

Photoexcitations in poly(*p*-phenylenevinylene) aggregates

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Abstract

Photo-induced electronic excitations of poly(*p*-phenylenevinylene) (PPV) aggregates are simulated and characterized using a recently developed linear-scaling localized-density-matrix (LDM) method. The intra- and inter-chain components of excitations are analyzed and quantified for different inter-chain distances. The excitations for the absorption and luminescence in PPV film and its derivatives are identified and are found analogous to those of H-aggregates. Their energy shifts upon aggregation are determined mainly by the inter-chain kinetic energy reduction and the Coulomb interaction of the electron–hole pair. It is concluded that the luminescence is caused by the intra-chain electron–hole pairs. © 2001 Elsevier Science B.V. All rights reserved.

Important progress has been made towards the commercialization of polymer light emitting diode (LED) [1–3]. PPV and its derivatives are among the most studied light emitting polymers. Pristine poly(*p*-phenylenevinylene) (PPV) films have distinctive vibronic features in their absorption spectra which indicate that the corresponding excitations in pristine PPV films are intra-chain in nature [4–6]. This has been explained by the fact that the inter-chain couplings in PPV aggregates are relatively weak. Subjected to high pressures, the absorption and emission spectra of PPV films red shift alike [7]. This was interpreted that the excitations for the absorption and luminescence acquire inter-chain components as the inter-chain distances decrease [7]. The absorption spectra of poly(2-methoxy,5-(2'ethyl-hexyloxy)-*p*-phenylenevinylene) (MEH-PPV) and cyano-substituted PPV

(CN-PPV) thin films shift little in energy compared to their counterparts in dilute solutions, while the corresponding emission spectra of thin films have large red shifts [8–10]. One view is that the excitations responsible for the absorptions in MEH-PPV and CN-PPV must be intra-chain since their absorption spectra in dilute solutions and films differ little [8,9]. Because the emission spectra of thin films and dilute solutions are quite different, the luminescences in the films are thus likely caused by the inter-chain excitations [8,9]. This was seemingly supported by the appearance of distinctively different excitations in CN- and MEH-PPV films observed in transient photoluminescence [8,9] and transient photo-induced absorption studies [8]. Another view is that the excitations responsible for the luminescence are intra-chain, and the red shifts of emission spectra are caused by the excitations that migrate to the longer conjugated chains in films or aggregates [11].

Numerical calculations have been used to help understand the microscopic pictures of the optical

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excitations in these conjugated systems. Most simulations have been performed on single chain (see, for example, [12–14]). Several recent calculations were carried on PPV dimers [15–17]. The tight-binding calculations have been performed on a PPV dimer to investigate the nature of the inter-chain excitations [15]. The inter-chain excitations were proposed to be responsible for the emissions in MEH-PPV and CN-PPV. The time-dependent Hartree–Fock calculations based on the Pariser–Parr–Pople (PPP) Hamiltonian have been employed to study the effects of inter-chain interaction on the absorption spectrum of a dimer [16]. In both studies, the inter-chain couplings are modelled as decaying exponentially versus the inter-chain distance. Cornil et al. [17] performed a detailed calculation on a series of PPV dimers with varying inter-chain distances and orientations. Intermediate neglect of differential overlap in spectroscopy (INDO/S) Hamiltonian [18] was employed in their single electron excitation configuration interaction (CIS) calculations, and all π orbitals were included explicitly while the σ electrons excluded. They concluded that the luminescence is mainly induced by the intra-chain polaron-excitons. To resolve the above confusions resulted from different experiments and calculations, detailed numerical simulations are needed to examine the photoexcitation dynamics in large three-dimensional PPV aggregates.

We report here our numerical study of the photo-induced excitations in PPV aggregates. Two types of PPV aggregates are investigated. One type is arranged according to the PPV crystal structure [19,20], which is denoted as type I. The structure of a four-chain type I aggregate is depicted in Fig. 1a. The C–C bond lengths along the benzene ring are set to 1.39 Å, and all the angles on the benzene are set to 120°. The C–H bond lengths are 1.09 Å. The single and double bond lengths in the vinylene group are 1.44 and 1.33 Å, respectively. Each chain is aligned along the x -axis and there are 3.28 and 1.64 Å displacements along x -direction from C to A and from B to A, respectively. Two chains are either parallel (as A and C) or tilted to each other with an angle of 76° (as A and B). The axes of C and B are displaced by (4.00, 3.12 Å) and (–0.31, 4.53 Å) in y – z plane from that of A. Chain

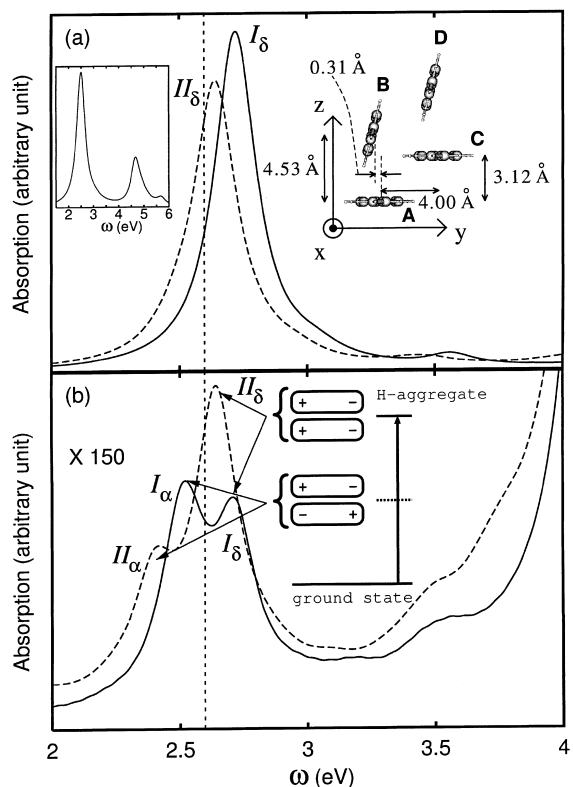


Fig. 1. Absorption spectra for 4-4 PPV aggregates. The solid lines are of type I, and the dashed lines for type II. The electric field is polarized (a) along the chain axis and (b) perpendicular to the plane of A. $\gamma = 0.1$ eV. The inset in (a) is the absorption spectrum of an 8-4 aggregate with the crystal structure. The inset in (b) depicts two typical types of excitations in an H-aggregate. The arrows indicate the types of excitations for the absorption peaks.

D is added with the same corresponding displacement vectors and angles with respect to B and C, see Fig. 1a. Each PPV chain is made of multiple repeating units. To model the PPV solid under high pressure [7], we reduce the inter-chain distances of type I by 10% to enhance the inter-chain couplings, and the resulting structures are denoted as type II. The photo-induced excitations in I and II are calculated with the LDM method [20–22]. Semiempirical complete neglect of differential overlap in spectroscopy (CNDO/S) Hamiltonian [23,24] is used in the calculation. Upon the application of an external field, the reduced single electron density matrix ρ may be expressed as

$\rho = \rho^{(0)} + \delta\rho$, where $\rho^{(0)}$ is the ground state reduced single electron density matrix and $\delta\rho$ is the induced density matrix by the external field. $\delta\rho$ contains the excited state information, for instance, the optical properties, and can be determined by solving its Heisenberg equation of motion within the time-dependent Hartree–Fock or random phase approximation [25,26]. The reduced density matrix $\delta\rho^v$ for individual photo-induced excited state v with energy Ω_v can be projected from $\delta\rho$.

The absorption spectra of two four-chain aggregates of type I and II are shown in Fig. 1, and each chain has four repeating units (denoted as 4-4). The solid lines are of type I, and the dash lines for II. Two polarized electric fields are applied. Fig. 1a depicts the absorption spectra for the electric field polarized along the x -axis. The absorption spectrum of II red shifts as compared to that of I, which is consistent with the experimental observation that the pressure on PPV films induces the red shift of absorption spectra [7]. The dash line at $\omega \approx 2.6$ eV represents the optical gap of a single four unit PPV chain. This indicates that the absorption spectra of PPV films actually blue shift compared to that of single chain or the dilute solution. Aggregate I has a large blue shift for the absorption (I_δ) while II has a much smaller one (II_δ). When the electric field polarizes along the z -axis, the absorption spectra change dramatically, which are plotted in Fig. 1b. A new peak (I_α or II_α) appears for each aggregate. This is the so-called Davydov splitting [27]. Each aggregate I or II has total four such excitations, and the other two are denoted as β and γ . Note that the signals in Fig. 1b are amplified by 150 times as compared to those in Fig. 1a, which implies that the oscillator strengths of I_α and II_α are very small. Similarly β and γ have very small oscillator strengths as well. This is the

reason why the excitations I_α and II_α cannot be detected in the absorption spectra. Among these four excitations for each aggregate δ mode has the highest energy, and γ the second highest. The energies of α and β are very close. For instance, the energy difference between I_α and I_β is 0.02 eV. For aggregate I, I_β has the lowest energy, while for II, II_α the lowest. After the photoexcitation, I_δ (II_δ), decays nonradiatively into the low lying modes I_α or I_β (II_α or II_β) from which the emission occurs. The inset in Fig. 1a is the absorption spectrum of a type I aggregate made of four 8-unit chains (denoted as 8-4).

Our calculated results agree with the observed absorption and emission spectra of PPV [7]. Now the question is what exactly the characteristics of these photo-induced excitations are in these systems. We examine first the inter-chain composition of each excitation. The inter-chain component of the density matrix $\delta\rho^v$ for excitation v may be measured by the probability P^v of finding the electron–hole residing separately at two different chains:

$$P^v \equiv \frac{\sum_{i,j}^{\text{inter-chain}} |\delta\rho_{ij}^v|^2}{\sum_{i,j} |\delta\rho_{ij}^v|^2}, \quad (1)$$

where the sum on the numerator is over the inter-chain components of $\delta\rho^v$, i.e., the atomic orbitals i and j belong to different chains; and the sum on the denominator is over all pairs of i and j . The P^v values of four types of excitations are shown for 4-4 PPV aggregates I and II in Table 1. While P^v of type II aggregates are an order of magnitude larger than those of I, they are only 5% or less. Thus, we conclude that *the excitations in both I and II aggregates are intra-chain modes*.

We examine the nature of photo-induced excitations by calculating their induced charge

Table 1
 P^v values of four types of excitations α , β , γ , and δ for 4-4 PPV aggregates I and II

v	ω (eV)	P^v	v (eV)	ω	P^v
I_α	2.51	0.0049	II_α	2.40	0.051
I_β	2.49	0.0036	II_β	2.41	0.037
I_γ	2.54	0.0026	II_γ	2.49	0.029
I_δ	2.72	0.0039	II_δ	2.64	0.040

distributions $(\delta\rho_{ii}^v + \delta\rho_{ii}^{v\dagger})/\sqrt{2}$. Fig. 2 shows the induced charge distributions of the two 4-4 aggregates I and II. The horizontal axis is the index of each unit which starts from the unit one of chain A and end at the unit four of chain D. The vertical axis shows the induced charge distribution. The dash lines represent the net charge of individual units. Figures are arranged from top to bottom with the increasing energy, and left (right) panel is for type I (II) aggregates. For I_α and II_α , the net charges of individual units along x -direction are alternating from minus to plus in A and C and from plus to minus in B and D. This implies that the intra-chain transition dipole moments for A and B (or C and D) are of opposite phases. In

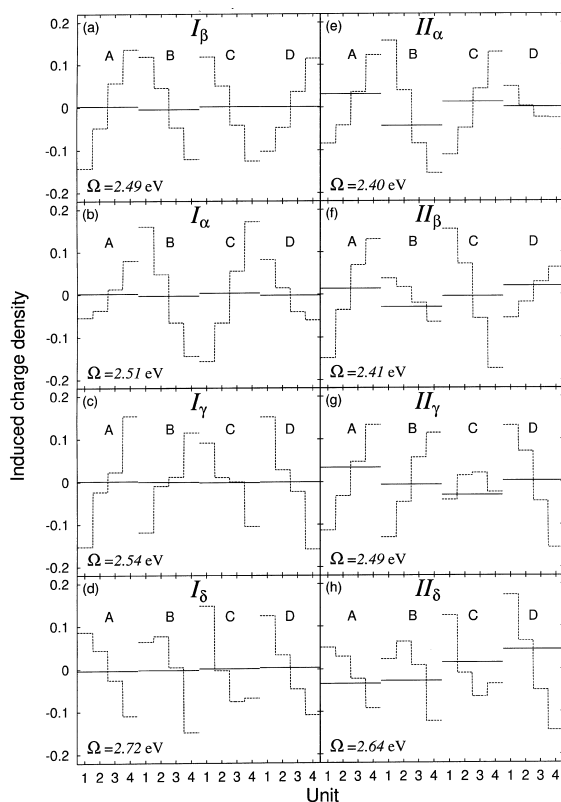


Fig. 2. The induced charge distributions in 4-4 PPV for type I aggregate (a)–(d) and for type II aggregate (e)–(h). The solid lines indicate the net charge of each chain, and the dashed lines stand for the charges of individual units on different chains. The excited energies Ω are shown for each excitation.

contrast, the charge distribution is from plus to minus for I_δ and II_δ in all the chains, which implies that the transition dipole moments of all chains are of the same phase. This results in that I_α (II_α) has a lower energy than I_δ (II_δ). Similarly, I_β and I_γ (II_β and II_γ) have smaller overall transition dipole moments and thus lower energies than I_δ (II_δ). This is analogous to the excitations in H-aggregates [28], and explains the reason why the absorption spectra in Fig. 1a blue shift compared to that of single chain.

A closer look reveals the difference in the induced charge distributions between the crystal and reduced structures. We calculated the total charge of each chain, which is shown by a solid line in Fig. 2. For the crystal structure I, the total induced charges of individual chains are virtually zero, indicating that no charge transfer occurs. However, the induced charges on individual chains are not zero for II_α , II_β , II_γ , and II_δ implying that the charge transfer occurs for the reduced structure II. Thus, *the larger inter-chain interaction induces the charge transfer among different chains.*

To understand the energy shifts, we examine the excited state energy Ω_v

$$\Omega_v = \text{Tr}([\delta\rho^v, [\rho^{(0)}, \delta\rho^{v\dagger}]]h^{(0)}) + \sum_{mn} (2\delta\rho_{mm}^{v\dagger}v_{mn}\delta\rho_{nn}^v - \delta\rho_{nm}^{v\dagger}v_{mn}\delta\rho_{mn}^v), \quad (2)$$

where $h^{(0)}$ is the ground state Fock matrix and v_{mn} is the Coulomb interaction between orbital m and n . ρ^v is normalized by setting $\text{Tr}(\rho^{(0)}, [\delta\rho^{v\dagger}, \delta\rho^v]) = 1$ [29,30]. We decompose Ω_v into kinetic and Coulomb component, and further intra- and inter-chain components for kinetic part. The intra- and inter-chain components are defined by whether the hopping matrix element is intra- or inter-chain. These components are listed in Table 2. The Coulomb induced shifts are positive for I_δ and II_δ and negative for others. This is consistent with the H-aggregate picture. The inter-chain components of kinetic energy induced shifts are all negative, and this means that the inter-chain hoppings reduce the kinetic energies. These reductions are much larger for the reduced structures II as compared to those of the crystal structures I due to the fact that the inter-chain interactions decay exponentially versus

Table 2
Components of energy shifts for the excitations α , β , γ , and δ of two 4-4 PPV aggregates I and II (in eV)^a

	Kinetic (intra)	Kinetic (inter)	Coulomb	Total
I _{α}	0.009	-0.027	-0.073	-0.090
I _{β}	0.001	-0.022	-0.085	-0.105
I _{γ}	0.013	-0.015	-0.042	-0.045
I _{δ}	0.075	-0.023	0.067	0.119
II _{α}	0.046	-0.231	-0.017	-0.202
II _{β}	0.066	-0.199	-0.054	-0.187
II _{γ}	0.063	-0.137	-0.035	-0.110
II _{δ}	0.122	-0.158	0.075	0.040

^aThe kinetic, Coulomb and total energies of a PPV oligomer with four units are 3.25, -0.66, and 2.60 eV, respectively.

the distance and are thus much larger for the reduced structures. This results in larger red shifts for II _{α} , II _{β} , and II _{γ} , since both the kinetic energy and the Coulomb interaction induce the red shifts, and little shifts for II _{δ} since the kinetic and Coulomb terms tend to cancel with each other. For type I aggregates, the inter-chain hoppings are much weaker, and thus, the Coulomb term dominates. This results in the blue and red shifts for the absorption and luminescence spectra, respectively [17]. It is important to point out that the intra-chain energy shifts are not zero and tend to compensate the effects of the inter-chain components. This comes from the fact that the inter-chain interactions induce the changes to the intra-chain portions of the excited state wave functions.

Since the type II aggregate have larger inter-chain hoppings than type I aggregate, it is employed to investigate the excitations in CN- and MEH-PPV films where larger average inter-chain hoppings are expected as compared to those of PPV films [10]. Our calculated results agree well with the observed absorption and emission spectra of these PPV derivatives [8,9,31]. For example, the small shift of II _{δ} as compared to the larger blue shift of I _{δ} (Fig. 1) is consistent with the experimental observations that CN- and MEH-PPV films have little shifts of their absorption spectra with respect to those of the dilute solutions [8,9,31]. The interplay between the inter-chain kinetic and Coulomb terms in Table 2 appears to explain well the spectra shifts of absorption and luminescence for CN- and MEH-PPV aggregates

and solutions [8–10]. Thus, the corresponding excitations in CN- and MEH-PPV films are likely intra-chain modes as well. This is significant and calls for the reinterpretations of many experiments [8–10,31,32].

We have shown that the excitations for both absorption and luminescence are similar to those of H-aggregates for I and II. CN- and MEH-PPV films have much more complex structural features. However, the excitations which have large oscillator strengths are those where the individual transition dipole moments on adjacent PPV chains are in phase and add up constructively. The Coulomb interaction should increase the energies of these excitations which are then compensated by the inter-chain kinetic energy. This results in small or little energy shifts for the absorption spectra upon aggregation. The excitations that are made of the individual transitions on adjacent chains with opposite phases should have very small oscillator strengths and thus cannot be detected in the absorption spectra. Both Coulomb attractions and the inter-chain hoppings would lower their energies and thus induce large red shifts in the emission spectra of films or aggregates. Therefore, we assert that our conclusions derived from the above calculations on aggregates I and II remain valid for CN- and MEH-PPV films. The distinctive excitations were observed in the transient optical spectroscopy, and it was interpreted that the excitations for absorption and emission were inter- and intra-chain, respectively [8–10]. Our calculation demonstrates that they are both intra-chain excitations but have very different transition moments. The varying values of radiative decay rates of pristine, MEH- and CN-PPV films [9] are likely caused by different structural motifs. To convince ourselves the generality of our conclusions based on the CNDO/S calculations, we carried out MNDO-Parametric Method 3 (PM3) [33] calculations on these systems and found that the results are similar. Brédas and co-workers have considered the nuclear relaxation of the excited states, and found that the relaxation stabilizes the intra-chain excitations [17]. Thus, the inclusion of nuclear dynamics should not alter our conclusion that the emission comes from the intra-chain electron-hole pairs.

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