Effect of interchain coupling on conducting polymer luminescence: excimers in derivatives of poly(phenylene vinylene)

M. W. Wu and E. M. Conwell

Center for Photoinduced Charge Transfer, Chemistry Department, University of Rochester, Rochester, New York 14627

and Xerox Corporation, Wilson Center for Technology, 114-22D, Webster, New York 14580

Abstract

Optical excitation of a chain in a polymer film may result in formation of an excimer, a superposition of on-chain excitons and charge-transfer excitons on the originally excited chain and a neighboring chain. The excimer emission is red-shifted compared to that of an on-chain exciton by an amount depending on the interchain coupling $t_\perp$. Setting up the excimer wavefunction and calculating the red shift, we determine average $t_\perp$ values, referred to a monomer, of 0.52 eV and 0.16 eV for poly(2,5-hexyloxy p-phenylene cyanovinylene), CN-PPV, and poly[2-methoxy, 5-(2′-ethyl-hexyloxy)-1, 4 p-phenylene vinylene], MEH-PPV, respectively, and use them to determine the effect of interchain distance on the emission.

PACS Numbers: 78.66.Qn, 71.20.Hk, 71.35.+z, 78.55.-m
The existence of polaron pairs or charge transfer excitons in poly(\(p\)-phenylene vinylene), PPV, and derivatives was first suggested to explain the magnetic field effect on photoconductivity and the long-lived photoinduced absorption found in PPV and some of its derivatives. Wavefunctions and energy levels of charge transfer (CT) excitons have been calculated for PPV. As noted in Ref. CT excitons would show little absorption or emission polarized parallel to the chains because there is little component of the dipole moment along the chains. The observation of strong absorption or emission polarized parallel to the chains requires that the wavefunction be a superposition of exciton wavefunctions along the two chains with the CT exciton wavefunctions, i.e., an excimer. The mixture of these wavefunctions results in a red shift of the emission of the excimer compared to that of an isolated chain. This shift can be determined by comparing emission from a film with that from a dilute solution of the polymer. Such a red shift has been seen in CN-PPV, ladder poly(paraphenylene) (L-PPP) and a series of \(\pi\)-conjugated polybenzobisthiazoles.

Photoinduced absorption measurements on MEH-PPV films and L-PPP films revealed a photogenerated species with a long lifetime, \(\sim \) ns, at least several times as long as the radiative lifetime. The suggestion was made that the photogenerated species is polaron pairs; it was reinforced by the observation that these long-lived pairs are not generated in dilute solution. Conwell has maintained that the long-lived pairs are excimers both in the cases of MEH-PPV and CN-PPV. A calculation of the most probable configurations of adjacent chains of MEH-PPV and of CN-PPV showed that emission is much less probable from excimers of the former polymer because of the large interchain distance. Recently, Samuel et al. reported that the emission from MEH-PPV is also downshifted in going from solution to film although the shift is less than half as much as that seen for CN-PPV. Also, they find that the emissive state is longer lived in film than in solution. However, the emission from MEH-PPV retains some vibronic structure, which is not expected for an excimer and indeed not seen for CN-PPV. They suggest, therefore, that the emission from MEH-PPV is also due to an interchain excitation, but the interchain interaction is weaker than that in CN-PPV. This is just what should be expected in view of the larger interchain
distance 4.1 Å found for MEH-PPV as compared to 3.4 Å for CN-PPV. In the much studied case of excimers formed by molecules, such as pyrene, in solution the molecules assume the intermolecular distance corresponding to the minimum energy for the excimer, determined by the balance of attractive \( \pi \)-wavefunction overlap and core repulsion. In a polymer film constraints on the chains result in a range of interchain distances and relative orientations, none of them necessarily optimum for excimer formation. The result is, understandably, a wide range of excimer emission frequencies and efficiencies, with the possibility of retention of the phonon structure for weakly coupled chains.

To calculate the frequency of the excimer emission from PPV derivatives, we use a simplified microscopic model for a PPV chain introduced by Rice and Gartstein. The two chains are taken to be finite but very long, parallel and coterminous. Chain deformation is neglected. The excimer wave function is taken to be the sum of exciton wavefunctions on chain 1 and chain 2, \(|\Psi_1\rangle\) and \(|\Psi_2\rangle\) respectively, and CT excitons \(|\Psi_{12}\rangle\) with the hole on chain 1, the electron on chain 2, and \(|\Psi_{21}\rangle\) with the position of electron and hole reversed. Setting up these wavefunctions, in what follows we determine the coefficient \(R\) of \(|\Psi_{12}\rangle\) and \(|\Psi_{21}\rangle\) in this sum by a variational method. The value of \(R\) depends on the interchain coupling. Comparing our predicted red shift with the experimental shift, we determine average values of \(t_\perp\) for CN-PPV and MEH-PPV. The former is found to be several times as large, as is appropriate to the smaller interchain distance for that case.

We start from a model Hamiltonian for the two coupled conjugated polymer chains: \(H = H_1 + H_2 + V_{12} + H_\perp\). \(H_i\) \((i = 1, 2)\) describes intrachain interactions for the \(i\)th chain. \(V_{12}\) stands for the long-range Coulomb interaction between electron (e) and hole (h), separated on different chains. \(H_\perp\) represents the coupling of the two chains. The \(H_i\) are given by

\[
H_i = \sum_{n\sigma} \left[ \alpha_0 (a_{in\sigma}^\dagger a_{in\sigma} + b_{in\sigma}^\dagger b_{in\sigma}) - t (a_{in+1\sigma}^\dagger a_{in\sigma} + b_{in+1\sigma}^\dagger b_{in\sigma} + \text{H.C.}) \right] \\
- \sum_{mn\sigma\sigma'} U(n - m) b_{in\sigma}^\dagger b_{in\sigma} a_{im\sigma}^\dagger a_{im\sigma'},
\]

where \(b_{in\sigma}^\dagger\) and \(a_{in\sigma}^\dagger\) create an electron in the conduction band and a hole in the valence band,
respectively, each with spin $\sigma$, located at the $n$th monomer in the $i$th chain. In writing this Hamiltonian, we measure energies from the center of the gap, so $\alpha_0$ denotes the distance from midgap of the center of each band. $t$ is the hopping integral between nearest neighbour monomers. From the first term of Eq. (1) one can get the single electron and single hole energy spectra: $\varepsilon_{ike} = \varepsilon_{ikh} = \alpha_0 - 2t \cos(ka)$, with $a$ representing the length of a monomer. Accordingly, $W = 4t$ is the band width. From the excitation spectra, neglecting the Coulomb interaction, one can easily get the energy gaps for e-h excitation, i.e., the minimum energy required to create an e-h pair on one polymer chain, $E_g = 2(\alpha_0 - 2t)$. The quantity

$$U(n - m) = U\delta_{nm} + \frac{V}{|n - m|} (1 - \delta_{nm})$$

(2)

represents the intrachain Coulomb interaction, with $U$ standing for the on-monomer e-h interaction and $V$ the nearest-neighbour monomer e-h interaction. The interchain Coulomb interaction is given by

$$V_{12} = - \sum_{mn\sigma s} V_1(n - m) b_{1\sigma n}^\dagger b_{2\sigma m}^\dagger a_{1ms}^\dagger a_{2ms} - \sum_{mn\sigma s} V_1(n - m) b_{1\sigma n}^\dagger b_{1\sigma m}^\dagger a_{2ms}^\dagger a_{2ms} ,$$

(3)

with

$$V_1(n - m) = \frac{V_1}{\sqrt{(n - m)^2 + B}} .$$

(4)

Here $B = \kappa_\parallel d^2/(\kappa_\perp a^2)$ and $d$ stands for the perpendicular distance between the two chains. $\kappa_\parallel$ and $\kappa_\perp$ are dielectric constants along and perpendicular to the polymer chains, respectively. The Hamiltonian

$$H_\perp = t_\perp \sum_{n\sigma} (b_{1\sigma n}^\dagger b_{2\sigma n} + \text{H.C.}) + t_\perp \sum_{n\sigma} (a_{1\sigma n}^\dagger a_{2\sigma n} + \text{H.C.})$$

(5)

represents the single-particle interchain hopping process. We assume that $t_\perp$ falls off exponentially according to

$$t_\perp = t_0 e^{-\mu d} = t_0 \exp(-\mu a \sqrt{B\kappa_\perp/\kappa_\parallel}) .$$

(6)

The intrachain wavefunction $|\Psi_i\rangle$ ($i = 1, 2$) for the $i$th chain can be acquired as follows. We first construct a two-particle wave function of the singlet e-h pair excitation on the $i$th chain as
\[ |\Psi_i\rangle = \frac{1}{\sqrt{2}} \sum_{nm\sigma} \phi_{nm} a_{1n\sigma}^\dagger b_{1m-\sigma}^\dagger |0\rangle \]  \hspace{1cm} (7)

with \( |0\rangle \) denoting the ground state. \( \phi_{nm} \) is assumed to be real and is normalized according to \( \sum_{nm} \Phi_{nm}^2 = 1 \). From \( H_i |\Psi_i\rangle = E |\Psi_i\rangle \), we obtain the lowest excitonic bound state with energy \( E_1 \):

\[ (E - 2\alpha_0)\phi_{n-m} = -2t(\phi_{n-m+1} + \phi_{n-m-1}) - U(n - m)\phi_{n-m} \]  \hspace{1cm} (8)

Similarly, we can construct two-particle charge-transfer (CT) wavefunctions as

\[ |\Psi_{12}\rangle = \frac{1}{\sqrt{2}} \sum_{nm\sigma} \phi_{nm} a_{1n\sigma}^\dagger b_{2m-\sigma}^\dagger |0\rangle \]  \hspace{1cm} (9)

and

\[ |\Psi_{21}\rangle = \frac{1}{\sqrt{2}} \sum_{nm\sigma} \phi'_{nm} a_{2n\sigma}^\dagger b_{1m-\sigma}^\dagger |0\rangle \]  \hspace{1cm} (10)

\( \phi_{nm} \) and \( \phi'_{nm} \) can differ from each other by a global phase. Here we take this phase as 1 so \( \phi_{nm} = \phi'_{nm} \). \( \phi_{nm} \) can be determined from \( (H_1 + H_2 + V_{12}) |\Psi_{12}\rangle = E |\Psi_{12}\rangle \) and is given by the equation

\[ (E - 2\alpha_0)\phi_{n-m} = -2t(\phi_{n-m+1} + \phi_{n-m-1}) - V_1(n - m)\phi_{n-m} \]  \hspace{1cm} (11)

with the normalization condition \( \sum_n \phi_n^2 = 1/N \) (Here we have assumed \( \phi_n \) to be real). Again we only need the lowest CT excitonic bound state with energy \( E_2 \) from Eq. (11).

The variational wave function of the excimer \( |\Psi\rangle \) can be constructed from the wavefunctions of the on-chain exciton \( |\Psi_i\rangle \) with exciton energy \( E_1 \) and the wave functions of CT exciton \( |\Psi_{12}\rangle \) and \( |\Psi_{21}\rangle \) with CT exciton energy \( E_2 \):

\[ |\Psi\rangle = \frac{1}{\sqrt{2 + 2R^2}} (|\Psi_1\rangle + a|\Psi_2\rangle + R|\Psi_{12}\rangle + R'|\Psi_{21}\rangle) \]  \hspace{1cm} (12)

Here \(|a| = 1 \) and \(|R| = |R'| \). We further assume all quantities are real. It can be seen that only if \( R = R' \) and \( a = 1 \) can it be possible to have the total energy \( E = \langle \Psi |H|\Psi \rangle < E_1 \). Then
\[ E = \left( E_1 + R^2 E_2 + 2\Gamma R \right) / \left( 1 + R^2 \right), \]  

(13)

where \( \Gamma \equiv \langle \Psi_i | H_\perp | \Psi_{12} \rangle = \langle \Psi_i | H_\perp | \Psi_{21} \rangle \). \( R \) is determined by minimizing \( E \), which gives

\[ R = -\sqrt{\frac{(E_2 - E_1)^2 + 4\Gamma^2 - (E_2 - E_1)}{2\Gamma}}. \]  

(14)

For the numerical calculations, we employ a chain of \( N = 400 \) unit cells for each of the polymers and use periodic boundary conditions. The values of various unknown parameters must be chosen to give the correct gap and exciton binding energy. For MEH-PPV the optical absorption edge is at 2.1 eV \cite{18}. The single particle energy gap of MEH-PPV has been measured as 2.45 eV \cite{19} and thus 0.35 eV. The intrachain Coulomb potential coefficient \( V \) is of the order of the Coulomb attraction between an electron and a hole separated by one monomer, which is \( \sim 1/2 \) eV \cite{15}. Choosing \( \alpha_0 = 3.2 \) eV, \( t = U = 1 \) eV \cite{15} and \( V = 0.44 \) eV, we calculate for MEH-PPV \( E_g = 2.4 \) eV, the exciton creation energy \( E_1 = 2.065 \) eV and its binding energy \( \epsilon_b = 0.335 \) eV. For CN-PPV the optical absorption edge is at \( \sim 2.3 \) eV \cite{8}. It is reasonable to assume that the exciton binding energy is similar to that of PPV and MEH-PPV. With \( \alpha_0 = 3.3 \) eV, \( t = U = 1 \) eV, and \( V = 0.4 \) eV, we obtain \( E_g = 2.6 \) eV, the exciton creation energy \( E_1 = 2.285 \) eV and \( \epsilon_b = 0.315 \) eV. To evaluate the CT wave function we use \( \kappa_\parallel = 8, \kappa_\perp = 3 \) and \( V_1 = V \). It is also necessary to have a value for \( t_\perp \) to obtain the CT wavefunctions \( |\Psi_{12}\rangle \) and \( |\Psi_{21}\rangle \) and the CT exciton energy from Eqs. (9) through (11). In principle it is possible to calculate a value for \( t_\perp \) given the positions of all the atoms in a pair of monomers on adjacent chains. We could use the atom positions determined by the procedure of Ref. \cite{12} to give minimum energy. The resulting \( t_\perp \) would not be representative of the film, however, because its amorphous nature implies, as discussed earlier, a wide range of interchain distances and relative orientations. We therefore determined what could be considered an average \( t_\perp \) by finding what value is required to obtain from the equations and parameters given above the red shift of the excimer emission. The result, referred to a monomer in each case, was \( t_\perp = 0.52 \) eV for CN-PPV films, 0.16 eV for MEH-PPV films.
To determine the dependence on $d$ of the excimer emission it is necessary to know how $t_\perp$ decreases with increasing distances between the chains. For PPV the coupling between C atoms on neighboring chain is mediated by H atoms, the C-H distances being the smallest. Also the wavefunction of the 2p level on H, which is coupled to the carbon p orbital, decays much less rapidly than the carbon p orbital. The resulting value of $\mu$ in Eq. (6) is $1.18 \text{ Å}^{-1}$. The change of exciton emission energy $E$ with interchain distance for this value of $\mu$ is shown in Fig. 1. It is seen that as $d$ increases, $E$ tends rapidly to the exciton energy $E_1$. We plot also in Fig. 1 the probable contribution of the CT exciton to the excimer state, $P = R^2/(1+R^2)$, as a function of distance $d$. It is seen that, at the most probable interchain distance for CN-PPV, $P \sim 1/2$, but decreases rapidly with increasing $d$. For MEH-PPV $P$ is always smaller. If direct coupling between C atoms on neighboring chains dominates over C-H coupling, $\mu$ would be $2.013 \text{ Å}^{-1}$ and the changes with distance would be even more rapid.

In summary, we have set up wave functions for excimers in CN-PPV and MEH-PPV, and compared them with experimental red shifts of the excimer emission to evaluate the average interchain transfer integral in films of these materials. Due to the large electronegativity of the CN group, which makes the interchain distance smaller, $t_\perp$ is much larger for that case. We use the $t_\perp$ values to determine how the emission frequency varies with interchain spacing.

We acknowledge the support of the National Science Foundation under Science and Technology Center grant CHE912001.
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FIGURES

FIG. 1. Plots of the emission energy $E$ (solid curves) and probability of CT exciton contribution to the excimer wave function, $P$ (dot-dashed curves) for CN-PPV and MEH-PPV. Dotted lines show the exciton energy $E_1$. 
