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Signatures of excitons and polaron pairs in the femtosecond excited-state absorption spectra of phenylene-based conjugated polymers and oligomers

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Abstract

We present results of broadband femtosecond transient absorption measurements in thin films of several phenylene-based π-conjugated materials. We compare results for unsubstituted poly(phenylene vinylene) (PPV), polyflourene, and a substituted five-ring oligomer of PPV. We observe universal spectral features in all materials, implying a common origin for the photoexcited species in all members of this family. In each material, we observe two photoinduced absorption (PA) features in the visible region in addition to a stimulated emission (SE) feature. The first PA feature shows strong dependence of the dynamics on excitation intensity, and correlates precisely with the SE feature, proving that this feature is due to the primary emissive exciton. The second PA feature shows dynamics independent of intensity. In the oligomers, this feature grows quadratically with respect to the first PA feature, as a result of nonlinear interactions of the primary excitons. In the polymers, however, the second feature grows linearly with intensity, and indicates an ultrafast decay channel to nonemissive interchain species due to defects.

Keywords: femtosecond transient absorption, conjugated polymers, photoexcitations

1. Introduction

Accompanying the widespread development of π-conjugated molecules for optoelectronic applications, there has been a resurgence of interest in their fundamental optical properties [1]. Just as the benzene molecule played a fundamental role in the development of modern quantum chemistry, so phenylene-based materials such as poly(*para*-phenylene vinylene) (PPV) and poly(*para*-phenylene) (PPP) have become the most widely studied class of luminescent conjugated polymers. In particular, there have been numerous investigations into the time-resolved transient absorption (TA) features of these materials on ultrafast (fs-ps) timescales [2-8]. Despite abundant data, however, there is still no widespread agreement on the origin of these features, and whether the signatures of photoexcitations are common to disparate members of the family.

In this paper, we compare the dominant TA signatures and dynamics, as a function of both wavelength and excitation density, for thin films of several phenylene-based π-conjugated materials. To supplement our earlier systematic measurements of a substituted five-ring oligomer of PPV (MEH-DSB) [7,8], we present new results for both unsubstituted PPV and poly(9,9-dioctylfluorene) (PFO). We observe universal spectral features and dynamics in all materials, implying a common origin for the photoexcited species in all members of this family, independent of side-chain substitution, chain length, or the exact nature of the polymer unit cell. In each of the three materials, we observe two photoinduced absorption (PA) features in the visible region in addition to a stimulated emission (SE) feature at the energy of the strong luminescence. The first PA band peaks in the near-infrared, shows strong dependence of the dynamics on excitation intensity, and correlates precisely with the SE feature, proving that this feature is due to the primary emissive exciton. The second higher energy PA feature shows dynamics independent of intensity. In the oligomers, this second band grows quadratically with respect to the first PA band; these secondary species (identified as interchain excitons or polaron pairs) are created as a result of nonlinear interactions of the excitons, either sequential re-excitation, or bimolecular annihilation. In the polymers, the secondary species are formed in a lin-

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ear process directly from the excitons, implying a lower binding energy, as well as a vital role of defects.

2. Experimental

PFO thin films were prepared by spin-coating from solution. Multilayered thin films of the PPV precursor polymer were prepared by ionic self-assembly with alternating layers of a negatively charged, transparent polymer, and thermally converted to PPV [9].

Our instrumentation for fs high-sensitivity, broadband chirp-free TA studies has been described elsewhere [10]. The samples were excited in vacuum at 3.1 eV, corresponding to near-resonant band-edge excitation. As a measure of transmission changes we use the differential transmission (DT), defined as follows: $DT = (T - T_0)/T_0 = \Delta T/T_0$, where T_0 and T are transmissions in the absence and in the presence of the pump, respectively. DT is related to the pump-induced absorption change ($\Delta\alpha$): $\Delta\alpha = -\frac{1}{d}ln(1+DT)$ (d is the sample thickness).

3. Fs transient absorption: PFO and PPV

The chirp-free DT spectra of PFO at several pump-probe delay times are shown in Fig. 1. The main spectral features are a broad PA band extending from 480-800 nm, along with a region of SE at wavelengths below about 480 nm. Two overlapping PA bands, PA_1 at 750 nm and PA_2 at around 600 nm, can be distinguished; these bands, as well as the region where the SE dynamics were measured (440 nm) are indicated in Fig. 1.

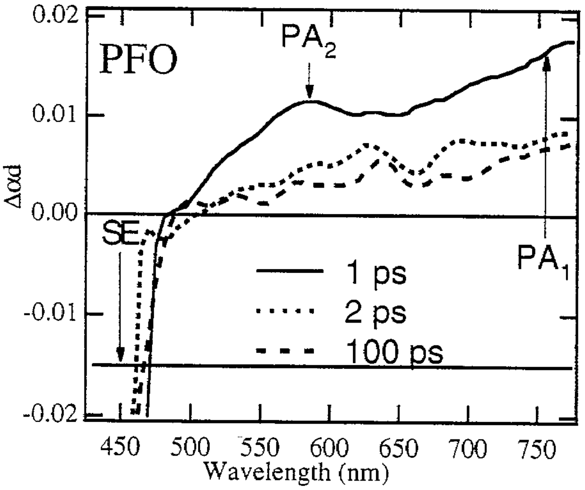

Fig. 1. $\Delta\alpha d$ spectra of PFO thin film for various delay times.

The dynamics of the two PA bands in PFO for different excitation densities are shown in Fig. 2. The solid line in Fig. 2(b) shows that the dynamics (scaled) of PA_2 at a pump fluence of 14 $\mu J/cm^2$ are indistinguishable from the dynamics obtained when pumping at 138 $\mu J/cm^2$ (solid circles). A similar pump-independent decay was also observed in MEH-DSB in the same spectral region, with similar time constants, attributed to interchain polaron pairs [7,8].

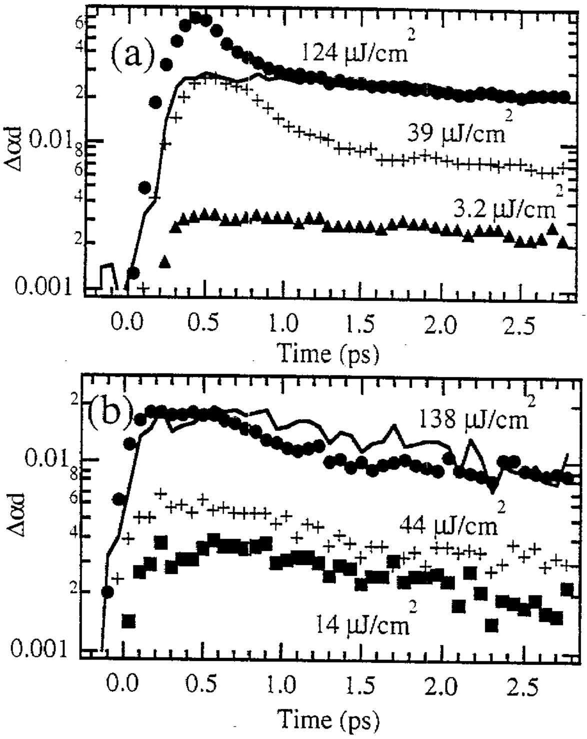

Fig. 2. Dynamics of $\Delta\alpha d$ in PFO as a function of pump fluence for (a) PA_1 (750 nm); (b) PA_2 (600) nm.

In contrast, the dynamics of PA_1 show a strong pump dependence [Fig. 2(a)]. At the highest fluence, a fit of the early-time data to a double exponential yields time constants of 200 fs and 4.5 ps. In MEH-DSB, similar dynamics were seen in this spectral region, with a fast component of 450 fs. In MEH-DSB, the fast decay component for PA_1 closely matched the rise-time of PA_2, supporting the idea that the formation of the species which gives rise to PA_2 occurs at the expense of the PA_1 species. For PFO, the fast decay of PA_1 is close to the resolution limit of our experiment, making it difficult to prove whether this decay is complementary with the rise-time of the PA_2 band. With our resolution the time constants are similar.

The dynamics of the SE match those of PA_1 at all pump intensities, provided that the sample does not photodegrade during the experiment. This implies that the same species is responsible for both the SE and PA_1, namely the emissive singlet exciton. This is identical to the results obtained with MEH-DSB films [7,8].

The chirp-free DT spectra of PPV self-asssembled multilayers (SAMs) at several pump-probe delay times are shown in Fig. 3. The spectral features are very similar to those observed in PFO and MEH-DSB. Two overlapping PA bands, PA_1 at 750 nm and PA_2 at around 600 nm, can be distinguished, along with an SE band (550 nm). Although the two PA bands cannot be clearly separated spectrally, their identification as due to different species is demonstrated by analyzing the intensity-dependent dynamics.

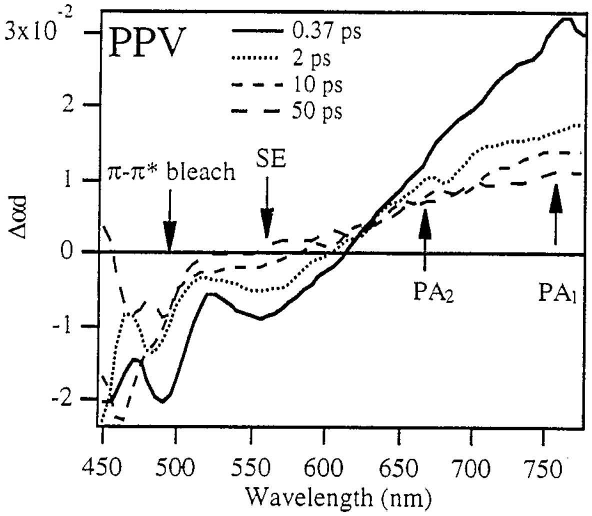

Fig. 3. $\Delta\alpha d$ spectra of PPV multilayer for various delay times.

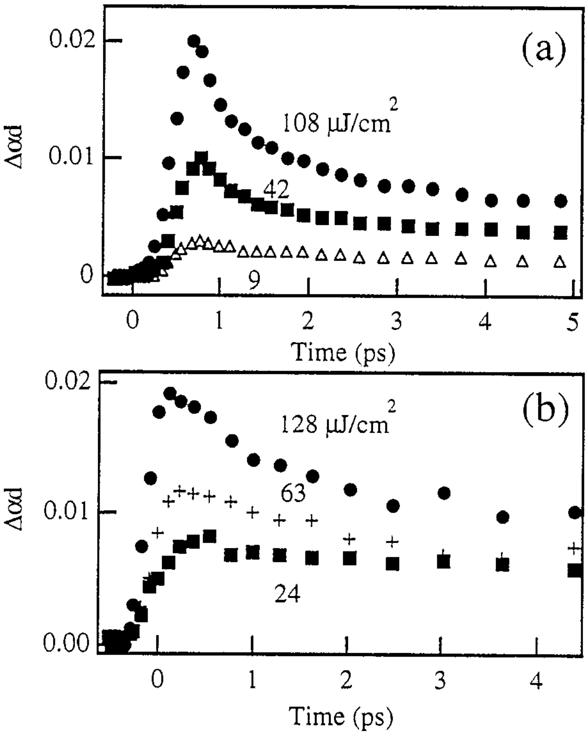

Fig. 4. Dynamics of $\Delta\alpha d$ in PPV as a function of pump fluence for (a) PA_1 (750 nm); (b) PA_2 (660) nm.

The dynamics of the two PA bands in PPV for different excitation densities are shown in Fig. 4. The dynamics of PA_1 and PA_2 are clearly different, as observed for both PFO and MEH-DSB, and the two bands also have distinct intensity-dependence. In this case, a slight dependence on intensity can be discerned for the PA_2 feature, but it is much weaker than that observed for the primary exciton PA band, just as in the other materials. The two bands overlap substantially, leading to a mixture of the dynamics due to each type of excitation at any given wavelength. The broad width of the two spectral features is likely due to the presence of increased inhomogeneous broadening.

4. Discussion

The evidence is quite strong, based on the above comparison of similar photoinduced spectral features and intensity-dependent dynamics, that the photoexcitations created in all phenylene-based polymers and oligomers are similar. We observe compelling evidence for two types of excitations. In all cases, the primary excitation in oligomers and polymers is the luminescent exciton, with a broad PA band peaking in the near-infrared (~ 800 nm). A separate PA_2 feature due to a secondary species can be unambiguously identified in the red spectral region (~ 600-700 nm) for all materials from this family which we have studied to date.

In pristine samples, the PA_1 feature invariably has dynamics and intensity-dependence which match exactly those of the stimulated emission, and it is widely agreed that this feature represents a transition from the primary intrachain exciton to a higher excited state. The strong intensity-dependent decay arises due to a combination of bimolecular annihilation, and amplified spontaneous emission.

The PA_2 feature has been widely assigned to interchain excitons, or bound polaron pairs [1,4,7,8]. However, there has been no detailed study of this feature in a range of related materials, and our data offers new insight into the generation mechanism of these interchain species. Our previous results have demonstrated that PA_2 in MEH-DSB oligomers arises only as a byproduct of nonlinear interactions of the primary excitons [7,8]. These interactions can be of two types: 1) direct excitation of a doubly-excited state (biexciton) by an intense fs pulse, followed by relaxation to the interchain pair; 2) indirect excitation of the biexciton by bimolecular annihilation. In either case, such nonlinear interactions lead to a *quadratic* dependence of the magnitude of PA_2 relative to the magnitude of PA_1. This dependence is shown for MEH-DSB in Fig. 5(a).

However, the case is very different for both PPV and PFO *polymers* [Fig. 5(b) and (c)]. For both of the polymers, the magnitudes of both PA_1 and PA_2 scale linearly with pump fluence, indicating that the generation of interchain pairs is much more facile in the polymers, and does not require overcoming a substantial potential barrier. The assignment of this feature to bound interchain pairs is supported by the lack of intensity-dependent decay for these species up to very high excitation density (of order 10^{20} cm^{-3}). This implies geminate recombination of a tightly bound, localized pair; the average separation of excitations at such high densities is only tens of Angstroms. The efficient generation of such interchain pairs directly from intrachain excitons is evidence of strong interchain interactions. However, the dramatic qualitative difference between the oligomer and polymer results argue for an additional effect. We suggest that the binding energy of the primary exciton is substantially lower in the polymers than in the oligomer, removing a potential energy barrier to charge separation onto adjacent chains. While the exciton binding energy has been measured to be 0.2 eV in MEH-PPV [11] and 0.3 eV in PFO [12], no systematic investigation of the binding energy in oligomers has been reported.

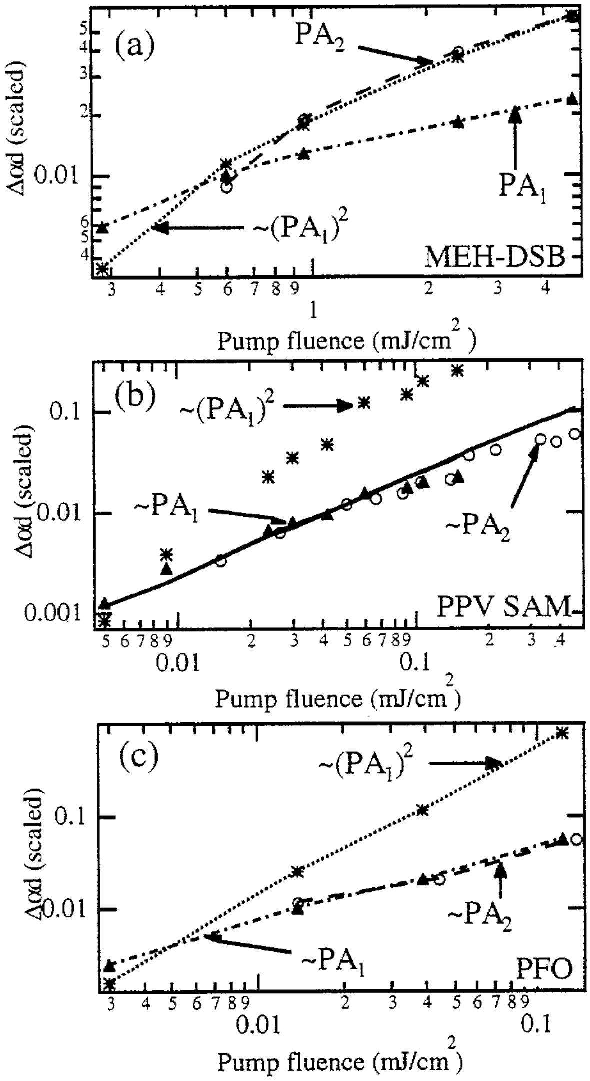

Fig. 5. Dependence of the magnitude of the two PA bands on pump fluence for (a) MEH-DSB; (b) PPV SAM; (c) PFO.

Our results also show another exciton quenching mechanism which is universal to all three materials: the effect of photochemical defects. The presence of these defects (created at high fluence or with prolonged excitation even in "inert" atmospheres) leads to very fast (ps) quenching of the SE band, and the growth of a competing PA band which is closely related to the PA$_2$ band observed even in pristine materials. Hence, energetically, the presence of a photochemically-created deep trap (which destroys the exciton with a charge-transfer reaction) leads to qualitatively similar behavior as the "intrinsic" interchain pair. This suggests that even in pristine materials, a small percentage of defects plays an important role in facilitating the formation of non-emissive interchain states.

4. Conclusion

We have identified two universal photoinduced spectral features common to several phenylene-based polymers and oligomers, and assign them to the primary intrachain exciton, and secondary interchain bound pairs, respectively. The generation mechanism for the secondary species, however, is quite different for oligomers and polymers. In the oligomer, the interchain pairs are created only due to strong nonlinear interactions, which allow the excitations to overcome a substantial potential energy barrier to charge separation. However, in the polymers the direct generation of interchain states on ps timescales suggests that this potential energy barrier is removed (likely due to a reduced binding energy of the intrachain exciton).

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