

Impact of Energetic Disorder and Localization on the Conductivity and Mobility of Organic Semiconductors

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Abstract—The impact of the energetic disorder and the charge localization on the conductivity, mobility and carrier concentration is investigated both theoretically and experimentally. This study gives three fundamental results: (i) the magnitude of the conductivity is strongly dependent on the spatial charge localization but (ii) the conductivity as a function of temperature and Fermi level is independent on the shape of the Density of States (DOS). On the other hand (iii) the mobility is strongly influenced by the DOS, hence the DOS affect the mobility only indirectly through the charge concentration. We show that many experimental observation and theoretical investigations can be merged in a simple physical framework based on hopping and percolation. The spatial localization and energetic disorder are the key elements to reach an unified picture of the mobility of organic semiconductors.

Index Terms—Energetic disorder, Localization, DOS, Conductivity, Mobility, Hopping, Percolation

I. INTRODUCTION

In the last years, the performances of organic semiconductors have seen impressing improvements and plastic-based circuits have been possible thanks to the development of new materials, fabrication processes and intensive physical and modeling activities. The most advanced organic electronic systems already in commercial production are high-efficiency, very bright and colorful displays based on organic light emitting diodes (OLEDs). The organic thin-film transistor (OTFT) is the basic building block of plastic-based circuits and it has been recently demonstrated [1] that it can be used also to achieve light emissions. A third important class of devices are the organic photovoltaic cells (OPC), which are promising and cost-effective systems to harvest the solar energy. The operation of OLED, OTFT and OPC is strongly dependent on the conductivity and mobility of the organic semiconductors, used as active layers in the devices. Therefore, a clear understanding of the charge carrier transport in organic semiconductors is of crucial importance in order to improve the opto-electronic properties of the devices based on these materials.

Aim of this work is to investigate the role of energetic disorder and spatial localization on the charge transport properties of organic semiconductors. Specifically, their relative

importance on conductivity, mobility and charge concentration is evaluated by means of a unified physical scenario based on two widely accepted ingredients: hopping and percolation.

II. THEORY

Charge carriers in disordered organic materials are localized in molecules or polymer sub-chains henceforth called sites. Each site is characterized by energy and position in the random lattice. The capability G_{da} of a charge carrier (electron or hole) to move from one site to another is proportional to the occupation probability f of the site that releases the carrier, called donor, the non-occupation probability $[1 - f]$ of the site that receives the carrier, called acceptor, and the hopping rate ν_{da} between the two sites: $G_{da} = G_0 f(E_d, E_F) [1 - f(E_a, E_F)] \nu_{da}$ where E_d , E_a are the energy of donor and acceptor sites, respectively, E_F is the Fermi level and $f(E, E_F) = 1 / \{1 + \exp[(E - E_F)/(k_B T)]\}$ is the Fermi-Dirac occupation probability of a site at energy E . The tunneling rate between two sites (ν_{da}) is defined by the Miller-Abraham hopping model [2]: $\nu_{da} = \nu_0 \exp[-2\alpha r_{da}] \exp[-(E_a - E_d + |E_a - E_d|)/(2k_B T)]$ being ν_0 the attempt-to-escape frequency, α the inverse of the localization radius of a charge carrier, r_{da} the distance between the donor and acceptor sites, k_B the Boltzmann constant and T the material temperature.

According to the percolation theory [3], the conductance of an organic semiconductor can be obtained by considering all the microscopic conductances $G_{da} > G_c$ where G_c is the critical percolation conductance of the system. When the percolation limit is reached, a charge carrier can always find a path to move from one site to another and all the sites are connected. The system conductivity can be calculated as:

$$\sigma = \sigma_0 \exp(-s_c) \quad (1)$$

where σ_0 is a constant prefactor and s_c is the exponent of the critical percolation conductance G_c when the percolation threshold is reached. The conductivity of an organic material can be calculated when the exponent s_c is known, and the

latter can be determined solving the following equation:

$$B_c - \frac{N_b(s_c, E_F)}{N_s(s_c, E_F)} = 0 \quad (2)$$

where $B_c = 2.8$ for a 3-D amorphous system [3]. N_b and N_s are the density of bonds and the density of sites, respectively, and they are integral functions of the DOS [3], [4]:

$$N_b = 4\pi \int_0^{\frac{s_c}{2\alpha}} dr_{da} r_{da}^2 \left\{ \left[\int_{E_F - U_r}^{E_F + U_r} dE \text{DOS}(E) \right]^2 - \int_{E_F}^{E_F + U_r} dE_d \text{DOS}(E_d) \int_{E_F - U_r}^{E_d + U_r} dE_a \text{DOS}(E_a) - \int_{E_F - U_r}^{E_F} dE_d \text{DOS}(E_d) \int_{E_F}^{E_d + U_r} dE_a \text{DOS}(E_a) \right\} \quad (3)$$

$$N_s = \int_{E_F - U_0}^{E_F + U_0} dE \text{DOS}(E) \quad (4)$$

where $U_r = k_B T (s_c + 2\alpha r_{da})$ and $U_0 = U_{r=0} = k_B T s_c$. The relation between the charge concentration c and the Fermi energy level is given by the equation:

$$c = \int_{-\infty}^{\infty} dE \text{DOS}(E) f(E, E_F) \quad (5)$$

Therefore, after defining the DOS, by means of Eqs. 1-4, s_c and the conductivity can be calculated in the typical range of carrier concentration of organic semiconductors: $c = [10^{13}, 10^{19}] \text{cm}^{-3}$ (which gives $E_F = [-0.7, -0.1] \text{eV}$) and for the most relevant DOS functions: the exponential g_E , the double exponential g_{2E} and the Gaussian g_G one:

$$g_E = \frac{N_t}{2E_t} \exp\left(-\frac{|\Delta E|}{E_t}\right) \quad (6)$$

$$g_{2E} = \frac{N_t}{2E_t} \exp\left(-\frac{|\Delta E|}{E_t}\right) + \frac{N_d}{2E_d} \exp\left(-\frac{|\Delta E|}{E_d}\right) \quad (7)$$

$$g_G = \frac{N_t}{\sqrt{2\pi}E_g} \exp\left[-\left(\frac{\Delta E}{\sqrt{2}E_g}\right)^2\right] \quad (8)$$

where $\Delta E = (E - E_0)$, E_t , E_d , E_g are the characteristic energies related to the disorder, E_0 is the reference energy and N_t , N_d are the total number of tail and deep states, respectively. The DOS used in this work (Eqs. 6-8) are plotted in the inset of Fig. 3 and their parameters are: $N_t = 10^{20} \text{cm}^{-3}$, $N_d = 10^{18} \text{cm}^{-3}$, $E_t = 35 \text{meV}$, $E_d = 70 \text{meV}$, $E_g = 100 \text{meV}$ and $E_0 = 0 \text{eV}$.

III. RESULTS AND DISCUSSION

In order to easily compare the conductivity and mobility calculated for different charge localization in the organic material, we define the dimensionless parameter $\theta = \alpha \times d$ where $d^3 = 1/N_t$ is the average distance between two sites. If θ is close to 1 (or less), the charges in the semiconductor are weakly localized in the energy sites, whereas if θ is close to 10 (or greater), the charges are strongly localized.

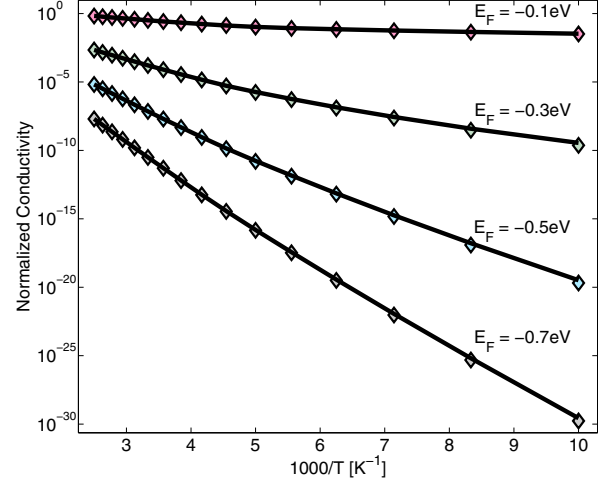


Fig. 1. Conductivity normalized to its highest value plotted vs temperature for several Fermi energies at $\theta = 1$. Symbols are calculated with g_E (Eqs. 1-4, 6), solid lines with g_{2E} (Eqs. 1-4, 7).

Solving the Eqs. 1-4, the conductivities for the different DOS are calculated and plotted in Figs. 1 and 2. Fig. 1 shows a material with weak localization; symbols represent the single exponential DOS (g_E - Eq. 6) and solid lines the double exponential DOS (g_{2E} - Eq. 7). Being $g_{2E} > g_E$ when $E_F < -0.5 \text{eV}$ (see the inset of Fig. 3), the function g_{2E} models an organic semiconductor with broader deep energy-states disorder with respect to one modeled by g_E . Since the conductivities calculated with the DOS g_E and g_{2E} have the same temperature and Fermi-energy dependences, it results that the deep-states do not determine the material conductivity.

Fig. 2 represents a material with strong localization; the symbols are calculated with an exponential DOS (g_E - Eq. 6), solid lines are calculated using a Gaussian DOS (g_G - Eq. 8). The DOS have the same number of total states but a complete different shape. Once again the conductivities calculated with the DOS g_E and g_G perfectly overlap in the whole range of temperature and Fermi-energy. This confirms and extends the previous results, leading to the conclusion that the conductivity of disordered organic materials does not depend on the shape of DOS but only on the total number of states available to the hopping.

The role of the spatial charge localization on the conductivity can be understood by comparing the results drawn in Figs. 1 and 2. It is worth noting that they can be directly compared because in both pictures the conductivity is normalized to the highest value (1, where $\theta = 1$). When the charge in a molecular/polymer site is more spatially localized, the conductivity strongly decreases and it is more temperature dependent. This is physically consistent with the fact that when the molecules or polymer chains are randomly packaged, the π -orbitals are weakly overlapped and the charge carriers need high-energy phonons to accomplish the hopping.

The mobility is calculated as the ratio $\mu = \sigma / (q \times c)$, where σ and c are calculated according to Eqs. 1-4 and 5,

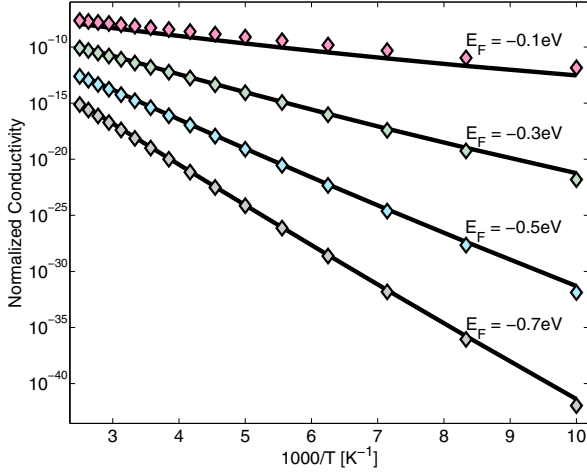


Fig. 2. Conductivity normalized to the highest value used in Fig. 1 plotted vs T for several Fermi energies at $\theta = 10$. Symbols are calculated with g_E (Eqs. 1-4, 6), solid lines with g_G (Eqs. 1-4, 8).

respectively and q is the elementary charge. The results are drawn in Figs. 3 and 4 for several DOS (Eqs. 6-8) and different charge localizations. In both figures, independently on the localization, the mobilities (calculated with various DOS) almost perfectly overlap in the high-concentration regime, where the DOS have the same magnitude. On the other hand, increasing the number of states per unit energy, the mobility decreases and this is evident in the low-concentration regime.

This can be explained as follows: (i) the conductivity as a function of Fermi level (i.e. charge concentration) is independent of the DOS; (ii) whereas, according to Eq. 5, the sensitivity of charge concentration on the Fermi energy is larger by increasing the density of states per unit of energy in the DOS. For these reasons, according to the DOS and to the parameters defined (see Fig. 3, Eqs. 6-8), for small carrier concentrations, hence low energies ($E < -0.5eV$), $g_{2E} > g_E > g_G$ which give $\mu_{2E} < \mu_E < \mu_G$. Therefore, the DOS influence the mobility only indirectly through the charge concentration. As a consequence, the energetic disorder impacts on the DOS broadness and eventually on the mobility: larger energetic disorder implies lower mobility.

The effect of the energetic disorder on the mobility becomes more evident by reducing the temperature. For example, in Fig. 3 when the concentration is $c = 10^{15} \text{ cm}^{-3}$, μ_{2E} is about ten-times smaller than μ_G at $T = 300K$ and two order of magnitude smaller at $T = 200K$. The same trends are displayed in Fig. 4 for high spatial localization: the larger is the disorder, the larger is the temperature dependence.

In the light of the proposed analysis, the findings can be merged in a unique picture: the conductivity is a general property of a disordered organic semiconductor; whereas the mobility depends on the shape of the DOS, which in turn is strongly influenced by the device fabrication process [6].

Finally, by means of the physical-based numerical framework described in section II, the mobility is compared to two

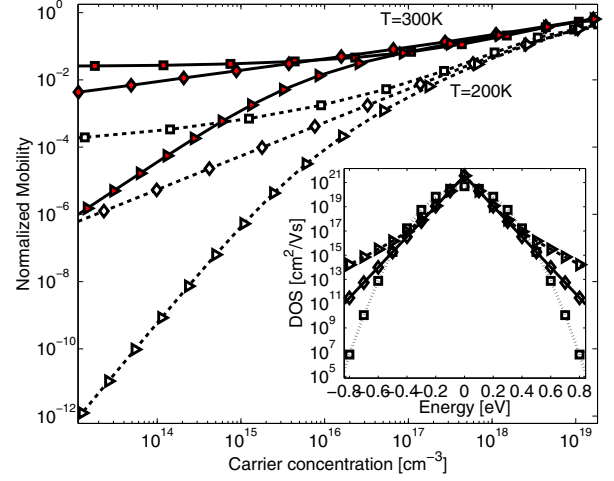


Fig. 3. Mobility normalized to its maximum value for a material with small localization $\theta = 1$. Symbols correspond to different DOS: $\diamond = g_E$ (Eq. 6), $\triangleright = g_{2E}$ (Eq. 7), $\square = g_G$ (Eq. 8).

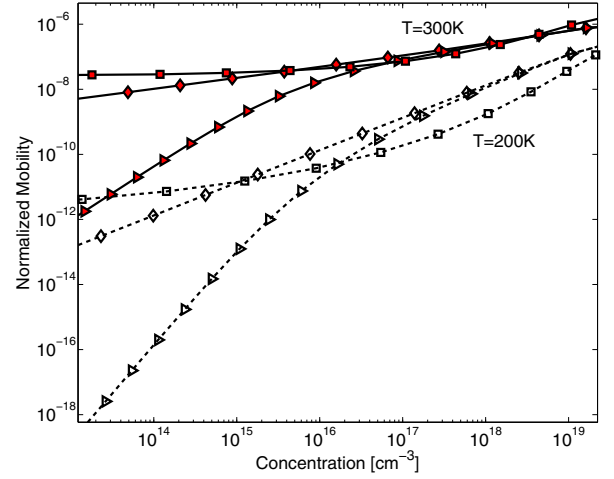


Fig. 4. Mobility normalized to the highest value used in Fig. 3 for a material with large localization $\theta = 10$. Symbols correspond to different DOS: $\diamond = g_E$ (Eq. 6), $\triangleright = g_{2E}$ (Eq. 7), $\square = g_G$ (Eq. 8).

widely accepted mobility models [3], [5] and the results are displayed in Figs. 5 and 6, respectively.

The Vissenberg and Matters model [3] assumes a single exponential DOS and it was proposed to model the field-effect mobility of OTFTs. Since the model is based on the theory adopted in this paper (Eqs. 1-4), the perfect match between the analytical model and the calculated numerical solution does not surprise. However, the latter gives important information about the spatial localization which results $\theta = 4$; it means that the pentacene has an intermediate level of charge localization.

The Pasveer et al. model [5] has been shown to fit the solution of the Master equation under the assumption of a Gaussian DOS. It was used to model the mobility of both OLEDs [5] and OTFTs [7]. The numerical solution of the percolation problem (Eqs. 1-4) with a Gaussian DOS g_G is compared with the

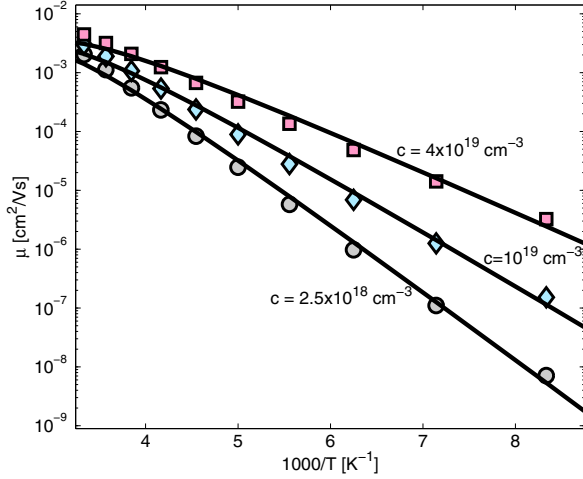


Fig. 5. Symbols are the mobility in a pentacene TFT as a function of temperature T calculated with the Vissenberg et al. model [3]. It agrees perfectly with the experimental data presented in the same work. Solid lines are calculated with Eqs. (1-6), the calculated physical parameters are: $\sigma_0 = 3.2 \times 10^4 S/cm$, $\alpha^{-1} = 2.2 \times 10^{-8} cm$, $E_t = 33.2 meV$, and $N_t = 1.47 \times 10^{21} cm^{-3}$.

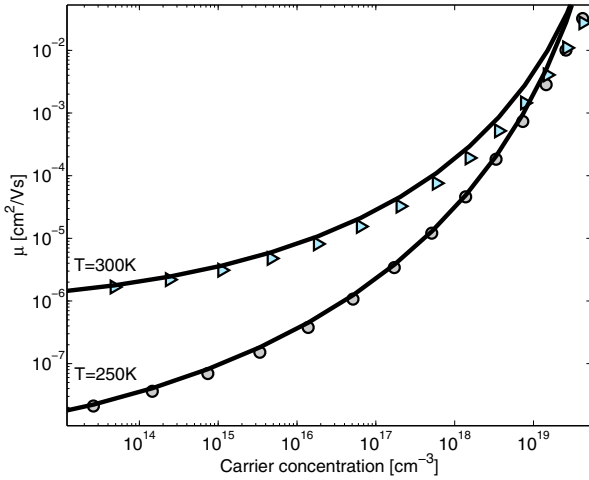


Fig. 6. Symbols are the mobility in a NRS-PPV as a function of concentration c for several temperatures T calculated with the Pasveer et al. model [5]. Solid lines are calculated with Eqs. (1-5, 8); the calculated physical parameters are: $\sigma_0 = 10^{19} S/cm$, $\alpha^{-1} = 1.8 \times 10^{-8} cm$, $E_g = 40.5 meV$, and $N_t = 1.7 \times 10^{20} cm^{-3}$.

model in Fig. 6; they are almost perfectly overlapped in the whole range of concentrations and temperatures. In this case this result is not obvious at all because the same result comes from two different approaches. The comparison of the models' physical parameters (DOS width E_g , total number of states N_t and localization α^{-1}) are in agreement too. This indicates that the percolation theory is fully consistent with the Master equation and it is an effective and faster way to solve the problem of carrier hopping in disordered media.

IV. CONCLUSION

In this paper we have discussed the impact of energetic disorder and spatial localization on the conductivity, mobility and charge concentration. The analysis have been carried out my means of a numerical framework based on two generally accepted concepts: carrier hopping and percolation theory. It was shown that localization and disorder are the key parameters to explain the transport in organic semiconductors.

In order to investigate the role of the energetic disorder, three relevant DOS functions have been considered: a single exponential g_E , a double exponential g_{2E} and a Gaussian g_G . It was shown that the conductivity is insensitive to the shape of the DOS and that the energetic disorder does not affect this material property. On the other hand, the charge carrier concentration depends on the DOS and, as a consequence, it strongly impacts on the concentration and temperature mobility dependence. More specifically, increasing the disorder the mobility decreases and it is more temperature dependent.

The spatial localization of charge carriers in the molecule or polymer sub-chains has been analyzed as well. The increase of the localization leads to a strong reduction of the conductivity; this is physically ascribed to a weak overlap of the π -orbitals, resulting in a reduction of the hopping rate. Same considerations hold for the mobility since the localization does not affect the charge concentration.

Finally, the numerical framework was used to model the mobility of several materials with different DOS and it was compared with two relevant and generally accepted models [3], [5]. The agreement is good in both cases and thus the two theories can be unified by means of the proposed physical framework.

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