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Intensity-dependent relaxation dynamics and the nature of the excited-state species in solid-state conducting polymers

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Femtosecond transient-absorption dynamics are presented for an oligomer and a number of polymers from the poly(arylene vinylene) family for excitation densities in the range from 10^{18}–10^{21} cm^{-3}. We report careful studies of the wavelength and pump-intensity dependence of the photoinduced absorption in a model five-ring oligomer, 2-methoxy-5-(2′-ethylhexyloxy)-distyryl benzene. We show that a single photoexcited species, the intrachain exciton, is responsible for all observable spectral features at low excitation densities. At higher excitation densities, nonlinear relaxation processes are observed in both polymers and the oligomer, consistent with exciton-exciton annihilation as a nonlinear-decay mechanism. [S0163-1829(97)00128-8]

The optical properties of conjugated polymers have generated widespread interest, both because these materials serve as model systems for understanding the electronic properties of quasi-one-dimensional semiconductors,[1,2] and because they have a strong potential for use as active materials in optoelectronic devices.[3] Conjugated polymers from the poly(arylene vinylene) family have been extensively studied by femtosecond (fs) and picosecond (ps) transient-absorption (TA) spectroscopy,[4–9] since new subgap absorption features arise in these materials on ultrafast time scales due to energy and structural relaxation to form polarons, bipolarons, and polaron excitons. However, considerable controversy still surrounds the interpretation of the photoinduced spectral features, and the nature of the excited-state species on ultrafast time scales. This controversy centers around several fundamental questions in solid-state polymer samples: (1) is the initial photoexcitation best described as a strongly localized molecular (Frenkel) exciton or a delocalized (Wannier) exciton? (2) Are more than one photoexcited species created at early times ($\leqslant 1$ ps)? (3) How are the relaxation pathways affected by the presence of defects due to photochemical changes, chemical impurities, or structural disorder?

The enduring nature of this controversy has arisen in part because measurements by different groups have yielded dramatically different conclusions. In particular, based on ultrafast TA studies, several authors have reached the conclusion that in poly(phenylene vinylene) (PPV) films all of the TA features can be explained as arising from a single photoexcited species: an intrachain exciton.[4,7] Other authors have concluded that at least two distinct species are created at early times, and that the quantum efficiency for generating the second species (‘‘spatially indirect excitons,’’ or bound interchain polaron pairs) in films can be as high as 90%.[5,6,8] The principal arguments for this second species have been (1) The dynamics of the stimulated emission (SE) and photoinduced absorption (PA) features were distinctly different under the experimental conditions used in several studies, indicating that the features have distinct origins;[5,6,8,9] (2) The PA band has relaxation dynamics which are independent of intensity, indicating geminate recombination of a bound pair.[5] Direct comparison of these results has been complicated by the fact that various studies were performed over a wide range of excitation densities, and with samples having uncontrolled degrees of photo-oxidation. For example, while some results have interpreted the decreased fluorescence efficiency in films as evidence for formation of secondary species,[5] more recent results have demonstrated that in pristine samples of PPV it is possible to model the observed fluorescence dynamics and quantum efficiency without assuming a second species.[10,11] In addition to being of fundamental interest, a resolution of this controversy is essential to optimize optoelectronic devices made from this unique class of materials.

While many works have appeared examining the nature of the initial photoexcitations in various members of the poly(arylene vinylene) family, no previous study has bridged the range of experimental conditions and materials used in these works to provide an unambiguous picture of both the intrinsic photoexcitation pathways and the origin of the conflicting observations of past studies. In this paper, we provide a detailed study of the TA features in several poly(arylene vinylenes) over a wide range of excitation densities. These measurements establish that many of the conflicting results outlined above can be understood as arising from a combination of intensity-dependent interactions of the primary photoexcited species (intrachain excitons) at high excitation densities, and extrinsic photochemical defects. The production of these defects can proceed very rapidly for the extremely high photon fluences used in many pulsed experiments, even in ‘‘inert’’ environments.

The majority of measurements presented in this paper were taken using the five-ring PPV oligomer 2-methoxy-5-(2′-ethylhexyloxy)-distyryl benzene (MEH-DSB), with structure shown in the inset to Fig. 1.[12] To demonstrate the generality of the results obtained, measurements were also performed in thin film samples of the polymers poly(p-phenylene vinylene) (PPV), poly[2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV), and poly(3-hexylthiophene) (P3HT). MEH-DSB was prepared and purified as described in Ref. 12, and thin films were deposited by vacuum sublimation onto sapphire substrates. MEH-PPV and P3HT samples were prepared as previously described,[13,14] and cast onto glass substrates in air. PPV samples were made by thermal conversion (80 °C for 2 h, then 140 °C for 2 h, and finally 220 °C overnight) of a stan-

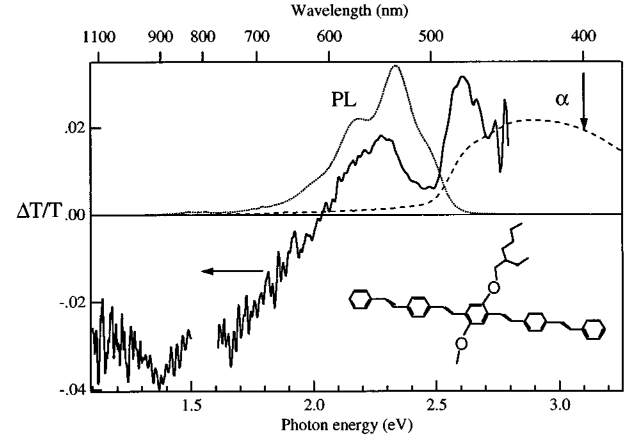

FIG. 1. The photoinduced transmission change $\Delta T/T$ (solid line) in a MEH-DSB thin film. A region of positive $\Delta T/T$ occurs, peaking at 535 nm, resulting from SE. The PA (negative $\Delta T/T$) peaks at $\approx$900 nm. The absorption coefficient, α, (dashed line) and PL (dotted line) are also plotted for comparison. The pump beam photon energy (3.1 eV) is indicated by the vertical arrow. The structure of MEH-DSB is shown in the inset.

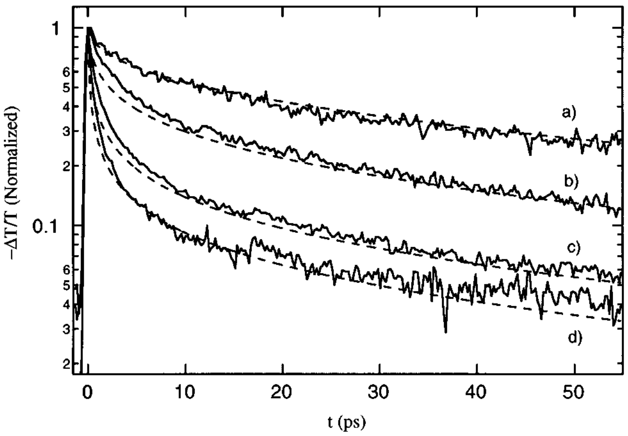

FIG. 2. Normalized time dependence of $-\Delta T/T$ at 800 nm (1.55 eV) in a thin film of MEH-DSB, for varying photon flux. Flux values from upper to lower curves are (a) $8.9\times10^{13}\ \mathrm{cm}^{-2}$; (b) $2.7\times10^{14}\ \mathrm{cm}^{-2}$; (c) $8.3\times10^{14}\ \mathrm{cm}^{-2}$; (d) $1.3\times10^{15}\ \mathrm{cm}^{-2}$. The dashed lines are a fit to the data using Eq. (1) (see text).

dard sulfonium-salt precursor polymer.[15] All samples were measured under vacuum (<5 mTorr) to inhibit photo-oxidation processes.

MEH-DSB serves as an ideal model compound for the poly(arylene vinylene) family. High optical quality samples can be prepared by vacuum sublimation with control over the degree of crystallinity by changing substrate temperature.[12] All films in this study were amorphous. Samples of high purity which have never been exposed to oxygen are easily prepared. Thin films of MEH-DSB are highly luminescent, with the photoluminescence (PL) quantum efficiency estimated to be approximately 15%.[12] The π–π^* absorption maximum occurs at 430 nm (2.9 eV), so that near-band-edge resonant pumping is achieved using our 400-nm (3.1-eV) pump beam. Several authors have pointed out the advantages of studying oligomers when trying to identify the intrinsic excitations in polymers.[16–18] The absorption and emission line shapes of oligomers and polymers are quite similar, indicating similar degress of structural relaxation in the excited state, despite a substantial upshift of the π–π^* transition energy in oligomers as a result of spatial confinement. In addition, the excited-state absorption features are also quite similar between polymers and oligomers. Oligomers are easily purified to a single chain length, so that additional energy relaxation channels due to a distribution of conjugation lengths are absent. Finally, in MEH-DSB the principal TA features are spectrally separated enough to allow unambiguous assignment despite their broad spectral linewidth. The need for a simple molecular system which allows insight into the broader class of materials is highlighted by the many existing conflicting studies of poly(arylene vinylene) polymers as outlined above.

Femtosecond TA studies were carried out using a regeneratively amplified Ti:sapphire laser (Clark-MXR CPA-1000) emitting 100-fs pulses of 1-mJ energy at a wavelength of 800 nm (1.55 eV) and a repetition rate of 1 kHz. The majority (90%) of the fundamental beam was frequency doubled to provide the pump excitation source at 400 nm (3.1 eV), with incident energy controlled with a calibrated neutral-density filter wheel. The remainder of the fundamental was attenuated to $<2\ \mu$J and either used directly as a probe beam, or focused through a 1-mm sapphire plate to generate a broadband white-light continuum probe pulse with spectral components from 450–1100 nm. The differential transmission ($\Delta T/T$) is defined as follows: $\Delta T/T=(T-T_0)/T_0$, where T_0 and T are transmissivities in the absence and in the presence of the pump, respectively. In the small signal limit ($\Delta T/T\ll 1$), $\Delta T/T$ is proportional to an absorption change $\Delta\alpha$: $\Delta T/T\approx-\Delta\alpha d$ (d is the sample thickness).

$\Delta T/T$ spectra at a fixed delay time between pump and probe pulses were recorded with a 0.15-m spectrometer coupled to a liquid-N_2-cooled charge-coupled device array camera by averaging the signal over 1000–2000 pulses. This measurement provides information on the spectral distribution of the excited-state absorption over a broad spectral range (0.45–1.1 μm). TA dynamics at a fixed probe wavelength were measured by mechanically chopping the pump beam at a frequency of 140–500 Hz, and measuring the modulation of the transmitted probe intensity using synchronous (lock-in) detection. A computer-controlled delay line in the probe path was used to vary the arrival time of the probe pulse relative to the pump. The pump beam pulse width was broadened to approximately 150 fs at the sample plane.

The principal TA spectral features in MEH-DSB are shown by the solid line in Fig. 1, and are similar to those reported for many poly(arylene vinylenes).[19] The bleaching signal (positive $\Delta T/T$) in the region of the absorption band arises due to the depopulation of the ground-state electrons;[19] the positive $\Delta T/T$ signal peaking at 535 nm (2.32 eV), coinciding with the PL (dotted line in Fig. 1), is assigned to SE;[19] the broad PA peak (negative $\Delta T/T$) peaking at $\sim$900 nm (1.38 eV) has an origin which remains controversial.

Figure 2 shows the normalized ultrafast PA dynamics of MEH-DSB probed at 800 nm (1.55 eV), within the broad near-infrared PA band, for values of the photon flux ranging from 8.9×10^{13}–$1.3\times10^{15}\ \mathrm{cm}^{-2}$. The magnitude of the peak

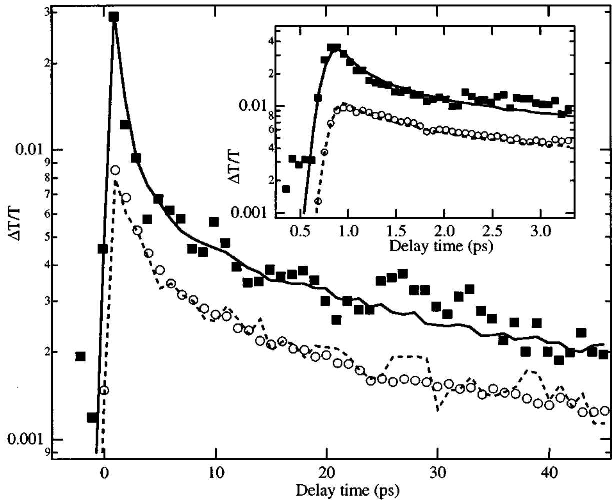

FIG. 3. A comparison of the dynamics of the SE at 535 nm (2.32 eV) and the PA at 850 nm (1.46 eV) at two fluences. The symbols show the SE (solid squares, photon fluence= 6.0×10^{15} cm^{-2}; open circles, 1.2×10^{15} cm^{-2}). The lines represent the PA, taken at the same fluences, and scaled by a factor of -0.3, such that the maxima of the two features coincide. The inset shows an expanded view of the same data on a shorter time scale.

$\Delta T/T$ at zero delay scales nearly linearly with pump intensity at low intensities, with saturation occurring above a flux of approximately 10^{15} cm^{-2}. From Fig. 2 it is apparent that the dynamics are dramatically changed at high excitation densities. From the measured absorption coefficient in MEH-DSB films at 400 nm, a photon flux of 10^{15} cm^{-2} in our measurement corresponds to an excitation density of 2.2×10^{20} cm^{-3}, neglecting the effects of variation along the film depth due to absorption of the pump beam. As the photon flux rises above a threshold of a few $\times10^{14}$ cm^{-2}, increasing contributions from ultrafast relaxation processes are observed. These results indicate that nonlinear relaxation processes occur on ultrafast time scales, rapidly depleting the excited-state population of the species which contribute to the PA band at 800 nm. We will return to a discussion of the intensity-dependent dynamics, but first we present a comparison of the main TA spectral features.

One of the principal arguments for interchain bound pairs as an intrinsic photoexcitation has been the reported lack of correlation between the dynamics of the SE band and the near-ir PA band. Since both the PA band (as above) and the time-resolved photoluminescence[20] have been shown to have intensity-dependent dynamics, it is clearly insufficient to compare the PA and SE features at a single pump intensity; the evolution of the two features must be carefully measured over a range of intensities. Figure 3 shows a comparison of the PA dynamics in MEH-DSB [measured at 850 nm (1.46 eV)] with the SE dynamics [measured at 535 nm (2.32 eV)]. Special care was taken to avoid photodegradation during these measurements. The squares and circles represent the SE measured at photon fluxes of 6×10^{15} cm^{-2} and 1.2×10^{15} cm^{-2}, respectively. The lines are the PA dynamics measured at the same fluxes, and scaled (by a factor of -0.3) to have the same maxima as the corresponding SE curves. The inset to the figure shows an expanded view of the dynamics on a shorter time scale. It is evident from Fig. 3 that when care is taken to compare the dynamics at the same intensity in pristine samples, the dynamics of the SE and PA features are identical. *These data indicate that in the model PPV oligomer MEH-DSB, the excitation responsible for the PA in the spectral region from* 750–1100 *nm (*1.13–1.65 *eV) is the same as that for the SE: the intrachain exciton.* We turn now to a discussion of the intensity-dependent relaxation of the PA feature as shown in Fig. 2.

To gain insight into the nature of the pump-dependent dynamics, the data of Fig. 2 were modeled using a nonlinear rate equation taking into account bimolecular decay processes. The bimolecular annihilation of excitons in organic solids has been studied extensively, both theoretically[21,22] and experimentally.[23–25] In the exciton-exciton annihilation process, the energy from one exciton is transferred to a nearby exciton, which rapidly relaxes nonradiatively back to the lowest excited state. This results in a net reduction in the exciton population. Molecular systems in which annihilation dynamics have been directly observed include phthalocyanine derivatives[23,25] and C_{60},[24] which have extended π-electron structures similar to those found in conjugated polymers. Exciton-exciton annihilation in poly(arylene vinylenes) has been recently proposed to explain the sublinear intensity dependence of the magnitude of the cw PL,[20,26] and the intensity dependence of the PL dynamics on the 100-ps time scale,[20] but this process has been previously explicitly ruled out for the PA feature in luminescent conjugated polymers.[5,8,27] Earlier work proposed annihilation as a decay mechanism in conducting polymers, but without any investigation of intensity dependence.[28] Although these studies have implied the presence of bimolecular effects, because of the ultrafast nature of the annihilation process such indirect measurements cannot give insight into the physical mechanism of the luminescence quenching. The intensity-dependent decay data as shown in Fig. 2 represent the first direct measurement of these effects with subpicosecond resolution in this class of materials.

A generic rate equation which includes exciton-exciton annihilation can be written[21,25]

$$\frac{dN}{dt}=G(t)-\frac{N}{\tau}-\gamma(t)N^2. \tag{1}$$

The functional form of the time-dependent nonlinear decay rate $\gamma(t)$ is sensitive to the effective dimensionality and the role of diffusion in the annihilation process.[22] For a three-dimensional system in the strong diffusion limit, $\gamma(t)=\text{const}$, while in the diffusion-free limit $\gamma(t)\propto t^{-1/2}$. Since the time scales for the nonlinear decay in Fig. 2 involve only the first few ps, diffusion cannot be expected to play a dominant role. For the purposes of illustration, the intensity-dependent data of Fig. 2 have been fit to Eq. (1), using $\gamma(t)=\beta t^{-1/2}$, as shown by the dashed lines in Fig. 2. The fits shown were obtained using only two adjustable parameters: $\tau=150$ ps and $\beta=5.3\times10^{-21}\ \mathrm{cm}^3/\sqrt{ps}$. The evolution of relaxation dynamics for photon fluxes from 9×10^{13}–1.3×10^{15} cm^{-2} is reproduced with reasonable accuracy, considering that the details of the nonlinear interaction are likely quite complex, and that in disordered solid-state films of conjugated polymers (even at low excitation densities) nonexponential decay dynamics are commonly ob-

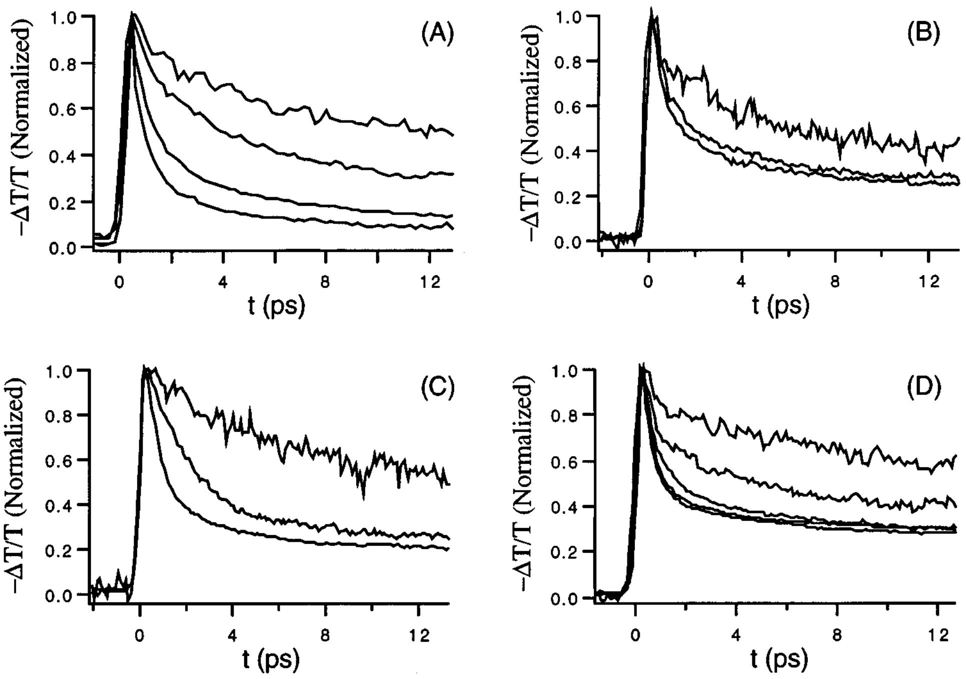

FIG. 4. Normalized $-\Delta T/T$ scans at varying photon fluences for thin films of four different poly(arylene vinylenes): (a) MEH-DSB, (b) PPV, (c) MEH-PPV, and (d) P3HT. Photon fluences for these measurements, from upper to lower curves, respectively, are (a) as listed in Fig. 2; (b) $1.0\times10^{14}\,\mathrm{cm}^{-2}$, $3.3\times10^{14}\,\mathrm{cm}^{-2}$, $1.0\times10^{15}\,\mathrm{cm}^{-2}$; (c) $1.0\times10^{13}\,\mathrm{cm}^{-2}$, $3.1\times10^{14}\,\mathrm{cm}^{-2}$, $9.3\times10^{14}\,\mathrm{cm}^{-2}$; (d) $8.7\times10^{13}\,\mathrm{cm}^{-2}$, $2.6\times10^{14}\,\mathrm{cm}^{-2}$, $8.0\times10^{14}\,\mathrm{cm}^{-2}$, $2.4\times10^{15}\mathrm{cm}^{-2}$, $6.7\times10^{15}\,\mathrm{cm}^{-2}$.

served. The largest deviations from this simple rate equation are evident on the ps time scale, and it is possible that other nonlinear interactions at short times contribute to the observed relaxation dynamics.

For the purposes of the present paper, however, a simple picture can explain the salient photophysics of this model PPV oligomer. At low excitation densities, the dominant TA features arise from excited-state absorption and stimulated emission from intrachain singlet excitons, and at higher excitation densities nonlinear interaction of these singlet excitons leads to progressively faster recombination dynamics. It should be noted that this nonlinear decay on the ps time scale is absent in TA measurements performed over the same intensity range in solution. This indicates that the three-dimensional interaction of excitons on separate chains provides the dominant nonlinear decay channel in thin films.

We have clearly shown that nonlinear processes consistent with exciton-exciton annihilation contribute strongly to the dynamics of the near-infrared PA band in MEH-DSB. In order to test whether these results are more general, the PA dynamics were probed at 800 nm (1.55 eV) as a function of intensity in a number of poly(arylene vinylene) polymers. These results are shown in Fig. 4 for (a) MEH-DSB, (b) pure PPV, (c) MEH-PPV, and (d) P3HT. In all four materials we observe the same general form of intensity-dependent dynamics. The detailed dependence of the dynamics on photon flux in each material is different, which is not surprising since the position of the pump beam relative to the $\pi-\pi^*$ absorption band, and the probe beam relative to the excited-state absorption band, is different in each case. Since the polymer films [(b) through (d) in Fig. 4] were thick compared with the absorption depth of the pump beam, a simple quantitative analysis of the type shown in Fig. 2 is not useful: the variation of excitation-density within the film is not included. A more complete quantitative model which includes these effects, as well as including terms which would allow for nonexponential decay at low intensities, is not necessary for the conclusions drawn in this paper. It is important to note that in both PPV and MEH-PPV, intensity-dependent decay dynamics are observed *at the same probe wavelengths* where previous measurements ruled them out.[5,6] This demonstrates that one of the principal arguments in favor of bound interchain polaron pairs as a dominant photoexcitation in poly(arylene vinylene) films is incorrect.

Although the results presented thus far demonstrate clearly that the dynamics of the SE and PA in MEH-DSB are correlated over the intensities presented, they *do not* provide an explanation of the lack of correlation between these features presented in previous work. In our studies of MEH-DSB, as the intensities were increased substantially above the levels presented in Fig. 3 (to become comparable to those used in previous reports) it became evident that at sufficiently high carrier densities the SE undergoes a very rapid decay, which is not matched by the PA. Moreover, at these same intensities we see evidence for rapid photodegradation of the samples (irreversible reduction of the magnitude of both PA and SE features) in a few tens of seconds, after which the samples again appear stable. We hypothesize that the lack of correlation between the two features is a byproduct of both photo-oxidation and high excitation densities; under these conditions, a second ultrafast relaxation pathway becomes efficient, corresponding to the creation of a second species with significant quenching of the stimulated emission. This hypothesis is consistent with recent reports that the effects of deliberate photo-oxidation, when studied at excitation densities in excess of 10^{20} cm^{-3}, lead to dramatic quenching of the SE, but have a relatively minor effect on the PA band.[27]

It has also recently been reported that the SE quantum efficiency varies strongly within films of the same polymer depending on the preparation conditions and solvent used to cast thin films.[29] It is clearly probable that some of the discrepancies in previous studies of the SE and PA dynamics are directly traceable to differences in the chemical purity and microscopic morphology of the samples, and that future studies must attempt to quantify these differences so that direct comparison can be made between results of different groups. We have demonstrated, however, that the presence of nonlinear (intensity-dependent) recombination dynamics is a general feature of poly(arylene vinylenes), even when relatively little care is taken to control chemical purity of the polymers.

It should also be noted that we find a second PA signature in MEH-DSB in the wavelength range between 620–700 nm (1.77–2.0 eV). This band has decay dynamics distinct from both the SE, and the PA feature from 750–1100 nm (1.13–1.65 eV), but given the broad spectral extent of the PA band in Fig. 1, this second feature is only evident from a detailed comparison of dynamics at different wavelengths. The longer-lived nature of the second band leads to an apparent blueshift of the PA band at longer times, similar to that recently reported for another PPV derivative, BuEH-PPV.[30] Our measurements could only detect this second feature at values of the photon flux $>10^{15}$ cm^{-2}, implying that it is due to a secondary species created only at high excitation densities, perhaps as a byproduct of the nonlinear interaction of intrachain excitons. For the purposes of this paper, it suffices to say that its presence does not account for the SE quenching observed in solid-state samples, and does not alter the assignment of the SE and the PA between 750–1100 nm (1.13–1.65 eV) to a single excited-state species. If this second band overlapped significantly with either the SE or the primary PA bands, then the dynamics of the latter two bands would not match so exactly. Such an overlap of bands in other poly(arylene vinylenes) may in fact help to explain why the SE and PA bands in these materials do not match exactly; in MEH-DSB, it is fortuitous that the bands are sufficiently distinct to allow unambiguous separation. A more detailed investigation of the intensity dependence of this second PA band in MEH-DSB will be presented in Ref. 31.

In summary, we have performed careful measurements of the decay dynamics of the PA band around 800 nm and the SE at 535 nm in the model oligomer MEH-DSB over a range of excitation densities. We have observed nonlinear recombination dynamics consistent with exciton-exciton annihilation in both features. Comparison of the decay dynamics for PA and SE shows that both of these bands arise from photogenerated intrachain excitons as the primary photoexcited species at low excitation densities. In addition we have observed pump-dependent PA dynamics in a variety of conducting polymers indicating that similar nonlinear interactions are a general feature of the excited-state recombination dynamics in many conjugated polymers from the poly(arylene vinylene) family. A second PA band with distinct dynamics was observed, however it does not influence the SE and primary PA bands. Given the similarities between the absorption and luminescence line shapes, the TA spectral features, and the nonlinear recombination dynamics in our model oligomer and in the broader class of arylene-vinylene polymers, our data is strongly suggestive that the intrinsic photoexcitations in all poly(arylene vinylenes) are intrachain excitons. In terms of the ongoing debate about the magnitude of the exciton binding energy, these results provide no direct measurement. However, the nonlinear interaction of these excitons at high excitation densities provides an explanation for many of the discrepancies of previous studies. To prove that the photoexcitation mechanisms in all of these materials are identical, however, will take further careful studies of the wavelength and intensity dependence of the transient excited-state absorption in polymer films which are known to be pristine. These studies are beyond the scope of this paper, but will be critical to claim a comprehensive understanding of these materials.

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