UNESCO/IUPAC Postgraduate Course in Polymer Science

Lecture:

CONJUGATED POLYMERS FOR OPTOELECTRONIC APPLICATIONS

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Conductive materials
Polymer batteries
Smart windows
Solar cells
Organic light emitting diodes
Field effect transistors
Mechanical actuators
Non-linear optics

What physical phenomena are behind these applications

Why conjugated polymers are used in these applications

Today electronics - mostly based on inorganic semiconductors (Si, GaAs etc.)

Approaching technology – semiconductive polymers

- low-cost production (printing technologies)
- low-energy consuming production lines (Si production consumes energy)
- flexible components (all plastic electronics)
- large variety of chemical structures
- brings better possibility of tailoring for specific properties

Example of recently commercialized π-conjugated polymer:

Samsung has introduced its latest OLED screen of 40'', a resolution of 1280x800 (WXGA), a contrast ratio of 5000:1 and a very limited thickness. (2005)

Polymer is the active light-emitting material here!

Polymers for electronic applications must be conductive or semiconductive

$$\vec{j} = \sigma \vec{E}$$

$$\vec{j} = e n_f \vec{v}$$

$$\vec{v} = \mu \vec{E}$$

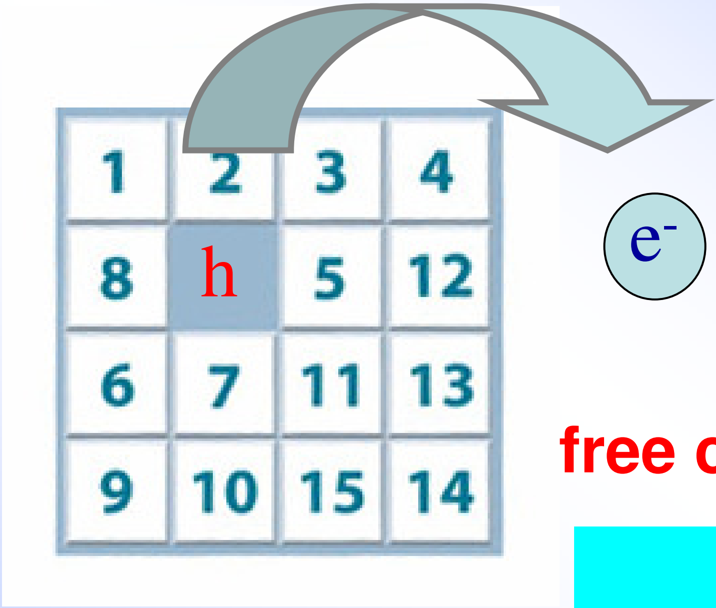
$$\sigma = e n \mu$$

e .....elemental charge
n_f ...concentration of free (movable) charges
v .....mean drift velocity of free charges
μ ....charge carrier mobility
E ..... applied electric field

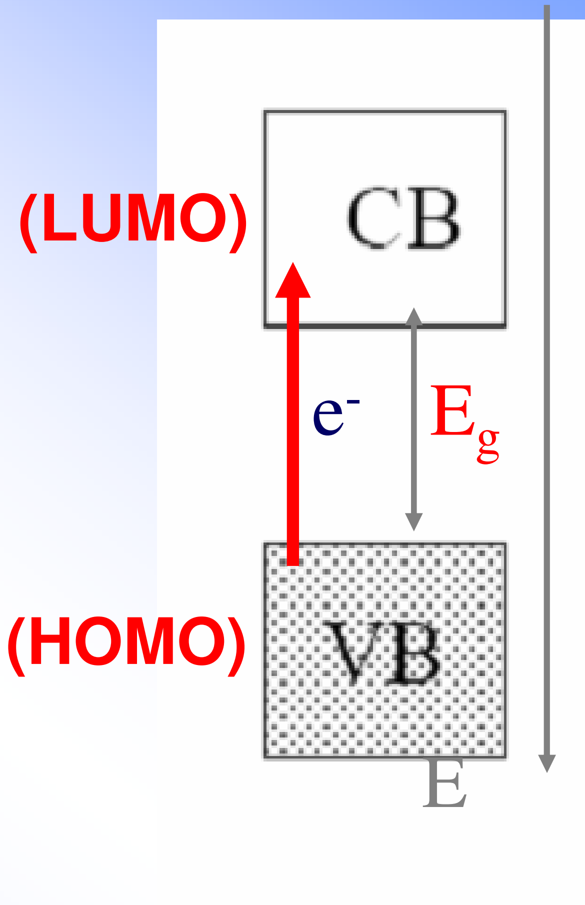
Polymer must contain charges - electrons, (or positive holes)

These charges must be mobile
(ions would be too slow for active electronic devices)

How to create free charges
How to transport charge between electrodes



How to move an electron?



free charges wanted

$$n_{free} = N_c \exp\left(-\frac{E_g}{2kT}\right)$$

Most polymers:

$E_g >> 3$ eV $\quad N_{free} < 100\ m^{-3}$

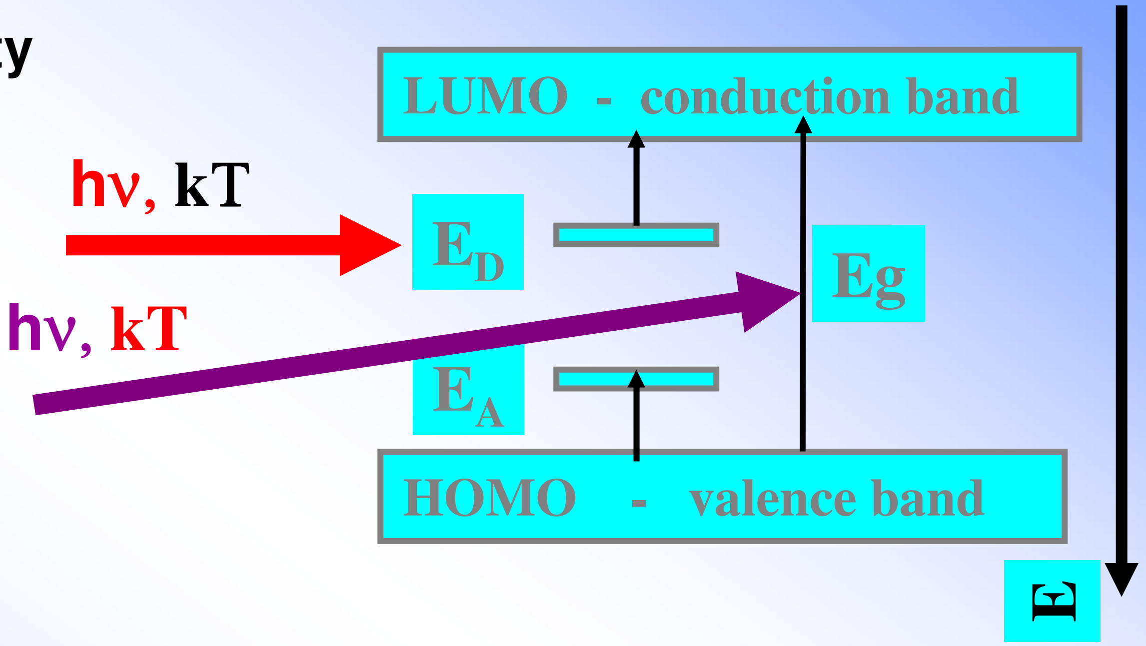
X Silicon crystal

$E_g = 1.1$ eV $\quad N_{free} \sim 10^{17}\ m^{-3}$

How to create free charges

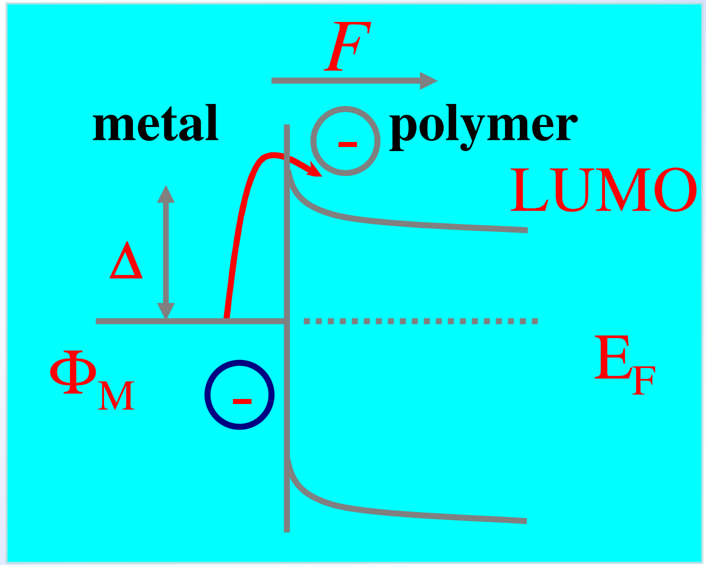
Ionization of an impurity (acceptor or donor):

Thermal excitation
Phototoexcitation

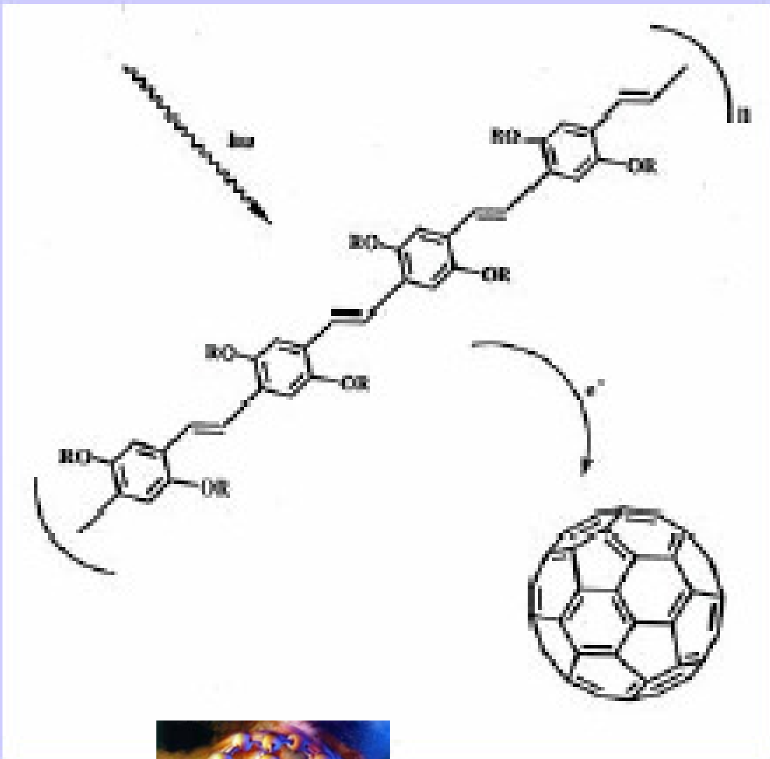


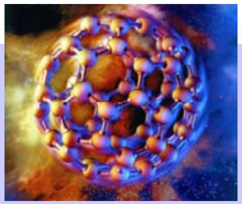
Injection from electrode (with applied electric field *F* electron can overcome potential barrier Δ between a metal contact and polymer)

$$j(F) = AT^2 \exp\left[-\frac{\Delta - \left(e^3 F / 4\pi\varepsilon\varepsilon_0\right)^{1/2}}{kT} \right]$$

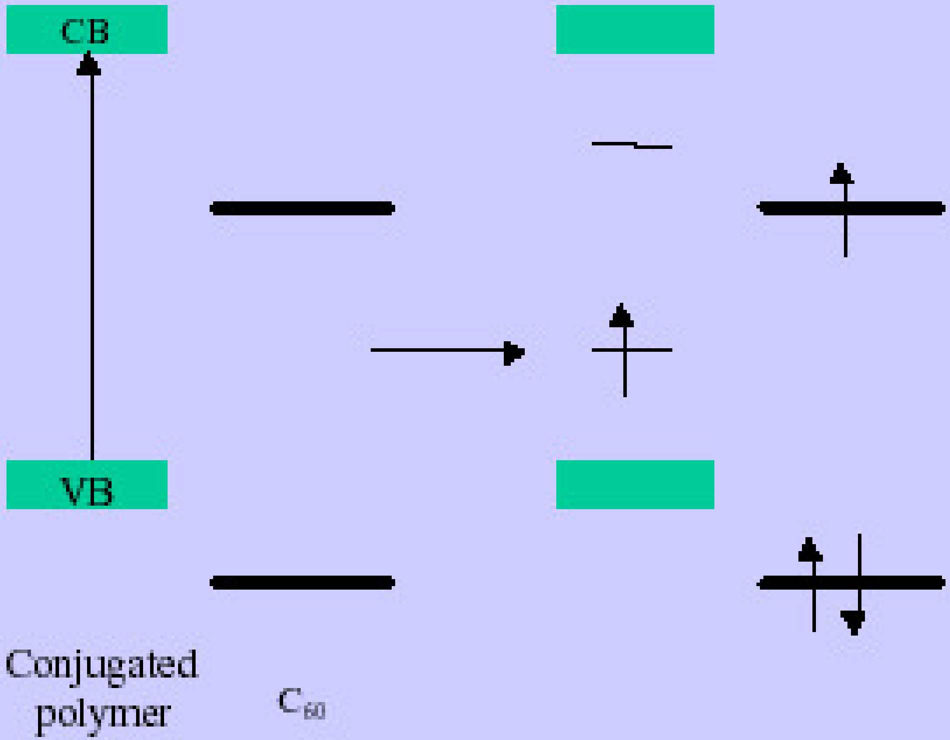


Example of creation of free charges at the interface between polymer and acceptor



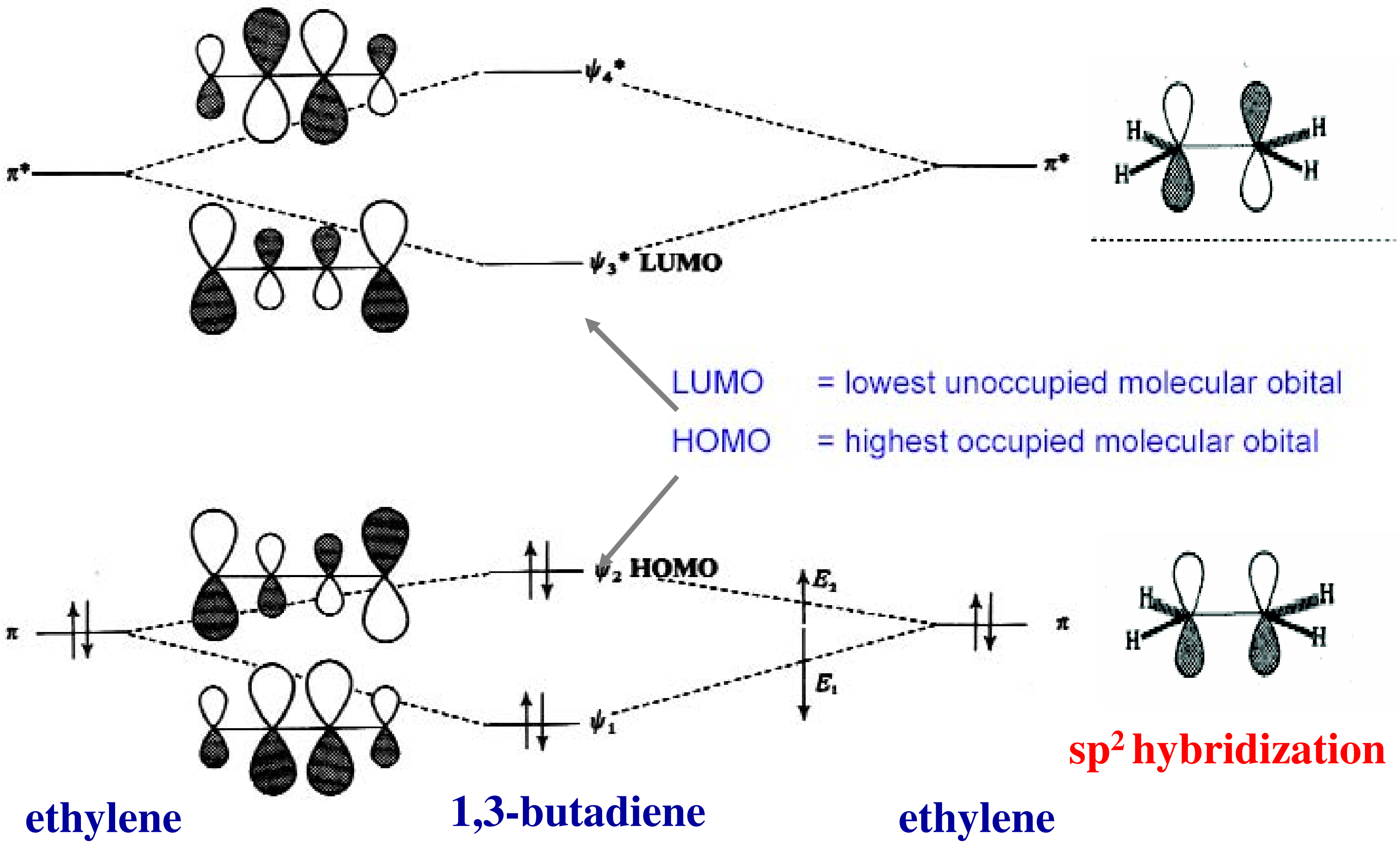


strong acceptor



N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, *Science* **258**, 1474 (1992).

Development of energy levels when going from ethylene to butadiene …

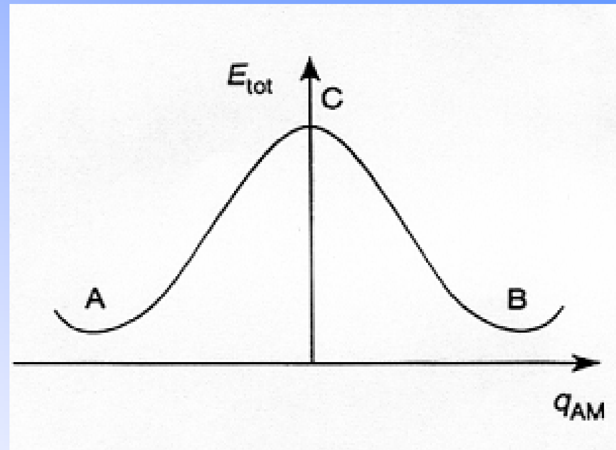


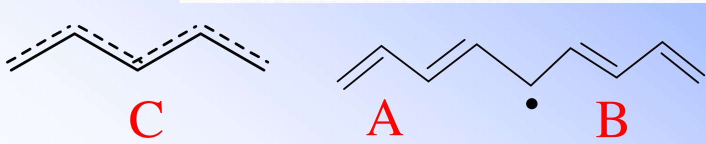
… and to polyacetylene

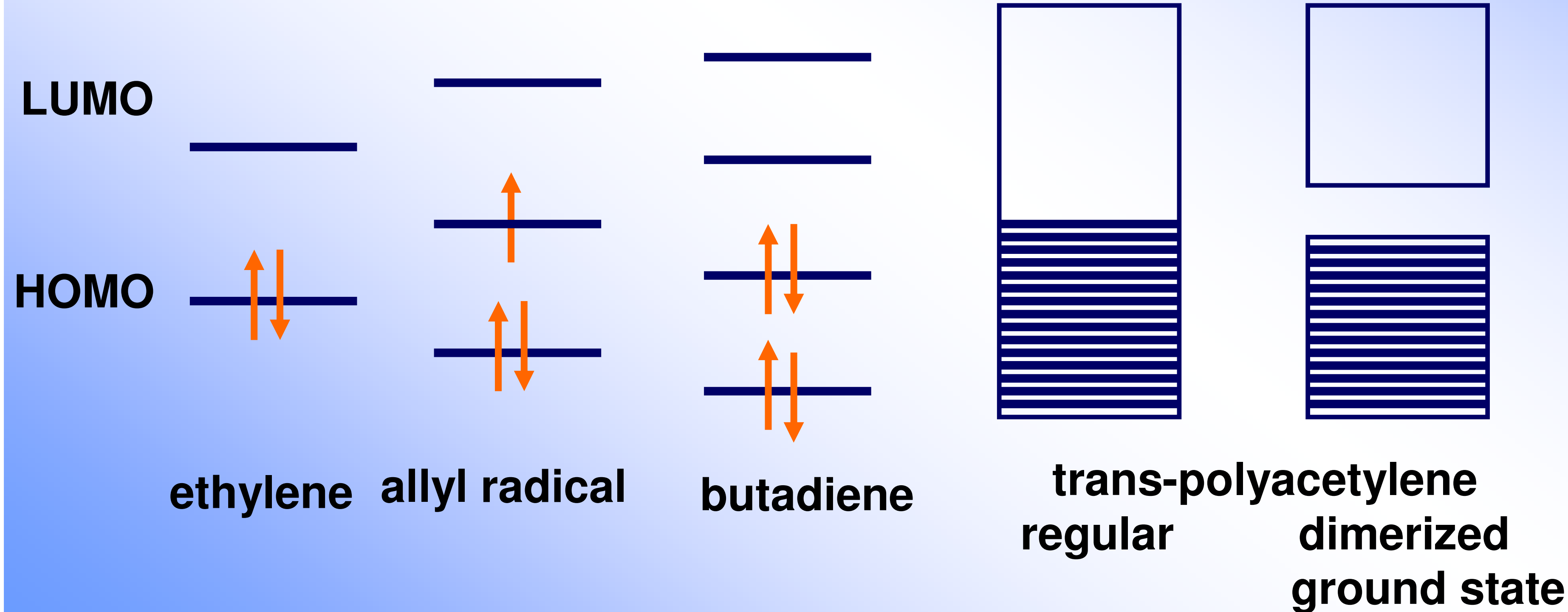
$CH_2{=}CH\text{-}CH{=}CH_2$

$CH_2{=}CH{-}\dot{C}H$

$CH_2{=}CH_2$

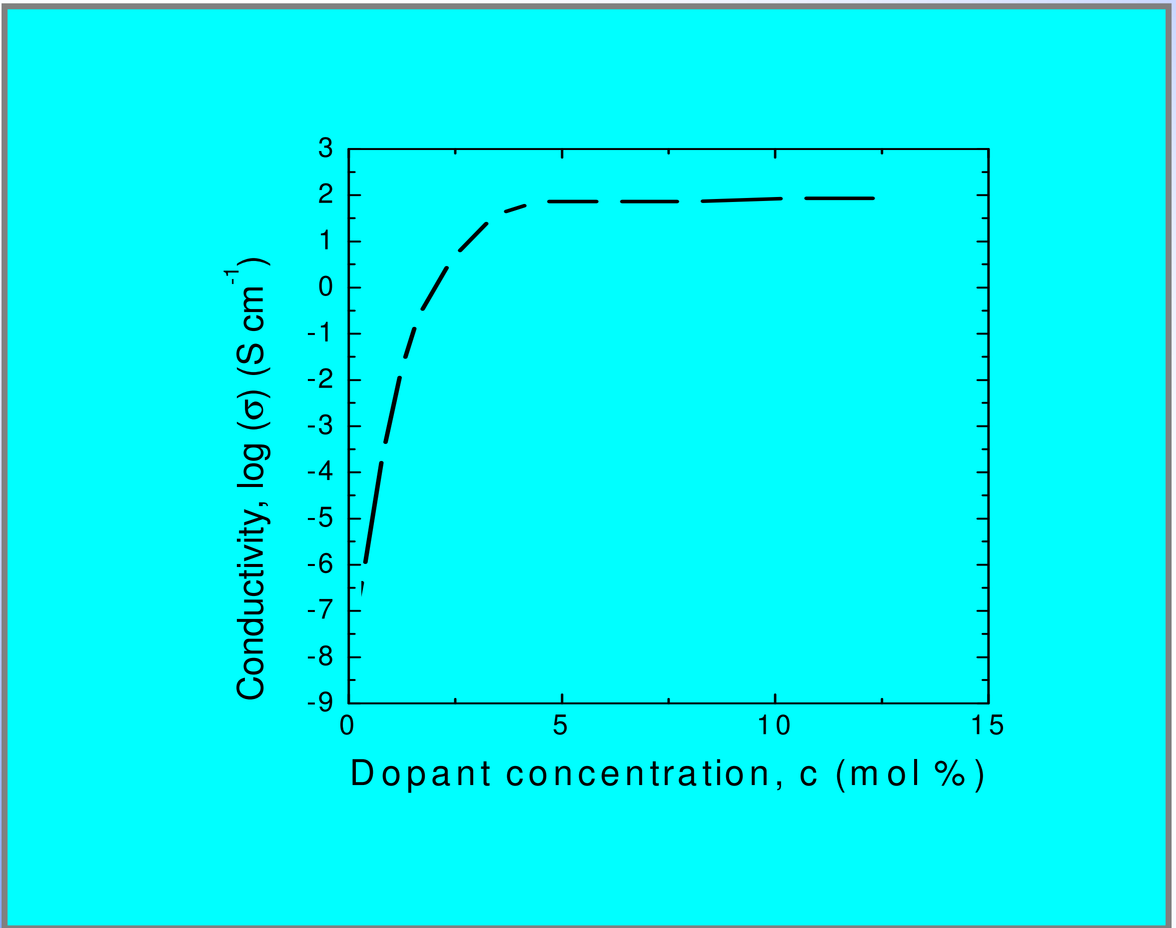






Trans-polyacetylene is a semiconductor with Eg ~ 1.6 eV

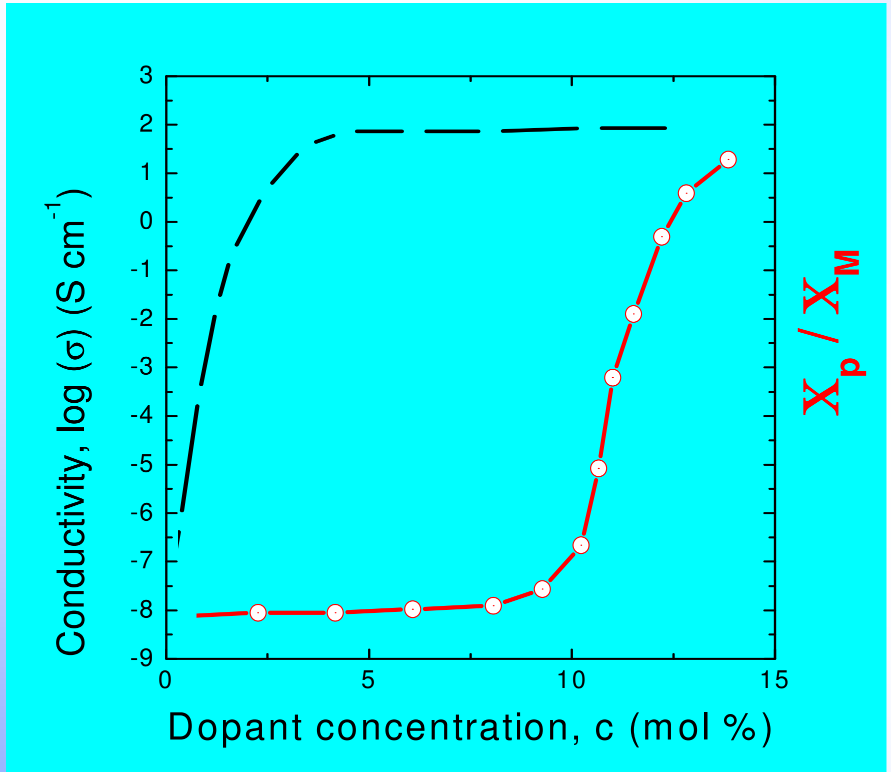
Polyacetylene doping



Nobel prize 2000

Alan J. Heeger
Alan G. MacDiarmid
Hideki Shirakawa

Dramatic change in conductivity at low dopant concentration !



Free electrons in conductors:

Pauli susceptibility:

$$X_P = 3\, n\, \mu_B \,/\, 2\, \varepsilon_F$$

spins of free electrons

In doped trans-polyacetylene conductive species do not have spin!!!!

Su - Schrieffer - Heeger Hamiltonian
one-dimensional π-conjugated chain

$$H_{SSH} = H_{el} + H_{lat}$$

$$H_{el} = \sum_{n,\sigma} t_{n,n+1}\left(c^{+}_{n+1,\sigma}c_{n,\sigma} + c^{+}_{n,\sigma}c_{n+1,\sigma}\right)$$

$$H_{lat} = \sum_{n}\left[\frac{p_n^2}{2M} + \frac{K}{2}\left(u_{n+1} - u_n\right)^2\right]$$

$$t_{n,n+1} = t_0 + \alpha\left(u_n - u_{n+1}\right)$$

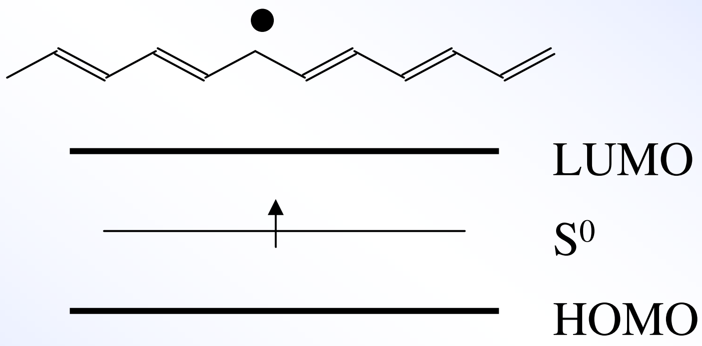
$c^{+}_{n,\sigma}$, $c_{n,\sigma}$ are the creation, resp. anihilation operators of an electron with spin projection σ in the π-orbital of the n_{th} carbon atom

u_n is the diplacement along the chain of the n_{th} CH unit from its position in the undimerized chain

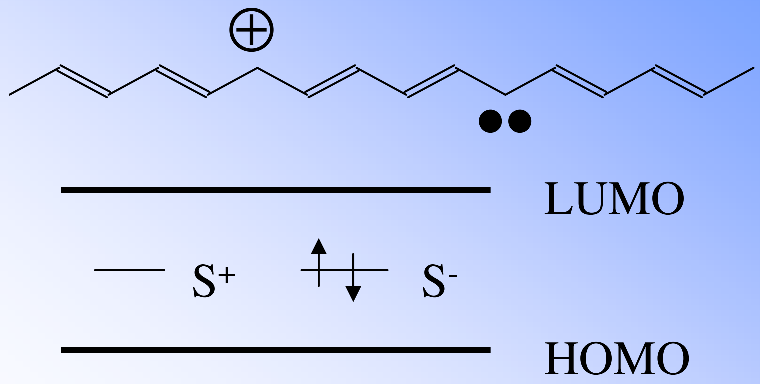
$t_{n,n+1}$ is electron hopping amplitude

reflects electron-phonon interaction

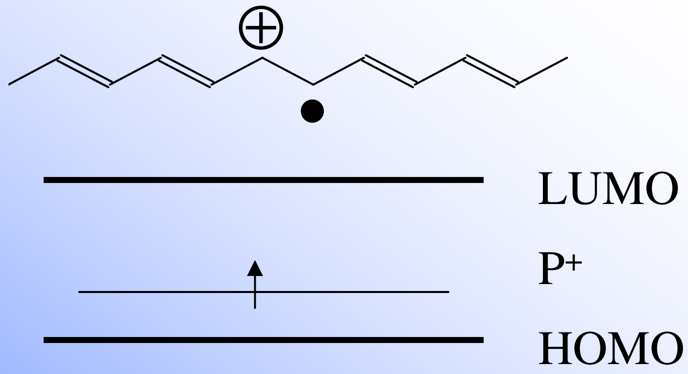
Neutral soliton (Free radical)



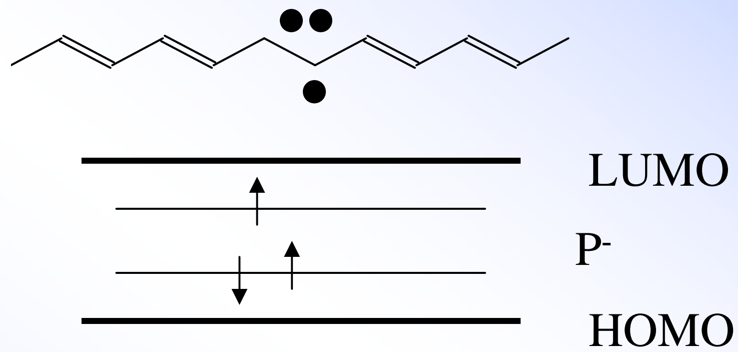
Charged soliton (Carbocation, Carbanion)



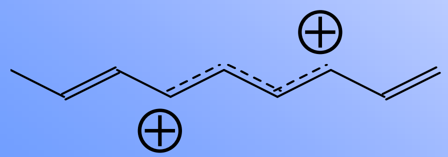
Positive polaron (Radical-cation)



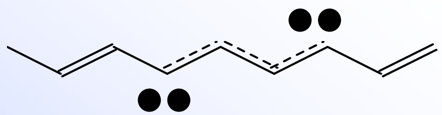
Negative polaron (Radical-anion)



Positive Bi-polaron (Carbodication)



Negative Bi-polaron (Carbodianion)



Soliton on the coast of Kuaii

- solitons are moved without dispersion
- solitons do not interact between each other

Normally waves (at water surface, acoustic, electromagnetic,) propagate with dispersion (they loose their shape and their amplitude decreases in time).

X soliton wave – keeps its shape without dispersion.

" Solitary wave " can be found as disastrous tidal waves initiated by earth quakes under the Pacific Ocean (Tsunami)

Free soliton motion possible only in trans-polyacetylene.

" degenerate ground state "

In other conjugated polymers motion of a soliton changes the energy.

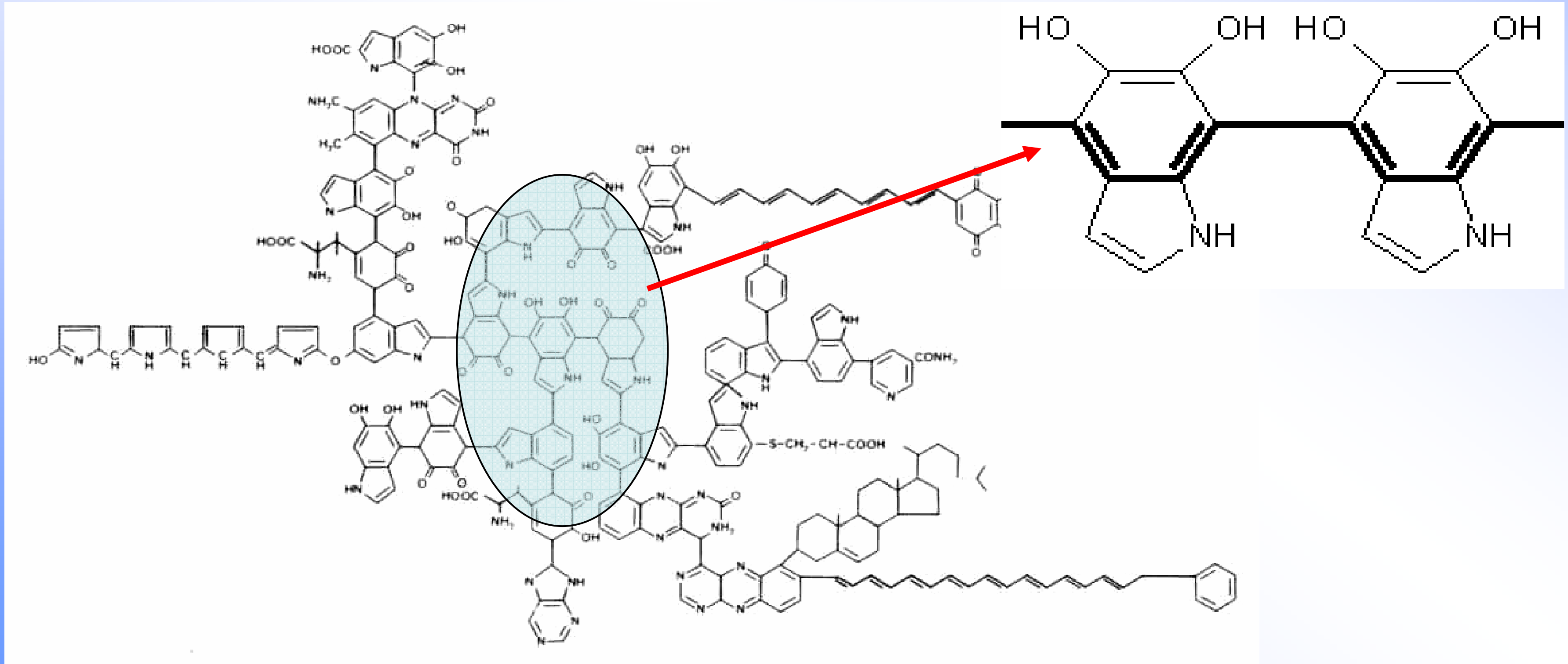
" non-degenerate ground state polymers "

The defect is moving. The electrons change their partners, not their position. This requires a slight displacement of the ions to invert short and long bond lengths.

Creation of solitons

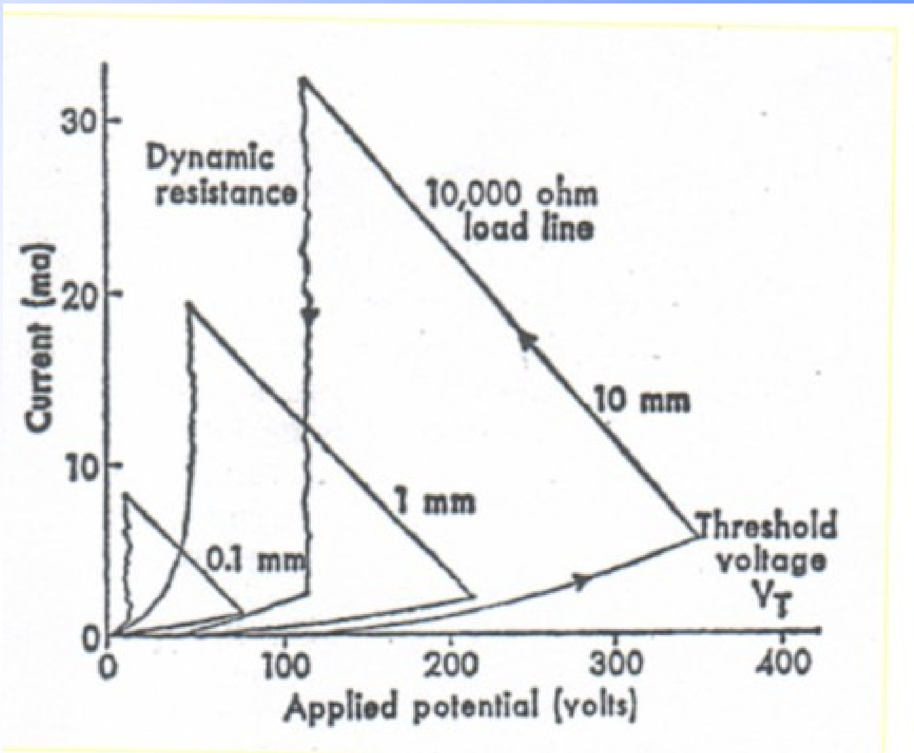
1) **during the synthesis or isomerization**
   (only about 400 radicals / 10^6 carbon atoms)
2) **chemical doping**
3) **photogeneration**
4) **charge injection**

McGinness, Corry and Proctor, of the University of Texas Cancer Center, Houston, reported in *Science* (183, 853; 1974) that melanins can be 'switched' from a poorly conducting to a highly conducting state at fairly low electric fields
(from 10^4 Ω cm to 10^2 Ω cm at a field 300 V cm^{-1})
Large conduction is of electronic origin and it fully reversible
Melanin can be considered the acetylene-black.



Melanin based electrical switch

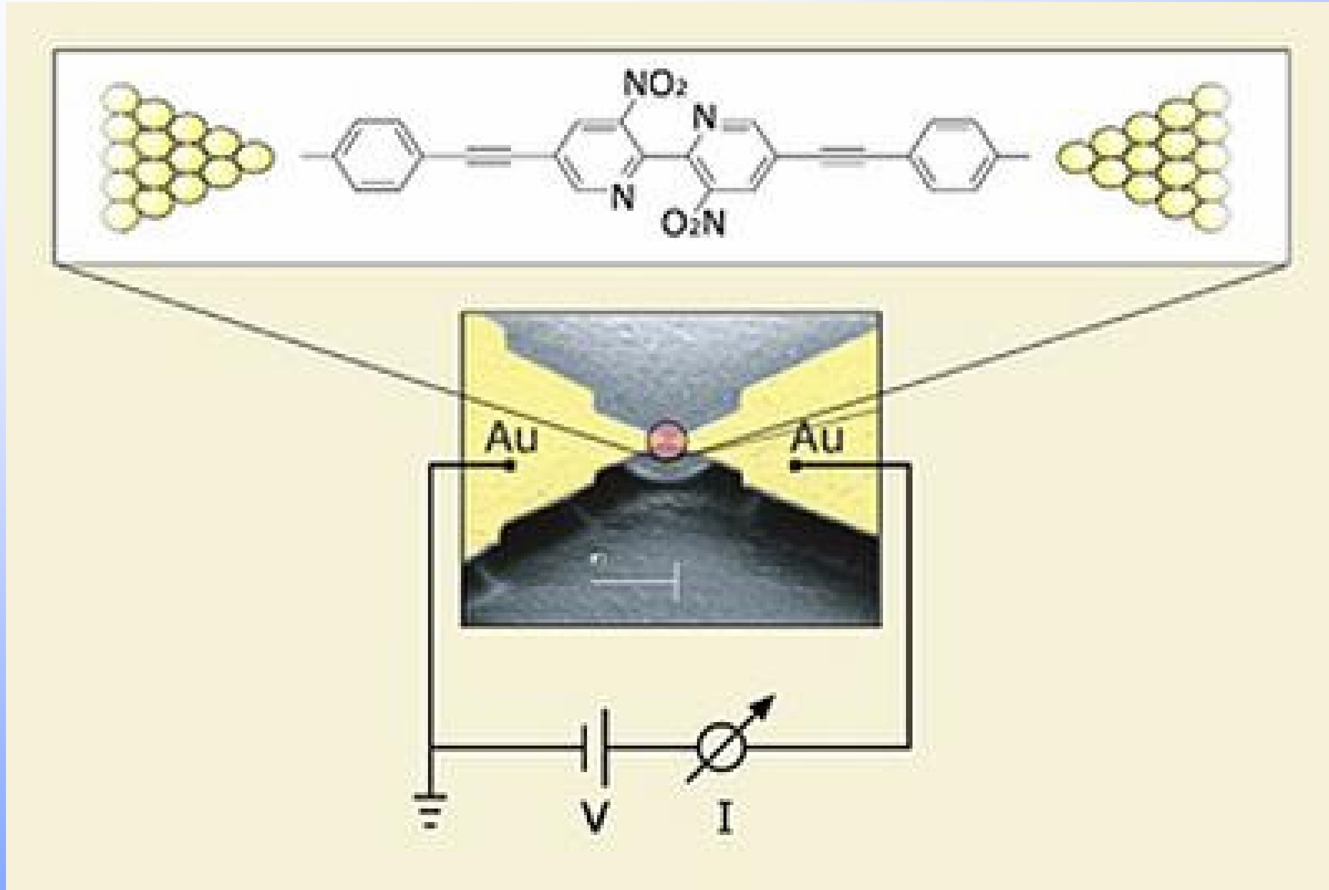
"Credit generally goes to the most famous discoverer, not to the first ."
R. Dulbecco*, *Nobel laureate



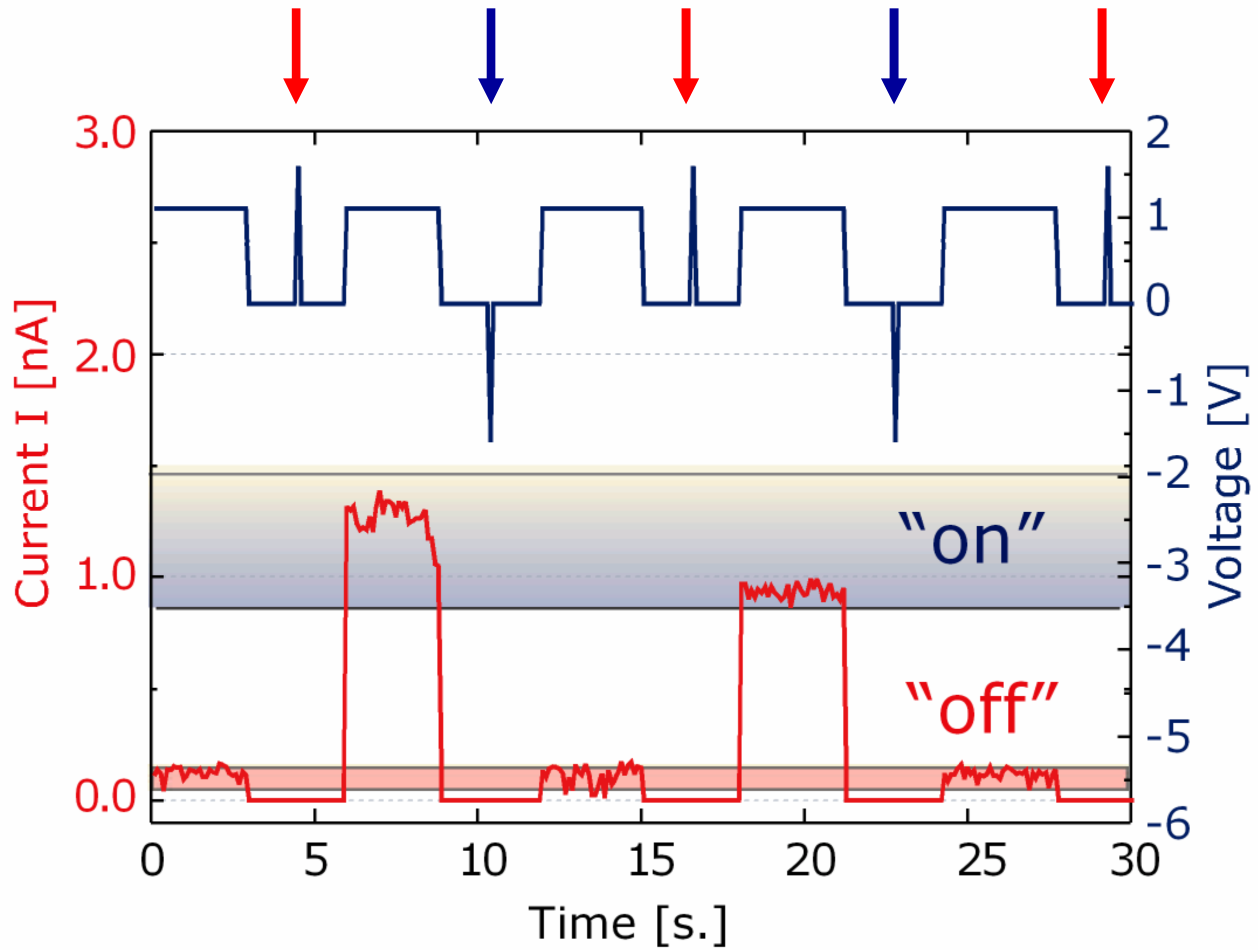
„Current voltage characteristics of melanin prepared by autoxidation of L-Dopa sandwiched between copper electrodes, for various sample thicknesses. The current through a melanin sample is dependent on its history, and will be given by the lower curve unless threshold voltage has been exceeded, in which the cell is switched from the "off" to the "on" state with a much higher conductivity. This process is reversible and is not a breakdown in the usual sense.“

McGinness et al. *Science* (183, 853; 1974)

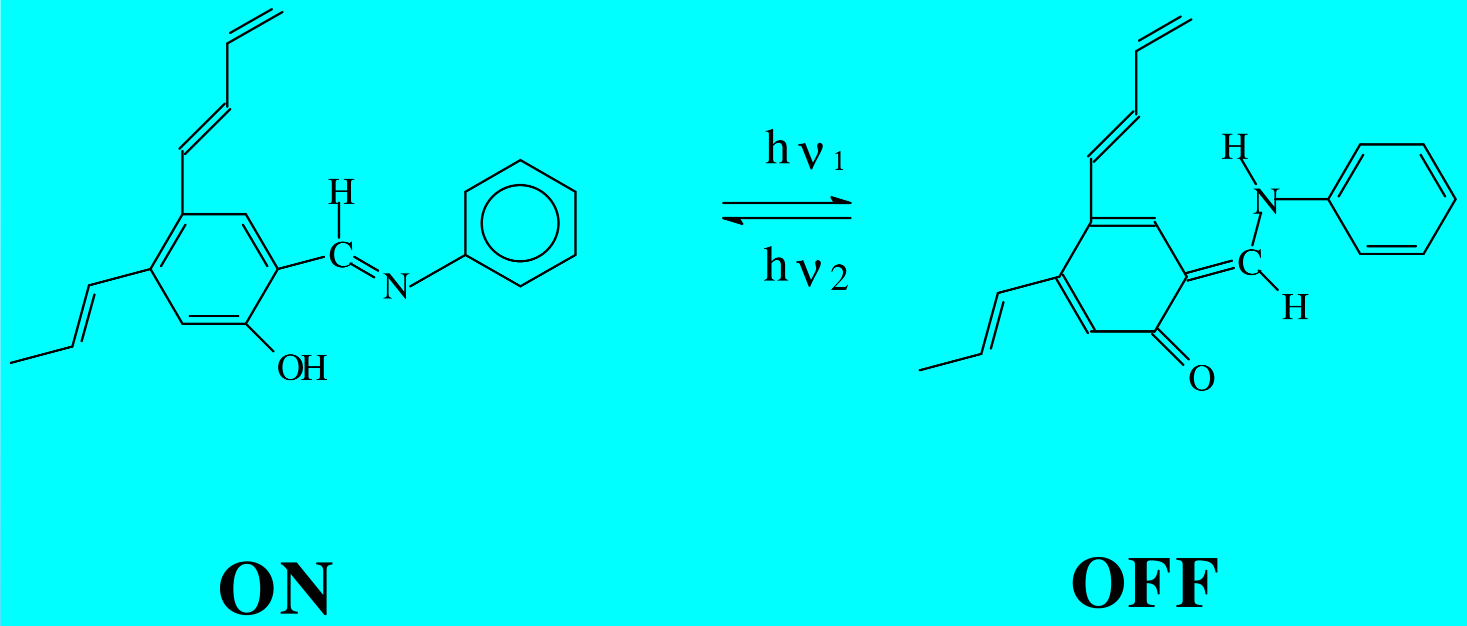
Swiss branch of IBM introduced molecular memory based on the conjugated molecule. It is able to write information using applied voltage and read it repeatedly



Write-read cyclus of the molecular memory



Opto-electrical switch



Photochromic side-group can interrupt the electron conjugation upon illumination.

Polyacetylene - Doping

1) Vapor:

$(CH)_x + ½ \, xy \, I_2 \rightarrow (CH^{y+})_x + xy \, I^-$

$xy \, I^- + xy \, I_2 \rightarrow xy \, I_3^-$

$(CH^{y+})_x + xy \, I_3^- \rightarrow [(CH^{y+}) (I_3^-)_y]_x$

2) Electrochemical:

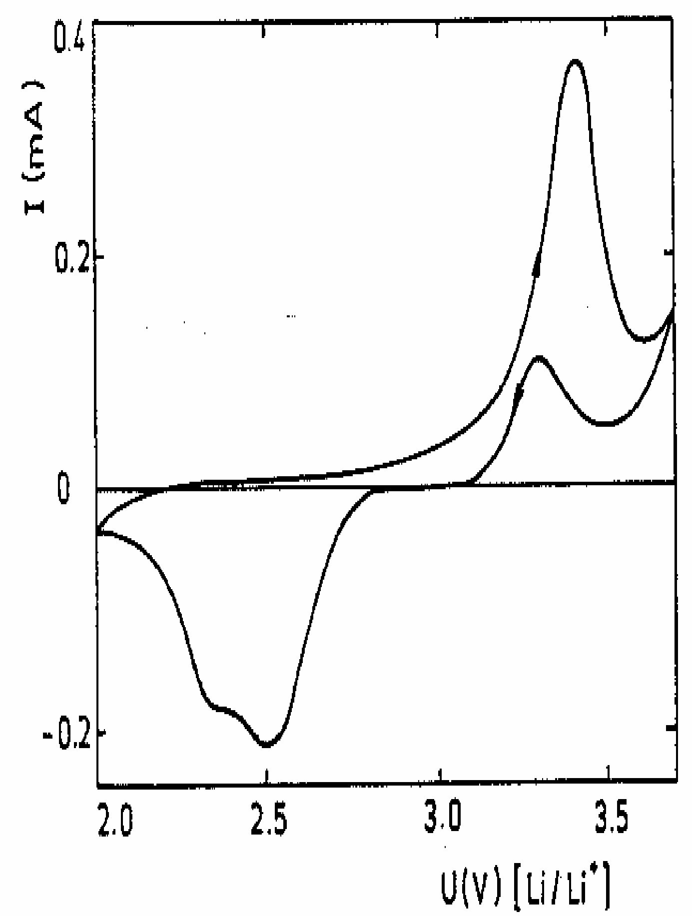
for example $n\text{-}Bu_4N^+ClO_4^-$/THF vs. Li^+/Li

$(CH)_x + xy \, e^- \rightarrow (CH^{y-})_x$

$(CH^{y-})_x + xy \, (n\text{-}Bu_4N^+) \rightarrow [(n\text{-}Bu_4N^+)_y(CH^{y-})]_x$

vs. Li: $U > 3.1$ V $\Rightarrow (CH_y^+)_x$

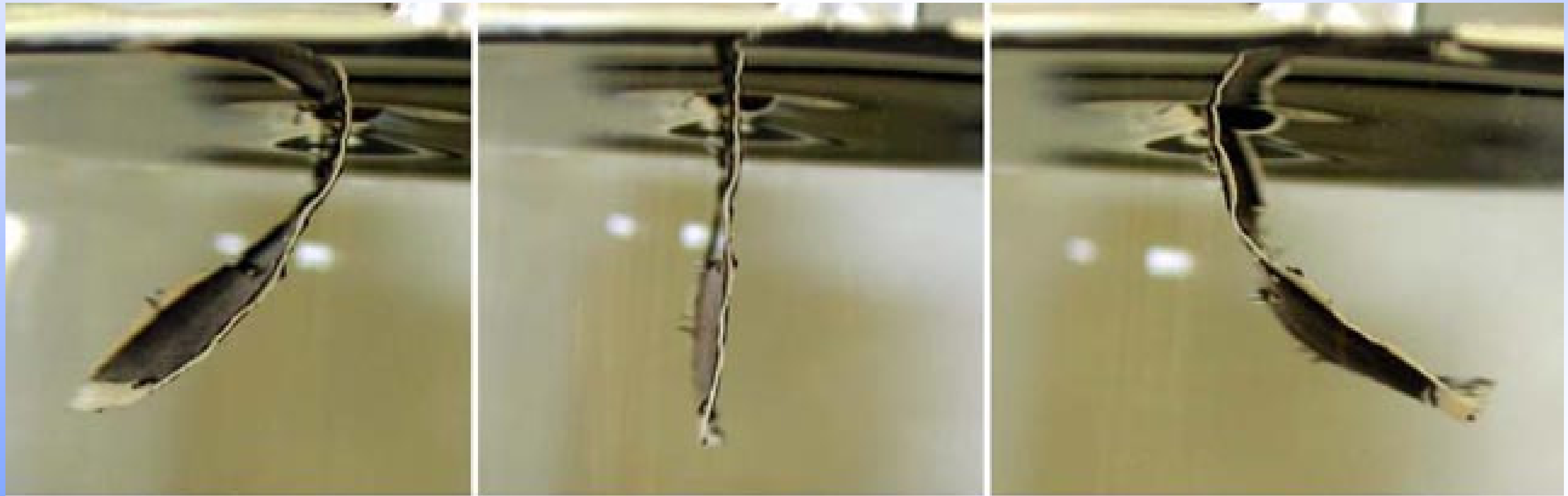
$U < 1.8$ V $\Rightarrow (CH_y^-)_x$



Mechanical actuators

Electrochemical doping (swelling of the polymer) - dedoping
Bimetallic-like structure: to materials with two different expansion coefficient
Expansion ratio about 2 %

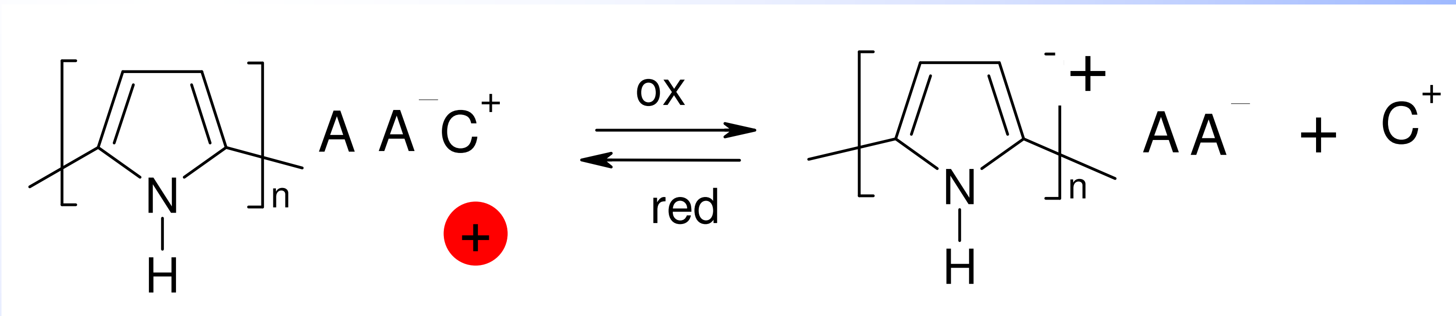
+U 0 -U

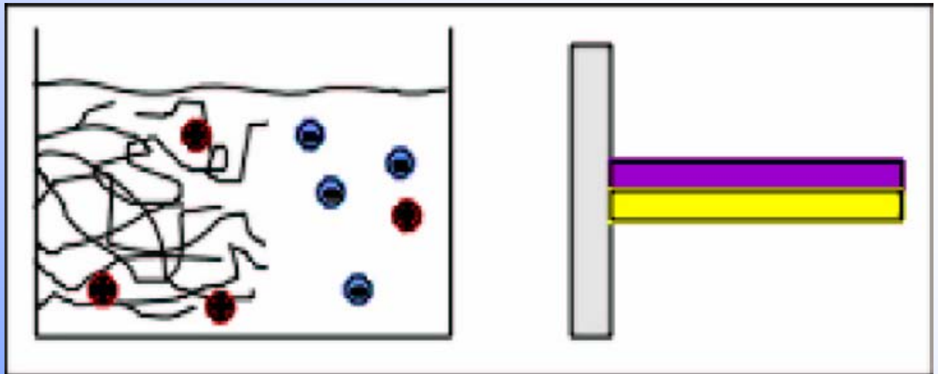


Possible application:
Artificial muscle, application in biological environment

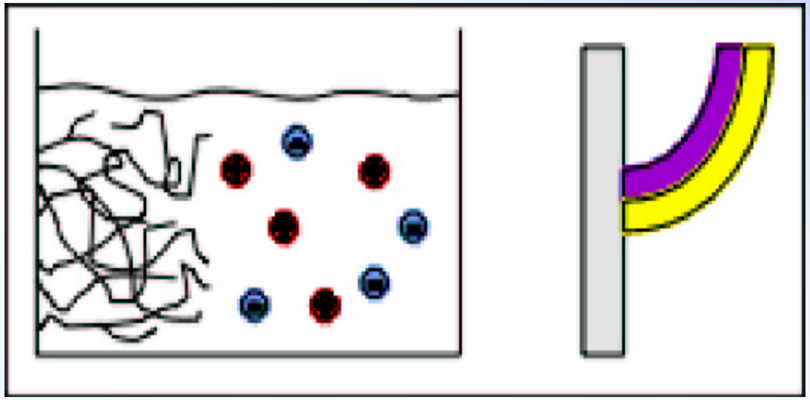
Large anion

Example: **Polypyrrol doped by dodecylbenzenesulhonate anions (DBS⁻) in a water solution of sodium dodecylbenzenesulphonate**





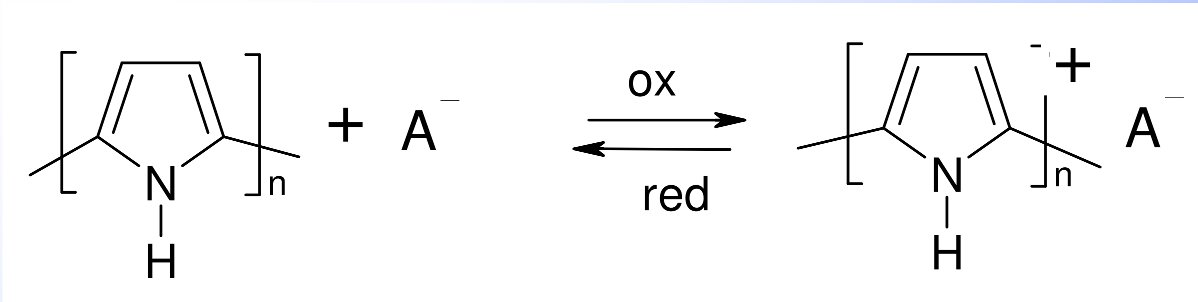
V = -1 : cations neutralize negatively charged polymer- expansion (polymer in reduced state)

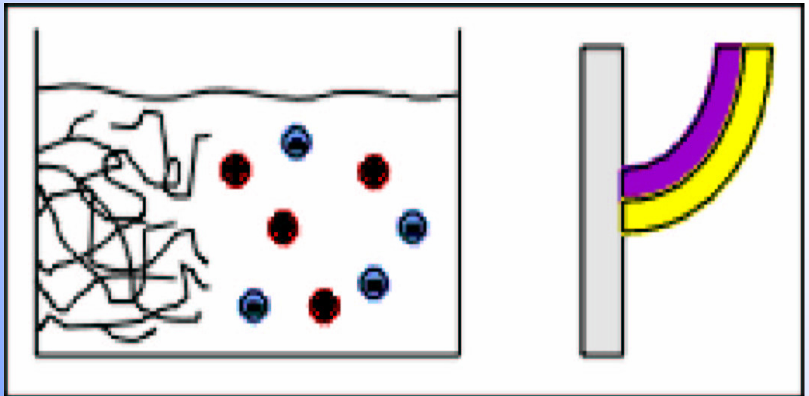


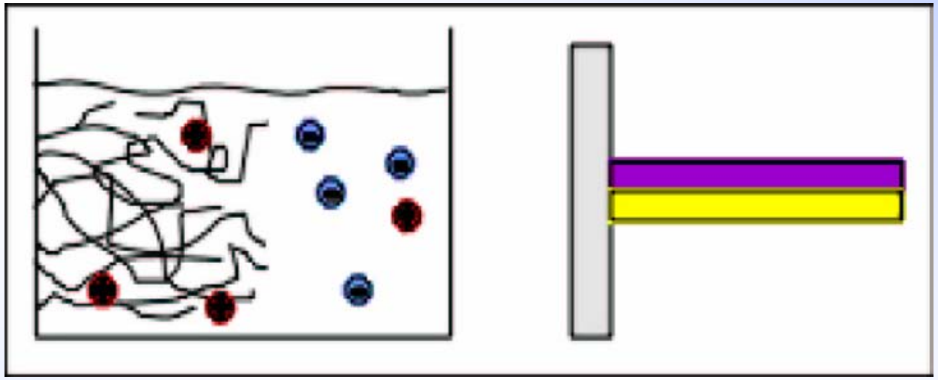
V = 0 : cations are expelled - contraction (polymer in oxidized state)

Small anions

Example: **Polypyrrol in $Li^{+}ClO_4^{-}$ electrolyte**



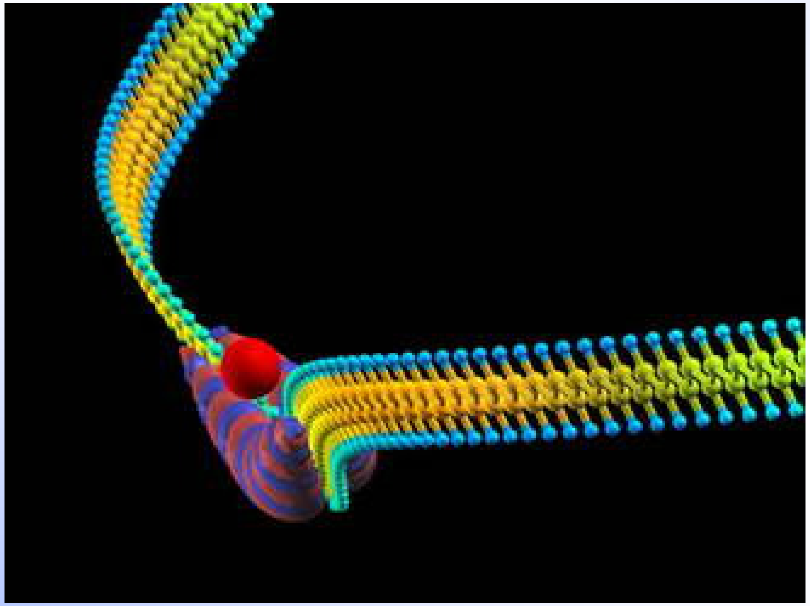


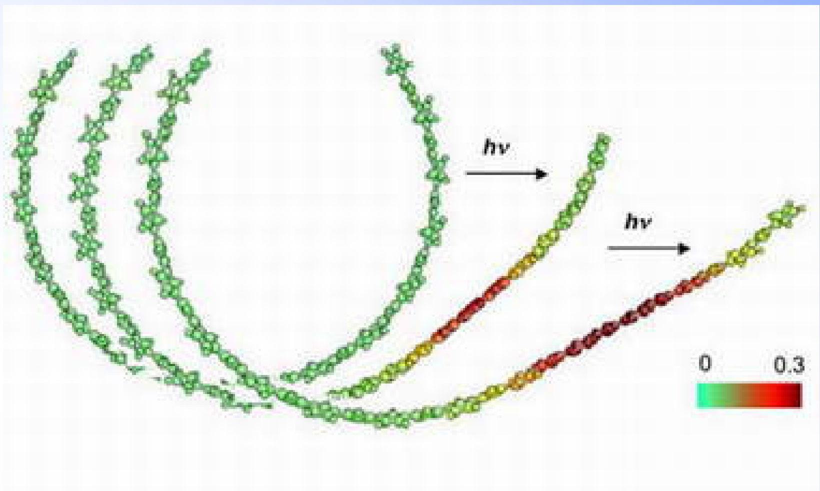


V = 0 : anions expelled - contraction (polymer in neutral state)

V = 1 : anions atracted to negative polymer - expansion (polymer in oxidised state)

Molecular „muscles“

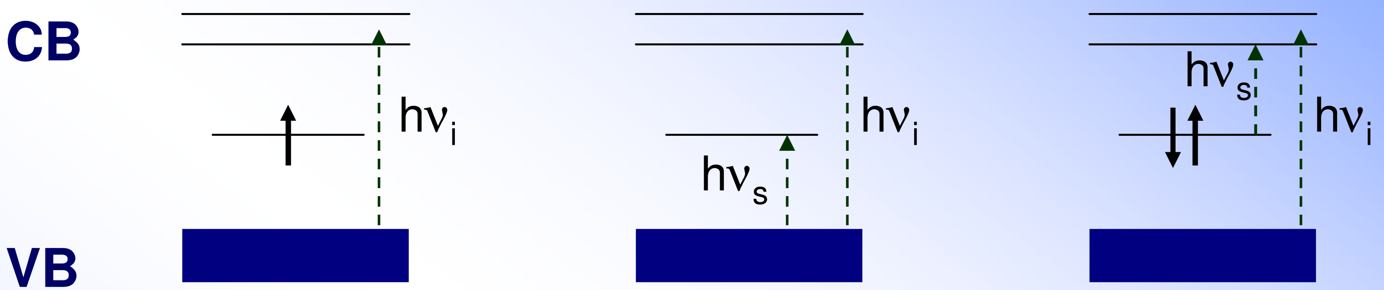




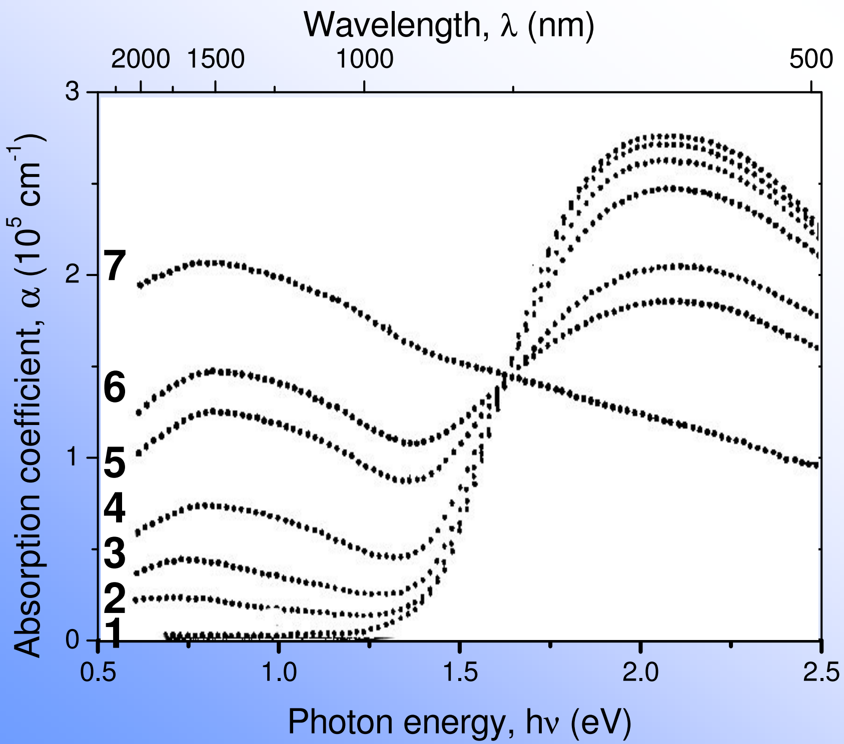
Charge induces morphology changes in a polymer chain

Source: Sidney Yip, Xi Lin, Massachusetts Institute of Technology

Optical transitions in trans-polyacetylene upon doping

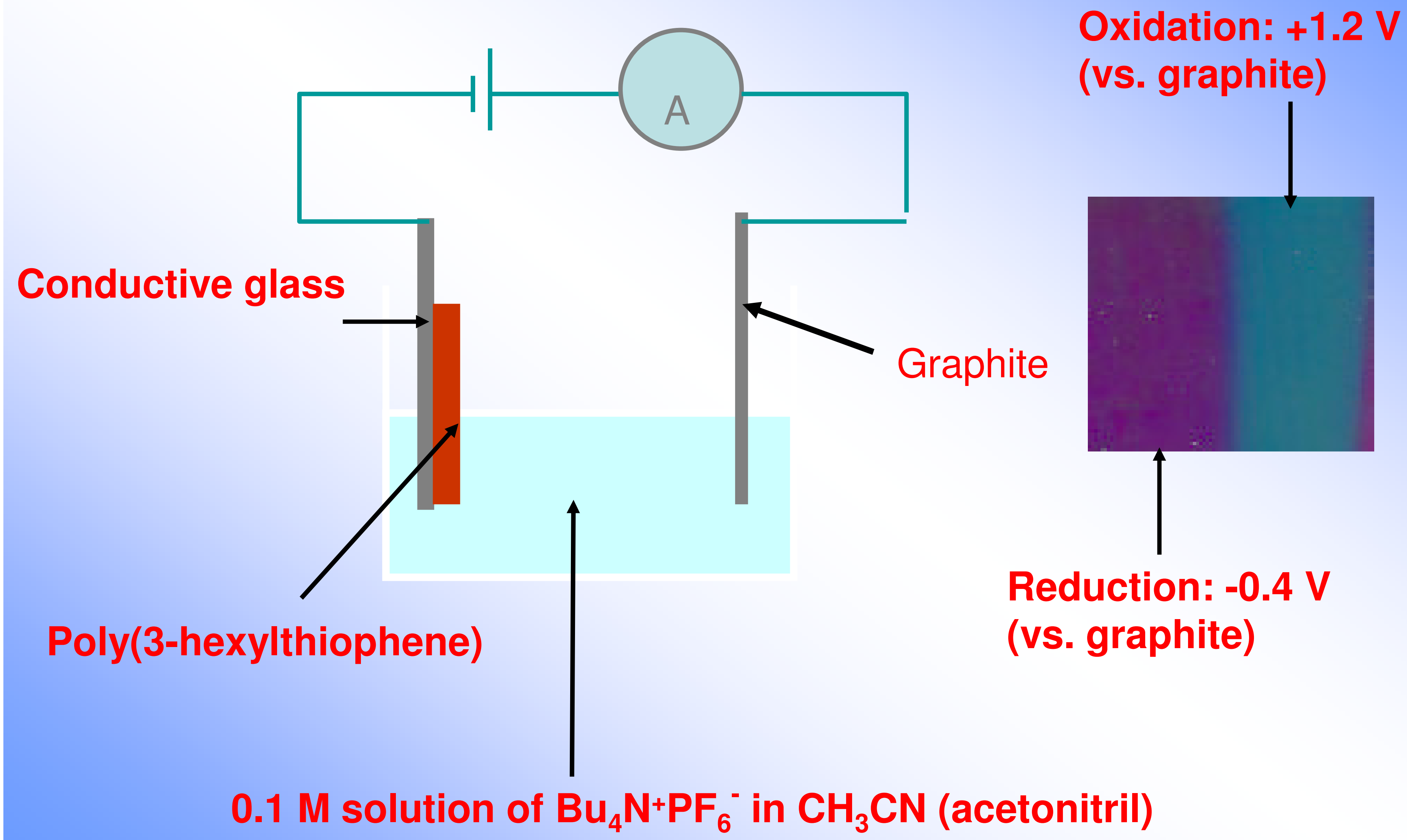


Energy diagram of trans-polyacetylene with valence band, conduction band and soliton energy level, with corresponding inter-band ($h\nu_i$) and mid-gap ($h\nu_S$) optical transitions.

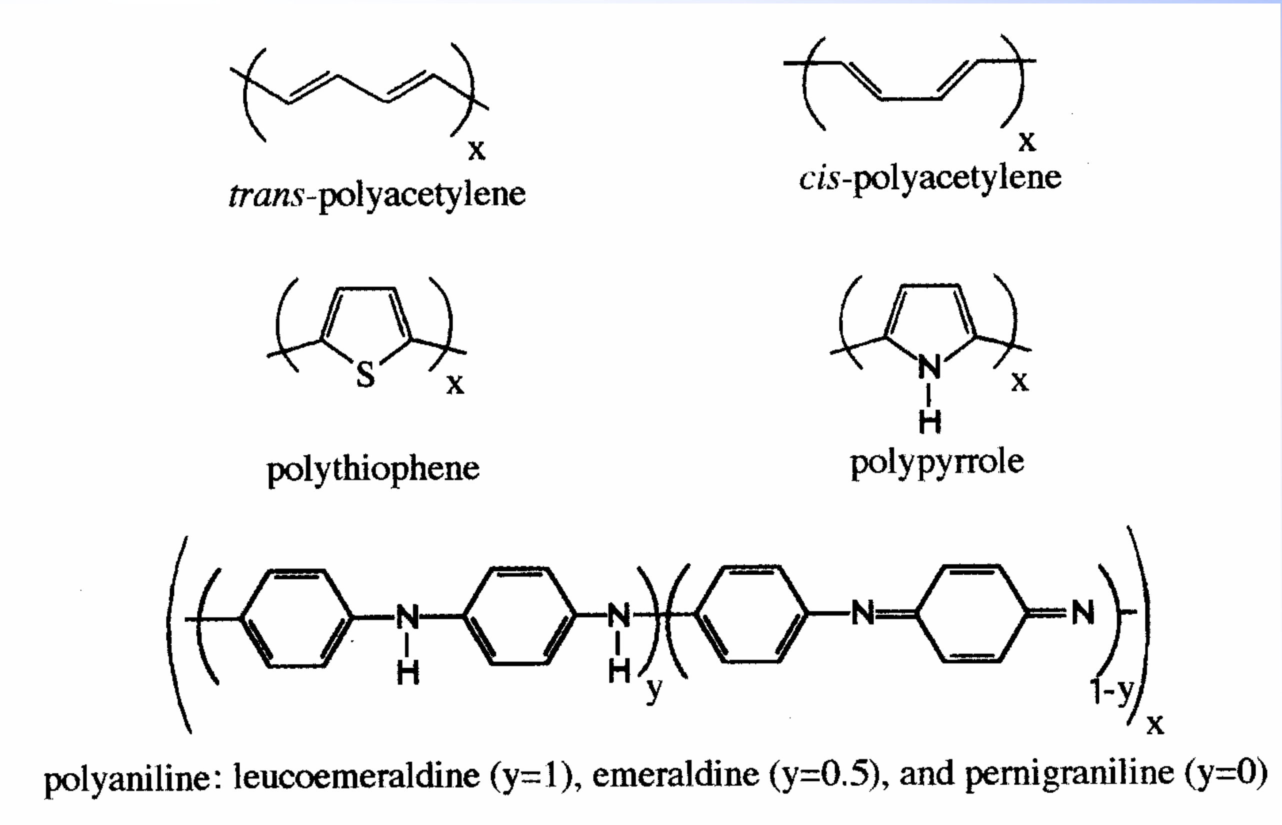


Optical absorption of trans-polyacetylene upon electrochemical doping with perchlorate ions. Molar concentrations of the dopant 0 ÷ 0.078 for the curves 1 – 7, respectively. (according to Feldblum et al. 1982)

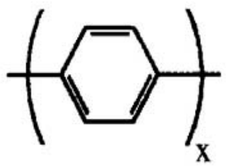
Smart windows



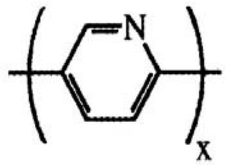
π-conjugated polymers electrically conducting after doping



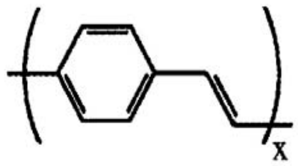
Semiconducting polymers



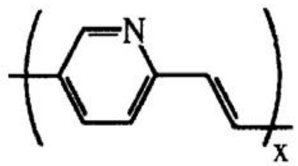
poly(*p*-phenylene)



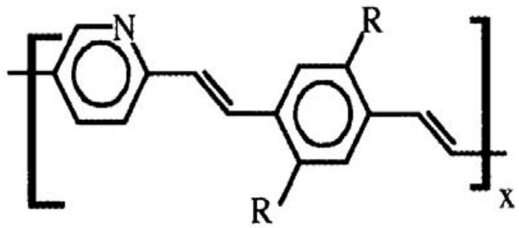
poly(*p*-pyridine)



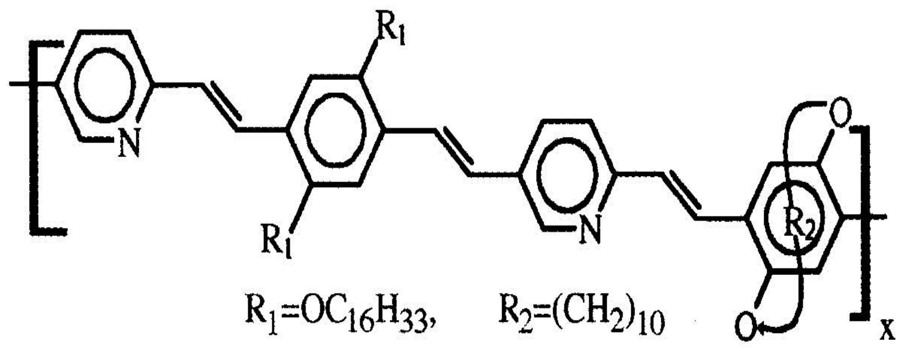
poly(*p*-phenylene vinylene)



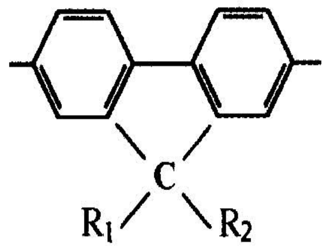
poly(*p*-pyridyl vinylene)



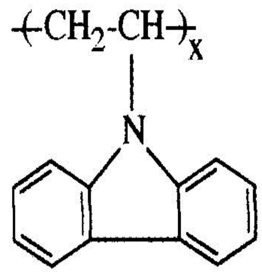
poly(*p*-pyridyl vinylene phenylene vinylene)



"strapped" poly(*p*-pyridyl vinylene phenylene vinylene)

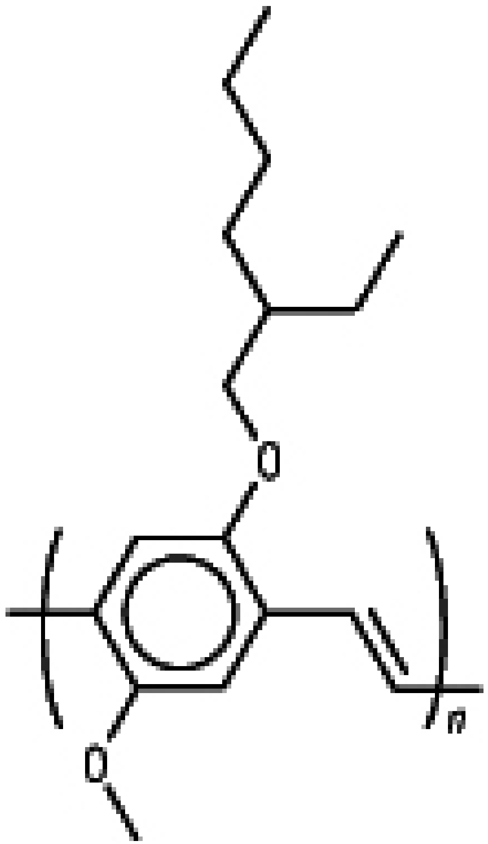


poly(fluorene)

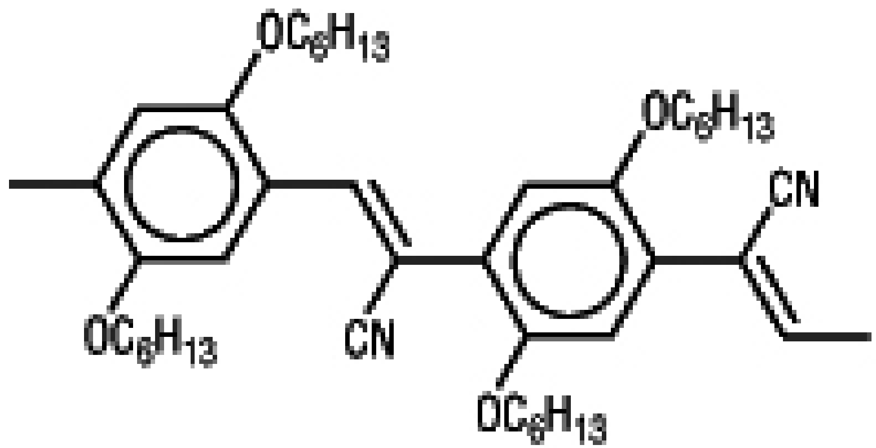


poly(N-vinyl carbazole)

p-type polymers
holes mobile

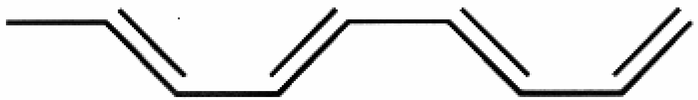


n-type polymer
electrons mobile



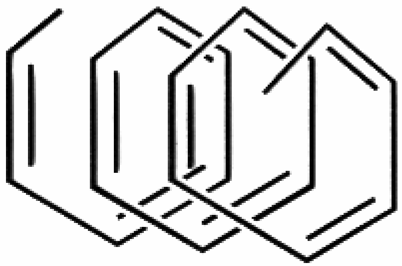
Structure considerations - isomers

a *TRANS-TRANSOID*



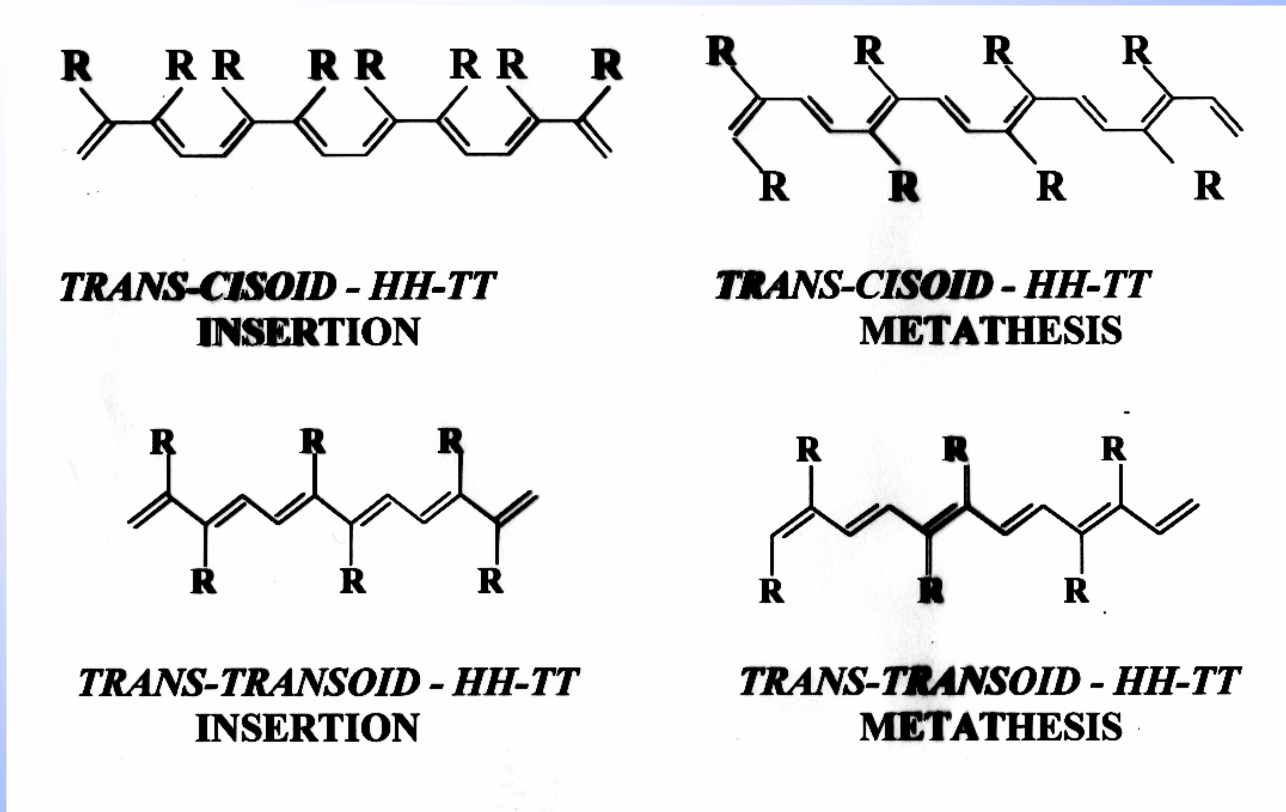
b *TRANS-CISOID*

c *CIS-TRANSOID*

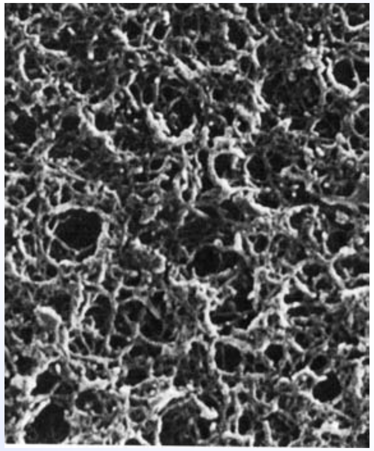


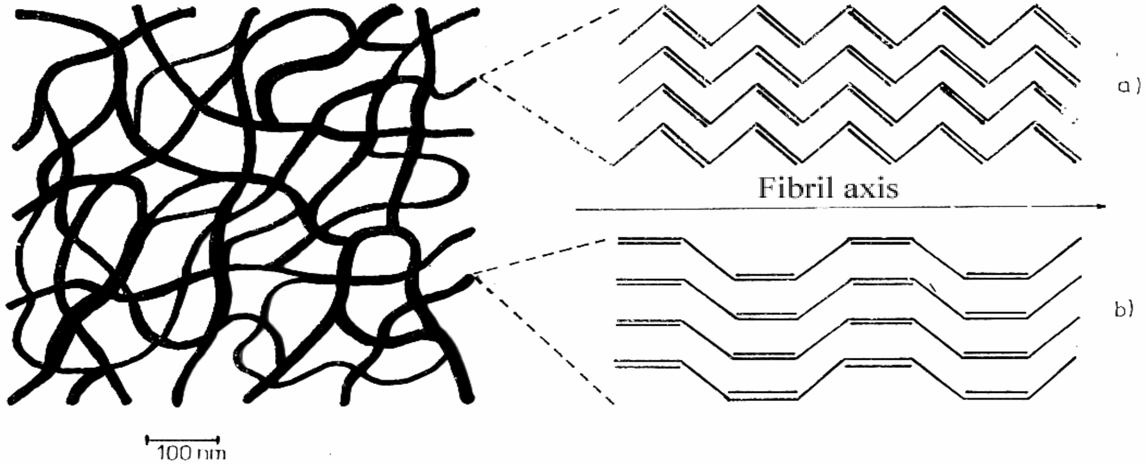
d *CIS-CISOID*

Structure considerations – regioregularity

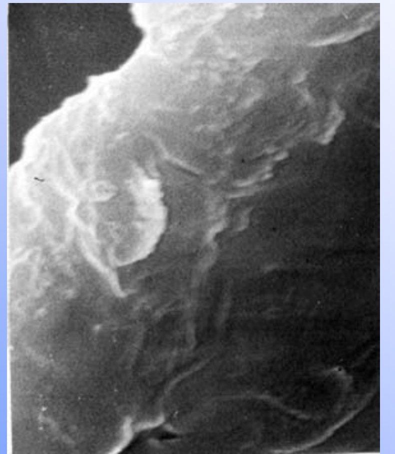


Depends on the polymerization mechanism

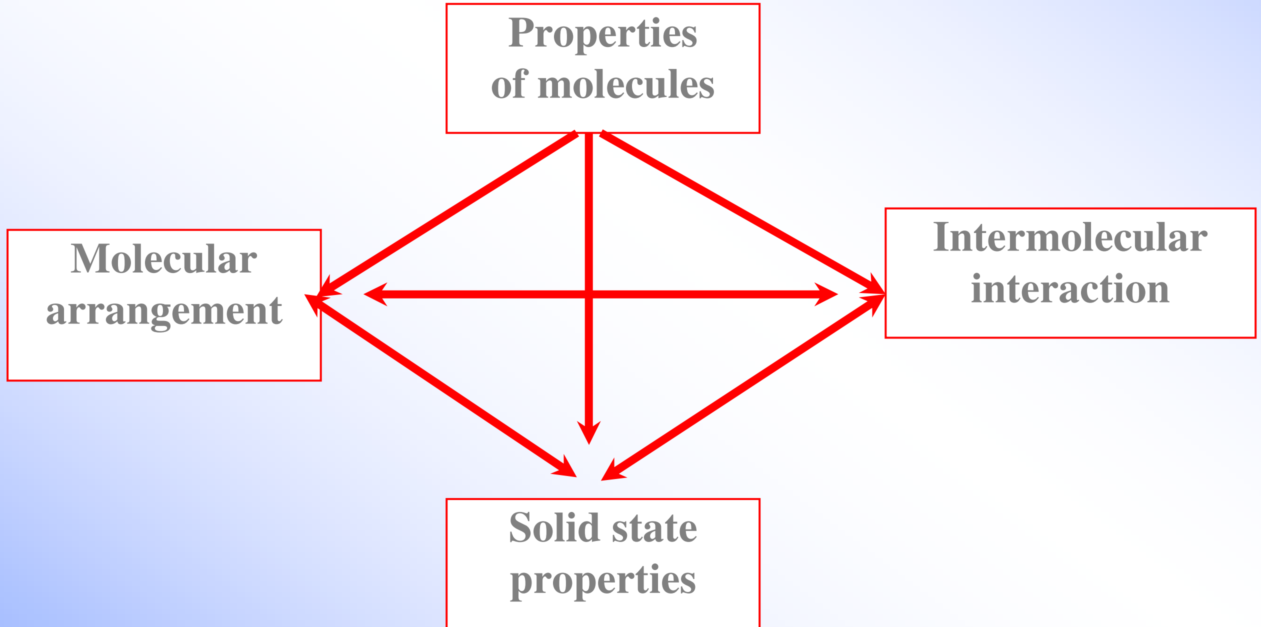




SEM of polyacetylene prepared by Shirakawa method in toluene



SEM of polyacetylene prepared by $Ti(OBu)_4$/ EtMgBr catalyst in diethylether



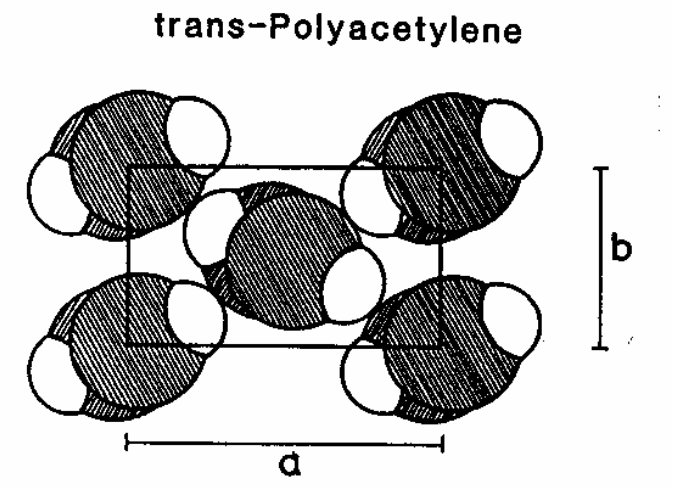
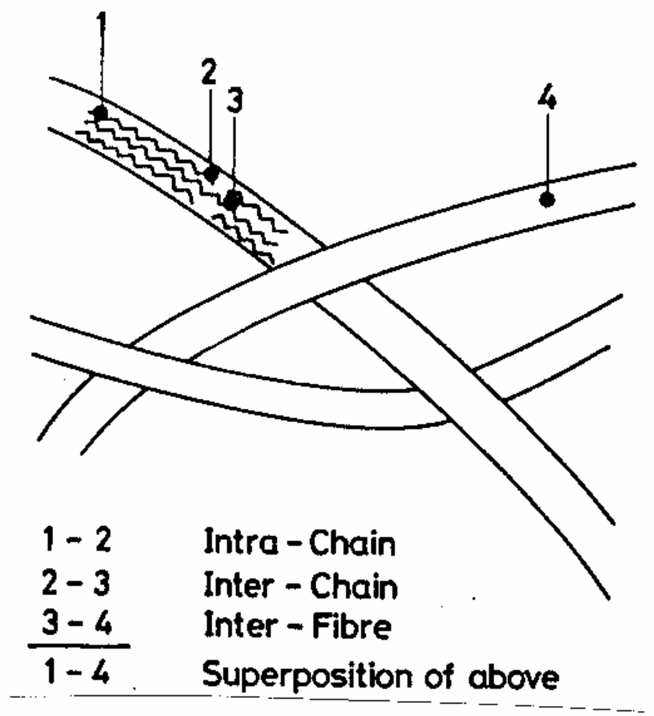


Fig. 4. Elementary cell of trans-polyacetylene, *a–b* plane. The polymer chains are perpendicular to the *a–b* plane

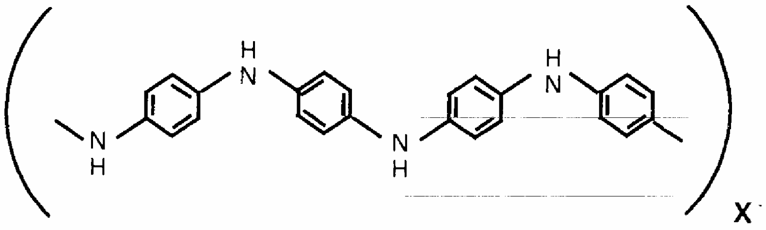


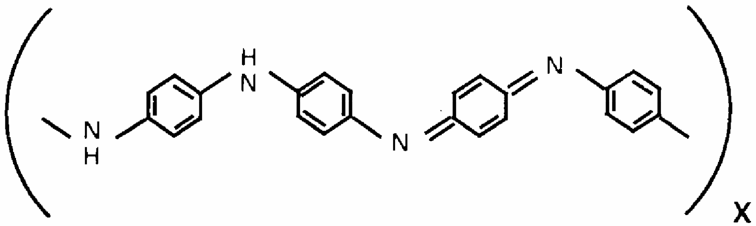
Polymers:

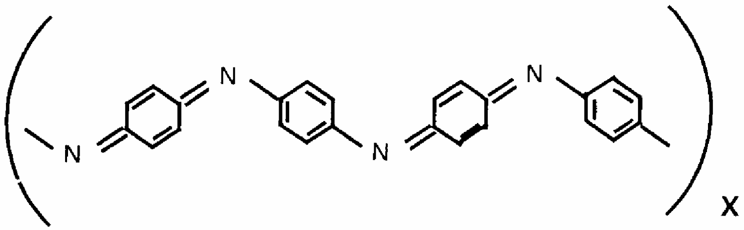
weak intermolecular interaction
stronger intramolecular interaction
hopping betweeen polymer segments

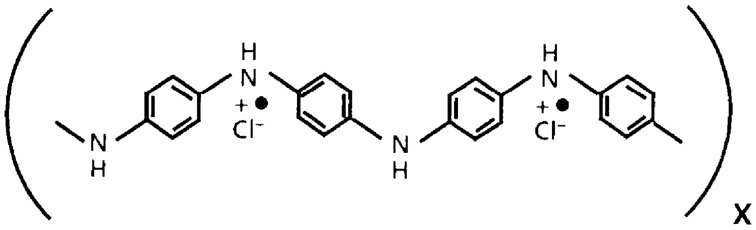
Polyaniline

modifications

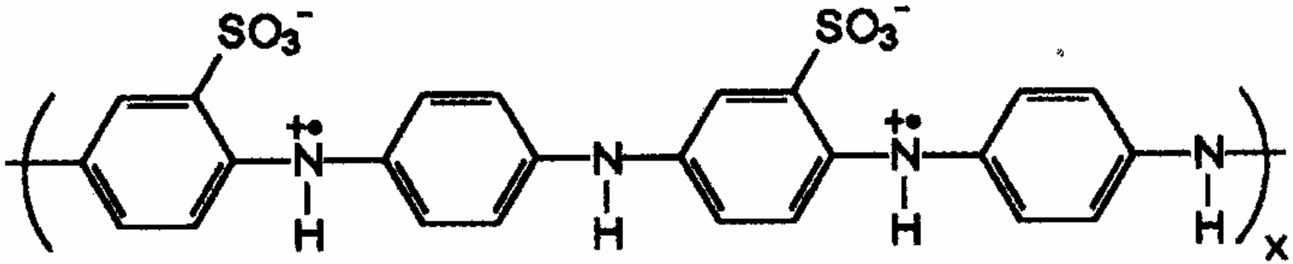
a)  LEB — colourless

b)  EB — blue

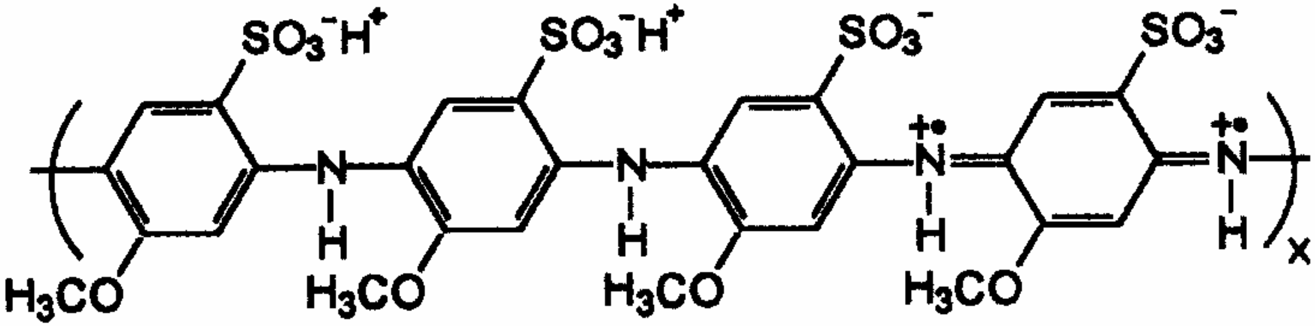
c)  PNB — violet

d)  ES — green

Sulfonated polyaniline:
Exapmple of „self-doped“ polymer

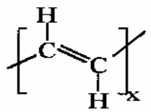
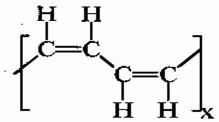
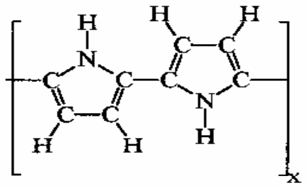
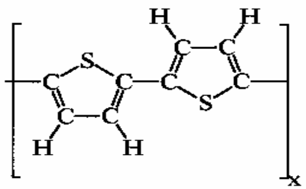
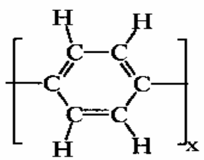
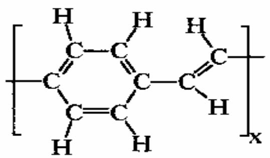


50% sulfonated polyaniline (EB-SPAN)

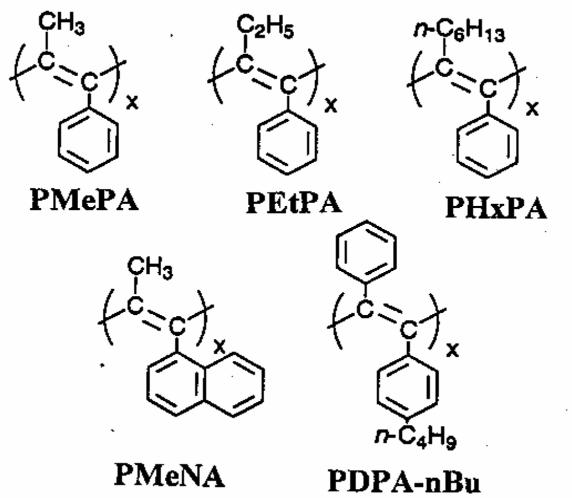


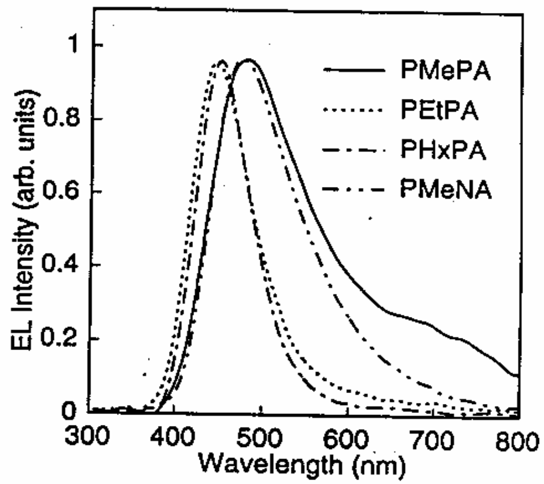
100% sulfonated polyaniline (NSPAN)

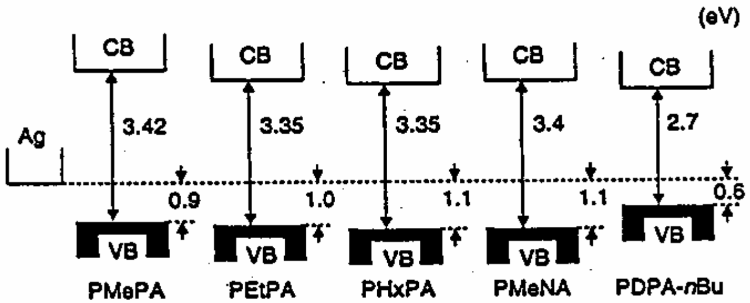
Color tuning
by chemical structure

POLYMER	STRUCTURE	Eg(eV)
trans-polyacetylene		1.4
cis-polyacetylene		2.0
polypyrrole		2.5
polythiophene		2.0
poly(p-phenylene)		3.0
poly(phenylenevinylene)		2.4

Color tuning of polymer by substitution with side groups



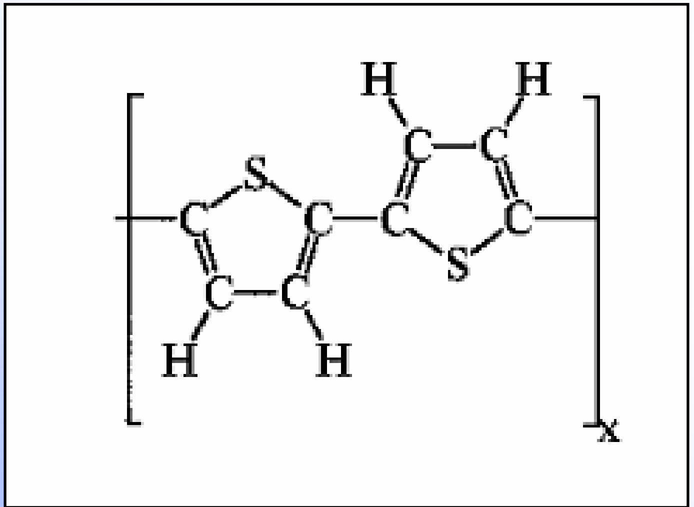


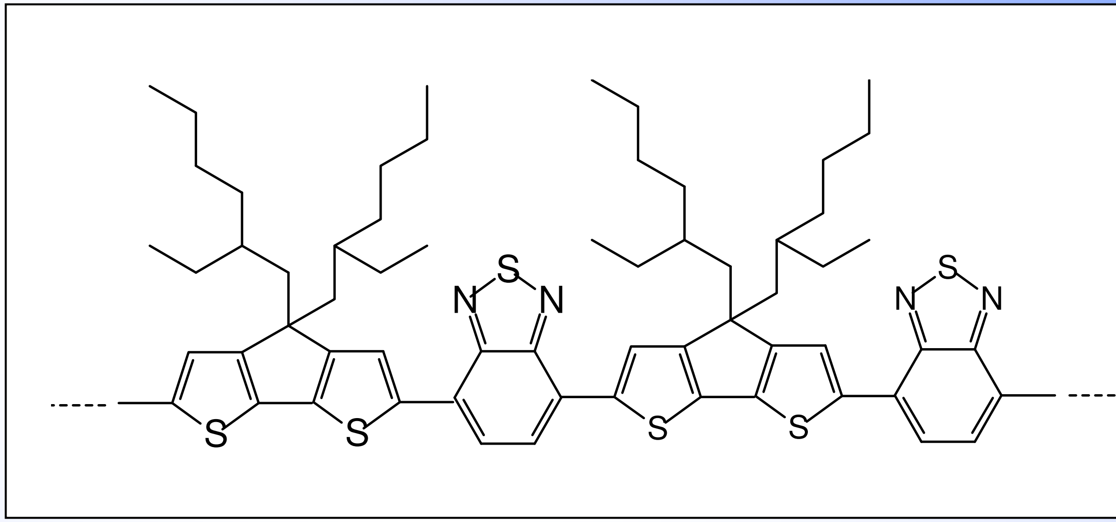


Estimated electronic energy levels

(From: M. Hirohata *et. al.*, Jpn. J. Appl. Phys. Part 2, Vol. 36 (1997), No.3A, pp. L 302-305.)

How to absorb maximum of light





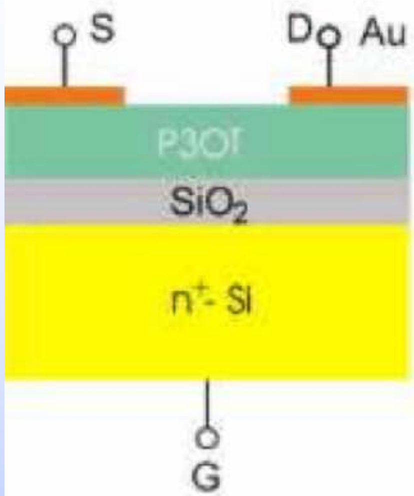
E_g = 2.0 eV

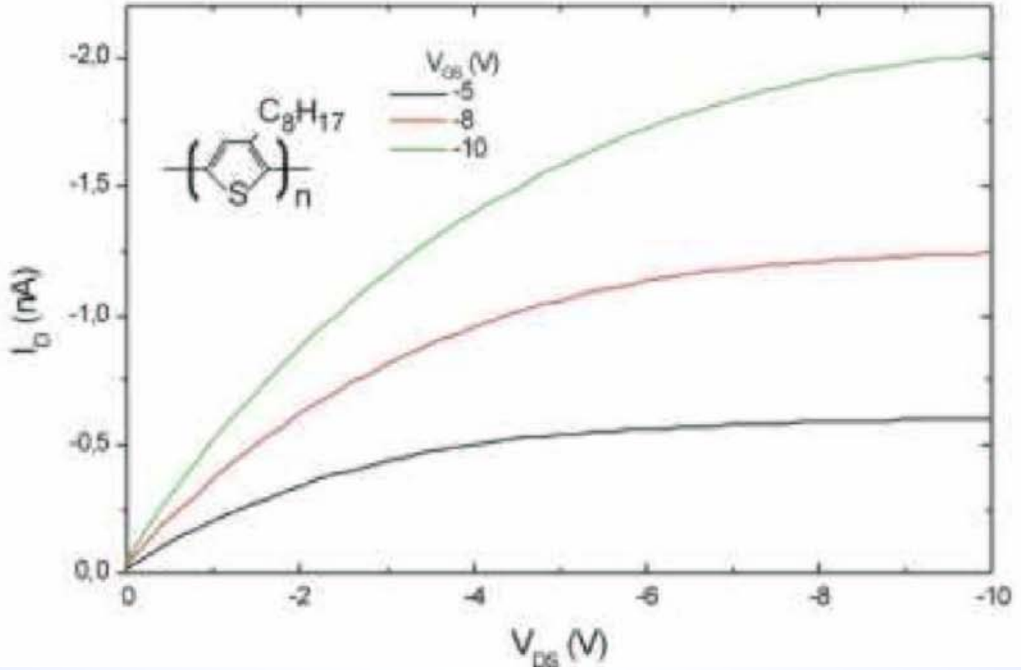
E_g = 1.4 eV

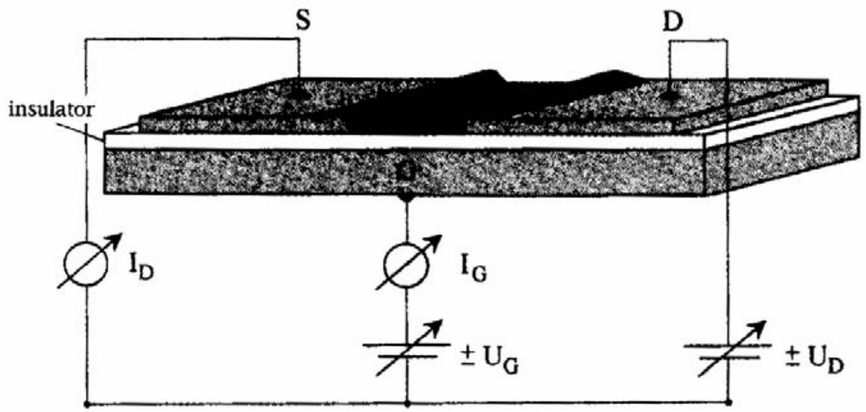
absorbs all the visible light
close to silicon E_g = 1.1 eV

Zhu, Z. et al., J. Macromol. Sci. A, 44 (12), 2007, 1249-1253

Organic Field Effect Transistor (FET)

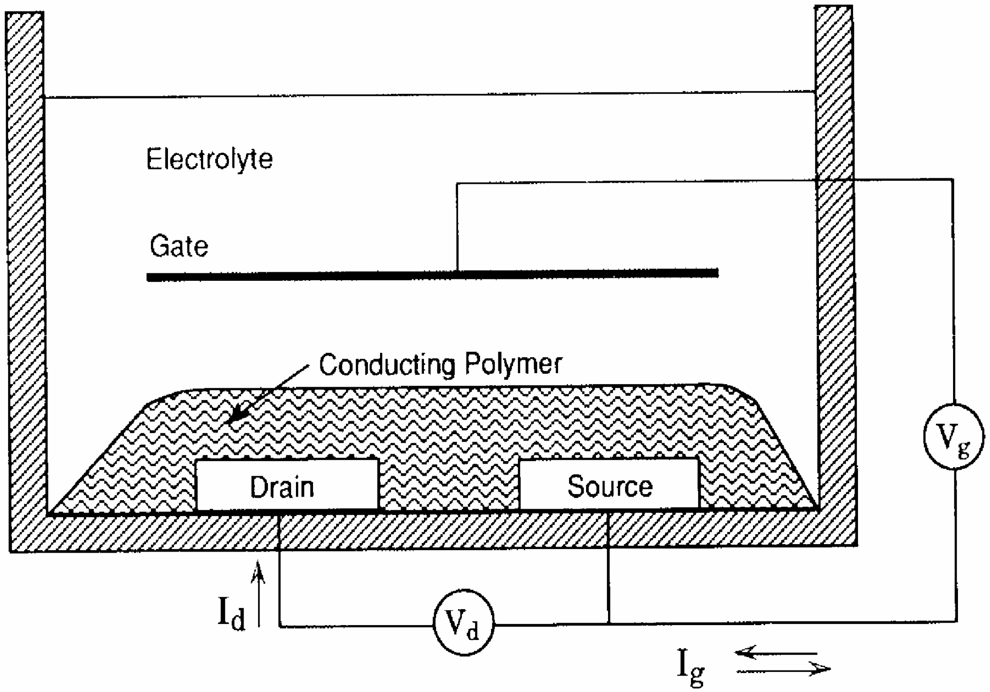






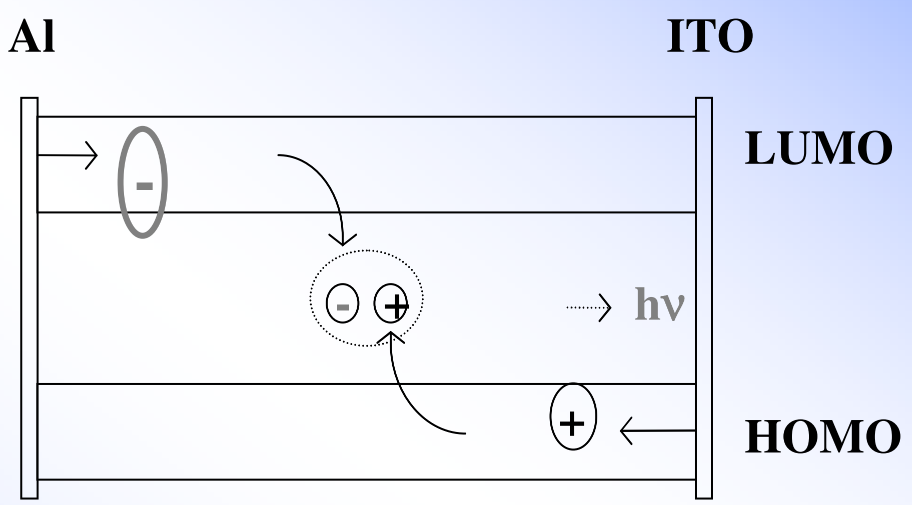
$$\left(\frac{\partial I_D}{\partial U_G}\right)_{U_D=const.} = \pm \frac{L}{D} \boldsymbol{\mu} C_i U_D$$

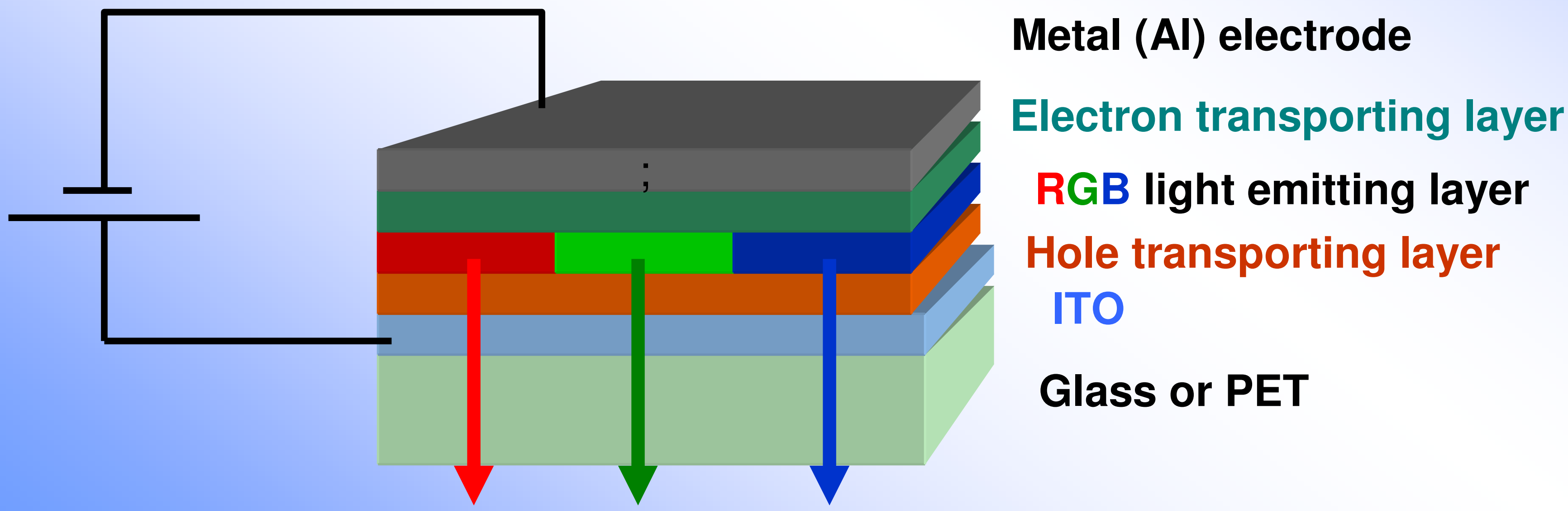
Electrochemical FET sensor



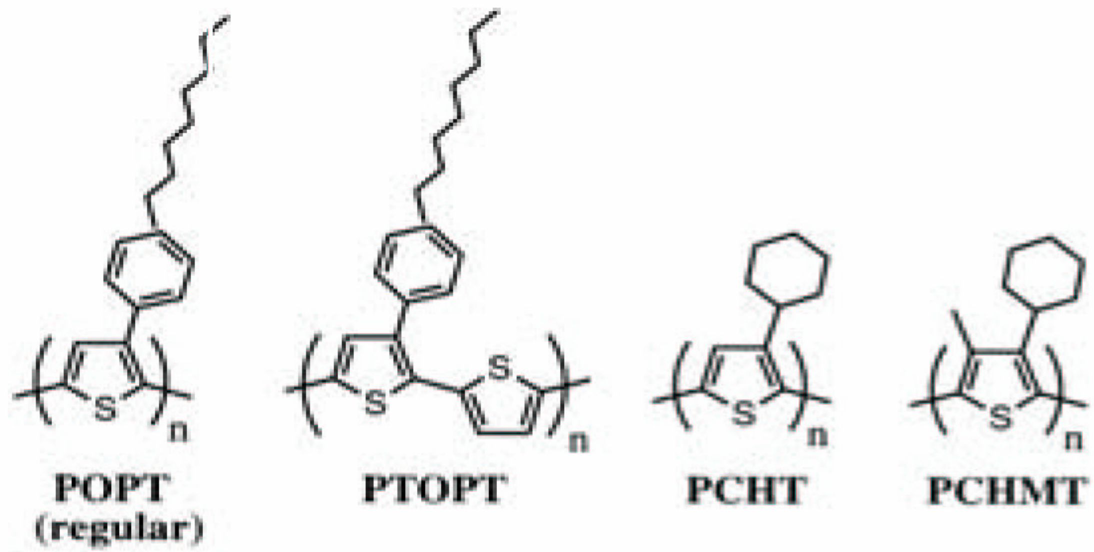
conducting polymer = poly(3-methylthiophene)
sensitivity 10^{-15} mole of an oxidant
(Thackeray et al. 1985)

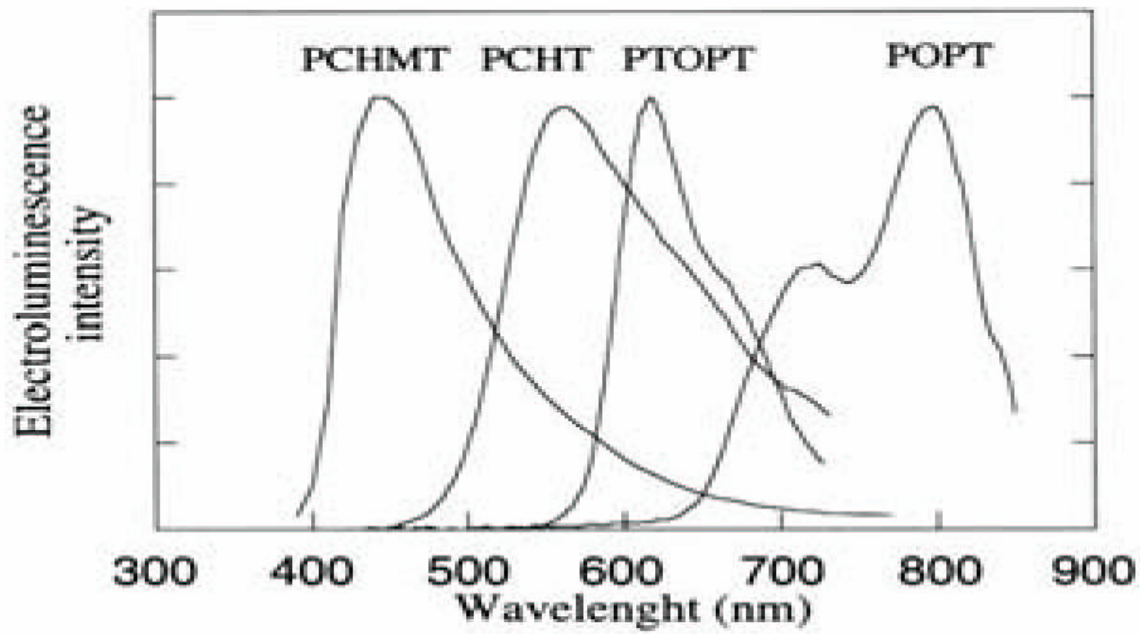
Organic Light - emitting diodes (OLED)





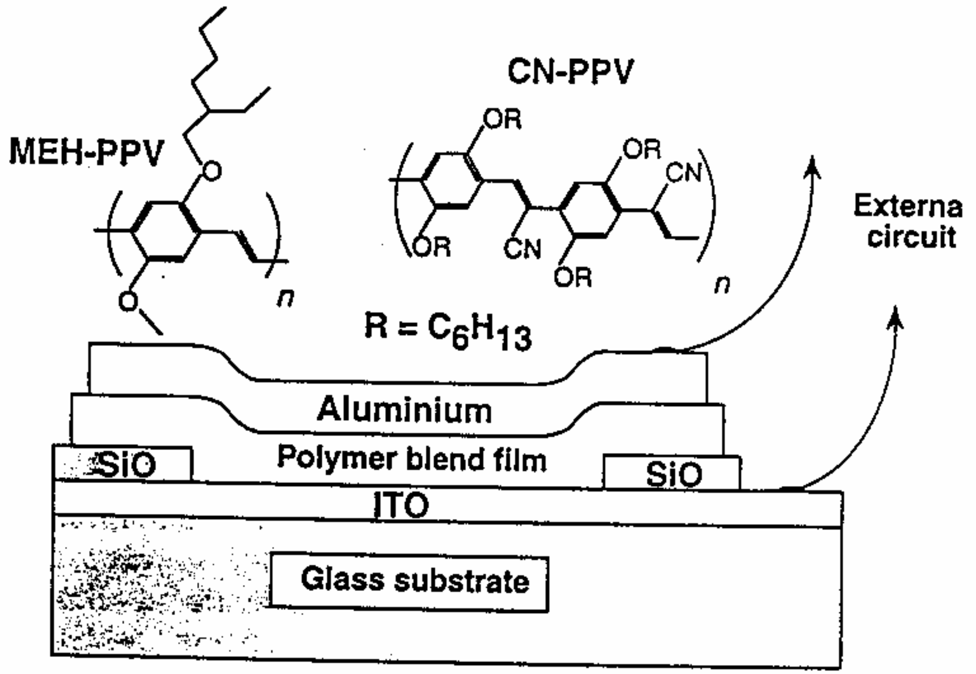
How to tune colour ???

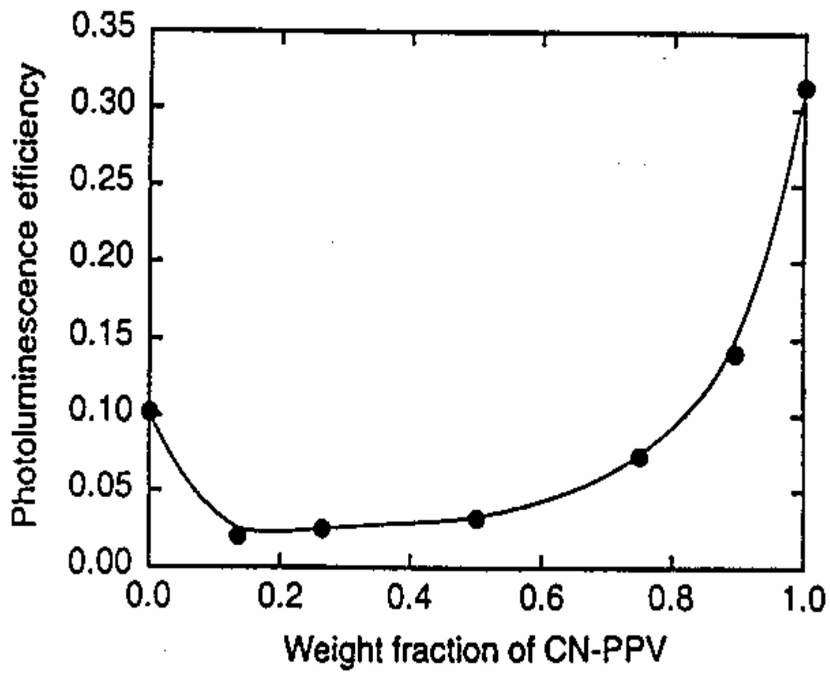





wise
view™

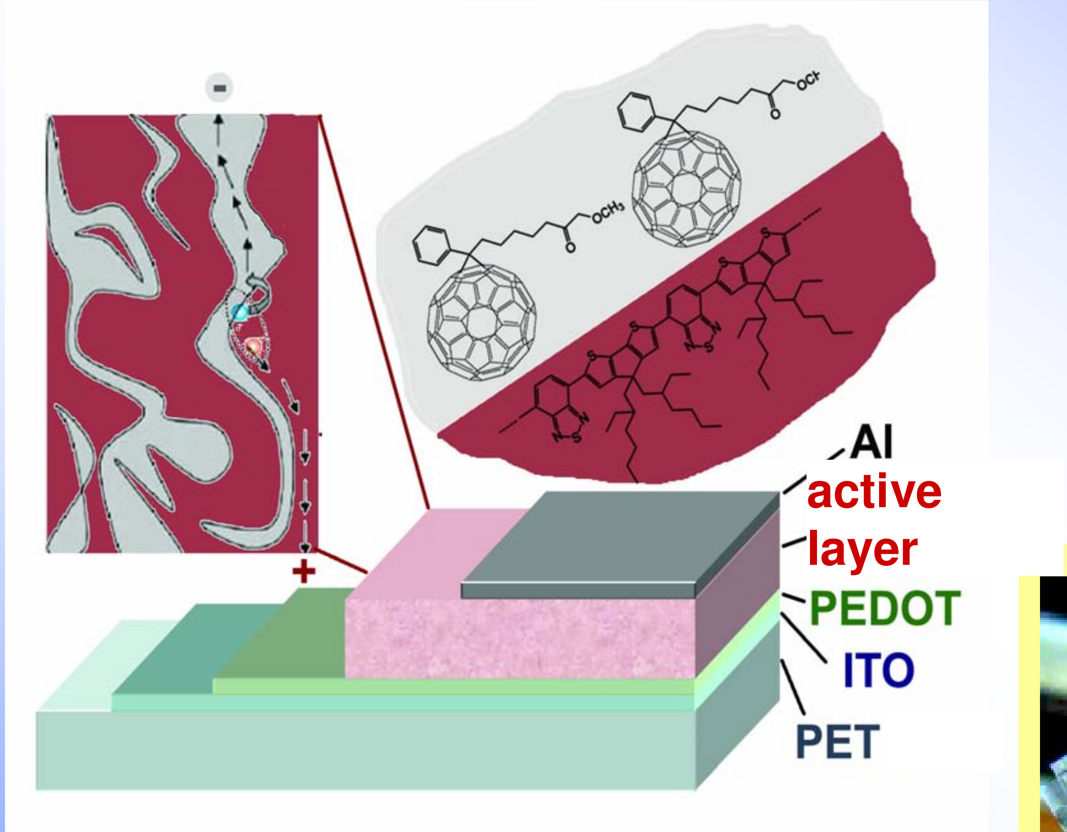
Efficient photodiodes from interpentrating polymer blends

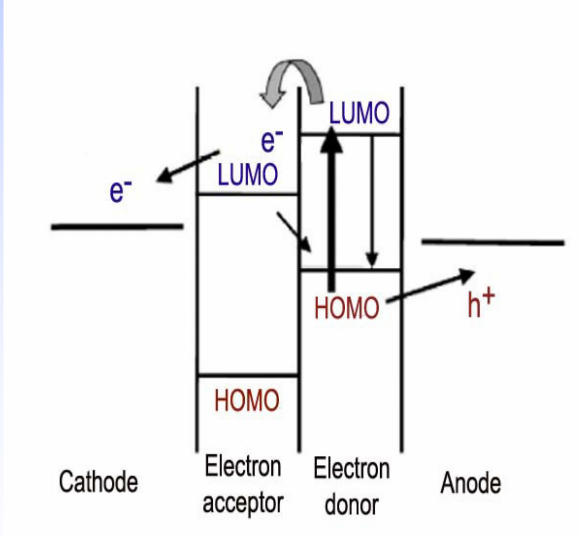




(J.J.M. Halls et.al., *Nature* **376**, 498, 1995)

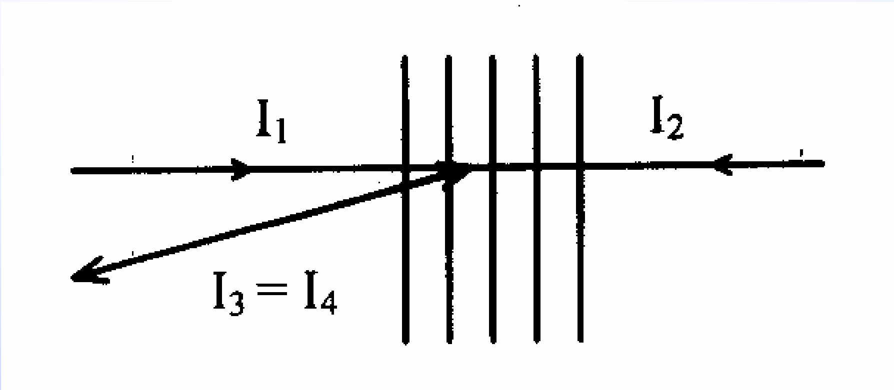
Polymer solar cells - flexible devices

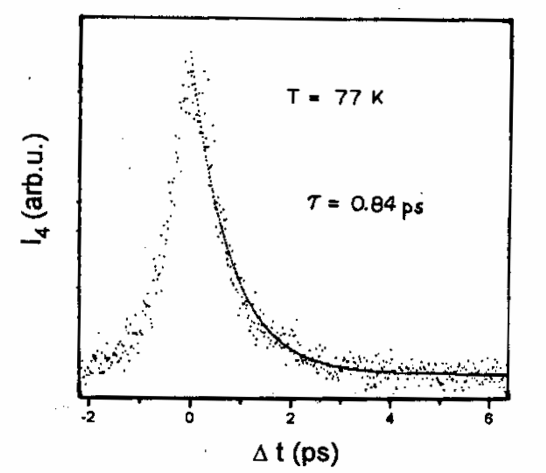




High nonlinearity of electron polarization
Refractive index depends on incident light intensity

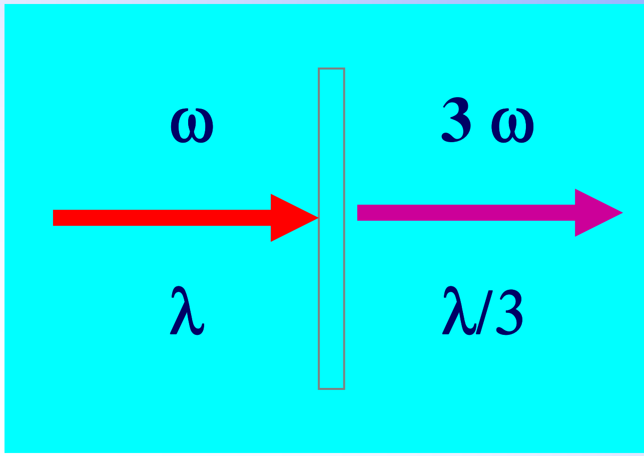
Ultrafast holography



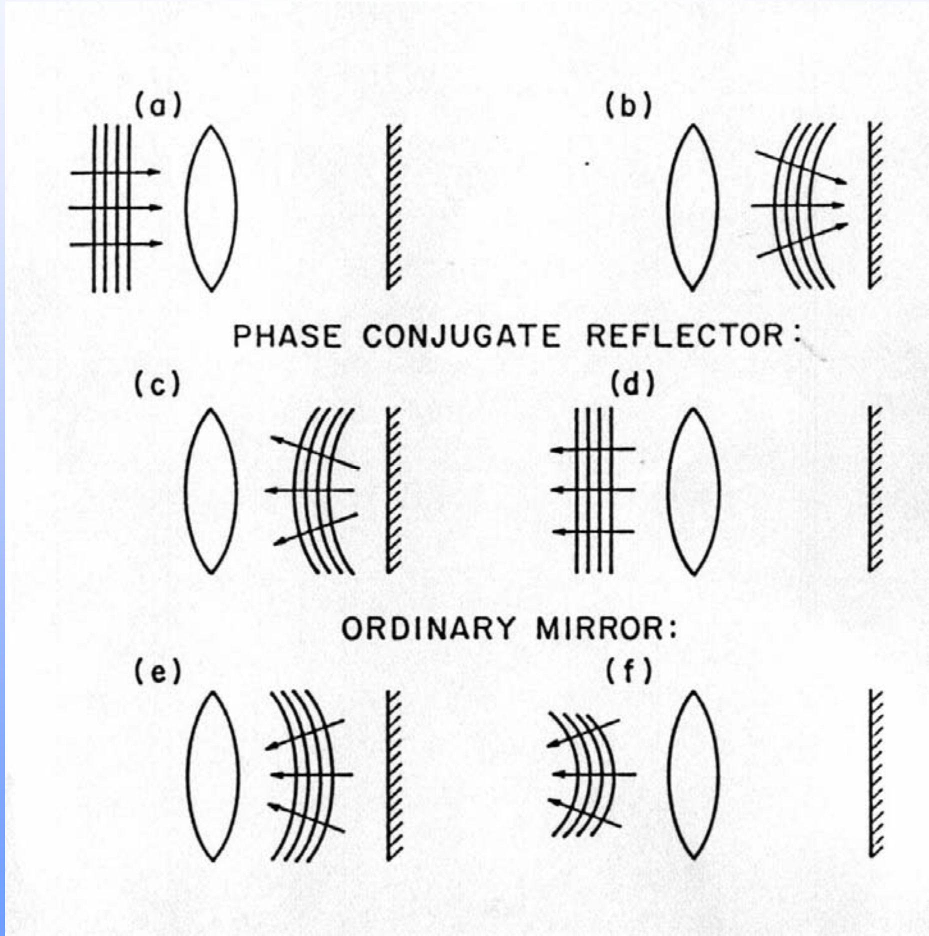


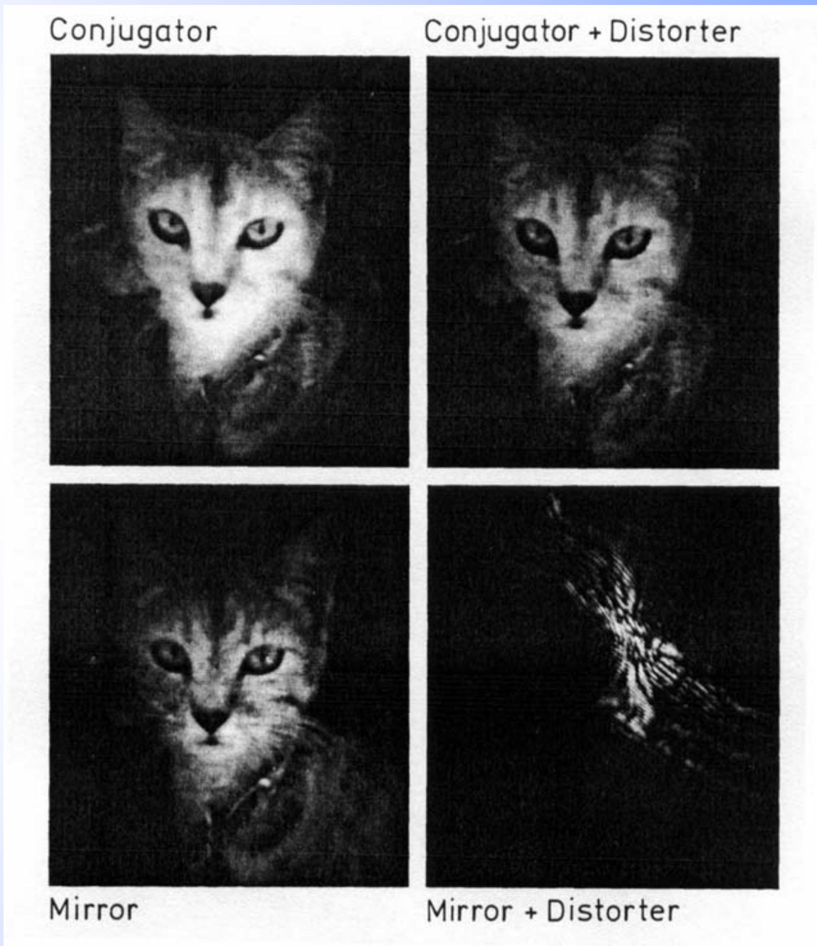
$\chi^{(3)}_{PA} \simeq 10^{-10}$ esu. AT 602 nm

Third harmonic generation

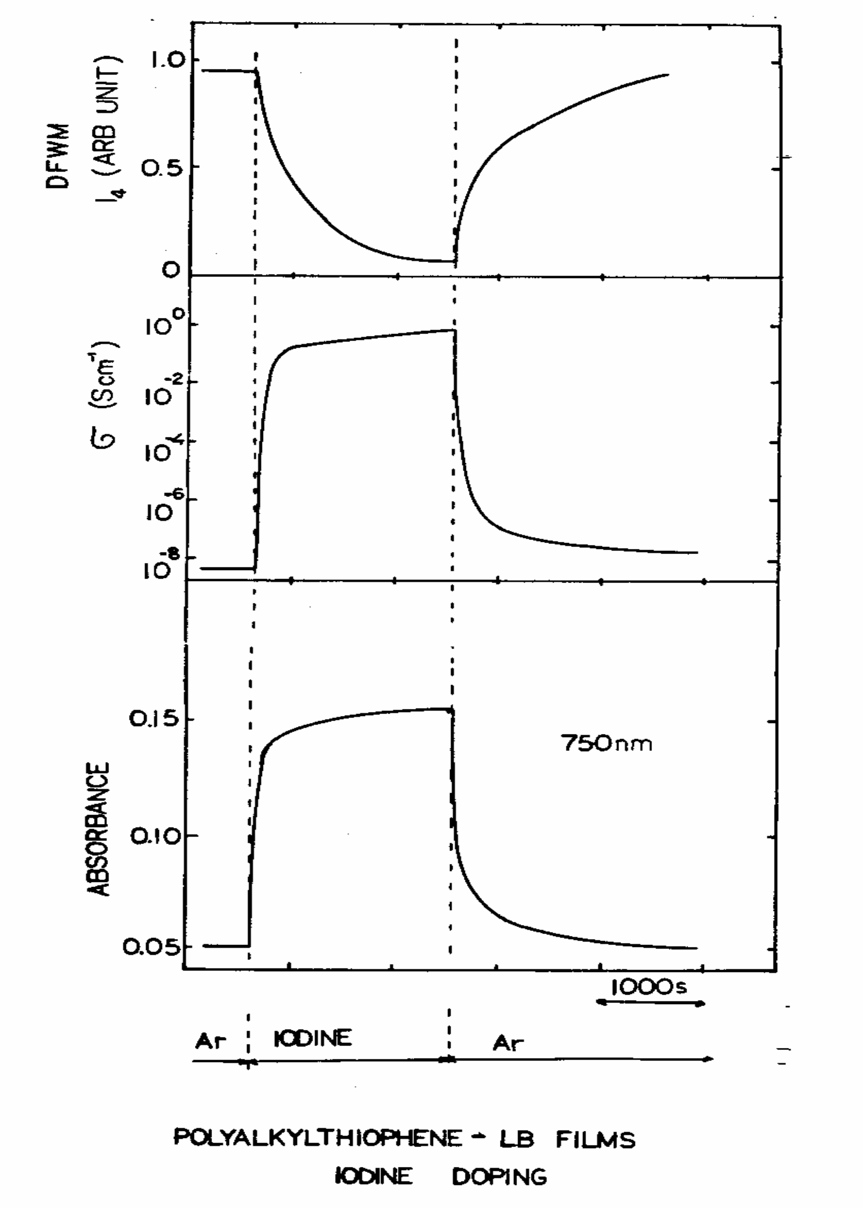


Example of optical nonlinearity
Phase - Conjugated Mirror : recovery of distorted light beam





Combination of various effects induced by doping



Multi-functional gas-sensor

Optical nonlinearity

Electrical conductivity

Optical absorbance

UNESCO/IUPAC Postgraduate Course in Polymer Science

END

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•http://www.imc.cas.cz/unesco/index.html
•unesco.course@imc.cas.cz