Theory of the singlet exciton yield in light-emitting polymers

William Barford

Department of Physics and Astronomy, University of Sheffield, Sheffield, S3 7RH, United Kingdom
Cavendish Laboratory, University of Cambridge, Cambridge, CB3 0HE, United Kingdom

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 inter-molecular inter-conversion from inter-molecular weakly bound polaron pairs (or charge-transfer excitons) to intra-molecular excitons. This theory is applicable to parallel polymer chains. A crucial aspect of the theory is that both the intra-molecular and inter-molecular excitons are effective-particles, which are described by both a relative-particle wavefunction and a center-of-mass wavefunction. This implies two electronic selection rules. (1) The parity of the relative-particle wavefunction implies that inter-conversion occurs from the even parity inter-molecular charge-transfer excitons to the strongly bound intra-molecular excitons. (2) The orthonormality of the center-of-mass wavefunctions ensures that inter-conversion 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 inter-conversion is then predominately a multi-phonon 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 inter-conversion rate in the triplet manifold is significantly smaller than that of the singlet manifold, and indeed it is comparable to the inter-system 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%

PACS numbers: 78.67.-n, 77.22.-d

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, although its value remains controversial. Lin et al. claim that the singlet yield only exceeds the statistical limit in large electric fields, while Segal et al. report a singlet exciton yield of only 20%. A photoluminescence detected magnetic resonance investigation suggests that inter-chain (or bimolecular) recombination is spin-dependent.

Many theoretical attempts have been made to explain the enhanced singlet exciton yield. Bittner et al. assume that intra-chain 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 argue that a multi-phonon process in the triplet channel also leads to faster intra-molecular singlet exciton formation.

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

Most of the recent experimental and theoretical work is reviewed in ref. In this paper we develop a model of inter-chain 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, inter-molecular inter-conversion occurs from the charge transfer to the lowest energy exciton states. This process is then limited by multi-phonon 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), while the charge-transfer states are quasi-degenerate, the triplet exciton formation rate is considerably smaller than the singlet exciton rate.

Multi-phonon emission has already been discussed as a possible factor in determining the overall singlet exciton
FIG. 1: The energy level diagram of the quasi-degenerate 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 intra-molecular odd parity excitons or inter-molecular even parity excitons. (In each case these correspond to the lowest pseudo-momentum members of each exciton family, as described in Section III.) Also shown are the respective lifetimes (or inverse rates) for the inter-conversions within the same spin manifolds and inter-system crossing (ISC) between the spin manifolds. $\Delta$ is the exchange energy between $S_X$ and $T_X$.

yield in intra-molecular processes$^{15,22}$. However, our model differs from these works by emphasizing the important role of the intermediate inter-chain charge-transfer states.

In the next section we introduce the relevant rate equations and derive an expression for the singlet exciton yield as a function of the characteristic relaxation times. In the following section the microscopic model of inter-molecular inter-conversion is described and the inter-conversion rates are calculated.

II. BASIC MODEL AND THE RATE EQUATIONS

Fig. 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$^{23}$. If the inter-system-crossing (ISC) between $T_{CT}$ and $S_{CT}$ (with a rate $1/\tau_{ISC}$) competes with the inter-conversion 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 inter-conversion 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 intra-molecular loosely bound excitons or weakly bound positive and negative polarons on neighboring chains. Intra-molecular charge-transfer states are Mott-Wannier excitons whose relative electron-hole wavefunctions are odd under electron-hole exchange$^{24}$. 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 quasi-degenerate$^{24,25}$. Similarly, the inter-molecular 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 quasi-degenerate. 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 inter-conversion to the intra-molecular excitons from the inter-chain charge-transfer excitons.

The strongly bound excitons, $S_X$ and $T_X$, are intra-molecular states. The inter-conversion 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 bi-molecular inter-conversion is described more fully in the next section. In this section we describe the kinetics by classical rate equations. The use of classical rate equations is justified if rapid inter-conversion follows the ISC between $T_{CT}$ and $S_{CT}$, as then there will be no coherence or recurrence between $T_{CT}$ and $S_{CT}$. We also note that since inter-conversion 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, 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.

The rate equations are:

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

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

\[
\frac{dN_{S_X}}{dt} = \frac{N_{S_{CT}}}{\tau_{S_{CT}}} - \frac{N_{S_X}}{\tau_{S_X}},
\]

\[
\frac{dN_{T_X}^\pm}{dt} = \frac{N_{T_{CT}}^\pm}{\tau_{T_{CT}}} - \frac{N_{T_X}^\pm}{\tau_{T_X}},
\]

Notice 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

\[
\frac{dN_{S_{CT}}}{dt} = \frac{dN_{T_{CT}}^\pm}{dt} = \frac{dN_{S_X}}{dt} = \frac{dN_{T_X}^\pm}{dt} = 0
\]

we obtain the singlet exciton yield, $\eta_S$, defined by,

\[
\eta_S = \frac{N_{S_X}/\tau_{S_X}}{N_{S_X}/\tau_{S_X} + N_{T_X}/\tau_{T_X}} \equiv \frac{N_{S_X}/\tau_{S_X}}{N/\tau},
\]

as

\[
\eta_S = \frac{3 + \gamma}{4(1 + \beta + \gamma)},
\]

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\(^{19}\) and the singlet exciton yield becomes\(^{19}\)

\[
\eta_S = \frac{1 + \gamma}{1 + 3\beta + 4\gamma},
\]

In practice, as we shall show, $\tau_{T_{CT}} \gg \tau_{S_{CT}}$ so $\beta \approx 0$. We note that $\eta_S$ is a function only of the relative life-times of $S_{CT}$ and $T_{CT}$, and the ISC rate. The singlet yield is plotted in Fig. 2 as a function of $\gamma$. We now describe the calculation of the relative rates.
FIG. 2: The singlet exciton yield, $\eta_S$, versus $\gamma = \tau_{IS} / \tau_{TCT}$. $\beta = \tau_{SCT} / \tau_{TCT}$. Solid curves from Eq. (7), dashed curves from Eq. (8).

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

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

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

(9)

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

$$H_{\text{inter}}^{1} = -t_{\text{inter}} \sum_{i\sigma} \left( c_{i\sigma}^{(1)} c_{i\sigma}^{(2)} + c_{i\sigma}^{(2)} c_{i\sigma}^{(1)} \right),$$

(10)

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

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

(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, $|\nu_a\rangle$:

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

(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, $H_{\text{inter}}$ mixes these electronic states. In particular, it causes an inter-conversion from the inter-chain excitons (or weakly bound polaron pairs) to the intra-chain 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,

$$|\iota\rangle = |P^+, P^-; Q_1, Q_2\rangle.$$  

(13)
The inter-chain 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 $H^1_{\text{inter}}$. Thus, the final state is an intra-molecular exciton on chain 1 (denoted by $|a\rangle$), leaving chain 2 in its ground electronic state,

$$|f\rangle = |a; Q_1^{(1)}1^1A_g; Q_2^{(2)}\rangle.$$  \hfill (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 intra-molecular excited states of semi-conducting conjugated polymers are Mott-Wannier excitons described by

$$|a; Q\rangle = \sum_{r,R} \psi_n(r; Q) \Psi_j(R)|r, R\rangle.$$  \hfill (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 $R + r/2$,

$$|r, R\rangle = \frac{1}{\sqrt{2}} \left( c_{r+\pi/2,1}^{(1)} c_{r-\pi/2,1}^{(1)} + c_{r+\pi/2,2}^{(1)} c_{r-\pi/2,2}^{(1)} \right) |1^1A_g\rangle.$$  \hfill (16)

$c_{m\sigma}^{(1)}$ and $c_{m\sigma}^{(2)}$ are the valence and conduction Wannier orbital operators, respectively, approximately defined by,

$$c_{m\sigma}^{(1)} = \frac{1}{\sqrt{2}} \left( c_{2m-1,1}^{(1)} + c_{2m,1}^{(1)} \right)$$  \hfill (17)

and

$$c_{m\sigma}^{(2)} = \frac{1}{\sqrt{2}} \left( c_{2m-1,1}^{(2)} - c_{2m,1}^{(2)} \right),$$  \hfill (18)

where $m$ is the unit cell index. The $\pm$ symbol in Eq. \hfill (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 wavefunction labelled 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 $n$.

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

is the center-of-mass wavefunction, 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 pseudo-momentum, $\beta = \pi j/(N+1)d$, where $j$ satisfies $1 \leq j \leq N$ 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 \hfill (20), $n = 1$ corresponds to the $S_X$ and $T_X$ families of intra-chain excitons, while $n = 2$ corresponds to the $S_{CT}$ and $T_{CT}$ families of intra-chain excitons. The lowest energy member of each family has the smallest pseudo-momentum, namely, $j = \hfill (20)$.

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

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

where $\tilde{\psi}_n$ represents the inter-chain effective-particle wavefunction. $n = 1$ (i.e. even electron-hole parity) for the lowest energy inter-chain 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,

$$|r, R; 2\rangle = \frac{1}{\sqrt{2}} \left( c_{r+\pi/2,1}^{(2)} c_{r-\pi/2,1}^{(1)} + c_{r+\pi/2,2}^{(2)} c_{r-\pi/2,2}^{(1)} \right) |1^1A_g\rangle^{(1)} |1^1A_g\rangle^{(2)}.$$  \hfill (21)

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

$$k_{I \to F} = \frac{2\pi}{\hbar} \langle F | H^1_{\text{inter}} | I \rangle^2 \delta(E_F - E_I).$$  \hfill (22)
where the initial and final B-O states are,
\[ |I\rangle = |P^{+}, P^{-}; Q_1, Q_2\rangle |\nu_{P^{+}}\rangle_1 |\nu_{P^{-}}\rangle_2 \]  \hspace{1cm} (23)
and
\[ |F\rangle = |a; Q_1\rangle_1 |1A_g; Q_2\rangle_2 |\nu_a\rangle_1 |\nu_{1A_g}\rangle_2 , \]  \hspace{1cm} (24)
respectively.

A. Electronic matrix elements

The corresponding electronic matrix element is,
\[ \langle f | H^1_{\text{inter}} | i \rangle = (2) \langle 1 | a; Q_1\rangle_1 \langle r' | H^1_{\text{inter}} | r, R \rangle \langle r, R | 1 | Q_1, Q_2\rangle_2 . \]  \hspace{1cm} (25)
Using Eq. (15) and Eq. (20) this is,
\[ \langle f | H^1_{\text{inter}} | i \rangle = \left( \frac{2}{N+1} \right) \sum_{r'} \sum_{R'} \sum_{r,R} \psi_n(r'; Q_1) \tilde{\psi}_n(r; Q_1, Q_2) \sin(\beta R') \times \]  \hspace{1cm} (26)
\[ \langle r', R' | H^1_{\text{inter}} | r, R \rangle \langle r, R | 1 | Q_1, Q_2\rangle_2 . \]
This matrix element is evaluated by expressing \( H^1_{\text{inter}} \) in terms of the valence and conduction Wannier orbital operators. Retaining terms that keep within the exciton sub-space we have,
\[ H^1_{\text{inter}} = -t_{\text{inter}} \sum_{m,\sigma} \left( c_{ma}^{\dagger} (1) c_{ma}^{\dagger} (2) c_{ma} (1) c_{ma} (2) \right) + \text{H.C.} \]  \hspace{1cm} (27)
Then,
\[ \langle f | H^1_{\text{inter}} | i \rangle = -t_{\text{inter}} \sum_{m,\sigma} \left( \psi_n(r'; Q_1) \tilde{\psi}_n(r; Q_1, Q_2) \sin(\beta R') \sin(\beta R) \times \right. \]  \hspace{1cm} (28)
\[ \left. \langle r', R' | H^1_{\text{inter}} | r, R \rangle \langle r, R | 1 | Q_1, Q_2\rangle_2 \right). \]
By exploiting the orthonormality of the basis functions,
\[ \langle r', R' | r, R \rangle = \delta_{r',r} \delta_{R',R}, \]  \hspace{1cm} (29)
as well as the \( \sin(\beta R) \) functions,
\[ \left( \frac{2}{N+1} \right) \sum_{R} \sin(\beta R') \sin(\beta R) = \delta_{\beta',\beta}, \]  \hspace{1cm} (30)
we have the final result for the electronic matrix element,
\[ \langle f | H^1_{\text{inter}} | i \rangle = -t_{\text{inter}} \sum_{r} \psi_n(r'; Q_1) \tilde{\psi}_n(r; Q_1, Q_2) . \]  \hspace{1cm} (31)

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

1. Inter-conversion occurs between excitons with the same centre-of-mass pseudo-momentum, \( \beta_j \).
2. Inter-conversion occurs between excitons with the same electron-hole parity. Thus, \( |n' - n| = \text{even} \).

Since the lowest energy inter-chain excitons have even electron-hole parity this implies that \( H^1_{\text{inter}} \) connects them to \( S_X \) and \( T_X \), and not to the intra-molecular \( S_{CT} \) and \( T_{CT} \). Moreover, since the inter-chain exciton will have relaxed to its lowest momentum state, \( H^1_{\text{inter}} \) converts it to the intra-chain exciton in its lowest momentum state, and not to higher lying momentum states.
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 $\Delta E_1^\nu_1$ for the $1$th chain. If $\Delta Q_1 = 0$ then $\Delta E_1^\nu_1 = \Delta E_1^0$ and thus $\Delta E_2^\nu_2 = -\Delta E_1^0$.

**B. Vibrational overlaps**

We now discuss the contribution of the vibrational wavefunctions to the total matrix element. Inter-molecular inter-conversion is an iso-energetic process which occurs from the lowest pseudo-momentum state of the charge-transfer manifold and the lowest vibrational levels of this state to the lowest pseudo-momentum state of the intra-molecular 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,

$$k_{I \rightarrow F} = \frac{2\pi}{\hbar} |(f|H_{\text{inter}}^1|i)|^2 \sum_{\nu_1 \nu_2} F_{0\nu_1}^{(1)} F_{0\nu_2}^{(2)} \delta(E_F - E_1)$$

$$= \frac{2\pi}{\hbar} |(f|H_{\text{inter}}^1|i)|^2 \sum_{\nu_1 \nu_2} F_{0\nu_1}^{(1)} F_{0\nu_2}^{(2)} \delta(\Delta E_1^{\nu_1} + \Delta E_2^{\nu_2}) \quad (32)$$

where

$$F_{0\nu_1}^{(1)} = |(1)\langle 0_{P^+}|\nu_a^1 \rangle (1)|^2 \quad (33)$$

and

$$F_{0\nu_2}^{(2)} = |(2)\langle 0_{P^-}|\nu_{1A_g}^1 \rangle (2)|^2 \quad (34)$$

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

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

and

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

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

Using the identity,

$$\delta(x + y) = \int \delta(x - z) \delta(y + z) dz \quad (37)$$
we can re-write Eq. (32) as,

\[ k_{I \rightarrow F} = \frac{2\pi}{\hbar} |\langle f |H_{\text{inter}}^1|i\rangle|^2 \int \sum_{\nu_1\nu_2} F_{0\nu_1}^{(1)} F_{0\nu_2}^{(2)} \delta(\Delta E_{\nu_1}^0 - E)\delta(\Delta E_{\nu_2}^0 + E) dE. \]  

(38)

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

\[ D(E) = \sum_{\nu_2} F_{0\nu_2}^{(2)} \delta(\Delta E_{\nu_2}^0 + E) \]  

(39)

and

\[ A(E) = \sum_{\nu_1} F_{0\nu_1}^{(1)} \delta(\Delta E_{\nu_1}^0 - E), \]  

(40)

respectively, we have the familiar rate expression for bi-molecular electron transfer,

\[ k_{I \rightarrow F} = \frac{2\pi}{\hbar} |\langle f |H_{\text{inter}}^1|i\rangle|^2 \int D(E)A(E) dE. \]  

(41)

A useful simplification to this expression arises by noting that the geometric distortions of the polarons and exciton polarons (namely the 1\textsuperscript{1}B\textsubscript{u} or 1\textsuperscript{1}B\textsubscript{u} states) from the ground state structure are very similar.\textsuperscript{32} Thus, the Huang-Rhys parameter (proportional to \(\Delta Q_1^0\), as defined in Fig. 3) for the 1\textsuperscript{1}B\textsubscript{u} and 1\textsuperscript{1}B\textsubscript{u} states relative to the positive polaron is negligible. Therefore,

\[ F_{0\nu_1} \sim \delta_{0\nu_1}, \]  

(42)

and thus the change of energy of chain 1 is,

\[ \Delta E_{\nu_1}^0 \equiv \Delta E_{1}^0, \]  

(43)

where \(\Delta E_{1}^0\) is the 0 \(\rightarrow\) 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,

\[ \Delta E_{\nu_2}^0 = -\Delta E_{1}^0. \]  

(44)

The vibrational level, \(\nu_2\), of the final 1\textsuperscript{1}A\textsubscript{g} state of chain 2 to which inter-conversion from the negative polaron initially occurs is given by,

\[ \nu_2 = (\Delta E_{2}^0 - \Delta E_{\nu_2}^0)/\hbar\omega = (\Delta E_{2}^0 + \Delta E_{1}^0)/\hbar\omega \]

\[ = (E_2(P^-;0P^-) - E_2(1\textsuperscript{1}A_g;0_{11}A_g) + E_1(P^+;0P^+) - E_1(a;0_a))/\hbar\omega \]

\[ = (\Delta E_{\text{CT}} - \Delta E_a)/\hbar\omega, \]  

(45)

where

\[ \Delta E_{\text{CT}} = (E_1(P^+;0P^+) - E_1(1\textsuperscript{1}A_g;0_{11}A_g)) + (E_2(P^-;0P^-) - E_2(1\textsuperscript{1}A_g;0_{11}A_g)) \]  

(46)

and

\[ \Delta E_a = E_1(a;0_a) - E_1(1\textsuperscript{1}A_g;0_{11}A_g) \]  

(47)

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

The condition expressed in Eq. (13) implies that the energy integral in Eq. (38) is restricted to the value of \(E = \Delta E_{1}^0\), and thus the rate becomes,

\[ k_{I \rightarrow F} = \frac{2\pi}{\hbar} |\langle f |H_{\text{inter}}^1|i\rangle|^2 \sum_{\nu_2} F_{0\nu_2}^{(2)} \delta(\Delta E_{\nu_2}^0 + \Delta E_{1}^0) \]

\[ = \frac{2\pi}{\hbar} |\langle f |H_{\text{inter}}^1|i\rangle|^2 F_{0\nu_2}^{(2)} \rho_f(E). \]  

(48)
\( \rho_f(E) \) is the final density of states on chain 2, defined by,

\[
\rho_f(E) = \sum_{\nu_2} \delta(\Delta E_2^{\nu_2} + \Delta E_1^0),
\]

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

\[
F_{0\nu_2}^{(2)} = \left| \langle 0 | \rho_1 | \nu_1, A_\nu \rangle \right|^2 = \frac{\exp(-S_p)S_p^{\nu_2}}{\nu_2!}
\]

we have the final result that,

\[
k_{I \to F} = \frac{2\pi}{\hbar} \left| \langle f | H_{\text{inter}}^1 | i \rangle \right|^2 \rho_f(E) \frac{\exp(-S_p)S_p^{\nu_2}}{\nu_2!}.
\]

This equation, along with the definition of \( \langle f | H_{\text{inter}}^1 | i \rangle \) in Eq. (41), is our final expression for the inter-conversion 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 iso-energetic transition there is vibrational relaxation to the lowest vibrational level of the \( 1^1A_g \) state of chain 2 via the sequential emission of \( \nu_2 \) 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 multi-phonon process. In the next section we estimate these rates.

### IV. ESTIMATE OF THE INTER-CONVERSION RATES

Since inter-conversion from the inter-molecular to the intra-molecular charge-transfer excitons is forbidden by symmetry, we now only discuss inter-conversion to the lowest excitons, \( S_X \) or \( T_X \). (As remarked in footnote 39, inter-conversion to higher-lying exciton states is allowed, but if this happens recombination is an intra-molecular process via the intra-molecular charge-transfer excitons.) Thus, the state label \( a \) is now either \( S_X \) or \( T_X \), and the number of phonons emitted, \( \nu_2 \), is either \( \nu_S \) or \( \nu_T \), as determined by Eq. (45).

Within the Mott-Wannier basis the exciton wavefunction overlaps are easy to calculate. Using \( t_{\text{inter}} = 0.1 \text{ eV} \), the interchain distance as 4 Å and standard semi-empirical Coulomb interactions gives

\[
\sum_r \psi_{S_X}(r) \tilde{\psi}_{S_{\text{CT}}}(r) \approx 1.0
\]

and

\[
\sum_r \psi_{T_X}(r) \tilde{\psi}_{T_{\text{CT}}}(r) \approx 0.9.
\]

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, with a similar value calculated for ‘ladder’ PPP in ref. 34. From the figures in ref. 34, 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 \( S_p \approx 0.5 \).  

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

The ISC rate is also not accurately known, with quoted values ranging from 0.3 ns, 4 ns and 10 ns. Nevertheless, despite this uncertainty, we see that the estimated triplet inter-conversion 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,

\[
\frac{k_{S\rightarrow S}}{k_{T\rightarrow T}} = \left| \frac{\sum \psi_{S_n}(r) \psi_{S_{CT-n}}(r)}{\sum \psi_{T_n}(r) \psi_{T_{CT-n}}(r)} \right|^2 \left| \exp(-S_p) \right|^{S_p \over S_T}
\]

Thus,

\[
\frac{k_{S\rightarrow S}}{k_{T\rightarrow T}} = 1.2S_p(\nu_T - \nu_S) \nu_T \nu_S
\]

This ratio increases as \( S_p \) decreases, because then multi-phonon emission becomes more difficult. The ratio also increases as the exchange energy, \( \hbar \omega(\nu_T - \nu_S) \), increases for any \( \nu_S \) or \( \nu_T \) if \( S_p < 1 \).

V. DISCUSSION AND CONCLUSIONS

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

1. The parity of the relative-particle wavefunction implies that inter-conversion occurs from the even parity inter-molecular charge-transfer excitons to the strongly bound intra-molecular excitons and not to the intra-molecular charge-transfer excitons (namely, the first odd parity exciton). (However, if the inter-chain charge transfer excitons lie higher in energy than the second family of even parity intra-chain exciton, recombination will be an intra-molecular process.)

2. The orthonormality of the center-of-mass wavefunctions ensures that inter-conversion 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 inter-conversion is then predominately a multi-phonon 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 wavefunctions, 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. As a consequence, the inter-conversion 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 is expected 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. 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 wavefunction and center-of-mass wavefunction, respectively) are no longer independent quantum numbers. Inter-conversion 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 inter-conversion to higher lying states is suppressed in favor of the lowest lying exciton. This prediction is confirmed by a recent quantum mechanical calculations by Beljonne et al. 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. 55) increases.

We note that the effective-particle description is still valid when there is self-trapping. In this case the center-of-mass wavefunctions are not the particle-in-the-box wavefunctions appropriate for a linear chains (Eq. 54), 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 ortho-normalized functions inter-conversion 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 inter-chain charge-transfer excitons lie energetically below high-lying even-parity families of intra-molecular excitons, and thus recombination is an inter-chain inter-conversion process and not an intra-molecular process via the intra-molecular charge-transfer excitons. Intra-molecular recombination is not desirable because although inter-conversion from the intra-chain 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 inter-molecular interconversion rates are also increased when the electron-intra-chain charge-transfer excitons is slower in the triplet manifold than the singlet manifold, both rates are expected to be faster than the ISC rate. This suggests that the singlet exciton yield is enhanced in rigid, well-conjugated polymers.

Acknowledgments

I thank N. Greenham, A. Köhler, and C. Silva (Cambridge) for useful discussions. I also gratefully acknowledge the financial support of the Leverhulme Trust, and thank the Cavendish Laboratory and Clare Hall, Cambridge for their hospitality.

E-mail address: W.Barford@sheffield.ac.uk

*Permanent address.

1 Y. Cao, I. D. Parker, Y. Gang, C. Zhang, and A. J. Heeger, Nature 397, 414-417 (1999).
2 K. H. Ho, J.-S. Kim, J. H. Burroughes, H. Becker, F. Y. L. Sam, T. M. Brown, F. Cacicelli, and F. H. Friend, Nature 404, 481-484 (2000).
3 J. S. Wilson, A. S. Dhoot, A. J. A. B. Seeley, M. S. Khan, A. Köhler, and R. H. Friend, Nature 413, 828-831 (2001).
4 M. Wohlgennant, K. Tandon, S. Mazumdar, S. Ramasesha, and Z. V. Vardeny, Nature 409, 494-497 (2001).
5 M. Wohlgennant, K. M. Jiang, Z. V. Vardeny, and P. A. J. Janssen, Phys. Rev. B88, 197401 (2002).
6 M. Wohlgennant, C. Yang, and Z. V. Vardeny, Phys. Rev. B66, 241201-4 (2002).
7 A. S. Dhoot, D. S. Ginger, D. Beljonne, Z. Shuai, and N. C. Greenham, Chem. Phys. Lett. 360, 195-201 (2002).
8 L. C. Lin, H. F. Meng, J. T. Shy, S. F. Horng, L. S. Yu, C. H. Chen, H. H. Liaw, C. C. Huang, K. Y. Peng, and S. A. Chen, Phys. Rev. Lett. 90, 36601 (2003).
9 These predictions have been questioned by R. Österbacka, Phys. Rev. Lett. 91, 219701, 2003, A. S. Dhoot and N. C. Greenham, ibid, 219702, M. Schott, Phys. Rev. Lett. 92, 59701, 2004, and W. Barford, submitted.
10 M. Segal, M. A. Baldo, R. J. Holmes, S. R. Forrest, and Z. G. Soos, Phys. Rev. B68, 075211 (2003).
11 M. Wohlgennant, C. Yang, and Z. V. Vardeny, Phys. Rev. B66, 241210 (2002).
12 M. N. Kohrak and E. R. Bittner, Phys. Rev. B62, 11473-11486 (2000).
13 S. Karabunarliev and E. R. Bittner, Phys. Rev. Lett. 90, 057402 (2000).
14 S. Karabunarliev and E. R. Bittner, J. Chem. Phys. 119, 3988-3995 (2003).
15 T.-M. Hong and H.-F. Meng, Phys. Rev. B63, 075206 (2001).
16 Z. Shuai, D. Beljonne, R. J. Silbey, and J. L. Bredas, Phys. Rev. Lett. 84, 131-134 (2000).
17 A. Ye, Z. Shuai, and J. L. Bredas, Phys. Rev. B65, 045208 (2002).
18 K. Tandon, S. Ramasesha, and S. Mazumdar, Phys. Rev. B67, 045109 (2003).
19 M. Wohlgennant and Z. V. Vardeny, J. Phys.: Condens. Matter 15, R83-R107 (2003).
20 A. Köhler and J. Wilson, Organic Electronics, 4, 179 (2003).
21 A. Köhler and D. Beljonne, Advanced Functional Materials, 14, 11, (2004).
22 A. L. Burin and M. A. Ratner, J. Chem. Phys. 109, 6092-6102 (1998).
23 Furthermore, there is an efficient electric-field-induced electron-hole mixing, so all the electron-hole pairs become charge-transfer excitons.
24 W. Barford, R. J. Bursill, and R. W. Smith, Phys. Rev. B66, 115205 (2002).
25 This prediction is confirmed in PPV-DOO, where $E(SCT) \sim 3.2 \text{ eV}$ and $E(TCT) \sim 3.1 \text{ eV}$.
26 S. Frolov, Z. Bao, M. Wohlgennant, and Z. V. Vardeny, Phys. Rev. B65, 205209 (2002).
27 A. P. Monkman, H. D. Burrows, L. J. Hartwell, L. E. Horsburgh, I. Hamblett, and S. Navaratnam, Phys. Rev. Lett. 86, 1358-1361 (2001).
28 See Charge and Energy Transfer Dynamics in Molecular Systems, V. May and O. Kuhn, Wiley-VCH, Berlin (2000).
29 In centro-symmetric light emitting polymers $n = 1$ and $j = 1$ corresponds to the $1^1B_u$ state, and $n = 2$ and $j = 1$ corresponds to the $m^1A_g$ state in the singlet sector, while in the triplet sector $n = 1$ and $j = 1$ corresponds to the $1^3B_u$ state, and $n = 2$ and $j = 1$ corresponds to the $1^3A_g$ state.
However, $H_{\text{inter}}$ can connect the inter-chain excitons to other even parity intra-chain excitons, if the former lie higher in energy. In that case the electron-hole recombination can be regarded as an intra-chain processes, as the states must relax via the intra-chain charge-transfer excitons, $S_{\text{CT}}$ and $T_{\text{CT}}$.

30 W. Barford, R. J. Bursill, and M. Yu Lavrentiev, Phys. Rev. B63, 195108 (2001).
31 M. Liess, S. Jeglinski, Z. V. Vardeny, M. Ozaki, K. Yoshino, Y. Ding, and T. Barton, Phys. Rev. B56, 15712 (1997).
32 E. E. Moore, W. Barford, and R. J. Bursill, Relaxation energies and excited state structures in poly(para-phenylene), submitted to Phys. Rev. B.
33 D. Hertel, S. Setayesh, H.-G. Nothofer, U. Scherf, K. Müllen and H. Bässler, Advanced Materials, 13, 65 (2001).
34 S. Frolov, M. Liess, P. Lane, W. Gellermann, and Z. Vardeny, Phys. Rev. Lett. 78, 4285 (1997).
35 W. Barford and E. E. Moore, An estimate of the inter-system crossing time in light-emitting polymers, submitted to Phys. Rev. B.
36 D. Beljonne, A. Ye, Z. Shuai, and J. L. Brédas, Adv. Funct. Mater., 14, 684 (2004)