

# Charge transport modeling in organic light emitting diodes

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## Abstract

We present a microscopic theory of charge transport and electrode injection in organic light emitting diodes which accounts for most of the molecular aspects of these materials.

The rational optimization of classical semiconductor optoelectronics devices required a good knowledge of the basic transport and light emission processes. The same work should be done in organic devices where charge transport and electrode injection stand as a crucial points for device optimization.

Until now, most of the transport models used in organic light emitting diodes are directly derived from the semiconductor physics of analogous silicon devices [1, 2].

We believe that the physics of transport and charge injection is very different in molecular and polymer materials than in inorganic solids. The reason for this special behavior are related on one side to the large polarisabilities of organic conjugated molecules [3] and to permanent dipoles on part of those of interest [4], and on the other hand on the high electron-phonon interactions leading to the presence of clearly identified polaronic state in polymers [5, 6, 7, 8].

The presence of disorder in most OLED (Organic Light Emitting Diode) materials acts also in synergy with both Coulomb interactions and electron-phonon interactions: a slow carrier in a disordered material interacts with other electrons and dipoles in a much stronger way than a fast one and relaxes the lattice more efficiently than a fast one.

Instead of applying the transport results established for the semiconductors, the work of our group aims to develop truly molecular model applicable to soft matter. Some of the aspects of this work is illustrated below.

## 1. The nature of the charge excitations and their transport

In conjugated polymers such as polypara-phenylene vinylene (PPV), extra electrons and holes are undoubtedly trapped

by the lattice in the form of polarons [5, 6, 7, 8]. The polaronic character is reinforced by disorder [9]. Band conduction is thus forbidden in the polymeric materials. Except at very high fields larger than  $1MV/cm^2$ , the transport processes are limited by the jumps from chain to chain induced by the temperature and the electric field.

In disordered molecular materials like hydroxyquinoline Alq<sub>3</sub>, the charge carriers are also localised on single molecules due to the weak effective transfer integral from molecule to molecule. This effect acts in synergy with disorder, molecular polarization and lattice relaxation. Charge transport also occurs through field dependent hopping processes [10].

In nearly perfect molecular crystals such as anthracene or pentacene, extended states control the transport properties at low temperatures.

## 2. Field dependence of the mobility in polymers like PPV

The most widely used dependence of the mobility with temperature and field for holes in PPV [11, 13] is

$$\mu(F) = \mu_0 \exp \left[ -\frac{\Delta}{k_B T} + B \left( \frac{1}{k_B T} - \frac{1}{k_B T_0} \right) \sqrt{F} \right] \quad (1)$$

with typically  $\Delta$  with typically  $\Delta = 0.5eV$ ,  $B = 3 \times 10^5 eV(Vm)^{-1/2}$ ,  $T_0 = 400 - 600K$  and  $\mu_0 = 3.5 \times 10^{-3} m^2/Vs$ . This dependence has been "established" by computer simulations to account for mobilities of disordered materials like molecularly doped polymers and amorphous glasses [15].

On the other hand, we developed a microscopic theory of the mobility of the charge carriers in conjugated polymer systems based on polaron drift along the chain and hopping from chain to chain [16]. Figure 2 illustrates on the same scale the mobilities used by the authors adopting relation 1 to account for low fields (curves  $B_1$  and  $B_2$ ) [11, 12] and high fields data (curves  $C_1$  and  $C_2$ ) [13, 14].

It is interesting to compare the hypothesis on which both models are based. The works of Bässler and coworkers

ers leading to relation 1 are based on the argument that transport occurs by hopping through Gaussian manifold of localized states that are distributed in energy and distance. The principal assumption of their formalism is that electron-phonon coupling is sufficiently weak that the polaronic effects may be neglected.

The jump rate is calculated according to Miller and Abrahams [17] who have developed a weak coupling single phonon, hopping theory. The main difference between that model and the ours is that our model is essentially multiphonon, based on hopping theories developed by Holstein and Emin [18] and accounts for the polymer character of the segments.

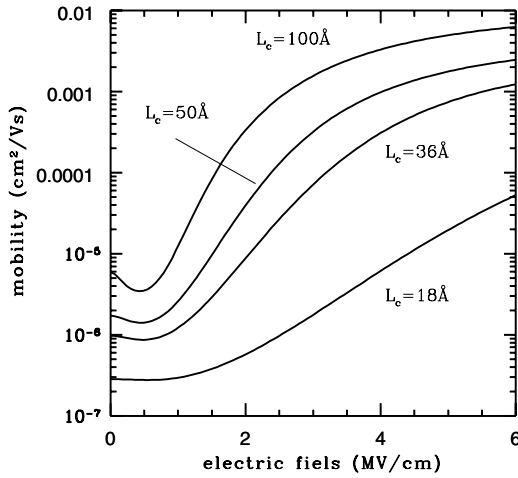


Figure 1: Field dependent mobilities for different conjugation lengths of the polymers. The minimum in the mobility for long chains is tightly related to the anisotropy of the charge transport. It corresponds to a zone of fields where the velocity of the charges is rather independent of the field.

### 3. Charge injection from an electrode

The difference  $E_0$  between the electrode work function and the electron affinity or the ionization potential of the molecular material is the origin of the injection barrier. But the charge accumulation at the interface due to the presence of the coulomb image force results into strong modifications of the bare barrier. Fig. 2 represents the actual barrier  $W_0$  as a function of bare barrier  $E_0$ . Points correspond to data obtained by the experiment [19] in Alq<sub>3</sub>, while the lines are the theory developed in references [20, 21]. The only parameters of the model is the distance  $x_1$  between the electrode and the first conjugated site of the polymer.

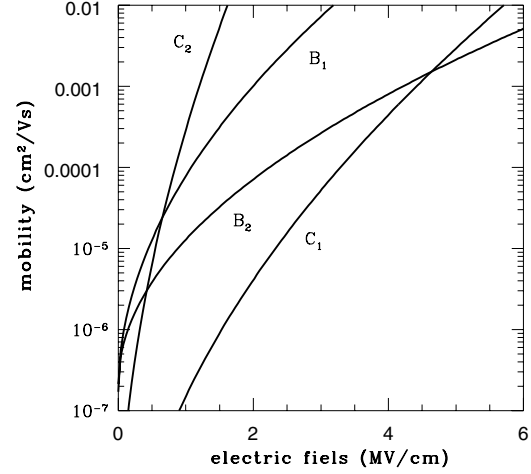


Figure 2: Field dependent mobilities obtained from equation (1) for different sets of parameters used in the literature:  $B_1$  corresponds to reference [11],  $B_2$  to reference [12],  $C_1$  corresponds to reference [13] and  $C_2$  to reference [14].

## 4. Organic-organic interface

Charge accumulation at interfaces is both due to oxydo-reduction potential differences between the molecular species and mobility variations close to the interfaces. The study of these effects, which can be very destructive for the OLED's and should be kept under control, required a numerical code described in section 5.

## 5. The numerical code

Most of the transport and injection elements have been included into a numerical code able to describe transport into multilayer OLED's. Transport is described by multiphonon hopping [18] between discrete sites

$$\Omega = \Omega_0 \exp \left[ -\frac{(W + \Delta/2)^2}{W k_B T} \right] \sim \Omega_D \exp \left( -\frac{\Delta}{k_B T} \right)$$

where  $W$  is the depth of the molecular trap and  $\Delta$  is the energy difference between the sites.

The field dependence of the mobility is included into  $\Omega_D$  and can be changed according to any empirical or calculated relation  $\mu(F)$  through the relation

$$\mu(F) = \frac{\Omega_D q a^2}{k_B T} \left( \frac{\sinh \frac{q F q}{2 k_B T}}{\frac{q F q}{2 k_B T}} \right)$$

Injection is treated very carefully by including thermoionic injection, image force, electrical double layer and direct tunneling to any site.

Although this code is very complete and accounts for the molecular aspects of the system, it contains a reasonable number of parameters.

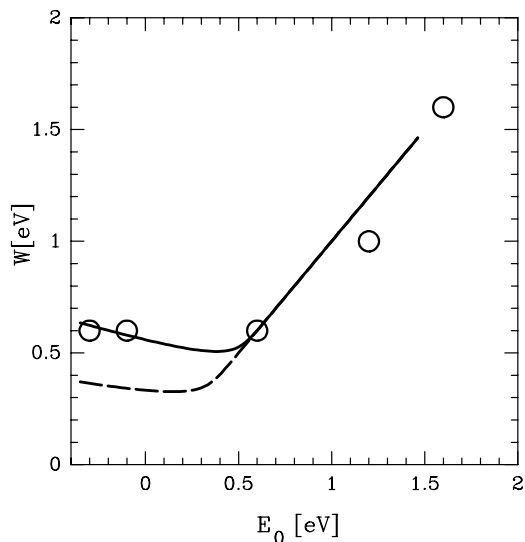


Figure 3: The internal workfunction as a function of the bare  $E_0 \equiv E_{LUMO} - E_F$  for  $x_1 = 3\text{Å}$  (full line) and  $x_1 = 6\text{Å}$  (dashed line) (see text). Points correspond to data obtained by the experiment, Ref. [19].

Apart from the mobilities and energy levels, five parameters (two per contact and one to relate the external and the internal efficiency) were required to fit the multilayer data of figure 4. The data included the voltage-current and voltage-light experimental curves for several related devices (with different ETL/HTL layer thicknesses).

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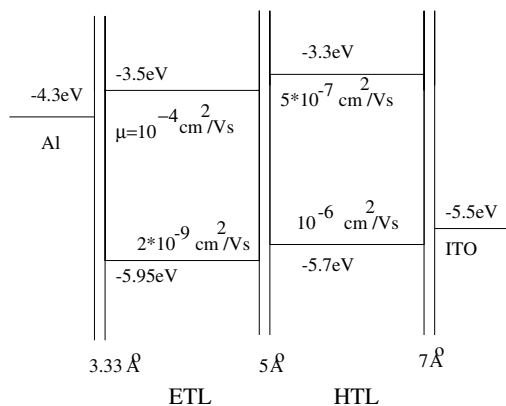


Figure 4: A scheme of a bilayer device prepared in our laboratory, with the properties reproduced in the simulation. For the electron transport layer (ETL) we used the material based on  $Zn(q-2-COOEt)_2$ , for the hole transport layer (HTL) we used the CN derivative of bicarbazyl (electroluminescent). The values for LUMO and HOMO level, as well as the workfunctions at electrodes were measured independently. The parameters for the contact and mobilities were deduced in part from related single layer devices.

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