Organic Electronics

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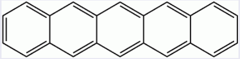
Outline

1. Introduction
   - Difference organic/inorganic semiconductors
   - From molecular orbitals to the molecular crystal
2. Organic Light Emitting Diodes
   - Basic Principals
   - Multilayer OLEDs
3. Organic Thin Film Transistors
   - OTFT Structure
   - Transport in organic semiconductors
4. Organic Photovoltaic Cells
   - Differences to inorganic solar cells
5. Summary

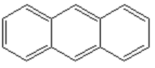
What is organic electronics?

- Electronics with carbon-based materials
- Two different groups:

Small-molecular materials



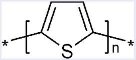
Pentacene



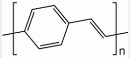
Anthracene

mainly prepared by thermal evaporation

Polymers



Polythiophene (PT)



Polyphenylen-vinylene (PPV)

prepared by solution processing (spin-coating, inkjet printing)

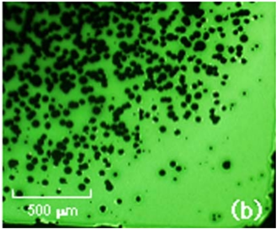
Advantages of organic semiconductors

- Light weight
- Mechanical flexibility
- Chemical modifications possible
- Easy and cheap processing (e.g. ink-jet printing, spin coating)

Readius from Polymer Vision

Disadvantages of organic materials

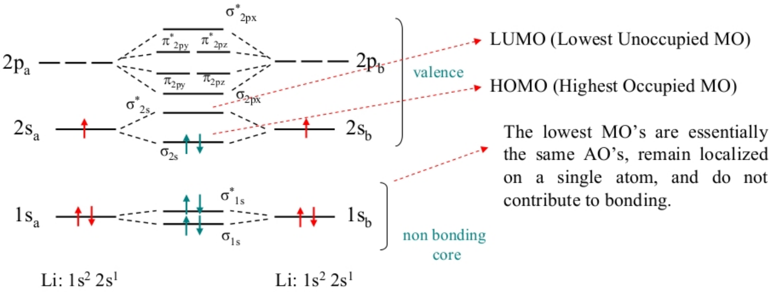
- Poor cristallinity
- Low mobility $\Longrightarrow$ low speed of devices
- Possible degradation under environmental influences



Dark spots on a ITO/α-NPD/Alq_3/Al OLED from: Kim et al.

Appl. Phys. Lett. 89, 132108 (2006)

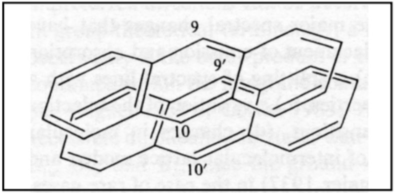
Molecular Orbitals



- Interaction between the atomic orbitals leads to bonding and anti-bonding molecular orbitals
- Splitting determined by the interaction between the atoms

Physical Dimers

- Special arrangement of two molecules close to one another, without the formation of chemical bonds
- Described by the following Hamiltonian: $H = H_1 + H_2 + V_{12}$ where H_1 and H_2 are the Hamiltonians of the isolated molecules and V_{12} describes their interaction



Anthracene sandwich physical dimer

Ground States of a Physical Dimer

Approximation of the ground state wavefunction as the product of the two molecular states:

Dimer Ground State

$$\Psi_g = \Psi_1 \Psi_2$$

The resulting energy of the ground state is the sum of the two molecular states, but shifted by the coulombic binding energy W:

Ground State Energy

$$E_g = E_1 + E_2 + \underbrace{< \Psi_1 \Psi_2 | V_{12} | \Psi_1 \Psi_2 >}_{W}$$

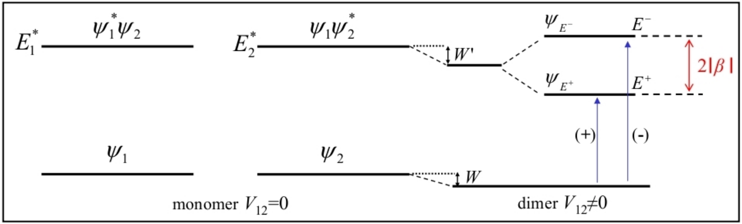
Excited States of a Physical Dimer

First Excited State (case of identical molecules)

$$\Psi_E = \frac{1}{\sqrt{2}}\left(\Psi_1^*\Psi_2 \pm \Psi_1\Psi_2^*\right)$$

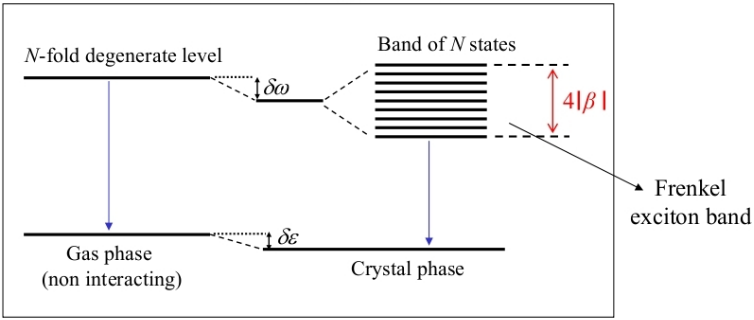
Excited State Energy

$$E^{\pm} = E_1^* + E_2 + \underbrace{< \Psi_1^*\Psi_2 | V_{12} | \Psi_1^*\Psi_2 >}_{W'} \pm \underbrace{< \Psi_1^*\Psi_2 | V_{12} | \Psi_1\Psi_2^* >}_{\beta}$$

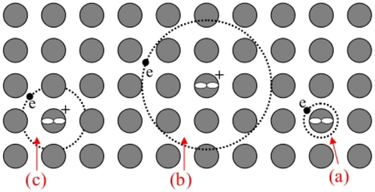


Linear Molecular Crystal

For not only two molecules but a linear array of N benzene rings, one gets the following energy levels:



Excitons



(a) Frenkel exciton: correlated e⁻-h⁺ pair that is located on the same molecule and moves as a unit through the crystal lattice.

The radius of the exciton is defined as the mean distance between electron and hole (≤ 5Å)

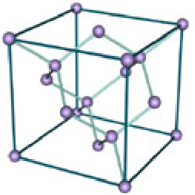
(b) Wannier-Mott exciton: the radius (between 40-100Å) is one order of magnitude larger than the intermolecular separation. This is typical in inorganic systems, where the interaction energy is great and the dielectric constant is high.

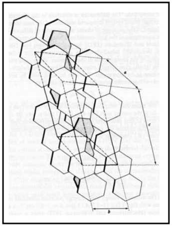
(c) Charge-transfer exciton: the exciton radius is only one or two times the nearest-neighbour intermolecular distance. Typical of organic systems.

Binding energy in inorganic semiconductors: 1-40 meV
in organic materials: 100-300 meV (→ stable at 300K)

Comparison Germanium and Anthracene

	Germanium	Anthracene
Melting point[$^\circ C$]	937	217
Intrinsic conductivity @ 300K [$\frac{1}{\Omega cm}$]	0.02	$\approx 10^{-22}$
Electron mobility @ 300K [$\frac{cm^2}{Vs}$]	4500	1.06
Hole mobility @ 300K [$\frac{cm^2}{Vs}$]	3500	1.31

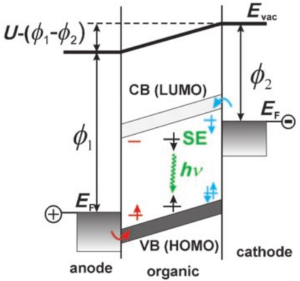




Organic Light Emitting Diodes (OLEDs)

- Principal of OLEDs first demonstrated in 1963 by Pope in anthracene
- First comparably efficient OLED by Tang and van Slyke in 1987 using Alq_3

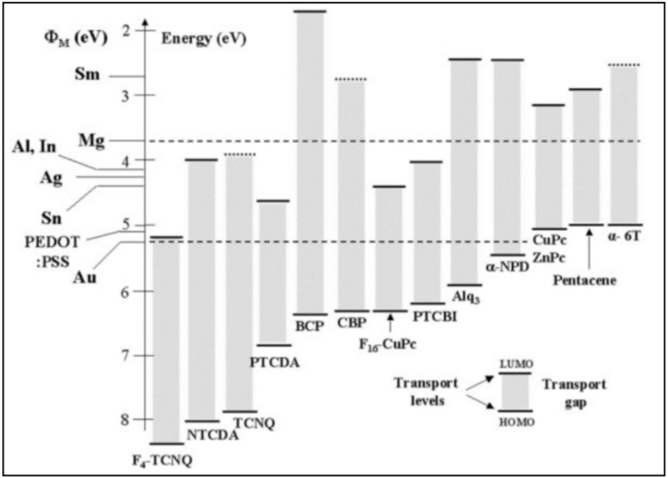
Charge Carrier Injection



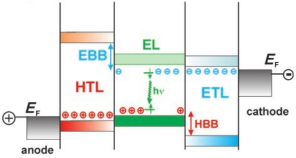
from N.Koch, ChemPhysChem 2007, 8, 1438 – 1455

Charge carriers need to overcome a potential barrier in order to get into the semiconductor
$\rightarrow$ Metal with high workfunction (Φ_1) for hole injection and one with low workfunction (Φ_2) for electron injection

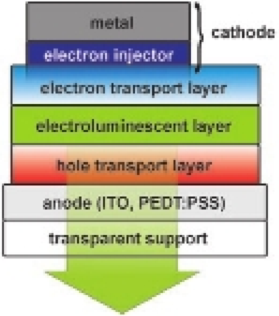
Level Alignment of some Organic Materials and Metals



Multilayer OLEDs



Hole and electron transfer layers to decrease the injection barriers

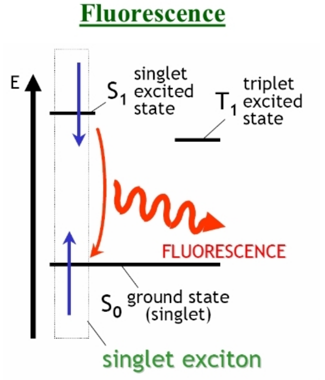


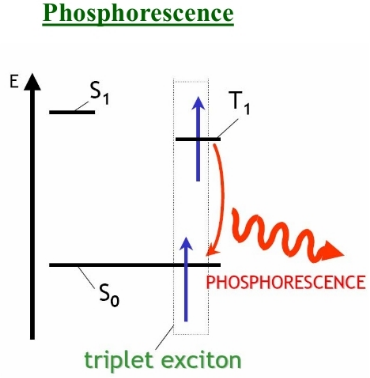
Tranparent anode needed (here: ITO)

Figures from N.Koch, ChemPhysChem 2007, 8, 1438 – 1455

Exciton Recombination

Fluorescence vs. Phosphorescence

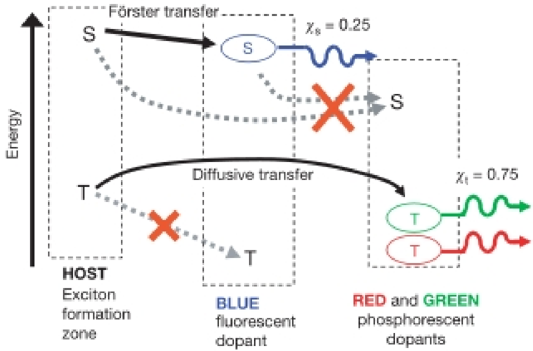


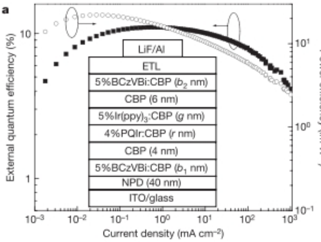


fast process $\approx$ 1ns

relatively slow process > 1ns

White Organic Light Emitting Diodes

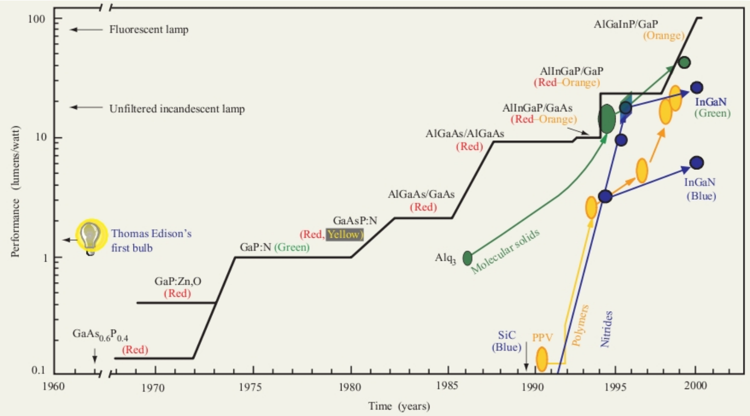




from Sun et al., NATURE 2006, Vol 440, 908-912

Use of triplet excitons for non-blue light emission

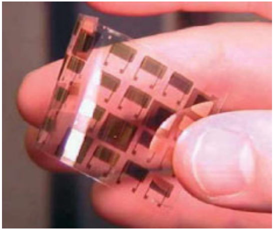
OLED Performance



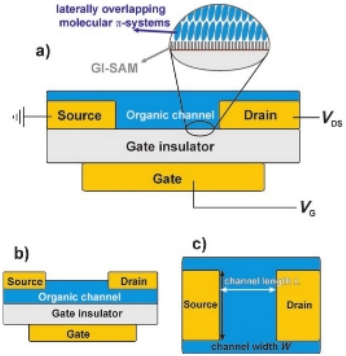
from Shaw and Seidler,"Organic Electronics: Introduction", IBM J. RES. & DEV.,Vol. 45

Organic Thin Film Transistors

- Possible use in active matrix flat panel displays, "electronic paper" displays, sensors or radio-frequency identification (RFID) tags
- In competition with a:Si:H which is normally used in active matrix displays



OTFT Structure



- Low conductivity in the channel without any gate voltage
- Formation of positive (negative) accumulation layer at the semiconductor-insulator interface upon application of a negative (positive) gate voltage
- High crystallinity needed to obtain high mobilities → use of SAMs

Typical Transistor Characteristic

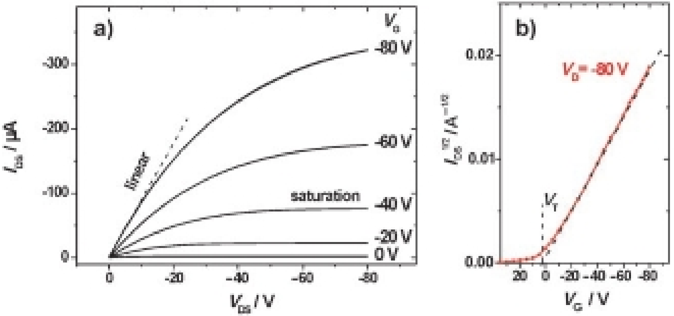
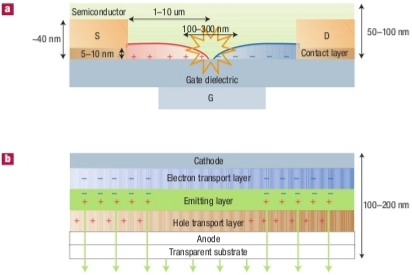


Figure 14. Examples of a) I_{DS}–V_{DS} output characteristics and b) I_{DS}–V_G characteristics of a prototypical OTFT comprising a SiO_2–hexamethyldisilazane (HMDS) gate insulator, Au top contacts, and P3HT as organic semiconductor. The hole mobility extracted from (b) was $\approx 10^{-2}$ $cm^2 V s^{-1}$. Device data kindly provided by D. Neher and P. Pingel (Universität Potsdam).

Combining OLED and OTFT

The Organic Light Emitting Transistor



from

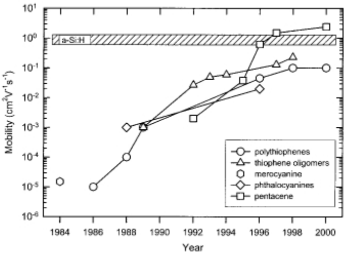
Muccini, nature materials, Vol. 5 (2006), p. 605-613

Useful for example in active matrix displays. No separate OLEDs and OTFTS needed → thinner and less complicated arrangement

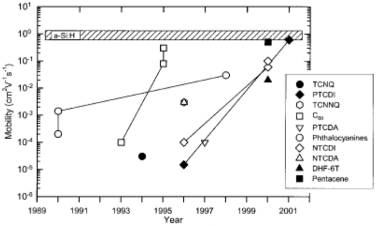
Charge Carrier Mobility

Mobility measurable with the help of TFTs: $I_{DS,sat} = \frac{W}{2L} C\mu \left(V_G - V_T\right)^2$

Hole mobility



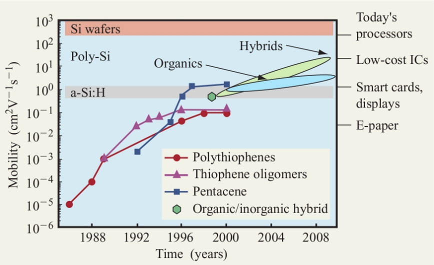
Electron mobility



Three orders of magnitude lower than in inorganic semiconductors

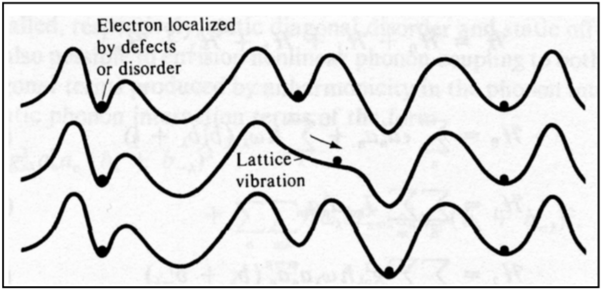
Why is the mobility so low?

- Weak inter-molecular coupling leads to high effective mass
- Amorphous material → thermally activated hopping transport, no band transport
- Polycrystalline material → scattering at grain boundaries
- "Self-trapping" of charge carriers - the polaron



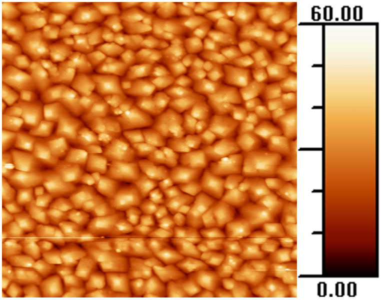
Hopping Transport

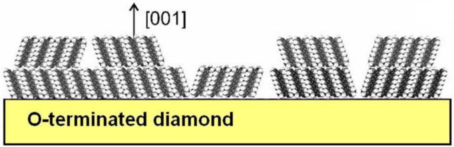
- In amorphous solids (also a-Si:H) the charge carriers are highly localised due to disorder
- Phonon assisted transport → mobility increases with rising temperature $\mu \propto exp(-E/kT)$

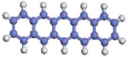


Polycrystalline Pentacene

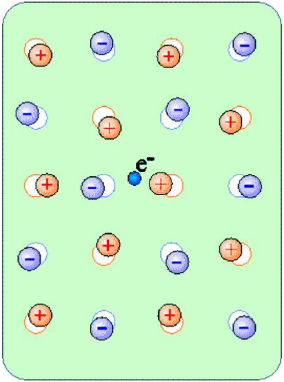
When diffusing from one grain to another, charge carriers get scattered at the defects introduced by the grain boundaries. These boundaries hence reduce the effective mobility.





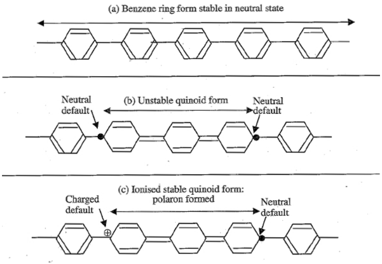


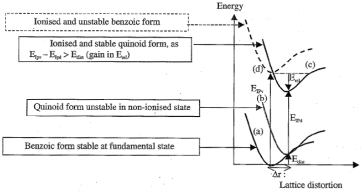
The Polaron in Ionic Materials



- Rearrangement of the lattice under the influence of the electric field of the charge carrier
- Resulting potential well hinders the motion of the charge, thus reducing its mobility

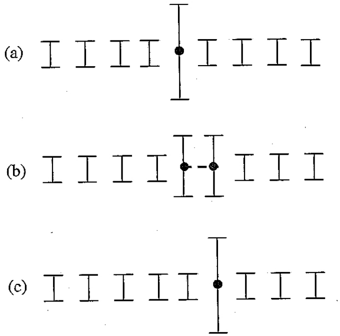
Polarons in π-conjugated Polymers





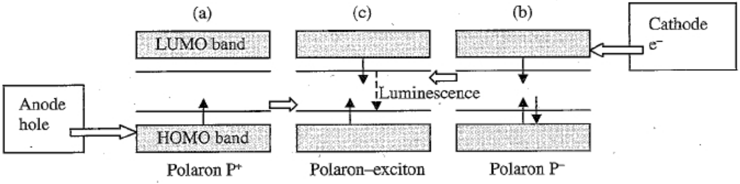
- Polymer rearranges itself in the presence of a charge carrier (here a hole), in order to be in the state of lowest energy.
- This configuration change goes in hand with a lattice distortion.

Polaron Transport



- In order to move the charge carrier the deformation needs to move too → low mobility of the polaron.
- Presence of phonons is increasing the mobility of the polaron.

Polaron-Excitons in OLEDs



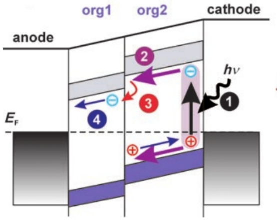
- Injection of positively and negatively charged polarons at the electrodes.
- Migration of the polarons in the external field.
- When the two oppositely charged polarons meet they form a polaron-exciton, which can eventually recombine.

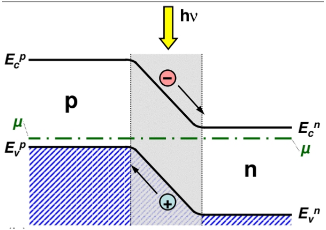
Organic Photovoltaic Cells

- Photovoltaic effect in single layer organic molecules first observed in the 1970s, later on also for polymers
- Cells consisting of a single material reach only very low efficiencies → combination of at least two materials necessary

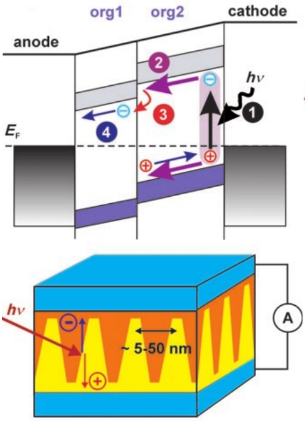
Why two dissimilar materials?

- Photon absorption leads to the formation of a neutral exciton, which is stable at room temperature
- Exciton dissociation is increased at organic-organic interfaces with proper band alignment



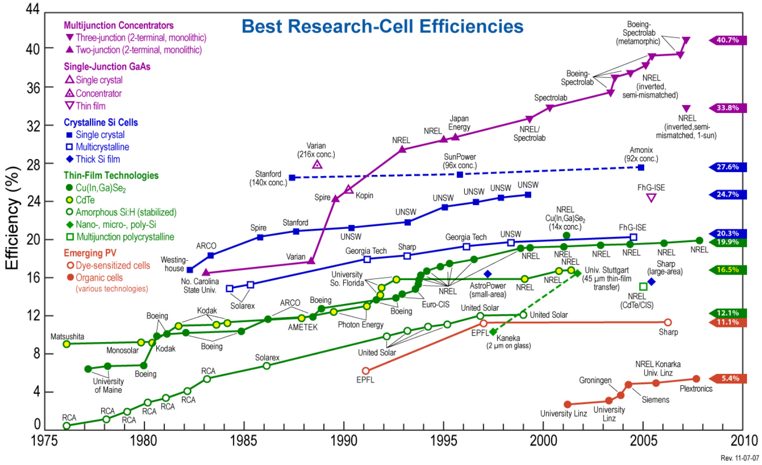


Operation Principle of OPVCs



- Exciton formation by absorption of a photon
- Diffusion of the neutral exciton to the organic-organic interface (diffusion length up to a few tens of nanometers)
- Dissociation of the exciton at the interface
- Collection of the charge carriers at the electrodes

OPVC Performance



Summary

- Organic semiconductors offer a low cost alternative to established semiconductors when it comes to large area and low cost applications
- First OLED applications are already on the market. OTFTs and OPVCs will most probably follow.
- Improvements on the material side are still needed (e.g. better solubility of small molecular crystals or doping possibilities)