

Toward a Unified Treatment of Electronic Processes in Organic Semiconductors

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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. On the basis of these findings, a self-consistent model of doped (purposely or not) organic semiconductors is proposed in which the equilibrium free carrier density, n_f , is a small fraction of the total charge density, a superlinear increase in conductivity with doping density is universal, n_f increases with applied electric field, and the carrier mobility is field dependent regardless of crystallinity.

Introduction

No self-consistent treatment of excitonic processes,^{1–3} doping,^{4–10} and carrier transport^{11–17} 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 of these processes are controlled by the same factors, primarily electrostatic forces and the spatial extent of the charge carrier wave functions, thereby providing a unified conceptual foundation upon which more detailed models can be based. The most widely recognized difference between organic and inorganic semiconductors is that the former generate excitons (electrically neutral, mobile excited states) upon light absorption whereas the latter directly form free electrons and holes. The reasons for this difference in the charge photogeneration mechanism are well known.¹ They were recently discussed in a broader context where it was shown that the more fundamental distinction is that between excitonic semiconductors (XSCs), which includes some inorganic semiconductors, and conventional semiconductors (CSCs).^{2,3} The factors that lead to excitonic behavior are quite fundamental 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, μ .

Excitonic Semiconductors

There are two primary reasons for the formation of excitons upon illumination of XSCs at room temperature: (1) the low dielectric constant, ϵ , of XSCs compared to that of CSCs and (2) the small Bohr radii of carriers, r_B .⁹ The former occurs partly because organic SCs consist mainly of elements in the first two rows of the periodic table whose electrons are more tightly bound than those of inorganic SCs, which often consist of more polarizable elements from the 3rd–5th rows. The latter occurs because the relatively weak intermolecular bonds result in narrow bandwidths and high effective masses of carriers in XSCs¹ compared to the strong interatomic bonds (wide bands) in most CSCs. In a semiconductor with hydrogen-like wave

functions (such as silicon), the Bohr radius of the electronic state is estimated to be¹⁸

$$r_B = r_0 n^2 \epsilon \left(\frac{m_e}{m_{\text{eff}}} \right) \quad (1)$$

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 a vacuum, and m_{eff} is the effective mass of the electron in the semiconductor (usually less than m_e in CSCs but greater than m_e in XSCs).^{1,19}

A charge carrier becomes free from its electrostatic attraction to an opposite charge (modeled here as a Coulomb potential) if the energy of attraction is less than $k_B T$, that is, less than Boltzmann's constant times the absolute temperature. This occurs at r_c , the critical distance between the two charges

$$r_c = \left(\frac{q^2}{4\pi\epsilon\epsilon_0 k_B T} \right) \quad (2)$$

where q is the electronic charge and ϵ_0 is the permittivity of free space.

Excitonic behavior is observed if $r_c > r_B$. Note that eqs 1 and 2 are equally valid for both excited-state and ground-state processes. Excitonic behavior is also observed when r_B is greater than the particle radius, but these “quantum confined” structures are not considered here. We define a quantity, γ , that approximately distinguishes between conventional and excitonic semiconductors

$$\gamma = \frac{r_c}{r_B} \approx \left(\frac{q^2}{4\pi n^2 \epsilon_0 k_B r_0 m_e} \right) \left(\frac{m_{\text{eff}}}{\epsilon^2 T} \right) \quad (3)$$

$\gamma > 1$: Excitonic semiconductor, XSC

$\gamma < 1$: Conventional semiconductor, CSC

Equation 3 is a rough approximation for several reasons. Among them, organic SCs are usually low-dimensional materials.¹ Therefore, the parameters r_c , r_B , ϵ , and m_{eff} do not have the spherical spatial symmetry implied by the derivation of eq 3. To more accurately describe organic SCs would require a tensor equation. Furthermore, the effective carrier mass, m_{eff} , is not well defined in XSCs in which carrier transport typically

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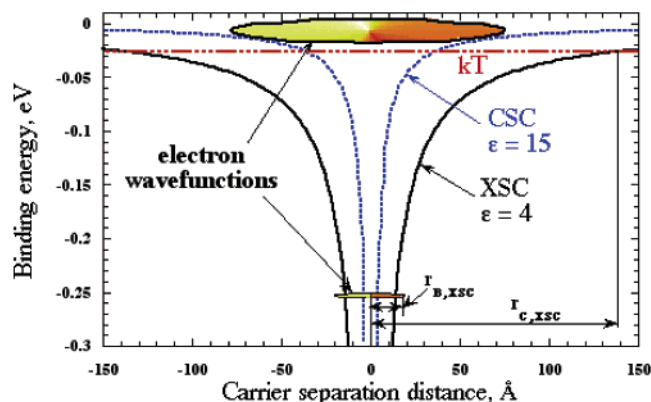


Figure 1. Schematic of the most fundamental differences between CSCs and XSCs showing r_B and r_c for XSCs. The calculations assume a Coulomb potential with the positive charge at 0 Å. This general scheme applies to all electrostatic attractions in the semiconductor, not just to photogenerated carriers.

occurs via a hopping mechanism rather than via delocalized band transport.¹ Also, ϵ is a bulk quantity and is valid only over distances of many lattice spacings; whereas, for the tightly bound wave functions that occur in some XSCs, the effective ϵ can approach its molecular value of 1.0.¹⁸ In other words, the potential wells deviate from the Coulomb form when the separation distance between charges is small. Despite the approximations, eq 3 is valuable in defining the parameters that are responsible for the distinct differences in behavior between the two types of semiconductors. Moreover, $\gamma \gg 1$ in most organic XSCs, making the distinction clear in most cases despite the approximations. 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.

The marked differences in photovoltaic behavior between XSCs and CSCs have been discussed recently.^{2,3} Briefly, when $\gamma < 1$ (CSCs), charge carriers are photogenerated throughout the bulk wherever light is absorbed. In contrast, when $\gamma > 1$ (XSCs), excitons photogenerated in the bulk dissociate primarily at a p–n heterojunction, resulting in the creation of electrons in one phase, already separated from holes on the opposite side of the heterojunction. This results in qualitatively different limitations on the achievable open circuit photovoltage, V_{oc} , in the two types of solar cells;^{2,3} CSCs are usually limited to the equilibrium built-in electrical potential difference, $V_{oc} < \phi_{bi}$, whereas XSCs commonly achieve $V_{oc} > \phi_{bi}$. Nevertheless, the thermodynamic limitations on the photoconversion efficiency are identical for the two semiconductor types.²⁰

Doping Organic Semiconductors

Doping organics to quasi-metallic levels has been well studied;^{1,21,22} in contrast, doping to semiconducting levels is just beginning to be explored quantitatively.^{6,7,10} We recently described doping in a highly crystalline molecular XSC model system^{8,9,23} in which the free charge carrier density, $n_f < 10^{10} \text{ cm}^{-3}$, is very low in the undoped material. This system allows a quantitative understanding of doping and free carrier generation in XSCs. Spatially and temporally stable n-type doping^{8,9} is achieved with a zwitterionic dopant molecule that is a reduced derivative of the host molecule (Figure 2). In solution, both the host and the dopant have identical reduction potentials and, when mixed together, form aggregates in which the dopant electron is delocalized over a number of host molecules.²⁴ The only energetic difference between the electron on the dopant and the

electron on one of the host molecules is that caused by the electrostatic attraction to the positive charge bound to the side chain of the dopant. All subsequent discussions assume n-type doping, but the relation to p-type doping is obvious.

The conductivity of the doped PPEEB films increases superlinearly with increasing dopant concentration, n_d (Figure 3).^{8,9} This superlinear increase has been observed in all quantitative studies of doping in monomeric^{5–7,25} and polymeric XSCs^{10,22,26–28} of which we are aware. Its origin has been the subject of much inquiry.^{5,9,25} A simple model based on the factors contained in γ can explain the apparent universality of this superlinear increase in conductivity with doping density in XSCs.⁹

Pearson and Bardeen²⁹ first reported that the activation energy for free carrier production, E_a , in doped silicon decreases with increasing dopant concentration at low temperature. The same phenomenon was later observed in doped germanium and was discussed by several groups.^{30–32} This behavior occurs because the electrostatic attraction of the dopant electron to its positive countercharge is significant at low temperature, and it decreases as more electrons and positive dopant counterions are added. The decrease in E_a leads to a superlinear increase in n_f and, therefore, in conductivity, σ . This is observed only at low temperature in CSCs^{30–32} (where they become XSCs, eq 3) because $E_{a,max}$, the maximum activation energy at very dilute dopant concentration, is on the order of 15 meV. However, the low dielectric constant and the small Bohr radii that are characteristic of XSCs (Figure 1, $\gamma > 1$) typically result in an $E_{a,max}$ of hundreds of meV. Therefore, E_a is expected to control n_f in XSCs even at room temperature.¹⁰ This fact can explain much of the electrical behavior of XSCs. In the simple case of doped PPEEB films, n_f is expected to vary as⁹

$$n_f = n_d \exp\left(\frac{-E_a}{k_B T}\right) \quad (4)$$

where Boltzmann statistics are valid because $E_a \gg k_B T$. We attribute the superlinear increase in σ with n_d in the PPEEB films to the increasing polarizability of the film caused by the addition of dopant cations with their highly polarizable electrons (most of which are in electrostatically bound but delocalized states), as described by eq 5.^{9,30}

$$\sigma = q \mu_n n_d \exp\left(\frac{-E_{a,max} + \beta n_d^{1/3}}{k_B T}\right) \quad (5)$$

where $E_a = E_{a,max} - \beta n_d^{1/3}$ and β is a fitting parameter of order $q^2/4\pi\epsilon\epsilon_0$. The increase in σ above the expected linear increase with n_d is a function of the distance between bound carriers, $(n_d - n_f)^{1/3} \approx n_d^{1/3}$, rather than the distance between free carriers, $n_f^{1/3}$.^{9,30} This occurs because the high value of $E_{a,max}$, 0.23 eV, ensures that n_f is only a small fraction of n_d at room temperature. Over the range of our data, n_d is 100 to 10 000 times greater than n_f .

Being based wholly on considerations of electrostatics and the spatial extent of the carrier wave functions, this explanation may be generalized to other doped XSCs despite differences in chemical structure, purity, and crystallinity. The observed superlinear increase in conductivity with doping density is expected to be, and apparently is, a universal attribute of excitonic semiconductors,^{5–10,22,25–28} including inorganic SCs at low T .^{29–32} One consequence of $\gamma > 1$ is that it may be impossible to produce shallow (i.e., mostly ionized) dopants in XSCs at room temperature, independent of the chemistry or

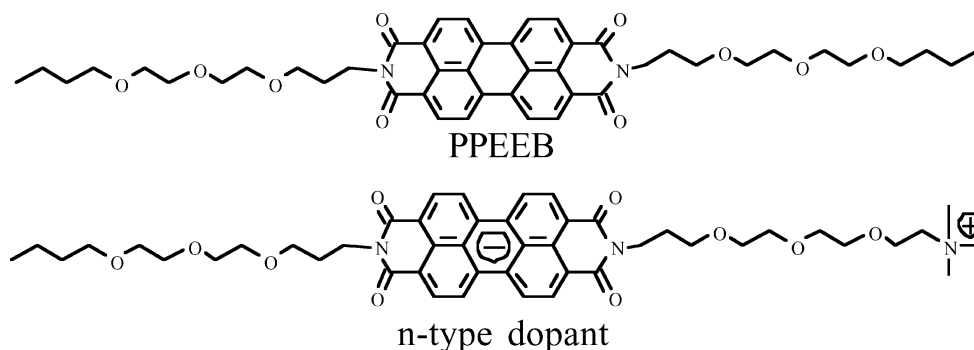


Figure 2. Chemical structure of the host semiconductor, PPEEB, a liquid crystal perylene diimide that is solid at room temperature, and its substitutional n-type dopant, a reduced derivative of PPEEB with a covalently attached counterion. There are no mobile ions in these doped films.

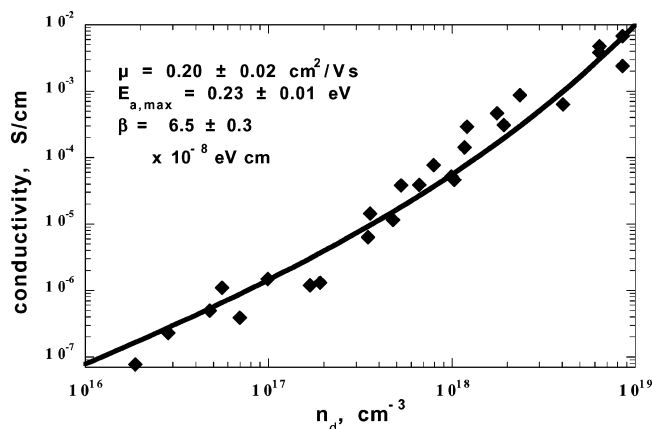


Figure 3. Conductivity of PPEEB films (at a field $F = 0.9 \text{ V}/\mu\text{m}$) versus dopant concentration, n_d . Data are from ref 9 and are fit to eq 5.

redox potentials of the dopant and host. This follows because E_a for strong dopants is determined by the factors contained in γ , not by the difference in potential between the dopant and its respective bandedge. In the doped PPEEB films, the dopant electron potential was exactly at the bandedge when measured in solution, but the electron in the solid films was still localized near the dopant molecule in a $\sim 0.23 \text{ eV}$ potential well because of the electrostatic attraction between it and its conjugate cation. Even if the dopant potential were to lie outside the band gap of the XSC, the charge carrier would relax to the bandedge and be localized near neighboring molecules because of the electrostatic force. Identical effects should occur in nominally undoped, but charged-defect-rich materials such as π -conjugated polymers.

In many nominally undoped XSCs, the total equilibrium charge density may be larger than expected. The carrier density usually estimated or measured in XSCs is n_f .^{1,28,33–36} This is often assumed to be a constant, equivalent to the total charge density in the semiconductor. Although this assumption is approximately valid for most CSCs, it is incorrect for XSCs because $\gamma > 1$. The equilibrium magnitude of n_f may derive from several sources such as the number of intrinsic carriers, n_i ; the number of purposely added dopants, n_d ; and the number of carriers produced from adventitious doping, $n_a = n_{a1} + n_{a2} + \dots$, caused by impurities, crystal imperfections, grain boundaries, surface states, bent or twisted bonds in a conducting polymer backbone, and so forth. In all but the best single-crystal XSCs, n_i is negligible. Equation 4 and its discussion shows that even in almost ideal thin films, $n_d \gg n_f$ because $\gamma > 1$. In less ideal systems in which n_a predominates, the same electrostatic considerations must hold. In general, therefore, $n_d + n_a \gg n_f$ in

doped (purposely or not) XSCs. Jarrett et al. reached a similar conclusion in a recent study of doped π -conjugated polymers.¹⁰

Defect-carrier generation may be especially prominent in π -conjugated polymers because their conducting backbone consists of a semi-infinite chain of high-energy covalent π bonds. The inevitable twists and bends in the backbone of these *quasi-amorphous* polymer films produce a high density of electronic states in the band gap, some of which will be charged.³⁶ I refer to this as “covalent disorder”. Another source of defect carriers comes from the difficulties in purifying high molecular weight polymers. It is estimated, for example, that $n_f \approx 10^{15}–10^{17} \text{ cm}^{-3}$ in poly(phenylene vinylene) type polymers,³⁶ whereas the total defect density is estimated to be $\sim 10^{19} \text{ cm}^{-3}$.³⁷ There are no purposely added dopants, $n_d = 0$, in these materials, and n_i is insignificant. The electrical properties are therefore controlled by n_a , at least at low fields where the injected carrier density, n_{inj} , is insignificant.

On the other hand, all covalent bonds are contained within the individual molecules in molecular XSCs, thus no covalent bonds exist between the molecular units. Morphological defects result in mostly low-energy perturbations, only a few of which will be charged. This I refer to as “noncovalent disorder”. The estimated free carrier density in these materials ($n_f \approx 10^9–10^{14} \text{ cm}^{-3}$)^{1,8,34,35,38} is substantially lower than that in π -conjugated polymers. It is often appropriate, therefore, to distinguish between molecular materials with noncovalent disorder, and π -conjugated polymers with covalent (and noncovalent) disorder, although the distinction in terms of charge density is primarily quantitative, not qualitative. Many XSCs, especially those with covalent disorder, are adventitiously doped to such a high level that their electronic behavior resembles that of purposely doped molecular XSCs.

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 . This fact is often overlooked in transport models; n_f *should* be an increasing function of applied field, F , in purposely or adventitiously doped XSCs because $\gamma > 1$. We are not referring to injected carriers, n_{inj} , whose number is obviously F -dependent. Nor is this effect applicable to materials in which $n_f \ll n_{\text{inj}}$, such as single-crystal XSCs¹ or molecularly “doped” polymers.^{13,17}

The Poole–Frenkel (PF) mechanism^{1,39,40} treats the effect of F on the number of carriers trapped in Coulomb potential wells in an isotropic solid (Figure 4) and, therefore, describes also the current density, J . We expect this mechanism (modified

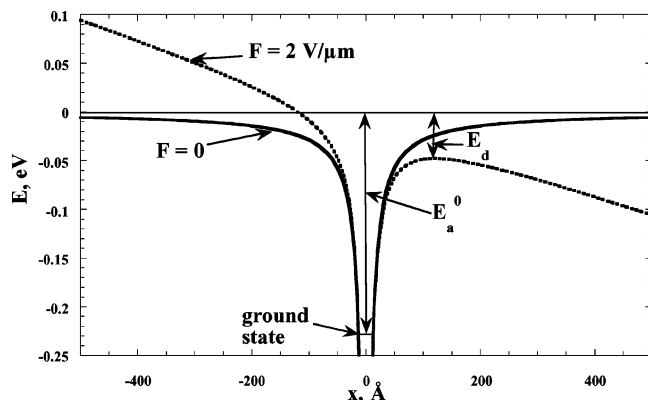


Figure 4. The activation energy for thermal emission of a charge carrier out of a Coulomb potential well decreases with the square root of the applied field, $F^{1/2}$ (Poole–Frenkel mechanism, eq 6).

below by a field-dependent mobility) to semiquantitatively describe the J – F characteristics of many purposely and adventitiously doped XSCs.

The dark current in the PF mechanism increases with $\exp(F^{1/2}/kT)$ as the field decreases the height of the electrostatic potential well binding the carrier to its countercharge (Figure 4)⁴⁰

$$J = q \mu_n F n_d \exp\left(\frac{\left(-E_a^0 + \left(\frac{q^3}{\pi \epsilon_0 \epsilon}\right)^{1/2} F^{1/2}\right)}{kT}\right) \quad (6)$$

Equation 6 is written for the simplest case (approximately applicable to the doped PPEEB films) in which n_d dominates J , n_a is negligible, μ_n is a constant, and there is only a single E_a^0 . The increase in current with $\exp(F^{1/2}/kT)$ occurs because n_f is proportional to $\exp(F^{1/2}/kT)$.⁴⁰ This point is sometimes misunderstood, and it may be asserted that the PF mechanism predicts an $\exp(F^{1/2}/kT)$ dependence of the *mobility*. The PF mechanism should apply (at least approximately) to all XSCs in which $n_d + n_a \gg n_f$ and for fields in which $n_f > n_{inj}$. It may be difficult to experimentally distinguish PF-controlled currents (eq 6) from n_{inj} -controlled, space-charge-limited currents (SCLC, $J \sim F^2$) in π -conjugated polymers.⁴⁵ However, the PF mechanism appears to be unavoidable in doped XSCs because $\gamma > 1$; it will influence the J – V behavior starting from zero field. At high field, n_{inj} may (or may not, depending on the assumed mechanism) eventually overwhelm n_f . Beyond this point, SCLC may be superimposed on the underlying PF currents. Pure SCLC behavior, however, is expected only in systems in which $n_f \ll n_{inj}$, for example, in molecularly doped polymers.^{13,17}

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) described above, although in practice, n_f and μ may be coupled. Field-dependent mobilities are most unambiguously observed in materials that have very low values of n_f , such as molecularly doped polymers.^{13,17} Models of charge transport in such XSCs explain the field dependence of the carrier mobility by assuming a Gaussian distribution of hopping site energies^{13,17} and/or by assuming a random distribution of fixed dipoles in the film (a correlated medium).^{15,41,42} These mechanisms have also been applied to the description of conduction in π -conjugated polymers.^{15,16,43,44}

A mobility of the empirical form^{14,16,41}

$$\mu = \mu_0(T) \exp(\alpha(T)F^{1/2}) \quad (7)$$

is often employed where the T dependences of μ_0 and α are unknown and probably material dependent. 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, or when more concentrated, multipoles, decrease the carrier mobilities relative to the flat band case. Carriers must either move around such barriers or be thermally emitted over them (in a PF-like mechanism) to contribute to the current. For example, despite their highly crystalline nature, we expect the random dipole mechanism to apply approximately to the mobility of carriers in the doped PPEEB films. Dipoles are formed by the electrons electrostatically bound at an average distance of r_B (eq 1) to their dopant counterions. They are free to orient in almost any direction and therefore will minimize any existing *static* electric fields. In this sense, they are not the random permanent dipoles treated by existing models. However, charge transport is affected by the *rate* at which the dipoles reorient with respect to the charge hopping rate. Because the dipoles in doped XSCs reorient by what is, in essence, a charge-hopping process, these two rates should be similar. Thus, the dipoles will begin to reorient on the time scale of hopping transport, but they will not have time to reach an equilibrium configuration. The dipole field will lag the charge-hopping process. Thus, the charge carrier will experience a not-quite-random distribution of dipoles, and there will be an energetic correlation between the site energies visited by the mobile charge.^{16,41} This mechanism, although apparently not previously considered, would seem to result in the same field-dependent mobility as described in previous models.^{13,15–17,41,42} In most cases where there is a substantial dipole density in the XSC, μ is expected to be field dependent. The internal dipole density of doped (purposely or not) XSCs should be approximately equal to the total internal charge density $\approx n_d + n_a \gg n_f$. Nominally undoped π -conjugated polymers and other defect-rich XSCs are expected, therefore, to have a large dipole density resulting in a field-dependent carrier mobility.

Summary

In summary, we propose a general organizing principle, γ (eq 3), that approximately distinguishes between XSCs and CSCs. It is a function of dielectric constant, the spatial delocalization of the carrier wave function, r_B , temperature, and so forth. 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, n_f , 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. Thus, the factors described in γ strongly influence the excitonic, doping, and transport properties of XSCs. In many organic materials that are not purposely doped, there is a substantial density of extrinsic charges. This is especially true for π -conjugated polymers. These materials behave similarly to purposely doped molecular XSCs. The increase in carrier mobility, μ , with electric field and temperature is expected to be a general feature in all materials with a substantial dipole density derived either from fixed dipoles, as in molecularly doped polymers, or from slowly orienting dipoles, as in purposely doped or adventitiously doped XSCs. Both n_f and μ are expected to be functions of *both* temperature and field in doped XSCs because $\gamma > 1$.

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