Singlet and Triplet Exciton Formation Rates in Conjugated Polymer Light-Emitting Diodes

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By applying a molecular orbital perturbation approach, we calculate the formation rates for singlet and triplet molecular excitons associated with intermolecular charge-transfer processes. It is found that the interchain bond-charge correlation has a strong influence on the relative probabilities for generating singlet and triplet excitons. Most importantly, application of our approach to a model system for poly(paraphenylenevinylene) shows that the ratio between the electroluminescence and photoluminescence quantum yields generally exceeds the 25% spin-degeneracy statistical limit.

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Electroluminescence (EL) in conjugated polymers has attracted wide interest because of the huge potential for application in display devices [1]. Polyparaphenylene vinylene (PPV) and its derivatives are among the most prominent polymeric materials to demonstrate large EL efficiency. There is a generally accepted concept that the EL efficiency is limited to 25% of that of photoluminescence (PL), based on the statistics of spin multiplicity; namely, for recombination of a pair of electron and hole (both spin $\frac{1}{2}$), there are four microstates in total, with three triplet states and one singlet state [2].

A polymer light-emitting-diode (LED) device usually consists of a layer of luminescent organic conjugated polymer, sandwiched between two metal electrodes. In the performance of such devices, electrons and holes are first injected from the electrodes into the polymer layer. The charge carriers then migrate through the organic layer, usually via interchain hopping processes, and eventually form intrachain excitons. The radiative decay of the singlet excitons gives rise to emission of photons out of the device, i.e., luminescence. The quantum efficiency for EL can be defined as a product of three factors: $\eta_{\mathrm{EL}} = \eta_1\eta_2\eta_3$, where $\eta_1 =$ (No. of emitted photons)/(No. of optically active singlet excitons); $\eta_2 =$ (No. of optical excitons)/(No. of excitons); $\eta_3 =$ (No. of excitons)/(No. of injected carriers). The singlet excitons can decay both radiatively and nonradiatively, so that $\eta_1 < 1$; η_2 is the center of interest of this Letter: We show below that the probabilities of forming singlet and triplet excitons can be different, thus, η_2 is not necessarily equal to 25%; η_3 is the probability for carriers given rise to intramolecular excitons. At the same time, the PL quantum efficiency can be also decomposed as $\eta_{\mathrm{PL}} = \eta_1\eta_4$, where η_1 is the same as for EL, and $\eta_4 =$ (No. of optical excitons)/(No. of absorbed photons). Usually, $\eta_3 < \eta_4 \sim 1$ [3], so $\eta_{\mathrm{EL}}/\eta_{\mathrm{PL}} = \eta_2\eta_3/\eta_4 < \eta_2$.

Very recently, Cao *et al.* found that the ratio of quantum efficiencies of EL with respect to PL in a substituted PPV-based LED can reach as high as 50% [4]. Since these authors attributed the 25% limit to be a consequence of the formation of strongly bound excitons, they conjectured that either the exciton binding energy is small or that the cross section for an electron-hole pair to form a singlet bound state is significantly higher than that to form a triplet. Note, however, that in PPV the splitting between the lowest singlet and triplet excitons has been calculated to be on the order of 0.7 eV [5], which is large enough to inhibit any possible contribution from thermalized triplet excitons to luminescence [6]. We then consider the second alternative. After all, in the low energy scattering process of neutrons with protons (both with spin $\frac{1}{2}$), the cross section of singlet is about 20 times as large as that of triplet [7]. To take account of possible different cross sections for singlet and triplet states, the expression for η_2 discussed above should be written as $\eta_2 = \sigma_S/(\sigma_S + 3\sigma_T) = \sigma_{S/T}/(\sigma_{S/T} + 3)$, where $\sigma_{S(T)}$ is the cross section for singlet (triplet), and $\sigma_{S/T} = \sigma_S/\sigma_T$. For $\sigma_S = \sigma_T$, then we get $\eta_2 = 25\%$, the statistic limit; for $\sigma_S = 3\sigma_T$, $\eta_2 = 50\%$; for $\sigma_T = 0$, $\eta_2 = 100\%$.

Thus, from the above analysis, we conclude that, for moderately strongly bound excitons, there are at least two possible ways to have $\eta_{\mathrm{EL}}/\eta_{\mathrm{PL}} > 25\%$: (i) The cross section for singlet exciton formation is larger than that of triplet, and (ii) $\eta_3 > \eta_4$, which is unusual. In this work, we apply the molecular orbital (MO) theory to a two-chain model to calculate the formation probabilities of singlet and triplet excitons. We will not discuss here the processes associated with η_3 and η_4.

The one-chain model Hamiltonian is the Pariser-Parr-Pople (PPP) model, which reads

$$H = -\sum_{\langle\mu\nu\rangle s} t_{\mu\nu}(c^{+}_{\mu s}c_{\nu s} + \mathrm{H.c.}) + U\sum_{\mu} n_{\mu\uparrow}n_{\mu\downarrow} + \sum_{\mu<\nu} V(r_{\mu\nu})n_\mu n_\nu \,. \tag{1}$$

The first term represents the π-electron (with spin s) hopping integral ($t_{\mu\nu}$) between nearest-neighbor carbon sites; the second and the third terms are the electron-electron diagonal density-density interaction: $n_{\mu s} = c_{\mu s}^{+} c_{\mu s}$, $n_{\mu} = \sum_s n_{\mu s}$. The long-range interaction for the π electrons of conjugated carbon systems is described by the Ohno-Klopman potential with $U = 11.13$ eV [8]. The hopping integrals are set to standard parameters: Within the vinylene linkage, $t_s = -2.2$ eV for single bonds (1.46 Å) and $t_d = -2.6$ eV for double bonds (1.35 Å); in the phenylene rings, all integrals are set to be $t_b = -2.4$ eV. We then apply the single configuration interaction (SCI) approach to calculate the intrachain exciton states. Hereafter, we apply the following convention: indices $i, j, \ldots$ for occupied MO; $a, b, \ldots$ for virtual MO; $p, q, r, s, \ldots$ for generic MO; $\mu, \nu, \ldots$ for atomic basis (sites). The spin-adapted exciton wave functions can be obtained from SCI as

$$|x1\rangle = \frac{1}{\sqrt{2}} \sum_{i_1 a_1} Z_{i_1 a_1} (a_{1\uparrow}^{+} i_{1\uparrow} \pm a_{1\downarrow}^{+} i_{1\downarrow}) |\text{HF-SCF}\rangle, \tag{2}$$

where the index 1 indicates the polymer chain 1, $+$ and $-$ represent singlet and triplet excited states, respectively. Z_{ia} is the CI coefficient (wave function) associated with an electronic configuration built by promoting one electron from occupied MO i to virtual MO a; $|\text{HF-SCF}\rangle$ denotes the Hartree-Fock self-consistent-field ground state Slater determinant.

For a system consisting of two interacting chains, we can form two initial states to mimic the charge transport processes in EL devices:

$$\begin{aligned} |in_1\rangle &= \frac{1}{\sqrt{2}} (L_{2\uparrow}^{+} H_{1\uparrow} \pm L_{2\downarrow}^{+} H_{1\downarrow}) |\text{HF-SCF}\rangle; \\ |in_2\rangle &= \frac{1}{\sqrt{2}} (L_{1\uparrow}^{+} H_{2\uparrow} \pm L_{1\downarrow}^{+} H_{2\downarrow}) |\text{HF-SCF}\rangle, \end{aligned} \tag{3}$$

with $+$ for singlet and $-$ for triplet. L_2 is the LUMO (lowest unoccupied molecular orbital) of chain 2, and H_2 the HOMO (highest occupied molecular orbital) of chain 2, etc. Here, by virtue of Koopmans' theorem, we assume that the injected electron is located in the LUMO level of one conjugated chain and the hole in the HOMO level of the other chain; this is reasonable since the electron (hole) can relax from higher unoccupied (lower occupied) orbitals to the lowest (highest) one. $|in_1\rangle$ $\{|in_2\rangle\}$ describes an initial state with an electron in chain 2 $\{1\}$ and a hole in chain 1 $\{2\}$. Supposing that the final exciton state takes the form expressed in Eq. (2), where chain 1 is the luminescence center, then the processes starting from the two initial states of Eq. (3) correspond to electron transport (ET) and hole transport (HT), respectively.

Suppose the two chains are coupled, e.g., by H'. A general expression for H' (that includes both one-electron and two-electron parts) reads

$$H' = \sum_{pq} h_{pq} p^{+} q + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle p^{+} q^{+} s r,$$

each term has a mixing of (chains) 1 and 2 spin-orbital indices; h_{pq} is the hopping integral, $t^{\perp}$, in the MO representation: $h_{pq} = \sum_{\mu_1 \nu_2} t^{\perp}(\mu_1, \nu_2) \Psi_{p\mu_1} \Psi_{q\nu_2}$. The following convention is applied:

$$\langle aj || ib \rangle = \langle aj | ib \rangle - \langle aj | bi \rangle, \quad \langle aj | ib \rangle = [ai | jb], \quad \text{and} \quad \langle pq | rs \rangle = \sum_{\mu\nu\sigma\tau} \Psi_{p\mu} \Psi_{q\nu} \Psi_{r\sigma} \Psi_{s\tau} [\mu\sigma | \nu\tau].$$

ψ is the LCAO coefficient of the one-electron wave function, and $[\mu\sigma | \nu\tau]$ is the Coulomb integral in the site representation (for instance, the Hubbard $U = [\mu\mu | \mu\mu]$).

It is then readily possible to evaluate the transition rates from the interchain electron-hole pair states [Eq. (3)] to the on-chain exciton [Eq. (2)], namely, the matrix elements of $\langle x1 | H' | in_1 \rangle$ and $\langle x1 | H' | in_2 \rangle$. After some algebra, it is found that the zero differential overlap term largest in absolute value, $[11 | 22]$, does actually not contribute; most importantly, the only relevant Coulomb integrals are of the types $[11 | 12]$ or $[22 | 21]$, i.e., the interchain charge-bond interaction. For simplicity, hereafter we keep the dominant contributions with only one center in each chain, denoted as $X^{\perp}(\mu_1, \nu_2)$. This term has been found to reduce the dimerization in polyacetylene [9–11] and also has been considered by Rice and Gartstein in the context of photoinduced charge-transfer phenomena [12]. We have made a simple estimate of its value for two butadiene molecules cofacially separated by 4 Å, from an *ab initio* Slater-type-orbital–3-Gaussian calculation. We find in this case that $t^{\perp}$ is about 4 times as large as $X^{\perp}$. However, their relative magnitude can be modified if an orthogonal site basis is used: In this case, even the sign of X could be altered if the electron interaction potential is highly screened [10,11]. For simplicity, we assume an exponential dependence on distance for both $t^{\perp}$ and $X^{\perp}$:$e^{-\zeta r}$, ζ being fixed at 1.4 Å^{-1}, and we treat the ratio of $X^{\perp}/t^{\perp}$ as a variable.

We do not consider disorder explicitly in the Letter. Instead, we consider two limiting cases: (i) weak intermolecular coupling, the electronic states are localized on single chains; and (ii) strong coupling, the electronic states are coherent combinations of localized states. The strength of coupling is related to energetic disorder: A strong disorder induces excitation localization [13]. In the first case, the on-chain excitation is given by Eq. (2), and the initial charge-transfer states are expressed in Eq. (3). In the second case, there are two Davydov states: $|D_1\rangle = (|x1\rangle + |x2\rangle)/\sqrt{2}$, $|D_2\rangle = (|x1\rangle - |x2\rangle)/\sqrt{2}$, with $|x2\rangle$ for the exciton wave function localized on chain 2. The $|D_1\rangle$ state is optically allowed if the two chains are aligned parallel to each other, while $|D_2\rangle$ is dark ($|x1\rangle$ and $|x2\rangle$ are optically allowed themselves). Here, the initial charge pair states are no longer described by Eq. (3); they should be $|D_3\rangle = (|in1\rangle + |in2\rangle)/\sqrt{2}$ and $|D_4\rangle = (|in1\rangle - |in2\rangle)/\sqrt{2}$. We then find the following expressions for the transition rate:

$$\begin{gathered}\langle D_1|H'|D_3\rangle = C_1 - C_2 \pm (C_3 + C_4),\\ \langle D_1|H'|D_4\rangle = 0, \qquad \langle D_2|H'|D_3\rangle = 0,\\ \langle D_2|H'|D_4\rangle = C_1 + C_2 \pm (C_3 - C_4),\end{gathered}$$

where, again, +/− stand for singlet/triplet, and the C terms are defined as

$$C_1 = \sum_{a_1} Z_{H_1 a_1} \sum_{\mu_1 \nu_2} \Psi_{a_1 \mu_1} \Psi_{L_2 \nu_2} \{t^{\perp}_{\mu_1 \nu_2} + X^{\perp}_{\mu_1 \nu_2}\}, \tag{4a}$$

$$C_3 = \sum_{i_1 a_1} Z_{i_1 a_1} \sum_{\mu_1 \nu_2} \Psi_{a_1 \mu_1} \Psi_{H_1 \mu_1} \Psi_{i_1 \mu_1} \Psi_{L_2 \nu_2} X^{\perp}_{\mu_1 \nu_2}. \tag{4b}$$

C_2 is obtained by replacing (a_1, H_1, L_2) by (i_1, L_1, H_2) in Eq. (4a), and C_4 by replacing (H_1, L_2) by (L_1, H_2) in Eq. (4b). C_1 (C_2) represents the hopping of electron (hole) from LUMO (HOMO) of molecule 2 to all the virtual (occupied) orbitals of molecule 1. Note that, usually, the hopping integral is negative and X is positive. So, from Eq. (4a), it is seen that the renormalization effect of the X term tends to reduce $t^{\perp}$. C_3 and C_4 are pure correlation effects which allow one to distinguish singlet from triplet excitations in charge-transfer processes.

The ratio of cross sections for singlet and triplet in the weak coupling limit is given as the following: for ET: $\sigma_{S/T} = [(C_1 + C_3)/(C_1' - C_3')]^2$; for HT: $\sigma_{S/T} = [(-C_2 + C_4)/(-C_2' - C_4')]^2$. In the strong coupling limit, the effects of electron transfer and hole transfer are coherently mixed, constructively for D_1 and destructively for D_2. The ratio of singlet/triplet formation cross sections for Davydov states can then be expressed as

$$\text{for } D_1\text{: } \sigma_{S/T} = \left(\frac{C_1 - C_2 + C_3 + C_4}{C_1' - C_2' - C_3' - C_4'}\right)^2;$$

$$\text{for } D_2\text{: } \sigma_{S/T} = \left(\frac{C_1 + C_2 + C_3 - C_4}{C_1' + C_2' - C_3' + C_4'}\right)^2.$$

The C' terms in the denominators are defined in the same way as the C terms in the numerators, but the former are evaluated with the triplet exciton wave function (Z) and the latter with the singlet. Thus, even for $X = 0$, there is still a slight difference between singlet and triplet exciton formation processes. The expressions of $\sigma_{S/T}$'s show that the cross sections for forming singlet and triplet excitons can be very different if the interchain bond-charge correlation X is taken into account. The correlation effect for the Davydov state D_1 is much more pronounced than in the weak coupling case, because electron and hole contributions are constructive for correlation terms $(C_3 + C_4)$ and destructive for mean field terms $(C_1 - C_2)$. However, for the D_2 excited state, it is constructive for mean field terms $(C_1 + C_2)$ and destructive for correlation terms $(C_3 - C_4)$. Thus, the correlation effect is expected to be much less important for D_2 than for D_1.

To estimate the magnitude of this effect, we have carried out numerical calculations for two six-ring PPV oligomers interacting in a cofacial arrangement with an interchain distance of 4 Å. In Fig. 1, we depict the evolution of the singlet vs triplet cross sections ratio as a function of $X^{\perp}/t^{\perp}$ for the weak and strong coupling cases.

For vanishingly small X value, the correlation effect is negligible. The singlet to triplet ratio is then always around 1.27, which amounts to an η_2 value of 29.7%, *slightly larger* than the statistical limit of 25%. This is due to the difference in the CI coefficients for the singlet and triplet excitons, the contribution from the HOMO-LUMO excitation configuration being larger for the singlet exciton than for the triplet exciton.

From Fig. 1(a), in the weak coupling limit, we find that the electron-transport channel favors triplet exciton formation for $0.2 < X^{\perp}/t^{\perp} < 1$, while the hole-transport channel slightly favors the singlet [14]. This is good

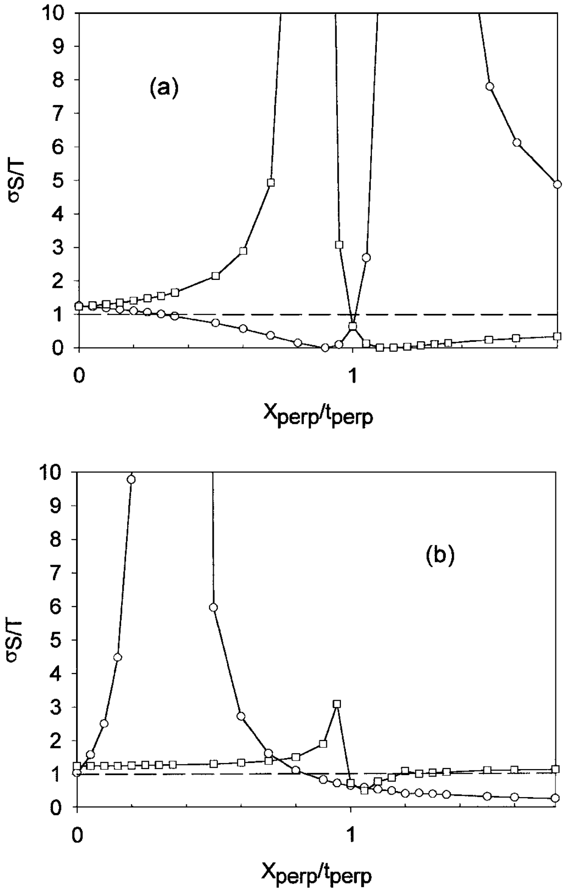

FIG. 1. Evolution of the ratio between singlet exciton and triplet exciton formation cross sections $\sigma_{S/T}$ as a function of $X^{\perp}/t^{\perp}$: (a) in the case of weak coupling, circles for electron transport, squares for hole transport; and (b) in the coherent case (Davydov states), circles for optically active D_1 state, squares for D_2.

news for PPV and its derivatives, since there usually exist deep trap centers that inhibit electron transfer, and, in most cases, holes are therefore the majority charge carriers [15]. The ratio becomes large only when $X^{\perp}$ is comparable to $t^{\perp}$, namely, for hole trapping, $X^{\perp}/t^{\perp} \sim 0.8$, and for electron trapping, $X^{\perp}/t^{\perp} \sim 1.2$. It must be borne in mind that usually $X^{\perp}/t^{\perp} \ll 0.8$. Thus, for weak coupling, we expect not much difference between the formation probabilities of singlet and triplet excitons and an η_2 of ~ 0.3.

In the case of full coherence, Fig. 1(b), the two Davydov states have different behaviors as X is increasing. For the optically active state, $|D_1\rangle$, there occurs a resonance for $X^{\perp}/t^{\perp}$ ranging from 0.15 to 0.5 (the denominator becomes extremely small in this range). This is the consequence of the amplified correlation effect discussed above. For the optically forbidden state $|D_2\rangle$, the ratio is around unity for most of the $X^{\perp}/t^{\perp}$ values (with singlet slightly more favorable), since here the correlation effect of the X term is negligible.

In the experiments of Cao *et al.* [4], electron-transport materials are blended into PPV to ensure balanced injections of holes and electrons. This is expected to improve the coherence between electrons and holes, so that the scenario associated with the limiting case of D_1 in Fig. 1(b) becomes applicable. In this case, a modest $X^{\perp}/t^{\perp} = 0.12$ gives $\sigma_{S/T} = 3$; namely, $\eta_2 = 50\%$.

A feature omitted in this work is the consideration of the energy conservation factor, namely, the dissipation into the lattice of the binding energies of both singlet and triplet excitons. We note that the triplet state lies, in general, about 0.7 eV below the singlet exciton; this fact thus favors the formation of singlets over triplets.

In summary, we have calculated the formation cross section ratios of singlet with respect to triplet excitons in PPV through charge-transfer processes. It is found that correlation effect of bond-charge type distinguishes singlet from triplet exciton formation rates. The correlation effect is evaluated to be very much pronounced for the optically allowed Davydov exciton state, where even a very small bond-charge interaction can bring a large difference in singlet and triplet formation cross sections. The ratio between the electroluminescence and photoluminescence quantum efficiency yields is found to generally exceed the 25% spin-degeneracy statistical limit.

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