Field Effect on the Singlet and Triplet Exciton Formation in Organic/Polymeric Light-Emitting Diodes

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Recently, both experimental and theoretical evidence indicate that the electrically-generated singlet and triplet exciton formation ratio ($r_{S/T}$) in conjugated polymers can exceed the 1:3 spin statistics limit. However, the extent that the electric field influences $r_{S/T}$ is in controversy. By measuring the rates of photo- and electrophosphorescence and fluorescence, Wilson et al.[6] concluded that the ratio $r_{S/T}$ is independent of the external electric field; Lin et al.[8] found that the ratio increases monotonically with the electric field by measuring the relative densities of singlet and triplet exciton in EL and PL processes; from a quantum-dynamical calculation, Tandon et al.[11] observed an abrupt increase in the ratio with respect to the electric field. In this work, we apply a correlated quantum-chemical approach coupled with a first-order perturbation, to investigate the relationship between the formation ratio and the electric field. We have calculated the influences of the electric field on the singlet and triplet exciton states as well as on the electron−hole free pair (charge-transfer) state. *It is found that for p*-phenylene-vinylene oligomer, the formation ratio of singlet excitons with respect to triplet excitons increases with the electric field.

I. Introduction

Wide interest has been attracted by π-conjugated polymers, because their electroluminescence (EL) has a huge potential for application in display devices. The polymers as EL-active materials possess the advantages of flexibility, low operating voltage, tunable color, and so on. The conjugated polymers light emitting diodes (PLEDs) usually consist of a layer of a luminescent organic conjugated polymer sandwiched between two metal electrodes. Electrons and holes are injected from the electrodes into the polymer layer. Through interchain hopping processes, the charge carriers migrate in the polymer layer, and then they recombine to form intrachain excitons. The radiative decay of excitons gives rise to the emission of photons, namely, electroluminescence.

The quantum efficiency for EL is defined as the ratio of the number of radiatively-decayed excitons over the number of electrons injected. It can be expressed as $\eta_{EL} = \eta_1\eta_2\eta_3$, where η_1 is the ratio of the number of emitted photons over the number of emissive singlet excitons, η_2 is the ratio of the number of optical excitons over the total number of excitons, and η_3 is the ratio of the total number of excitons over the total number of injected carriers. We note that η_1 expresses the efficiency of the radiative decay of the singlet excitons; η_2, the efficiency of forming optically-active excitons; and η_3, the efficiency of forming bound states during the carriers transport process. According to simple spin statistics, in the process of charge recombination, there are four possible spin micro-states, three of which are nonemissive triplet excitons, one of which is singlet exciton. If the charge carriers' recombination is a spin-independent process then η_2 is 25%, and then the maximum quantum efficiency, η_{max}, of the PLEDs would be limited to 25%.[1]

Recently, however, Cao et al.[2] and Ho et al.[3] found that η_{max} can be as large as 45% to 50% in the derivatives of poly(paraphenylenevinylene) (PPV), by improving either the electron transport or the internal molecular interfaces. By measuring the photoinduced absorption (PA) and photoinduced absorption-detected magnetic resonance (PADMR) for a series of conjugated oligomers and polymers, Wohlgenannt et al.[4,5] have found that the ratio of formation cross sections of singlet and triplet excitons, $r_{S/T}$, is strongly material dependent and in all cases larger than 1. Wilson et al.[6] have studied this ratio directly in working PLED devices of platinum-containing polymer and monomer. They found that for a monomer device, the average ratio is about 22%, while for a polymer it can go up to 57%. They showed that this ratio is independent of the thickness of the film, the temperature, and the electric field. Dhoot et al.[7] have measured the densities of singlet and triplet excitons in the PLED devices, and found that the ratio is about 83%. Lin et al.[8] have measured the relative densities of singlet and triplet excitons both in PL and EL processes, and they found a remarkable dependence of the ratio on the applied electric field. All of these studies show a large variation in singlet formation rates ranging from 22% to 83%.

Despite the reason behind these results remaining unclear, it is now generally accepted that the singlet and triplet excitons can be formed at different rates and the 25% spin statistics limit can usually be overcome in conjugated polymers. Theoretically, several models have been employed to explain why η_2 is not fixed at 25%. Bittner et al.[9] have simulated the intrachain collision of positive and negative polarons through a mixed quantum/classical molecular dynamics approach. Their results show that the formation rate of singlet excitons is larger than that of triplet ones. Shuai et al.[10] have applied the Fermi-Golden-Rule (FGR) to calculate the matrix elements for the exciton formation process in a coupled two-chain model, and found that the intermolecular bond-charge correlation (X-term) induces

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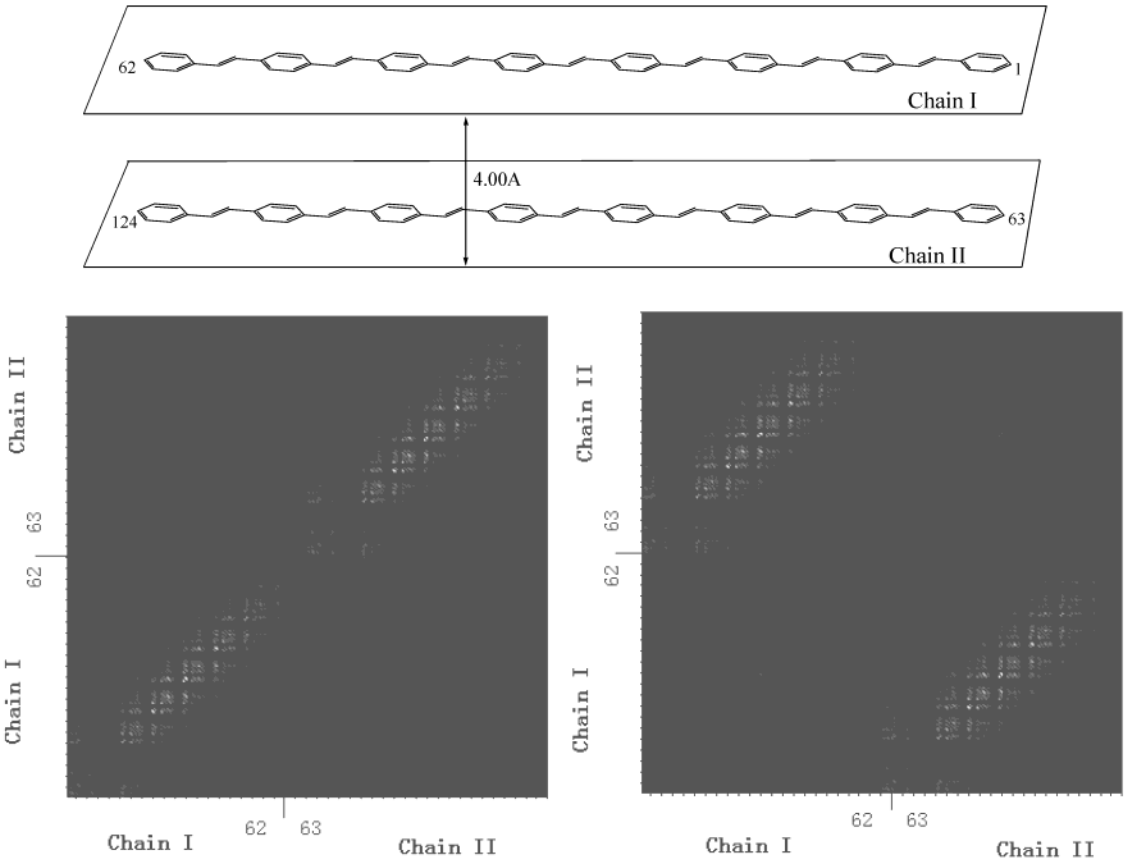

Figure 1. Electron−hole wave function for the lowest singlet excitonic state (left) and the lowest singlet CT state (right) of the cofacial OPV8 dimer in zero field; the distance between the two molecules is 4.00 Å.

spin-dependent exciton formation rates. For PPV, they conclude that η_2 can generally exceed the 25% limit. Tandon et al.[11] developed a model based on two interacting short polyene molecules, which can be solved by employing the exact dynamic evolution method. They found that the materials dependence of $r_{S/T}$ can be described by the effective bond-alternation parameter δ. In addition, they have questioned the applicability of FGR in calculating the spin-dependent exciton formation rates, based on an exact and analytic manipulation for a dimer of ethylene (N=2). While very recently, Shuai et al.[12] found that, only for N=2, the formation rate ratio is independent of the bond-charge correlation; for a longer chain or for a different molecular structure, the X-term comes to play an important role. Shuai et al.[12] concluded that FGR is applicable. Hong and Meng[13] have also suggested a so-called phonon-bottleneck mechanism based on the spin−orbital coupling and the peculiar triplet excited-state structure, which is a totally different view. So far, a clear and commonly-accepted theoretical understanding is not available.

The electric field has influences on many properties, such as charge carry density and mobility.[14] However, the extent to which the electric field can influence the $r_{S/T}$ in PLEDs is in controversy. From Wilson et al.,[6] the $r_{S/T}$ is almost independent of the strength of the applied field. While from Lin et al.,[8] the $r_{S/T}$ strongly increases with electric field strength. By using a time-dependent approach to the interchain charge transfer, Tandon et al.[11] found that there exists a range of field strength where $r_{S/T}$ increases suddenly.

In the present work, we use INDO Hamiltonian coupled to a single configuration interaction (SCI) method to calculate the singlet and triplet excitons and interchain charge transfer states for a cofacial PPV configuration. Then we study the change of energy for excitonic states and charge transfer states when an electric field is applied on the dimers. And then, according to time-dependent first-order perturbation, we modeled the electric field effects on the ratio of the formation cross section of singlet and triplet excitons. Our results show that in the presence of an electric field perpendicular to the molecular plane, the $r_{S/T}$ smoothly increases with electric field. However, when the electric field is parallel to the molecular plane of the conjugated polymers, for a small field strength the $r_{S/T}$ is almost independent of the electric field.

II. Theoretical Methodology

The electroluminscence in a conjugated polymer consists of the following processes: (i) injection of electrons and holes, (ii) charge transport between polymeric interchains, (iii) charge recombination and formation of singlet or triplet excitons, and (iv) the radiative decay of singlet excitons (disregard of intersystem crossing). In the present work, we focus on (iii), and we study the electric field effect on the ratio of formation rates for singlet excitons over triplet excitons.

We choose the highly luminescent system, the oligomers of paraphenylene vinylene (OPV) with 4, 6, 8, and 10 phenyl rings (denoted as OPV4, OPV6, OPV8, and OPV10), as our model molecular systems. The individual oligomer structures are optimized by the semiempirical AM1 method[15] as implemented in the AMPAC package.[16] Then we construct the corresponding dimer by simply putting two oligomers together in the configuration shown in Figure 1, to mimic the charge separation and recombination situation in the PLED device. In fact, the molecular aggregation in the PLED device is quite complicated; there are different distances between chains with different length.

For simplicity, it is assumed that the two cofacial *p*-phenylenevinylene oligomers chains are separated by 4 Å, which is a typical interchain distance. From a time-dependent first-order perturbation theory, or the Fermi Golden Rule, the formation probability from an initial state (the charge separated state) to the final state (the intrachain exciton state) can be expressed as

$$p = \left|\frac{\langle i|H'|f\rangle \sin(\omega_{fi}t/2)}{E_i - E_f}\right|^2 \tag{1}$$

where *p* represents the exciton formation probability. The formation rate is the time derivative of the above quantity

$$\sigma = \frac{\mathrm{d}p}{\mathrm{d}t} = \frac{|\langle i|H'|f\rangle|^2 \sin(\omega_{fi}t)}{2\hbar E_{fi}} \tag{2}$$

H′ is the perturbation operator; $|i\rangle$ and $|f\rangle$ represent the initial state and final state wave functions, and E_i and E_f are the corresponding energy levels, respectively while ω_{fi} is equal to $(E_\mathrm{f} - E_\mathrm{i})/\hbar$. In our model, for the singlet exciton formation cross section (σ_S), $|i\rangle$ and $|f\rangle$ represent the lowest singlet charge transfer state and the singlet exciton state, respectively; while for triplet exciton formation cross section (σ_T), $|i\rangle$ and $|f\rangle$ mean the lowest triplet charge transfer state and triplet exciton state, respectively. Ye and co-workers[10b,10c] have shown in a coupled-cluster equation of motion study that from an initial charge-separated state, the probability to form the lowest exciton state is about 3 orders of magnitude larger than that to form other higher-lying exciton states. In this work, we focus on the energy denominator, and the electronic coupling term is assumed to be unaffected by the electric field. Then, by following Karabunarliev and Bittner[17] and Tandon et al.[11] the ratio $r_{S/T}$ of the formation cross section of the singlet and triplet is

$$r_{S/T} = \frac{\sigma_S}{\sigma_T} = \left(\frac{E_{CT}^T - E_{T1}}{E_{CT}^S - E_{S1}}\right) = \left(\frac{E_b^T}{E_b^S}\right) \tag{3}$$

where $E_\mathrm{CT}^{T/S}$ represents the energy of the triplet/singlet charge transfer state, respectively; $E_{T1/S1}$means the energy of triplet or singlet excitonic state; and $E_b^{T/S}$ is the binding energy of the triplet or singlet exciton. Here we have neglected the oscillatory time-dependent factor. In fact, we only consider the amplitude. We have neglected the electron−phonon coupling. Also, since this is obtained by first-order perturbation, when the initial and final states get close, the approach is not valid.

The central issue of this work is to calculate the energy of the charge transfer (CT) state and the exciton state. Here, we calculate the excited states of the cofacial chains by using INDO Hamiltonian coupled to the single configuration interaction (SCI) method[18,19] with Mataga-Nishimoto parametrization[20] for the two-electron interaction potential. When the electric field is applied on the dimers, the two-molecules-system Schrödinger equation is written as

$$(\hat{H} + \hat{H}_{EF})\Psi_n = E_n'\Psi_n \tag{4}$$

where $\hat{H}$ is the time-independent molecular dimer Hamiltonian without an external field; $\hat{H}_{EF}$ is the applied electric field operator. The range of the electric field strength is up to 10^7 V/cm, close to and slightly higher than those in the experiments of Wilson et al[6] or Lin et al.[8] E_n' represents the energy of the nth state in the electric field. Once we get $E_{CT}^{T/S}$ and $E_{T1/S1}$ in different electric fields, the ratio $r_{S/T}$ of the formation cross section of singlet and triplet excitons can be easily obtained from eq 3.

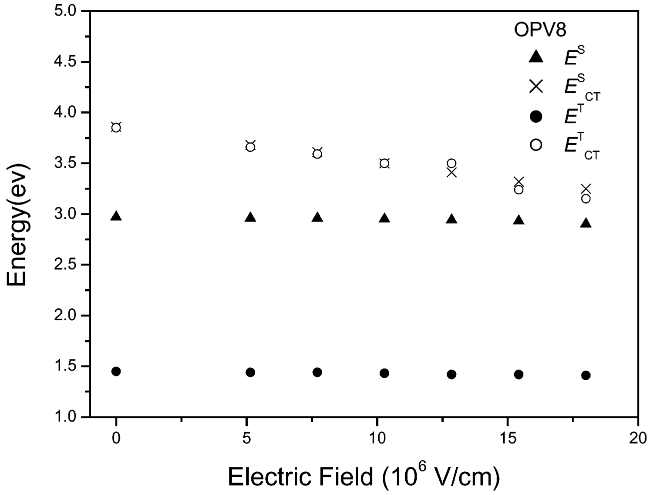

Figure 2. Dependence of the excited-state energies for the cofacial OPV8 dimers on the field strength. Here, the applied electric field is perpendicular to the molecular plane. The up-triangle, cross, hollow circle, and filled circle represent the lowest singlet exciton, the lowest singlet CT state, the lowest triplet CT state, and the lowest triplet exciton, respectively.

III. Results and Discussion

(i) Electric Field Effect on the Energies of Excited States. Through the supermolecular method, we can identify the lowest excitonic state and CT state of dimers. Within the SCI approach, an excited state can be pictured as a linear combination of different excitations from occupied molecular orbitals to virtual orbitals. It can be equivalently viewed as a combination of electron−hole pair excitation with different separation. We can project the many-body wave function into the electron−hole subspace.[21]

The electron/hole wave functions for the lowest excited state in the OPV8 cofacial dimer are displayed in Figure 1. Each data point (x_i,y_i) in the figure represents the probability $|\Psi(x_i,y_i)|^2$ of finding the electron on site x_i and the hole on site y_i, and the brightness is related to the value of $|\Psi(x_i,y_i)|^2$ at point (x_i,y_i). The brighter the zone is, the bigger the probability of finding the electron and the hole on this zone. The molecular exciton state is shown at the left side of the lower panel in Figure 1. It is clearly seen that the brightest region concentrates on the cross line from the lower left to the upper right corners. This indicates that the highest probabilities of finding the electron and hole is on the same chain (intrachain) and the electron and hole are very close, either in chain I or in chain II. However, for the interchain CT state, shown in the right-hand side of Figure 1, we find that the brightest region concentrates on the cross line from the upper left to the lower right corners, which means the highest probability of finding the electron (hole) in one chain is very high only if the hole (electron) is on another chain. In this way, we can easily identify the molecular exciton and the interchain charge transfer states from the quantum chemical calculations.

The calculated energies of excitons and CT states are given in Figure 2 for the electric field perpendicular to the molecular plane and in Figure 3 for the parallel field. From Figure 2, we observed that, (i), the energies of the excited states decrease with the electric field strength; and for the CT state, the decrease is even more pronounced than the molecular exciton state; and

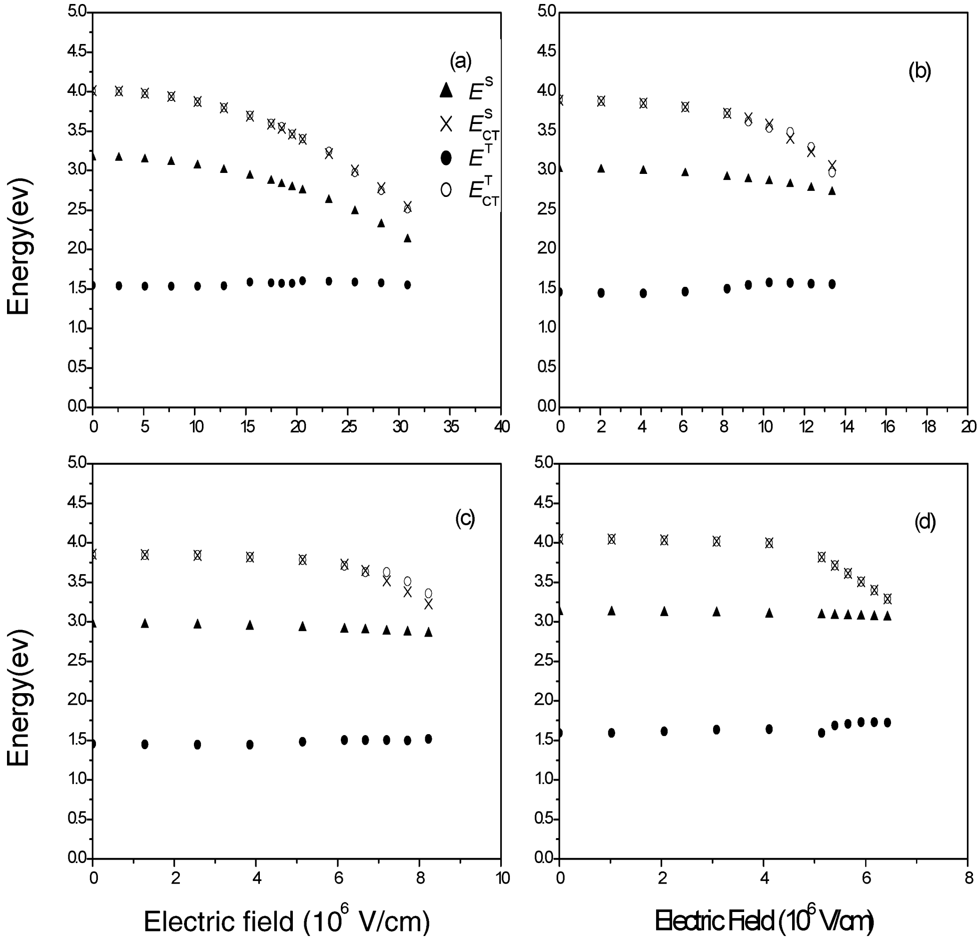

Figure 3. Dependence of excited-state energies for the cofacial dimers on the conjugation length and the field strength. Here, the parallel electric field is applied along the molecular plane. The up-triangle, cross, hollow circle, and filled circle represent the lowest singlet exciton, the lowest singlet CT state, the lowest triplet CT state, and the lowest triplet exciton, respectively. (a), (b), (c), and (d) correspond to OPV4, OPV6, OPV8, and OPV10, respectively.

(ii), the singlet exciton is more sensitive to the electric field than that of triplet exciton. These results can be understood from an electric dipole point of view: When the electric field is applied on the dimer, the energy of the point-dipole will decrease as the following relation

$$E = -\mu \cdot F_{EF} = -|\mu|\cdot|F_{EF}|\cdot\cos\theta \qquad (5)$$

where E is the decrease in energy for the point-dipole in the electric field (F_{EF}). μ is the dipole moment of the excited state and θ is the angle between the vector of the electric field and the vector of the point-dipole; here it is zero. As we know, the CT state is the interchain charge pair while the exciton is the intrachain electron hole bound state. The instantaneous dipole moment of the CT state is much larger than that of the excitonic state because the distance between the electron and the hole for the CT state is longer than that of excitonic states. According to eq 5, the decrease in energy for the CT state is faster than that of the exciton state. As for the triplet exciton, its induced dipole moment is smaller than that of the singlet exciton because the triplet state is of a much more localized character.[22] As a result, the decrease in energy of the singlet exciton is more sensitive to the electric field than that of the triplet exciton. Note here that the perpendicular electric field does not change the relative position of the electron and the hole of the CT states. This is confirmed by Figure 4 where it can be seen that the position the electron and hole of the lowest CT state in the vertical electric field (1.5×10^7 V/cm) is the same as that in a zero electric field (see the right side of Figure 1).

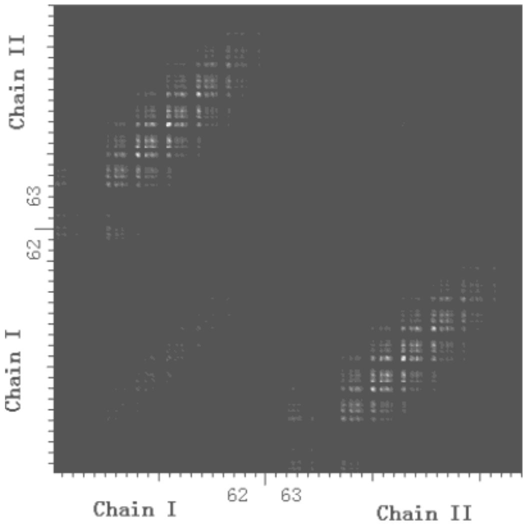

Figure 4. Electron−hole wave functions for the lowest singlet CT state of OPV8 with the electric field perpendicular to the molecular plane. Here, the field strength is 1.5×10^7 V/cm. The distance between the two molecules is 4.00 Å.

When a parallel electric field is applied along the molecular plane, it is seen clearly from Figure 3(c) that for a small electric field strength, all energies of the excited states remain unchanged. When the electric field is increased to a certain value, the energies of the excited states start to decrease, especially for the CT state. This can be rationalized by the point-dipole

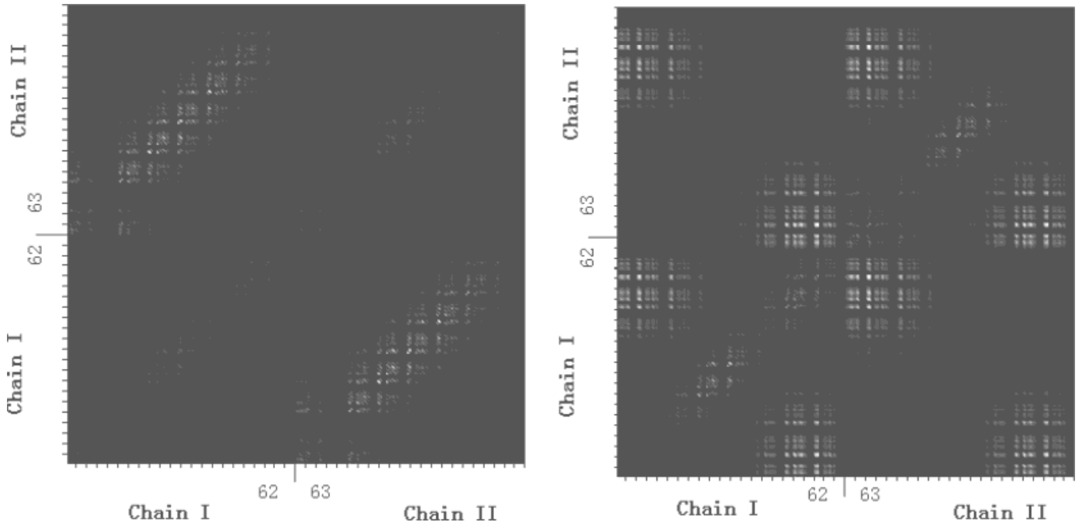

Figure 5. Electron−hole wave function of the lowest singlet CT state for OPV8 within the electric field parallel to the molecular plane. The field strength is 3.8×10^6 V/cm for the left side, and 7.7×10^6 V/cm for the right side, respectively.

picture. When the direction of the electric field is parallel to the OPV8 molecule plane, the direction of the dipole of the CT states is perpendicular to that of the electric field, namely $\theta = \pi/2$; we therefore have $E = 0$. However, the relative position of the electron and the hole will generally change in order to decrease the energy of the CT state in such an electric field; the hole will move along the direction of the electric field in the molecular chain while the electron moves in the opposite direction. Note that for the cofacial dimer structure at a fixed distance, there exists a finite binding energy for the CT state. Thus there exists a threshold field strength that breaks the CT pair down, below which the CT energy is almost independent of the field.

To confirm this rationalization, we illustrate in Figure 5 the electron−hole pair wave function of the lowest single CT state; the left side of the figure is for small field strength, and the right side for large field strength. We find that the position of the electron and hole of the lowest CT state in a small electric field is unchanged. However, for a large electric field, it can be clearly seen that there are many more bright zones; that is, the distribution of the electron and hole in the CT state deviates considerably from that of a low field strength. This indicates that the direction of the instantaneous dipole for the CT state is no longer perpendicular to the direction of the electric field, which eventually results in a decrease in the energy of the CT state.

From Figure 2, we also find that in the presence of a perpendicular electric field the dependence of the excitation energy on the electric field is not affected by the conjugated length. Namely, the field dependence of excited-state energy for OPV4, OPV6, OPV8, and OPV10 are all similar. However, for the parallel electric field case, we find from Figure 3 that the variation of the energies of the CT states with the electric field is sensitive to the conjugation length. This is related to the fact that the electron and hole move toward the opposite direction along the corresponding chains. In general, the longer the conjugation length, the lower the threshold field strength, and the larger the induced dipole moment along the electric field direction.

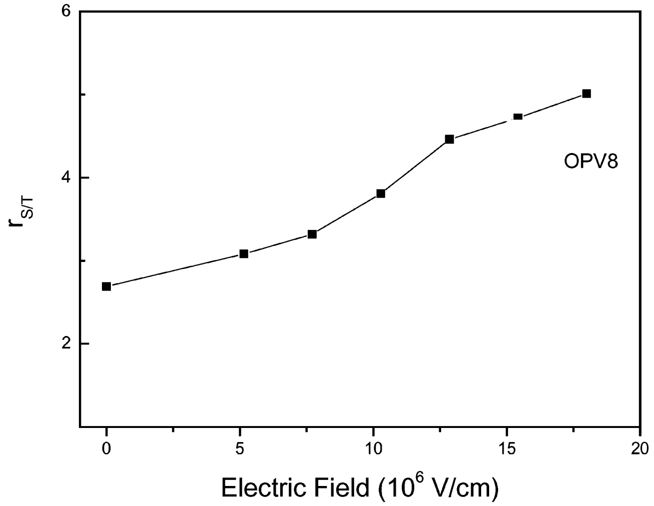

Figure 6. Electric field effect on the ratio of the formation cross section of singlet and triplet excitons for OPV8 dimer. The applied field is perpendicular to the molecular plane.

(ii) Field Effect on the Ratio of the Formation Cross Section Singlet and Triplet Exciton. We now turn to investigate the influence of the electric field on the ratio $r_{S/T}$ of the formation cross section of singlet and triplet excited states, according to eq 3. The results are given in Figure 6 for a perpendicular field and in Figure 7 for a parallel electric field. We find that in the presence of an electric field, the $r_{S/T}$ increases with the electric field strength, which is in good agreement with the experimental conclusions of Lin et al.[8] When a parallel electric field is applied along the molecular plane, we note from Figure 7 that for a small field strength the $r_{S/T}$ remains almost unchanged. This is due to the fact that all energies of excited states do not vary with the electric field as discussed above; while in a large electric field, the $r_{S/T}$ for the OPV6, OPV8, and OPV10 with longer chains increase rapidly with the field strength. From our analysis based on the point-dipole picture, the perpendicular electric field does not alter the excited-state instantaneous dipole for the CT state. Therefore, the $r_{S/T}$ do not relate to the conjugated length of the dimer. However, in a parallel electric field, the electron and hole of the CT states will move toward opposite directions along the corresponding chain, which leads to the increase of the dipolar vector in the direction of the electric field. The dipole moment of the CT state in the direction of the electric field is larger than that of the exciton state. The longer the conjugation length, the larger the dipole. As a result, for the long oligomer, its $r_{S/T}$ is more sensitive to the applied electric field. As for OPV4, the $r_{S/T}$ is almost unaffected by the electric field. This is due to the fact

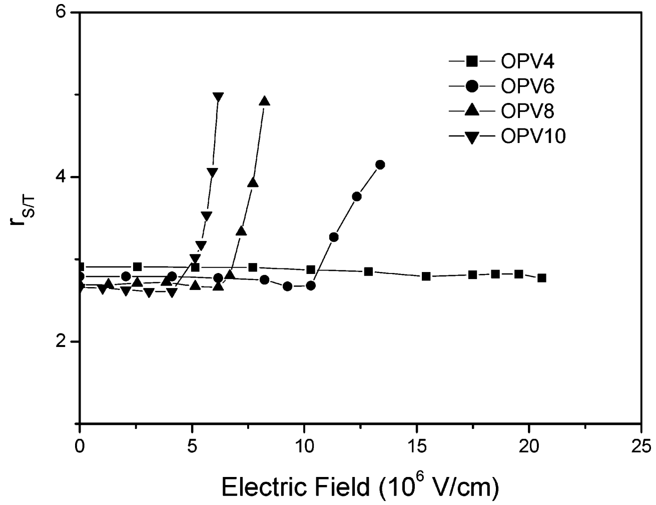

Figure 7. Electric field effect on the ratio of the formation cross section of singlet and triplet excitons for dimers with a different conjugated length. Here, the applied electric field is parallel to the molecular plane.

that the conjugation length of PPV4 is very small, and thus the dipole moment of the CT state in the direction of the electric field is also very small. Therefore, the decrease in energy of the singlet exciton state is almost equal to that of the CT state in the electric field, and the same is true for the case of triplet exciton and CT states. Consequently, the $r_{S/T}$ in OPV4 remains almost unchanged within the scope of the electric field considered in this study. It should be pointed out that the divergence in Figure 7 is an artifact due to the first-order perturbation, when the initial charged state is very close in energy to the final exciton state.

IV. Conclusions

To conclude, we apply a correlated quantum chemical approach coupled with a first-order perturbation; we calculated the energies of the singlet and triplet exciton states as well as the charge transfer states in a vertical or parallel electric field for the *p*-phenylene vinylene oligomers and the effect of the electric field on the formation ratio of singlet and triplet excitons, $r_{S/T}$. We find that in the presence of an electric field perpendicular to the molecular plane, the $r_{S/T}$ increases smoothly with the field strength. However, for the parallel electric field, when the field strength is larger than the threshold field strength, the $r_{S/T}$ increases rapidly with the field strength, and it is sensitive to the conjugation length. The longer the conjugation, the faster the increase of the $r_{S/T}$ with the electric field strength; while the field strength is smaller than the threshold field strength, the $r_{S/T}$ remains unchanged. We have rationalized these behaviors from a point-dipole picture. Our theoretical results support the experimental findings by Lin et al.[8]

Obviously, the exciton binding energies are sensitive to both interchain and intrachain polarization effects.[23,24] The surrounding effect should have influences on the exciton formation ratios. Our two-chain model has addressed part of this effect. A multichain model deserves further study.

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