Excimers in light-emitting conjugated polymers

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The electronic structures of the low-lying excited states for two parallel chains of poly (*p*-phenylene-vinylene) with arbitrary relative positions are studied. The interchain interaction is treated microscopically. The energy and charge transfer fraction of the (light-emitting) lowest singlet state are found to depend sensitively on the horizontal shift of the two chains, which is in turn determined by the packing geometry. Our predictions of the excimer-forming geometry and the relative (dipole-forbidden) photoluminescence lifetimes are in excellent agreement with experiments. [S0163-1829(98)07529-8]

The physics of electroluminescent conjugated polymers, especially poly(*p*-phenylene vinylene) (PPV), has been of major interests since the first demonstration of a light-emitting diode (LED) based on such materials.[1] Despite the ensuing extensive studies, the photophysical process underlying both the photoluminescence (PL) and electroluminescence (EL) in solid state is still not completely settled. Recently, it has been observed that the light-emitting species in some PPV derivatives (CN-PPV and Br-PPV) are found to be quite different from the others, both in terms of spectrum and lifetime.[2,3] The fact that a major difference in the spectra exists between chemically very similar derivatives is surprising. Since no such spectral difference is observed in the solutions, the interchain interaction is believed to be the origin. Excimer formation[4,5] has been proposed as a possible explanation.

Assuming the intrachain electronic structure is not affected by the side groups, the question is how does the packing geometry determine the emission process. In order to answer the question, we study in this paper a two-chain model including microscopic interchain interactions. Configuration interaction among exciton (EX) and charge-transfer (CT) states, common in smaller organic molecules,[6,7] are found to be indispensable in obtaining the correct excited states for polymer films as well. Our key result is that the electronic structure of the emitting state (lowest singlet excited state) depends sensitively not only on the interchain distance, but also the relative horizontal shift of the two chains in a dramatic way. Based on the packing geometry obtained from computer simulation by Conwell *et al.*,[8] a significant CT component is found in the emitting state for CN-PPV, but it is negligible in MEH-PPV and PPV. These results completely agree with the conjecture based on experimental data that excimers are formed in the first but not in the latter two.[2,3] Furthermore, three experimental signatures of excimers, large Stokes shift, broad emission spectrum, and, most importantly, long radiative lifetime,[2] all agree with our calculation. Our results are opposite to the intuitive interpretation[8] in one crucial aspect. We found that the emitting state is always of even parity, implying the transition to the ground state is dipole forbidden. Vibrational coupling to a higher odd parity state is necessary for the transition to happen, with the transition rate inversely proportional to the square of the energy splitting of the two

states due to interchain interaction. This implies that the larger the interchain interaction (and therefore the CT component), the smaller the transition rate is, instead larger as Conwell *et al.* claimed. This explains the extraordinarily long radiative lifetime of CN-PPV,[3] which has a quite large CT component by our calculation.

Consider two chains **a** and **b**, such that **b** is displaced from **a** by a rigid translation vector $d\mathbf{e}_z + \mathbf{D}_h$. $\mathbf{e}_z$ is the unit vector normal to the symmetry plane (approximately the benzene plane) of chain **a**. $\mathbf{D}_h$ is the horizontal shift parallel to the plane. The Hamiltonian for the π electrons contains four pieces:

$$H = H_0^a + H_0^b + H_i + Hc. \tag{1}$$

The first two are intrachain tight-binding Hamiltonians for chains **a** and **b**, respectively. H_i is the interchain hopping and H_C the Coulomb interaction. In second quantized form,

$$H_0^{a,b} = -\sum_{(ij),\sigma} t_{ij} \hat{c}_{i\sigma}^{a,b\dagger} \hat{c}_{j\sigma}^{a,b} + \text{H.c.} \tag{2}$$

Here $\hat{c}_{i\sigma}^{a,b}$ is the annihilation operator of electrons on carbon site i and spin σ of chain **a** and **b**, respectively. We include only the nearest-neighbor intrachain hopping. t_{ij} is equal to t for benzene bonds, t_1 for single bonds, and t_2 for double bonds [see inset of Fig. 1(b)]. For the interchain hopping,

$$H_i = -\sum_{n=1}^{N} \sum_{\lambda=1}^{8} \sum_{\sigma=\pm 1} \sum_{i=1}^{m} t_{\lambda i} [\hat{c}_{nf(\lambda,i)\sigma}^{b\dagger} \hat{c}_{n\lambda\sigma}^a + \text{H.c.}]. \tag{3}$$

Here n is the index for the unit cells and N is the total number of cells in each chain. λ is the index for the carbon atoms within each unit cell [see inset of Fig. 1(b)]. One-to-many interchain electron hopping is allowed from carbon site λ on chain **a** to site $f(\lambda,i)$ on chain **b** with hopping integral $t_{\lambda i}$. m is the maximal number of i. Hopping from **b** to **a** is in the H.c. part of H_i. Note that the π electrons are assumed to be superpositions of carbon p_z orbitals only. Both intrachain and interchain carbon-hydrogen couplings are ignored. The eigenstates of H_a and H_b are the Bloch states, with the annihilation operators $\hat{A}_{k\alpha\sigma} = \sum_{n\lambda} e^{ikna} \zeta_\lambda^\alpha(k) \hat{c}_{n\lambda\sigma}^a$, $\hat{B}_{k\alpha\sigma} = \sum_{n\lambda} e^{ikna} \zeta_\lambda^\alpha(k) \hat{c}_{n\lambda\sigma}^b$, where a is the lattice constant. k lies in the first Brillouin zone
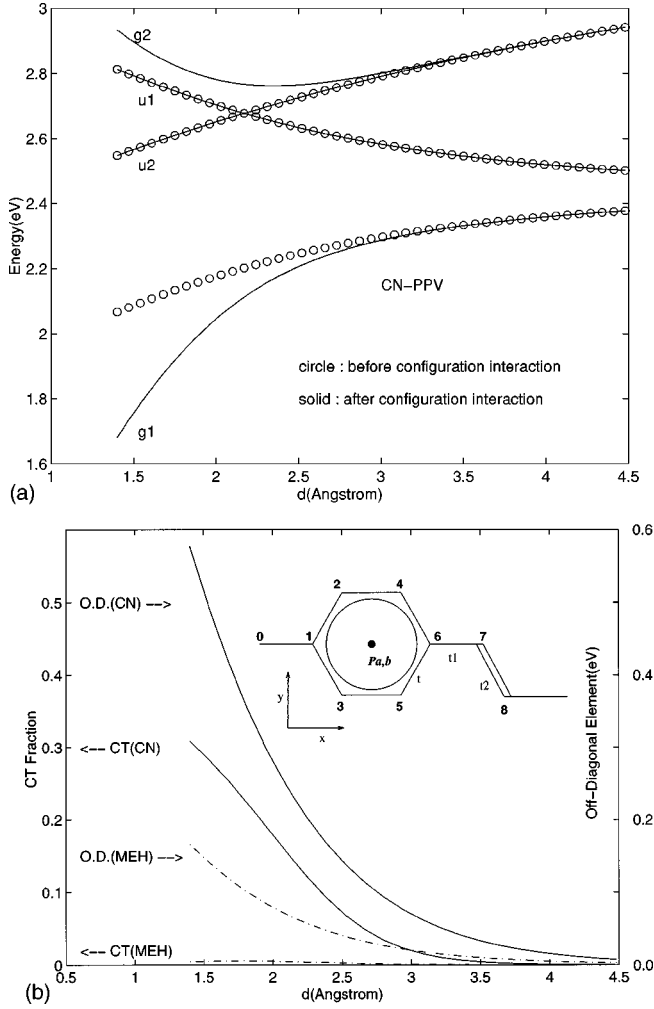
FIG. 1. (a) The energies of the low-lying excited states $\varepsilon_{u1,2}$ and $\varepsilon_{g1,2}$ (solid lines) are shown as functions of vertical interchain distance d. The horizontal shift D_h for CN-PPV is used. Exciton energies $\varepsilon_{EX}^{\pm}$ (lower two circle lines) and CT energies ε_{CT} (upper circle line) before configuration interaction are also shown. In practice, $A = 12.8$ eV, $\mu = 1.18$ Å are used for $t_{\lambda i}$. The result is almost independent on m, the maximal number of interchain hoppings from each site, as long as $m > 3$. (b) The CT fractions $|\langle CT - |g1\rangle|^2$ and the off-diagonal matrix element $\langle CT - |\tilde{H}_i|EX-\rangle$(real) of $|g1,2\rangle$ for CN-PPV(solid) and MEH-PPV(dash-dot) are shown.

$[-\pi/a, \pi/a]$. $\alpha = 1 \cdots 8$ is the band index. In terms of $\hat{A}_{k\alpha\sigma}$ and $\hat{B}_{k\alpha\sigma}$, $H_{a,b}$ is in diagonized form: $H_a = \Sigma_{k\sigma\alpha}E_\alpha^0(k)\hat{A}_{k\alpha\sigma}^\dagger\hat{A}_{k\alpha\sigma}$, $H_b = \Sigma_{k\sigma\alpha}E_\alpha^0(k)\hat{B}_{k\alpha\sigma}^\dagger\hat{B}_{k\alpha\sigma}$. The band structure $E_\alpha^0(k)$ is well known.[9] The lower four bands are filled in the ground state. In terms of the Bloch states, H_i becomes

$$H_i = -\sum_{k\alpha\alpha'\sigma} T_{\alpha\alpha'}(k)\hat{A}_{k\alpha\sigma}^\dagger\hat{B}_{k\alpha'\sigma} + \text{H.c.},$$

$$T_{\alpha\alpha'}(k) = N\sum_{\lambda=1}^{8}\sum_i t_{\lambda i}\zeta_\lambda^\alpha(k)\zeta_{f(\lambda,i)}^{\alpha'*}(k). \quad (4)$$

The hopping integral is assumed to be the form $t_{\lambda i} = A \exp(-\mu r_{\lambda i})$, where $r_{\lambda i}$ is the distance between site λ

on chain **a** and site $f(\lambda, i)$ on chain **b**, which depends on, besides λ and i, both the vertical distance d and horizontal shift D_h between the two chains. μ is the size of the carbon p_z orbital and A is a fitting parameter.[10] In order to simplify our problem, we include only the middle two bands, the conduction ($\alpha = c$) and the valence band ($\alpha = v$), and rewrite the Hamiltonian in terms of the electron operators $\alpha_{k,\sigma} \equiv \hat{A}_{kc\sigma}$, $\gamma_{k,\sigma} \equiv \hat{B}_{kc\sigma}$, and hole operators $\beta_{-k,-\sigma} \equiv \hat{A}_{kv\sigma}^\dagger$, $\delta_{-k,-\sigma} \equiv \hat{B}_{kv\sigma}^\dagger$. Within such a two-band approximation, the total Hamiltonian becomes $H = \tilde{H}^a + \tilde{H}^b + \tilde{H}_C + \tilde{H}_i$. Here $\tilde{H}^a = \Sigma_{k\sigma}E_e(k)\alpha_{k\sigma}^\dagger\alpha_{k\sigma} + E_h(k)\beta_{k\sigma}^\dagger\beta_{k\sigma}$. $\tilde{H}^b$ can be obtained by making the substitution $\alpha \to \gamma$ and $\beta \to \delta$. The renormalized single-particle spectra for electrons and holes are $E_e(k) = E_c(k) + \Delta E_c$, $E_h(k) = -E_v(k) + \Delta E_v$. The band edge renormalizations ΔE_c and ΔE_v are integrals involving the Bloch wave functions and the Coulomb potential $V(r)$. The Coulomb part $\tilde{H}_C$ splits further into five pieces: $\tilde{H}_C = H_{C1}^a + H_{C2}^a + H_{C1}^b + H_{C2}^b + H_C^{ab}$, with

$$H_{C1}^a = \frac{1}{2}\sum_{kk'q\neq 0} V_1(q)(\alpha_{k+q\sigma}^\dagger\alpha_{k'-q\sigma'}^\dagger\alpha_{k'\sigma'}\alpha_{k\sigma}$$
$$+ \beta_{k+q\sigma}^\dagger\beta_{k'-q\sigma'}^\dagger\beta_{k'\sigma'}\beta_{k\sigma}$$
$$- 2\alpha_{k+q\sigma}^\dagger\beta_{k'-q\sigma'}^\dagger\beta_{k'\sigma'}\alpha_{k\sigma}) \quad (5)$$

and

$$H_{C2}^a = \sum_{kk'q} V_2(q)\alpha_{k+q\sigma}^\dagger\beta_{-k-\sigma}^\dagger\beta_{-k'+q-\sigma'}\alpha_{k'\sigma'}. \quad (6)$$

As before, $H_{C1,2}^b$ can be obtained by the substitution $\alpha \to \gamma$ and $\beta \to \delta$. The interchain Coulomb interaction $H_C^{a,b}$ is

$$H_C^{ab} = \frac{1}{2}\sum_{kk'q} V_{ab}(q)(\alpha_{k+q\sigma}^\dagger\gamma_{k'-q\sigma'}^\dagger\gamma_{k'\sigma'}\alpha_{k\sigma}$$
$$+ \beta_{k+q\sigma}^\dagger\delta_{k'-q\sigma'}^\dagger\delta_{k'\sigma'}\beta_{k\sigma} - \alpha_{k+q\sigma}^\dagger\delta_{k'-q\sigma'}^\dagger\delta_{k'\sigma'}\alpha_{k\sigma}$$
$$- \gamma_{k+q\sigma}^\dagger\beta_{k'-q\sigma'}^\dagger\beta_{k'\sigma'}\gamma_{k\sigma}). \quad (7)$$

In order to get the eigenstates of the Hamiltonian, we first break the total Hamiltonian into "free" and "interaction" parts: $H = H_0 + \tilde{H}_i$, with $H_0 = \tilde{H}^a + \tilde{H}^b + \tilde{H}_C$. There are four low-lying singlet excited states for the "free" Hamiltonian H_0. They are the exciton in chain **a**, the exciton in chain **b**, and two CT states for which the electron and hole reside on different chains. $\tilde{H}_i$ causes mixing (configuration interaction) among those four states. The resulting 4×4 eigenvalue problem can be further reduced to two 2×2 problems, for even and odd parity subspaces, respectively. Diagonization of the two 2×2 matrices gives the physical eigenstates.

The basis states for singlet elementary excitations in the two-band approximation are $|k\rangle_A$, $|k\rangle_B$, $|k\rangle_C$, and $|k\rangle_D$, which are defined as[11] $|k\rangle_A \equiv (1/\sqrt{2})(\alpha_{k\uparrow}^\dagger\beta_{-k\downarrow}^\dagger + \alpha_{k\downarrow}^\dagger\beta_{-k\uparrow}^\dagger)|0\rangle$, $|k\rangle_B \equiv (1/\sqrt{2})(\gamma_{k\uparrow}^\dagger\delta_{-k\downarrow}^\dagger + \gamma_{k\downarrow}^\dagger\delta_{-k\uparrow}^\dagger)|0\rangle$, $|k\rangle_C \equiv (1/\sqrt{2})(\gamma_{k\uparrow}^\dagger\beta_{-k\downarrow}^\dagger + \gamma_{k\downarrow}^\dagger\beta_{-k\uparrow}^\dagger)|0\rangle$, and $|k\rangle_D \equiv (1/2)(\gamma k\uparrow\dagger\beta-k\downarrow\dagger + \gamma k\downarrow\dagger\beta-k\uparrow\dagger)|0\rangle$, and $|k\rangle_D \equiv (1/\sqrt{2}) \times (\alpha_{k\uparrow}^\dagger\delta_{-k\downarrow}^\dagger + \alpha_{k\downarrow}^\dagger\delta_{-k\uparrow}^\dagger)|0\rangle$. The ground state $|0\rangle$ is the state with no electrons and holes. The electron and hole are in the

same chain for $|k\rangle_A$ and $|k\rangle_B$, while they are in different chains for $|k\rangle_C$ and $|k\rangle_D$. All the basis states have zero total momentum. They span four subspaces, which are decoupled from one another without $\tilde{H}_i$. The matrix elements of H_0 within each subspace are

$$_A\langle k'|H_0|k\rangle_A = {}_B\langle k'|H_0|k\rangle_B$$

$$= [2E_c(k) + \Delta E_g]\delta_{k'k} - V(k'-k),$$

$$_C\langle k'|H_0|k\rangle_C = {}_D\langle k'|H_0|k\rangle_D$$

$$= [2E_c(k) + \Delta E_g]\delta_{k'k} - V_{ab}(k'-k),$$

where

$$V(k'-k) = V_1(k'-k) + V_2(0)$$

$$= \frac{1}{N}\left[\sum_{n\neq 0} e^{-iR(k'-k)}\frac{V}{R(n)} + U\right],$$

$$V_{ab}(k'-k) = \frac{1}{N}\left[\sum_n e^{-iR(k'-k)}\frac{V}{R_\perp(n)}\right]. \quad (8)$$

We have used the relation $E_v(k) = -E_c(k)$ for PPV band structure. $R(n)[R_\perp(n)]$ is the distance between two unit cells in the same(opposite) chain(s) differing in indices by n. Anisotropy of the dielectric constant is also included.[12] The bandgap renormalization $\Delta E_g = \Delta E_c + \Delta E_v$, together with the on-site and off-site Coulomb energies U and V are treated as adjustable parameters. The lowest states, denoted by $|A\rangle$, $|B\rangle$ $|C\rangle$ $|D\rangle$ in these subspaces can be expanded as $|A,B\rangle = \Sigma_k \Phi_{EX}(k)|k\rangle_{A,B}$, $|C,D\rangle = \Sigma_k \Phi_{CT}(k)|k\rangle_{C,D}$. The energies are ε_{EX} for $|A\rangle, |B\rangle$ and ε_{CT} for $|C\rangle, |D\rangle$. Parity eigenstates can be constructed out of them: $|EX\pm\rangle \equiv \sqrt{1/2}(|A\rangle \pm |B\rangle)$, $|CT\pm\rangle \equiv \sqrt{1/2}(|C\rangle \pm |D\rangle)$. As mentioned before, there is no matrix element between $+$ and $-$ states. We can, therefore, consider them separately. For the diagonal matrix elements, we have $H_0|EX\pm\rangle = \varepsilon_{EX}^\pm|E\pm\rangle$, $H_0|CT\pm\rangle = \varepsilon_{CT}^\pm|E\pm\rangle$. Using Eq. (4), the off-diagonal matrix element becomes

$$\langle CT\pm|\tilde{H}_i|EX\pm\rangle = \frac{1}{2}\sum_k \Phi_{CT}^*(k)\Phi_{EX}(k)[-T_{cc}^*(k) \pm T_{vv}^*(k)$$

$$\pm T_{vv}(k) - T_{cc}(k)]. \quad (9)$$

It turns out that $\langle CT+|\tilde{H}_i|EX+\rangle = 0$ because the transition amplitudes $T_{\alpha\alpha}$ is real and the same for $\alpha = c, v$. Consequently, there is no configuration interaction between EX and CT states for the $+$ subspace, and we need to diagonize the 2×2 matrix for the $-$ subspace only:

$$\begin{pmatrix} \varepsilon_{EX}^- & \langle CT-|\tilde{H}_i|EX-\rangle \\ \langle CT-|\tilde{H}_i|EX-\rangle^* & \varepsilon_{CT}^- \end{pmatrix}. \quad (10)$$

Note that $\varepsilon_{EX}^\pm = \varepsilon_{EX}$ and $\varepsilon_{CT}^\pm = \varepsilon_{CT}$ so far. Davydov splitting between $\varepsilon_{EX}^\pm$[13] is phenomenologically included by the replacement $\varepsilon_{EX}^\pm \rightarrow \varepsilon_{EX} \pm m^2/d^3$, where m is the transition dipole and d is the interchain distance.

Davydov splitting is a purely many-body Coulomb effect, which couples the exciton states $|A\rangle$ and $|B\rangle$. In order to couple $|A\rangle$ and $|B\rangle$, a term proportional to $\gamma^\dagger \delta^\dagger \alpha \beta$ (simultaneous interchain transfer of an electron-hole pair due to Coulomb interaction) is required in H. The coefficient of such a term is hard to know without the detailed knowledge of some integrals involving the the atomic wave functions. Since our treatment of the Coulomb interaction is not very microscopic, with parameters U and V so chosen such that the intrachain exciton energy ε_{EX} is equal to the experimental value, the transition moment m for the $\varepsilon_{EX}^\pm$ splitting can only be introduced as a fitting parameter. On the other hand, the interchain hopping Hamiltonian H_i is a purely one-body effect. The configuration interaction due to H_i are then treated much more microscopically. Note that, unlike H_i, Davydov splitting does not mix $|EX\rangle$ with $|CT\rangle$. Therefore, it does not affect the CT fraction as much as H_i does.

Let us turn to the inversion symmetry (parity) of the problem now. Consider the symmetry of a single chain, say, **a**, first. The lattice structure is invariant under inversion with respect to the point P_a, the center of benzene [see inset of Fig. 1(b)]. For Bloch states, we have $|k,\alpha\rangle \leftrightarrow \eta|-k,\alpha\rangle$, $\eta = \pm 1$. $\leftrightarrow$ means inversion with respect to P_a. In terms of the Wannier functions, the symmetry manifests itself as $\zeta_\lambda^\alpha(k) = \eta\zeta_{\bar{\lambda}}^\alpha(-k) = \eta\zeta_\lambda^{\alpha*}(k)$, with $\lambda \leftrightarrow \bar{\lambda}$ under inversion. More explicitly, $(\lambda\bar{\lambda}) = (1,6),(2,5),(3,4),(7,0)$, and $(8,-1)$. λ less than 1 means carbon site in the previous unit cell. Explicit calculation of $\zeta_\lambda^\alpha(k)$ shows that $\eta = 1$ for $\alpha = v$, and $\eta = -1$ for $\alpha = c$, which implies $|k\rangle_A \leftrightarrow -|-k\rangle_A$. Combined with the fact that the envelope functions $\Phi_{EX,CT}(k)$ are both even functions of k, we have $|A\rangle \leftrightarrow -|A\rangle$, i.e., the exciton is of odd parity (dipole allowed). In the case of two chains, the point of inversion symmetry becomes the middle point P of the symmetry points P_a of chain **a** and P_b of chain **b**. The parity of the states can be easily seen to be $|A\rangle \Leftrightarrow -|B\rangle$, $|C\rangle \Leftrightarrow -|D\rangle$. $\Leftrightarrow$ means inversion with respect to P. Finally, we have $|EX,CT+\rangle \Leftrightarrow -|EX,CT+\rangle$ and $|EX,CT-\rangle \Leftrightarrow |EX,CT-\rangle$. The interesting point here is that the $-$ subspace, which contains the lowest state, is of even parity and dipole forbidden to decay radiatively to the ground state. Quantum lattice fluctuations must be considered to yield a finite radiative lifetime. In fact, similar situation has been reported for a pair of thiophene oligomers.[14]

In the following we present our results. First of all, since the energies of intrachain excitations have been studied intensively[9] and is not our main concern here, we simply choose $V(=U)$ such that the exciton creation energy ε_{EX} is 2.43 eV. The renormalized bandgap $E_e(0) + E_h(0)$ is chosen to be 3.4 eV. We consider two PPV derivatives CN-PPV and MEH-PPV, with packing geometries determined from computer simulations.[8] The horizontal shift D_h is $(2,\sqrt{3})b$ for CN-PPV and $(9/4, -\sqrt{3}/4)b$ for MEH-PPV.[8] $b = 1.4$ Å is the carbon bond length. Consider CN-PPV first. In Fig. 1(a), we plot the energies $\varepsilon_{u1,2}$ and $\varepsilon_{g1,2}$ of the lowest four excited states $|u1,2\rangle$ and $|g1,2\rangle$ for a range of vertical interchain distance d with fixed D_h. u,g means ungerade (odd) and gerude (even). At large d, we have $|u1,2\rangle \simeq |EX+\rangle, |CT+\rangle$ and $|g1,2\rangle \simeq |EX-\rangle, |CT-\rangle$. $|g1\rangle$ is always the lowest excited state. Even though it is dipole forbidden, it must be responsible for the PL photon emission. By definition, an excimer is formed if such a state has a significant CT component.[6,7] The CT fraction of $|g1\rangle$ is shown in Fig. 1(b).

Indeed, the excimer character is clear when $d \lesssim 3$ Å, which is not far from the the ground state equilibrium interchain distance $d_0 = 3.3$ Å.[8] Since $\varepsilon_{g1}(d)$ decreases rapidly with d, the two chains must come closer to each other due to the attractive force when excited. The new equilibrium distance d^* depends on both the exciton density and the molecular force field between these two chains. Two characteristic energy differences are of particular interest here: $\Delta\varepsilon_1 \equiv \varepsilon_{g1}(\infty) - \varepsilon_{g1}(d^*)$ and $\Delta\varepsilon_2 \equiv \varepsilon_{g1}(d_0) - \varepsilon_{g1}(d^*)$. Experimentally, $\Delta\varepsilon_1$ is the difference in solution and film PL photon energies, while $\Delta\varepsilon_2$ is the net Stokes shift due to interchain lattice relaxation, i.e., the apparent Stokes shift minus the optical phonon energy. For CN-PPV, $\Delta\varepsilon_1 \simeq 0.35$ eV and $\Delta\varepsilon_2 \simeq 0.25$ eV.[2,3] Since the transition dipole m responsible for Davydov splitting is unknown in our model, we adjust it such that $\varepsilon_{g1}(\infty) - \varepsilon_{g1}(d_0) = (0.35 - 0.25)$ eV. The corresponding transition diople length is 1.6 Å. The actual final lattice configuration in films is, however, very difficult to predict due to two reasons. (a) Polymers are heavy molecules with large atomic weight. It is not likely that a significant shrinkage of interchain distance can be caused by the excitation of a single electron-hole pair. A finite exciton density(exciton number per monomer) is required. d^* is therefore determined by the exciton density, instead of a single exciton. Because the magnitude of exciton density is presently unknown, a reliable prediction seems unlikely. (b) In the solution we need only to consider a pair of polymers in order to determine d^*. In films, however, the force experienced by a particular chain is affected by many neighboring chains and is much more complicated. Strictly speaking, our two-chain approach is accurate in predicting only the initial tendency toward excimer formation, but not the final configuration, which may contain distortions involving more than two chains, or relaxations other than vertical distance shrinkage, e.g., rotation and horizontal displacement. We can, however, give a simple estimate of d^* based on the Leanard-Jones form of the molecular force field $U(d) = C[(1/2)(d_0/d)^{12} - (d_0/d)^6]$. d^* is the minimum point of $\varepsilon_{g1}(d) + U(d)$. C is so chosen such that $\Delta\varepsilon_2 = 0.25$ eV, from which we predict $d^* \simeq 2.35$ Å, where the CT fraction is about 15 %. The actual equilibrium configuration may be even lower in energy and have an even larger CT component.

Surprisingly, when we apply the same procedure to MEH-PPV, with $\boldsymbol{D}_h = (9/4, -\sqrt{3}/4)b$, the story becomes totally different. For the same range of d as before, the off-diagonal element in Eq. (10) is nearly zero, and the $|g1\rangle$ state remains basically $|\text{EX}-\rangle$ [see Fig. 1(b)]. Consequently, the light-emitting state remains basically the exciton as in the solution $(d = \infty)$. Since the slope of $\varepsilon_{g1}(d)$ at $d_0 = 4.05$Å is vanishingly small, d_0 and d^* almost coincide with each other. This explains the very small solution-film PL difference and Stokes shift observed in MEH-PPV.[15] Similar results are obtained for PPV, with $\boldsymbol{D}_h = (-1.79, 3.17)$ Å and $d_0 = 3.26$ Å,[16] agreeing with the fact that excimers are also absent in the PL spectrum of PPV.[2] The difference between these three PPV derivatives becomes conspicuously transparent when we scan the off-diagonal term $\langle\text{CT}-|\tilde{H}_i|\text{EX}-\rangle$, which is real due to certain symmetry, and the CT fraction of $|g1\rangle$, over a range of $\boldsymbol{D}_h$ for some fixed d [see Figs. 2(a),2(b)]. Since $\langle\text{CT}-|\tilde{H}_i|\text{EX}-\rangle$ is the superposition of hopping
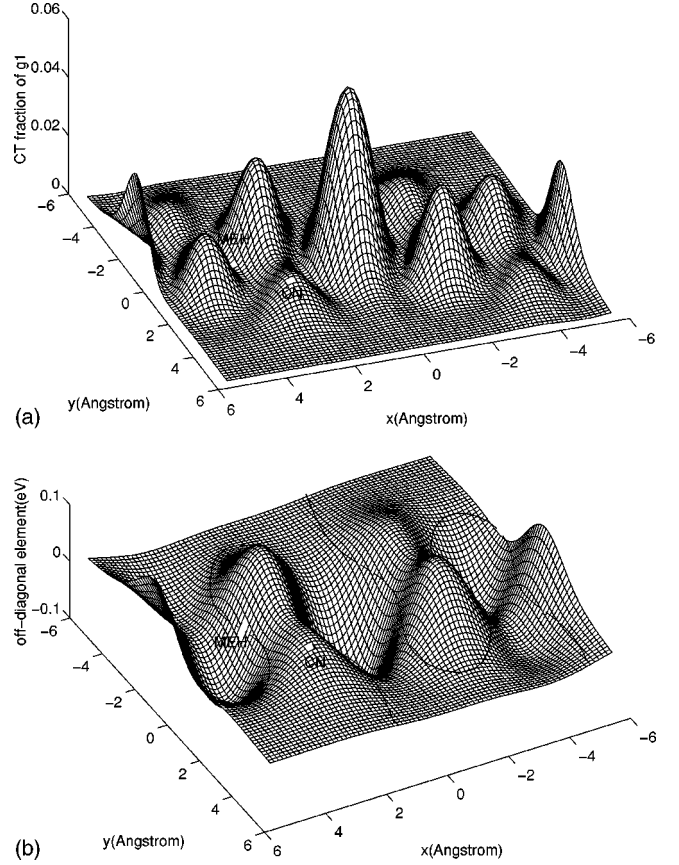

FIG. 2. (a) The CT fraction $|\langle\text{CT}-|g1\rangle|^2$ of the light-emitting state $|g1\rangle$ are shown for an area of D_h. d is fixed at 3.3 Å. The CT fraction for CN-PPV is about 10 times larger than that of MEH-PPV. Surface elements at D_h of CN-PPV and MEH-PPV are removed for clarity. The central peak at (0,0) corresponds to the geometry that two chains are right on top of each other. (b) The off-diagonal matrix element $\langle\text{CT}-|\tilde{H}_i|\text{EX}-\rangle$ for the $-$ subspace are plotted for the same area of D_h. The contour of zero is shown to emphasize that MEH-PPV happens to be in a geometry of vanishing CT-EX mixing due to inteference.

terms, which involves the complex Wannier wave fuctions $\zeta_\lambda^\alpha(k)$, between many different pairs of carbon orbitals, large variations are expected due to the quantum interferences (cancelations). The landscapes of all the figures changes little as long as d is in the physical range of $2.5 - 4.5$ Å. CN-PPV happens to be close to a local maximum, while MEH-PPV is close to the contour of $\langle\text{CT}-|\tilde{H}_i|\text{EX}-\rangle = 0$. PPV is already in the flat region away from all the peaks. $\Delta\langle\text{CT}-|\tilde{H}_i|\text{EX}-\rangle/\Delta d$ can be viewed as the effective attractive force due to one excitation, which is equal to -0.094 eV/Å for CN-PPV and -0.0095 eV/Å for MEH-PPV, if Δd is chosen to be 0.5 Å. In addition to the spectra, our model also explains the lifetimes of PL and photoinduced absorption (PA),[17] in particular the large difference in PL lifetimes between MEH-PPV (1.2 ns) (Ref. 18) and CN-PPV (17 ns).[3]

The symmetry-forbidden transition rate r_g from $|g1\rangle$ to $|0\rangle$, via vibrational coupling to $|u1\rangle$, is given by[19]

$$r_g = r_u \left(\frac{1}{\varepsilon_{u1} - \varepsilon_{g1}}\right)^2 \sum_i \langle q_i^2\rangle \left(\frac{\partial}{\partial q_i}\langle u1|\Delta H(\boldsymbol{q})|g1\rangle\right)_0^2.$$

$$\text{(11)}$$

q is the collective lattice coordinates. r_u is the transition rate from $|u1\rangle$ to $|0\rangle$, which is actually equal to the rate from $|A\rangle$ to $|0\rangle$ for a single chain. ε_{u1} and ε_{g1} are excited state energies at the relaxed lattice configuration. $\langle q_i^2 \rangle$ is the mean square lattice quantum fluctuation. Consider, for example, the lattice displacements in chain **a** only. Since they effect the electronic states in chain **a** but not in chain **b**, the exact inversion symmetry of $|u1\rangle$ is broken, and the emission is slightly dipole allowed. r_u is inversely proportional to the PL radiative lifetime τ_{PL}^f in films, while r_g is inversely proportional to the PL radiative lifetime τ_{PL}^s in solutions. Using the relation $1/\tau_{\text{PL}}^f \sim (\varepsilon_{u1} - \varepsilon_{g1})^{-2}$, we can predict the relative τ_{PL}^f of the derivatives. For MEH-PPV, we simply take $d^* = d_0$

$= 4.05$ Å, at which $\varepsilon_{u1} - \varepsilon_{g1} = 0.17$ eV from our calculation. For CN-PPV, the lattice is relaxed substantially and the actual value of d^* is hard to find. However, we can approximate $\varepsilon_{u1} - \varepsilon_{g1}$ by $2\Delta\varepsilon_1 = 0.7$ eV, assuming that the even and odd states split evenly off the the unperturbed value $\varepsilon_{g1}(\infty)$. The ratio between their τ_{PL}^f is predicted to be $(0.7/0.17)^2 = 17$, consistent with the experimental value 17 ns/1.2 ns $= 14.2$.

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