Essential optical states in $\pi$-conjugated polymer thin films

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We develop a theory of the electronic structure and photophysics of interacting chains of $\pi$-conjugated polymers to understand the differences between solutions and films. While photoexcitation generates only the exciton in solutions, the optical exciton as well as weakly allowed exciters are generated in films. Photoinduced absorption in films is primarily from the lowest excimer. We are also able to explain peculiarities associated with photoluminescence, including delayed photoluminescence and its quenching by electric field.

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The photophysics of dilute solutions and thin films of $\pi$-conjugated polymers (PCPs) are often remarkably different [1, 2, 3]. Solutions exhibit behavior characteristic of single strands, and the different behavior of films is due to interchain interaction and disorder. Microscopic understanding of the effects of interchain interaction has remained incomplete even after intensive investigations. As discussed below, the experimental results themselves are controversial. Further, while theoretical works on interchain interactions have examined a variety of issues [4], few authors [5] have investigated the interchain species that dominate thin film photophysics [1, 2, 3].

The key controversy in PCP films involves the apparent generation of polaron-pairs (bound electron-hole pairs on neighboring chains) or even free polarons upon photoexcitation. The reduced photoluminescence (PL) of films, nonexponential time decay of PL, delayed PL lasting until milliseconds, and electric-field induced quenching of the same are cited as evidence for the polaron-pair [1, 2, 3]. The mechanism of their formation is controversial. Transient absorptions in films are also not understood. Two distinct ultrafast photoinduced absorptions (PAs) are seen in solutions as well as in films with weak interchain interactions, such as dioctyloxy-poly-paraphenylenevinylene (DOO-PPV) [7]. The low energy PA1 appears at a threshold energy of 0.7 eV and has a peak at $\sim 1$ eV, while the higher energy PA2 occurs at $\sim 1.3$–$1.4$ eV. Comparison of PA and PL decays [7] and other nonlinear spectroscopic measurements [8] have confirmed that these PAs are from the 1B$_g$ optical exciton, in agreement with theoretical work on PCP single chains [8, 9]. In contrast, PA and PL decays in PCPs with significant interchain interactions (for e.g., poly[2-methoxy,5-(2'-ethyl-hexyloxy)-$\pi$-phenylenevinylene], MEH-PPV) are uncorrelated [1, 11]. PA measurements to previously inaccessible wavelengths [12]. The authors have detected a new relatively weak PA at $\sim 0.35$–$0.4$ eV in PCP films [12], which they label P$_1$. The authors ascribe P$_1$ to free polaron absorption, and suggest instantaneous photogeneration of both polarons and excitons. Such branching of photoexcitations would be in agreement with previous claim of the observation of infrared active vibrations in MEH-PPV in fs time [13], but is difficult to reconcile with (i) the large exciton binding energies deduced from PA1 energy [7, 8, 9], and (ii) microwave conductivity measurements [14] and THz spectroscopy [15], which find negligible polaron generation in solutions and films. Interestingly, samples that exhibit P$_1$ absorption also exhibit induced absorptions PA$_1$ and PA$_2$ [12], in apparent contradiction to the polaron-pair picture [1, 11] (unless PAs from the latter and the exciton occurred at the same energies). Taken together, the above experiments indicate the strong need for systematic theoretical work on interacting PCP chains.

In the present Letter, starting from a microscopic $\pi$-electron Hamiltonian, we determine the complete energy spectrum of interacting PCP chains. We find a 1:1 correspondence between the “essential states” that determine the photophysics of single strands [8, 10] and the dominant excited states, including excited interchain species, in films. We are able to explain consistently, (i) the branching of photoexcitations, (ii) the peculiarities associated with PL, and (iii) ultrafast PA over the complete experimental wavelength region for PCP films.

Our calculations are within an extended two-chain Pariser-Parr-Pople Hamiltonian $H = H_{\text{intra}} + H_{\text{inter}}$, where $H_{\text{intra}}$ and $H_{\text{inter}}$ correspond to intra- and inter-chain components, respectively. $H_{\text{intra}}$ is written as,

\[ H_{\text{intra}} = - \sum_{\nu, (ij), \sigma} t_{ij}(c^{\dagger}_{\nu,i,\sigma}c_{\nu,j,\sigma} + H.C.) + U \sum_{\nu,i} n_{\nu,i,\uparrow}n_{\nu,i,\downarrow} + \sum_{\nu, i, j} V_{ij}(n_{\nu,i} - 1)(n_{\nu,j} - 1) \]

where $c^{\dagger}_{\nu,i,\sigma}$ creates a $\pi$-electron of spin $\sigma$ on carbon atom
of oligomer $\nu$ ($\nu = 1,2$), $n_{\nu,i,\sigma} = c_{\nu,i,\sigma}^\dagger c_{\nu,i,\sigma}$ is the number of electrons on atom $i$ of oligomer $\nu$ with spin $\sigma$ and $n_{\nu,i} = \sum_{\sigma} n_{\nu,i,\sigma}$ is the total number of electrons on atom $i$. The hopping matrix element $t_{ij}$ is restricted to nearest neighbors and in principle can contain electron-phonon interactions, although a rigid bond approximation is used here. $U$ and $V_{ij}$ are the on-site and intrachain intersite Coulomb interactions. We parametrize $V_{ij}$ as

$$V_{ij} = \frac{U}{\kappa \sqrt{1 + 0.6117 R_{ij}^2}}$$  \hspace{1cm} (2)$$

where $R_{ij}$ is the distance between carbon atoms $i$ and $j$ in Å, and $\kappa$ is the dielectric screening along the chain due to the medium. Based on previous work [17] we choose $U = 8$ eV and $\kappa = 2$. We write $H_{\text{inter}}$ as

$$H_{\text{inter}} = H_{\text{inter}}^\text{ee} + H_{\text{inter}}^\text{exc}$$  \hspace{1cm} (3)$$

$$H_{\text{inter}}^\text{ee} = -t_{\perp} \sum_{\nu,\nu',i,\sigma} (c_{\nu,i,\sigma}^\dagger c_{\nu',i,\sigma} + H.C.)$$  \hspace{1cm} (4)$$

$$H_{\text{inter}}^\text{exc} = \frac{1}{2} \sum_{\nu < \nu',i,j} V_{ij}^\perp (n_{\nu,i} - 1)(n_{\nu',j} - 1)$$  \hspace{1cm} (5)$$

In the above, $t_{\perp}$ is restricted to nearest interchain neighbors. We choose $V_{ij}^\perp$ as in Eq. 2 with a background dielectric constant $\kappa_\perp \leq \kappa [3]$. To get a physical understanding of the effect of $H_{\text{inter}}$, we begin with the case of two ethylene molecules in the molecular orbital (MO) limit $U = V_{ij} = 0$, placed one on top of the other such that the overall structure has a center of inversion. The ethylene MOs are written as,

$$a_{\nu,\lambda,\sigma}^\dagger = \frac{1}{\sqrt{2}} [a_{\nu,1,\sigma}^\dagger + (-1)^{\lambda-1} a_{\nu,2,\sigma}^\dagger]$$  \hspace{1cm} (6)$$

where $\lambda = 1(2)$ corresponds to the bonding (antibonding) MO. The spin singlet one-excitation space for the two molecules consists of the four spin-bonded valence bond (VB) diagrams shown in Fig. 1(a). We refer to the two intramolecular excitations $|\text{exc1}\rangle$ and $|\text{exc2}\rangle$ as excitons (we ignore for the moment that true excitons require two intramolecular excitations $\nu,\lambda,\sigma$), and the other two, $|P_1^+ P_2^-\rangle$ and $|P_1^- P_2^+\rangle$, consist of charged molecules and are the polaron-pairs. The exciton and polaron-pair wavefunctions are given by,

$$|\text{exc1}\rangle = \frac{1}{\sqrt{2}} a_{2,1,1}^\dagger a_{1,2,1}^\dagger (a_{1,1,1}^\dagger a_{1,2,1}^\dagger - a_{1,1,1}^\dagger a_{1,2,1}^\dagger)|0\rangle$$  \hspace{1cm} (7)$$

$$|P_1^+ P_2^-\rangle = \frac{1}{\sqrt{2}} a_{2,1,1}^\dagger a_{1,2,1}^\dagger (a_{1,1,1}^\dagger a_{1,2,1}^\dagger - a_{1,1,1}^\dagger a_{1,2,1}^\dagger)|0\rangle$$  \hspace{1cm} (8)$$

Nonzero $H_{\text{inter}}$ mix these pure states to give excimers. Consider first the $H_{\text{inter}}^{\text{ee}} = 0$ limit. Matrix elements of $H_{\text{inter}}^{\text{exc}}$ are zero between $|P_1^+ P_2^-\rangle$ and $|P_1^- P_2^+\rangle$ but nonzero between $|\text{exc1}\rangle$ and $|\text{exc2}\rangle$, indicating that while the polaron-pair states are degenerate for $H_{\text{inter}}^{\text{ee}} \neq 0$, the exciton states form new nondegenerate states $|\text{exc1}\rangle \pm |\text{exc2}\rangle$ (see Fig. 1(b)). The dipole operator $\mu = e \sum_{\nu,i} r_{\nu,i} (n_{\nu,i} - 1)$, where $r_{\nu,i}$ gives the location of atom $i$ on oligomer $\nu$, couples the ground state to only the even parity exciton state. We now switch on $H_{\text{inter}}^{\text{ee}}$, which mixes $|\text{exc1}\rangle - |\text{exc2}\rangle$ and $|P_1^+ P_2^-\rangle - |P_1^- P_2^+\rangle$, to give the two excimer states in Fig. 1(c). From the expression for $\mu$, both exciters are dipole-forbidden from the ground state. The optical exciton $|\text{exc1}\rangle + |\text{exc2}\rangle$ and the polaron-pair $|P_1^+ P_2^-\rangle + |P_1^- P_2^+\rangle$ are not affected by $H_{\text{inter}}^{\text{ee}}$ in this symmetric case. We make an important observation: the transverse component of $\mu$, perpendicular to the molecular axes, couples the two excimer states with the polaron-pair state, indicating allowed optical transition from the lower excimer to the polaron-pair.

We now go beyond the two ethylenes and make the following observations.

(i) Fig. 1 applies also to the $U = V_{ij} = 0$ limit of identical oligomers of arbitrary PCPs facing one another. The lowest one-excitations, across the highest occupied and lowest unoccupied MOs of the oligomer pairs, are split by $H_{\text{inter}}$ to give the same four eigenstates of Fig. 1. Wu and Conwell, and Meng had concluded the same for a simpler $H_{\text{inter}}^{\text{ee}}$ [6]. We have confirmed this for $H_{\text{inter}}$ in Eqs. 3-5 from configuration interaction (CI) calculations involving the configurations of Fig. 1 for long PPV oligomers. To identify wavefunctions as polaron-pair, excimer, etc., we choose an orbital set consisting of the canonical Hartree-Fock orbitals of the individual molecular units, and perform CI calculations using these localized MOs. The localized basis allows calculations of ionicities of individual oligomers. The expected ionicities are 0 and 1 for the exciton and the polaron-pair, respectively, and fractional for the excimers.

(ii) Fig. 1 applies also to higher energy excitations involving arbitrary pairs of MOs of PCP oligomers. Note that interchain species here are in their excited states. Again, we have verified this from CI calculations involving highly excited pairs of MO configurations of PPV.
TABLE I: SCI excited states of two symmetrically placed 8-unit PPV oligomers for $\kappa_{\perp} = 2$, $t_{\perp} = 0.03$ and 0.1 eV (numbers in parentheses are for $t_{\perp} = 0.1$ eV.) Here $j$ and $E_j$ are quantum numbers (without considering symmetry) and energy, respectively. Ionicity is the charge on the chains. The states are arranged not according to their energies, but according to the manifolds they belong to (see text). The $\mu_{G,j}$ and $\mu_{ij}$ are the dipole couplings between the ground state and state $j$, and between excited states, respectively.

| $j$ | $E_j$ (eV) | Ionicity | $\mu_{G,j}$ | $\mu_{ij}$ |
|-----|------------|----------|-------------|------------|
| 2 (2) | 2.77 (2.67) | 0.06 (0.26) | 0 | — |
| 3 (4) | 2.83 (2.81) | 0 (0) | 6.52 (6.52) | — |
| 5 (5) | 3.00 (3.00) | 1 (1) | 0 | 0.99 (2.04)$^a$ |
| 6 (8) | 3.02 (3.12) | 0.94 (0.74) | 0 | — |
| 4 (3) | 2.92 (2.81) | 0.08 (0.29) | 0 | — |
| 7 (7) | 3.06 (3.06) | 0 (0) | 0 | — |
| 8 (9) | 3.12 (3.12) | 1 (1) | 0 | — |
| 9 (10) | 3.14 (3.24) | 0.92 (0.64) | 0 | — |
| 14 (11) | 3.39 (3.26) | 0.18 (0.38) | 0 | 6.66 (6.91)$^b$ |
| 16 (15) | 3.42 (3.42) | 0 (0) | 6.83 (6.83)$^b,c$ |
| 18 (19) | 3.52 (3.46) | 1 (1) | 0 | 7.68 (7.68)$^b$ |
| 20 (26) | 3.55 (3.67) | 0.82 (0.55) | 0 | 7.41 (6.69)$^b$ |

$^a$i=2. $^b$All dipole couplings are with states in lowest manifold near 1B$_u$ with the same character (see text). $^c$ The mA$_g$.

TABLE II: SCI excited states near the optical exciton of two-chain PPV with 5 and 7-units for $\kappa_{\perp} = 2$, $t_{\perp} = 0.1$ eV.

| $j$ | $E_j$ (eV) | Ionicity | $\mu_{G,j}$ | $\mu_{ij}$ |
|-----|------------|----------|-------------|------------|
| 2 | 2.74 | 0.23 | 1.45 | — |
| 3 | 2.89 | 0.07 | 4.99 | 0 |
| 4 | 3.04 | 0.14 | 2.07 | 0 |
| 5 | 3.07 | 1.00 | 0 | 2.03 |
| 6 | 3.16 | 0.45 | 0.31 | 0 |
| 7 | 3.21 | 0.53 | 0.57 | 0 |

oligomers, using the localized basis.

(iii) The results of (i) and (ii) indicate that for $U = V_{jj} = 0$ but $H_{\text{inter}} \neq 0$, the two-chain energy spectrum consists of a series of overlapping energy manifolds, with each manifold containing an exciton, a polaron-pair and two excimers, as in Fig. 1. We speculate that similar energy manifolds persist for nonzero $U$, $V_{ij}$. We have verified this conjecture within the single-CI (SCI) approximation for the complete two-chain Hamiltonian, including all one-excitations, and using the localized MO basis set. We have summarized our SCI results in Table I for two interacting symmetrically placed parallel PPV oligomers at a distance of 0.4 nm. Identification of excitons, polaron-pairs and excimers from their ionicities is possible even at higher energies. Table I also lists relevant transition dipole couplings. PA from the lowest excimer ($i = 2$) to the lowest polaron-pair ($j = 5$) is still allowed. PA in single-chain PCPs is from the 1B$_u$ exciton to an even higher energy two-photon state the mA$_g$ [9], and to an even higher energy two-photon state the mA$_g$ [10]. Table I shows that, (i) exactly as near the 1B$_u$, a pair of excimers and a polaron-pair occur near the mA$_g$, and (ii) longitudinal transition dipole-couplings between interchain states near the 1B$_u$ and interchain states of the same character near the mA$_g$, are of the same strength as that between the 1B$_u$ and mA$_g$ excitons.

We now relax the inversion symmetry condition to take disorder into account approximately. We consider two oligomers of different lengths, arranged face to face with only one end matching (see insert Fig. 2). In Table II we show the results of SCI calculations for PPV oligomers 5- and 7-units long, again for interchain separation 0.4 nm. The key differences from the centrosymmetric case are: (i) there are now two optical excitons ($j = 3, 4$), which have acquired weak ionic character, (ii) characterization of states as excimers ($j = 2, 6,$ and 7) and polaron pairs ($j = 5$) are still valid, and (iii) the excimers have acquired weak transition dipole couplings with the ground state. We have shown the energy region near the optical exciton...
only. Instead of giving similar details for higher energy states, we will calculate PA.

The key results that emerge from Tables I and II are: (i) direct photogenerations of the optical exciton and the two lowest excimers, one below and one above the exciton, are allowed, and (ii) the exciters, and not free polarons or the polaron-pair play a crucial role in PCP films. While we have shown calculations of interchain interaction effects for ideal and simple cases, our results remain qualitatively intact for three or more oligomers, different relative orientations and distances.

Our calculations therefore provide the foundation for understanding PCP films qualitatively, and perhaps even semi-quantitatively. The reduced PL and its non-exponential behavior in films are related to the lowest excimer. Nonradiative relaxation of the exciton to the lowest excimer competes with direct radiative relaxation. It is likely that PL and PA in films after a few hundred fs are largely from the weakly emissive lowest excimer. The allowed component in the excimer’s wavefunction comes from the optical exciton, making it likely that their emission profiles are similar. This conjecture is supported by very recent observations of (i) weak emission from an intermolecular species in dendritic oligothiophenes [18], and (ii) PA from excimers in pentacene films [19]. Delayed PL [1, 2] is from both the excimers, with the upper excimer relaxing directly to the ground state as well as via the exciton. The polaron-pair component of the excimers’ wavefunctions ensures that the relaxation processes are slow, as the electron and the hole are partly on different chains. The quenching of the delayed PL by external electric field is understandable. The transverse dipole coupling between the two excimers and the polaron-pair indicates that an external electric field will mix these energetically proximate states strongly [9], as we have confirmed numerically (not shown). Increased ionicity of the excimers’ wavefunction diminishes both the radiative decay to the ground state and the nonradiative decay to the exciton. This mechanism provides a natural explanation for the immediate reappearance of the delayed PL upon removal of the field.

A direct test of our theory comes from comparisons of calculated and experimental PAs. In Fig. 2(a) we compare PAs calculated for a single 8-unit PPV oligomer with that from the lowest excimer in a two-chain system consisting of a 7-unit and a 9-unit oligomer. Fig. 2(b) shows PA calculations for the same two-chain system for other parameters. The similarity between the two-chain PA in Fig. 2 and the experimental PA spectra of Sheng et al. [12] for films is striking. PA$_1$ in the single chain corresponds to the transition from the 1B$_u$ to the m_A$^g$. The initial and final states of PA$_1^P$ absorptions in the two-chain systems are both excimers. The near identical energies of this absorption in solutions and films [12], and the absence of correlation between PA and PL decays in the latter [1, 11], can therefore both be explained.

The P$_1$ absorption in the two-chain system in Fig. 2 is from the lowest excimer to the lowest polaron-pair. Its strength is indeed a measure of interchain interaction [12], but it is unrelated to free polarons. Our interpretation of P$_1$ resolves the apparent disagreement between ultrafast spectroscopy [12] and other measurements [14, 15]. We predict that the polarizations of P$_1$ and PA$_1^P$ are different.

In summary, excimers and polaron-pairs occur not only near the optical edge of PCP films, but also at high energies. The 1B$_u$ and m_A$^g$ excitons, together with the excimers and polaron-pairs derived from these states constitute the essential optical states of PCP films. We have presented the first applications of this concept here. Application to copolymers [20] is clearly of interest.

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