

Carrier generation mechanisms for photoconductivity in conjugated polymers

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We study theoretically the origin of photoconductivity in conjugated polymers. The charge carriers are released when excitons dissociate through the deep levels within the semiconductor bandgap caused by either oxidation (carbonyl group) or structure defects. Our results explain the recent observations of the temperature-independent photocurrent in the sweep-out regime and the transient photocurrent at high excitation. The tightly bound exciton versus semiconductor band controversy on the photocarrier generation process is clarified.

The origin of photoconductivity (PC) in conjugated polymers has been under intense study recently but controversies remain.¹⁻³ The basic question is how the excitons, with possibly large-binding energy, dissociate into free carriers. The carbonyl group introduced by oxidation has been demonstrated to quench the excitons efficiently.^{4,5} Besides, excitons are known to dissociate at the polymer/metal junction, and interchain effects were shown to enhance the dissociation process.⁶ Barth and Bäessler measured the intrinsic PC by eliminating the oxidation and junction exciton quenching,² and conclude that in such a pure sample the excitons have to overcome a binding energy of 0.34 eV through thermal activation or electric field tunneling in order to dissociate into free carriers. The temperature and field dependence of the PC quantum yield was shown to be consistent with the Onsager model.^{8,2} This picture is, however, inconsistent with the PC measurement in the sweep-out regime by Moses *et al.*,¹ which shows that the effective activation energy decreases with the film thickness, contradictory to the constant value (exciton binding energy) as the Onsager model would predict. Moses *et al.* thus propose that the temperature dependence of PC is mainly due to thermal activation out of the deep levels (traps) into which the carriers fall along their passage to the electrode, and the carrier generation process itself is temperature independent. This behavior is interpreted as the evidence of a small exciton binding energy,¹ contrary to other studies.^{9,10}

Large binding energy and weak temperature dependence can be reconciled if the predominant carrier generation channel for photoconductivity is not thermal activation but mediated by the defect levels. In order to confirm this possibility, in this paper, we study theoretically the exciton dissociation process through defects, including the carbonyl group and two kinds of structure defect, shown in Fig. 1. We found that all of them introduce deep levels within the energy gap. If the exciton binding energy is smaller than the deep level binding energy, the electron of the exciton can drop into the deep level through multi-phonon emission while the hole is released to be the free carrier, when the level is initially empty. The reversed process happens when the level is initially occupied. This is a relaxation instead of an activation process. Carriers can therefore be generated at zero temperature and have in general a weakly temperature-dependent rate. Our prediction about the relation between exciton

quenching rate and oxygen density agrees with experiment.⁵ Furthermore, we use the experimental quantum yield for pure samples oxygen-free to predict the density of structure defects based on our calculation. The result is consistent with the estimate of the average chain length. Quenching through structural defects is found to be the predominant carrier generation process at a typical density level of the structural defects. The observed temperature-independence of the photocurrent¹ is therefore not due to the smallness of the exciton binding energy, but to the high-quenching efficiency of the deep levels. These results provide a unifying picture for the experiments and clarify the controversy about the origin of the photo-carrier generation process. In addition to the steady-state PC, we also explain the unusual transient observed at very high excitation⁷ by the saturation of the defects due to a high exciton density.

The π -electron system for a perfect conjugated polymer is modeled as a one-dimensional infinite lattice with alternating values of hopping integrals t_1 and t_2 for the p_z orbitals. For conjugated polymers with a more complicated unit cell like poly(*p*-phenylene vinylene) (PPV), t_1 and t_2 can be taken as parameters that reproduce the conduction and valence band structure. The valence band lies between $-|t_1 + t_2|$ and $-|t_1 - t_2|$, while the conduction band occupied the range between $|t_1 - t_2|$ and $|t_1 + t_2|$. The structural defect is

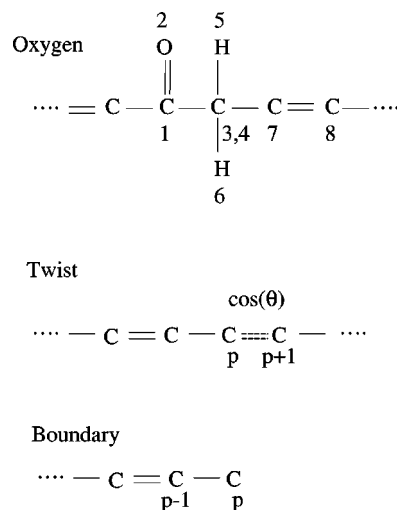


FIG. 1. The structures of the three kinds of defects.

introduced by changing one of the hopping integrals t_1 to $t'_1 = t_1 + \Delta t$. Physically a smaller t'_1 can be caused by a chain twist or distortion, which reduces the p_z orbital overlap. Our calculation applies, however, to a larger t'_1 as well. The chain boundary corresponds to $\Delta t = -t_1$. Assume the defect bond is between sites p and $p+1$. For a perfect chain, the Schrödinger equation for the wavefunction $|\psi\rangle$ is $L\psi=0$, with $L = \varepsilon I - H$, where ε is the energy eigenvalue, I is the identity matrix, and H is the Hamiltonian. More explicitly, the matrix element $L_{\mu\nu}$ is $\varepsilon\delta_{\mu\nu} - t_1\delta_{v,\mu+1} - t_2\delta_{v,\mu-1}$ for odd μ , and $\varepsilon\delta_{\mu\nu} - t_2\delta_{v,\mu+1} - t_1\delta_{v,\mu-1}$ for even μ . μ, ν are site indices. With the defect, L is changed to $L + \Delta L$, where $\Delta L = -\Delta t(\delta_{\mu,p}\delta_{v,p+1} + \delta_{\mu,p+1}\delta_{v,p})$. The eigenvalue equation becomes $(1 + L^{-1}\Delta L)|\psi\rangle = 0$. The inverse of the matrix L is given by $L_{\mu\nu}^{-1} = \sum_{k,\sigma=\pm} u_{\mu}^{\sigma}(k)u_{\nu}^{\sigma*}(k)/(\varepsilon - \varepsilon_k^{\sigma})$, where $\varepsilon_k^{\pm} = \pm\sqrt{t_1^2 + t_2^2 + 2t_1t_2\cos(2ka)}$ is the dispersion for the conduction band (+) and for the valence band (-). Here, k is the wave number, $2a$ is the size of the unit cell containing two sites, ka is in the Brillouin zone $[-\pi/2, \pi/2]$, $u_{\mu}^{\pm}(k)$ is the component of the Bloch wave function at site μ . The energy eigenvalue ε can be determined by the equations for ψ_p and ψ_{p+1}

$$\begin{pmatrix} 1 - \Delta t L_{p,p+1}^{-1} & -\Delta t L_{p,p}^{-1} \\ -\Delta t L_{p+1,p+1}^{-1} & 1 - \Delta t L_{p+1,p}^{-1} \end{pmatrix} \begin{pmatrix} \psi_p \\ \psi_{p+1} \end{pmatrix} = 0. \quad (1)$$

Localized state with an energy within the gap, i.e., $-|t_1 - t_2| < \varepsilon < |t_1 + t_2|$, are introduced by the defect when $-2t_1/\Delta t < 1$ for $t_2 > t_1$, and $-2t_1/\Delta t > 1$ for $t_2 < t_1$. The defect level energy ε_d , appearing in pairs of the same magnitude but opposite sign, is given by¹¹

$$\varepsilon_d^{\pm} = \pm \frac{1}{A-1} [t_1(1+A) - \sqrt{4t_1^2A + t_2^2(A-1)^2}], \quad (2)$$

where $A \equiv (2t_1/\Delta t + 1)^2$. For the localized states outside the energy bands, the expression becomes $\varepsilon_{d,out}^{\pm} = \pm [t_1(1+A) + \sqrt{4t_1^2A + t_2^2(A-1)^2}]/(A-1)$. The component of the wavefunction at site $q \neq p$ can be related to ψ_p by

$$\frac{\psi_q}{\psi_p \Delta t} = \frac{-1}{-\varepsilon^2 + t_1^2 + t_2^2} \frac{1}{\sqrt{1-B^2}} \gamma^{\frac{q-p}{2}} (\varepsilon + t_1 + t_2 \gamma^{-1}), \quad (3)$$

where $B = 2t_1t_2/(-\varepsilon^2 + t_1^2 + t_2^2)$ and $\gamma = (\sqrt{1-B^2} - 1)/B$. For odd $q-p$, we simply change $p-q$ to $p-q-1$. The details of the derivation and the physical picture will be published elsewhere.¹¹ The localized state energies are shown in Fig. 2 as a function of Δt for $t_1 > t_2 > 0$. Both $t_{1,2}$ and the wave function ψ have been chosen to be positive without loss of generality. The Fermi level is always at the zero of energy. The localized states outside the bands are irrelevant to the process of exciton quenching, so we concentrate on the states within the band gap (deep levels) below. In addition to the localized electronic state, the structural defect usually causes localized phonon mode as well. Free carriers can be captured by the deep level through multiphonon emission.

The first specific case we consider is bond twisting, for which the bond t_1 is twisted permanently by an angle θ . We assume that the local mode profile follows the electronic wave function, because the very existence of the local pho-

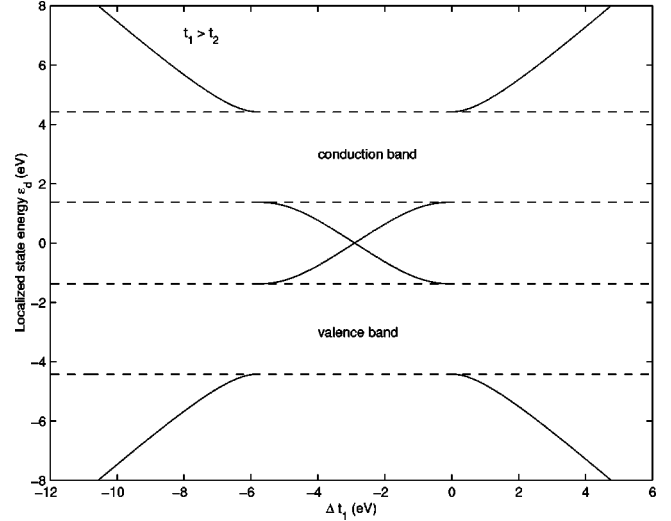


FIG. 2. The localized state energy for the case $t_1 > t_2$ is shown when one of the t_1 bonds is changed to $t_1 + \Delta t_1$. The localized state inside the gap occurs when $-2t_1 < \Delta t_1 < 0$, otherwise the localized state occurs outside the bands.

non mode itself is due to the localization of the electron. The second kind of structural defect is the boundary of a semi-infinite chain. Localized electronic and phonon modes occur simultaneously at the boundary. For the electronic part, we set Δt equal to $-t_1$, such that the hopping is zero. The deep level is located at $\varepsilon = 0$. The coupling between the local mode and the electron is assumed to be through the modulation of the last bond. The third case is the carbonyl group with an oxygen atom attached to the carbon backbone. Each of the atomic orbitals contributing to the π -conjugation is labeled by a number (Fig. 1). Note that the bonding beyond site 7 is exactly the same as the unoxidized case. Sites 3 and 4 are sp^3 orbitals roughly perpendicular to the sp^2 plane (x - y plane). They participate in the π -electron wavefunction through hyperconjugation.¹³ Their hopping integrals with the same p_z orbital are the same in magnitude but opposite in sign, because they are on opposite sides of the x - y plane. The hopping integrals of the bonds around the oxygen defect are summarized by $t_{12} = t_O$, $t_{13} = t_{37} = -t_{14} = -t_{47} = t_h$, $t_{35} = t_{46} = t_H$, where t_O is the hopping between the p_z orbitals of carbon and oxygen, t_h is the hopping for hyperconjugation, and t_H is the hopping between hydrogen $1s$ and the carbon sp^3 orbitals. We choose $t_h = \frac{1}{2} \cos(\phi)t_2$. $\phi = 25.16^\circ$ is the angle between the tetrahedral sp^3 bonds and the neighboring p_z orbital. For the diagonal on-site energy, we choose $\varepsilon_H = \varepsilon_C = 0$ for hydrogen because the CH bond is covalent. For oxygen, we choose $\varepsilon_O = 2t_1$ (Ref. 13) to account for its stronger attraction to electrons than carbon. We found by numerical diagonalization that there are two localized states. One is below the valence band with heavy weighting on the oxygen atom (oxygen level), and another one is inside the gap (deep level). The Fermi level is between the top of the valence band and the deep level. The obvious local phonon mode with strong coupling to the deep electron level is the oscillation of the C=O double bond.

The capture rate P_k for a free electron with momentum k is determined by the non-adiabatic part of the Hamiltonian.¹²

$$\begin{aligned}
P_k &= \frac{2\pi}{\hbar^2\omega} |\langle \psi_k, \chi_{k,0} | H^{NA} | \psi_d, \chi_{k,p} \rangle|^2 \\
&= 2\pi\omega \left| \left\langle \psi_k \left| \frac{\partial}{\partial Q} \right| \psi_d \right\rangle_{Q^*} \right|^2 I_k(p),
\end{aligned} \tag{4}$$

where $\psi_{k,d}$ and $\chi_{k,d}$ are the wave function for the electronic and lattice parts, respectively. $k(d)$ corresponds to a free (defect) state, ω is the angular frequency of the local mode, I_k is the lattice factor,¹² and Q is the dimensionless normal coordinate of the local phonon mode. The minimum of total energy is at $Q=0$ if the electron is free, and shifted to Q^* when the electron is captured. $p \equiv (\varepsilon_k^+ - \varepsilon_d^+)/\hbar\omega$ is the number of phonons emitted. For the case of an exciton, the electron can drop into the level while the hole is released to the valence band and becomes a free charge carrier, if the binding energy of the exciton is smaller than the binding energy of the deep level. The excess energy is carried by the hole kinetic energy and the local phonon. The exciton quenching rate P_{ex} becomes¹¹ $P_{ex} = \sum_k |\phi(k)|^2 P_k [p(k)] \theta[p(k) - 1]$, where $\phi(k)$ is the exciton wave function. Now the number of emitted phonons p is a function of the hole momentum k , because the hole kinetic energy in the final state depends on k . Energy conservation gives $p(k) = [t_1 - t_2 - E_B - E_d(Q^*) - T(k)]/\hbar\omega$, where $T(k) = \varepsilon_0^- - \varepsilon_k^-$ is the hole kinetic energy, and E_B is the exciton binding energy. The step function in P_{ex} guarantees that the quenching occurs only when the final state is indeed lower than the initial state by more than the energy of one phonon. In practice we take the exciton wave function $\phi(k)$ to be a Lorentzian with width $1/a_B$, where a_B is the exciton Bohr radius. Lorentzian is considered to be the most reasonable line shape because it corresponds to exponential decay in the real space. Our result, however, is not sensitive to the choice of the line shape. The exciton wave function provides an averaging over the k region around conduction-band bottom, so only the value of a_B , which sets the extension of the wave function is important. The process of hole capture and electron release can be considered in the same way. The only difference is that the emitted phonons need to compensate the energy difference between the deep level and the valence band instead of the conduction band. We consider only the electron capture process below, because hole is believed to be more mobile than electron and accounts for the major part of the PC.³

For convenience we define the capture rates $1/\tau_1^{ex} \equiv P_{ex}N_c$ and $1/\tau_1^f(k) \equiv P_k N_c$. Here, $N_c = N/2$ is the number of repeat units in the chain. The time constants $\tau_1^{ex,f}$ have the advantage of being independent of the system size. For a chain with N_d defects, the capture rate is $P_k N_d = n_d/\tau_1$, where the defect density $n_d = N_d/N_c$ is the number of defects per repeat unit. The results of the calculations are summarized in Table I. $1/\tau_1^{ex}$ for the twist defect is shown in Fig. 3. For $\theta < 1.03$, $p(k) < 1$, and the quenching cannot occur. The parameters suitable for PPV are used here:^{13,14} $t_1 = -2.9$ eV, $t_2 = -1.52$ eV, $t_H = -4$ eV, $\varepsilon_0 = 2t_1$, $E_B = 0.3$ eV, and $a_B = 5$ a. $\hbar\omega = 0.18$ and 0.17 eV and $\alpha = 4.1$ and 3 eV/Å for C=C and C=O bond, respectively. The rates are temperature-independent and apply to $\hbar\omega\beta \gg 1$, which covers room temperature and below.

TABLE I. The local mode displacement Q^* , the new minimum of total energy $E_d(Q^*)$, the capture rates for free electron $1/\tau_1^f$ and the exciton $1/\tau_1^{ex}$ per unit defect density are shown for three types of deep level defects. $1/\tau_1^f$ is evaluated at the conduction bottom $ka = \pi/2$.

Defect type	Q^*	$E_d(Q^*)$ (eV)	$1/\tau_1^f$ (ns ⁻¹)	$1/\tau_1^{ex}$ (ns ⁻¹)
Twist ($\theta = 3\pi/8$)	0.32	0.76	57	3.2×10^3
Boundary	1.0	-0.10	1.4×10^{-2}	4.5
Oxygen	0.35	0.77	4.6	3.6×10^2

The photocarrier generation can be described by a set of rate equations for the exciton number per unit cell $n_{ex}(t)$ and the defect filling fraction $f(t)$, where t denotes time. Assume that there are n_d defects per unit cell with volume v . The density of free carriers is $n_{df}(t)$ in this simple model. For a photon flux I_p and an absorption coefficient α_p , the rate equation becomes

$$\begin{aligned}
\frac{dn_{ex}}{dt} &= \alpha_p v I_p - \frac{1}{\tau_r} n_{ex} - \frac{1}{\tau_1} n_d (1-f) n_{ex}, \\
\frac{df}{dt} &= \frac{1}{\tau_1} n_{ex} (1-f) - \frac{1}{\tau_2} f^2 n_d.
\end{aligned} \tag{5}$$

Here, τ_r is the radiative lifetime of the exciton and τ_1 is τ_1^{ex} for simplicity. The free hole capture rate $1/\tau_2$ is taken as an adjustable parameter. We consider two special cases of the solutions: (1) A δ -function laser pulse which sets the initial condition $n_{ex} = n_0$ and $f = 0$; (2) The steady state where all the quantities are constant. The solution for the first case under the condition $n_0 > n_d$ is shown in Fig. 4. The parameters used are $\tau_r = 1.0$ ns (Ref. 15) and $1/\tau_1 = 3.6 \times 10^2$ ns⁻¹ for oxygen defect (Table I). τ_2 is chosen to be 10 times τ_1 . The qualitative behavior is independent of τ_2 , as long as it is not too large to prevent the defect saturation. The carrier number $n_{df}(t)$ saturates much faster than the decay of the exciton, so the photocarrier generation process occurs

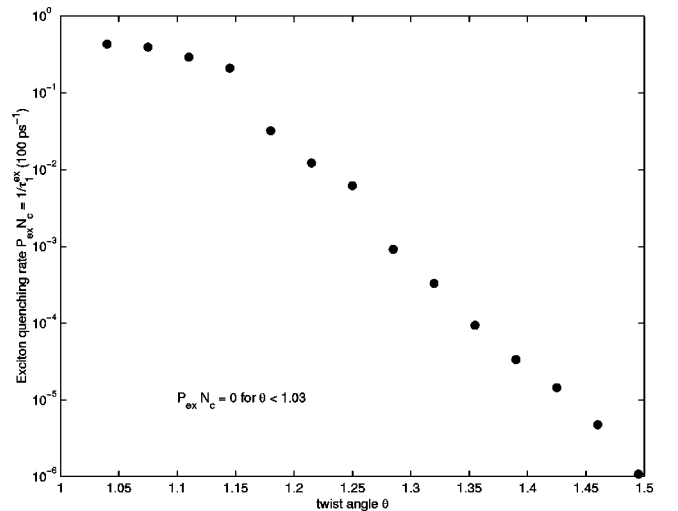


FIG. 3. The exciton quenching rate per unit defect density $1/\tau_1^{ex}$ is plotted as a function of double bond twist angle θ (in radian). The bond is broken when $\theta = \pi/2$.

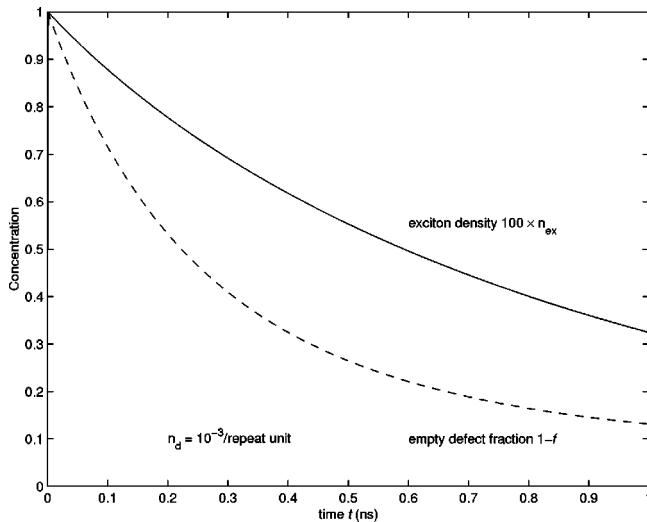


FIG. 4. The dynamics of exciton decay n_{ex} and the defect filling f is shown for the system excited by a short optical pulse, which generates an initial exciton density n_0 of 10^{-2} /cell. The defect density $n_d = 10^{-3}$ /cell. The exciton decay lifetime is about 1 ns, while the defect is filled in about 0.25 ns.

only in the first quarter of the exciton lifetime when there are still empty defects available. This explains the striking behavior observed in two-pump PC experiments,⁷ which shows that the carrier generation process does stop much earlier than the exciton lifetime. The steady state carrier generation quantum yield ζ is defined as the ratio between the photon absorption rate and the carrier generation rate:

$$\zeta = \frac{(1-f)n_{ex}n_d/\tau_1}{\alpha_p I_p v} = \frac{(1-f)n_d/\tau_1}{(1-f)n_d/\tau_1 + 1/\tau_r}, \quad (6)$$

which is equal to the ratio between the exciton quenching rate $(1-f)n_d/\tau_1$ and the total decay rate. The quantum yield decreases with the pumping intensity, because of the saturation of the deep level by the pump.

The quantum yield of photoluminescence (PL) was found to be reduced to one half when there is one oxygen atom per

400 PV units,⁵ corresponding to $n_d = 1/400$. The exciton quenching lifetime τ_{nr} or the nonradiative lifetime is equal to $\tau_1/n_d = 1.1$ ns. The PL quantum yield is $\tau_{nr}/(\tau_r + \tau_{nr})$. For $\tau_r = 1$ ns, the quantum yield is 0.53, close to the value of 0.5 observed in the experiment. For other oxygen densities, the PL yield basically follows the above relation, within about 30 % discrepancy, with τ_{nr} inversely proportional to the n_d for $n_d < 1/100$.⁴ For larger oxygen densities, our independent defect assumption does not hold. So the prediction is not expected to be very reliable. As for the case of a structural defect, the carrier generation quantum yield ζ was found to be 1.2×10^{-3} in a high purity sample without oxidation.¹ The photocurrent is away from saturation so $f \approx 0$, and the yield takes a simple form $\zeta = n_d \tau_r / \tau_1$. Note this expression is independent of the adjustable parameter τ_2 . Because there is no oxygen in the sample, the exciton quenching is due only to the structural defect. We assume the main defect is the midgap level at the chain boundary. Since half of them are filled, the empty defect density n_d is $1/N_c$. Using the value $1/\tau_1 = 4.5$ ns⁻¹ (Table I), we obtain $N_c = 3.7 \times 10^3$. N_c can be estimated independently from the molecular weight analysis. It is usually in the order of 10^3 . For example,¹⁶ the average molecular weight of RO-PPV, with monomer molecular weight about 400, has recently been determined to be 2×10^6 , corresponding to $N_c = 5 \times 10^3$, again consistent with our prediction. For the inert samples, there is no oxygen defect. We consider only the midgap level at the boundary and ignore the twists. In fact, the shallow level at small twist angle does not capture the exciton efficiently. Large twist angle close to $\pi/2$ is not that different from the chain boundary. The ‘‘intrinsic’’ photocurrent of pure samples can therefore be primarily accounted for by the structural defects. It is disorder sensitive, and not mainly determined by intrinsic properties like the exciton binding energy.

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¹D. Moses, J. Wang, G. Yu, and A. Heeger, Phys. Rev. Lett. **80**, 2685 (1998).

²S. Barth and H. Bässler, Phys. Rev. Lett. **79**, 4445 (1997).

³*Primary Photoexcitations in Conjugated Polymers: Molecular Exciton Versus Semiconductor Band Model*, edited by N. Sariciftci (World Scientific, Singapore, 1997).

⁴H. Antoniadis, L. Rothberg, F. Papadimitrakopoulos, M. Yan, M. Galvin, and M. Abkowitz, Phys. Rev. B **50**, 14 911 (1994).

⁵M. Yan, L. Rothberg, F. Papadimitrakopoulos, M. Galvin, and T. Miller, Phys. Rev. Lett. **73**, 744 (1994).

⁶D. Vacar, E. Maniloff, D. McBranch, and A. J. Heeger, Phys. Rev. B **56**, 4573 (1997); C. H. Lee, G. Yu, K. Pakbaz, D. Moses, N. S. Sariciftci, F. Wudl, and A. J. Heeger, Synth. Met. **70**, 1353 (1995).

⁷L. Rothberg, M. Yan, A. Fung, T. Jedju, E. Kwock, and M. Galvin, Synth. Met. **84**, 537 (1997).

⁸L. Onsager, Phys. Rev. **54**, 554 (1938).

⁹M. Chandross, S. Mazumdar, S. Jeglinski, X. Wei, Z. Vardeny, E. Kwock, and T. Miller, Phys. Rev. B **50**, 14 702 (1994).

¹⁰S. Alvarado, P. Seidler, D. G. Lidzey, and D. D. C. Bradley, Phys. Rev. Lett. **81**, 1082 (1998).

¹¹H. F. Meng and T. M. Hong (unpublished).

¹²M. Lannoo and J. Bourgoin, *Point Defects in Semiconductors* (Springer, Berlin, 1981).

¹³C. A. Coulson, B. O’Leary, and R. B. Mallion, *Hückel Theory for Organic Chemists* (Academic Press, London, 1978).

¹⁴P. Gomes da Costa and E. Conwell, Phys. Rev. B **48**, 1993 (1993).

¹⁵N. Greenham, I. Samuel, G. Hayes, R. Phillips, Y. Kessener, S. Moratti, A. Holmes, and R. Friend, Chem. Phys. Lett. **241**, 89 (1995).

¹⁶J. H. Hsu, W. S. Fann, P. H. Tsao, K. R. Chuang, and S. A. Chen, J. Phys. Chem. A **103**, 2375 (1999).