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Theory of singlet exciton yield in light-emitting polymers

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The internal electroluminescent quantum efficiency of organic light-emitting diodes is largely determined by the yield of singlet excitons formed by the recombination of the injected electrons and holes. Many recent experiments indicate that in conjugated polymer devices this yield exceeds the statistical limit of 25% expected when the recombination is spin independent. This paper presents a possible explanation for these results. We propose a theory of electron-hole recombination via intermolecular interconversion from intermolecular weakly bound polaron pairs (or charge-transfer excitons) to intramolecular excitons. This theory is applicable to parallel polymer chains. A crucial aspect of the theory is that both the intramolecular and intermolecular excitons are effective particles, which are described by both a relative-particle wave function and a center-of-mass wave function. This implies two electronic selection rules. (i) The parity of the relative-particle wave function implies that interconversion occurs from the even parity intermolecular charge-transfer excitons to the strongly bound intramolecular excitons. (ii) The orthonormality of the center-of-mass wave functions ensures that interconversion occurs from the charge-transfer excitons to the lowest branch of the strongly bound exciton families, and not to higher lying members of these families. The interconversion is then predominately a multiphonon process, determined by the Franck-Condon factors. These factors are exponentially smaller for the triplet manifold than the singlet manifold because of the large exchange energy. As a consequence, the interconversion rate in the triplet manifold is significantly smaller than that of the singlet manifold, and indeed it is comparable to the intersystem crossing rate. Thus, it is possible for the singlet exciton yield in conjugated polymers to be considerably enhanced over the spin-independent recombination value of 25%.

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I. INTRODUCTION

The internal electroluminescent quantum efficiency of organic light-emitting diodes is largely determined by the yield of singlet excitons formed by the recombination of the injected electrons and holes. Singlet exciton yields in light-emitting polymers exceeding the spin-independent recombination value of 25% have now been reported by a large number of groups,[1–7] although its value remains controversial. Lin *et al.*[8] claim that the singlet yield only exceeds the statistical limit in large electric fields,[9] while Segal *et al.*[10] report a singlet exciton yield of only 20%. A photoluminescence-detected magnetic resonance investigation[6] suggests that interchain (or bimolecular) recombination is spin dependent.

Many theoretical attempts have been made to explain the enhanced singlet exciton yield. Bittner *et al.*[11–13] assume that intrachain electron-hole recombination occurs via vibrational relaxation through the band of exciton states between the particle-hole continuum and lowest bound excitons. Since vibrational relaxation is faster in the singlet channel than the triplet channel, because the lowest singlet exciton lies higher in energy than the lowest triplet exciton, a faster formation rate for the singlet than the triplet exciton is predicted. Hong and Meng[14] argue that a multiphonon process in the triplet channel also leads to faster intramolecular singlet exciton formation.

The different rates for singlet and triplet exciton formation predicted in the literature for interchain recombination[15–17] arise largely from the assumption that an interchain density-dependent electron transfer term is an important factor in the recombination mechanism. This term couples states of the same ionicity. Since the interchain charge transfer states are predominately ionic, while the intrachain triplet exciton has more covalent character than the intrachain singlet exciton, the rate for the singlet exciton formation is correspondingly greater.

Most of the recent experimental and theoretical work is reviewed in Refs. 18 and 19. In this paper we develop a model of interchain electron-hole recombination between pairs of parallel polymers that involves intermediate, loosely bound (“charge-transfer”) states that lie energetically between the electron-hole continuum and the final, strongly bound exciton states. We argue that as a consequence of electronic selection rules, intermolecular interconversion occurs from the charge transfer to the lowest energy exciton states. This process is then limited by multiphonon emission, which decreases approximately exponentially with the energy gap between the pair of states. Since the lowest singlet and triplet exciton energies are split by a large exchange energy (of ca. 0.7 eV[20]), while the charge-transfer states are quasidegenerate, the triplet exciton formation rate is considerably smaller than the singlet exciton rate.

Multiphonon emission has already been discussed as a possible factor in determining the overall singlet exciton yield in intramolecular processes.[14,21] However, our model differs from these works by emphasizing the important role of the intermediate interchain charge-transfer states.

In Sec. II we introduce the relevant rate equations and derive an expression for the singlet exciton yield as a function of the characteristic relaxation times. In Sec. III the microscopic model of intermolecular interconversion is described and the interconversion rates are calculated.

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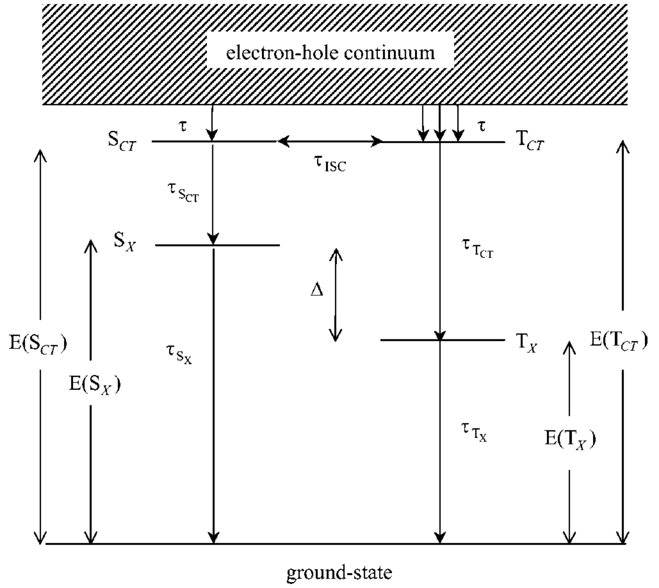

FIG. 1. The energy-level diagram of the quasidegenerate singlet and triplet charge-transfer excitons (denoted by S_{CT} and T_{CT}, respectively) and the lowest singlet and triplet excitons (denoted by S_X and T_X, respectively). S_{CT} and T_{CT} may be either intramolecular odd-parity excitons or intermolecular even-parity excitons. (In each case these correspond to the lowest pseudomomentum members of each exciton family, as described in Sec. III.) Also shown are the respective lifetimes (or inverse rates) for the interconversions within the same spin manifolds and intersystem crossing (ISC) between the spin manifolds. Δ is the exchange energy between S_X and T_X.

II. BASIC MODEL AND THE RATE EQUATIONS

Figure 1 shows the energy-level diagram for this model. The electrons and holes are injected into the polymer device with random spin orientations. Under the influence of the electric field the electrons and holes migrate through the device, rapidly being captured (in less than 10^{-12} s) to form the weakly bound charge-transfer singlet and triplet excitons S_{CT} and T_{CT}, respectively. We assume that no spin mixing occurs during this process, and thus, the ratio of S_{CT} to T_{CT} is 1:3 (Ref. 22). If the intersystem-crossing (ISC) between T_{CT} and S_{CT} (with a rate $1/\tau_{ISC}$) competes with the interconversion from T_{CT} to the triplet exciton T_X, (with a rate $1/\tau_{T_{CT}}$) and $1/\tau_{T_{CT}}$ is smaller than the interconversion rate $(1/\tau_{S_{CT}})$ from S_{CT} to the singlet exciton S_X, then the singlet yield is enhanced.

The charge-transfer states might be either intramolecular loosely bound excitons or weakly bound positive and negative polarons on neighboring chains. Intramolecular charge-transfer states are Mott-Wannier excitons whose relative electron-hole wave functions are odd under electron-hole exchange.[23] A crucial characteristic of these states is that because of their odd electron-hole parity, the probability of finding the electron and hole on the same molecular repeat unit is zero. Thus, they experience very small exchange interactions, and therefore, the singlet and triplet states are quasidegenerate.[23,24] Similarly, the intermolecular weakly bound positive and negative polarons—although now possessing even electron-hole parity—also experience weak exchange interactions as necessarily the electron and hole are on different repeat units, and thus, singlet and triplet states are also quasidegenerate. Furthermore, since the charge-transfer excitons are also weakly bound with relatively large electron-hole separations, there exist efficient spin-flipping mechanisms, such as spin-orbit coupling, or exciton dissociation via the electric field or by scattering from free carriers and defects. In this paper we focus on interconversion to the intramolecular excitons from the interchain charge-transfer excitons.

The strongly bound excitons, S_X and T_X, are intramolecular states. The interconversion process from S_{CT} to S_X and from T_{CT} to T_X depends on the nature of S_{CT} and T_{CT}. The mechanism for bimolecular interconversion is described more fully in Sec. III. In this section we describe the kinetics by classical rate equations. The use of classical rate equations is justified if rapid interconversion follows the ISC between T_{CT} and S_{CT}, as then there will be no coherence or recurrence between T_{CT} and S_{CT}.[27] We also note that since interconversion is followed by rapid vibrational-relaxation (in a time of $\sim 10^{-13}$ s), these processes are irreversible.

We first consider the case where ISC occurs directly via the spin-orbit coupling operator. This operator converts the $S_z = \pm 1$ triplets into the singlet,[14] and vice versa. Let N_{S_X}, $N_{S_{CT}}$, $N_{T_X}^{\pm}$, and $N_{T_{CT}}^{\pm}$ denote the number of S_X, S_{CT}, and the $S_z = \pm 1$ T_X and T_{CT} excitons, respectively. N/τ is the number electron-hole pairs created per second. Then the rate equations are

$$\frac{dN_{S_{CT}}}{dt} = \frac{N}{4\tau} + \frac{N_{T_{CT}}^{\pm}}{\tau_{ISC}} - N_{S_{CT}}\left(\frac{1}{\tau_{ISC}} + \frac{1}{\tau_{S_{CT}}}\right), \tag{1}$$

$$\frac{dN_{T_{CT}}^{\pm}}{dt} = \frac{N}{2\tau} + \frac{N_{S_{CT}}}{\tau_{ISC}} - N_{T_{CT}}^{\pm}\left(\frac{1}{\tau_{ISC}} + \frac{1}{\tau_{T_{CT}}}\right), \tag{2}$$

$$\frac{dN_{S_X}}{dt} = \frac{N_{S_{CT}}}{\tau_{S_{CT}}} - \frac{N_{S_X}}{\tau_{S_X}}, \tag{3}$$

and

$$\frac{dN_{T_X}^{\pm}}{dt} = \frac{N_{T_{CT}}^{\pm}}{\tau_{T_{CT}}} - \frac{N_{T_X}^{\pm}}{\tau_{T_X}}. \tag{4}$$

Note that the $S_z = 0$ component of the T_{CT} exciton is *converted directly* to the $S_z = 0$ component of the T_X exciton and cannot contribute to the singlet exciton yield.

When these equations are solved under the steady-state conditions that

$$\frac{dN_{S_{CT}}}{dt} = \frac{dN_{T_{CT}}^{\pm}}{dt} = \frac{dN_{S_X}}{dt} = \frac{dN_{T_X}^{\pm}}{dt} = 0, \tag{5}$$

we obtain the singlet exciton yield η_S defined by

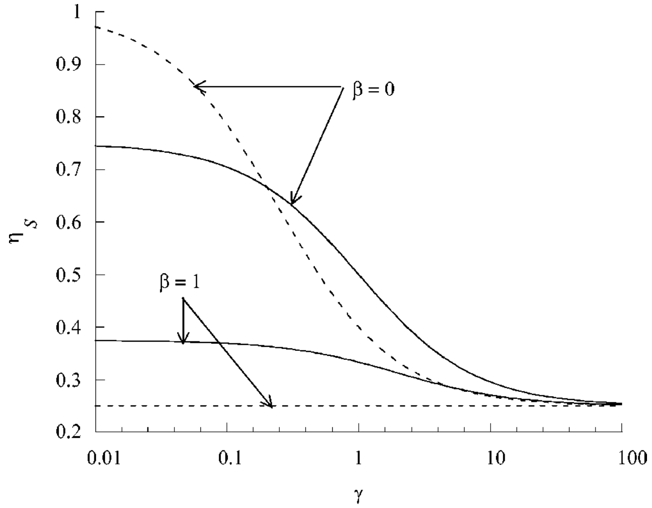

FIG. 2. The singlet exciton yield η_S versus $\gamma = \tau_{ISC}/\tau_{T_{CT}}$. $\beta = \tau_{S_{CT}}/\tau_{T_{CT}}$. Solid curves from Eq. (7); dashed curves from Eq. (8).

$$\eta_S = \frac{N_{S_X}/\tau_{S_X}}{N_{S_X}/\tau_{S_X} + N_{T_X}/\tau_{T_X}} \equiv \frac{N_{S_X}/\tau_{S_X}}{N/\tau}, \tag{6}$$

as

$$\eta_S = \frac{3+\gamma}{4(1+\beta+\gamma)}, \tag{7}$$

where $\beta = \tau_{S_{CT}}/\tau_{T_{CT}}$ and $\gamma = \tau_{ISC}/\tau_{T_{CT}}$.

Alternatively, we might consider ISC via a spin-randomization process, whereby the charge-transfer excitons are scattered into charge-transfer triplets with a probability of $3/4$ and charge-transfer singlets with a probability of $1/4$. Then the rate equations are those of the Appendix of Ref. 9 and the singlet exciton yield becomes[18]

$$\eta_S = \frac{1+\gamma}{1+3\beta+4\gamma}. \tag{8}$$

In practice, as we shall show, $\tau_{T_{CT}} \gg \tau_{S_{CT}}$ so $\beta \approx 0$. We note that η_S is a function only of the relative lifetimes of S_{CT} and T_{CT}, and the ISC rate. The singlet yield is plotted in Fig. 2 as a function of γ. We now describe the calculation of the relative rates.

III. DERIVATION OF THE INTER-MOLECULAR INTER-CONVERSION RATE

The Born-Oppenheimer (B-O) Hamiltonian for a pair of coupled polymer chains is

$$H = \sum_{\ell=1}^{2} H_{intra}^{(\ell)} + H_{inter}, \tag{9}$$

where $H_{intra}^{(\ell)}$ is the intrachain B-O Hamiltonian for the ℓth chain and H_{inter} is the interchain B-O Hamiltonian. We split the interchain Hamiltonian into two components: the interchain one-electron Hamiltonian H_{inter}^1 and the interchain two-electron Hamiltonian H_{inter}^2. H_{inter}^2 predominately describes the Coulomb interactions between the π electrons on neighboring chains. H_{inter}^1 describes electron transfer between chains. For parallel chains with nearest-neighbor electron transfer this is

$$H_{inter}^1 = -t_{inter} \sum_{i\sigma} (c_{i\sigma}^{(1)\dagger} c_{i\sigma}^{(2)} + c_{i\sigma}^{(2)\dagger} c_{i\sigma}^{(1)}), \tag{10}$$

where $c_{i\sigma}^{(\ell)\dagger}$ ($c_{i\sigma}^{(\ell)}$) creates (destroys) a π electron on site i of chain ℓ and t_{inter} is the interchain hybridization integral. If the chains are weakly coupled, then we may regard H_{inter}^1 as a perturbation on the approximate Hamiltonian

$$\tilde{H} = \sum_{\ell=1}^{2} H_{intra}^{(\ell)} + H_{inter}^2. \tag{11}$$

Within the Born-Oppenheimer approximation the electronic and nuclear degrees of freedom are described by the Born-Oppenheimer states. A Born-Oppenheimer state $|A\rangle$ is a direct product of an electronic state, $|a;\{Q\}\rangle$, and a nuclear state associated with that electronic state, $|\nu_a\rangle$

$$|A\rangle = |a;\{Q\}\rangle|\nu_a\rangle. \tag{12}$$

The $\{Q\}$ label indicates that the electronic state is parametrized by the nuclear coordinates.

The stationary electronic states are the eigenstates of the approximate Hamiltonian $\tilde{H}$. Thus, the perturbation H_{inter}^1 mixes these electronic states. In particular, it causes an interconversion from the interchain excitons (or weakly bound polaron pairs) to the intrachain excitons by transferring charge from one chain to another.

We take the initial electronic state to be a positive polaron on chain 1 and a negative polaron on chain 2

$$|i\rangle = |P^+, P^-; Q_1, Q_2\rangle. \tag{13}$$

The interchain Coulomb interaction between the chains creates a weakly bound charge-transfer exciton, to be described below. The labels Q_1 and Q_2 indicate the independent normal coordinates of chains 1 and 2, respectively.

We consider the situation where the negative polaron is transferred from chain 2 to chain 1 by H_{inter}^1. Thus, the final state is an intramolecular exciton on chain 1 (denoted by $|a\rangle$), leaving chain 2 in its ground electronic state

$$|f\rangle = |a;Q_1\rangle^{(1)}|1A_g;Q_2\rangle^{(2)}. \tag{14}$$

Before proceeding it will be useful to review the theory of excitons in conjugated polymers. In the weak-coupling limit (namely, the limit that the Coulomb interactions are less than or equal to the band width) the intramolecular excited states of semiconducting conjugated polymers are Mott-Wannier excitons described by[22]

$$|a;Q\rangle = \sum_{r,R} \psi_n(r;Q)\Psi_j(R)|r,R\rangle. \tag{15}$$

$|r,R\rangle$ is an electron-hole basis state constructed by promoting an electron from the filled valence band Wannier orbital at $R-r/2$ to the empty conduction band Wannier orbital at $R+r/2$,

$$|r,R\rangle = \tfrac{1}{\sqrt{2}}(c^{c(\ell)\dagger}_{R+r/2,\uparrow}c^{v(\ell)}_{R-r/2,\uparrow} \pm c^{c(\ell)\dagger}_{R+r/2,\downarrow}c^{v(\ell)}_{R-r/2,\downarrow})|1^1A_g\rangle . \qquad (16)$$

$c^{v(\ell)\dagger}_{m\sigma}$ and $c^{c(\ell)\dagger}_{m\sigma}$ are the valence and conduction Wannier orbital operators, respectively, approximately defined by

$$c^{v(\ell)\dagger}_{m\sigma} = \tfrac{1}{\sqrt{2}}(c^{(\ell)\dagger}_{2m-1\sigma} + c^{(\ell)\dagger}_{2jm\sigma}) \qquad (17)$$

and

$$c^{c(\ell)\dagger}_{m\sigma} = \tfrac{1}{\sqrt{2}}(c^{(\ell)\dagger}_{2m-1\sigma} - c^{(\ell)\dagger}_{2m\sigma}), \qquad (18)$$

where m is the unit cell index. The ± symbol in Eq. (16) refers to singlet $(+)$ or triplet $(-)$ excitons.

R is the center-of-mass coordinate, and r is the relative coordinate of the effective particle. $\psi_n(r;Q)$ is a hydrogen-like electron-hole wave function labeled by the principle quantum number n, which describes the effective-particle. This has the property that under electron-hole reflection (namely, $r \to -r$) $\psi_n(r;Q)=\psi_n(-r;Q)$ for odd n and $\psi_n(r;Q)=-\psi_n(-r;Q)$ for even n, and

$$\Psi_j(R) = \sqrt{\frac{2}{N+1}}\sin(\beta R) \qquad (19)$$

is the center-of-mass wave function, which describes the motion of the effective-particle on a linear chain. N is the number of unit cells. For each principle quantum number n, there is a *band* of excitons with different pseudomomentum $\beta = \pi j/(N+1)d$, where j satisfies $1 \leqslant j \leqslant N$ and d is the unit-cell distance. Thus, every exciton-state label a corresponds to two independent quantum numbers: n and j. As described in Ref. 23, $n=1$ corresponds to the S_X and T_X families of intrachain excitons, while $n=2$ corresponds to the S_{CT} and T_{CT} families of intrachain excitons. The lowest energy member of each family has the smallest pseudomomentum, namely, $j=1$.[28]

It is also convenient to describe the intermolecular weakly bound polaron pairs as charge-transfer excitons described by

$$|P^+,P^-;Q_1,Q_2\rangle = \sum_{r,R} \tilde{\psi}_n(r;Q_1,Q_2)\Psi_j(R)|r,R;2\rangle, \qquad (20)$$

where $\tilde{\psi}_n$ represents the interchain effective-particle wave function. $n=1$ (i.e., even electron-hole parity) for the lowest energy interchain excitons. $|r,R;2\rangle$ is an electron-hole basis state constructed by promoting an electron from the filled valence band Wannier orbital at $R-r/2$ on chain 1 to the empty conduction band Wannier orbital at $R+r/2$ on chain 2,

$$|r,R;2\rangle = \tfrac{1}{\sqrt{2}}(c^{c(2)\dagger}_{R+r/2,\uparrow}c^{v(1)}_{R-r/2,\uparrow} \pm c^{c(2)\dagger}_{R+r/2,\downarrow}c^{v(1)}_{R-r/2,\downarrow})|1^1A_g\rangle^{(1)}|1^1A_g\rangle^{(2)}. \qquad (21)$$

With this background to the theory of excitons we now proceed to derive the transfer rate. The isoenergetic interconversion rate from the initial to the final states is determined by the Fermi Golden Rule expression,

$$k_{I\to F} = \frac{2\pi}{\hbar}\langle F|H^1_{inter}|I\rangle^2\delta(E_F - E_I), \qquad (22)$$

where the initial and final B-O states are

$$|I\rangle = |P^+,P^-;Q_1,Q_2\rangle|\nu_{P^+}\rangle^{(1)}|\nu_{P^-}\rangle^{(2)} \qquad (23)$$

and

$$|F\rangle = |a;Q_1\rangle^{(1)}|1A_g;Q_2\rangle^{(2)}|\nu_a\rangle^{(1)}|\nu_{1^1A_g}\rangle^{(2)}, \qquad (24)$$

respectively.

A. Electronic matrix elements

The corresponding electronic matrix element is

$$\langle f|H^1_{inter}|i\rangle = {}^{(2)}\langle 1^1A_g;Q_2|^{(1)}\langle a;Q_1|H^1_{inter}|P^+,P^-;Q_1,Q_2\rangle . \qquad (25)$$

Using Eqs. (15) and (20) this is

$$\langle f|H^1_{inter}|i\rangle = \frac{2}{N+1}\sum_{r',R'} \psi_{n'}(r';Q_1)\sin(\beta' R') \times \sum_{r,R} \tilde{\psi}_n(r;Q_1,Q_2)\sin(\beta R) \times {}^{(2)}\langle 1^1A_g;Q_2|^{(1)}\langle r',R'|H^1_{inter}|r,R;2\rangle . \qquad (26)$$

This matrix element is evaluated by expressing H^1_{inter} in terms of the valence and conduction Wannier orbital operators. Retaining terms that keep within the exciton subspace, we have

$$H^1_{inter} = -t_{inter}\sum_{m\sigma}(c^{v(1)\dagger}_{m\sigma}c^{v(2)}_{m\sigma} + c^{c(1)\dagger}_{m\sigma}c^{c(2)}_{m\sigma}) + \text{H.c.} \qquad (27)$$

Then,

$$\langle f|H^1_{inter}|i\rangle = -t_{inter}\frac{2}{N+1}\sum_{r',r}\psi_{n'}(r';Q_1)\tilde{\psi}_n(r;Q_1,Q_2) \times \sum_{R',R}\sin(\beta' R')\sin(\beta R)^{(1)}\langle r',R'|r,R\rangle^{(1)}. \qquad (28)$$

By exploiting the orthonormality of the basis functions

$$\langle r',R'|r,R\rangle = \delta_{r'r}\delta_{R'R} \qquad (29)$$

as well as the $\sin(\beta R)$ functions

$$\frac{2}{N+1}\sum_R \sin(\beta' R)\sin(\beta R) = \delta_{\beta'\beta}, \qquad (30)$$

we have the final result for the electronic matrix element

$$\langle f|H^1_{inter}|i\rangle = -t_{inter}\sum_r \psi_{n'}(r;Q_1)\tilde{\psi}_n(r;Q_1,Q_2). \qquad (31)$$

Equations (30), (19), and (31) demonstrate the very significant result that interconversion via H^1_{inter} is subject to two electronic selection rules.

(i) Interconversion occurs between excitons with the same center-of-mass pseudomomentum β_j.

(ii) Interconversion occurs between excitons with the same electron-hole parity. Thus, $|n'-n|=\text{even}$.

Since the lowest energy interchain excitons have even electron-hole parity, this implies that H^1_{inter} connects them to S_X and T_X and not to the intramolecular S_{CT} and T_{CT}.[29] Moreover, since the interchain exciton will have relaxed to its lowest momentum state, H^1_{inter} converts it to the intrachain exciton in its lowest momentum state and *not to higher-lying momentum states*.

B. Vibrational overlaps

We now discuss the contribution of the vibrational wave functions to the total matrix element. Intermolecular interconversion is an isoenergetic process that occurs from the lowest pseudomomentum state of the charge-transfer manifold and the lowest vibrational levels of this state to the lowest pseudomomentum state of the intramolecular excitons at the same energy as the initial level. Thus, the vibrational levels in Eq. (23) are $\nu_{P^+}=0$ and $\nu_{P^-}=0$. However, the vibrational levels in Eq. (24) are determined by the conservation of energy.

Using Eq. (22) the rate is thus,

$$\begin{aligned} k_{I\to F} &= \frac{2\pi}{\hbar}|\langle f|H^1_{inter}|i\rangle|^2 \sum_{\nu_1\nu_2} F^{(1)}_{0\nu_1}F^{(2)}_{0\nu_2}\delta(E_F - E_I) \\ &= \frac{2\pi}{\hbar}|\langle f|H^1_{inter}|i\rangle|^2 \sum_{\nu_1\nu_2} F^{(1)}_{0\nu_1}F^{(2)}_{0\nu_2}\delta(\Delta E_1^{\nu_1} + \Delta E_2^{\nu_2}), \end{aligned} \tag{32}$$

where

$$F^{(1)}_{0\nu_1} = \left|{}^{(1)}\langle 0_{P^+}|\nu_a\rangle^{(1)}\right|^2 \tag{33}$$

and

$$F^{(2)}_{0\nu_2} = \left|{}^{(2)}\langle 0_{P^-}|\nu_{1^1A_g}\rangle^{(2)}\right|^2 \tag{34}$$

are the Franck-Condon factors associated with the vibrational wave function overlaps of chains 1 and 2, respectively. Likewise,

$$\Delta E_1^{\nu_1} = E_1(a;\nu_a) - E_1(P^+;0_{P^+}) \tag{35}$$

and

$$\Delta E_2^{\nu_1} = E_2(1^1A_g;\nu_{1^1A_g}) - E_2(P^-;0_{P^-}) \tag{36}$$

are the changes in energy of chains 1 and 2, respectively. These changes in energy are illustrated in Fig. 3.

Using the identity,

$$\delta(x+y) = \int \delta(x-z)\,\delta(y+z)dz \tag{37}$$

we can rewrite Eq. (32) as

$$\begin{aligned} k_{I\to F} = \frac{2\pi}{\hbar}|\langle f|H^1_{inter}|i\rangle|^2 \int \sum_{\nu_1\nu_2} F^{(1)}_{0\nu_1}F^{(2)}_{0\nu_2}\delta(\Delta E_1^{\nu_1} - E) \\ \times\,\delta(\Delta E_2^{\nu_2} + E)dE. \end{aligned} \tag{38}$$

Defining the spectral functions for the donor (chain 2) and acceptor (chain 1) as

$$D(E) = \sum_{\nu_2} F^{(2)}_{0\nu_2}\delta(\Delta E_2^{\nu_2} + E) \tag{39}$$

and

$$A(E) = \sum_{\nu_1} F^{(1)}_{0\nu_1}\delta(\Delta E_1^{\nu_1} - E), \tag{40}$$

respectively, we have the familiar rate expression for bimolecular electron transfer

$$k_{I\to F} = \frac{2\pi}{\hbar}|\langle f|H^1_{inter}|i\rangle|^2 \int D(E)A(E)dE. \tag{41}$$

A useful simplification to this expression arises by noting that the geometric distortions of the polarons and exciton polarons (namely, the 1^1B_u or 1^3B_u states) from the ground-state structure are very similar.[30] Thus, the Huang-Rhys parameter (proportional to ΔQ_1^2, as defined in Fig. 3) for the 1^1B_u and 1^3B_u states relative to the positive polaron is negligible. Therefore,

$$F_{0\nu_1} \sim \delta_{0\nu_1}, \tag{42}$$

and thus, the change of energy of chain 1 is

$$\Delta E_1^{\nu_1} \equiv \Delta E_1^0, \tag{43}$$

where ΔE_1^0 is the $0-0$ energy difference on chain 1 between the final exciton state and the positive polaron. This is illustrated in Fig. 3. By the conservation of energy, we therefore have

$$\Delta E_2^{\nu_2} = -\Delta E_1^0. \tag{44}$$

The vibrational level ν_2 of the final 1^1A_g state of chain 2 to which interconversion from the negative polaron initially occurs is given by

$$\begin{aligned} \nu_2 &= (\Delta E_2^0 - \Delta E_2^{\nu_2})/\hbar\omega = (\Delta E_2^0 + \Delta E_1^0)/\hbar\omega \\ &= (E_2(P^-;0_{P^-}) - E_2(1^1A_g;0_{1^1A_g}) + E_1(P^+;0_{P^+}) \\ &\quad - E_1(a;0_a))/\hbar\omega \\ &= (\Delta E_{CT} - \Delta E_a)/\hbar\omega, \end{aligned} \tag{45}$$

where

$$\begin{aligned} \Delta E_{CT} = [E_1(P^+;0_{P^+}) - E_1(1^1A_g;0_{1^1A_g})] \\ + [E_2(P^-;0_{P^-}) - E_2(1^1A_g;0_{1^1A_g})] \end{aligned} \tag{46}$$

and

$$\Delta E_a = E_1(a;0_a) - E_1(1^1A_g;0_{1^1A_g}) \tag{47}$$

are the $0-0$ transition energies of the charge-transfer exciton and the state $|a\rangle$, respectively.

The condition expressed in Eq. (43) implies that the energy integral in Eq. (38) is restricted to the value of $E=\Delta E_1^0$, and thus, the rate becomes

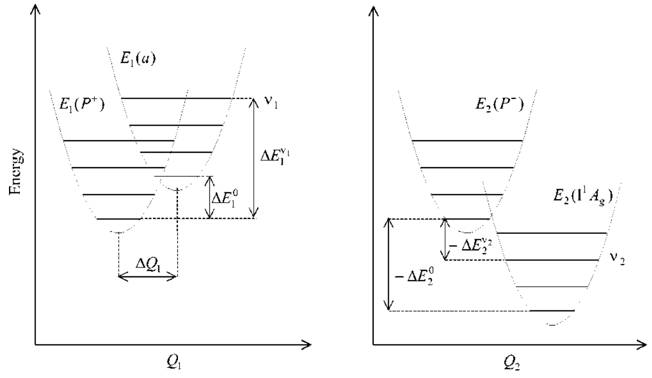

FIG. 3. Bimolecular electron transfer from chain 2 to chain 1. The initial state is a positive polaron on chain 1 and a negative polaron on chain 2, each in their lowest vibrational level. The electron transfer creates an exciton state in chain 1, with chain 2 in its ground state. The energy differences between the final and initial states are $\Delta E_\ell^{\nu_\ell}$ for the ℓth chain. If $\Delta Q_1=0$ then $\Delta E_1^{\nu_1}=\Delta E_1^0$ and thus $\Delta E_2^{\nu_2}=-\Delta E_1^0$.

$$\begin{aligned} k_{I\to F} &= \frac{2\pi}{\hbar}|\langle f|H^1_{inter}|i\rangle|^2 \sum_{\nu_2} F^{(2)}_{0\nu_2}\delta(\Delta E_2^{\nu_2}+\Delta E_1^0) \\ &= \frac{2\pi}{\hbar}|\langle f|H^1_{inter}|i\rangle|^2 F^{(2)}_{0\nu_2}\rho_f(E). \end{aligned} \tag{48}$$

$\rho_f(E)$ is the final density of states on chain 2, defined by

$$\rho_f(E)=\sum_{\nu_2}\delta(\Delta E_2^{\nu_2}+\Delta E_1^0), \tag{49}$$

which is usually taken to be the inverse of the vibrational energy spacing. Inserting the expression for the Franck-Condon factor,

$$F^{(2)}_{0\nu_2}=\left|{}^{(2)}\langle 0_{P^-}|\nu_{1^1A_g}\rangle^{(2)}\right|^2=\frac{\exp(-\mathsf{S}_p)\mathsf{S}_p^{\nu_2}}{\nu_2!}, \tag{50}$$

we have the final result that

$$k_{I\to F}=\frac{2\pi}{\hbar}|\langle f|H^1_{inter}|i\rangle|^2\rho_f(E)\frac{\exp(-\mathsf{S}_p)\mathsf{S}_p^{\nu_2}}{\nu_2!}. \tag{51}$$

This equation, along with the definition of $\langle f|H^1_{inter}|i\rangle$ in Eq. (31), is our final expression for the interconversion rate. S_p is the Huang-Rhys factor for the polaron relative to the ground state, defined as $E_d/\hbar\omega$, where E_d is the reorganization (or relaxation) energy of the polaron relative to the ground state. After the isoenergetic transition, there is vibrational relaxation to the lowest vibrational level of the 1^1A_g state of chain 2 via the sequential emission of ν_2 phonons. The number of phonons emitted corresponds to the difference in energies between the initial charge-transfer and final exciton states, given by Eq. (45). This is a multiphonon process. In Sec. IV, we estimate these rates.

IV. ESTIMATE OF THE INTERCONVERSION RATES

Since interconversion from the intermolecular to the intramolecular charge-transfer excitons is forbidden by symmetry, we now only discuss interconversion to the lowest excitons, S_X or T_X. (As remarked in footnote,[29] interconversion to higher-lying exciton states is allowed, but if this happens recombination is an intramolecular process via the intramolecular charge-transfer excitons.) Thus, the state label a is now either S_X or T_X, and the number of phonons emitted, ν_2, is either ν_S or ν_T, as determined by Eq. (45).

Within the Mott-Wannier basis the exciton wave function overlaps are easy to calculate. Using $t_{inter}=0.1$ eV,[17] the interchain distance as 4 Å and standard semiempirical Coulomb interactions gives

$$\sum_r \psi_{S_X}(r)\tilde{\psi}_{S_{CT}}(r)\approx 1.0 \tag{52}$$

and

$$\sum_r \psi_{T_X}(r)\tilde{\psi}_{T_{CT}}(r)\approx 0.9. \tag{53}$$

The polaron Huang-Rhys parameter S_p is not accurately known for light-emitting polymers. However, we expect it to be similar to the S_X exciton Huang-Rhys parameter. The relaxation energy of the S_X exciton has been experimentally determined as 0.07 eV in PPV,[31] with a similar value calculated for ‘ladder’ PPP in Ref. 32. From the figures in Ref. 33, we estimate the relaxation energy to be 0.12 eV in ladder PPP (where the phenyl rings are planar) and 0.25 eV in PPP (where the phenyl rings are free to rotate). Thus, taking the relaxation energy as 0.1 eV and $\hbar\omega=0.2$ eV implies that $\mathsf{S}_p\sim 0.5$.

Now, using $\hbar\omega=0.2$ eV$(\equiv\rho_f^{-1})$, $\mathsf{S}_p\sim 0.5$ and assuming that the energy difference between the strongly bound singlet exciton (S_X) and the *intramolecular* charge-transfer excitons of ∼0.8 eV is approximately the energy difference between the singlet exciton and the *intermolecular* charge-transfer excitons, we can estimate the interconversion rate for the singlet exciton. This is $k_{S_{CT}\to S_X}\sim 7.5\times 10^{11}$ s^{-1} (or $\tau_{S_{CT}}\sim 1$ ps). Similarly, using an exchange gap of ∼0.7 eV gives $k_{T_{CT}\to T_X}\sim 1\times 10^8$ s^{-1} (or $\tau_{T_{CT}}\sim 10$ ns). Thus, the triplet interconversion rate is much slower than the singlet interconversion rate.

The ISC rate is also not accurately known, with quoted values of 0.3 ns (Ref. 21), 4 ns (Ref. 34), and 10 ns (Ref. 35). Nevertheless, despite this uncertainty, we see that the estimated triplet interconversion rate is comparable to or slower than the ISC rate, which from Eq. (7) implies a large singlet exciton yield.

Generally, the ratio of the rates is

$$\frac{k_{S_{CT}\to S_X}}{k_{T_{CT}\to T_X}}=\frac{|\sum_r \psi_{S_X}(r)\tilde{\psi}_{S_{CT}}(r)|^2\exp(-\mathsf{S}_p)\dfrac{\mathsf{S}_p^{\nu_S}}{\nu_S!}}{|\sum_r \psi_{T_X}(r)\tilde{\psi}_{T_{CT}}(r)|^2\exp(-\mathsf{S}_p)\dfrac{\mathsf{S}_p^{\nu_T}}{\nu_T!}}. \tag{54}$$

Thus,

$$\frac{k_{S_{CT}\rightarrow S_X}}{k_{T_{CT}\rightarrow T_X}} = 1.2\mathsf{S}_p^{-(\nu_T-\nu_S)}\frac{\nu_T!}{\nu_S!}. \tag{55}$$

This ratio increases as S_p decreases because then multiphonon emission becomes more difficult. The ratio also increases as the exchange energy $\hbar\omega(\nu_T-\nu_S)$ increases for any ν_S or ν_T if $\mathsf{S}_p<1$.

V. DISCUSSION AND CONCLUSIONS

We propose a theory of electron-hole recombination via intermolecular interconversion from intermolecular weakly bound polaron pairs (or charge-transfer excitons) to intramolecular excitons. This theory is applicable to parallel polymer chains. A crucial aspect of the theory is that both the intramolecular and intermolecular excitons are effective particles, which are described by both a relative-particle wave function and a center-of-mass wave function. This implies two electronic selection rules.

(i) The parity of the relative-particle wave function implies that interconversion occurs from the even parity intermolecular charge-transfer excitons to the strongly bound intramolecular excitons and not to the intramolecular charge-transfer excitons (namely, the first odd-parity exciton). (However, if the interchain charge transfer excitons lie higher in energy than the second family of even-parity intrachain exciton, recombination will be an intramolecular process.)

(ii) The orthonormality of the center-of-mass wave functions ensures that interconversion occurs from the charge-transfer excitons to the lowest branch of the strongly bound exciton families and not to higher lying members of these families.

These selection rules imply that interconversion is then predominately a multiphonon process determined by the Franck-Condon factors. These factors are exponentially smaller for the triplet manifold than the singlet manifold because of the large exchange energy.

There is also a contribution to the rates from the overlap of the relative-particle wave functions, which again are smaller in the triplet manifold because the triplet exciton has a smaller particle-hole separation and has more covalent character than its singlet counterpart.[17] As a consequence, the interconversion rate in the triplet manifold is significantly smaller than that of the singlet manifold, and indeed, it is comparable to the ISC rates. Thus, it is possible for the singlet exciton yield to be considerably enhanced over the spin-independent value of 25% in conjugated polymers.

Any successful theory must explain the observation that the singlet exciton yield is close to 25% for molecules and increases with conjugation length.[3,5] This theory qualitatively predicts this trend for two reasons. First, the effective-particle description of the exciton states is only formally exact for long chains. This description breaks down when the chain length (or more correctly, conjugation length) is comparable to the particle-hole separation. In this case separation of the center-of-mass motion and the relative-particle motion is no longer valid. Then the quantum numbers n and j, which describe the relative-particle wave function and center-of-mass wave function, respectively, are no longer independent quantum numbers. Interconversion is then expected to take place between all the states lying between the charge-transfer state and the lowest exciton state. However, as the chain length increases interconversion to higher lying states is suppressed in favor of the lowest-lying exciton. This prediction is confirmed by a recent quantum-mechanical calcuation by Beljonne *et al.*[36] The second reason that the singlet exciton yield is enhanced in polymers over molecules is that the Huang-Rhys parameters decrease as the conjugation length increases, and thus, the relative rate [given by Eq. (54)] increases.

We note that the effective-particle description is still valid when there is self-trapping. In this case the center-of-mass wave fuctions are not the particle-in-the-box wave functions appropriate for a linear chains [Eq. (19)], but they are the ortho-normalized functions appropriate for the particular potential well trapping the effective particle. The key point is that because these are orthonormalized functions interconversion occurs between a pair of states with the same center-of-mass quantum numbers as described in this paper.

This theory has been formulated for an idealized case of sufficiently long, parallel polymer chains. The applicability of this theory for polymer light-emitting displays needs verifying by performing calculations on oligomers of arbitrary length and arbitrary relative conformations.

Finally, we remark that this theory presents strategies for enhancing the singlet exciton yield. Ideally, the polymer chains should be well conjugated, closely packed, and parallel. The last two conditions ensure that the interchain charge-transfer excitons lie energetically below high-lying even-parity families of intramolecular excitons, and thus, recombination is an interchain interconversion process and not an intramolecular process via the intramolecular charge-transfer excitons. Intramolecular recombination is not desirable because although interconversion from the intrachain charge-transfer excitons is slower in the triplet manifold; than the singlet manifold, both rates are expected to be faster than the ISC rate. The relative intermolecular interconversion rates are also increased when the electron-lattice coupling is reduced. This suggests that the singlet exciton yield is enhanced in rigid, well-conjugated polymers.

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