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Origins of aggregation quenching in luminescent phenylenevinylene polymers

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Abstract

We measure transient absorption, gain and bleaching of a model conjugated polymer in solution where aggregation of the polymer has been deliberately controlled. Evidence is presented that photoexcitation of aggregated polymer chains leads to creation of interchain non-emissive polaron pairs in large quantum yield. This is shown to be consistent with film behavior and accounts for low luminescence quantum yields in the solid state. It also explains the recent reports of rapidly formed species with characteristic infrared active vibrations. Our data support a picture where polaron pairs mostly recombine to form the ground state directly, in stark contrast to their presumed recombination mechanism in electroluminescent devices where they have been postulated to form only excited singlet and triplet states.
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Keywords: Phenylenevinylene; Photoexcitation; Photoluminescence (PL); Excited state dynamics

1. Introduction

The potential application of luminescent conjugated polymers in optoelectronic devices has stimulated research into the yield and the dynamics of elementary excitations in this class of material [1–5]. The nature of the photogenerated elementary excitations and their relaxation dynamics are of both theoretical and practical importance. It has been observed that the photoluminescence (PL) quantum yield drops substantially when the polymer is transformed from solute into neat thin films. This is now generally accepted as an effect of polymer chain-aggregation that results in the rapid formation of a large quantum yield of interchain excited state species that relax non-radiatively [1]. Nevertheless, a number of issues regarding the nature of interchain excitations and their formation mechanism remain incompletely resolved. Most importantly, the morphology dependence of the branching ratios for forming non-luminescent species has not been investigated sufficiently to provide prescriptive information on how to avoid forming them.

Many researchers have studied solvatochromism associated with conjugated polymer chain-aggregation in solution [6–11]. We have recently showed that we can reproduce the phenomenology associated with solid state conjugated polymer PL while working in solutions where the same polymer is deliberately aggregated by varying the fraction of “good” and “bad” solvent for the polymer [12,13]. In particular, we observe the following “film-like” behaviors upon aggregation in solution: (1) a red-shift to the spectrum; (2) a reduction in the PL quantum yield even while there is no substantial change in the excited state lifetime; (3) a long-lived tail to the PL that we ascribe to “back-transfer” [14,15] from interchain excitations. The present paper describes studies of the transient absorption of the aggregated solutions of MEH–poly(2-methoxy-5-(2′-ethylhexyloxy)-(phenylenevinylene)) (PPV). Our main purpose in using controlled aggregation in solution is to try to unambiguously determine the signature of interchain excited species in photoinduced absorption (PA) experiments and to use this information to ascertain their prevalence and their fate. The importance of understanding the interchain excitations derives directly from the hypothesis that they are responsible for the reduced quantum yield of emission in polymer thin films relative to solution.

Using PA to track interchain excitations has been somewhat confusing and controversial since triplet states, polaron pairs, bipolarons and singlets have all been reported to absorb in PPV films in the near-infrared [6]. Very beautiful pump–dump experiments by Frolov et al. [3] suggest that the vast majority of excitations are singlets and that the nanosecond PA in DOO–PPV derives from triplets. The work by Yan et al., however, appears to implicate polaron pair absorption as the cause of long-lived PA [1]. One potential resolution to this uncertainty was proposed by Klimov et al. [2] who

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showed that some of the PA can be created by non-linear processes that occur at high intensity in PA experiments, since the experiments of Yan et al. [1] were performed under those conditions. Unfortunately, this explanation suggests that the quantum yield under low excitation intensity would be comparable to that in solution and that is not the case.

The present work compares transient absorption spectra and dynamics in dilute unaggregated and aggregated solutions as well as in films of MEH–PPV. All of our work is performed at intensities where non-linear effects are small. Moreover, work in aggregated solutions most likely eliminates impurity and damage effects on the spectroscopy. We are able to observe triplet formation and quantify it. We have also succeeded in inferring the near-infrared spectrum of an interchain species we believe to be polaron pairs. We find that the recombination of polaron pairs is much faster in solution than in a film and that the vast majority of pairs recombine to form the ground state directly. The latter observation is surprising and has potentially important consequences for electroluminescent devices based on conjugated polymer films.

2. Experimental

The synthesis and characterization of the MEH–PPV have been described previously [17]. Solutions of 0.1 mg of MEH–PPV per ml of solvent are prepared and put in supersonic bath for 0.5 h prior to measurement. Two solvents are used. The first one is pure toluene, which is a good solvent for MEH–PPV. The second one is a 50–50 vol.% mixture of toluene and hexane. The solution concentrations are adjusted to have absorbance of 0.15 at 400 nm in a 1 mm length cuvette since 400 nm is the excitation wavelength used in our experiment. MEH–PPV films are spin-cast from toluene solution (4 mg/ml and 2000 rpm spin rate) and kept under N_2 flow during the experiment. All measurements are carried out at room temperature. As a practical matter, the polymer dissolved in solution is much less prone to photodegradation than in the film, and its optical properties remain unchanged over a long period of time and extensive illumination.

Steady-state absorption spectra are recorded in a HP8452A diode array spectrometer while steady-state PL spectra are measured with a SPEX Fluorolog instrument. We use a standard pump-probe set-up for the transient absorption measurements. A Clark-MXR Ti:Sapphire laser system generates the 800 nm pulses with about 100 fs FWHM at 1 kHz repetition rate. White light continuum is generated by focusing a small portion of the laser pulses into a 1 mm thick sapphire plate and is used as a probe. The rest of the 800 nm light is frequency-doubled to make 400 nm pulses that excite the sample after being synchronously chopped at 500 Hz so that every other pump pulse strikes the sample. The pump and probe are focused colinearly on the sample with parallel polarization. After the sample, single wavelengths from the probe are separated by a spectrometer and detected with silicon photodiodes. A standard phase-sensitive technique is used to collect the transient absorption signal that we report as fractional changes in probe transmission, $\Delta T/T$. Pump pulse fluences were below 500 μJ/cm^2 to avoid intensity-dependent effects. The independence of the dynamics on intensity and the linearity of $\Delta T/T$ with intensity were verified experimentally. For the measurement of transient absorption spectra at 500 ps delay (Fig. 4), we used a Nd:YAG laser pump-probe set-up with 50 ps time resolution. The sensitivity of the optical multichannel analyzer used in the Nd:YAG set-up is low at ~900 nm and causes the spectral shape at close to 900 nm to be less reliable.

3. Results and discussion

The absorption and PL spectra of MEH–PPV in pure and mixed solvents are shown in Fig. 1(a). The absorption spectrum in mixed solvent shows a red-shift although the peak absorbance and the absorbance at 400 nm are little changed from that of the pure solvent. The red-shift has been shown to result from increased conjugation length due to chain-packing in the aggregated regions of MEH–PPV in the mixed solvent [13]. The PL spectrum in the mixed solvent is also red-shifted and, despite the fact that the absorbances in the two solutions are the same, the PL intensity in mixed solvent is only about half of that in pure toluene. This means the PL quantum yield drops by 50% in the mixed solvent.

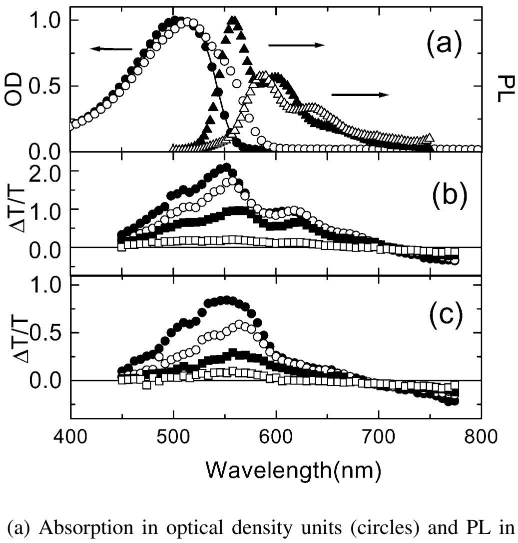

Fig. 1. (a) Absorption in optical density units (circles) and PL in counts (triangles) spectra of MEH–PPV in pure toluene (solid) and mixed solvent (open) of 50% toluene and 50% hexane. Absolute values are in arbitrary units but relative intensities between samples are correct. (b) Transient difference spectra at various delays for MEH–PPV in toluene. From top to bottom, the pump-probe delays are 1, 10, 100, 500 ps. (c) Transient difference spectra at the same delays for MEH–PPV in mixed solvent under the same conditions. In both (b) and (c), $\Delta T/T$ values are multiplied by 100.

It is important to point out that the excitation used in the measurement is a weak lamp so that the observed quantum yield drop cannot be due to any intensity-dependent effect such as exciton–exciton annihilation. A much more detailed discussion of the structural reasons for the spectral changes in PL and absorption in aggregated solutions can be found elsewhere [13].

Fig. 1(b) and (c) present the spectrum of $\Delta T/T$ at several pump-probe delays in good and poor solvent, respectively. Three distinct phenomena can be largely separated by wavelength and so we treat them one at a time. It is clear that the reddest portion of the transient spectrum (700–850 nm) represents excited state absorption (PA). As is clear from a comparison with the steady-state PL, the increase in transmission in the central portion of the spectrum (600–700 nm) is associated primarily with stimulated emission (SE) that results in probe amplification. The bluest portion of the transient spectrum (450–550 nm) also exhibits increases in probe intensity when the sample is pumped and we ascribe these primarily to ground state bleaching since there is very little PL at these wavelengths.

It is most pedagogically clear to treat the SE first since this can be unambiguously assigned to singlet states. The transient gain decay dynamics when probed at 650 nm reflect mostly SE and are shown in Fig. 2. In both unaggregated and aggregated solution, the decays can be well fit with a single-exponential having lifetime of 300 ps. Both solutions have little absorption at this probe wavelength. The fact that the lifetime of S_1 in both solutions is the same makes it exceedingly unlikely that the PL quantum yield drop in the mixed solvent is because the radiative and non-radiative rates change in concert. We believe that the reduced PL reflects the fact that many of the absorbed photons create interchain species on a very rapid timescale, faster even than our sub-picosecond resolution.

One would expect the interchain species to appear somewhere in the PA spectrum. The time decays of the PA when probed at 750 nm are shown in Fig. 3. The results cannot be fit with a single-exponential decay. In both the aggregated and the non-aggregated solutions, there is a long-lived component with lifetime of ≥1 ns. Previous work ascribed long-lived PA in MEH–PPV films in the near-infrared to interchain polaron pairs [1]. However, this is unlikely to be the correct explanation for the long-lived PA in Fig. 3 since its magnitude in pure solvent is almost twice that in the mixed solvent. One would expect the opposite because the aggregation of chains in the mixed solvent would favor the formation of interchain species. Given that its amplitude scales with the amplitude of the PA assigned to S_1 when we go from pure to mixed solvent, it is plausible to assign it to triplet absorption. To test this hypothesis, we degassed the solution of MEH–PPV in pure solvent and monitored its PA spectrum at long delay time (500 ps) where singlets have mostly vanished. The results are illustrated in Fig. 4. The magnitude of the PA spectrum decreases when purged with N_2, and recovers when subsequently purged with air. The triplet population can be affected by the ‘degassing’ process because of enhanced rate of O_2-assisted intersystem cross-

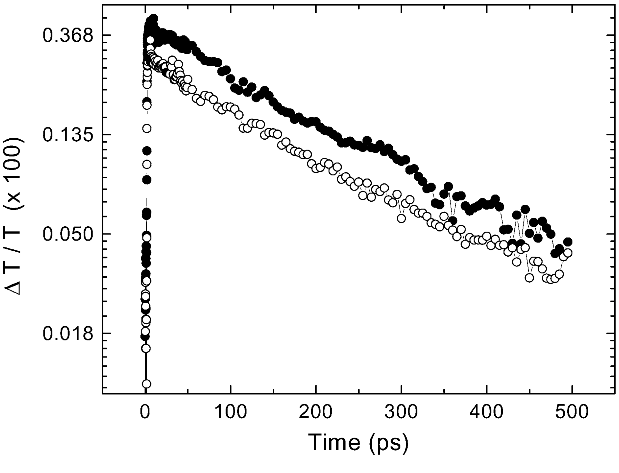

Fig. 2. Transient decays of MEH–PPV transmission in pure (solid) and mixed (open) solvent when probed at 650 nm.

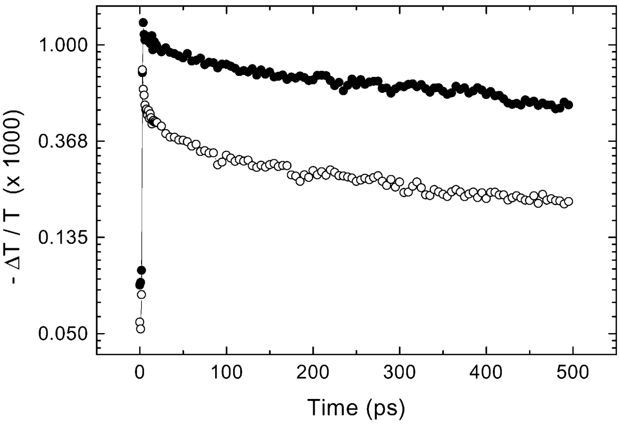

Fig. 3. Transient decays of MEH–PPV transmission in pure (solid) and mixed (open) solvent when probed at 750 nm.

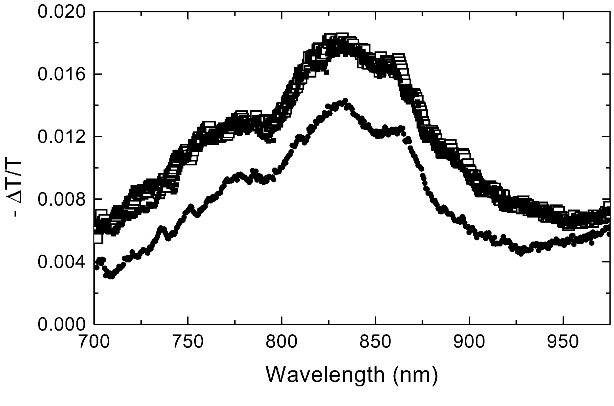

Fig. 4. Transient absorption spectra of MEH–PPV in pure toluene at 500 ps after photoexcitation when not purged (solid squares above), purged with N_2 (solid circles below) then purged again with air (open squares).

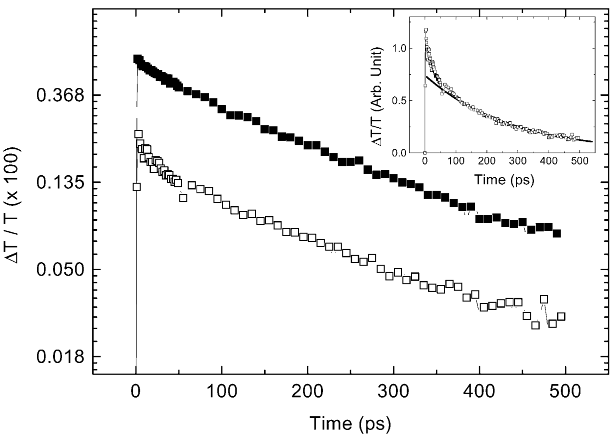

Fig. 5. Time decays of MEH–PPV in pure solvent at 500 nm (solid) and mixed (open) solvent at 550 nm. The inset shows the decay in the mixed solvent with a single-exponential fit (solid line) to the longer time component of the decay.

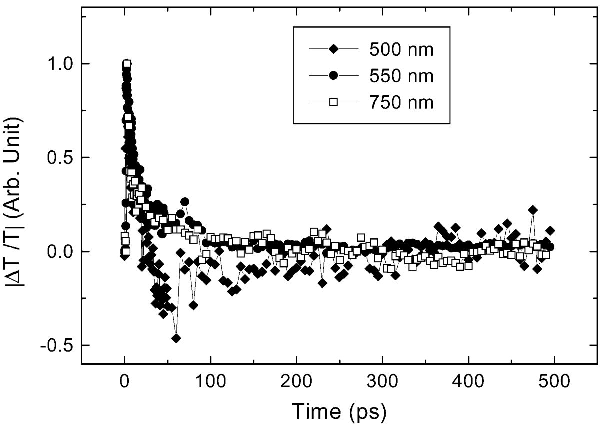

Fig. 6. Difference of decay dynamics between mixed and pure solvent cases where the spectra have been scaled to have identical long time components. This is presented for probe wavelengths 500 nm (solid diamonds), 550 nm (solid circles) and 750 nm (open squares) where the 750 nm decay is inverted for comparison.

ing (ISC) [18]. These data confirm our assignment of the long-lived solution PA as being due to T_1 absorption. Given that assignment, our PA data tell us that the triplet state has a lifetime of ∼1 ns in solution at ambient temperature.

Fig. 5 presents decay dynamics of $\Delta T/T$ in toluene at 500 nm and in toluene/hexane at 550 nm.[1] The transmission changes at these wavelengths are primarily from ground state photobleaching (PB) since both samples absorb but do not emit at these wavelengths. The PB signals reflect the ground-state population recovery dynamics and are, thus, an excellent indicator of branching ratios. The fact that the PB decay in the pure solvent can be approximately fit with a single-exponential lifetime of ∼300 ps suggests the majority of the excited states formed are singlet excitons (S_1) and that the ISC yield is low. From the small magnitude of long-lived component in the PB signal of both solutions, we infer that the ISC yield for T_1 is very small, around 5%. The much larger long-lived PA in Fig. 3 indicates that the triplet–triplet absorption cross-section at 750 nm must be much larger than that of the singlets.

The principal difference between the “good” and “poor” solvent PA decays in Fig. 3, is observed within the first 50 ps. The decay in the mixed solvent has a fast component that is not present in the pure solvent and we, therefore, believe that component to be associated with an interchain excited state species, presumably polaron pairs. In the remainder of the paper, we focus on confirming that assignment and considering its implications. The behavior of the bleaching recovery (Fig. 5) mirrors that of the PA (Fig. 3) where the decay in the mixed solvent also has an additional fast component not present in the pure solvent. The aggregated solution shows a 300 ps exponential component to the decay of the PB but also a much faster component. When the 300 ps exponential decay is extrapolated back to time zero, it accounts for ∼50% of the PB magnitude (cf. Fig. 5 inset). This suggests that the branching ratio of excitations into intrachain singlet exciton S_1 and interchain species is approximately 1:1 in this solution. If we assume negligible emission from the pathway where interchain excitations are created, this would account for the factor of two reduction in PL yield and SE magnitude. When probed at 550 nm, the signal in the pure solvent is from both PB and SE while the signal in the mixed solvent is still from PB but the conclusion is similar.

Since the fast-decay dynamics in PB and PA are only present in the mixed solvent, we can approximately extract them by subtraction. We scale the pure solvent decays so that the amplitudes of the long-lived components match those in the mixed solvent and then subtract them from the analogous mixed solvent data. The result of this procedure is shown in Fig. 6. The residual fast-decay components at 550 nm and 750 nm match extremely well, exhibiting 50 ps decay. The result at 500 nm is noisier but still approximately matches the other two decays. We conclude that the species with a 50% weight in the “poor” solvent PB is also the species responsible for the fast-decay component of the PA. Thus, the polaron pairs are formed on a subpicosecond timescale, have 50% quantum yield and recombine to form the ground state in 50 ps in the 1:1 toluene/hexane solvent mixture under study.

Armed with an understanding of the PA, PB and SE, we are able to deduce a spectrum for the interchain species. In particular, the difference of the PA spectra of the two solutions at 10 ps delay time should reflect the polaron pair PA. Fig. 7 illustrates this difference where the MEH–PPV PA spectrum in the mixed solvent has been multiplied by a factor of 2.5 so that the PA in both solutions will have same magnitude at long delay times (≫50 ps). Assuming

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[1] We use 500 nm to study bleaching recovery dynamics for the pure solvent and 550 nm for the mixed solvent as roughly comparable wavelengths due to the red-shift observed in the mixed solvent aggregated case.

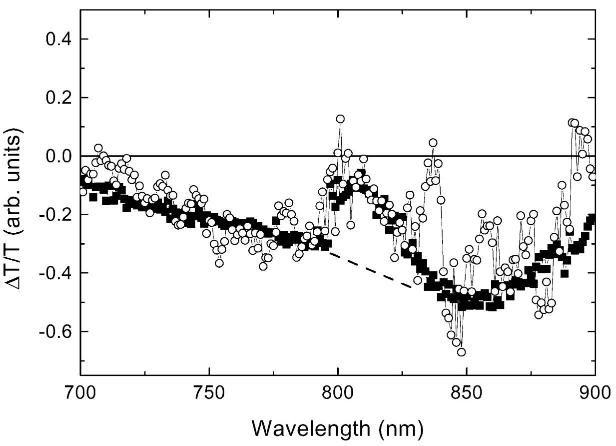

Fig. 7. Transient absorption difference spectrum as described in the text between MEH–PPV in mixed solvent and pure solvent at 10 ps after photoexcitation (open circles). The film spectrum 500 ps after photoexcitation is shown for comparison (solid squares). The spectral feature at approximately 800 nm is an artifact of the fact that this wavelength is the fundamental of the Ti:Sapphire laser and we do not believe the data there are accurate. The dotted line to guide the eye is probably closer to the true transient spectrum.

that S_1 and T_1 are the only species present at long times and that their extinction coefficients do not vary much with aggregation, the contributions of S_1 and T_1 will then be the same for both solutions.

For comparison, we did the same measurements on a MEH–PPV film cast from toluene solution. The steady-state PL and pump-probe SE are highly reduced in the film. The greater degree of chain-aggregation leads to much smaller yield for S_1 and concomitantly larger yield for the interchain non-radiative species. The PB and PA decays of the film are shown in Fig. 8, the PA data being in accord with previous literature measurements [1]. In the context of our current measurements, it is surprising that the film PA and PB both have substantial long-lived tails in addition to a fast initial decay component. Since the S_1 state is created with small yield, the long-lived component cannot be from T_1. We conclude *that both short and long decay components in the film PA and PB are predominantly from interchain species*, in agreement with the interpretation of previous work [1]. Further proof of this comes from the spectrum of long-lived PA in the film that is plotted along with the solution difference spectrum in Fig. 7. The excellent agreement between these is strong evidence for the assignment of the film PA spectrum as polaron pairs. Absorption detected magnetic resonance experiments suggest the polaron pair state absorbs at this wavelength as well [16], also in accord with our belief that the most prevalent species created in photoexcited MEH–PPV films and heavily aggregated solvents is polaron pairs.

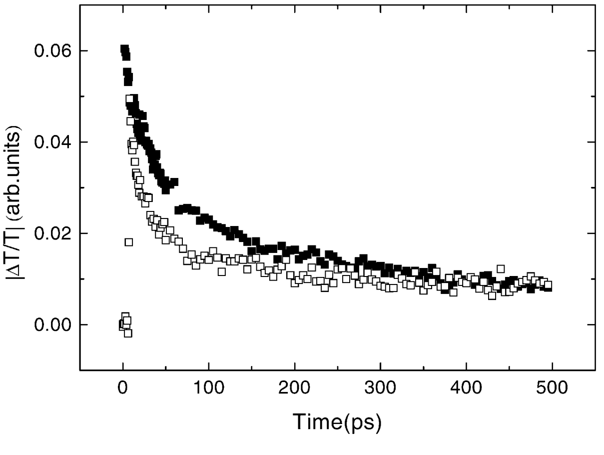

Fig. 8. Time decays of MEH–PPV film at 530 nm (open squares) and 850 nm (solid squares) where the 850 nm signal is inverted for comparison.

It remains to be understood why the decay dynamics for polaron pairs change so dramatically between the mixed solvent and the film. Qualitatively, we think the reason may simply be that the cluster size is small enough in solution that most photogenerated charge pairs cannot get very far apart. This type of explanation is in the spirit of the model of diffusive recombination dynamics of geminate polaron pairs posited by Bassler and Ries [19]. In the small clusters found in solution, the average recombination time is, therefore, more rapid than in films. The magnitude of long-lived “back-transfer” PL observed in time-correlated photon counting experiments [13] done on MEH–PPV in 1:1 mixtures of toluene/hexane is consistent with the absence of significant long-lived PA due to polaron pairs in the present experiments on analogous solutions.

4. Conclusions and implications

Transient absorption data on deliberately aggregated MEH–PPV in solution provide us with a self-consistent picture of the photophysics that is compatible with previous work on MEH–PPV films and solutions. We have accounted for the reduction of PL quantum yield in solutions of aggregated MEH–PPV, and identified the PA associated with the responsible competing pathway. We have demonstrated that the alternative pathway is formation of interchain species and assigned them as polaron pairs on the basis of their spectrum and the sensitivity of their recombination dynamics to environment. These polaron pairs form on a subpicosecond timescale. *Their high quantum yield explains recent observations of rapidly formed charged species characterized by infrared active vibrations* [4,20] and does not reflect small exciton binding energy nor is it the result of non-linear excitation processes [21]. In fact, we see that the excitons that do not ionize on the subpicosecond timescale while they are hot will form stable intrachain excitons that have large binding energy compared to *kT* and will not further dissociate into charge pairs [22]. We predict that rapid formation of infrared active vibrations characteristic of charged species [23] will not be observed in large yield for conjugated polymers in dilute solution with good solvents. The intrachain excitons formed after relaxation decay exponentially in about 300 ps, primarily to the ground state, via fluorescence or internal conversion. A small fraction (≈5%) intersystem cross to form triplet states.

We find that the polaron pairs formed in solution aggregates nearly all decay directly to the ground state within the first 50 ps after excitation. The existence of an efficient process involving polaron recombination to form ground states directly has important implications since polaron pair association is the essential process required to from excited states in organic light-emitting diodes (LED). It has been commonly assumed that the result of charge recombination is either excited singlet or triplet states and usually hypothesized to occur with statistical branching ratio [24]. *To the extent that there are other pathways such as direct formation of ground states, electroluminescence will be even more severely limited than has been thought previously in the molecular systems where it is prevalent.* While creation of polaron pairs by photoexcitation is certainly not identical to polaron recombination in light-emitting devices, it would appear to be a reasonable model. On the other hand, we already know that in some systems, formation of singlet excited states in LEDs must occur with high branching ratio since the LED is very efficient [25]. It will be interesting to see whether MEH–PPV is unusual in this regard.

We observe much more rapid decay dynamics for most of the polaron pairs in solution aggregates as compared to films. This may be the result of constrained diffusion in the relatively small polymer clusters formed in solution. Alternatively, it may be due to increased chain flexibility in solution that allows the polymer to assume configurations favorable for recombination. In future work, we hope to vary the size of the aggregate and observe how this affects the bleaching recovery dynamics.

Acknowledgements

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