

# Intermolecular Interaction Effects on the Ultrafast Depolarization of the Optical Emission from Conjugated Polymers

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We have investigated the effect of interchain interactions on the ultrafast depolarization of the photoluminescence from solid films of a conjugated polymer. Accurate control was exercised over the interchain separation by threading of the conjugated chains with insulating macrocycles or complexation with an inert host polymer. Our measurements indicate that excitation into the higher electronic states of a chain aggregate is followed by a fast ( $< 100$  fs) relaxation into lower excited states with an associated rotation of the transition dipole moment. These findings emphasize the need for consideration of initial excitonic delocalization across more than one polymeric chain.

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The great potential of conjugated polymers for optoelectronic applications has sparked intense interest in the nature of the primary photoexcitations in these materials. While these are now generally believed to be correlated electron-hole pairs (excitons) with binding energy of up to a few hundred meV [1], the extent of their initial delocalization and the following localization dynamics are still a matter of controversy. Recent measurements have indicated that the initially generated exciton may be delocalized across more than one conformational subunit for a variety of conjugated materials, e.g., for a polyphenylenevinylene (poly-PV) derivative in solution [2], oligomeric PV dimers [3], and supramolecular assemblies of PV molecules [4]. The strong electron-phonon coupling inherent to  $\pi$ -conjugated systems causes a subsequent dynamic localization on the time scale of nuclear oscillation periods ( $< 100$  fs) for excitons on a segment of a single chain [5,6] and also those delocalized over stacked chain segments [7,8]. The ensuing motion of the exciton through the material is then mediated by weaker electronic coupling between dipolar moments on interacting chromophores [9]. Currently, it is unclear whether the initial exciton localization dynamics in conjugated polymers occur predominantly on a single chain segment, or whether intermolecular interactions, in particular, in the solid state, are of significance. Recent observations of an ultrafast ( $< 100$  fs) depolarization of the photoluminescence (PL) from thin films of poly-thiophene [10] and concentrated solutions of a poly-PV derivative [11] have been attributed to dynamic excitonic localization. The latter study concluded that ultrafast exciton localization was an on-chain effect, as the ultrafast depolarization component was weaker for chains containing static conjugation breaks or shorter segments, for which the extent of the exciton changes less dramatically upon nuclear relaxation [5].

We demonstrate here that ultrafast rotation of the emitting electronic dipole moment can be a direct

result of interchain interactions in conjugated polymer films. For this purpose we have examined a polydiphenylenevinylene derivative (PDV) for which we have attained precise control over the chain packing through a range of novel approaches: by supramolecular complexation with a polyethyleneoxide (PEO) matrix polymer, by threading insulating  $\beta$ -cyclodextrin macrocycles onto the polymer backbone to form a rotaxane ( $\beta$ -CD-PDV), and through the casting process. All three methods independently indicate that the PL depolarization dynamics occurring within the first 100 fs are directly correlated with the initial delocalization of the excitation across more than one polymer chain.

The chemical structure of the conjugated material under investigation is shown in Fig. 1. The synthesis of PDV and its rotaxane formed with  $\beta$ -cyclodextrin has been described elsewhere [12]. PEO with molecular weight average of  $M_v = 100\,000$  g mol<sup>-1</sup> was purchased from Sigma Alrich and used without further purification. Film samples were made by dissolving the compounds in deionized water (15 mg/ml) and either spin-casting or drop-casting on Spectrosil B substrates to result in a film thickness of  $\sim 100$  nm or a few microns, respectively. The samples were prepared under N<sub>2</sub> atmosphere and kept under dynamic vacuum ( $10^{-5}$  mbar) for measurements. Thin-film transmission spectra were taken using a spectrophotometer (Perkin Elmer, Lambda 9). Time-resolved PL measurements were performed using an upconversion set-up that has already been described in detail elsewhere [13]. All materials were excited at a photon energy of 3.06 eV and pulse energy of 1 nJ using the frequency-doubled output from a Ti:sapphire laser supplying 70-fs pulses at 80 MHz repetition rate. The PL was gated optically using part of the fundamental at vertical polarization, focused onto a  $\beta$ -barium borate crystal. The PL intensity components polarized parallel ( $I_{\parallel}$ ) and perpendicular ( $I_{\perp}$ ) to the linear excitation polarization were recovered by adjusting the

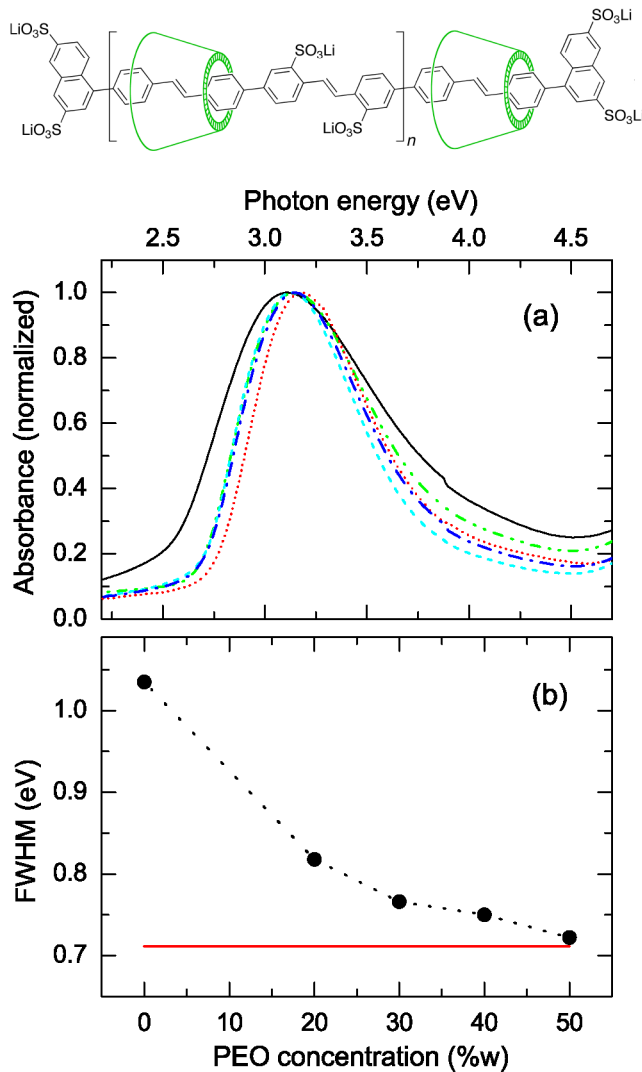


FIG. 1 (color online). Top: chemical structure of  $\beta$ -CD-PDV. The PDV structure is identical but without the (schematically represented)  $\beta$ -CD rings. The number average degree of polymerization is 11 for  $\beta$ -CD-PDV and 12 for PDV [12]. (a) Absorption spectra of spun-cast films of  $\beta$ -CD-PDV (red, dotted line) and PDV:PEO blend films with 0% (black, solid line), 20% (green, dash-dotted line), 40% (blue, dash-dotted line), and 50% (cyan, dashed line) PEO fraction by weight. PEO shows no absorption over this range. (b) FWHM of the absorption spectra as a function of PEO concentration. The value extracted from the thin film of  $\beta$ -CD-PDV is indicated as a (red) line.

latter with a half-wave plate and a Glan-Thompson polarizing prism. The PL anisotropy was calculated from these components as  $\gamma = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + 2I_{\perp})$ . All PL spectra were corrected for spectral response of the apparatus.

Figure 1(a) displays the absorption spectra for thin films of  $\beta$ -CD-PDV and of PDV blended with a range of different PEO fractions (0%–50% by weight). Anionic conjugated polymers based on PV units aggregate strongly in solution, making them useful materials for chemical and biological sensors [14,15]. It has been demonstrated that

such interchain interactions result from interpenetration of neighboring chains in solution, carried through the casting process into the solid film [16]. In accordance with these previous studies, we find evidence for interchain interactions in thin films of PDV in the occurrence of featureless, broad absorption peaks for the lowest electronic transitions (Fig. 1) and broadened room-temperature NMR spectra (not shown). The addition of PEO to the PDV solutions narrows the thin-film absorption spectra significantly from  $\sim 1$  eV at 0% to 0.72 eV at 50% PEO concentration [Fig. 1(b)]. Recent experiments have shown that titration of PDV with PEO in dilute (ppm) water solutions results in a 2.5-fold increase in PL efficiency over a similar concentration range, and a ninefold increase for thin films [17]. The combined PL efficiency and absorption data strongly suggest that PEO forms supramolecular complexes with PDV polymers in solution that disrupt the close interaction between neighboring conjugated chains in solution and thin films. Figure 1 also displays the absorption spectrum (a) and its FWHM [indicated in (b) by a line] of  $\beta$ -CD-PDV. Rotaxination of PDV with bulky, insulating macrocycles has been shown to result in a 2.6-fold increase of PL efficiency in solution [18], comparable to that for blends with high PEO fraction. Our data show that at high PEO fraction the FWHM of the PDV absorption approaches that of  $\beta$ -CD-PDV indicating that rotaxination is the most effective means of interrupting intermolecular interactions within the given parameter range. Closer inspection of the absorption spectra reveals that the energy of the lowest absorption peak of PDV is hardly affected by complexation with PEO (within a few tens of meV). The polyrotaxane absorption appears blueshifted by  $\sim 70$  meV, most likely as a result of weaker electronic coupling to its surroundings [19]. For all materials investigated, the most significant effect of aggregation on the absorption is an associated broadening, in agreement with a coupling between electronic states of more than one spectroscopic unit that leads to the splitting of the states as demonstrated theoretically and experimentally for stacked PV oligomers [8,20]. The distribution of oscillator strength between the split states of the aggregate depends sensitively on the relative orientation of the interacting chromophores [8]. The observed increase in the high-energy tail of the absorption with increasing aggregation suggests a prevalence of cofacial, aligned interacting chains in the PDV films.

Figure 2 displays (a) the PL spectra soon after excitation (300-fs delay) and (b) the time-integrated (TI) PL spectra for thin films of PDV:PEO blends and  $\beta$ -CD-PDV. The average energy of the emitted photons was extracted from the spectra through energy-weighted integration and is displayed in Fig. 2(c) and 2(d) as a function of PEO fraction (straight line for the rotaxane). The early-time spectra are collected after nuclear relaxation has occurred but before any significant amount of exciton migration through the film has been undertaken [9]. As a result, the average energy of photons emitted at early times is higher than the value extracted from the time-integrated spectra.

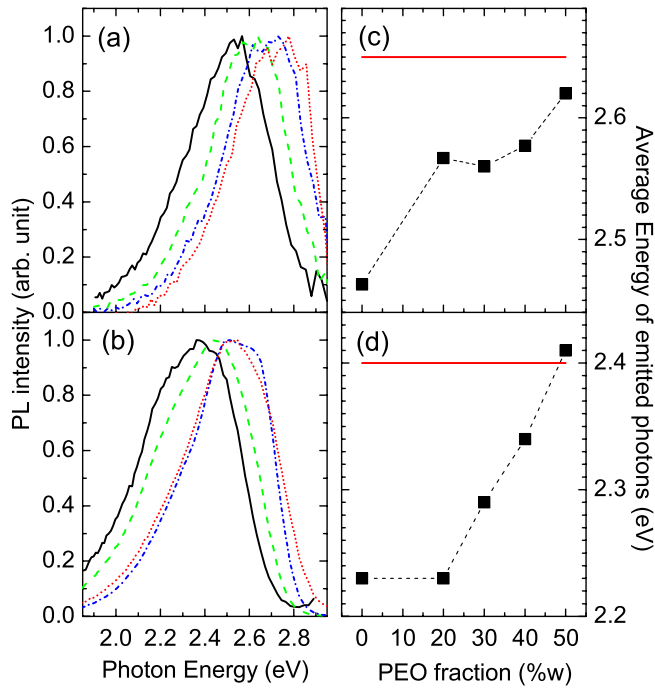


FIG. 2 (color online). (a) Time-resolved PL spectra at 300-fs delay and (b) time-integrated PL spectra for thin films of  $\beta$ -CD-PDV (red, dotted line) and PDV:PEO blends containing 0% (black, solid line), 30% (green, dashed line), and 50% (blue, dash-dotted line) of PEO. The average energy of the emitted photons extracted from the spectra is displayed in (c) for the early-time spectra and (d) for the time-integrated spectra (horizontal line for  $\beta$ -CD-PDV).

This discrepancy tends to narrow with increasing PEO fraction since a decrease in intermolecular interaction reduces the diffusivity of excitons in the material. Interestingly, the early-time spectra show a strong redshift in the emission with increasing intermolecular interaction: the emission from pure PDV films is shifted by 180 or 160 meV to the red compared to the emission from the rotaxane or the 50:50 blends with PEO, respectively. We propose that this redshift is caused by relaxation of the excitation into the lowest electronic states of the aggregate that is completed within the first hundred femtoseconds after excitation. With increasing intermolecular interaction this emission is found to decrease in energy, in agreement with quantum-chemical calculations performed on oligomeric PV pairs [8].

We have used this well-characterized model system to examine whether ultrafast transition dipole reorientation may be induced by intermolecular interactions between conjugated polymer chains. Figure 3(a) displays the PL polarization anisotropy decay within the first 5 ps after excitation for drop-cast films of rotaxinated PDV and PDV:PEO blends. It is evident from these data that increasing the separation between PDV chains has a strong effect on the initially recorded PL anisotropy  $\gamma(0)$ . For low PEO fraction  $\gamma(0)$  is very low ( $\sim 0.1$ ) but increases with increasing PEO fraction to 0.27 at 90% PEO content. The

rotaxane films show an initial PL anisotropy of 0.37 that is within experimental error of the value 0.4 expected for a random distribution of noninteracting transition dipole moments associated with a two-level system [21]. The values of  $\gamma(0)$  extracted from measurements on a range of films are displayed in Fig. 3(b) as a function of PEO concentration. It can be seen that four different mechanisms may induce an increase of  $\gamma(0)$ , all of which are linked to an increasing separation between the polymer chains. The first is rotaxination, which again proves to be most effective at separating the chains, the second is blending with an

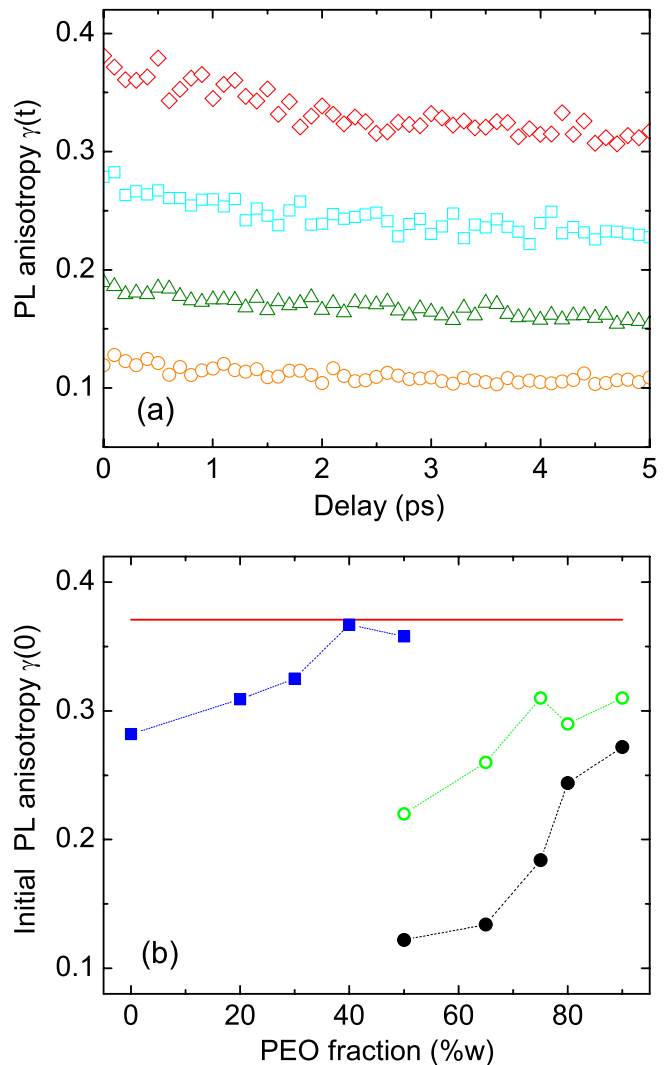


FIG. 3 (color online). (a) PL anisotropy decay for drop-cast films of  $\beta$ -CD-PDV (red diamonds) and PDV:PEO blends with 90% (blue squares), 75% (green triangles), and 50% (orange circles) PEO fraction by weight. (b) Initial anisotropy values  $\gamma(0)$  for spin-cast films at 2.6 eV detection energy (blue solid squares), drop-cast films at 2.6 eV (black solid circles), and drop-cast films at 2.8 eV (green open circles) for PDV:PEO blends as a function of PEO content. The value of  $\gamma(0)$  for the polyrotaxane is indicated as a line and was found to be independent of casting technique and detection energy between a measured range of 2.4–2.8 eV. The experimental error for  $\gamma(0)$  is 5%–10%.

increasing fraction of PEO. Third, choosing spin-casting instead of drop-casting leads to an increase in  $\gamma(0)$  in agreement with electron microscopy experiments that have demonstrated the differences in chain packing morphologies for the two casting techniques [22]. Fourth, increasing the PL detection energy for PDV:PEO films from the center of the early-time emission spectrum (2.6 eV) to the high-energy edge (2.8 eV) results in an increase of  $\gamma(0)$  consistent with emission being collected from more isolated chains in the arrangement distribution of interacting chains.

These results clearly demonstrate that stronger intermolecular coupling promotes an ultrafast initial depolarization of the induced transition dipole moment. For example, the initial PL anisotropy of 0.12 for drop-cast films would correspond to a rotation of the transition dipole moment by  $43^\circ$  if an initial value of 0.4 was assumed [21]. Convolution of an ultrafast decay component with the measured time trace of the excitation pulse (FWHM of 300 fs) indicates that an initial depolarization would have to occur on a time scale of less than 100 fs in order to be unobservable within our signal-to-noise ratio. Such fast processes correspond to strong electronic coupling, e.g., to nuclear vibrations, and cannot be described adequately within the framework of incoherent hopping mediated by weak dipole-dipole coupling. Recent observation of an ultrafast rotation of the transition dipole moment for solutions of a poly-PV derivative have been interpreted as an on-chain relaxation effect [11]: an exciton initially delocalized along a long conjugated segment may localize following relaxation of the nuclear lattice. For a bent segment, this may lead to a rotation of the electronic dipole moment within the time scale of the relaxation [6]. We demonstrate here that in solid films of conjugated polymers the ultrafast reorientation of the electronic transition dipole moment is strongly mediated by interchain interactions, rather than intramolecular relaxation. Photoexcitation primarily populates the upper level of the electronic states split through intermolecular electronic coupling, in accordance with a prevalence of small angles between adjacent chains [8]. The following relaxation to the lower electronic states results in an ultrafast redshift of the emission and induces a rotation of the transition dipole moment. Conceptually, this phenomenon may be understood considering the early model introduced by Kasha for the coupling between two chromophores that induces a splitting of an excitonic state into two nondegenerate states [23]. For identical interacting chromophores, simple vector addition arguments show that the resulting states of the aggregate are orthogonally polarized, so that a relaxation between the two will cause a strong depolarization of the emission. However, electronic coupling between conjugated polymer chains represents a more complex situation. Theoretical calculations indicate that the dynamics of exciton localization and relaxation between electronic states of two coupled, nonidentical chromophores should depend sensitively on the relative strengths of the energies associated with electronic cou-

pling, nuclear relaxation and the mismatch between the interacting chromophores [7]. The ultrafast depolarization dynamics we observe as a result of interchain interactions will therefore be mediated by coupling of the electronic oscillator to the phonon bath that leads to dynamic localization of the exciton within the time scale of a nuclear oscillation period [7,8].

In conclusion, we have demonstrated that for conjugated polymer films, intermolecular relaxation dynamics play an important role in the evolution of the excitonic state in the early ( $< 100$  fs) time regime after excitation. The formation of interchain aggregates is a very common phenomenon in the relatively disordered solids of conjugated polymers [24]. Our results indicate clearly that initial excitonic delocalization across more than one chain, and the subsequent relaxation dynamics need to be considered for a full understanding of the optoelectronic properties of these systems. Recent theoretical models for small interacting conjugated molecules placed at well-defined relative positions in solution have successfully incorporated initial excitonic delocalization as a result of intermolecular electronic coupling [3,4]. Our findings emphasize the need for the development of similar models that may be applied to describe the early intermolecular relaxation dynamics in more disordered conjugated polymer solids.

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