

# Toward a Unified Treatment of Electronic Processes in Organic Semiconductors

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# Toward a Unified Treatment of Electronic Processes in Organic Semiconductors

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## ABSTRACT

A quantitative study of n-type doping in highly crystalline organic semiconductor films establishes the predominant influence of electrostatic forces in these low-dielectric materials. Based on these findings, a self-consistent model of doped (purposely or not) organic semiconductors is proposed in which: 1) the equilibrium free carrier density,  $n_f$ , is a small fraction of the total charge density; 2) a superlinear increase in conductivity with doping density is universal; 3)  $n_f$  increases with applied electric field; and 4) the carrier mobility is field-dependent regardless of crystallinity.

## Introduction

No self-consistent treatment of excitonic processes, doping and carrier transport in organic semiconductors is yet available. There are existing models for the individual processes, but the assumptions made to model one process can be incompatible with those made to model another. Here we show that all these processes are controlled by the same factors, primarily electrostatic forces and the spatial extent of the charge carrier wavefunctions, and thereby provide a unified conceptual foundation upon which more detailed models can be based. The factors that lead to excitonic behavior are quite fundamental[1,2] and affect many characteristics of the material, not just the photogeneration process. We briefly describe the origin of excitonic behavior, doping processes in organic semiconductors, the native carrier density in XSCs and its relation to purposely doped materials and finally, the expected field-dependence of both the free carrier density,  $n_f$ , and the carrier mobility,  $\mu$ .

## Excitonic Semiconductors

In a semiconductor with hydrogen-like wavefunctions (such as silicon), the Bohr radius of the electronic state is estimated to be

$$r_B = r_0 n^2 \varepsilon (m_e / m_{eff}) \quad (1)$$

where  $r_0$  is the first Bohr radius of an electron in a hydrogen atom,  $n$  is the quantum number of the orbital,  $m_e$  is the mass of a free electron in vacuum and  $m_{eff}$  is the effective mass of the electron in the semiconductor. A charge carrier becomes free from its electrostatic attraction to an opposite charge at  $r_c$ , the critical distance between the two charges,

$$r_c = (q^2 / 4\pi\varepsilon\varepsilon_0 k_B T), \quad (2)$$

where  $q$  is the electronic charge and  $\varepsilon_0$  is the permittivity of free space.

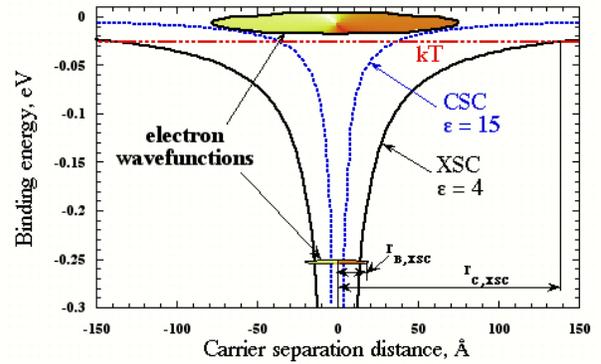
Excitonic behavior is observed if  $r_c > r_B$ . We define a quantity,  $\gamma$ , that approximately distinguishes between conventional and excitonic semiconductors:

$$\gamma = \frac{r_c}{r_B} \approx \left( \frac{q^2}{4\pi n^2 \varepsilon_0 k_B r_0 m_e} \right) \left( \frac{m_{eff}}{\varepsilon^2 T} \right) \quad (3)$$

$\gamma > 1$ : Excitonic semiconductor, XSC

$\gamma < 1$ : Conventional semiconductor, CSC

Equation 3 is only a rough approximation for several reasons which will be discussed. Note that CSCs become excitonic at low  $T$ , and therefore can provide a relevant comparison to organic XSCs at room temperature. A schematic representation of the factors described in eq. 3 is shown in Figure 1.



**Figure 1.** A schematic of the most fundamental differences between CSCs and XSCs showing  $r_B$  and  $r_c$  for XSCs. This general scheme applies to all electrostatic attractions in the semiconductor, not just to photogenerated carriers.

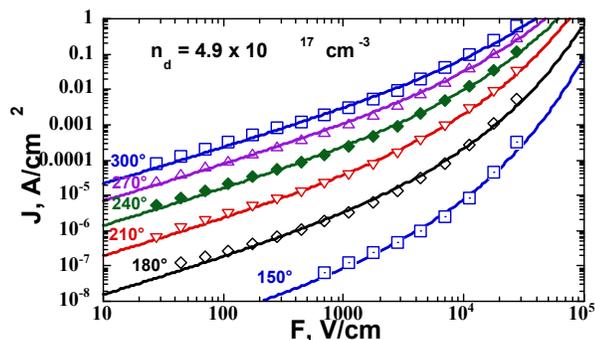
## Doping

The conductivity of doped XSC films increases *superlinearly* with increasing dopant concentration,  $n_d$ , in all quantitative studies of doping in monomeric and polymeric XSCs of which we are aware. A simple model based on the factors contained in  $\gamma$  can explain the apparent universality of this superlinear increase in conductivity with doping density in XSCs.[3]

Pearson and Bardeen first reported that the activation energy for free carrier production,  $E_a$ , in doped silicon decreases with increasing dopant concentration at low temperature. The low dielectric constant and the small Bohr radii that are characteristic of XSCs (Fig. 1,  $\gamma > 1$ ) typically result in  $E_{a,max}$  of *hundreds* of meV. Therefore,  $E_a$  is expected to control  $n_f$  in XSCs even at room temperature. This fact can explain much of the electrical behavior of XSCs. We attribute the superlinear increase in  $\sigma$  with  $n_d$  to the increasing polarizability of the film caused by addition

of polarizable dopants:[3] Identical effects should occur in nominally undoped, but charged-defect-rich materials such as  $\pi$ -conjugated polymers.

In many nominally undoped XSCs, the total equilibrium charge density may be far larger than expected. Defect carrier generation may be especially prominent in  $\pi$ -conjugated polymers because their conducting backbone consists of a semi-infinite chain of high-energy covalent  $\pi$ -bonds. The inevitable twists and bends in the backbone of these *quasi-amorphous* polymer films produce a high density of electronic states in the bandgap, some of which will be charged. Many XSCs, especially those with such “covalent disorder” are adventitiously doped to such a high level that their electronic behavior resembles that of purposely doped molecular XSCs.



**Figure 2.** Typical  $J$ - $F$  curves versus temperature for a polycrystalline film doped to  $n_d = 4.9 \times 10^{17} \text{ cm}^{-3}$ .

### Transport

The same spatial and electrostatic considerations that cause exciton formation, and cause most added dopant electrons to remain bound near their conjugate dopant counterions in XSCs, also effect carrier transport by controlling  $n_f$ . The Poole-Frenkel (PF) mechanism treats the effect of  $F$  on the number of carriers trapped in Coulomb potential wells in an isotropic solid and, therefore, describes also the current density,  $J$ . We expect this mechanism (modified by a field-dependent mobility) to semiquantitatively describe the  $J$ - $F$  characteristics of many purposely and adventitiously doped XSCs. Figure 2 shows typical  $J$ - $F$  curves of a liquid crystalline perylene diimide doped n-type to a density of  $n_d = 4.9 \times 10^{17} \text{ cm}^{-3}$ . The fits are to a modified PF equation.

The mobility of charge carriers in XSCs usually increases with increasing electric field. This process is formally independent of the field-assisted increase in  $n_f$  (e.g., the PF mechanism) although in practice,  $n_f$  and  $\mu$  are often coupled. The existence of a substantial density of bound charges in doped (purposely or not) XSCs causes spatial fluctuations in the conduction and valence band energies. These dipoles decrease the carrier mobilities relative to the “flat band” case. Nominally undoped  $\pi$ -conjugated polymers, and other defect-rich XSCs, are expected, therefore, to have a large dipole density resulting in a field-dependent carrier mobility.

### Summary

We propose a general organizing principle,  $\gamma$  (eq. 3), that approximately distinguishes between XSCs and CSCs. It is a function of dielectric constant, the spatial delocalization of the carrier wavefunction,  $r_B$ , temperature, etc. Light absorption by an XSC leads to electrostatically bound electron-hole pairs (excitons). Doping an XSC n-type leads primarily to electrons bound to their conjugate dopant ions. The number of free electrons increases with increasing dielectric constant and with increasing electric field. The mobility of the electrons is diminished and becomes field dependent whenever  $r_B$  is smaller than the spatial potential fluctuations.

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