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Effect of interchain coupling on a biexciton in organic polymers*

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The effect of interchain coupling on the formation and the stability of a biexciton is studied in poly (*p*-phenylene vinylene) chains in the framework of the tight-binding approach. We obtain an intrachain exciton and biexciton as well as an interchain exciton and biexciton through a double-photon excitation. It is found that a biexciton is energetically favourable to two single excitons even when there exists an interchain coupling. There is a turnover value $t_{\perp \mathrm{C}}$ of the interchain coupling for the formation of a biexciton, beyond which two excitons are combined into one biexciton. The binding energy of a biexciton is calculated to decrease with the increase of interchain coupling, which indicates that a biexciton is relatively stable in polymers with a weak interchain coupling. The conclusion is consistent with the experimental observations. In addition, a suggestion about how to improve the yielding efficiency or the formation of biexcitons in actual applications is given.

Keywords: biexciton, polymers, binding energy
PACC: 7135, 8120S, 3520V

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. They have become very promising functional materials in optoelectronic devices.[1−5] The electronic and the optical properties of these organic materials can be studied by using relatively simple models on the molecular structures, of which a one-dimensional tight-binding approximation has been widely used.[6,7] For an organic semiconductor, the bond structure is sensitively correlated to its electronic structure because of the strong electron–lattice interactions. Once the electronic structure is changed by external effects, such as through photoexcitation, the bond structure will undergo a change accordingly. Of course, the electronic structure will change with its bond structure too. The interdependence of electrons and bonds is an important characteristic of organic materials. Many peculiar phenomena of organic semiconductors result from the strong electron–lattice interactions. For example, after the polymer has been doped, its carriers are not electrons or holes any more, but polarons or bipolaons that are localized in space;[6] by photoexcitation the excited states are localized excitons or biexcitons, which are bound to have some special properties.[8,9]

It is well known that the lowest optical state in a polymer is an exciton,[10] which is found to be responsible for the light emission and photocurrent through the radiative decay and dissociation,[9] respectively. In addition, it has been predicted that two excitons in a polymer can be combined into a biexciton,[11,12] in that the energy of a biexciton is lower than that of two separated excitons. Klimov *et al* [13] have given clear experimental verification of biexcitons in a five-ring oligomer of PPV. In addition, some excitation intensity dependent phenomena observed in experiments, such as a hyperlinear increase in radiative quantum efficiency of poly (*p*-phenylene)-type ladderpolymer, reported by Kranzelbinder *et al*,[14] have also been attributed to the formation of biexcitons. In 2000, Sun *et al* [8] theoretically predicted a new characteristic that the polarization of a biexciton was opposite

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to the external electric field. Another similar polarization has also been obtained from the single-photon excitation of a charged polaron.[15] The abnormal polarization is not only applicable in a switching device, but it may also serve as a criterion to identify the formation of a biexciton in organic polymers.

There are some factors affecting the formation of an exciton or a biexciton in a single polymer. Size confinement effect was discussed by Pasquinelli and Yaron.[12] They indicated that there existed 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, otherwise the exciton–exciton interaction is not sufficiently strong to lead to the formation of a biexciton. On the other hand, the stability of an exciton or a biexciton before their radiative recombination is also affected by some elements (e.g. an external electric field,[16] sequential photon excitations[9] or defects[17]), which lead them to be dissociated into a polaron pair (involving a positive polaron and a negative polaron) or a bipolaron pair (involving a positive bipolaron and a negative bipolaron).

In addition, there exists an interchain coupling between the molecules in actual situations. For a single-photon excitation, the experimental data indicated that the interchain coupling could lead to the formation of interchain charge transfer states,[18,19] such as a bound polaron pair, which can remarkably reduce the yielding efficiency of the emissive exciton. Of course, even if we do not consider the interchain charge transfer, the interchain coupling does impede the formation of the emissive exciton as discussed in our other work.[20] For a double-photon excitation, although it is shown that a biexciton is energetically favourable to two separated excitons, the conclusion is obtained in a single polymer. As early as 1998, the effect of the interchain coupling on the biexciton was experimentally reported by Klimov *et al*,[13] and they indicated that a biexciton was not so stable in a solid-state film with strong interchain couplings as in a dilute solution with weak interchain couplings.[13] It is obvious that the interchain coupling plays an important role in the formation and the stability of a biexciton. However, the correlative physical picture is still obscure.

In the present paper, a system consisting of two PPV chains is modeled, by which we study the effect of interchain coupling on the formation and the stability of a biexciton in two steps. Firstly, four possible states photogenerated by a double-photon excitation in the system are presented, in which the formation and the competition between a biexciton and two excitons are mainly discussed; secondly, the effect of the interchain coupling on the stability of a biexciton is discussed. Here we give only a static picture by comparing the energies of different excitations. A more abundant content, such as the evolution time and yields, can be obtained by using a nonadiabatic evolution method. With the method, An *et al* [21] and Meng *et al* [22] have studied different single excitations in polymers, and obtained the yields of polaron pairs generated by photoexcitations. The remainder of the present paper is organized as follows. The model Hamiltonian is established and the scheme of a self-consistent calculation is outlined in Section 2. In Section 3 the results of our numerical computation are described and discussed. Finally, the conclusions drawn from the present study are summarized in Section 4.

2. Model

A PPV molecule as sketched in Fig.1, has been well described by using an extended Su–Schrieffer–Heeger (SSH) model.[9,23] The intrachain hopping integral $t_{n,n+1}$ between the nearest neighbour sites is written as

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

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

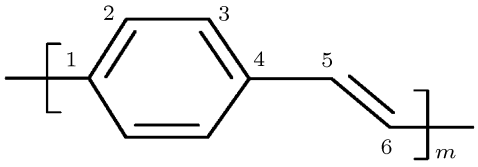


Fig.1. Schematic diagram of a PPV molecule with m repeat units.

With the electron–electron (e–e) interaction included, the Hamiltonian for the isolated jth chain is written as

$$H_j = H_{j,0} + H_{j,\text{e-e}}, \quad (1)$$

$$H_{j,0} = -\sum_{n,s} t_{j,n,n+1}(C^{+}_{j,n+1,s}C_{j,n,s} + C^{+}_{j,n,s}C_{j,n+1,s}) + \frac{1}{2}K\sum_{n}(u_{j,n+1}-u_{j,n})^2 + K'\sum_{n}(u_{j,n+1}-u_{j,n}), \quad (2)$$

$$H_{j,\mathrm{e-e}} = U\sum_{n} C^{+}_{j,n,\uparrow}C_{j,n,\uparrow}C^{+}_{j,n,\downarrow}C_{j,n,\downarrow} + V\sum_{n,s,s'} C^{+}_{j,n,s}C_{j,n,s}C^{+}_{j,n+1,s'}C_{j,n+1,s'}, \quad (3)$$

where $C^{+}_{j,n,s}(C_{j,n,s})$ is the creation (annihilation) operator of an electron at site n with spin $s(s=\uparrow,\downarrow)$ in the jth chain; K is the elastic constant; the third term in expression (2) is added to stabilize the free ends of the finite chain with N sites; K' is given by

$$K' = -\frac{2\alpha}{N-1}\sum_{\mu,n,s}{}' Z_{j,\mu,n,s}Z_{j,\mu,n+1,s} \quad (4)$$

with $\sum'$ denoting the sum over the occupied states; $H_{j,\mathrm{e-e}}$ is the e–e interaction in the jth chain, which is treated in the Hartree–Fock approximation[24] for simplicity.

In actual situations, we suppose two PPV chains ($j=1,2$) with a parallel alignment. The interchain coupling takes place between the nearest sites of the two chains, which is described in the following form:

$$H_{\perp} = -\sum_{n,s} t_{\perp}(C^{+}_{1,n,s}C_{2,n,s} + C^{+}_{2,n,s}C_{1,n,s}), \quad (5)$$

where $t_{\perp}$ is the interchain hopping integral.

To check the polarization of the system, we apply an inducing electric field E in the direction from left to right along the two chains. The interaction of electrons with the applied electric field E in the jth chain is written as

$$H_{j,E} = \sum_{n} eE(na+u_{j,n})(C^{+}_{j,n,s}C_{j,n,s}-1), \quad (6)$$

where a is the lattice constant.

The electronic eigenstate $\psi_{\mu,s} = \sum_{n,j} Z_{j,\mu,n,s}\,|n,j\rangle$ is obtained by solving the Schrödinger of the electronic Hamiltonian, which is dependent on bond displacement $u_{j,n+1}-u_{j,n}$. On the other hand, by minimizing the total energy, displacement $u_{j,n+1}-u_{j,n}$ is determined by the eigenstates

$$u_{j,n+1}-u_{j,n} = -\frac{2\alpha}{K}\sum_{\mu,s}{}' Z_{j,\mu,n,s}Z_{j,\mu,n+1,s} - \frac{K'}{K} + \frac{eE}{K}\Big(\sum_{\mu,s,m=1}^{n}{}' Z^2_{j,\mu,m,s} - n\Big). \quad (7)$$

It is obvious that displacement $u_{j,n+1}-u_{j,n}$ and eigenstate $Z_{j,\mu,n,s}$ depend on each other, which can be calculated iteratively. After obtaining the eigenstate $Z_{j,\mu,n,s}$, the net charge density in the jth chain can be calculated from the following formula:

$$\rho_{j,n} = \sum_{\mu,s}{}' |Z_{j,\mu,n,s}|^2 - 1. \quad (8)$$

3. Results and discussion

Referring to Ref.[9], we set the parameters of PPV as $\alpha = 102.9$ eV / nm, $t_0 = 2.66$ eV, $a = 0.122$ nm, and $K = 9900.0$ eV / nm^2. In addition, we find that the e–e interaction does not qualitatively change the results in our model, so it is fixed to be $U = 2.0$ eV, and $V = U/3$. By adjusting t_1 and t_2, we obtain an energy gap of $E_{\mathrm{g}} = 2.8$ eV between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital), which is consistent with the values from other studies on pristine PPV.[25,26]

When a polymer absorbs a single photon with energy close to the energy gap, an electron will be excited from HOMO to LUMO and leave a hole at HOMO, thereby forming an electron–hole pair. It has been indicated that, in an isolated polymer chain, the excited electron–hole pair interacts with the bond lattice to form a self-trapping state or a localized exciton.[10] If two photons are absorbed, a biexciton may directly or indirectly form.[10] The formation and competition between a biexciton and two excitons have been discussed with the Pariser–Parr–Pople (PPP) model[27] in a frozen molecular structure.[12] In a two-chain system, the interchain charge transfer due to the interchain coupling leads to more complex photoexcitation than in a one-isolated chain. Up to now, it has been commonly received that either an intrachain or an interchain exciton can form through a single-photon excitation.[18,19] While for a double-photon excitation in such a system, the photoexcited states including the competition between them are still unknown.

We firstly concern the possible states photogenerated by a double-photon excitation in a two-chain system, which can be obtained by solving the Schrödinger equation of Hamiltonian $H_1 + H_2 + H_{\perp}$ with different excitation modes. There may be many possibilities for the case of double-photon excitation in a two-chain structure, with interchain charge transfer considered. Here only four possible excited states are presented at an interchain coupling $t_{\perp} = 0.2$ eV. Figure

2(a) shows that the photoexcitation takes place only within the first chain (two electrons are excited from HOMO to LUMO, with the first chain initially endowed with a lattice distortion and the second chain perfectly dimerized), which apparently corresponds to a biexciton. To confirm it, we give the charge density distribution under an electric field. It is found that the polarization is antiparallel to the direction of the field.[8] Figure 2(b) shows that the photoexcitation takes place within both of the two chains (two electrons are excited from HOMO to LUMO, with both of the two chains initially endowed with a lattice distortion), which is attributed to two excitons due to the normal polarization appearing in either of the two chains. Figure 2(c) indicates a charge transfer state. Two electrons are excited from the first chain to the second one (two electrons are excited from HOMO to LUMO+1, with both of the two chains initially endowed with a lattice distortion). Therefore a positive bipolaron and a negative one form separately in the two chains. Figure 2(d) reveals that only one electronic charge transfer takes place between the chains. In this case (one electron is excited from HOMO to LUMO and another one excited from HOMO to LUMO+1, with both of the two chains initially endowed with a lattice distortion), an excited positive polaron and a negative polaron (or an excited negative polaron and a positive polaron) appear separately in the two chains. An excited polaron has been described in Ref.[15].

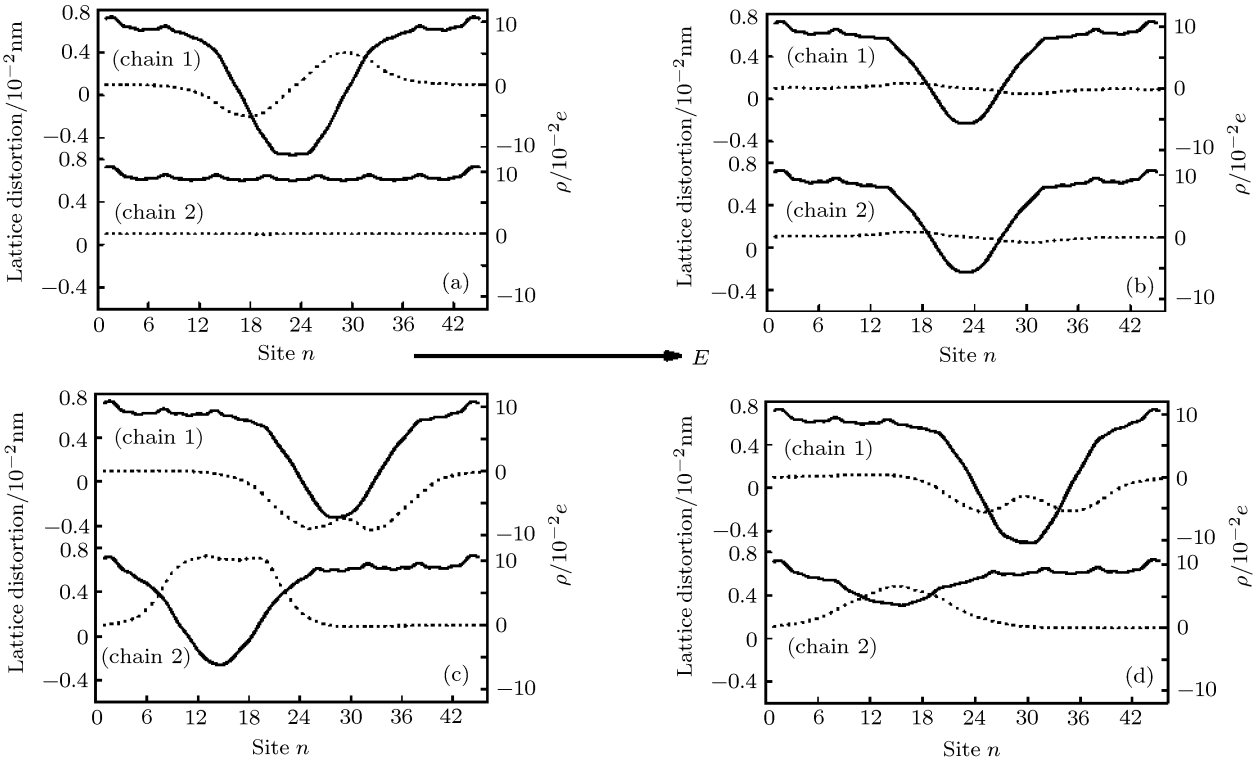


Fig.2. Possible states photogenerated by a double-photon excitation in the two-chain system at an interchain coupling $t_\perp = 0.2$ eV, where panel (a) indicates that the photoexcitation results in a biexciton in the first chain, panel (b) exhibits the photoexcitation leads to two excitons, panel (c) indicates the photoexcitation produces a positive bipolaron and a negative one, and panel (d) displays that the photoexcitation creates an excited positive polaron and a negative polaron, with the solid and dot lines showing the lattice distortion and charge density ρ, respectively.

Here we leave the interchain charge transfer states and consider only the biexciton and the exciton behaviours in a two-chain system. Dependences of the creation energy for a biexciton and two excitons on interchain coupling are shown with solid and dot lines in Fig.3 respectively. It is obtained that the creation energy of a biexciton is always smaller than that of two excitons, which indicates that a biexciton is energeti-

cally favourable to two single excitons even when there exists an interchain coupling. In addition, we find that there is a turnover value $t_{\perp C}$ ($t_{\perp C} = 0.4$ eV in present parameters) of the interchain coupling for the formation of a biexciton. When $t_\perp \leq t_{\perp C}$, both a biexciton and two excitons are obtained, and the difference between their energies is found to decrease with the increase of interchain coupling. We know that electronic states can spread between chains, which results in an interaction between the two excitons in different chains. The strength of the interaction can be reflected by calculating the difference between the creation energy of two excitons and that of two separated ones. The result is shown with the dash line in Fig.3. It is clear that the interaction increases with the increase of interchain coupling. Once the interchain coupling exceeds the critical value $t_{\perp C}$, the interaction between the two excitons becomes strong enough to combine them into a biexciton. In other words, when $t_\perp > t_{\perp C}$, only a biexciton can be obtained. Therefore, by changing external conditions, such as by applying a pressure, to adjust the aggregation of polymers or interchain coupling, we may change the yielding efficiency of biexcitons or excitons.

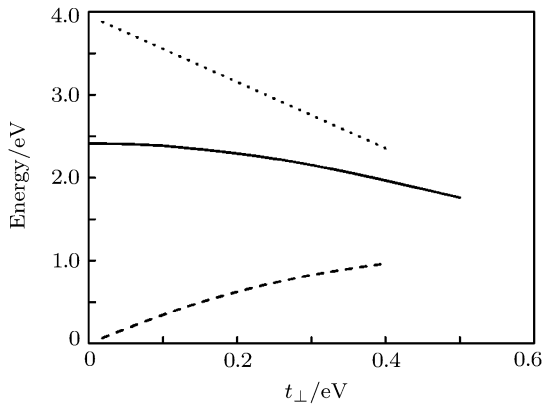


Fig.3. Dependences of the creation energy for a biexciton (solid line) and two excitons (dot line) on interchain coupling, where the dash line reflects the interaction energy between two excitons in different chains.

Now we come to consider the stability of a biexciton. It is indicated that an exciton and a biexciton may be dissociated into a polaron pair and a bipolaron pair before their radiative recombination, respectively. The difference in state energy between after and before dissociation, defined as the binding energy, determines the stability of either an exciton[28] or a biexciton.[29,30] Here the binding energy of a biexciton in different interchain couplings is calculated as shown in Fig.4. It is obtained that the binding energy decreases apparently with the increases of interchain coupling. So we speculate that a biexciton is relatively stable in polymers with a weak interchain coupling or in a dilute polymer solution, which is qualitatively consistent with the experimental observations reported by Klimov *et al.*[13] As the binding energy reflects the power of dissociating an exciton or a biexciton into free charges and the reverse process, a large binding energy means a high-efficient formation of a biexciton. The result implies that one can obtain the required biexcitons by controlling the aggregation of the polymer molecules for different applications in optoelectronic organic devices. For example, in a light emitting device, one would like to have a high density of biexcitons. A large binding energy will be favourable for the formation of a biexciton.

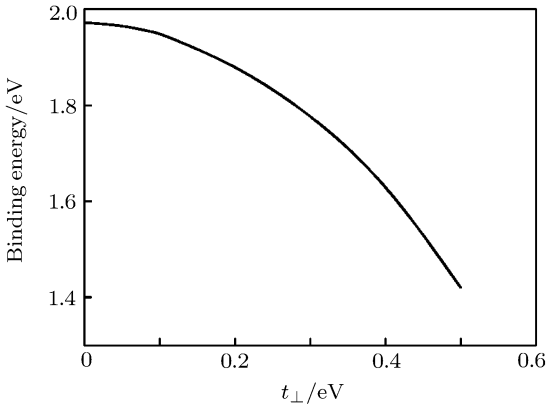


Fig.4. Dependence of the binding energy of a biexciton on interchain coupling.

In actual organic materials, the polymer chains are not equivalent in length and the interchain coupling may take place only in some segments of the molecules. To understand the photoexcitation in coupled molecules with different lengths, we consider the case where a short chain (shorter than a biexciton width δ', $\delta' = 28a$ in the present study) couples with a long one. It has been indicated that in an isolated chain, the ends confines a state and makes the energy increase. Here only a biexciton in the long chain, or the case corresponding to Fig.2(a), is obtained. However, the short chain has an effect on the biexciton as shown in Fig.5. It is found that a short chain is favourable to increasing the binding energy of a biexciton localized in the coupled chains. Therefore, we may increase the yielding efficiency of biexcitons through the synthesis of polymers to change their molecule size distribution and inter-molecular conformation.

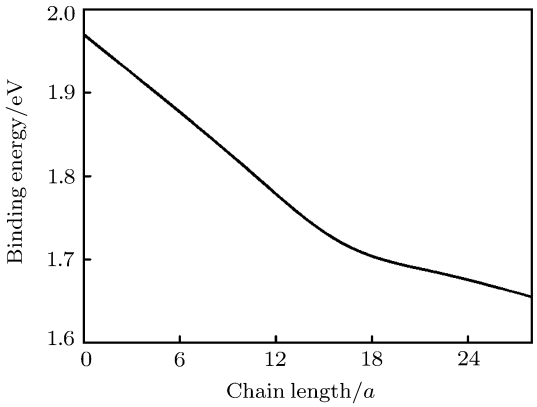


Fig.5. Effect of a short chain with different chain lengths on the binding energy of a biexciton.

4. Summary

It has been known that biexcitons have some characteristics different from those that excitons or other excitations have, such as abnormal polarization and the narrow spectral structure. They also have a high radiative recombination, which indicates that they have potential applications in solid-state lasers, photoelectronic and switching devices. Here we investigate the formation of biexcitons in actual PPV polymers by using an interchain coupling model. Both an intra- and inter-chain exciton and biexciton are obtained through a double-photon excitation. Through investigating the competition between a biexciton and two excitons, it is found that we may change the yielding efficiency of biexcitons or excitons by controlling the aggregation of the polymer molecules. The apparent reduction in biexciton binding energy with the increases of interchain coupling shows that a biexciton is more stable in polymers with a weak interchain coupling or in a dilute solution of polymers than in a solid sample, which is qualitatively consistent with the experimental observations. In addition, by studying the effect of a short chain, it is obtained that the yielding efficiency of biexcitons may be improved through the synthesis of polymers to change their molecule size distribution and inter-molecular conformation.

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