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EXCITON AND BIEXCITON SIGNATURES IN
FEMTOSECOND TRANSIENT ABSORPTION OF
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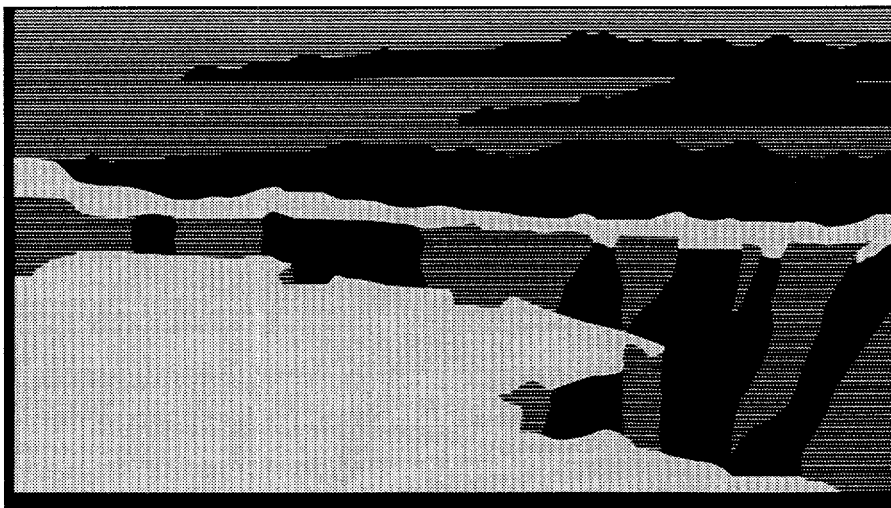
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Exciton and Biexciton Signatures in Femtosecond Transient Absorption of π -Conjugated Oligomers

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ABSTRACT

We report femtosecond transient-absorption studies of a five-ring oligomer of polyphenylenevinylene (PPV) prepared in two different forms: as solid-state films and dilute solutions. Both types of samples exhibit a photoinduced absorption (PA) band with dynamics which closely match those of the stimulated emission (SE), demonstrating unambiguously that these features originate from the same species, namely from intrachain singlet excitons. Photochemical degradation of the solid-state samples is demonstrated to dramatically shorten the SE dynamics above a moderate incident pump fluence, whereupon the dynamics of the SE and the long-wavelength PA no longer coincide. In contrast to solutions, solid-state films exhibit an additional short-wavelength PA band with pump-independent dynamics, indicating the efficient formation of non-emissive inter-chain excitons. Correlations in the subpicosecond dynamics of the two PA features, as well as the pump intensity-dependence provide strong evidence that the formation of inter-chain excitons is mediated by intrachain two-exciton states. At high pump levels, we see a clear indication of interaction between excited states also in dilute solutions. This is manifested as a superlinear pump-dependence and shortening of the decay dynamics of the SE. We attribute this behavior to the formation of biexcitons resulting from coherent interaction between two excitons on a single chain.

Key Words: π -conjugated oligomers, transient absorption, excitons, biexcitons

1. INTRODUCTION

Polymeric π -conjugated systems are often referred to as organic semiconductors. However, the photophysics of these systems is significantly different from that of classic inorganic materials. This difference is due to such features of polymeric systems as quasi-one-dimensionality of molecular structure, strong effects of lattice relaxation, and a significant level of disorder in solid-state samples. These lead to existence of new types of photoexcited species stabilized by lattice relaxation^{1,2} as well as to opening of new relaxation channels resulting in efficient picosecond (ps) and sub-ps deactivation of photoexcitations.^{2,3}

Despite numerous studies on the ultrafast photophysics of π -conjugated polymer systems such as poly(*para*-phenylene vinylene) (PPV) and its derivatives, great controversy persists regarding the nature and mechanisms of formation of the primary photoexcitations in these materials.⁴⁻¹⁶ It is widely accepted that in dilute solutions with weakly-interacting molecules, the dominant excitations are intrachain singlet excitons which have been described either as Coulombically bound electron-hole pairs^{17,18} or self-localized "polaron excitons."^{1,2} The situation is more complex in solid-state samples, where strong inter-molecular interactions can lead to the formation of non-emissive interchain species, also referred to as "indirect excitons," or bound polaron pairs.⁸⁻¹² These species have been cited by some authors as primary excitations in solid-state samples,⁹⁻¹¹ although this point of view is not universally accepted.^{6,13} The mechanism of formation of indirect excitons remains unclear, and there is at present no agreement regarding the proportion of intra- and inter-chain excitons generated by absorbed photons.^{9-11,13}

Another issue which has been actively debated recently is the existence of coherent many-particle states such as cooperatively-emitting excitons¹⁹ and biexcitons.²⁰ Both cooperative emission processes and biexciton effects

have been extensively studied in inorganic semiconductors (see, e.g., Refs. 21–23), however, for organic systems, experimental investigations of these effects have only recently begun.

In the present paper we apply the methods of femtosecond transient absorption (TA) to address such important issues of the photophysics of π -conjugated systems as (1) the mechanism for the generation of interchain species, (2) the role of intra- and interchain excitons in the evolution of the time-resolved nonlinear optical response, and (3) the existence of stable two-exciton states (biexcitons) and their effect on TA. To evaluate the role of intermolecular interactions, we study two different forms of the same material: dilute solutions and solid-state films. We demonstrate that in solutions, both the stimulated emission (SE) and the photoinduced absorption (PA) can be explained in terms of generation of a single species—intra-chain singlet excitons. In pristine films, in addition to the singlet exciton PA feature, we observe a new PA band which we attribute to non-emissive interchain excitons. The correlations in dynamics of the two PA features, as well as the pump intensity-dependence, indicate that the generation of inter-chain excitons is a nonlinear process mediated by intra-chain two-exciton states. We see clear signatures of interaction between photoexcitations also in solutions which can be attributed to formation of stable biexcitons with the oscillator strength enhanced due to coherent interaction of two excitons occupying a single chain.

2. EXPERIMENTAL

As a model system for our studies we have selected a five-ring PPV oligomer 2-methoxy-5-(2'-ethylhexyloxy)-distyryl benzene (MEH-DSB) (see molecular structure in Fig. 1). MEH-DSB can be prepared as high quality thin films by vacuum sublimation, and is also soluble.²⁴ Investigation of a model oligomer system allows us to avoid the effects of inhomogeneous broadening resulting from a distribution of conjugation lengths which is always present in amorphous polymer films. These distributions can lead to associated ultrafast "random-walk" energy relaxation dynamics⁵ which complicate the interpretation of experimental data on subpicosecond timescales. MEH-DSB was prepared and purified as described in Ref. 24. Solutions were prepared at a concentration of 5×10^{-4} g/ml in *p*-xylenes. Amorphous thin films (~100 nm thickness) were deposited by vacuum sublimation onto sapphire substrates and transferred into an optical cryostat in a dry box to minimize the effects of photo-oxidation. As several authors have discussed,^{16,25–27} the similarities in the optical and electronic properties of conjugated oligomers and polymers suggest that the results reported below are of general importance also for conjugated polymers.

TA studies were performed using a femtosecond pump-probe experiment. The samples were excited at 3.1 eV using 100-fs frequency-doubled pulses from a regeneratively amplified mode-locked Ti-sapphire laser (Clark-MXR CPA-1000). The pump-photon energy slightly exceeds the energy of the π - π^* transition in MEH-DSB (~2.9 eV), corresponding to near-resonant band-edge excitation. The transmission of the excited sample is probed by delayed pulses of a femtosecond continuum generated in a 1-mm-thick sapphire plate. 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. In the small signal limit ($DT \ll 1$), DT is proportional to an absorption change $\Delta\alpha$: $DT \approx -\Delta\alpha d$ (d is the sample thickness).

Time-resolved DT data were measured in two different experimental configurations. DT spectra at a fixed delay time Δt between pump and probe pulses were recorded with a 0.15-m spectrometer coupled to a liquid-nitrogen-cooled CCD camera by averaging the signal over 1000–2000 pulses. This type of measurement provides information on the spectral distribution of the nonlinear optical response over a broad spectral range (0.45–1.1 μ m) with an accuracy up to 10^{-3} in DT. In another configuration, DT spectra and single-wavelength DT dynamics were monitored with much higher accuracy (up to 10^{-5} in DT) using phase-sensitive detection with a lock-in amplifier synchronized to a chopped pump beam. In addition to the improved sensitivity, the above method can be used for recording chirp-free TA spectra by scanning the monochromator and simultaneously adjusting the relative pump-probe delay according to the calibrated chirp.²⁸

3. INTRA- AND INTERCHAIN PHOTOEXCITATIONS

To avoid photodegradation, for all measurements reported in this section the fluence w_p of individual pump pulses was kept below 5 mJ cm^{-2} . Furthermore, care was taken at each sample spot to keep the integrated pump fluence for the entire scan below $\sim 1 \text{ kJ cm}^{-2}$, a threshold above which irreversible photochemical changes could be detected in our measurements (see section 4).

Fig. 1 shows time-resolved DT spectra of the MEH-DSB solution along with single-wavelength DT dynamics (inset) recorded at three different spectral energies. The DT spectra show an intense positive band with two maxima at 2.45 eV and 2.6 eV. The 2.6-eV maximum occurs due to pump-induced bleaching of the ground state, whereas the maximum at ~ 2.4 eV, in the range below the absorption edge, can be assigned to SE, in agreement with TA data from Ref. 6 and the demonstration of efficient lasing in MEH-PPV solutions in Ref. 29.

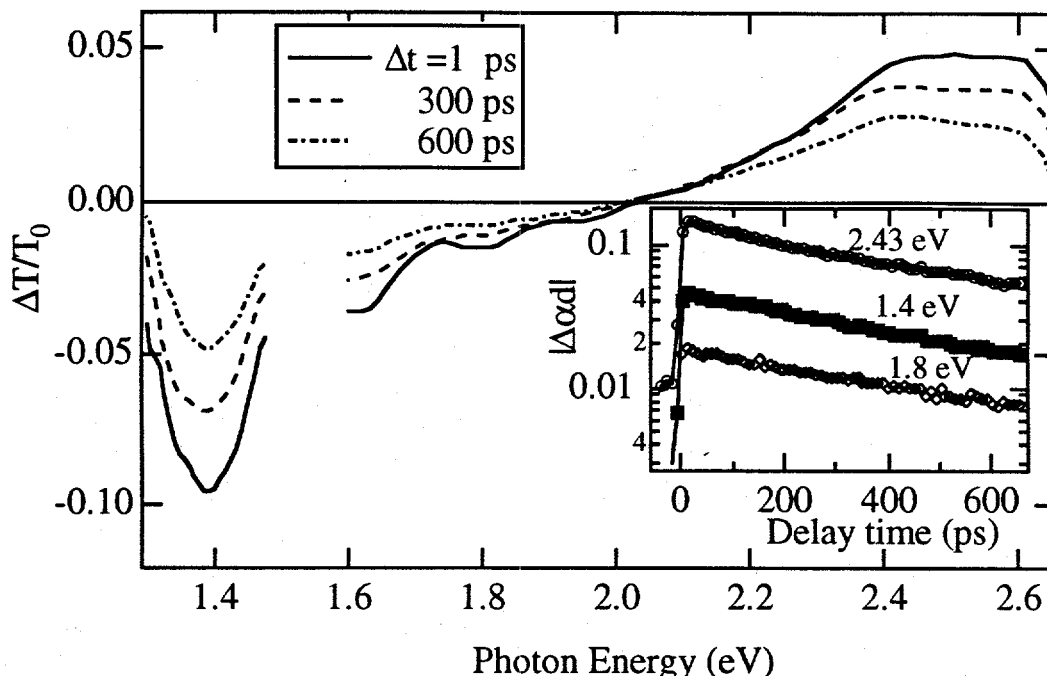


Figure 1. DT spectra of MEH-DSB solution recorded at $w_p = 0.17 \text{ mJ cm}^{-2}$ for different delay times Δt between pump and probe pulses. Insert: Nearly identical dynamics of SE (1.4 eV) and PA (1.4 and 1.8 eV) in solution samples, indicating a presence of one type of photoexcited species.

The third pronounced TA feature in solutions is a broad weakly-structured PA band extending from ~ 2 eV to ~ 1.3 eV. The DT dynamics recorded at the SE maximum and at two different spectral energies within the PA band (insert to Fig. 1) show nearly identical exponential decay, with a time constant of ~ 650 ps, indicating that both spectral features (SE and PA) originate from the same species. As these species are associated with the efficient SE, they can be assigned to intrachain singlet excitons, in agreement with previous measurements in MEH-PPV solutions.¹¹ The TA relaxation dynamics give a measure of a radiative lifetime of excitons in MEH-DSB: $\tau_r \approx 650$ ps, which is close to the reported values for MEH-PPV.²⁹

In Fig. 2 we show time-resolved DT spectra and single-wavelength DT time transients (insert) recorded for the MEH-DSB film. As different from solutions with relatively slow sub-nanosecond exponential DT dynamics, in films, the DT decay is much faster (ps time scale) and is strongly nonexponential. We also see the increase of the PA signal at ~ 1.8 eV, which is indicative of the formation of a new short-wavelength PA band. The fact that two distinct spectral bands are present in solid-state samples is confirmed by an analysis of single-wavelength DT dynamics. The 1.4-eV band (PA₁) shows much faster decay than the feature at 1.8 eV (PA₂) (see insert to Fig. 2). In addition to that, the dynamics of two PA features have very different pump dependences (Figs. 3 and 4). On the 3 ps time scale shown in Fig. 3, the PA₂ exhibits *pump-independent* and almost exponential decay with an initial fast relaxation time constant of about 6 ps [notice the overlap of the scaled time-transient of the lower intensity data (lines) and the higher intensity data (open triangles) in Fig. 3]. In stark contrast, the dynamics of PA₁ band are clearly nonexponential even at short delay times (see Fig. 4 and insert to this figure), and show a *pronounced pump intensity-dependence* which will be discussed below.

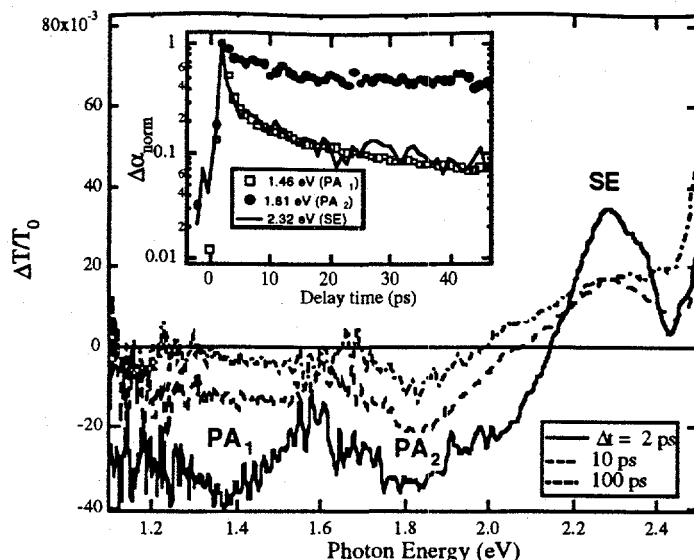


Figure 2. Two PA features in time-resolved DT spectra of MEH-DSB film ($w_p = 0.6 \text{ mJ cm}^{-2}$). Insert: Matching dynamics of the SE and PA₁ features along with distinctly different dynamics of the PA₂ feature.

The existence of two distinct PA bands with different dynamics in solid-state samples clearly indicates contributions from at least two different species to TA. Although the PA₁ decay dynamics are intensity-dependent, in pristine films they match very closely the SE dynamics on all timescales studied, and over a wide pump-intensity range (Fig. 4 and the inset to Fig. 1). This clearly shows that, as in solutions, the PA₁ feature arises from the same species as the SE, namely from emissive intrachain singlet excitons.

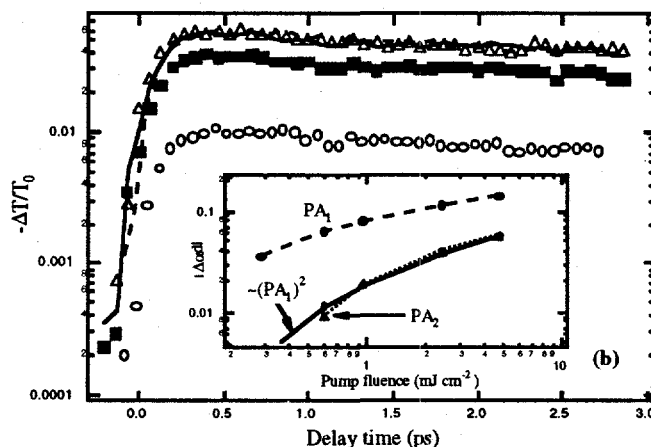


Figure 3. Time transients demonstrating pump-independent dynamics of the PA₂ feature, for $w_p = 6 \text{ mJ cm}^{-2}$ (open triangles), 3 mJ cm^{-2} (solid squares), and 0.6 mJ cm^{-2} (open circles). Solid and dashed lines are data taken at 3 and 0.6 mJ cm^{-2} , respectively, scaled to the 6 mJ cm^{-2} data. Inset: PA pump dependence indicating a quadratic correlation [$\text{PA}_2 \sim (\text{PA}_1)^2$] in the peak magnitudes of the PA₁ and PA₂ features.

We now examine in more detail the short-wavelength PA₂ band, which is only observed in solid-state samples. The fact that we do not see any associated SE features indicates that the PA₂ band might be related to the non-emissive interchain excitons predicted in Refs. 8–11. This explanation is consistent with the observed pump-independent dynamics (Fig. 3) which are expected for strongly correlated geminate electron-hole pairs located on closely separated chains.⁹ To explore the possible mechanisms for the generation of interchain species, we performed a careful study of the short-term PA₁ and PA₂ dynamics (Figs. 5 and 6). The build-up of the PA₁ band is very fast (Fig. 5, solid squares) and occurs essentially within the duration of the pump pulse. On the other hand, PA₂

shows a delayed build-up with a rise constant of about 500 fs (Fig. 5, open squares). Interestingly, this build-up is complementary to the initial fast decay of the PA₁ feature which is characterized by a time constant of about 450 fs.

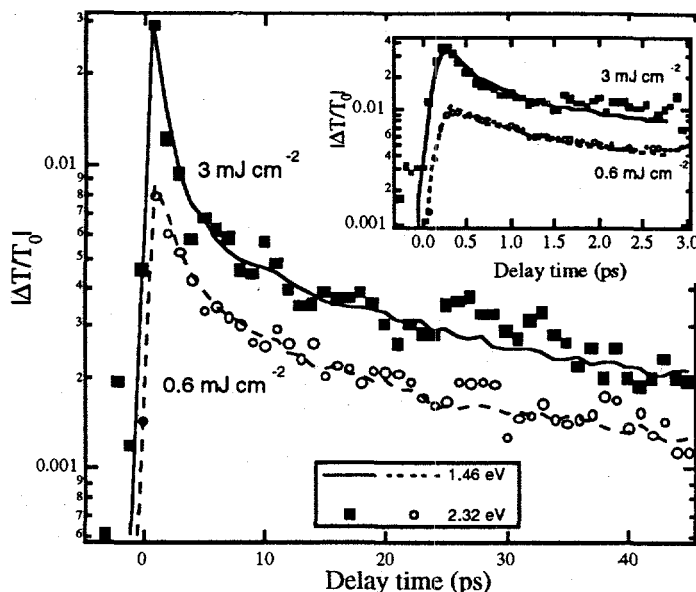


Figure 4. DT time transients recorded for two different pump fluences, demonstrating matching dynamics for the SE (2.32 eV) and PA₁ (1.46 eV) features in the pristine film on the time scale up to 45 ps. Insert: The same dynamics on the short time scale (up to 3 ps).

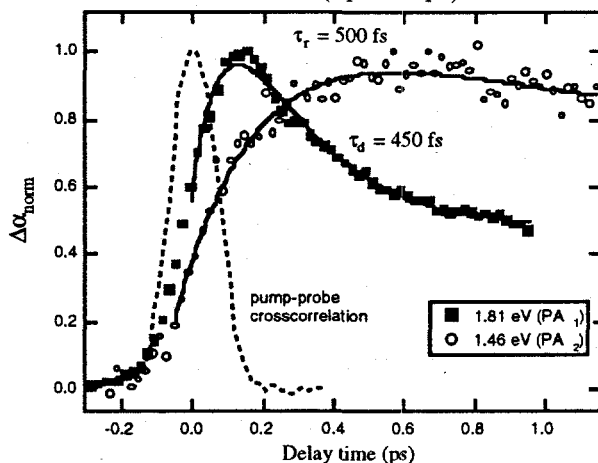


Figure 5. Complementary subpicosecond dynamics recorded for the PA₁ and PA₂ features in the film, plotted together with the pump-probe cross-correlation which defines the temporal resolution of the experiment.

We can derive further correlations related to the formation of the PA₂ band by fitting the decay of PA₁ at early times (< 3 ps), for different pump intensities, to a double exponential decay as shown in Fig. 6. Of course, since the PA decay is nonexponential over timescales from 1 ps–1 ns, such a double exponential fit cannot be used for a quantitative description of the decay over this whole range. However, at early times such a fit gives a good description of the dominant decay time constants and their relative magnitudes. As a result of this simple analysis we find that both the initial and subsequent decay time constants in our double exponential fit at early times are essentially independent of the pump fluence, and are close to 450 fs and 6 ps, respectively. The apparent intensity-dependent decay on the shortest timescales results from an evolution of the *relative magnitudes* of these two decay components. The pump intensity-dependence of the amplitudes of the fast (A_f) and the slow (A_s) components is displayed in the inset to Fig. 6. These data reveal the dependence $A_f \propto A_s^2$, which is indicative of two correlated components,

contributing to the PA₁ feature. Given the observed quadratic pump-dependence of A_f , and the ultrafast PA₁ build-up dynamics (see Fig. 5), it is reasonable to infer that the fast PA₁ component originates from doubly-excited chains (intrachain two-exciton states) which are generated during the pump laser pulse via sequential re-excitation of singly-excited molecules. Furthermore, the observed correlation in the initial fast decay of PA₁ and the build-up dynamics of the PA₂ band shown in Fig. 5 indicates that the generation of interchain species occurs at the expense of the doubly-excited molecules. This generation mechanism is confirmed by the quadratic correlation in the pump dependence of the PA₁ and PA₂ features shown in inset to Fig. 3.

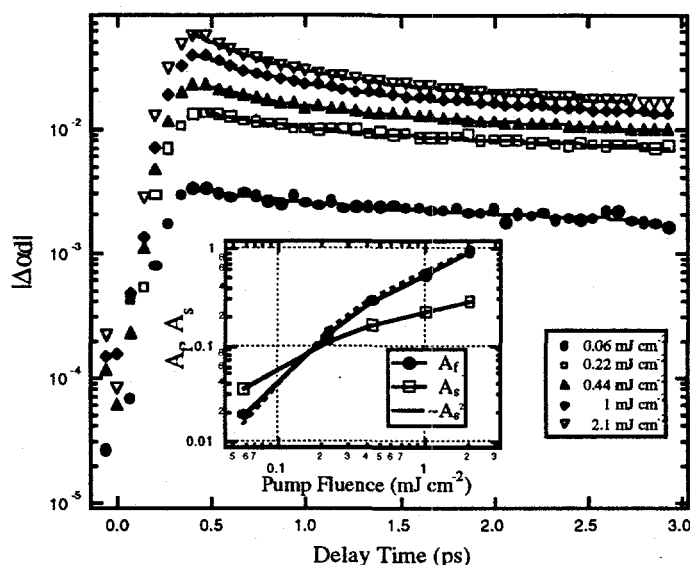


Figure 6. Pump-intensity dependent time transients of PA₁ feature at 1.46 eV (symbols) plotted together with double-exponential fits (lines). Data are shown for $w_p = 2.1 \text{ mJ cm}^{-2}$ (open triangles), 1 mJ cm^{-2} (solid diamonds), 0.44 mJ cm^{-2} (solid triangles), 0.22 mJ cm^{-2} (open squares), and 0.06 mJ cm^{-2} (solid circles). Inset: quadratic correlation in the pump-dependence of the magnitudes derived for the fast (A_f) and the slow (A_s) components from the double-exponential fits [$A_f \sim (A_s)^2$].

The above picture suggests that at high pump fluences the PA₁ absorption has two different components—a short-lived one, arising from doubly-excited chains, and a longer-lived component, associated with singly-excited intrachain species. The quadratic intensity-dependence of the magnitude of the two-exciton contribution leads to the experimentally observed pump-dependent decay of the PA₁ band. We emphasize here the difference between the intensity-dependent decay predicted for bimolecular exciton-exciton annihilation, which has been suggested to explain the relaxation dynamics in conjugated polymers by several authors,^{30–32} and the more complex correlated decay of singly- and doubly-excited excitons as suggested by the present results. In the former case, the nonlinearity occurs via the interaction and annihilation of excitons: a nonlinear decay process. In the latter case, the nonlinearity occurs during the generation process, within the pump pulsewidth, and results from sequential absorption of pump photons into one- and two-exciton states.

4. PHOTODEGRADATION IN SOLID-STATE FILMS

The interpretation of the ultrafast PA features in solid-state samples of PPV derivatives has been highly controversial.^{4,6–16} In films of PPV,^{9,10} methoxy-PPV,⁸ MEH-PPV,¹¹ BuEH-PPV,¹⁵ and a ladder-type poly(para-phenylene) derivative,¹² the SE and PA dynamics were observed to be different. Hence, for these materials it was concluded that the PA is entirely or partially due to species which are different from those responsible for the SE. However, correlations between the SE and PA decays have been reported for films of PPV,⁷ P3HT,³³ and poly(*p*-pyridyl vinylene).¹⁴ We believe that the reason for many of the inconsistencies in previously published experimental data is the uncontrolled photo-oxidation of the samples, which has a very strong effect on the TA (and especially the SE) dynamics.^{3,13,16,31}

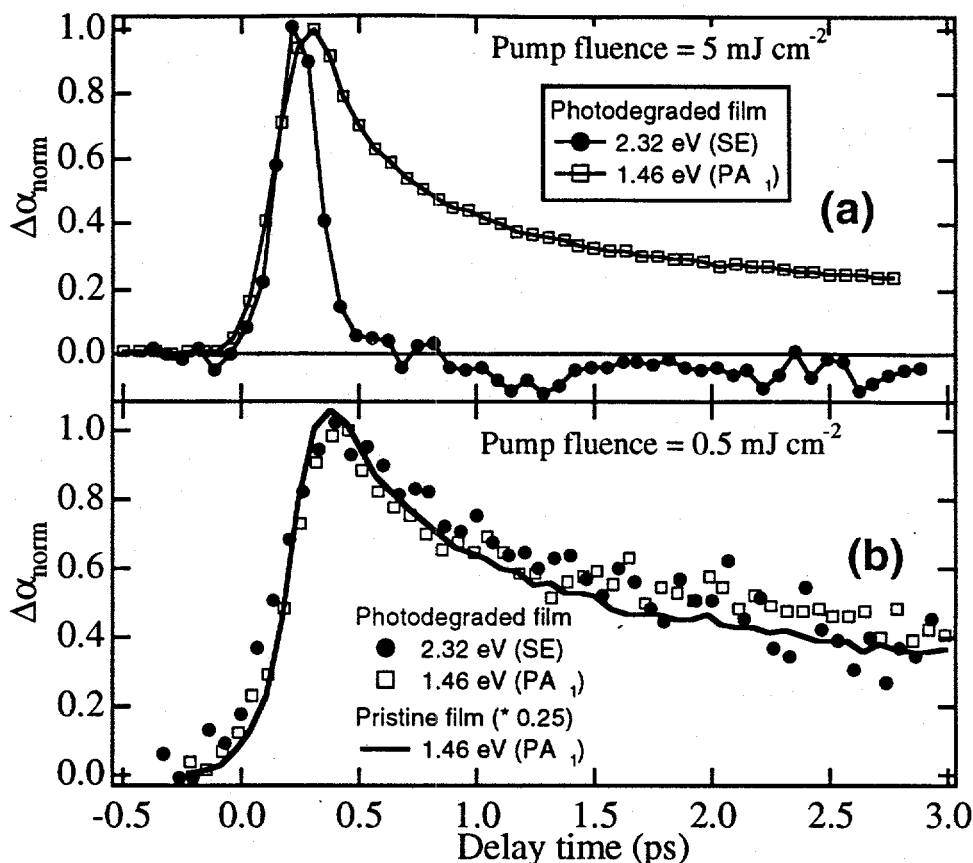


Figure 7. Comparison of the SE and PA_1 dynamics in the photodegraded film at high (a) and low (b) pump fluences. As different from pristine films, SE and PA_1 dynamics strongly deviate from each other at high pump levels.

Our measurements show that irreversible photochemical changes take place in MEH-DSB, even in an evacuated cryostat, under moderate pulsed excitation levels. Photochemical degradation is characterized by an overall reduction in the magnitude of DT, and a dramatic change in the dynamics of the SE emission as detailed below. These effects were observed at per pulse excitation levels above $\sim 4\text{--}5 \text{ mJ cm}^{-2}$ and when irradiating the films with a cumulative fluence greater than $\sim 1 \text{ kJ cm}^{-2}$ (e.g., during a single scan of the decay dynamics at a particular spot on the sample). In photodegraded (photo-oxidized) samples, at pump intensity above $\sim 4 \text{ mJ cm}^{-2}$ we see a drastic change in SE dynamics which no longer match those of the PA_1 band [Fig. 7(a)]. TA signal at 2.32 eV (SE maximum in pristine samples) rapidly switches from SE (positive DT) to PA (negative DT) [Fig. 7(a), solid circles], similar to the crossover previously observed in PPV films,¹⁰ where the difference in PA and SE dynamics was cited as evidence of a distinct species contributing to the near-IR PA band. Interestingly, by lowering the pump intensity we again return to the regime where PA and SE dynamics match each other [Fig. 7(b)], although the magnitude of the TA signal gets reduced by approximately a factor of four for both SE and PA.

Our observations can be explained within the following model. Prolonged laser irradiation of high enough intensity results in generation of defects via, e.g., loss of conjugation due to cleaving of the vinylene double bonds to form terminal carbonyl species as was previously suggested in Ref. 3. These defects contribute to TA by a negative PA_1 signal which is likely spectrally overlapping with SE. However, the defect states cannot be photoexcited directly by incident photons, but rather only via a charge transfer mediated by intrachain excitons. As in case of formation of interchain excitons, the charge transfer is only efficient at high pump intensities in the regime where a large number of molecules are doubly excited. Therefore, at low pump fluences the SE dynamics are not significantly affected by the presence of defects. The main effect of photodegradation in this case is the overall reduction of the TA signal (PA and SE) due to reduced concentration of conjugated molecules which also leads to the quenching of photoluminescence

(PL) observed previously in photodegraded samples.³⁴⁻³⁶ At high pump intensities, defect states get activated via a charge transfer mediated by doubly excited molecules. This results in a new defect-related PA feature, suppressing the SE. The sub-ps build-up of a new PA band [see Fig. 7(a)] is consistent with ultrafast growth dynamics of the PA₂ feature (Fig. 5) which is generated via a similar charge-transfer mechanism.

5. BIEXCITONS IN π -CONJUGATED SYSTEMS

It has been established that in case of inorganic semiconductors, high-level excitation can lead to formation of excitonic molecules or biexcitons.²¹ Biexcitons were first detected experimentally in wide-gap semiconductors, such as CdS and CuCl by their signatures in PL spectra.^{37,38} Observation of biexcitons in bulk semiconductors is hindered by their small binding energies which are typically in the range of several meV. Theoretical calculations show that the biexciton binding energy can be enhanced in case of spatially confined systems³⁹ which has been confirmed experimentally by measurements of semiconductor quantum-dot structures.⁴⁰ Recent calculations in Ref. 20 demonstrated that stable biexcitons can also exist in organic π -conjugated systems, although it remains unclear whether their properties are similar to those of biexcitons in inorganic semiconductors.

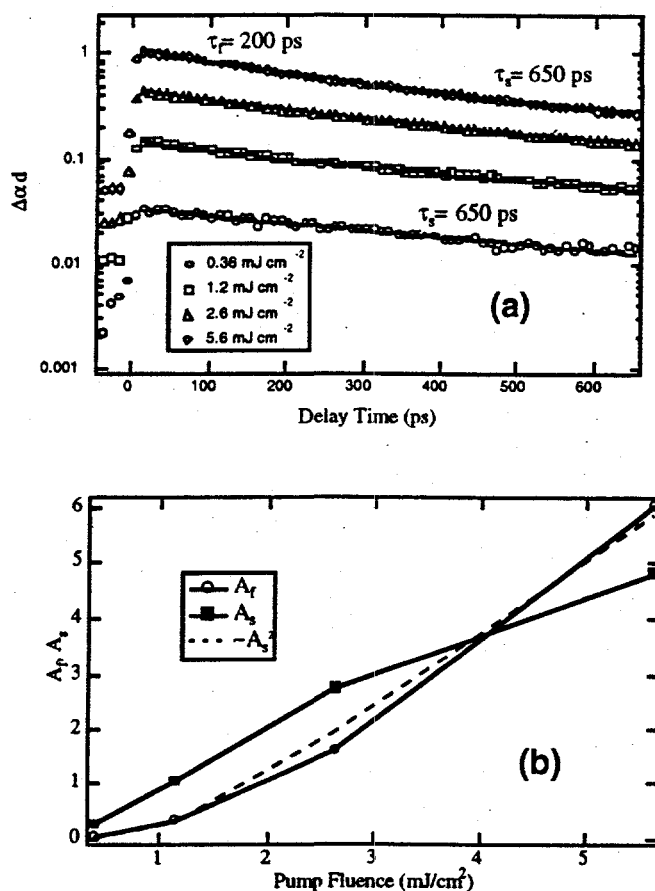


Figure 8. (a) Pump-intensity dependent dynamics of the SE in the solution sample along with double-exponential fits indicating the presence of two components with relaxation constants of ~ 200 and ~ 650 ps. (b) Quadratic correlations between amplitudes of the fast (A_f) and slow (A_s) SE components derived from the double-exponential fits.

The data from the previous section obtained for film samples clearly indicate the generation of doubly-excited molecules at high pump levels. However, due to efficient charge separation these species are unstable and decay on the sub-ps time scale with the accompanying formation of interchain excitations. These short-lived double excitations can be treated as "hot" unrelaxed biexcitons. If ultrafast decay of doubly-excited molecules is indeed associated with charge separation, we would expect that biexcitons can be stabilized in dilute solutions, for which charge transfer

is inhibited due to large molecular separation. To explore this issue we performed the TA studies of MEH-DSB solutions at pump levels up to $\sim 6 \text{ mJ cm}^{-2}$ which corresponds to excitation of more than one electron-hole pair per molecule on average. Shown in Fig. 8(a) are SE time transients recorded for several pump intensities. As described in Section 3, low-intensity scans can be well fitted to a single exponential decay with a time constant of around 650 ps. At pump levels exceeding $1\text{--}2 \text{ mJ cm}^{-2}$ the SE decay starts to deviate from a single exponential, indicating the presence of an additional faster component. A simple analysis of the data using a double exponential fit shows that all time transients can be well described using two time constants $\sim 200 \text{ ps}$ (fast decay) and $\sim 650 \text{ ps}$ (slow decay) which are essentially the same for all pump intensities. Analyzing the correlations between amplitudes of the fast (A_f) and slow (A_s) components [see Fig. 8(b)] we arrive at the relationship $A_f \propto A_s^2$, indicating the generation of doubly-excited molecules, a conclusion similar to that made in the previous section for solid-state films. However, as different from films, the decay of doubly-excited states in solutions occurs on a much longer time scale of hundreds of ps, supporting the assumption that in solid-state samples these states decay predominantly via charge-transfer processes.

In dilute solutions the inter-molecular interactions are suppressed, however, and the fact that the lifetime of doubly-excited molecules is shorter than that of a single exciton is indicative of strong interactions between excitations occupying a single chain. Another clear signature of coherent interactions is the superlinear increase of the magnitude of the SE at high pump levels seen in Fig. 9. By fitting the experimental data (solid circles in Fig. 9) to the power dependence w_p^m (dashed line in Fig. 8) we get $m = 1.5$. As TA measurements are not sensitive to PL photons, this superlinear growth cannot be explained by amplified spontaneous emission but rather indicates an increasing contribution from new species with enhanced oscillator strength.

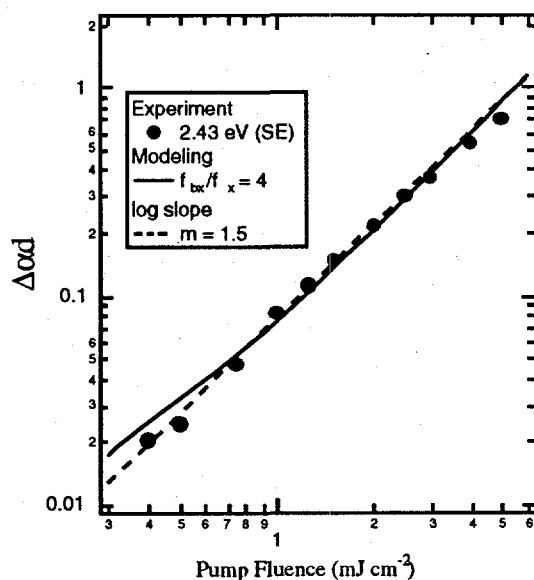


Figure 9. Superlinear pump dependence of the SE (symbols) along with a fit to a power dependence (dashed line) ($\text{SE} \propto w_p^m$ with $m=1.5$) and results of the modeling (solid line) assuming exciton and biexciton contributions to SE (see text).

It is known from studies of inorganic semiconductors that one of the effects associated with formation of biexcitons is the enhancement of the oscillator strength (f_{bx}) for the exciton-biexciton transition²² which is analogous to the effect of the giant oscillator strength in case of excitons weakly-bound to impurities.⁴¹ The enhancement factor $S = f_{bx}/f_x$ (f_x is the exciton oscillator strength) scales as a ratio of volumes of the wave function of the biexciton to that of the exciton (which can be understood in terms of the super-radiant emission of two coherent oscillators²²). As a result of the larger oscillator strength, the radiative decay of biexcitons is enhanced with respect to that of excitons, with the same enhancement factor S giving the ratio of the exciton to biexciton lifetimes. Both the shortening of the

SE decay time, and the correlated superlinear pump-dependence observed in solutions, give strong evidence towards the formation of stable biexcitons located on a single MEH-DSB chain.

The ratio of the slow and fast relaxation constants for the SE decay is around 3.3 which gives the estimate of the enhancement factor for the biexciton oscillator strength. We have also performed independent estimates of this factor by modeling the SE pump dependence. We assume that generation of biexcitons occurs during the laser pulse via re-excitation of singly-excited molecules. The exciton and biexciton contributions to SE are scaled in accordance with their oscillator strengths f_x and f_{bx} . As a result of the modeling (solid line in Fig. 8) we obtain $S = 4$ which is in a reasonable agreement with a value derived from decay dynamics. Since our measurements were limited to a single-length oligomer, it is not clear whether the observation of biexcitons in short-length π -conjugated systems is facilitated by spatial confinement. However, theoretical and experimental data available for inorganic semiconductors indicate a crucial role of quantum confinement in the stabilization of two-exciton states.^{39,40}

6. CONCLUSIONS

We have performed femtosecond TA studies of a five-ring PPV oligomer (MEH-DSB) prepared either as solid-state films or dilute solutions. In both types of samples, we see the signatures of singlet excitons in both PA and SE. However, the TA spectra of solid-state samples are strongly affected by intermolecular interactions resulting in an additional short-wavelength PA feature attributed to non-emissive interchain excitons. A close match of dynamics for the long-wavelength PA and SE in pristine films over a wide pump-intensity range demonstrates unambiguously that these features originate from the same species identified as intrachain singlet excitons. We observe clear correlations between the subpicosecond relaxation of the long-wavelength PA and the build-up dynamics of the short-wavelength PA component. These data, along with the observed quadratic correlation in pump intensity-dependence of the magnitude of the two PA features, indicate that the formation of the interchain species is mediated by two-exciton states (doubly-excited molecules or biexcitons) generated during the laser pulse by re-excitation of singly-excited molecules.

We observe a strong effect of photodegradation on TA in solid-state films, manifested as an overall reduction of the TA signal and a drastic shortening of SE dynamics at high pump levels. This is explained in terms of generation of defects which contribute to TA by a negative signal spectrally overlapping with SE. Defect states can only be activated at high pump fluences via a charge-transfer process mediated by intrachain two-exciton states. Therefore, in degraded films SE and PA₁ dynamics match each other at low pump intensity but are strongly different at high pump fluences.

We see clear signatures of exciton-exciton interaction in case of multiple photoexcitations occupying a single chain in dilute solutions. This is observed as a superlinear SE pump-dependence and a shortening of the SE decay time at high pump intensities. Both observations strongly point to the formation of stable biexcitons with enhanced oscillator strength, due to coherent exciton-exciton interactions.

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