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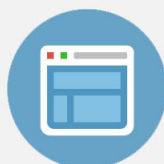
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Dynamics of exciton transfer in coupled polymer chains

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The dynamics of singlet and triplet exciton transfer in coupled polymer chains are investigated within the Su-Schrieffer-Heeger+Pariser-Parr-Pople model including both electron-phonon (e-p) coupling and electron-electron (e-e) interactions, using a multi-configurational time-dependent Hartree-Fock dynamic method. In order to explain the processes involved, the effects of on-site and long-range e-e interactions on the locality of the singlet and triplet excitons are first investigated on an isolated chain. It is found that the locality of the singlet exciton decreases, while the locality of the triplet exciton increases with an increase in the on-site e-e interactions. On the other hand, an increase in the long-range e-e interaction results in a more localized singlet exciton and triplet exciton. In coupled polymer chains, we then quantitatively show the yields of singlet and triplet exciton transfer products under the same interchain coupling. It is found that the yield of singlet interchain excitons is much higher than that of triplet interchain excitons, that is to say, singlet exciton transfer is significantly easier than that for triplet excitons. This results from the fact that the singlet exciton is more delocalized than the triplet exciton. In addition, hopping of electrons with opposite spins between the coupled chains can facilitate the transfer of singlet excitons. The results are of great significance for understanding the photoelectric conversion process and developing high-power organic optoelectronic applications. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4803163>]

I. INTRODUCTION

Organic materials, which are conductive, luminescent, and flexible and involve only low-cost processing,¹ are one of the ideal candidates for optoelectronic materials and have extensive application possibilities. Excitons consisting of an electron and a hole confined in one lattice configuration are important elementary excitations in organic materials.^{2,3} They can recombine radiatively and emit light in organic electroluminescence devices and can separate to form free charge carriers under the electric field in organic solar cells. From the work of Rothberg's group in 1990s,^{4,5} it is known that the most common excitation pathway in polymers involves the formation of nonemissive interchain excitons. This is because the basic process involves charge transfer between chains, unless the polymer chains are well-separated. Later on, a series of results with respect to the influence of interchain interactions on the absorption and emission of conjugated chains have been discussed,⁶⁻⁸ and the charge/neutral branching ratio in the photoexcitation of polymers has been further measured by Sheng *et al.*⁹ These results indicate that the interchain interaction plays an important role in determining the efficiency of optoelectronic devices.

Recently, An and co-workers¹⁰ have discussed interchain coupling effects on the dynamics of photoexcitations in conjugated polymers. It was shown that the yield of interchain excitons increases and that of intrachain excitons decreases with increasing interchain coupling. Similarly, Gao *et al.*¹¹ also

studied the effect of interchain couplings on exciton formation in two coupled PPV chains and showed that with increasing interchain coupling, an exciton needs a long time to form. Soon after, Meng and An also discussed interchain coupling effects on photoexcitations in two coupled polymer chains in the presence of an electric field.¹² The results showed that with increasing interchain coupling, interchain excitons are more readily generated, and the dissociation field decreases. The generation of the interchain excitons can effectively contribute to free-polaron generation. Because interchain excitons represent the intermediate but essential step between exciton formation and exciton dissociation,¹³ dynamic studies of exciton transfer are of great significance for understanding the photoelectric conversion process, carrier formation and collisions of carriers, and can provide important theoretical foundation for understanding the conductive and luminous efficiency of polymers.

It is important to note, however, that in previous work, only the electron-lattice interactions have been considered and the electron-electron (e-e) interactions have been ignored. Therefore, the different characteristics between singlet and triplet excitons cannot be distinguished. At present, the multi-configurational time dependent Hartree-Fock (MCTDHF) method^{14,15} based on multi-configurational interactions can give a rational illustration of the organic spin-eigenstates. This method uses multi-Slater determinants to describe the electronic wave functions and partly takes into account electron correlations on the basis of the traditional Hartree-Fock method.^{16,17} Within this method, the appropriate spin symmetry of the electronic wavefunction is taken into account, thus allowing us to investigate the properties of singlet and triplet

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excited states, respectively, and to discover the difference between them.

An outline of the model used in the calculations is given in Sec. II. We have investigated the effects of the on-site and long-range e-e interaction on the locality of the singlet and triplet excitons and point out the differences between the singlet and triplet exciton transfers between two coupled chains. This is discussed in Sec. III. Finally, a summary is given in Sec. IV.

II. MODEL AND METHOD

The model Hamiltonian we have adopted is the Su-Schrieffer-Heeger+Pariser-Parr-Pople (SSH+PPP) model^{15,18,19} with a Brazoskii-Kirova-type symmetry-breaking term.^{20,21} This Hamiltonian can be written as

$$H_{tot} = H_{latt} + H_{elec}. \quad (1)$$

The first term in Eq. (1) is the Hamiltonian of the lattice backbone, and describes the classical treatment of the elastic potential and kinetic energy of the sites,

$$H_{latt} = \frac{1}{2}K \sum_n (u_{n+1} - u_n)^2 + \frac{1}{2}M \sum_n \dot{u}_n^2, \quad (2)$$

where u_n is the lattice displacement of the n th site from its equidistant position, K is the elastic constant due to the σ bonds, and M is the mass of a CH group.

The second term in Eq. (1) is the Hamiltonian of the electronic part,

$$H_{elec} = H_{el} + H_{ee}. \quad (3)$$

In the above expression, the first contribution denotes the electron-phonon (e-p) interaction, expressed as²²

$$H_{el} = - \sum_{n,s} t_{nm} (c_{n,s}^\dagger c_{m,s} + c_{m,s}^\dagger c_{n,s}), \quad (4)$$

$$t_{nm} = \begin{cases} t_0 - \alpha(u_n - u_m) + (-1)^n t_e, & \text{intrachain hopping with } m = n \pm 1 \\ t_\perp, & \text{nearest neighbor interchain hopping,} \end{cases} \quad (5)$$

where $c_{n,s}^\dagger$ and $c_{n,s}$ are the operators which create and annihilate an electron at the n th site with spin s , t_0 is the transfer integral of π -electrons in a regular lattice, α is the e-p coupling constant, and t_e is introduced to lift the ground-state degeneracy for nondegenerate polymers. $t_\perp$ stands for the interchain transfer integral between adjacent sites on the two chains. The second contribution in Eq. (3) is the e-e interaction Hamiltonian and can be written as

$$H_{ee} = U \sum_{n,s} \left(c_{n,s}^\dagger c_{n,s} - \frac{1}{2} \right) \left(c_{n,-s}^\dagger c_{n,-s} - \frac{1}{2} \right) + \frac{1}{2} \sum_{n,m \neq n,s,s'} V_{nm} \left(c_{n,s}^\dagger c_{n,s} - \frac{1}{2} \right) \left(c_{m,s'}^\dagger c_{m,s'} - \frac{1}{2} \right), \quad (6)$$

where U is the on-site e-e interaction, and V_{nm} is the effect of the long-range e-e interactions which is included through the Ohno potential, defined as

$$V_{nm} = U / \sqrt{1 + (\beta r_{nm} / r_0)^2}. \quad (7)$$

The quantity β is referred to below as the shielding factor. Here, r_{nm} denotes the distance between sites n and m and can be written as

$$r_{nm} = \begin{cases} (n-m)r_0 + u_n - u_m, & \text{intrachain distance between } n \text{ and } m \\ \sqrt{[(n-m+n_0)r_0 + u_n - u_m]^2 + d^2}, & \text{interchain distance between } n \text{ and } m, \end{cases} \quad (8)$$

where $n_0 (=30)$ is the single polymer chain length, r_0 is the average bond length, and β is the shielding factor which determines the ratio between the on-site and intersite repulsion energies. d is the distance between the two chains.

The evolution of the electronic states can be written as

$$i\hbar |\dot{\Psi}\rangle = H_{elec} |\Psi\rangle. \quad (9)$$

The temporal evolution of the lattice is determined by the equation of motion for the atom displacements,

$$M \ddot{u}_n = -\nabla_n \langle \Psi | H_{latt} | \Psi \rangle - \nabla_n \langle \Psi | H_{elec} | \Psi \rangle. \quad (10)$$

The coupled differential equations (9) and (10) can be solved with a Runge-Kutta method of order 8 with step-size control.^{23,24} The parameters used here are taken to be those for *cis*-polyacetylene, i.e., $t_0 = 2.1$ eV, $\alpha = 3.2$ eV/Å, $K = 21.0$ eV/Å², $r_0 = 1.22$ Å, $t_e = 0.05$ eV, $M = 1349.14$ eV fs²/Å², $U = 4.1$ eV, $\beta = 3.4$, and $d = 4.0$ Å as developed by Miranda *et al.*¹⁵ specifically for the case where the Hamiltonian includes both on-site and long-range e-e interactions.

In the results below, we will use the optimized staggered order parameters to analyze and display the lattice,

$$\delta_n(t) \equiv (-1)^n (u_{n-1}(t) + u_{n+1}(t) - 2u_n(t)) / 4. \quad (11)$$

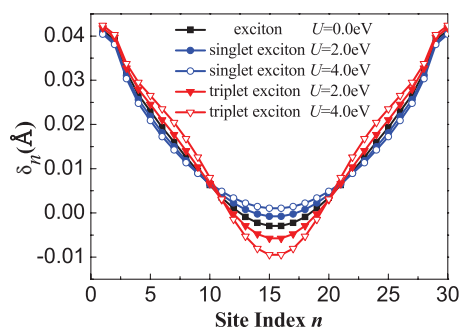


FIG. 1. Optimized staggered order parameters for singlet and triplet excitons for a number of different on-site e-e interaction strengths U in one polymer chain.

III. RESULTS AND DISCUSSIONS

The dynamics of exciton transfer between two coupled chains depend strongly on the locality of the excitons, so we first study the locality of the singlet and triplet excitons on an isolated polymer chain, where the effects of the on-site and long-range e-e interaction can be brought into focus. A short oligomer chain consisting of 30 CH units is adopted. To make explicit the effect of the on-site e-e interaction, we set β in Eq. (7) to be infinite so that the long-range e-e interactions are forced to zero. Fig. 1 shows the optimized staggered order parameters of the singlet exciton and the triplet exciton for various values of the on-site e-e interaction, U . For comparison, we also give the configuration of the SSH exciton ($U = 0$), as expected, there is no difference in configuration between singlets and triplets in this case. From the figure, it can be seen that the locality of the singlet exciton decreases, while the locality of the triplet exciton increases with increasing of U .

We then add the effect of the long-range e-e interactions. From Eq. (7), one can find that a decrease in β induces an increase in V_{nm} . Fig. 2 shows the optimized staggered order parameters of the singlet exciton (a) and the triplet exciton (b) as a function of the shielding factor β for fixed U . Both the singlet exciton and the triplet exciton become more localized as the shielding factors β decreases. That is to say, an increase in the long-range e-e interaction can result in a more localized singlet and triplet exciton. When both the on-site and the long-range e-e interactions are included, we get the configurations of the singlet exciton and the triplet exciton under the

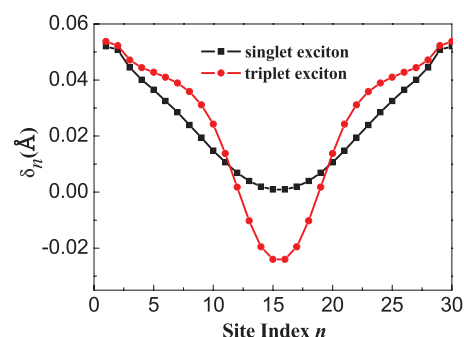


FIG. 3. Optimized staggered order parameters for singlet and triplet excitons calculated using the SSH+PPP model in one polymer chain.

SSH+PPP model. In Fig. 3, we show the optimized staggered order parameters for the singlet exciton and the triplet exciton for SSH+PPP model. It is remarkable that the singlet exciton is more delocalized than the triplet exciton, which indicates that the singlet and triplet excitons transfer processes should be different.

We next turn to a systematic study of the charge transfer processes of the singlet exciton and the triplet exciton in two polymer chains under the influence of the interchain coupling. In our simulations, two coupled parallel polymer chains opposite each other are considered, either of which is composed of 30 CH-units. The chain 1 units are labeled 1-30 and the chain 2 units are labeled 31-60. The initial lattice configurations and electronic structures can be obtained by minimizing the total static energy of the two-chain system in the absence of the e-e interactions.

In order to avoid abrupt changes, the interchain coupling strength is increased smoothly over a period of 100 fs, and then remains at a constant value. Fig. 4(a) shows the evolution of the lattice configurations for the singlet exciton under a moderate interchain coupling strength, $t_{\perp} = 0.25$ eV. A pre-existing localized singlet exciton lies initially in the middle of chain 1 while chain 2 remains in the dimerized state. Due to the interchain coupling, the electron and hole in the singlet exciton exchange between the two chains. The depth of the distortion on chain 1 decreases, and that on chain 2 increases as time goes on. After about 100 fs, the lattice deformations on the two chains have nearly the same depth, that is to say, complete delocalization of the singlet exciton has taken place. Fig. 4(b) shows the configurations of the two chains at 0 fs

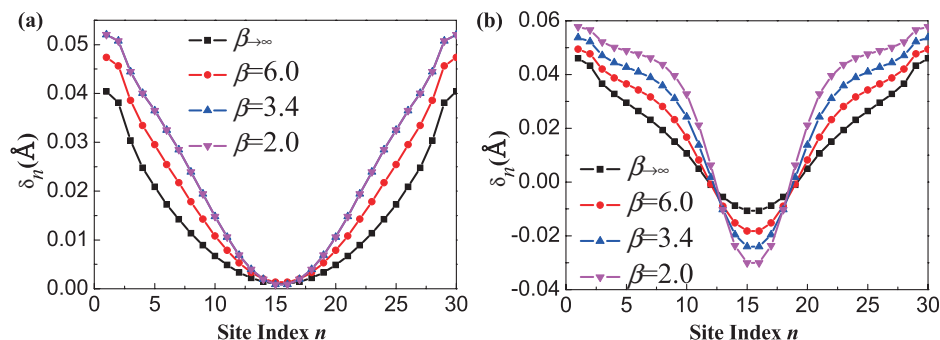


FIG. 2. Optimized staggered order parameters for singlet (a) and triplet excitons (b) for a number of different long-range e-e interaction strengths in one polymer chain.

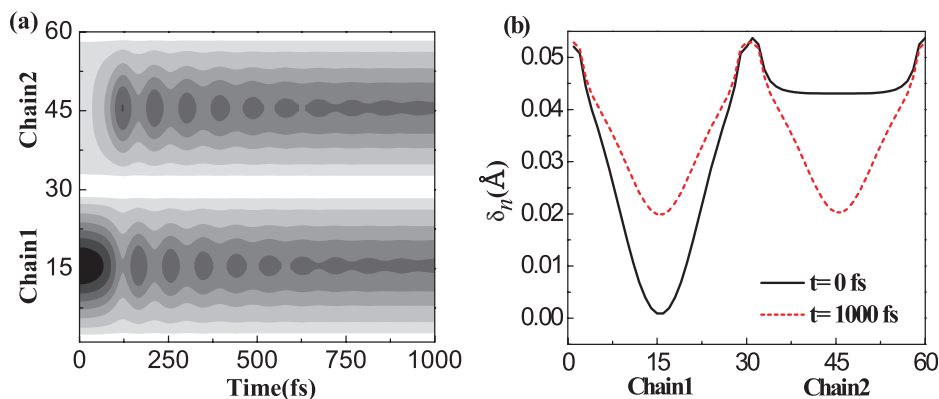


FIG. 4. (a) Evolution of the lattice configurations with time for an interchain coupling $t_{\perp} = 0.25$ eV for the singlet exciton and (b) the lattice configurations at time 0 fs and 1000 fs. The dark region corresponds to the singlet excitons.

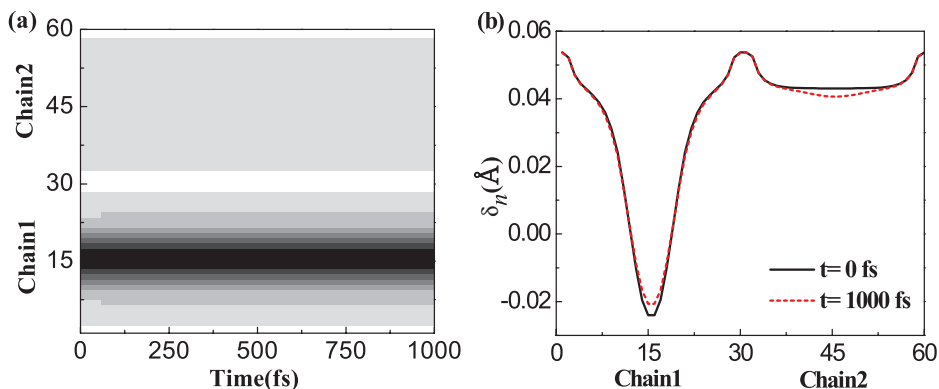


FIG. 5. (a) Evolution of the lattice configurations with time for an interchain coupling $t_{\perp} = 0.25$ eV for the triplet exciton and (b) the lattice configurations at time 0 fs and 1000 fs. The dark region corresponds to the triplet excitons.

and 1000 fs. At 1000 fs, two nearly identical lattice deformations finally emerge, which suggests that the charges separate equally onto the two chains.

The dynamics of the triplet exciton are dramatically different from the singlet exciton at the same interchain coupling strength. In Fig. 5(a), the initial state is a triplet exciton localized on chain 1 while chain 2 remains in the dimerized state. As time goes on, the depth of the distortion on chain 1 is approximately constant. In Fig. 5(b), at 1000 fs, there appears a shallow distortion on chain 2. By comparing the dynamic transfer process between the singlet exciton and the triplet exciton, the important message obtained is that the singlet excitons transfer between chains more easily than the triplet excitons do.

We now analyze the products and their yields after the charge transfer of the singlet exciton and the triplet exciton between two coupled chains. The exciton transfer products for the singlet exciton and the triplet exciton are shown in Fig. 6. We divide the products into four species: the intrachain excitons, including two states: (a) an exciton localized on chain 1 and a ground-state dimerized on chain 2; (b) an exciton localized on chain 2 and a ground-state dimerized on chain 1; the interchain excitons, including two states: (c) a hole-polaron on chain 1 bound to an electron-polaron on chain 2; (d) an electron-polaron on chain 1 bound to a hole-polaron on chain 2. Arithmetic operators “+” and “−” describe

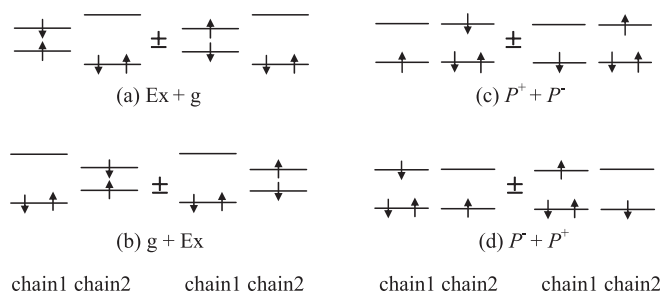


FIG. 6. The possible exciton transfer products, including intrachain excitons (Ex+g and g+Ex) and interchain excitons (enchained polaron-pairs), “+” corresponds to singlet spin-eigenstates, “−” corresponds to triplet spin-eigenstates.

TABLE I. The yields of exciton transfer products for $t_{\perp} = 0.25$ eV: (a) the singlet states and (b) the triplet states.

Exciton transfer products	Singlet yields (a)	Triplet yields (b)
Ex+g	0.25334	0.89391
g+Ex	0.24337	0.0026
$P^+ + P^-$	0.24846	0.04609
$P^- + P^+$	0.24846	0.04609

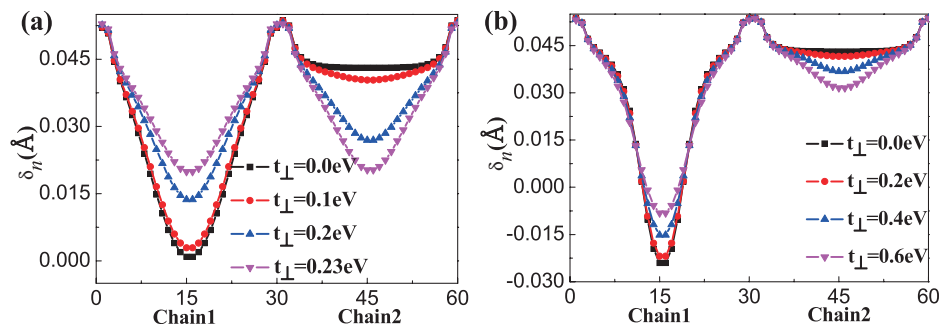


FIG. 7. The lattice configurations for a number of different interchain couplings: (a) the singlet states and (b) the triplet states.

superpositions of the two-slater determinants, “+” corresponds to singlet spin-eigenstates, “−” corresponds to triplet spin-eigenstates.

We also calculate the yields of these products, which are represented in Table I: (a) the singlet spin states, (b) the triplet spin states. For the singlet spin states, the yield of the intrachain excitons is about 49.7%, which is the sum of the two states (a) and (b) of Fig. 6. The yield of the interchain excitons also is about 49.7%, which is the sum of the two states (c) and (d) of Fig. 6. For the triplet states, the yield of the intrachain excitons is about 89.7%, and the yield of the interchain excitons is only about 10%. We can see that the yield of the interchain singlet excitons is far higher than the interchain triplet excitons. These results also quantitatively represent the fact that singlet excitons transfer more easily than the triplet excitons do.

Finally, we study the effects of the interchain coupling strength on the charge transfer process both for the singlet exciton and the triplet exciton. Fig. 7 shows the lattice configurations of the singlet states (a) and the triplet states (b) as a function of the interchain couplings strengths at evolution stable-states. For the singlet spin states, with an increase in the interchain coupling strength, the amplitude of the distortion on chain 1 decreases, and that on chain 2 increases. As an example, for $t_{\perp} = 0.2$ eV, there is a decrease in the displacement on chain 1, along with the emergence of a large distortion on chain 2. When $t_{\perp} \geq 0.23$ eV, complete delocalization of the singlet excitons has taken place. For the triplet spin states, on the other hand, for the same increase in the interchain coupling strength, the decrease in the amplitude of

the distortion on chain 1 is inconspicuous. Note for example, for $t_{\perp} = 0.2$ eV, the small decrease in the displacement on chain 1, along with the emergence of a small distortion on chain 2.

Following these observations, the effects of the interchain coupling strength on the yields of the interchain excitons both for the singlet and triplet states have also been studied. Fig. 8 shows the yields of the interchain excitons as a function of the interchain coupling strength at the evolution steady states. For the singlet spin states, with increasing interchain coupling strength, the yield of the interchain excitons increases, e.g., for $t_{\perp} = 0.1$ eV, the yield is 12%, and for $t_{\perp} = 0.2$ eV, the yield is 45%. When $t_{\perp} \geq 0.23$ eV, the yield of the interchain excitons can reach ratios of 50%. For the triplet spin states, with increasing interchain coupling strength, the increase in the yield of the interchain excitons is slow, e.g., for $t_{\perp} = 0.1$ eV, the yield is 1.5%, and for $t_{\perp} = 0.2$ eV, the yield is only 6%. Even for $t_{\perp} = 0.6$ eV, the yield of the interchain excitons is only 36%.

All the above discussions demonstrate the important point that the singlet excitons transfer more easily between two coupled chains than the triplet excitons do. We can give an explanation by calculating the localities of the singlet exciton and the triplet exciton. With an increase in the interchain coupling, the singlet exciton can easily spread to the neighboring chain. However, the triplet exciton still tends to keep its local status in one chain as the interchain coupling increases. As a result, for the triplet exciton, it is hard to transfer the charge to the neighboring chain. In addition, the hopping of electrons with opposite spins between the coupled chains can facilitate singlet exciton transfer.

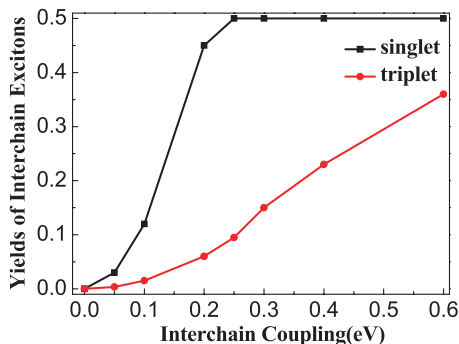


FIG. 8. The yields of the interchain excitons for a number of different interchain couplings for the singlet and triplet states.

IV. SUMMARY

We have simulated the exciton transfer process in two coupled polymer chains by solving the time-dependent Schrödinger equation and the lattice equation of motion nonadiabatically using the SSH+PPP model, including interchain e-p coupling and e-e interactions. The interchain coupling can favor exciton transfer as well as the formation of interchain excitons. More remarkably, with the same interchain coupling, the yield of interchain singlet excitons is higher than that of interchain triplet excitons. That is to say, the singlet excitons can be transferred more easily than the triplet excitons by the effects of the interchain couplings. The results can

be understood as arising from the fact that the singlet exciton is more delocalized than the triplet exciton, as is discussed in the first part of this work. Actually, the hopping of the electrons with opposite spins between chains can facilitate singlet exciton transfer. From previous work, it is known that the formation of interchain excitons can reduce luminous efficiency in organic LEDs, while interchain excitons can be dissociated easily and improve electrical conduction efficiency in organic solar cells. Consequently, the results given here can be used to understand the photoelectric conversion mechanism and discover distinct photoelectric conversion phenomena. At last, it should be mentioned that some two-electron processes, such as direct exciton hopping between molecules, are not involved and only accounted for in a mean-field way within the MCTDHF with fixed coefficients, as pointed out by Miranda *et al.*,¹⁴ for the description of such processes requires a formalism with time-dependent coefficients. However, it should also be noted that the MCTDHF with fixed coefficients catches the essential features of the electronic wavefunctions, such as the spin symmetry, specially, it provides a way to investigate the dynamic properties of singlet and triplet excited states of large interacting-electron systems with an acceptable computation cost at present. Further improvement of the formalism, such as considering time-dependent coefficients and/or more configurations, will be left in future.

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