Nanostructural properties 2010/11

Simple models of conjugated polymers

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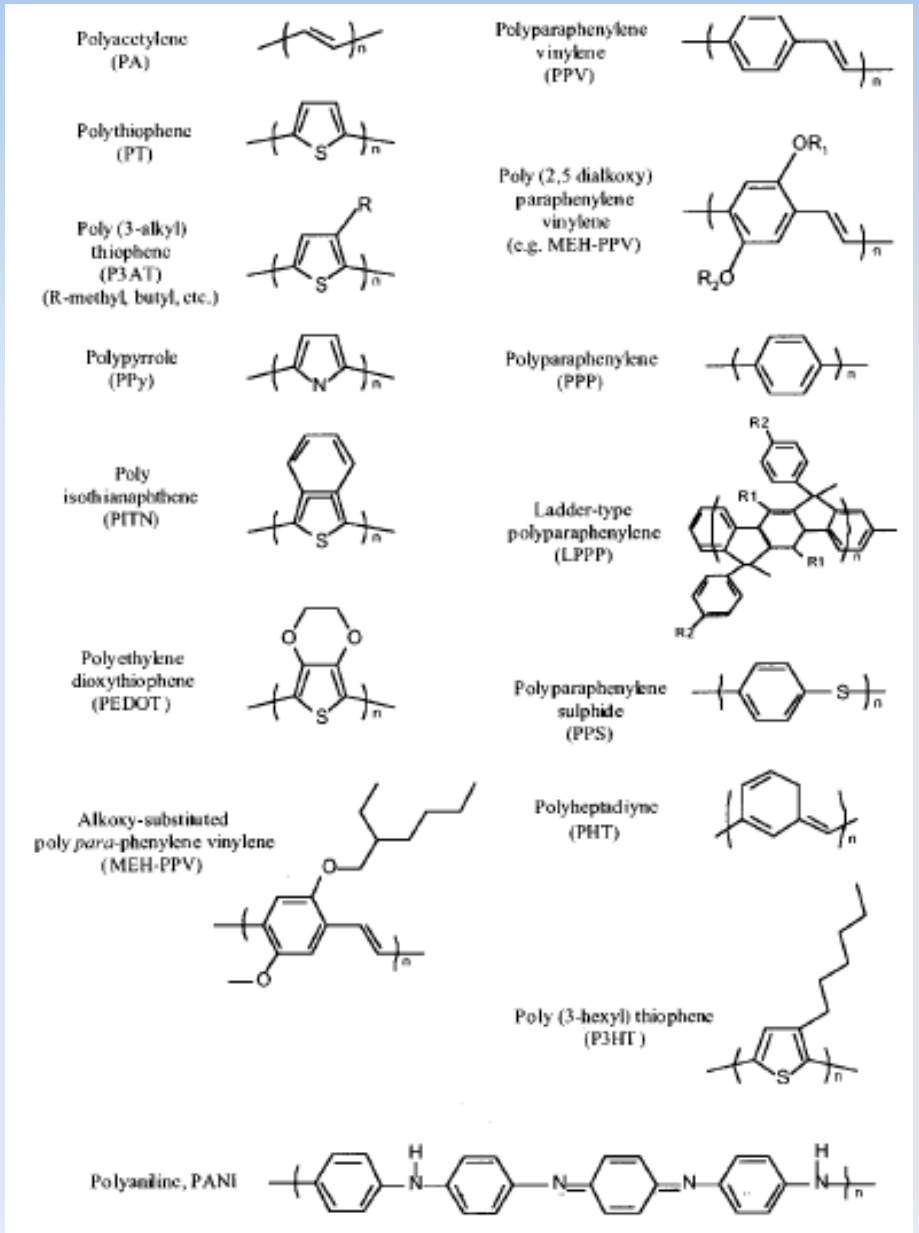
Polymer

A **polymer** is a large molecule (macromolecule) composed of **repeating structural units**

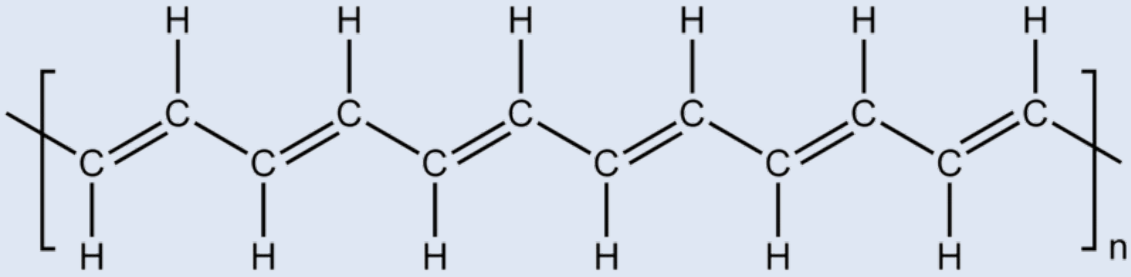
source:Wikipedia



Conjugated

A conjugated system is a molecular entity whose **structure** may be represented as a system of **alternating single and double bonds**

source:http://goldbook.iupac.org

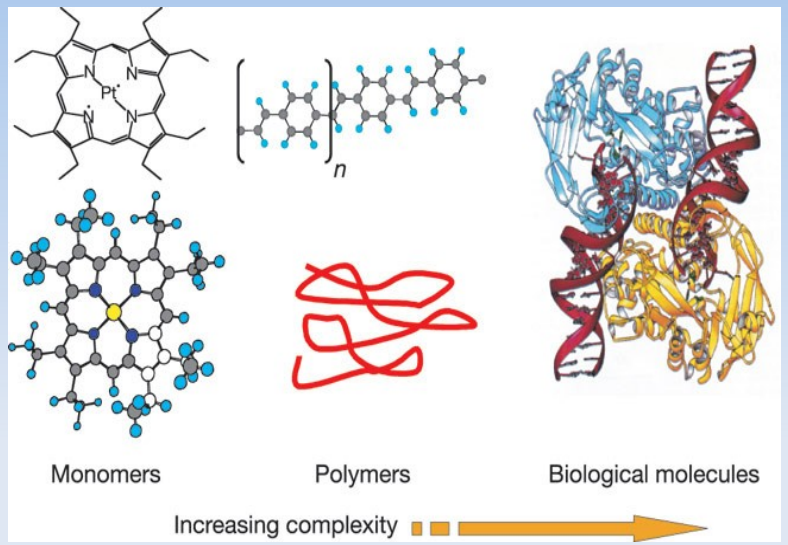


Organic Electronics

- Electronics

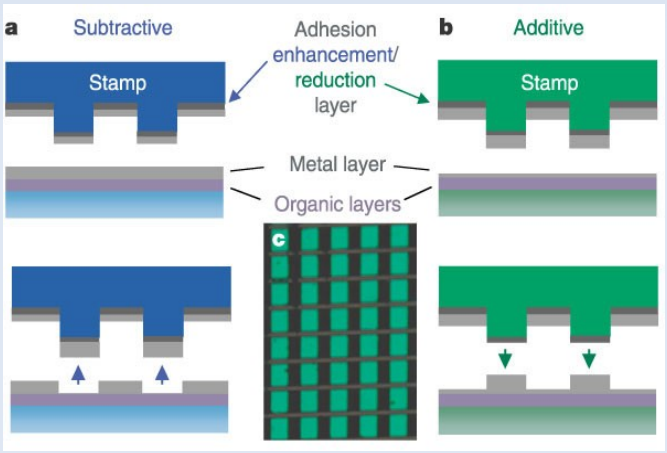
  Electronics is that branch of science and technology which makes use of the controlled motion of electrons through different media and vacuum.[...] Most electronic devices today use semiconductor components to perform electron control. The study of semiconductor devices and related technology is considered a branch of physics, whereas the design and construction of electronic circuits to solve practical problems come under electronics engineering.[Wikipedia]

Organic Electronics



S.R.Forrest Nature(2004)

Exploiting the possibilities of organic chemistry



Innovative fabrication methods (solution-based, printing)

Combines good mechanical and electric properties

Plastic Electronics!

Model

...a model [is], a **purposely extremely simplified approach to reality**, which can only account for certain aspects of reality, but for these in a convincing way. **Understanding without models is impossible**. However, a model is useful, only if one understands its **scope and limitations**.

Source: Kutzelnigg, W. (2007), What I like about Hückel theory. Journal of Computational Chemistry, 28: 25–34

Some important models

1. **The Free Electron (FE) model (!)**
2. **The Hückel Molecular Orbital (HMO) model**
3. **The Pariser-Parr-Pople (PPP) model (just results)**
4. **The Su-Schrieffer-Heeger (SSH) model (if time allows...)**

To be contrasted with *ab-initio* approaches: (Time Dependent)Density Functional Theory, Hartree-Fock, Post-HF,Many-Body Perturbation Theory, Quantum Monte Carlo, etc.

Models vs *ab-initio*

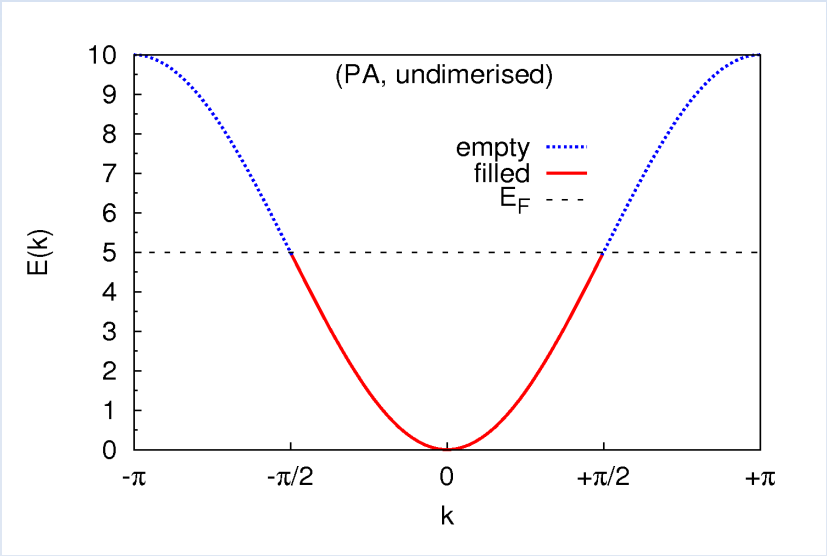
"**The computed numbers** are not only processed like data but they **look like data**, and a study of them may be no more enlightening than a study of real meteorological observations."

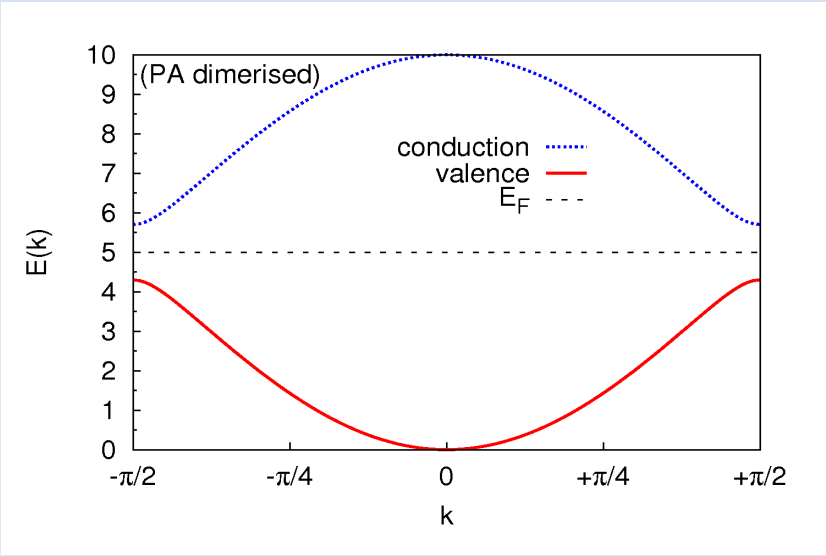
Source: E. N. Lorenz, The Nature and Theory of the General Circulation of the Atmosphere, Vol. 218 (World Meteorological Organization, Geneva, 1967)

Models are essential also to **interpret** the output of very accurate *ab-initio* simulations, e.g., as a **filter** to extract information.

PA Band Structure (see Notes)

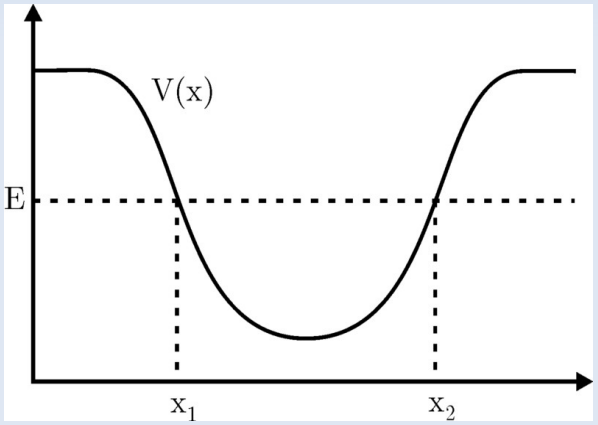
Metal or Semiconductor?
It depends on the structure!

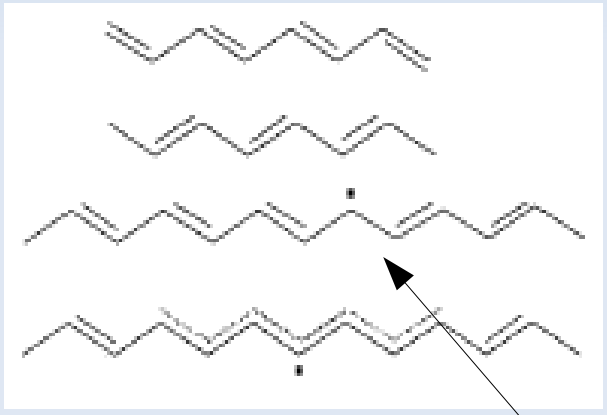




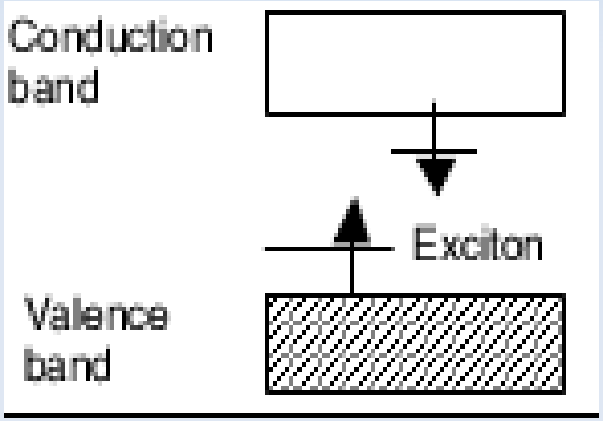
Polymer Chain Deformations

Polymer chains can deform about an electron-hole pair, polaron-exciton

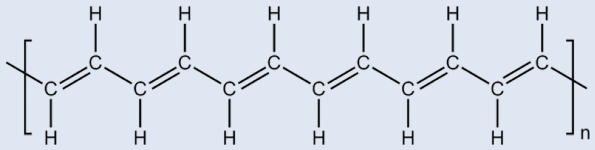




Heeger, Rev.Mod.Phys (2000)

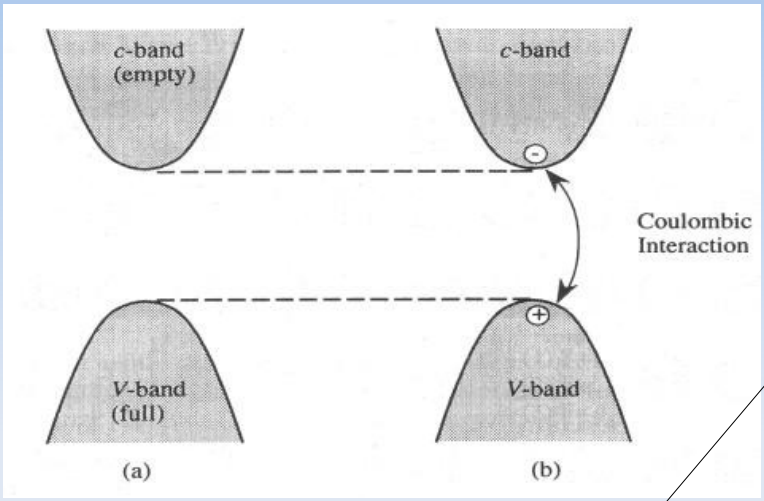


Moliton&Hiorns Polym. Int. (2004)



Local deformation, like a defect or an impurity level (localised state)

Excitons

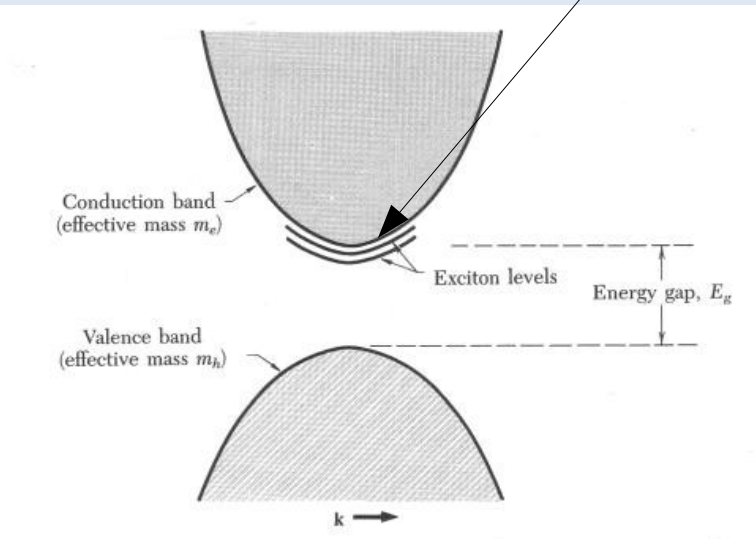


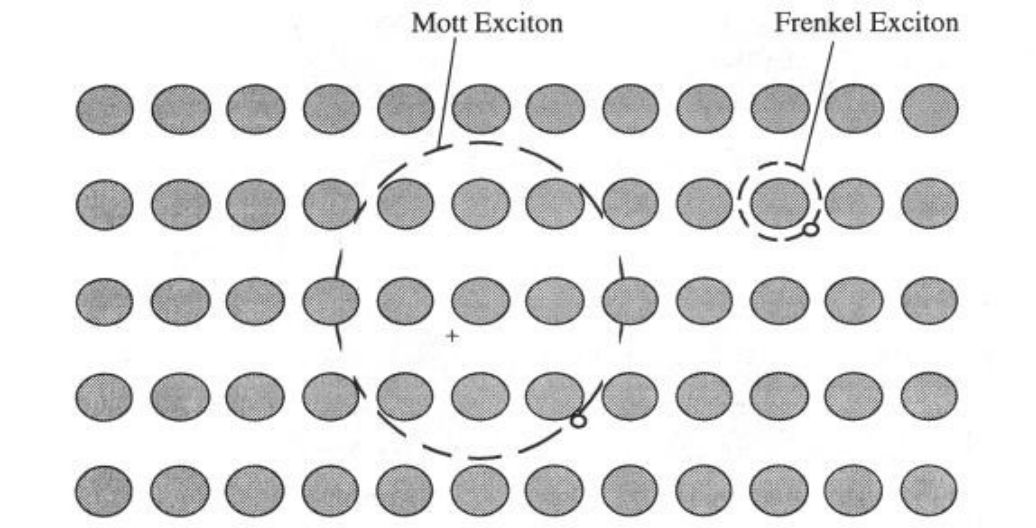
We neglected the electron-hole interaction (Coulomb)

Example: H atom

$$E_n = \frac{m_{eff}\, e^4}{2\left(4\pi\epsilon_0\epsilon_r\right)^2 \hbar^2 n^2}$$

Two types of exciton: weakly bound (Wannier-Mott) and strongly bound (Frenkel)





From:http://kottan-labs.bgsu.edu/

Excitons

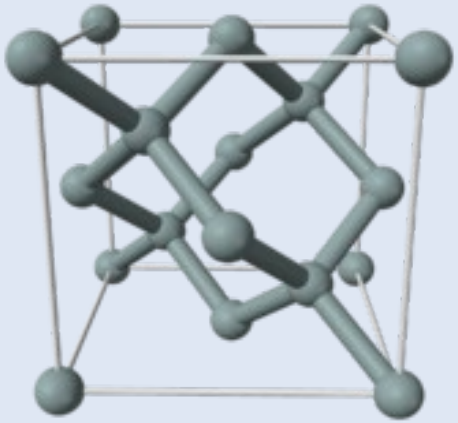
Energetic consideration:

- **Thermal energy(300K) ~0.025 eV**
- **Wannier-Mott excitons ~0.1 eV**
- **Frenkel excitons ~1.0 eV**

[1 eV/part = 23 kcal/mol]

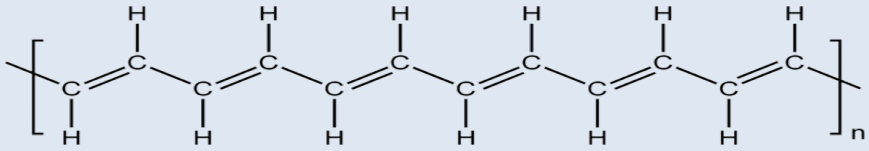
Message: it's hard to dissociate Frenkel excitons at room temperature! Interfaces needed

Si



Wannier-Mott

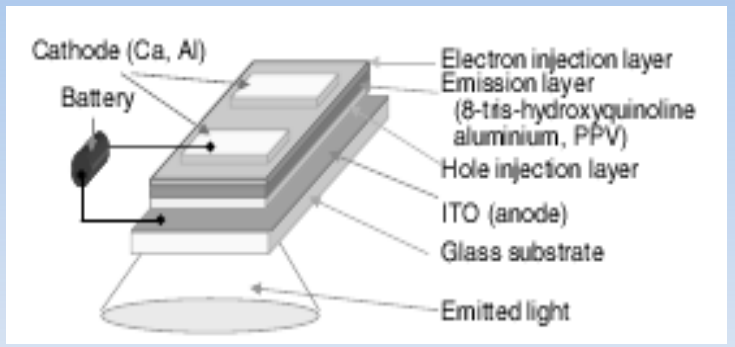
PA



Frenkel

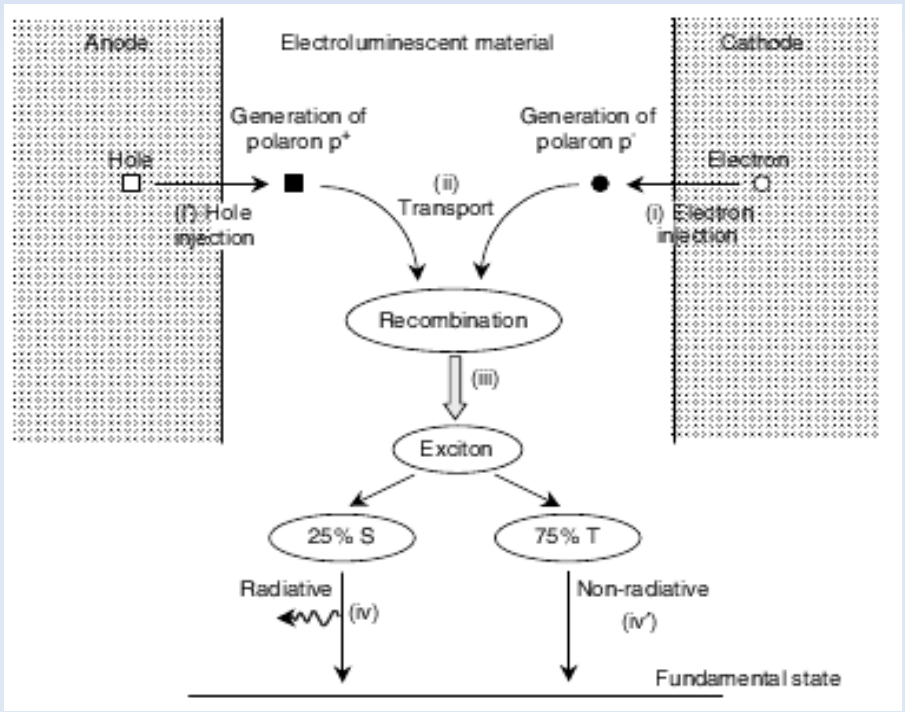
WHY? Electronic screening (ε_r) is more effective in 3D

Light-Emitting Devices (LEDs)



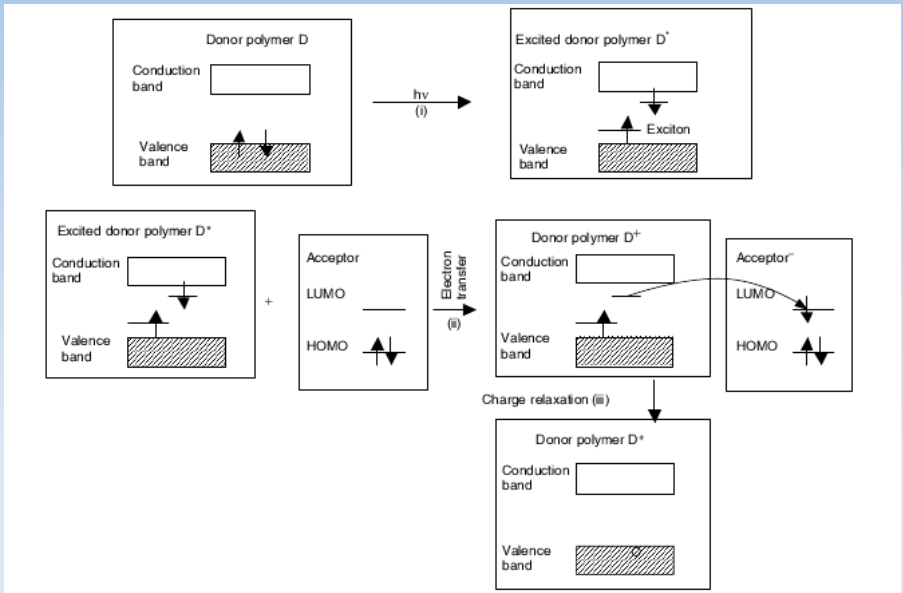
Low mobility is advantageous

Big issue: polymer degradation (Blue OLEDs)

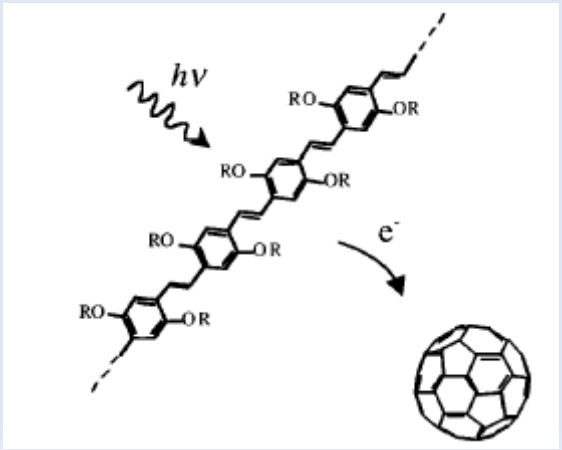


Moliton&Hiorns Polym. Int. (2004)

Solar Cells

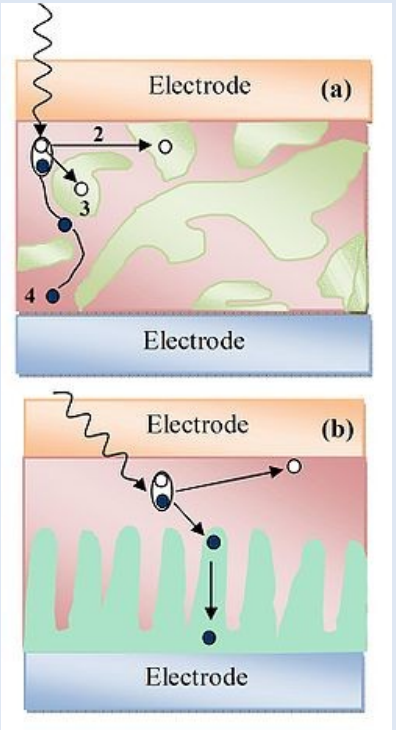


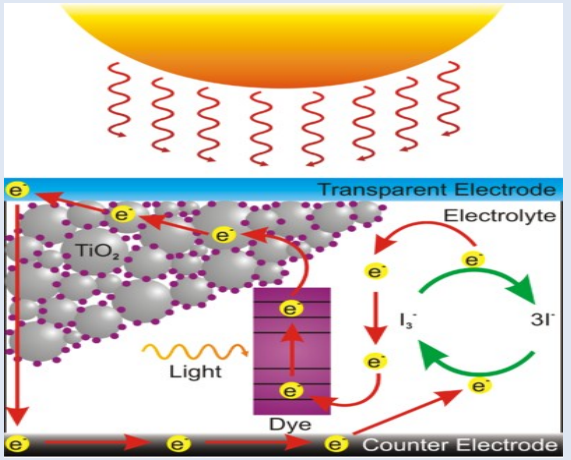
Moliton&Hiorns Polym. Int. (2004)



Competition between exciton relaxation and dissociation times

Low efficiency ~3%





Dye-sensitized solar cell (Grätzel)

Resources

- AJ Heeger *Rev. Mod. Phys*. **73** 681 (2001) [His Nobel lecture]
- A. Moliton & RC Hiorns *Polym. Int.* **53** 1397 (2004)
- W. Kutzelnigg *J. Comput. Chem.* **28** 25 (2007)
- ER Bittner *Quantum Dynamics* CRC Press (2010) [Chap. 8-9]
- My notes on: http://nano-bio.ehu.es/nanostructural-properties-201011 [as soon as possible]