un polimero?

Polimero: molecola ad alto peso molecolare costituita dalla ripetizione di un'unita' (monomero)

A-A



Monomero: composto a basso peso molecolare

Oligomero: corta catena polimerica

Copolimero: polimero costituito da due o piu' tipi di monomero

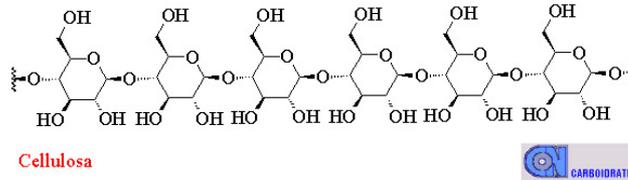
Random copolymer: A-B-B-A-A-B-A-B-A-B-B-B-A-A-B

Alternating copolymer: A-B-A-B-A-B-A-B-A-B-A-B-A-B

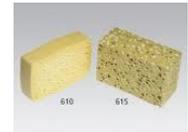
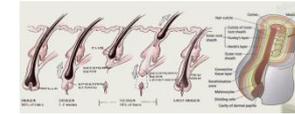
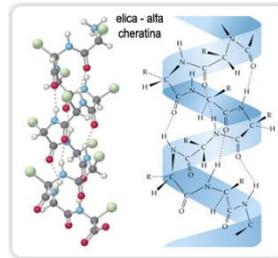
Block copolymer: A-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B

Polimeri naturali ...

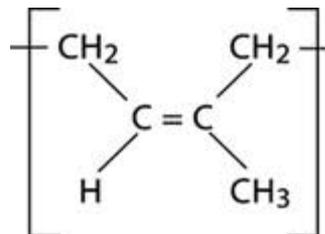
cellulosa



cheratina

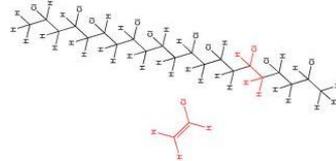


gomma naturale

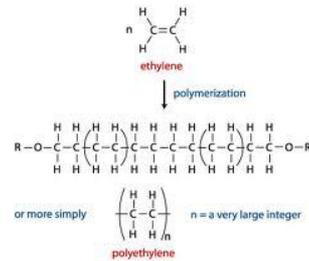


... e artificiali

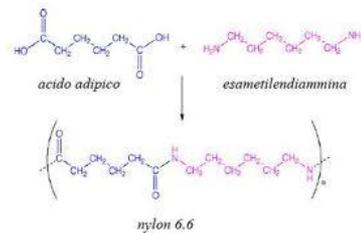
PVC



PE



PA
(nylon)



... e molti altri!

... diverse categorie di impiego

materiali plastici



elastomeri



fibre



... molti altri criteri di classificazione!

...

Degradabilità'

Risposta meccanica

Stechiometria del processo di sintesi

Meccanismo del processo di sintesi

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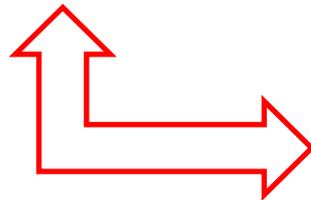
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Degradabilità

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Meccanismo del processo di sintesi



Polimerizzazione a stadi di equilibrio

Polimerizzazione a catena

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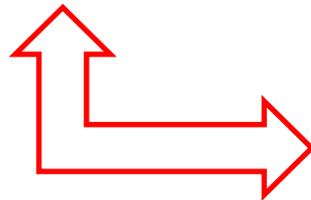
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Meccanismo del processo di sintesi



Polimerizzazione a stadi di equilibrio

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Polimerizzazione coordinata con catalizzatori (Ziegler-Natta)

Karl Ziegler e Carlo Natta mettono a punto la polimerizzazione stereospecifica (1954)

e ricevono per questo **il premio Nobel per la chimica (1963)**



«Professor Natta: Lei è riuscito a preparare mediante un nuovo metodo macromolecole che hanno una struttura spaziale regolare. **Le conseguenze scientifiche e tecniche della sua scoperta sono immense, e ancora non possono essere valutate pienamente**».

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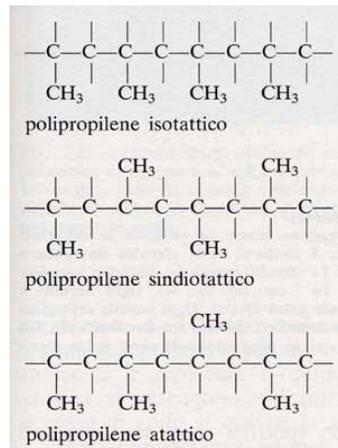
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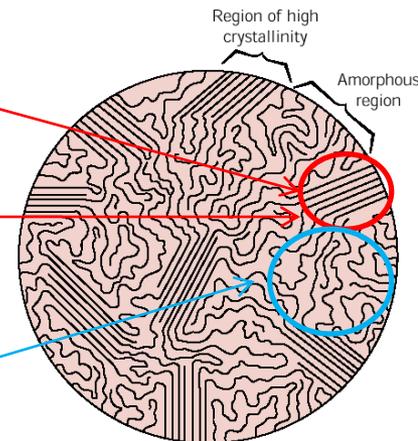


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high melting



low melting



Polimeri conduttivi: perche'?

I polimeri sono tradizionalmente utilizzati come **isolanti** nelle applicazioni elettriche ed elettroniche, grazie alla loro alta resistività (ruolo passivo)...



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... ma polimeri con caratteristiche di **conduttori o semiconduttori** permetterebbero la progettazione/realizzazione di svariati dispositivi elettronici e optoelettronici che sfruttino le straordinarie proprietà di questi materiali:

-proprietà meccaniche (leggerezza, robustezza, flessibilità elasticità...)



-facilità nella produzione e bassi costi



-semplice ingegnerizzazione (processi di sintesi, funzionalizzazione chimica...)



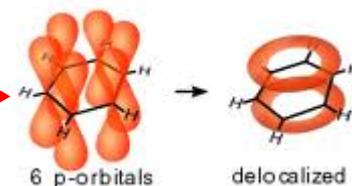
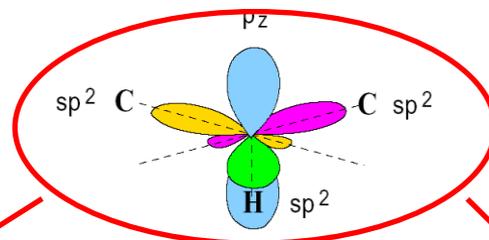
Polimeri conduttivi: come?

Due strategie chiave:

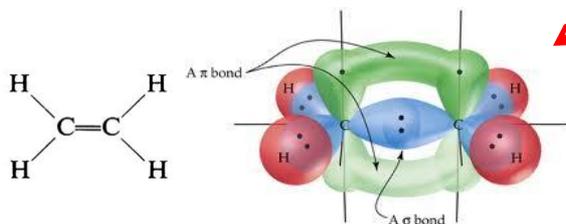
1) Coniugazione π : alternanza di legami singoli e doppi tra carboni



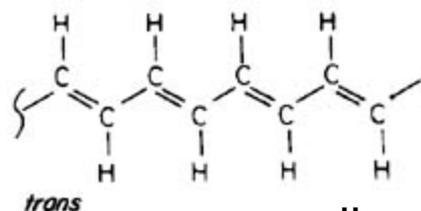
ibridizzazione sp^2



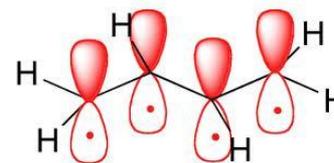
benzene



etilene



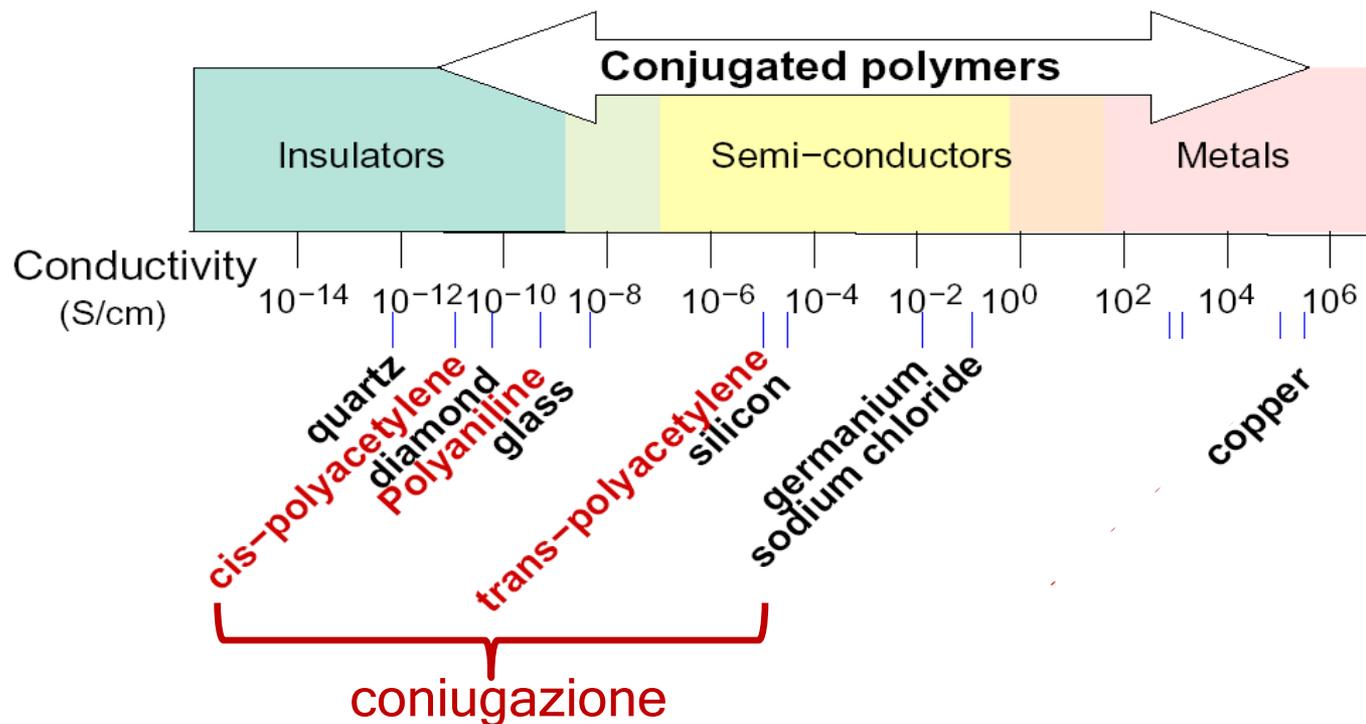
poliacetilene



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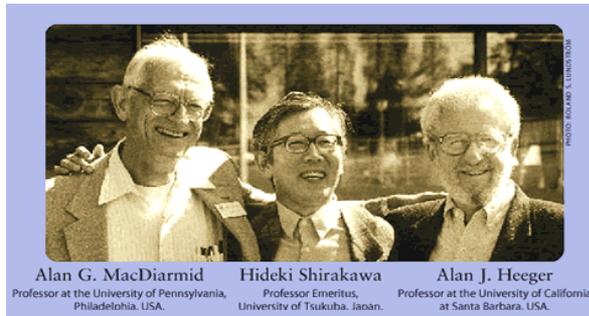


Polimeri conduttivi: come?

Due strategie chiave:

1) Coniugazione π : alternanza di legami singoli e doppi tra carboni

2) Drogaggio:



**2000 Nobel Prize in Chemistry
"For the discovery and development
of conductive organic polymers".**

an accidental discovery

At the beginning of the 1970s Shirakawa was studying the polymerisation of acetylene. In his reaction vessel polyacetylene appeared in the form of an unremarkable black powder. On one occasion a visiting researcher accidentally added one thousand times more catalyst than usual. Imagine the researchers' surprise when a beautiful silvery film formed on the surface of the liquid in the vessel. The obvious question was: "if the plastic film shines like a metal, can it conduct electricity, too?"

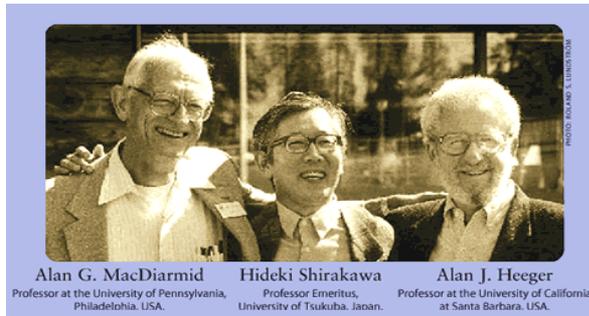
- Official Nobel Website

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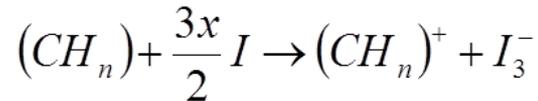


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p-doping:

rimozione di elettroni dal sistema

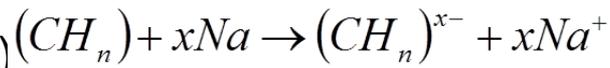
(ossidazione, tramite alogeni)



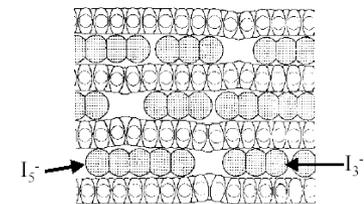
n-doping:

addizione di elettroni al sistema

(riduzione, tramite metalli alcalini)



Structure of I₂-doped trans-(CH)_x

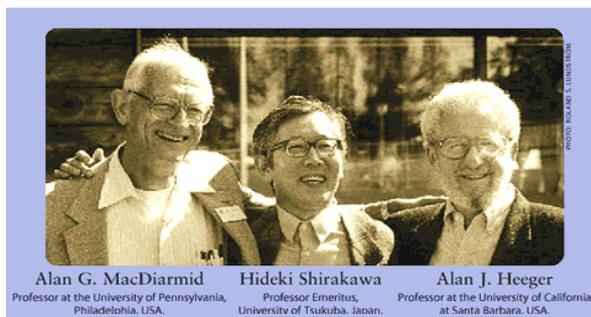


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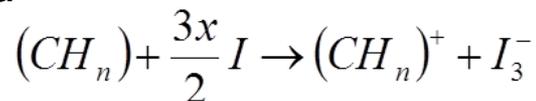


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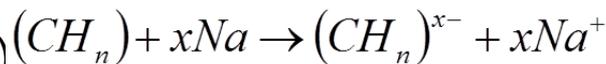


- Significant doping levels (until 10 mole %)

n-doping:

addizione di elettroni al sistema

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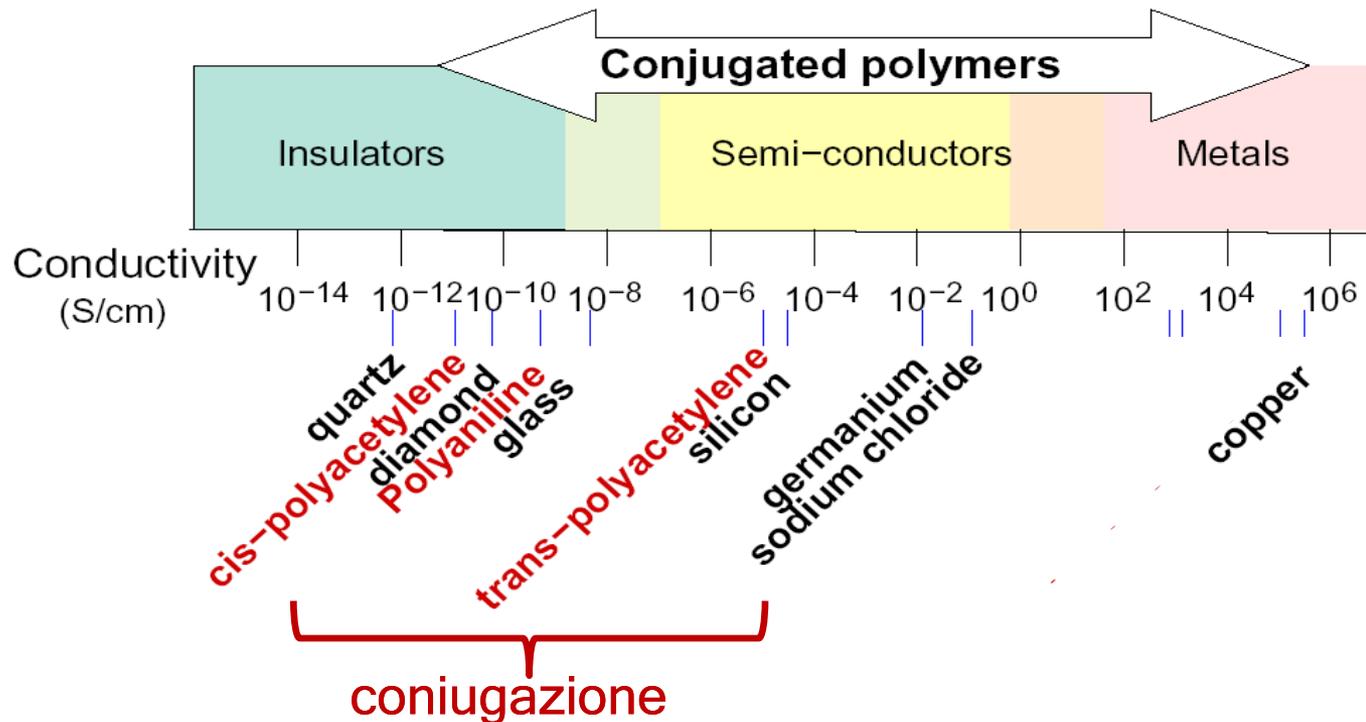


- There is a *charge transfer* between the incorporated dopant atom and the polymer chain = *the lattice is partially oxidized or reduced*

Polimeri conduttivi: come?

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1) Coniugazione π

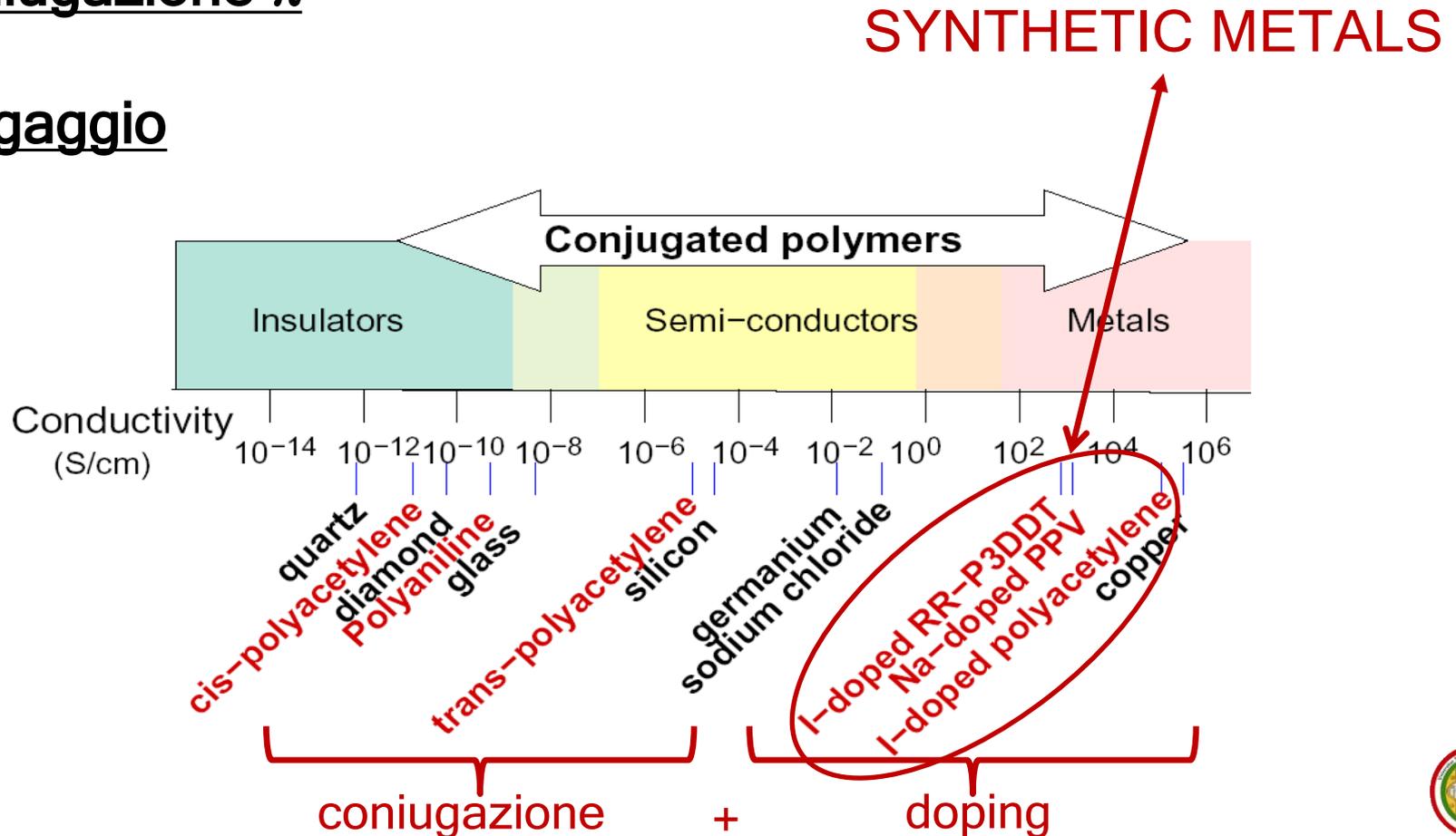


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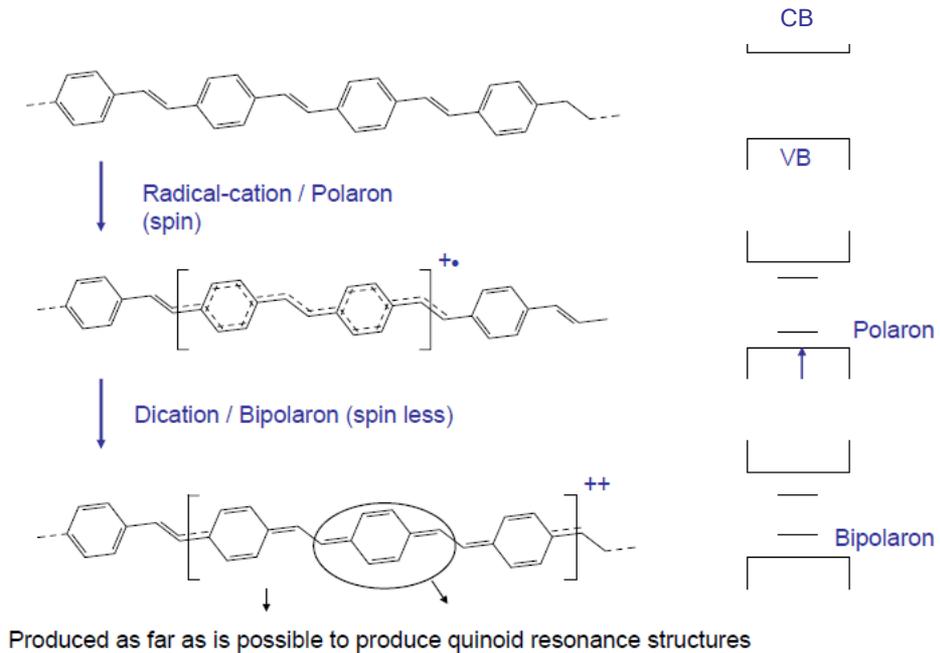
Meccanismi per la conducibilita'

L'aggiunta di una molecola con carattere donore o accettore produce una reazione redox.

A partire dal polimero "neutro" ...

il primo passo consiste nella formazione di un catione (o anione), detto **polarone**;

tale passo puo' poi essere seguito da un secondo trasferimento elettronico, con la formazione di un **bipolarone**.



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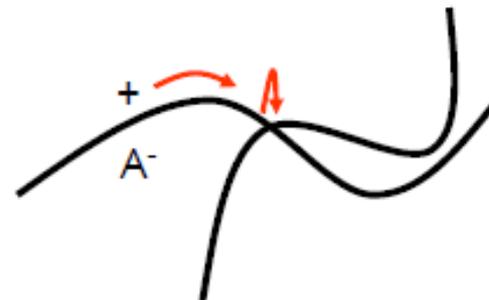
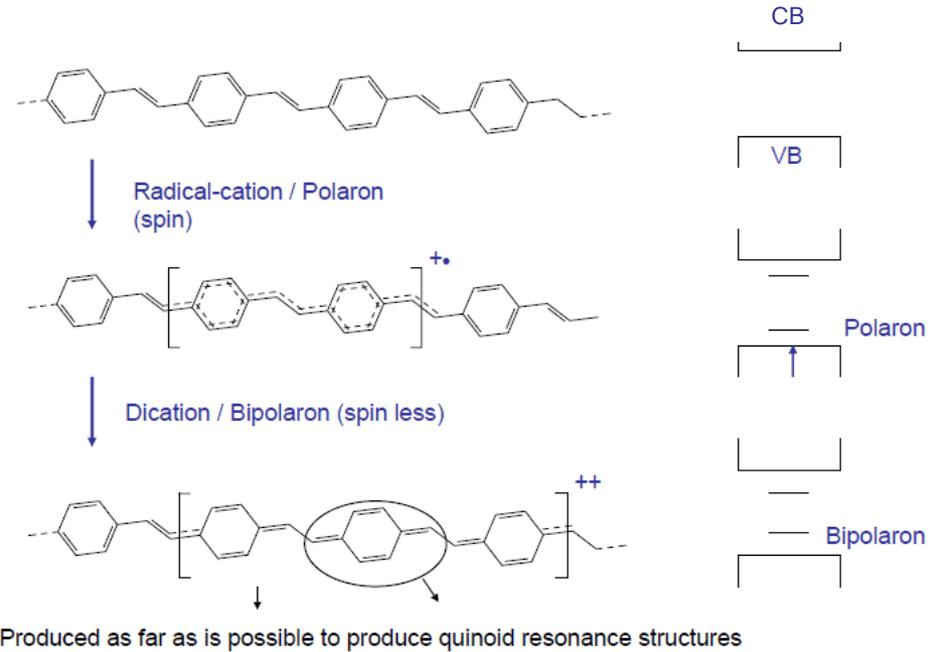
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Inoltre: **intrachain** vs. **interchain** (hopping) charge transport mechanisms

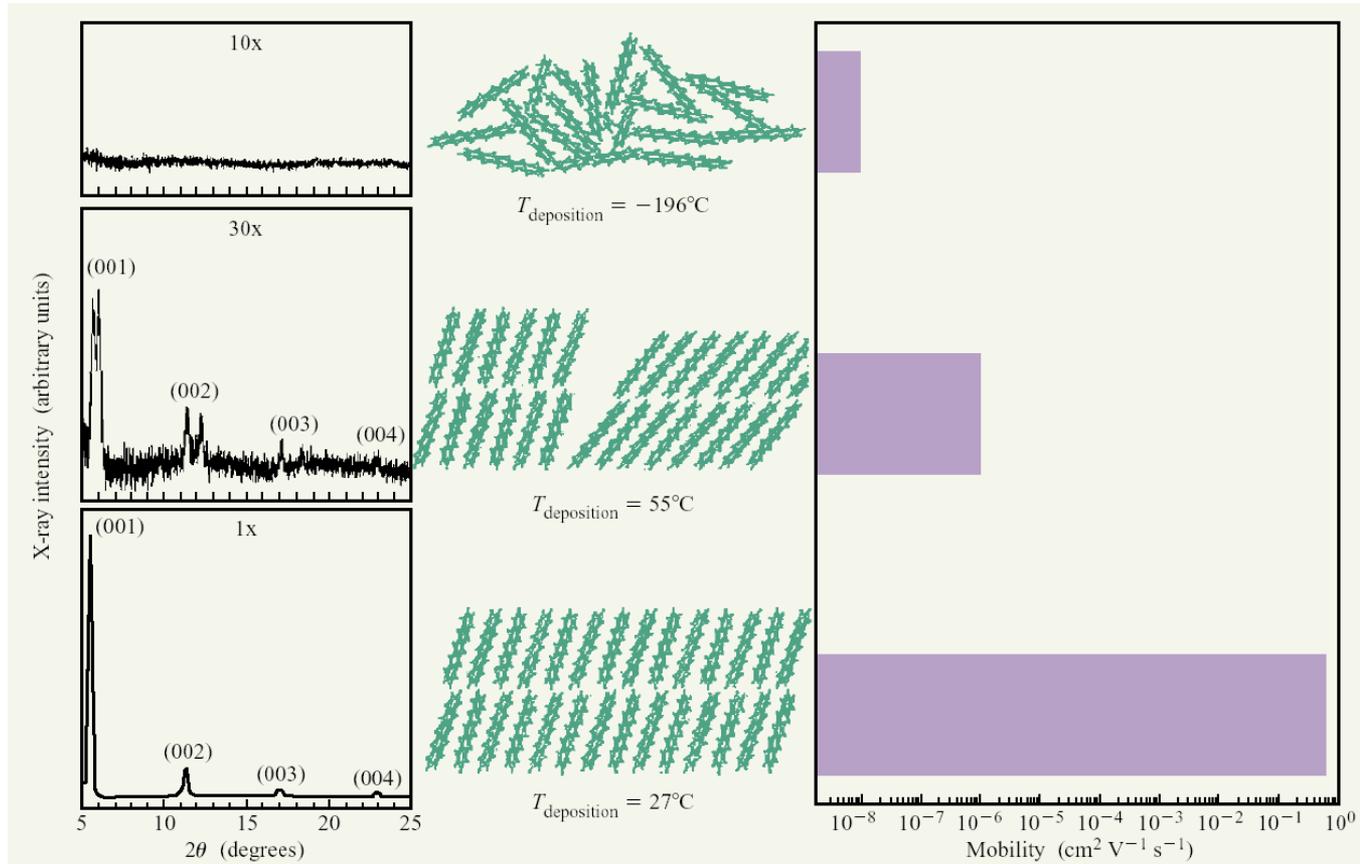


Interazioni inter-catena

X-ray diffraction

Microstructure

Mobility



Un campo in (fin troppo!) rapida espansione

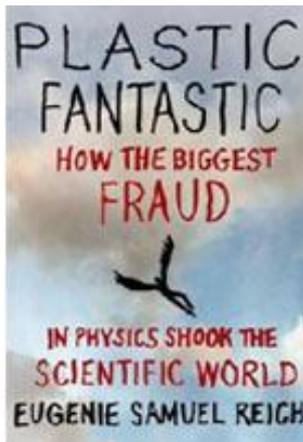
- J. H. Schön, et al (2000). "Ambipolar Pentacene Field-Effect Transistors and Inverters". *Science* 287 (5455):.
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- ... e MOLTI altri



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WITHDRAWN!



2002: Schön scandal was discovered!

First published in 2009
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Un campo in (fin troppo!) rapida espansione

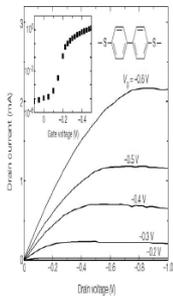
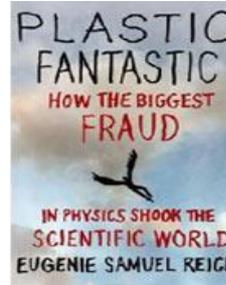


Figure 4. Triode characteristics from "SAMFET" Paper (XII). The figure has been compressed horizontally for comparison. Fig. 2: "SAMFET."

The same triode data for the SAMFET also appears to match other, much older data, represented as different materials:

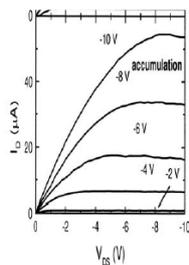


Figure 6. Triode characteristics from "Ambipolar Pentacene" (II) Fig. 2, lower part.; "Pentacene."

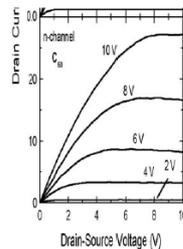
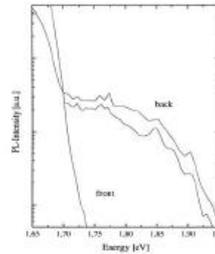


Figure 5. Triode characteristic from "SuperFETswitch" Paper (III). Fig. 1 lower part: "C₆₀."



Adapted from Figure 3.30 on page 48 of J. H. Schön (1997) *Anwendungen von CuGaSe₂ in der Photovoltaik*. Dissertation der Universität Konstanz, Band 329, UFO Atelier für Gestaltung und Verlag, Konstanz.



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Figure 2.1: In one of his earliest manipulations, Schön made changes, adding peaks to two curves. The result was a simpler story that fit better with other scientific literature

... e molte altre contraffazioni!

Un campo in (fin troppo!) rapida espansione

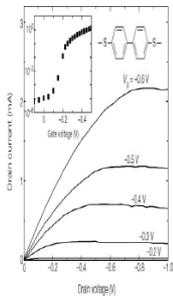
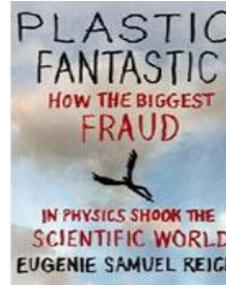


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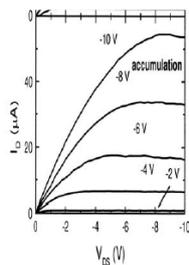


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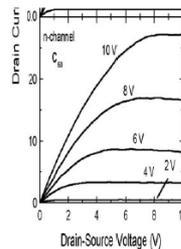
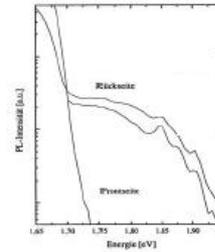
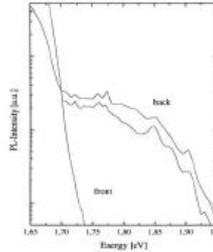


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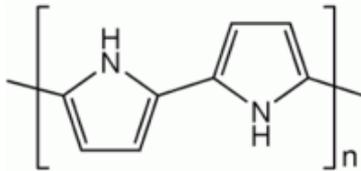
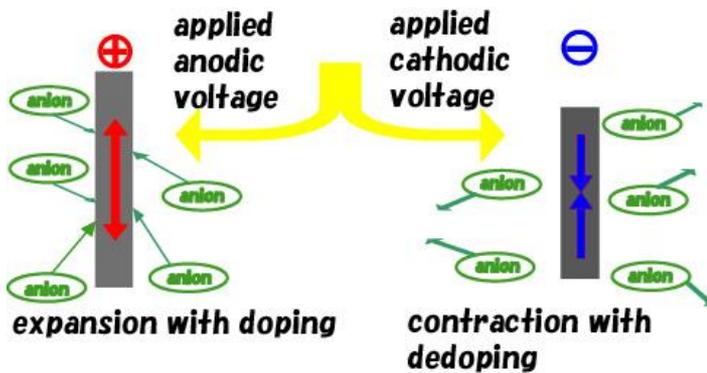
The beauty of science is that it is (slowly!) self-correcting

Applicazioni

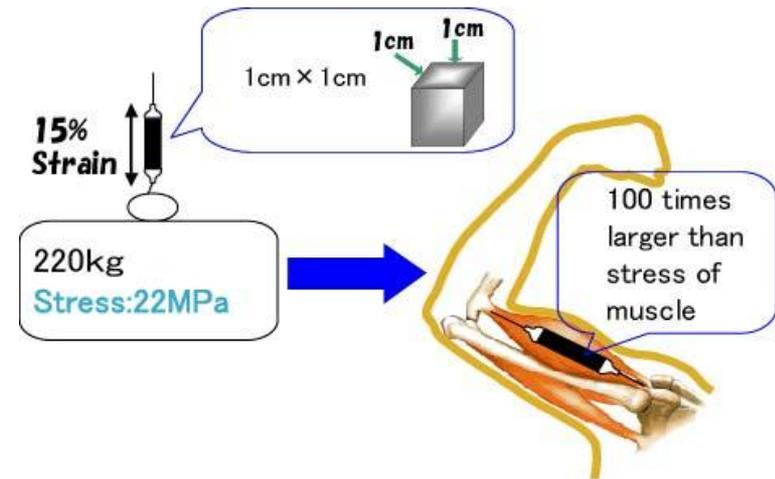


Applicazioni: attuatori

Meccanismo:

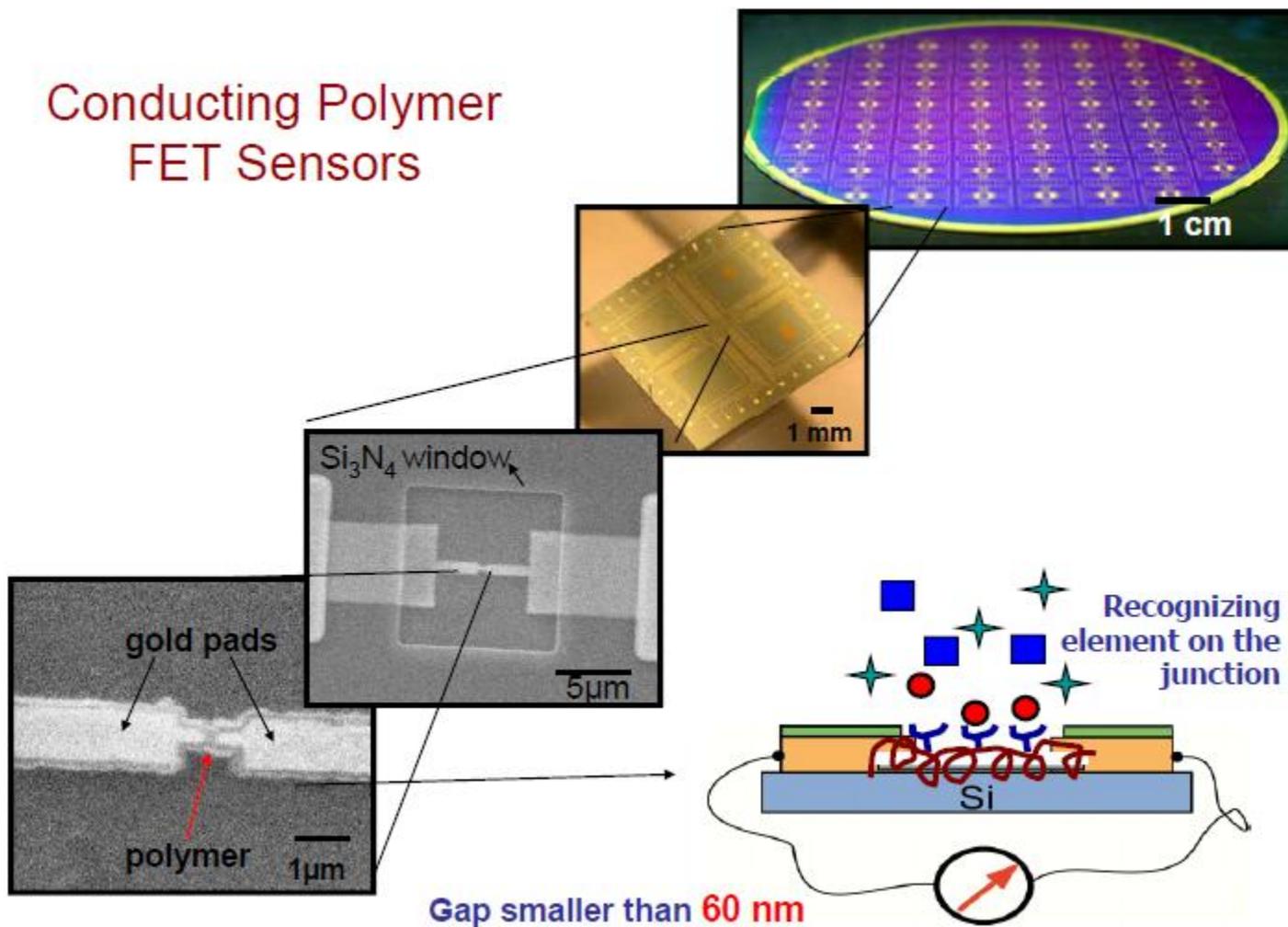


→ muscoli artificiali



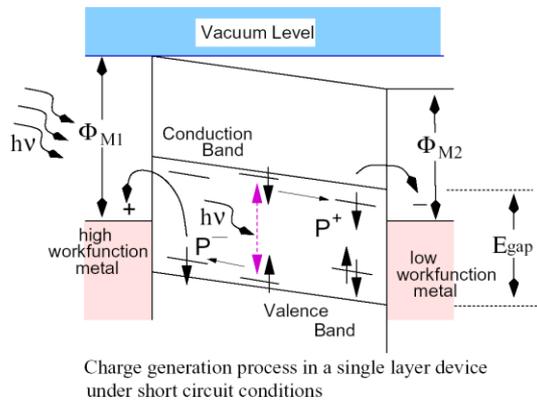
Applicazioni: FET sensors

Conducting Polymer FET Sensors

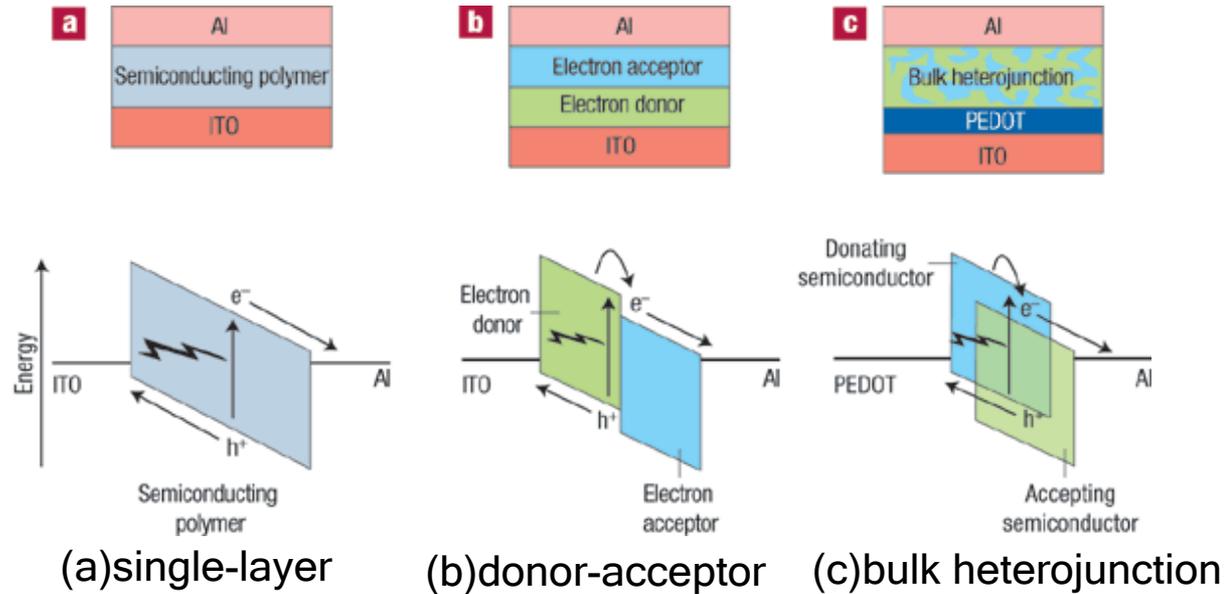


Applicazioni: celle solari organiche

Principio di funzionamento

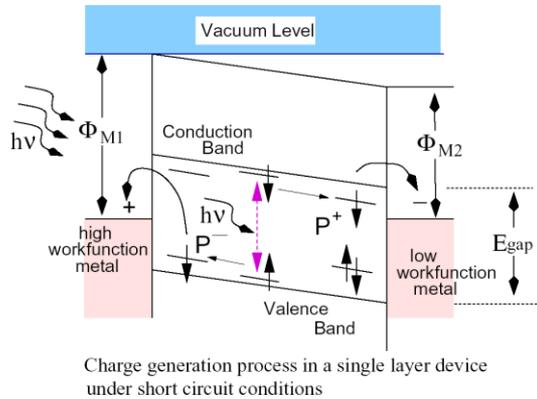


Possibili configurazioni del layer attivo

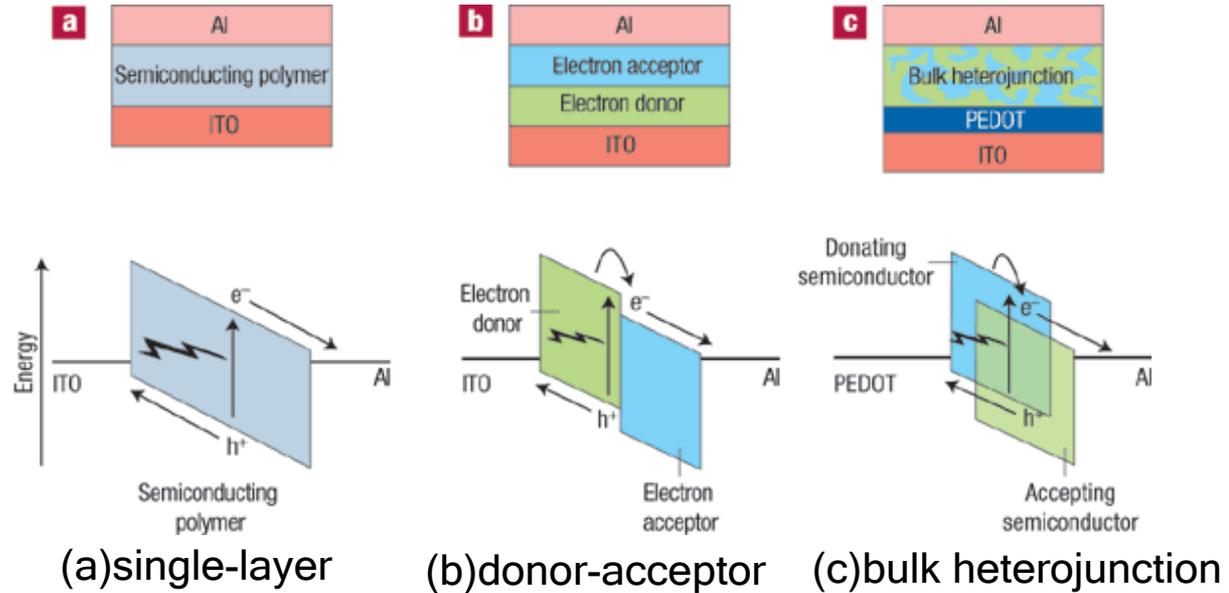


Applicazioni: celle solari organiche

Principio di funzionamento



Possibili configurazioni del layer attivo

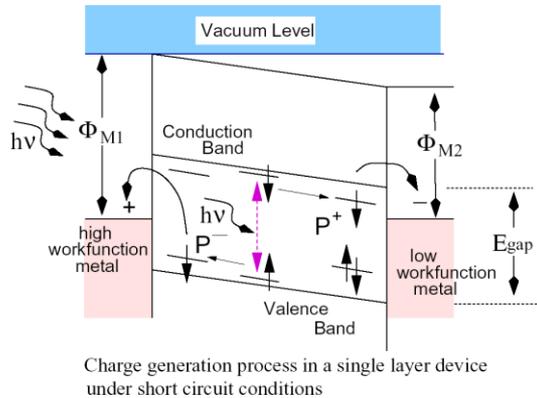


Celle fotovoltaiche ...

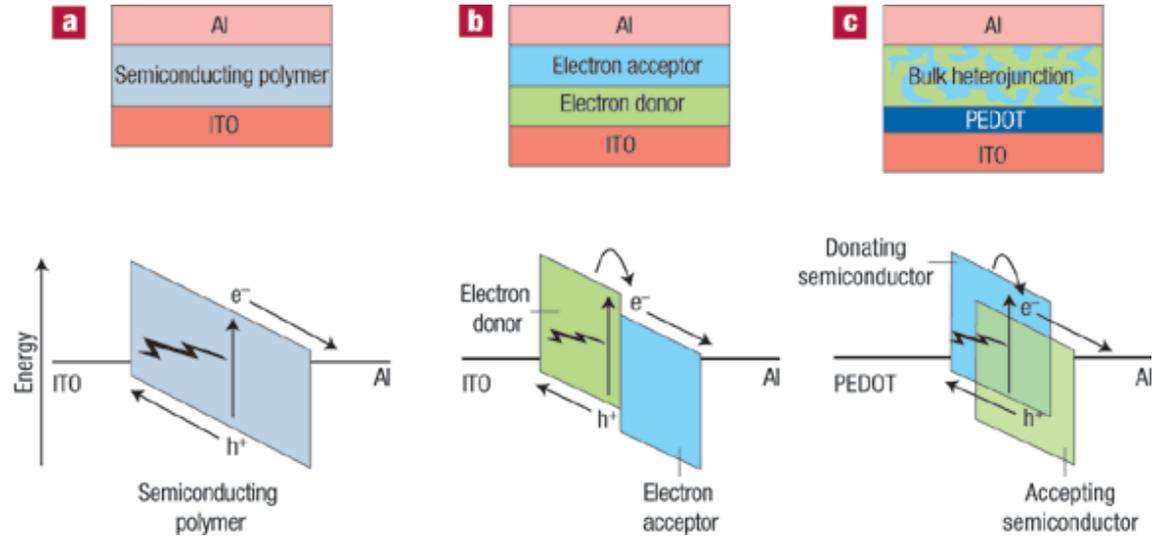


Applicazioni: celle solari organiche

Principio di funzionamento



Possibili configurazioni del layer attivo



(a) single-layer

(b) donor-acceptor

(c) bulk heterojunction

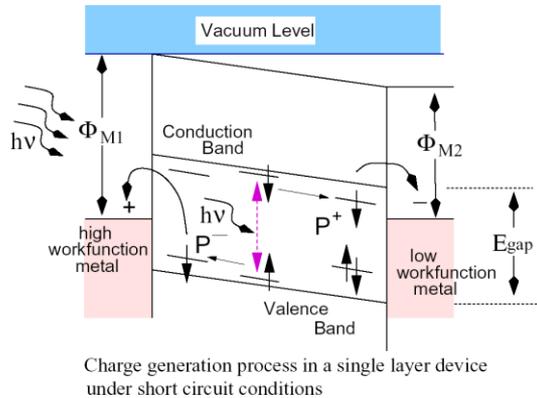
Celle fotovoltaiche ... stampabili a getto di inchiostro



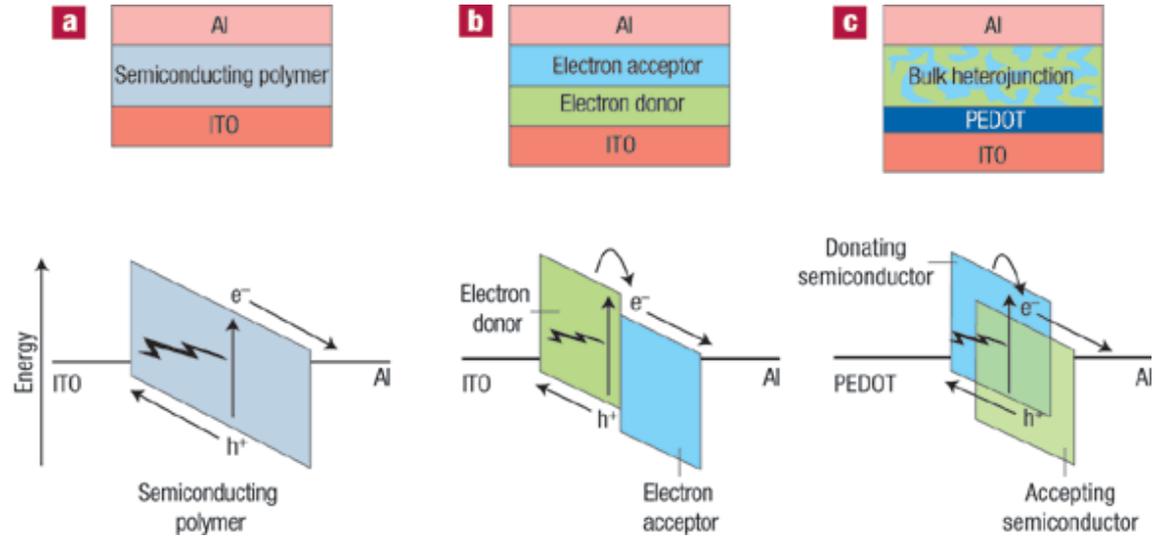
www.konarka.com

Applicazioni: celle solari organiche

Principio di funzionamento



Possibili configurazioni del layer attivo



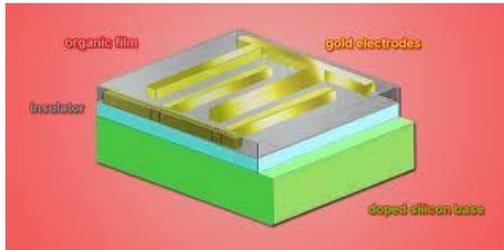
Celle fotovoltaiche ... stampabili a getto di inchiostro ... e abbigliamento fotovoltaico!



www.konarka.com



... e molte altre applicazioni!



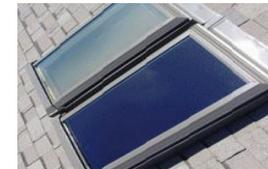
Field-effect transistor organico



Schermatura elettromagnetica



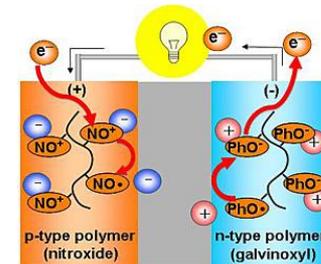
Laser a polimeri



“Smart” windows



Display

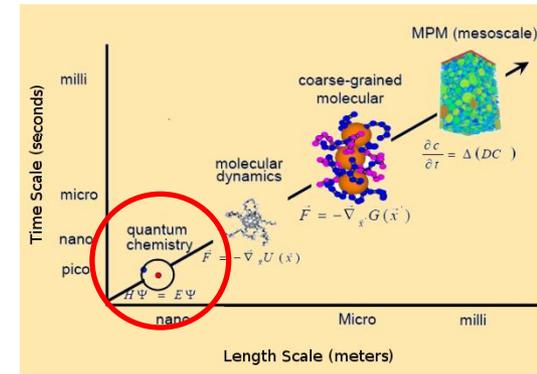
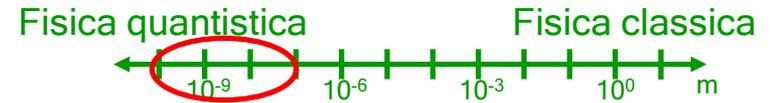


Batterie ricaricabili

La nostra ricerca

Fisica della materia computazionale

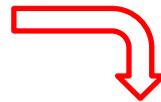
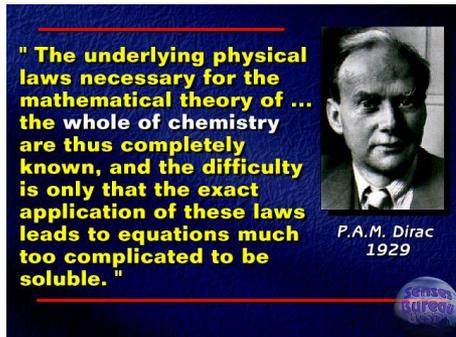
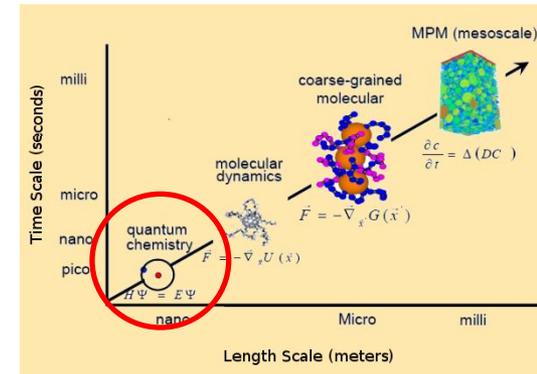
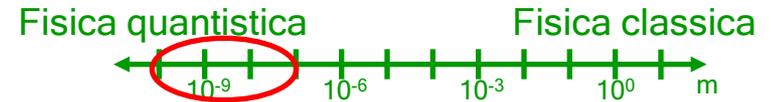
Sistemi alla nanoscala → fisica quantistica



La nostra ricerca

Fisica della materia computazionale

Sistemi alla nanoscala → fisica quantistica



Equazione di Schrödinger

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V(r, t) \psi$$

... ma per un tipico materiale

$$H(\mathbf{R}, \mathbf{r}) = \sum_{i \in el} \frac{p_i^2}{2m} + \sum_{I \in ion} \frac{p_I^2}{2M_I} + \frac{1}{2} \sum_{i \in el} \sum_{j \in el, j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i \in el} \sum_{I \in ion} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{I \in ion} \sum_{J \in ion, J \neq I} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

... non sappiamo risolverla analiticamente!

→ possiamo risolverla attraverso una simulazione numerica avendo costruito un opportuno modello teorico

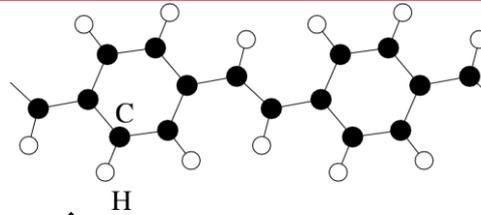


I never satisfy myself until I can make a mechanical model of a thing. If I can make a model I can understand it. (Lord Kelvin)

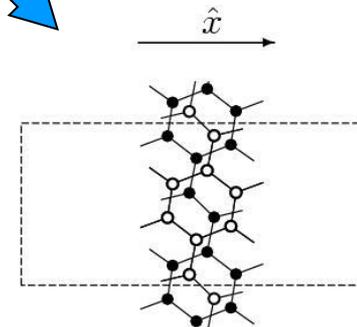
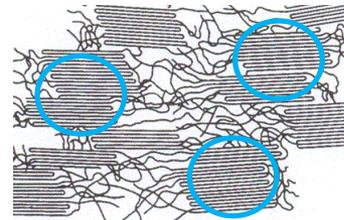
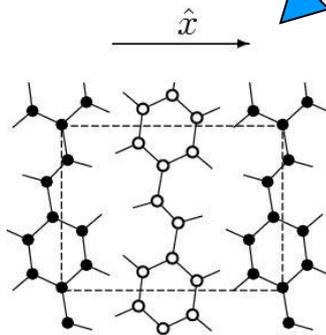


La nostra ricerca sui polimeri (semi)conduttori: effetti intercatena nel PPV

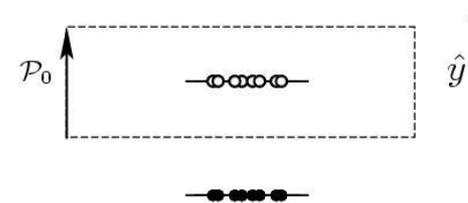
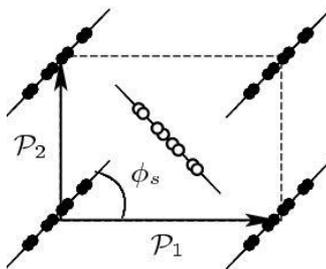
Isolated PPV chain



Solid state
packing



MEH-PPV
(π -stack)



D.Chen, et al, Phys. Rev. B 41, 6759 (1990)

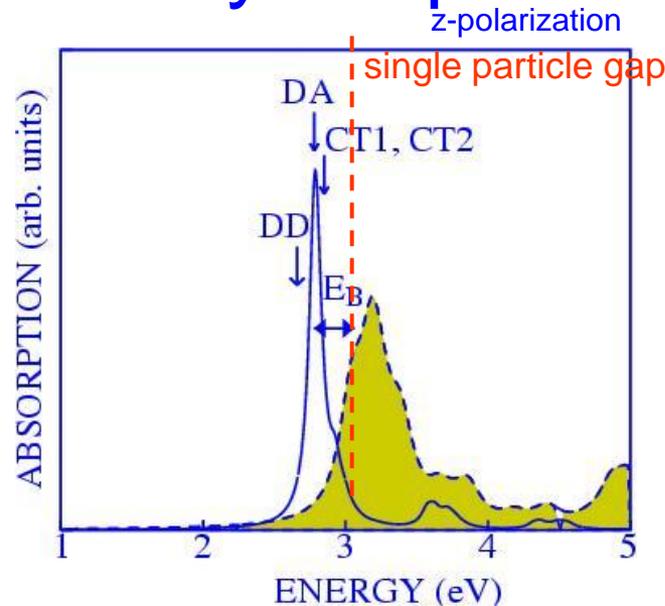
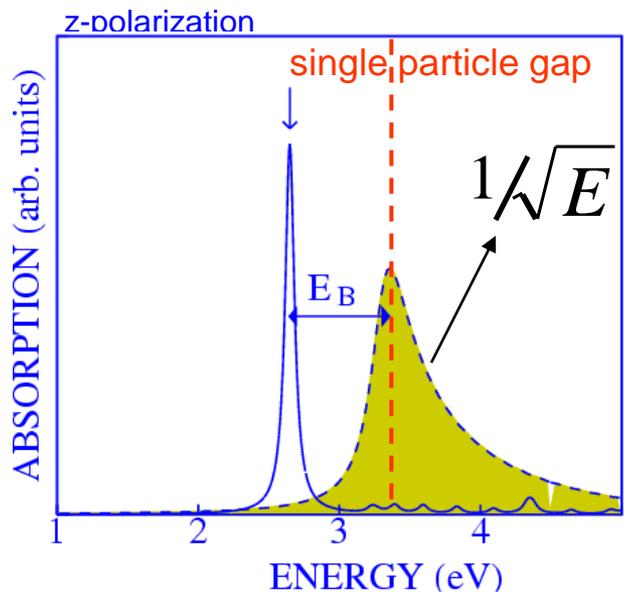
C.Y.Yang, F.Hide, M.A.Diaz-Garcia, A.J.Heeger, Y.Cao,
Polymer 39, 2299 (1998)



La nostra ricerca sui polimeri (semi)conduttori: effetti intercatena nel PPV

isolated chain

vs HB crystal phase



exciton \leftrightarrow 1D singularity suppression

→ exciton \leftrightarrow 1D singularity suppression

large binding energy $E_B \approx 0.6 \div 0.7$ eV

→ E_B is lowered to $0.2 \div 0.3$ eV

lowest singlet-exciton optically active

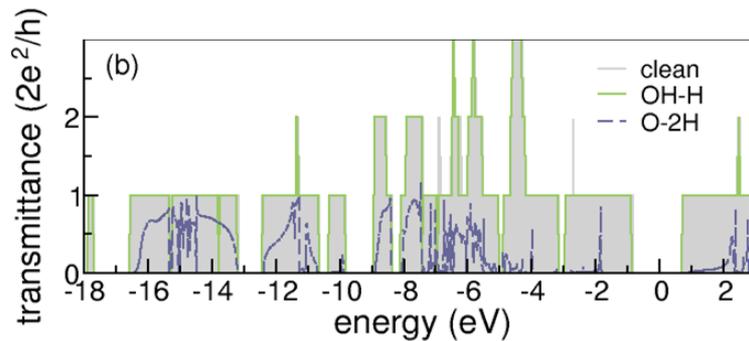
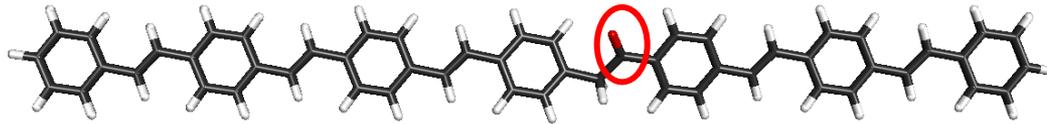
→ much richer excitonic structure

GOOD for LED

GOOD for PV

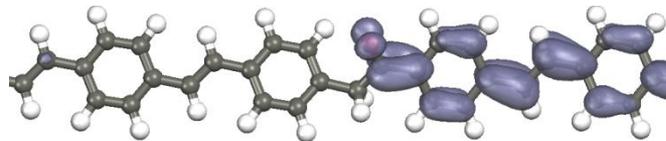


La nostra ricerca sui polimeri (semi)conduttori: difetti di ossigeno in PPV



The keto-defect completely blocks the ballistic charge flow along the chain ...

LUMO Keto



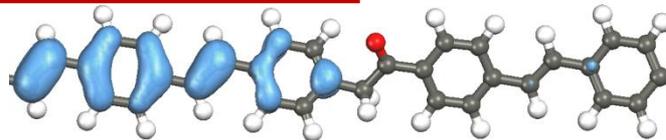
hole



electron



HOMO Keto



... but it helps the photoinduced current along the polymer chain:
promising route for **increasing photovoltaic efficiency!**

La nostra ricerca sui polimeri (semi)conduttori: la conduzione nel DNA

APPLIED PHYSICS LETTERS

VOLUME 79, NUMBER 23

3 DECEMBER 2001

Insulating behavior for DNA molecules between nanoelectrodes at the 100 nm length scale

A. J. Storm, J. van Noort, S. de Vries, and C. Dekker^{*)}
Faculty of Applied Sciences, Delft University of Technology, 2628 CJ Delft, The Netherlands

isolante

Direct measurement of electrical transport through DNA molecules

Danny Porath^{*}, Alexey Bezryadin^{*†}, Simon de Vries^{*} & Cees Dekker^{*}

^{*} Department of Applied Sciences, Delft University of Technology, 2628 CJ Delft, The Netherlands

semiconduttore

VOLUME 86, NUMBER 16

PHYSICAL REVIEW LETTERS

16 APRIL 2001

Metallic Conduction through Engineered DNA: DNA Nanoelectronic Building Blocks

A. Rakitin,¹ P. Aich,² C. Papadopoulos,¹ Yu. Kobzar,¹ A. S. Vedenev,^{1,3} J. S. Lee,² and J. M. Xu¹

¹Division of Engineering, Brown University, Providence, Rhode Island 02912

²Department of Biochemistry, University of Saskatchewan, 107 Wiggins Road, Saskatoon, Saskatchewan, Canada S7N 5E5

³Russian Academy of Sciences, Institute of Radioengineering and Electronics, Fryazino, Moscow district 141120, Russia
(Received 4 August 2000)

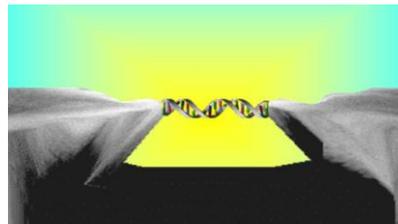
metallo

Proximity-Induced Superconductivity in DNA

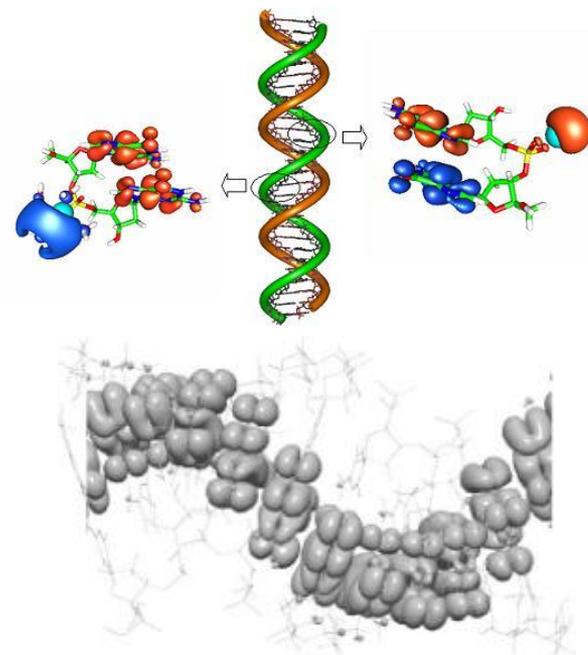
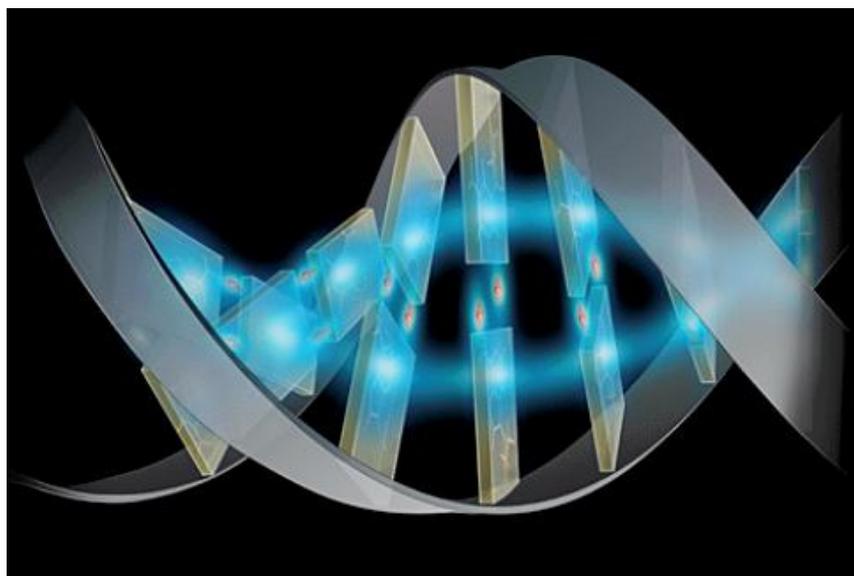
A. Yu. Kasumov,^{1,2*} M. Kociak,¹ S. Guéron,¹ B. Reulet,¹
V. T. Volkov,² D. V. Klinov,³ H. Bouchiat¹

superconduttore

???



La nostra ricerca sui polimeri (semi)conduttori: la conduzione nel DNA



Comportamento semiconduttore, bassa conducibilità.

TUTTAVIA la conoscenza della struttura elettronica del DNA ci permette di capire le strategie migliori per “ingegnerizzarlo” al fine di migliorarne le proprietà di conducibilità elettrica!!

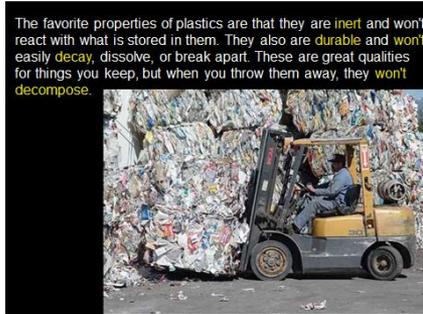
In conclusione...

Polimeri conduttivi: materiali “preziosi” dal punto di vista della fisica di base e delle applicazioni.

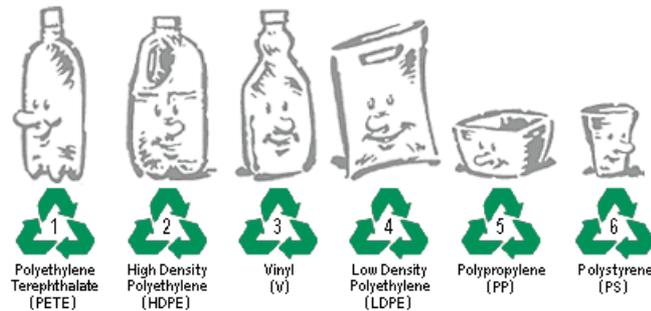
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MA:



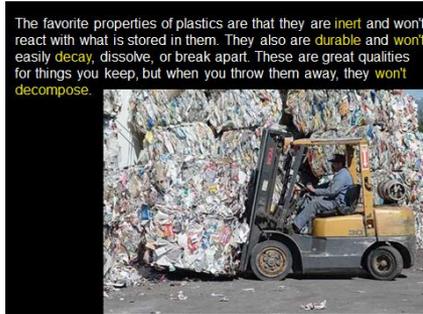
poiche' tipicamente non sono biodegradabili, e' necessario riciclarli, per poterli trasformare in qualcos'altro →



In conclusione...

Polimeri conduttivi: materiali “preziosi” dal punto di vista della fisica di base e delle applicazioni.

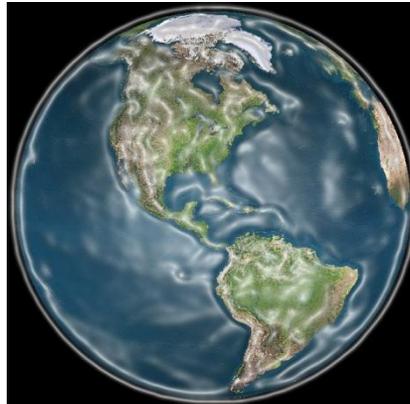
MA:



poiche' tipicamente non sono biodegradabili, e' necessario riciclarli, per poterli trasformare in qualcos'altro



Recycle or we will have a polymer planet.



Grazie per l'attenzione !

Recycle or we will have a polymer planet.

