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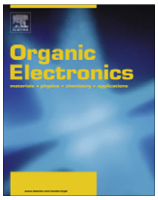

Biexcitons generation in a polymer by a femtosecond electric pump pulse

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ABSTRACT

By applying a femtosecond electric pump pulse to a polymer, biexcitons are obtained and the relation between its yield and the photoexciting process is also presented. The simulations are performed within the framework of an extended version of one-dimensional Su–Schrieffer–Heeger tight-binding model combined with a nonadiabatic evolution method. In the discussions, effects of both the photoexciting energy and intensity are considered. The main result is that the yield ratio of biexcitons and excitons increases rapidly with the photoexciting intensity, and there exists a critical photoexciting intensity, beyond which the yield efficiency of biexcitons is even higher than that of excitons. The result theoretically verifies that, by increasing the photoexciting intensity, we can obtain biexcitons efficiently, which is consistent with the experimental speculation.

1. Introduction

Organic polymers, such as poly(*p*-phenylene vinylene)s (PPVs), are highly conjugated linear macromolecules that are of great current interest because of their semiconductor-like properties and ease of processing. As a class of organic semiconductor, the bond structure of these materials is sensitively correlated to their electronic structure due to the strong electron–lattice interactions, which consequently results in many peculiar phenomena [1]. For example, in polymers or other organic semiconductors, the tightly bound electron–hole pairs (i.e., self-trapped excitons and their complexes) are the only primary photoexcited species [2–4]. All the applications of polymers in optoelectronic devices, such as polymer light-emitting diodes (PLEDs), organic photovoltaic (OPV) cells, and organic semiconductor lasers (OSLs), should benefit from the deeper understanding for these photoexcited species.

As we know, an exciton, consisting of a single electron–hole pair, is the lowest optical state in polymers [5]. Through the radiative decay and dissociation, such an element excitation will be responsible for the light emission [6] and photocurrent [7], respectively. Thus, the formation and the consequent evolution of an exciton should play an important role in the optoelectronic applications of polymers. However, the optoelectronic properties of polymers dominated solely by excitons are mostly linear. It has been found that, in some experimental conditions (e.g., at a high excitation intensity) [8,9], polymers will present an apparent nonlinear response, and thus possess potential applications in laser devices. In fact, the nonlinear phenomena have been widely attributed to the formation of exciton complexes [10], such as a biexciton involving double electron–hole pairs [8–12]. Biexcitons were firstly proposed, by their signatures in photoluminescence (PL) spectra, in conventional inorganic semiconductors, especially in some quantum confined systems (e.g., CuCl quantum dots [13], $In_xGa_{1-x}As/GaAs$ quantum wires [14], and InGaAs/GaAs quantum wells [15], etc.). From the 1990s, in organic charge-transfer solids [10], single-walled carbon nanotubes [16–19], and especially in polymers [8,9,11,12], extensive research has been carried out from both experimental and theoretical viewpoints to understand their nature and dynamics.

Up to now, the experimental data have indicated that formation of biexcitons is mostly excitation intensity dependent. In 1997, by increasing the excitation intensity Kranzelbinder et al. found a hyperlinear increase of the light emission of poly (*p*-phenylene)-type ladder polymer,

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and attributed it to the formation of biexcitons for their intrinsic high radiative quantum efficiency [8]. In the following year, with the method of femtosecond transient absorption (TA), Klimov et al. gave a clear experimental verification for the existence of biexcitons in a five-ring oligomer of PPV [9]. They emphasized that stable biexcitons can only exist in solutions of PPVs at high excitation intensities. Theoretically, more attention is paid to its formation mechanism. Mazumdar et al. considered different one-dimensional models to describe different classes of one-dimensional organics, and speculated that the exciton-to-biexciton transition should be a fundamental way upon the formation of biexcitons [20]. Within the Pariser–Parr–Pople (PPP) model, Pasquinelli and Yaron investigated the size confinement effect on the formation of biexcitons in a finite polymeric chain [21]. They indicated that there exists a critical chain length, below which the size confinement effect results in a strong enough exciton–exciton interaction leading to binding between them to form a biexciton. In addition, the characteristic of biexcitons under an external electric field was focused by Sun et al. They predicted that a polymer with a biexciton will present an apparent reverse polarization [22]. The abnormal polarization is not only applicable in an ultra-fast switching device, but it may also serve as a criterion to identify the formation of a biexciton.

Although some progress has been made for recognizing the nature and formation of biexcitons in organics, a theoretical investigation for the dependence of its yield on the photoexciting process is still lacking. In earlier theoretical treatment, the excited electrons have been supposed to lie in higher energy orbitals [22], while the photoexciting process was neglected. In one of our recent work [4], by applying a femtosecond electric pump pulse to a PPV molecule, we obtained the spontaneous electron transitions and theoretically simulated the photoexciting process. Here, we will focus on the biexciton photogeneration by using such a method, and further clarify the relation between its yield and the photoexcitations. The paper is organized as follows. The model and method are presented in Section 2. The results and discussions are shown in Section 3. Finally in Section 4, the conclusions are given.

2. Model and method

For excitons or biexcitons in organic semiconductors, most of the theoretical works were based on the Coulomb-correlated model [11,12,20], such as the PPP model [21], which is actually a rigid-band correlated electron model. Here, we employ the well-known Su–Schrieffer–Heeger (SSH) model [23], in which the strong electron–lattice interactions in polymers are emphasized. By a renormalization treatment for the benzene rings [24], a PPV molecule can be modeled as a one-dimensional chain. Thus, the Hamiltonian of a PPV chain can be written as

$$H = -\sum_n t_{n,n+1}(C^+_{n+1}C_n + C^+_n C_{n+1}) + \frac{1}{2}K\sum_n (u_{n+1} - u_n)^2 + \frac{1}{2}M\sum_n \dot{u}_n^2 + \sum_n eE(t)(na + u_n)(C^+_n C_n - 1), \tag{1}$$

where the physical quantities can be referred to Refs. [4,24]. The first term shows the electron hopping between the nearest neighboring sites of the system [expressed as H_e in Eqs. (5) and (6)]; the second term and the third one separately describes the classical treatment of the elastic potential and kinetic energy of the sites; the final term shows the effect of an external electric field. Here it should be emphasized that $E(t)$ in the Hamiltonian is a time-dependent AC field. To numerically simulate a photoexciting process, we choose $E(t)$ as a Gaussian form with width T centered at t_c,

$$E(t) = E_0 \exp\{-[(t - t_c)/T]^2\}\cos(\omega t), \tag{2}$$

in which, E_0 and ω separately shows the photoexciting intensity and frequency.

Here, the displacement u_n of a site n is not fixed, which will evolve with the electronic states due to the strong electron–lattice interactions. In the present model, u_n is developed upon the Newtonian equation of motion

$$M\ddot{u}_n = -K(2u_n - u_{n+1} - u_{n-1}) + 2\alpha(\rho_{n,n+1}(t) - \rho_{n-1,n}(t)) + eE(t)(\rho_{n,n}(t) - 1) - \lambda M\dot{u}_n. \tag{3}$$

$\rho_{n,n'}(t)$ is the electronic density matrix defined as

$$\rho_{n,n'}(t) = \sum_v \Phi^*_{v,n}(t) f_v \Phi_{v,n'}(t), \tag{4}$$

where $\Phi_{v,n}(t) = \langle n|\Phi_v(t)\rangle$. $n|\Phi_v(t)\rangle$ shows the evolution of an electronic state, which depends on the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\Phi_v(t)\rangle = \left(H_e + \sum_n eE(t)(na + u_n)C^+_n C_n\right)|\Phi_v(t)\rangle. \tag{5}$$

f_v in Eq. (4) gives the occupation of state $|\Phi_v(t)\rangle$ and is determined by the initial electron occupation (0, 1 or 2). A damping term is introduced in Eq. (3) to describe the energy dissipation into the surrounding medium by a tuning parameter λ [25].

In addition, to recognize the final states, we introduce instantaneous eigenstate $|\phi_\mu(t)\rangle$, which is obtained by the instantaneous eigen equation

$$\left[H_e + \sum_n eE(t)(na + u_n)C^+_n C_n\right]|\phi_\mu(t)\rangle = \varepsilon_\mu(t)|\phi_\mu(t)\rangle, \tag{6}$$

where we can see that the Hamiltonian is determined by the instantaneous site displacement u_n. $\varepsilon_\mu(t)$ is the eigen energy of instantaneous state $|\phi_\mu(t)\rangle$.

In present investigation, we set $|\Phi_v(t=0)\rangle = |\phi_v(t=0)\rangle$ at beginning. When a photoexcitation is applied, the state $|\Phi_v\rangle$ will experience an evolution determined by the coupled differential equations (3) and (5), which can be solved by the Runge–Kutta method of order eight with step-size control [26]. In the evolution process, it should be stressed that we employ a nonadiabatic approximation, by which the electron transitions between instantaneous eigenstates are allowed. The nonadiabatic effects are of crucial importance to describe the photoexciting process.

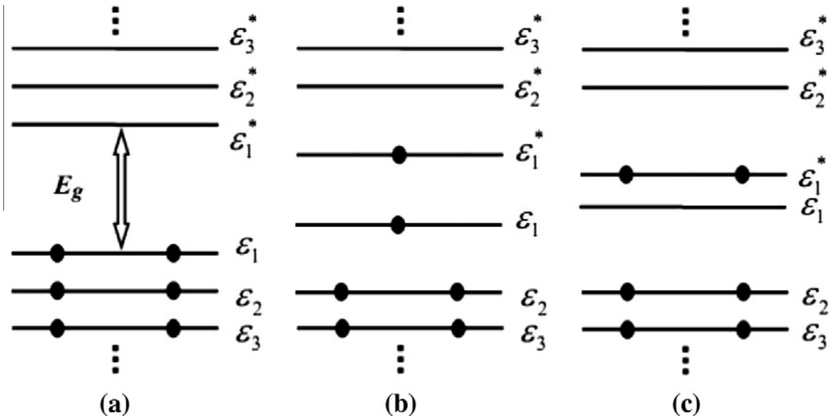

Fig. 1. Schematic diagram of the molecular orbitals for a PPV molecule in a ground state (a), an exciton (b), or a biexciton (c), where the filled circles indicate electrons with the spin omitted.

3. Results and discussion

As a model system for our studies, we select a six-ring PPV molecule (i.e., the chain length ($l = 34a$)). The other parameters can be referred to Refs. [4,24]. In the simulations, we start from a ground state, which is obtained by minimizing the total energy of a PPV molecule. If there is no any external perturbation, the molecule will keep its ground state unchanged. In this equilibrium state, we have $|\Phi_\mu(t)\rangle = |\phi_\mu(t)\rangle = |\phi_\mu(t=0)\rangle$ with the eigen energy ε_μ. Fig. 1(a) shows the schematic diagram of the molecular orbitals for a PPV molecule in a ground state, where we denote ε_μ $(\mu = 1, 2, \ldots)$ to be the μth occupied orbital counted from HOMO, and ε_μ^* $(\mu = 1, 2, \ldots)$ to be the μth unoccupied one counted from LUMO. Between HOMO and LUMO, we can see an apparent energy gap of E_g.

When the PPV molecule is photoexcited, electrons will gain energy and $|\Phi_v(t)\rangle$ evolves with time, which means that electrons may transit among the instantaneous eigenstates $|\phi_\mu(t)\rangle$. The "by-hand" simulations treat the transitions by moving electrons from the occupied orbitals to the unoccupied ones. As we know, transition $\varepsilon_1 \rightarrow \varepsilon_1^*$ with one electron leads to the formation of an exciton, while that with two electrons produces a biexciton, as shown in Fig. 1(b) and (c), respectively [22]. However, the "by-hand" simulations neglect the photoexciting process, and thus cannot give a quantitative relation between these photoexcited species and the photoexcitations. Here, let us excite the molecule by a femtosecond electric pump pulse with the form of Eq. (2), in which T is fixed to be 25 fs, and the photoexciting intensity and energy chosen to be E_0 = 4 MV/cm and $\hbar\omega = 2.6$ eV respectively. After that, the final state is firstly analyzed by calculating $F_\mu(t) = \sum_v f_v |\langle\phi_\mu(t)|\Phi_v(t)\rangle|^2$, which gives the electron occupation on instantaneous eigenstate $|\phi_\mu(t)\rangle$ at time t. The variations of $F_\mu(t)$ reflect electron transitions among the instantaneous eigenstates. As shown in Fig. 2(a), at beginning, the molecule keeps its ground state unchanged with electron occupation $F_\mu(t) = f_\mu$. At t_c = 40 fs, a photoexcitation is applied, and we find that electrons on the occupied orbitals gain energy to transit to the unoccupied ones with different probabilities. Especially, apparent transitions take

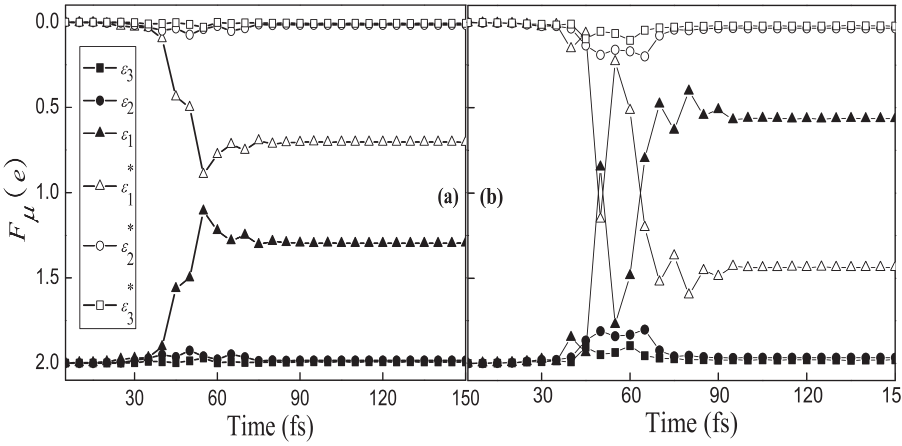

Fig. 2. Variations of occupation $F_\mu(t)$ on the six instantaneous eigenstates near the gap during the evolution of the PPV molecule. (a) The result with the photoexciting intensity E_0 = 4 MV/cm and energy $\hbar\omega = 2.6$ eV and (b) that with the photoexciting intensity E_0 = 10 MV/cm and energy $\hbar\omega = 2.3$ eV.

place between ε_1 and ε_1^*. About 30 fs later, the transitions stop, and the transferred electrons from ε_1 to ε_1^* are about 0.7e. The result is different from the ideal (or integral) transitions in the "by-hand" simulations, and it means that the photoexcited products obtained here are neither pure excitons nor biexcitons.

Now let us recognize the final state by considering all the possible electron transitions (0, e or 2e) from ε_1 to ε_1^*. As shown in Fig. 1, if there is no any electron transition, the molecule will keep its ground state (denoted as state S_0); if the transferred electrons are one electronic charge (e), the molecule lies in an exciton state (denoted as state S_1); while if the transferred electrons are two electronic charges (2e), the molecule lies in a biexciton state (denoted as state S_2). Here, we project the evolution state $|\Phi(t)\rangle$ onto these instantaneous eigenstates $|\phi_{S_k}\rangle$ (k = 0, 1 or 2) to determine their species. That is, $i_{S_k}(t) = |\langle\phi_{S_k}|\Phi(t)\rangle|^2$, which shows the yield i_{S_k} of one kind state S_k. The calculated results are shown in Fig. 3. It is found that, after the photoexcitation, the molecule may still keep its ground state with a probability of 41%, or lie in an exciton with a probability of 44%, or lie in a biexciton with a probability of 12%. In addition, we note that there are still missing some excited products with a total yield of 3%. By further checking the electron transitions between ε_μ and ε_μ^* shown in Fig. 2(a), we attribute these negligible products to the weak higher-energy transitions taking place from ε_μ and ε_μ^*, where $\mu \geqslant 2$.

From Fig. 3, we see that although we can obtain biexcitons, the yield is far below that of excitons. Next, we will focus on how to make the produce efficiency of biexcitons above that of excitons. To do so, effect of the photoexciting energy and intensity on such an issue will be separately discussed. Firstly, let us check the dependence of the yields of biexcitons and excitons on the photoexciting energy, as shown in Fig. 4, where the photoexciting intensity is fixed to be E_0 = 4 MV/cm. It is found that there exists a critical value of the photoexciting energy ($\hbar\omega_c = 2.56$ eV in present parameters), only over the value do biexcitons and excitons begin to be photogenerated. In fact, the critical value corresponds to the experimentally observed optical energy gap [27], beyond which electrons in the occupied orbitals will obtain enough energy to overcome the energy gap and transit to the unoccupied ones. As the orbitals are discrete, the transition probability is strong only at some photoexciting energies. As reported in Ref. [4], with the increase of the photoexciting energy there will appear a series of transition peak, which in turn corresponds to the transition $\varepsilon_1 \to \varepsilon_1^*$, $\varepsilon_2 \to \varepsilon_2^*$, and $\varepsilon_3 \to \varepsilon_3^*$, etc. For example, in present parameters the first transition peak appears near $\hbar\omega = 2.6$ eV. Consequently, at such a photoexciting energy, both biexciton and exciton have the largest yield (denoted as the peak yield as follows). However, the more worth noting is that, no matter how we change the photoexciting energy, the yield of biexcitons is always smaller than that of excitons.

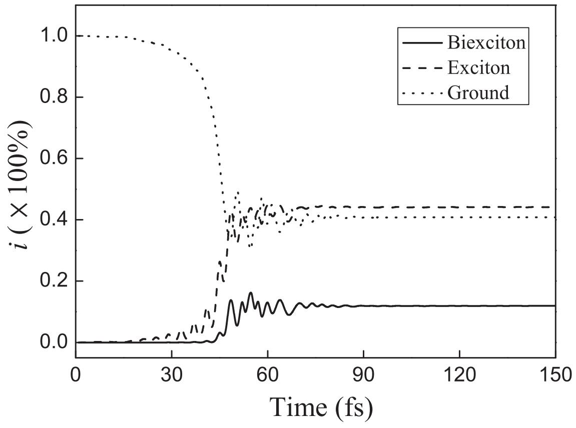

Fig. 3. Probabilities of the PPV molecule in a ground state (dotted line), an exciton (dashed line), and a biexciton (solid line) during the evolution with the photoexciting intensity E_0 = 4 MV/cm and energy $\hbar\omega = 2.6$ eV, respectively.

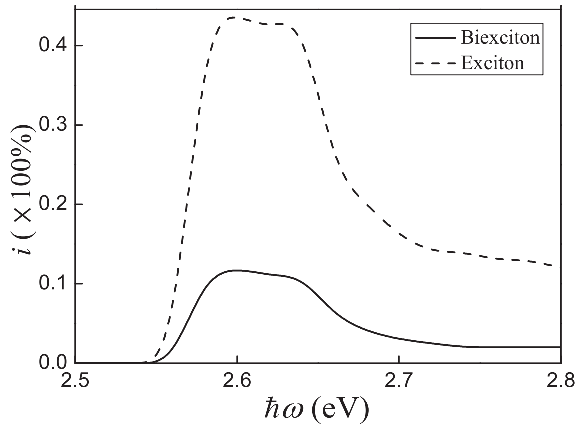

Fig. 4. Dependence of the yields of biexcitons and excitons on the photoexciting energy with the photoexciting intensity fixed to be E_0 = 4 MV/cm.

Then, let us focus on the effect of the photoexciting intensity on their yields. Fig. 5 shows the dependence of the peak yields of biexcitons and excitons on the photoexciting intensity E_0. It is found that there exists a critical intensity E_{0C} for the generations of biexcitons and excitons. In the case of $E_0 < E_{0C}$, the yield of excitons is always larger

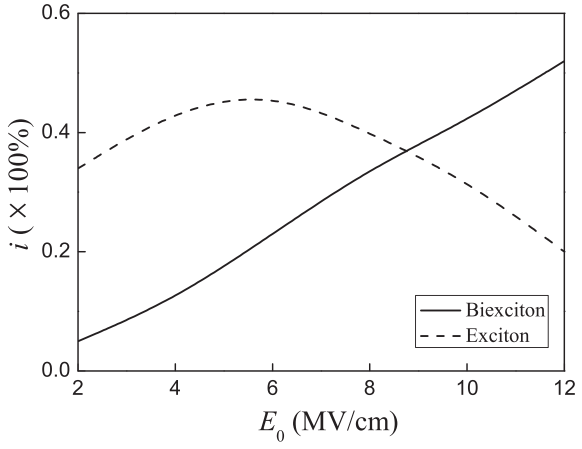

Fig. 5. Dependence of the peak yields of biexcitons and excitons on the photoexciting intensity E_0.

than that of biexcitons. Once the photoexciting intensity exceeds such a critical value, biexcitons are more favorable to be generated than excitons. The reason is that, by strong photoexciting intensity, the probability of the double-electron transition from ε_1 to ε_1^* will be apparently enhanced. Fig. 2(b) shows the variations of occupation $F_\mu(t)$ on the six instantaneous eigenstates near the gap during the evolution with the photoexciting intensity E_0 = 10 MV/cm and energy $\hbar\omega = 2.3$ eV, respectively. As can be seen, due to the higher probability of the double-electron transition, the electrons transiting from ε_1 to ε_1^* exceed one electronic charge (e) and reach about 1.5e (i.e., a situation known as a population inversion, which is a necessary condition for laser) [28,29]. Since the radiative recombination efficiency of biexcitons is higher than that of excitons, the results presented in Fig. 5 may dominate the experimentally observed excitation intensity dependent transition of the luminescence from a linear to a hyperlinear increase [8].

Finally, it should be stressed that, in the present model study, the photoexciting intensity E_0 can also have an apparent effect on the electronic structure of the PPV molecule. Here, we focus on its energy gap, and it is found that the gap will be reduced by the enhancement of E_0 due to the stark effect. As a result, the optical energy gap or the peak absorption in the optical spectra will appear a clear red-shift. For example, in present parameters the peak absorption appears near $\hbar\omega = 2.6$ eV in the case of E_0 = 4 MV/cm, while the peak absorption red-shift to $\hbar\omega = 2.3$ eV in the case of E_0 = 10 MV/cm, as presented in Fig. 2. In addition, the formation mechanism of biexcitons is a focused question. Mazumdar et al. [20] and Klimov et al. [9] attribute the biexciton formation to the sequential reexcitation of an exciton. Pasquinelli and Yaron [21] and Wang et al. [30] showed that two excitons can be bound to form a biexciton since the energy of a biexciton is less than the total energy of two separated excitons due to the self-trapping in a polymer. However, the process strongly depends upon the size confinement effect. That is, only in a limited system can the exciton–exciton interaction be strong enough to lead to the formation of a biexciton. In our model study, we attribute the biexciton formation to a two-photon process (i.e., double-electron transition), which directly results in the formation of biexcitons. Firstly, from Fig. 3 we can see that biexcitons and excitons are photogenerated at the same time and do not depend on each other. Secondly, we also consider the effect of the chain length on the yield ratio between biexcitons and excitons. It is found that, even in an infinite polymer chain, can biexcitons be more favorable to be generated than excitons by increasing the photoexciting intensity.

4. Conclusion

In view of the contribution of biexcitons to the nonlinear optoelectronic properties of organics and their potential applications in laser devices, we theoretically investigated the biexcitons photogeneration in a PPV molecule. Firstly, a quantitative relation between the biexciton yield and the photoexciting process was presented. Especially, we indicated that there exist a critical photoexciting intensity, beyond which biexcitons are more efficiently generated than excitons. The result may dominate the experimentally observed excitation intensity dependent transition of the luminescence from a linear to a hyperlinear increase due to the intrinsic high radiative quantum efficiency of biexcitons. Finally, the biexciton formation mechanism was briefly discussed, which corresponds to a two-photon process.

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