Charge carrier generation through reexcitations of an exciton in poly(*p*-phenylene vinylene) molecules

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Charge carrier generation due to reexcitations of an exciton in poly(*p*-phenylene vinylene) (PPV) molecules is studied theoretically in the framework of the tight-binding approach. Two different kinds of optical transitions for an exciton are suggested. It is found that the high-energy transition will dissociate the exciton into free charges, which is responsible for the photocurrent. The state from the low-energy transition is strongly field dependent. Only at a strong electric field does the exciton dissociate into free charges. The different quantum efficiency of charge carrier photogeneration in a solid-state PPV from that in a solution one is studied by including the effect of interchain couplings on the exciton dissociation.

I. INTRODUCTION

Organic semiconductors, including high conjugated polymers such as poly(*p*-phenylene vinylene)s (PPVs), have become very promising functional materials in optoelectronic devices—e.g., light-emitting diodes,[1,2] plastic lasers,[3] and photovoltaic cells,[4] as well as organic spin valves.[5] Extensive research has been carried out with the goal of understanding the photophysics and carrier characteristic of this class of materials. Compared to inorganic materials, the strong electron-lattice interaction of organic materials means the electronic and optical properties of these materials can be tailored over a wide range by relatively simple chemical modifications of the molecular structure. Despite many advances, a deeper understanding of the photoexcited species and the charge carrier photogeneration is still necessary in order to further improve the performance of these optoelectronic devices.

It has been predicted that polarons or bipolarons are the main charge carriers in organic polymers.[6,7] The photogeneration mechanism of these carriers and their yields have previously been the main focus of study.[8–21] As early as the 1960s, investigations were made of charge carrier photogeneration in some molecular crystals, such as anthracene crystals,[8,9] which were explained in terms of the Onsager theory of geminate recombination. In recent years, different experimental data have been interpreted to support two very different concepts concerning the charge carrier photogeneration in polymers. Miranda, Moses, and Heeger indicated that both charge carriers (polarons) and neutral excitons are independently generated via optical interband transitions[10,11] and the process is independent of the electric field. On the other hand, a number of experiments carried out on derivatives of poly(*p*-phenylene vinylene) (Refs. 16–18) and methyl-substituted ladder-type poly(*p*-phenylene) (m-LPPP) (Refs. 19–21) considered charge carrier generation as a two-step process, in which neutral excitons are first created due to photoexcitation and then dissociate into charge carriers through reexcitation with electric field or are temperature assisted. Although most of the experimental data favor the latter method, the mechanism of exciton dissociation is

still a heavily disputed question. By means of electric-field-modulated femtosecond pump-probe absorption spectroscopy,[19] Gulbinas *et al.* showed that two different exciton dissociation mechanisms take place depending on the excitation photon energy. When the excitation energy is relatively low, excitons slowly dissociate into charge pairs during the entire exciton lifetime and the process is strongly electric field dependent. When the excitation energy is high, charge pairs appear fast and require less assistance of an electric field for the exciton dissociation. Unfortunately, it is impossible to distinguish the "charge pairs" between free charge carriers participating in photocurrent and Coulombically bound charge pairs not participating in photocurrent.

In this paper, two kinds of optical transitions for an exciton in PPV molecules are suggested that are external electric field assisted, by which we theoretically explore the mechanism of charge carrier photogeneration due to exciton dissociation. Contribution of the "charge carriers" to the photocurrent is investigated. In addition, effects of the external electric field and interchain couplings on the exciton dissociation are also included to explain the different quantum efficiency of charge carrier photogeneration in a solid-state PPV from that in a solution. The presentation is organized as follows. The model Hamiltonian is established, and the scheme of a self-consistent calculation is outlined in Sec. II. In Sec. III we describe and discuss the results of our numerical computation. Finally, in Sec. IV our conclusions are summarized.

II. MODEL

Recently, theoretical investigations concerning the charge carrier photogeneration in polymers have been performed using the Pariser-Parr-Pople model.[22] However, the model does not include the effect of the lattices and it is actually a rigid-band correlated electron model. Here we suggest a tight-binding electron-lattice interacting model, which is originally proposed to describe a long trans-polyacetylene chain by the well-known Su-Schrieffer-Heeger (SSH) model.[23] By a renormalization treatment, the PPV molecule can be regarded as a one-dimensional chain and each repeat unit con-
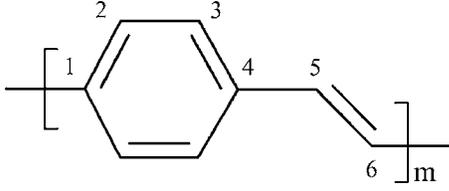
FIG. 1. Schematic diagram of a PPV molecule with m repeat units.

tains six sites along the chain direction. The structure sketch of a PPV molecule with m repeat units is shown in Fig. 1. In the framework of the tight-binding approach, there are six electron transfer integrals $t_{n,n+1}$ for each repeat unit, of which only four transfer integrals are independent due to the molecular spatial symmetry—i.e.,

$$t_{1,2} = t_{3,4} = t_1', \quad t_{2,3} = t_2', \quad t_{4,5} = t_{6,1} = t_3', \quad t_{5,6} = t_4'.$$

The above four parameters are simplified with two parameters t_1 and t_2 by writing the transfer integrals in the form

$$t_{n,n+1} = t_0 - \alpha(u_{n+1} - u_n) - t_1 \cos n\pi$$
$$+ t_2 \cos\left(\frac{n+1}{3}\pi\right)\delta\left(\frac{n+1}{3}, \text{int}\right),$$

where $\delta\left(\frac{n+1}{3}, \text{int}\right)=1$, if $\frac{n+1}{3}=\text{int}$, and $\delta\left(\frac{n+1}{3}, \text{int}\right)=0$, if $\frac{n+1}{3} \neq \text{int}$. t_0 is the electron hopping integral for a uniform bond structure, α is the electron-lattice interaction constant, and u_n is the displacement of a unit at site n. "int" indicates an integer.

If we include the effect of the external electric field E and the internal electron-electron (e-e) interaction, the Hamiltonian of a single PPV molecule chain is written as

$$H = H_0 + H_E + H_{e\text{-}e}, \tag{1}$$

$$H_0 = -\sum_{n,s} t_{n,n+1}(C_{n+1,s}^\dagger C_{n,s} + C_{n,s}^\dagger C_{n+1,s}) + \frac{1}{2}K\sum_n (u_{n+1}-u_n)^2$$
$$+ K'\sum_n (u_{n+1}-u_n), \tag{2}$$

$$H_E = \sum_n eE(na + u_n)(C_{n,s}^\dagger C_{n,s} - 1), \tag{3}$$

$$H_{e\text{-}e} = U\sum_n C_{n,\uparrow}^\dagger C_{n,\uparrow} C_{n,\downarrow}^\dagger C_{n,\downarrow} + V\sum_{n,s,s'} C_{n,s}^\dagger C_{n,s} C_{n+1,s'}^\dagger C_{n+1,s'} \tag{4}$$

where $C_{n,s}^\dagger$ ($C_{n,s}$) is the creation (annihilation) operator of an electron at site n with spin s ($s=\uparrow, \downarrow$). K is the elastic constant. The third term is to stabilize a PPV molecule with open ends, and K' is given by

$$K' = -\frac{2\alpha}{N-1}\sum_{\mu,n,s}{}' Z_{\mu,n,s} Z_{\mu,n+1,s}, \tag{5}$$

where N is the total site number of a PPV molecule. Σ' means sum over the occupied states.

H_E is the interaction of electrons with the applied electric field E and a the lattice constant. $H_{e\text{-}e}$ is the e-e interaction, which is treated with the Hartree-Fock approximation for simplicity. The electronic eigenstate $\psi_{\mu,s}=\Sigma_n Z_{\mu,n,s}|n\rangle$ is obtained by solving the Schrödinger equation of the electronic Hamiltonian, which is dependent upon the bond displacement $u_{n+1}-u_n$. On the other hand, by minimizing the total energy, the displacement $u_{n+1}-u_n$ is determined by the eigenstates

$$u_{n+1} - u_n = -\frac{2\alpha}{K}\sum_{\mu,s}{}' Z_{\mu,n,s} Z_{\mu,n+1,s} - \frac{K'}{K}$$
$$+ \frac{eE}{K}\left(\sum_{\mu,s,m=1}^{n}{}' Z_{\mu,m,s}^2 - n\right). \tag{6}$$

It is obvious that the displacement $u_{n+1}-u_n$ and eigenstate $Z_{\mu,m,s}$ depend upon each other, which can be calculated iteratively. Then we can obtain the charge density distribution

$$\rho_n = \sum_{\mu,s}{}' |Z_{\mu,n,s}|^2 - 1. \tag{7}$$

III. RESULTS AND DISCUSSION

For a PPV molecule, we set the parameters as $\alpha = 102.9$ eV/nm, $t_0 = 2.66$ eV, $a = 0.122$ nm, and $K = 9900.0$ eV/nm^2, referring to Refs. 24 and 25 and e-e interaction $U=2.0$ eV and $V=U/3$. By adjusting the magnitudes of t_1 and t_2, we get an energy gap of $E_g=2.8$ eV, which is consistent with other works on pristine PPV.[24–26]

Generally, in a photoexcitation process the photon energy is transferred to electrons and phonons, both of which are excited to higher-energy states. In organic materials the situation becomes more complex than in normal inorganic materials due to the much stronger electron-lattice interactions. As is well known, in the usual inorganic materials an exciton is an excited electron-hole pair confined by the Coulomb interaction. In polymers, the electron-lattice interaction, which is much stronger than the electron-hole Coulomb interaction, makes the exciton localized or self-strapped. It is well known that the band-edge transition in PPVs leads to the formation of an exciton, which is responsible for the PPV photoluminescence and electroluminescence. The schematic diagram for the energy levels of a PPV molecule and possible optical transitions are shown in Fig. 2, where we denote ε_i^v ($i=1,2,\ldots$) to be the ith energy level in the valence band counted from the top and ε_j^c ($j=1,2,\ldots$) to be the jth energy level in the conduction band counted from the bottom. The band-edge transition $P_0(\varepsilon_1^v \rightarrow \varepsilon_1^c)$ is indicated in Fig. 2(a). In this case, ε_1^v and ε_1^c go into the gap as discrete levels (ε_d and ε_u) and their electronic states become localized due to strong electron-lattice interactions. An exciton can be reexcited by a second photoabsorption, which may result in three optical transitions as shown in Fig. 2(b): transition P_1 from ε_u to ε_2^c, P_2 from ε_d to ε_2^c, and P_3 from ε_d to ε_u. It is known that transition P_3 will lead to the formation of a biexciton,[27] which has been widely studied.[28] Here we will give a detailed investigation of transitions P_1 and P_2.
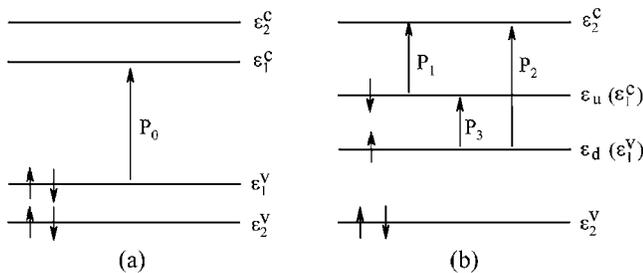
FIG. 2. Schematic diagrams for the energy levels of a PPV molecule with a ground state (a) and an exciton state (b). P_0 indicates the band-edge transition between ε_1^v and ε_1^c, which will result in an exciton; $P_1(\varepsilon_u \to \varepsilon_2^c)$, $P_2(\varepsilon_d \to \varepsilon_2^c)$, and $P_3(\varepsilon_d \to \varepsilon_u)$ separately indicates the optical transition of an exciton to a high-lying excited state.

Quantum mechanics tells us that, for a symmetrical system, each electronic state has a certain parity, either odd parity or even parity. Optical transitions are dipole allowed only between electronic states with opposite parities. In actual materials, the parity of the electronic states can be easily destroyed, such as by the effect of disorder or the assistance of an external electric field E. Figure 3 shows the dependence of the transition dipole moments for P_1 (solid line) and P_2 (dashed line) on the external electric field. It is found that both transitions P_1 and P_2 are electric field dependent. Transition P_2 will become permitted when an external electric field is included.

The lattice distortion and the charge density distribution after transition P_1 (denoted state S_{P_1}) are shown in Fig. 4, where we choose the conjugation length of the molecular chain as $L=124a$. Apparently, it is no longer an exciton as there appears a charge distribution confined to two local lattice defects. Through decomposing the intragap states [i.e., four discrete levels formed by transition P_1 with the upper two $(\varepsilon_1^c, \varepsilon_2^c)$ and the lower two $(\varepsilon_1^v, \varepsilon_2^v)$ being degenerate separately] into four different cases,[29] An et al. predicted that S_{P_1} is a mixed state consisting of an exciton and a polaron pair.

Now let us focus on the dissociation of state S_{P_1} by applying an external electric field E. Since state S_{P_1} consists of an exciton and a polaron pair, the dissociation process should include two steps if the exciton and the polaron pair are
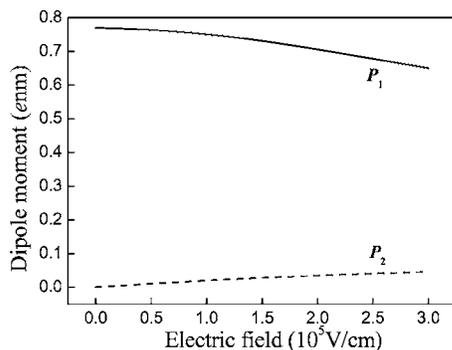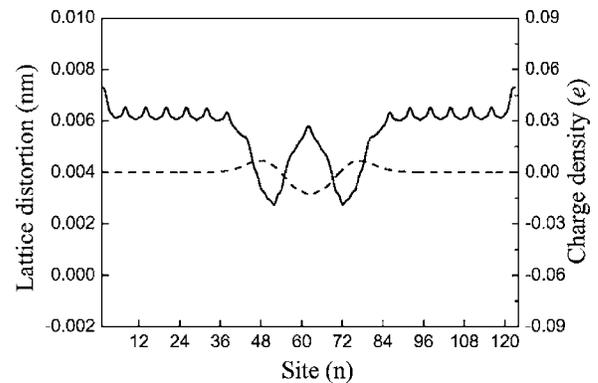
FIG. 4. High-lying excited state resulting from transition P_1 in the PPV molecule without electric field. The solid line shows the lattice distortion and the dashed line charge density distribution. The conjugation length of the molecular chain is $L=124a$.

independent: the dissociation of a polaron pair at a weak electric field and the dissociation of an exciton at a stronger electric field. However, the calculation only accounts for one electronic charge after the dissociation, which means that the exciton and the polaron pair in state S_{P_1} are not independent but coupled with each other. Figure 5 presents the dependence of induced charges on the electric field. As can be seen, the induced charges increase with the increase of the electric field and finally reach one electronic charge when $E \geq 0.3 \times 10^5$ V/cm. When $E < 0.3 \times 10^5$ V/cm, the energy resulting from the external electric field is not strong enough to dissociate state S_{P_1}. A result at $E=0.15 \times 10^5$ V/cm is shown in Fig. 6(a), where the direction of the electric field is from left to right along the molecular chain. The induced negative charges are confined on the left side and the positive ones on the right side of the chain, each with a localized lattice defect. As they are bound together, the induced charges (pair) have no contribution to the photocurrent. When $E \geq 0.3 \times 10^5$ V/cm, state S_{P_1} is dissociated into a negative polaron (P$^-$) and a positive polaron (P$^+$), as shown in Fig. 6(b), which contribute to the photocurrent. In short, free charge carriers can result from the exciton dissociation by transition P_1 and the process is strongly field dependent.

For transition P_2 (denoted state S_{P_2}), ε_2^v and ε_2^c also go into the gap as discrete levels and become localized states due to the strong electron-lattice interactions. Through de-

FIG. 3. Dependence of the transition dipole moments for P_1 (solid line) and P_2 (dashed line) on the external electric field.
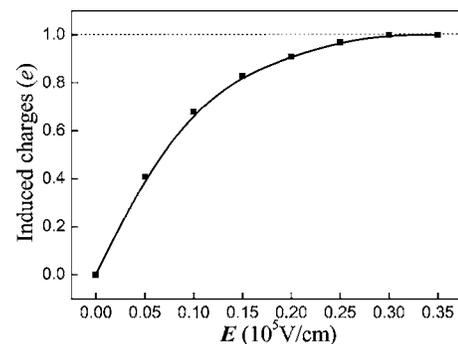
FIG. 5. Dependence of the induced charges in the PPV molecule after transition P_1 on the external electric field E.
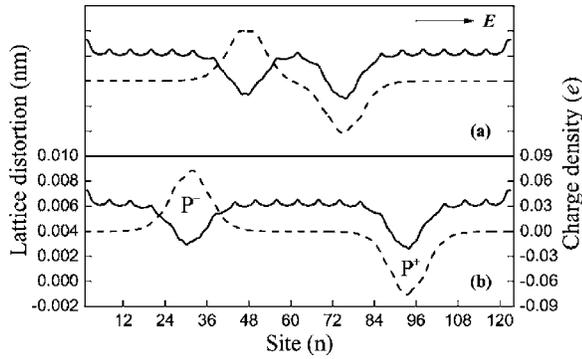
FIG. 6. High-lying excited states resulting from transition P_1 in the PPV molecule with an electric field $E = 0.15 \times 10^5$ V/cm (a) and $E = 0.3 \times 10^5$ V/cm (b). The direction of the applied electric field E is from left to right along the molecular chain. The solid line shows the lattice distortion and the dashed line charge density distribution.

composing the four intragap states of S_{P_2}, we find that the singly occupied state ε_2^c and the doubly occupied state ε_2^v constitute a negative polaron, while the singly occupied state ε_1^c and the unoccupied state ε_1^v constitute an excited positive polaron, which was found to have a reverse polarization character in our previous work.[30] Unlike transition P_1, the negative polaron and the excited positive polaron in S_{P_2} are found to be independent and the induced charge keeps one electronic charge unchanged with the variation of the electric field. Figure 7 shows the lattice distortion and the charge density distribution after transition P_2 with an electric field $E = 0.1 \times 10^5$ V/cm. Apparently, transition P_2 dissociates the exciton into a negative polaron (P^-) and an excited positive polaron ($\hat{P}^+$) contributing to the photocurrent.

Here it should be stressed that, although the exciton dissociations by transitions P_1 and P_2 are both electric field dependent, the two processes are very different. For transition P_1, the absorbed photon energy is not strong enough to dissociate the exciton into free charge carriers. That is, there exists a "potential barrier" between the S_{P_1} state and the free charge carriers, which can be reduced by an external electric
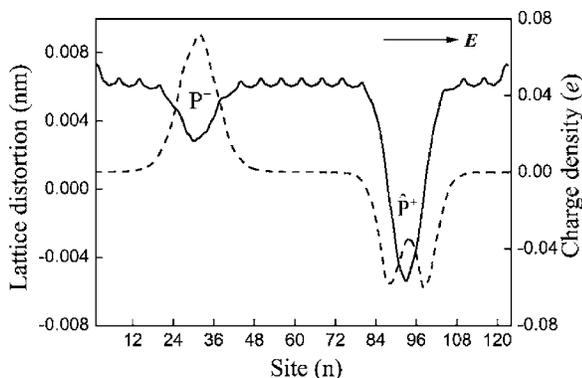
FIG. 7. High-lying excited state resulting from transition P_2 in the PPV molecule with an electric field $E = 0.1 \times 10^5$ V/cm. The direction of the applied electric field E is from left to right along the molecular chain. The solid line shows the lattice distortion and the dashed line charge density distribution.

field. For transition P_2, the absorbed photon energy directly dissociates the exciton, which does not need the assistance of an electric field. The applied electric field only ensures transition P_2 to be dipole allowed.

In actual organic materials such as solid films of polymers or oligomers used in organic light-emitting diodes (OLEDs), the molecules are not isolated and there are interchain interactions between the molecular chains. By recording the sub-picosecond transient complex conductivity using THz time-domain spectroscopy,[17] Hendry *et al.* showed that the quantum efficiency of charge photogeneration is two orders of magnitude smaller in a solution ($\sim 10^{-5}$) than in a solid film ($\sim 10^{-3}$) of MEH-PPV. Miranda *et al.* also indicated that polaron pairs can be photogenerated in a dilute solution of derivative PPVs with quantum efficiency $\sim 3\%$, about one-third of that for a solid film of the same polymer.[11] Apparently, interchain interactions can remarkably improve the quantum efficiency of charge carrier photogeneration.

From the work of Bounds *et al.* in the early 1980s,[31,32] we know that photoexcitations will lead to the formation of charge-transfer (CT) excitons by the interchain interactions in solid samples. A CT exciton has a relatively large radius, and its binding energy is roughly determined by the Coulombic force even in the organic materials. As a result, the photocurrent in solid samples mainly comes from the thermal dissociation of CT excitons into free charge carriers. The process may be responsible for the different quantum efficiency of charge carrier photogeneration in a solid-state sample from that in a solution one. Here we try to give a simple consideration about the effect of interchain interactions on the exciton dissociation. The Coulombic correlation between the chains is not included in the present work. Therefore, the results are only qualitatively helpful to understand the experimental observations. The interaction between two coupled PPV molecules with a parallel alignment, in the framework of the tight-binding approach, is described by

$$H_\perp = -\sum_{n,s} t_\perp (C_{1,n,s}^\dagger C_{2,n,s} + C_{2,n,s}^\dagger C_{1,n,s}), \qquad (8)$$

where $t_\perp$ stands for the transfer integral between sites labeled by same index n on each molecule chain.

For a two-chain system, photoexcitation will lead to two possibilities for the formation of exciton states. The first possibility is a strongly bound electron-hole pair forming an intrachain exciton.[33,34] The second possibility is the formation of a spatially indirect exciton,[35,36] which is formed as a result of interchain electron transfer (i.e., charge-transfer exciton). As is well known, the photoluminescence (PL) in PPVs has been attributed to the radiative decay of intrachain excitons. For this kind of exciton, dependences of the induced charges on the interchain couplings after transition P_1 are shown in Fig. 8. It is found that the induced charges increase with the interchain couplings. Therefore, an intrachain exciton is more easily dissociated in a solid film than that in a dilute solution, which is qualitatively consistent with the experimental observations. Theoretically, when the interchain coupling $t_\perp \geq 0.15$ eV, the induced charges will reach one electronic charge (at $E = 0.25 \times 10^5$ V/cm), which means that transition P_1 has dissociated the exciton into free
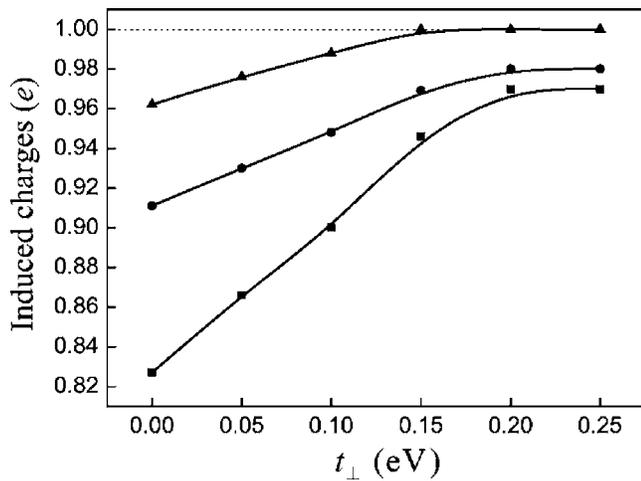
FIG. 8. Dependence of the induced charges in the two PPV molecules on the interchain couplings after transition P_1. Squares indicate an electric field $E=0.15\times10^5$ V/cm; circles and triangles separately indicate $E=0.2\times10^5$ V/cm and $E=0.25\times10^5$ V/cm.

charge carriers. Of course, in actual materials, the interchain coupling is usually smaller than $t_\perp=0.15$ eV. In addition, the Coulombic correlation between the electron and hole impedes exciton dissociation. Therefore, even if the interchain coupling is included, the intrachain exciton does not dissociate easily by transition P_1. To give a more reasonable explanation for some experimental observations about the exciton dissociation, additional physical processes should be taken into account, such as the interchain charge transfer, strong external fields, and, especially, the thermal effect. For example, in 1992, Frankevich *et al.* demonstrated the importance of the thermal effect in considering the formation and dissociation of a charge-transfer exciton.[35] Recently, Troisi

and Orlandi indicated that, in organic crystals, thermal molecular motions are sufficient to destroy the translational symmetry of the electronic Hamiltonian and make the band description inadequate for room-temperature organic crystals.[37]

IV. SUMMARY

Charge carrier photogeneration is important for photovoltaic cells or electrophotographic devices, while the opposite process (recombination of a charge pair into an exciton) determines the operation of light-emitting diodes. According to the experimental data favoring charge carriers resulting from exciton dissociation, we theoretically studied the process of exciton dissociation by considering two kinds of optical transitions for an exciton. The calculation supports the conclusion that photocurrent in conducting polymers may result from a dissociation of an exciton. It was found that the two kinds of optical transitions have a different dependence upon the external electric field. In addition, the interchain coupling has a certain effect on the exciton dissociation, which makes the different quantum efficiency of charge carrier photogeneration in a solid-state sample from that in a solution. The theoretical calculation is qualitatively consistent with the experimental observations. Further investigations should be done in the future that include additional physical processes, such as the interchain charge transfer, strong external fields, and the thermal effect.

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