

The role of long-lived dark states in the photoluminescence dynamics of poly(phenylene vinylene) conjugated polymers. II. Excited-state quenching versus ground-state depletion

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The two pulse fluorescence bleaching experiments reported in an earlier paper [J. Chem. Phys. **117**, 454 (2002)] are reanalyzed in the context of additional experiments. The fluorescence bleaching observed in that paper was originally ascribed to ground-state depletion. By analyzing the absorption saturation behavior and the magnitude of the pump-probe signal, we find that the absorption cross section of poly(phenylene vinylene) at 400 nm is two orders of magnitude too small to significantly deplete the ground state given the pump fluences used in that experiment. Instead, the observed depletion is due to a combination of exciton-exciton annihilation at early times and dark state luminescence quenching at later times. Different experiments have different sensitivities to the fluence-dependent quenching, with time-resolved experiments like transient emission and fluorescence decay time consistently underestimating the exciton-exciton annihilation rate. Experiments that measure the integrated fluorescence, such as fluorescence saturation and bleaching, result in a consistent value for the exciton-exciton annihilation constant of $6 \times 10^{-9} \text{ cm}^3/\text{s}$, while the dark state quenching constant is estimated to be at least $1.2 \times 10^{-8} \text{ cm}^3/\text{s}$. Indirect evidence based on the wavelength and sample dependence of the dark state formation suggest that the dark states are charge-separated polarons. The relatively large quenching constants are consistent with what has been observed in other conjugated polymers and suggest that the long-lived dark states in particular are effective quenchers, capable of quenching thousands of surrounding chromophores. © 2003 American Institute of Physics. [DOI: 10.1063/1.1540093]

I. INTRODUCTION

The photophysics of conjugated polymers is an area of active investigation due to their potential applications in light-emitting diodes and solar cells. The excited state structure of these materials is very complex, with several different types of states accessible via photoexcitation, including singlet excitons, charge-separated states, and triplet excitons. In a recent paper,¹ hereafter referred to as Paper I, we studied long-lived dark states in the conjugated polymer poly(phenylene vinylene) (PPV). In that work, we found that a preceding pump pulse could deplete the fluorescence excited by a subsequent probe pulse, and that by varying the delay between the pulses we could obtain information about the formation dynamics of long-lived dark states in the polymer. In the analysis of those experiments, the underlying assumption was that the physical origin of the fluorescence decrease was the depletion of the initial ground-state population by the pump pulse. In the present work, we investigate this process in more detail and come to the conclusion that ground-state depletion plays a negligible role. Instead, we find that both exciton-exciton annihilation (EEA) and dark state luminescence quenching are responsible for the observed decrease in the probe fluorescence signal. This new mechanism of depletion changes the conclusions of Paper I and requires a revision of our estimate that 10%–40% of the initially excited

chromophores end up in long-lived dark states. In reality, the fraction of initial excitations that remain as long-lived quenchers, most likely polarons, is smaller by an order of magnitude. But because these quenchers have an extremely large quenching rate, they still have a significant effect on the total fluorescence emitted from the sample even at relatively low concentrations.

The goal of the present work is twofold: First, to show that our earlier assumption about the origin of fluorescence bleaching in Paper I was mistaken, and second, to show that luminescence quenching by both excitons and dark states is significant even at relatively low ($\sim 1 \mu\text{J}/\text{cm}^2$) light intensities where the dynamics appears to be unaffected. We begin by directly extracting a value for the absorption cross section of a PPV chromophore at 400 nm ($\sigma_A^{400 \text{ nm}}$) from transient absorption and absorption saturation experiments. We find that the $\sigma_A^{400 \text{ nm}}$ of PPV is too small by a factor of 100 to explain the bleach depths observed experimentally, using our previous assumption that ground-state population depletion by the pump pulse is the mechanism of fluorescence bleaching. An alternative mechanism for the pump-induced fluorescence depletion is that the excitons created by the pump beam can interact with those excited by the probe beam. We find that different experiments have different sensitivities to the EEA process, but that a value for the EEA rate of $\gamma = 6 \times 10^{-9} \text{ cm}^3/\text{s}$ gives a satisfactory fit to both the bleaching data and the fluorescence yield data, while the decay rates of the fluorescence and transient emission predict a smaller γ .

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The new information available from this analysis is a value for γ_d , the quenching probability of the long-lived dark state, of $1.2 \times 10^{-8} \text{ cm}^3/\text{s}$. This large quenching rate, along with indirect evidence from the wavelength and sample dependence of the bleaching, suggests that the most likely candidate for the long-lived, fluorescence quenching dark state is a charge-separated polaron.

II. EXPERIMENT

The PPV samples are prepared via the precursor polymer route described previously.² The precursor polymer with a tetrahydrothiophenium leaving group is synthesized and dissolved in methanol. Films are spin cast on a 1 mm glass substrate and thermally converted under vacuum ($<30 \text{ mTorr}$) at 300°C for 3 hours. The resulting films have optical densities of around 0.5 at 400 nm. The sample is mounted in a cryostat held under vacuum. All the experiments are done at room temperature.

Excitation pulses are generated by second harmonic generation of the 800 nm output from a 40 kHz regenerative amplifier (Spectra Physics, Spitfire) in a 0.4 mm BBO crystal.¹ After second harmonic generation, the 800 and 400 nm pulses are separated with a dichroic filter. The 400 nm pulses are used as bleaching pulses and the 800 nm pulses are frequency-doubled again in a 0.1 mm KDP crystal to generate probe pulses which are delayed using two retro-reflectors. The pump and probe beams are generated using separate doublers because of the different path lengths and beam diameters used in the experiment, necessary to ensure that the probe always sees a uniform pump fluence. The first retro-reflector is mounted in a home-made 1 m travel motorized delay stage controlled by a personal computer and the second retro-reflector is mounted in a 5 cm delay stage (ATS03005, Aerotech). Both the bleaching and probe beams are focused onto the sample with a 15 cm lens. The spot sizes of bleaching and probe beams are 50 and 20 μm [full width at half maximum (FWHM)], respectively. Each beam profile is measured by translating a razor blade across the focus and fitting the data to a Gaussian profile. The peak fluence is then calculated by dividing the total pulse energy by $\pi\sigma^2$, where σ is the 1/e point of the fitted Gaussian. For two beam experiments, the average pump fluence seen by probed sample region is calculated by convolution of the two beam profiles. Since the probe beams are always at least a factor of two smaller than the pump beams, this results in a decrease of the effective probe fluence from the peak fluence of 10%–20% at most. The combination of spot sizes and fluences used in these experiments are well below the levels where amplified spontaneous emission has been observed in phenylene–vinylene polymers, and no signs of spectral narrowing were observed.^{3,4} There was no effect of laser repetition rate on the observed dynamics, from 40 to 4 kHz.

A calcite polarizer is used to purify and set the polarization of the bleach pulses to the magic angle (54.7°) with respect to the probe beam, although no polarization dependence of the bleaching signal was detected in later experiments. For bleach recovery experiments, the 400 nm probe beam is chopped with a mechanical chopper, and the fluorescence due to the probe is collected with a 5 cm lens from

the back side of the sample at an angle of about 30° from the sample surface normal. The fluorescence is detected with a photomultiplier tube and the signal is fed into a lock-in amplifier (SRS SR830). The probe fluence is about $2 \mu\text{J}/\text{cm}^2$.

Degenerate transient pump–probe experiments are performed using the same set-up for the bleach recovery experiment. The polarization of the pump beam is set to the magic angle with respect to the probe beam. After the sample, the probe is passed through a film polarizer set at 90° to the pump polarization to remove pump beam scattering noise. In this way unwanted rotational effects are avoided and the noise from pump scatter can be minimized. Silicon photodiodes are used to detect both the probe and reference 400 nm pulses. Standard lock-in detection and subtraction techniques are used to improve the signal-to-noise ratio. Low fluence pump–probe and bleach recovery experiments are done with the long delay stage with a pump fluence of $2 \mu\text{J}/\text{cm}^2$. No sign of a measurable coherent artifact, which would occur within the pulse duration and be sensitive to the relative polarizations of the pump and probe beams, was observed. Fluence dependence decay experiments are done with short delay stage. The fluence of the pump beam is varied from 2 to $40 \mu\text{J}/\text{cm}^2$ using neutral density filters.

Picosecond time-resolved fluorescence spectra are measured using a streak camera (Hamamatsu, streak scope C4334). The samples are excited with the beam coming in at an angle of about 20° from the sample surface normal. The fluorescence was collected normal to the sample surface, collimated and focused into a spectrometer (Spectra Pro-150) with a 150 grooves/mm grating to disperse the spectrum before the streak camera. The instrumental response time of this measurement is about 25 ps in a 1 ns sweep window.

III. RESULTS

Figure 1 shows a typical bleaching experiment, where an initial pump pulse depletes the fluorescence signal due to a following probe pulse. For the trace in Fig. 1, the pump fluence is $3.3 \mu\text{J}/\text{cm}^2$, corresponding to an excitation density of $6.6 \times 10^{17}/\text{cm}^3$ given the thickness of the PPV (50 nm) film and its transmission at the 400 nm excitation wavelength (50%). At this fluence level there was no discernible intensity dependence in the shape of the short time decays in our pump–probe experiments,⁵ and this is why we had earlier assumed that intensity-dependent effects like EEA could be safely neglected. Under this assumption, we attributed the bleaching to depletion of the ground state by the pump pulse which left less population to be excited by the following probe pulse. Further experiments have caused us to re-evaluate this assumption. The inset to Fig. 1 shows a comparison of the power dependence of the bleaching of PPV and the laser dye Coumarin 307 in dilute methanol. In order to deplete the fluorescence of the dye in solution by a similar amount requires on the order of $1 \text{ mJ}/\text{cm}^2$, two orders of magnitude larger than that required by PPV. Using a simple rate equation approach⁶ (where we assume that T_2 and excited-state vibrational relaxation are rapid relative to the pulse duration, allowing us to neglect stimulated emission), it is straightforward to show that the ground-state population

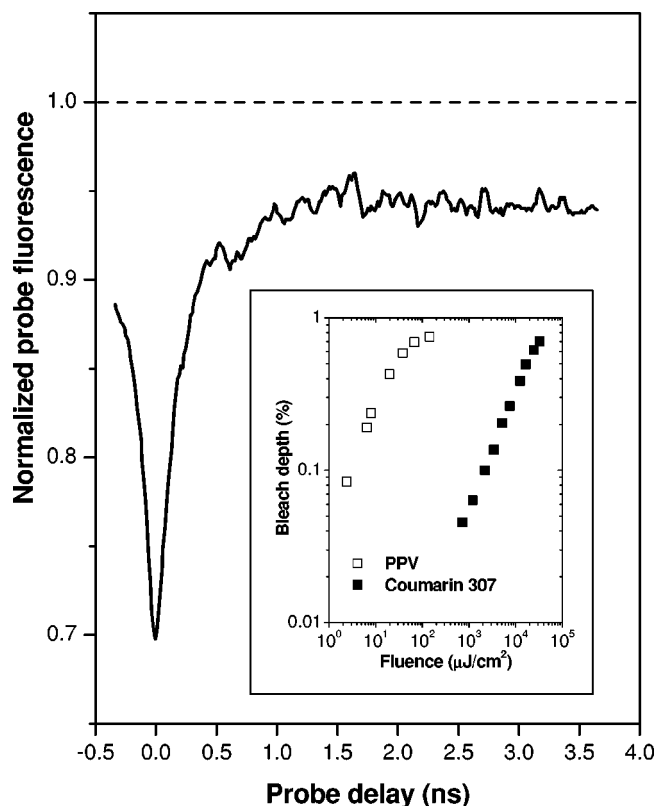


FIG. 1. Recovery time trace of PPV's fluorescence excited by a probe pulse following excitation by a pump pulse with a fluence of $3.3 \mu\text{J}/\text{cm}^2$. The inset shows the fluence dependence of the bleach depth at 0 delay for both PPV and Coumarin 307 in methanol.

left after a pump pulse is proportional to both the absorption cross-section σ_A and the pump fluence ϵ_{pu} , where ϵ_{pu} is in terms of photons/ cm^2

$$N_{\text{gr}}(0_+) = N_{\text{gr}}(0) \exp[-\sigma_A \epsilon_{\text{pu}}] \approx N_{\text{gr}}(0) [1 - \sigma_A \epsilon_{\text{pu}}]. \quad (1)$$

Here $N_{\text{gr}}(0)$ and $N_{\text{gr}}(0_+)$ are the ground-state populations before and after the excitations respectively. In these experiments, we measure the pulse energy and spot size, so we can estimate ϵ_{pu} to within an uncertainty of a factor of 1.5. For the experiments shown in Fig. 1, the fluence $\epsilon_{\text{pu}} = 6.6 \times 10^{12}$ photons/ cm^2 , which means that a σ_A on the order of 10^{-14} cm^2 is needed to achieve the observed bleach. Such a large cross section could only result from aggregation of PPV chromophores, and in the case of PPV such an aggregate would have predominantly H character, leading to a blue-shifted, enhanced absorption but no superradiance, as in the case of J-aggregates. Experimental studies of aggregates of small PPV oligomers by Oelkrug *et al.*^{7,8} clearly show H-aggregate type absorption, and σ_A 's of a similar magnitude have been observed in molecular J-aggregates.^{9,10} Such an enhanced cross section would be evidence of intermolecular electronic coupling and delocalization in PPV. An enhancement of the effective oscillator strength by a factor of 100 would suggest an absorbing state delocalized over ~ 100 chromophores.¹¹

In order to test this hypothesis, we performed other experiments to independently measure σ_A . In materials like

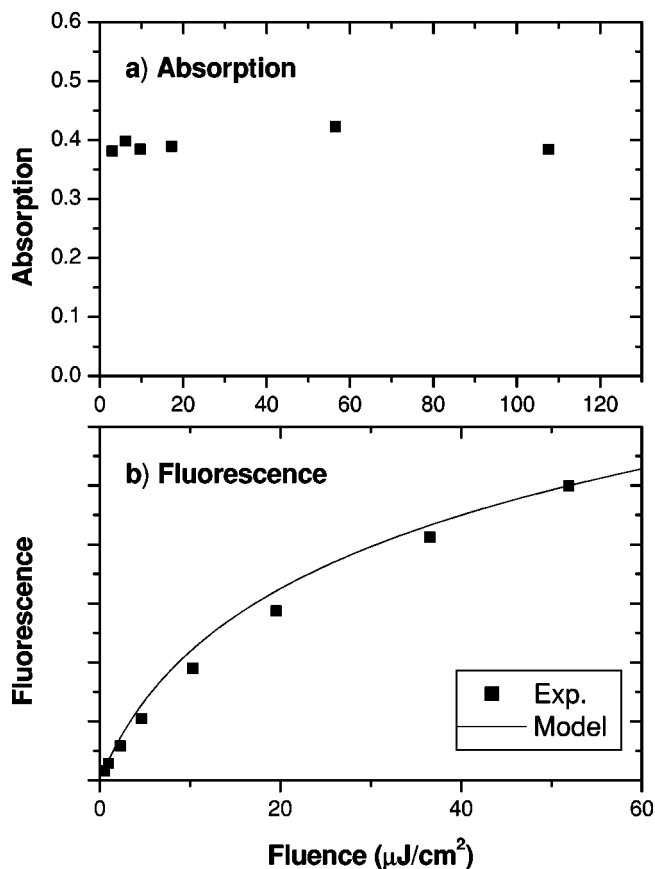


FIG. 2. (a) Fluence dependence of PPV absorption at 400 nm. (b) Fluence dependence of PPV fluorescence after excitation at 400 nm. The solid line is the calculated dependence using Eq. (4) and a model with $k_{\text{fl}}^{-1} = 180$ ps and $\gamma = 6 \times 10^{-9} \text{ cm}^3/\text{s}$.

PPV, the absorption coefficient $\alpha = \sigma_A N$ obtained from a linear absorption measurement does not necessarily yield a value for σ_A since the density of chromophores N is generally unknown as well. To measure σ_A directly, a nonlinear experiment is required. Figure 2 shows the simplest such experiments, namely single pulse absorption and fluorescence saturation measurements.⁶ For $\sigma_A = 10^{-14} \text{ cm}^2$, the absorption of an optically thin system is expected to saturate at fluences below $100 \mu\text{J}/\text{cm}^2$, again due to depletion of the ground state, and the effective absorption would decrease as the pulse saturates the transition. Figure 2(a) shows that PPV is not a particularly effective saturable absorber. Even at fluences in excess of $100 \mu\text{J}/\text{cm}^2$, where we begin to see photodamage in the material, the percent transmission remains constant. A different way to directly measure the absorption cross section is to analyze the magnitude of the transient absorption change due to the pump pulse. The fractional change of the probe transmission at the pump wavelength, again neglecting stimulated emission and hole-burning effects, is given by

$$\frac{\Delta T}{T} = T^{\exp(-\sigma_A \epsilon_{\text{pu}}) - 1} \quad \text{at } t=0. \quad (2)$$

Equation (2) has been used previously to analyze pump-probe signal levels in experiments on different conjugated polymers.¹² The underlying assumption in our application is

that the excited-state population has already shifted out of the probe window, and this is certainly the case in PPV, where the stimulated emission has been observed to shift to 525 nm within 50 fs of excitation.⁵ If the ground-state hole also shifts on this time scale, the transmission would partially recover and our estimate for σ_A would be too small. Spectrally resolved pump-probe data on PPV at room temperature shows no sign of a bleach that is changing its shape on this time scale, however.^{5,13} Excited-state absorption would also make the bleach appear smaller than it really is, although there is no sign of such an absorption at the fluence levels used in this experiment.⁵ Nevertheless, our estimates of σ_A should be taken as a lower bound. Both T and ΔT are measured in a pump-probe experiment, and typical data are shown in Fig. 5. At 400 nm, we find a peak $\Delta T/T$ of 2×10^{-4} with an excitation density of $6.6 \times 10^{18}/\text{cm}^3$, which yields a $\sigma_A = 6 \times 10^{-17} \text{ cm}^2$, similar to what has been obtained for other conjugated polymers in solution.¹⁴ This value may underestimate the absorption cross section, since it does not take the possibility of excited state absorption into account, which would cancel out part of the bleach and make it appear too small. From the data in Fig. 5, we know that there is the possibility of induced absorption at this wavelength. Nevertheless, it is unlikely that such an absorption would be strong enough to almost exactly cancel the induced transmission. The low value for σ_A is also consistent with the lack of absorption saturation in Fig. 2(a), since this value for σ_A requires a fluence of $10^{15}/\text{cm}^2$ or $1 \text{ mJ}/\text{cm}^2$ to generate a 10% saturation. In both cases, using experiments designed to specifically measure σ_A , the large cross section predicted by our previous analysis of the bleaching experiments in Paper I is not observed.

A final observation is that no anisotropy in the bleaching could be detected. If the pump pulse was preferentially depleting molecules oriented along its direction of polarization, then we would expect a probe pulse polarized orthogonal to the pump would see less fluorescence depletion. At low temperatures, PPV has a time-independent fluorescence anisotropy of ~ 0.2 , which shows that no significant reorientation of the transition dipoles occurs during the fluorescence lifetime. The amount of bleaching at short delays depends only on pump power, however, and not on its polarization relative to the probe. Similar bleaching experiments on Coumarin 307 did show the expected enhancement of the bleach when pump and probe polarizations were parallel, suggesting that the mechanism of bleaching is not the same in these two cases.

A more indirect way to measure the amount of excited-state population excited by a pump pulse is to measure the total amount of fluorescence from the sample. As the pump fluence increases, eventually all the molecules are placed in the excited state and increasing the pump power yields no increase in the fluorescence. Such an experiment is shown in Fig. 2(b). Here we see a dramatic rollover in the fluorescence, even at very low pump fluences of $1 \mu\text{J}/\text{cm}^2$. A similar rollover is observed in Coumarin 307 (inset) but at much higher fluence levels, consistent with its measured absorption cross section of 10^{-16} cm^2 at 400 nm. The origin of the fluorescence saturation in PPV is different from that ob-

served in the laser dye, and has been ascribed by previous authors to exciton-exciton annihilation (EEA).¹³

Efficient EEA has been demonstrated previously in PPV and a variety of conjugated polymers. In the simplest analysis, the evolution of the singlet exciton population is governed by the kinetic equation

$$\frac{dN_{\text{ex}}}{dt} = -(k_r + k_{nr})N_{\text{ex}} - \gamma N_{\text{ex}}^2 = -k_{\text{fl}}N_{\text{ex}} - \gamma N_{\text{ex}}^2, \quad (3)$$

where k_r is the radiative decay rate, k_{nr} is the sum of all nonradiative rates that couple the exciton to the ground state, and γ is the bimolecular annihilation constant. k_{fl} is the total rate of decay from the singlet exciton state, which is measured in a fluorescence lifetime experiment. More sophisticated theories¹⁵ take the spatial depletion and diffusion of excitons into account; in this case γ becomes time-dependent, i.e., $\gamma = \gamma'/\sqrt{t}$. In this paper we consider only the simplest case described by Eq. (3), since it is sufficient to model most of the data presented here. Estimates of γ in PPV at room temperature range from 3×10^{-9} to $4 \times 10^{-8} \text{ cm}^3/\text{s}$, with the lower values resulting from intensity dependent pump-probe measurements¹⁶ and the larger values from fluence dependent fluorescence yields like those in Fig. 2(b).¹⁷ Using Eq. (3), the analytical expressions for the amount of integrated fluorescence, the decay of the excited-state population, and the depletion of the fluorescence excited by a weak probe beam (whose contribution to EEA is negligible) are as follows:

$$N_{\text{ex}}(t) = \frac{N_{\text{ex}}(0)e^{-k_{\text{fl}}t}}{1 + N_{\text{ex}}(0)\frac{\gamma}{k_{\text{fl}}}(1 - e^{-k_{\text{fl}}t})}, \quad (4)$$

$$\text{Fl} = \int_0^\infty N_{\text{ex}}(t)dt = \frac{1}{\gamma} \ln \left(1 + N_{\text{ex}}(0)\frac{\gamma}{k_{\text{fl}}} \right), \quad (5)$$

$$\frac{\Delta \text{Fl}}{\text{Fl}} = \frac{\text{Fl}(\text{without pump}) - \text{Fl}(\text{with pump})}{\text{Fl}(\text{without pump})} = 1 - \frac{\ln \left(1 + N_{\text{ex}}(0)\frac{\gamma}{k_{\text{fl}}} \right)}{N_{\text{ex}}(0)\frac{\gamma}{k_{\text{fl}}}}. \quad (6)$$

Figures 2(b) and 3 show the power dependences of the fluorescence saturation and bleach depth respectively, along with calculated curves using Eqs. (5) and (6) with $\gamma = 6 \times 10^{-9} \text{ cm}^3/\text{s}$, $k_{\text{fl}}^{-1} = 180 \text{ ps}$. In both cases, this simple model fits the data reasonably well.

While this model does a good job of describing the behavior of quantities related to the integrated fluorescence, its ability to model the excited-state dynamics of PPV, as predicted by Eq. (4), is less satisfactory. For example, pump-probe data at 600 nm, which overlaps the stimulated emission and should directly reflect $N_{\text{ex}}(t)$, are not well-described by Eq. (4). The data, along with curves predicted using Eq. (4) and the values used for the data in Figs. 2(b) and 3, are shown in Fig. 4. We emphasize that the calculated curves in Fig. 4 are generated without any fittable param-

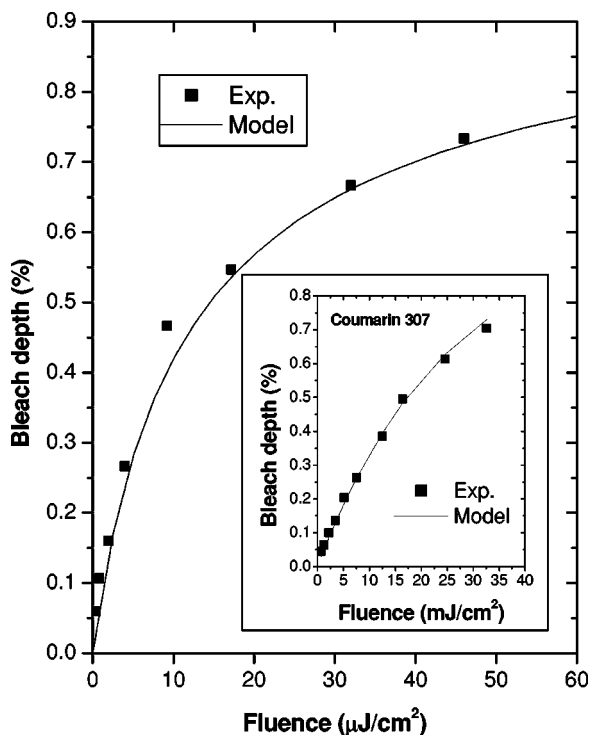


FIG. 3. Fluence dependence of PPV double beam fluorescence bleach experiment at 0 delay. The solid line is a model curve is with $k_{fl}^{-1} = 180$ ps and $\gamma = 6 \times 10^{-9}$ cm³/s. The inset shows the same experiment with Coumarin 307 in methanol solution, and in this case the solid line represents the calculated ground-state depletion due to an absorption cross-section 2.0×10^{-17} cm², which is obtained directly from the absorption spectrum.

eters: γ and k_{fl} are both obtained from separate experiments (the fluorescence saturation and decay, respectively). Not surprisingly, the curves do not give a quantitative match to the data. In particular, the standard EEA model predicts a faster decay at low powers and at short times than is observed experimentally. This lack of fluence dependence at fluences below $20 \mu\text{J}/\text{cm}^2$ was the basis of the assumption in Paper I that EEA did not affect those experiments. In reality, extracting γ from pump-probe data at any wavelength is problematic due to the complex nature of PPV's spectroscopy. Spectral shifting, nonexponential decays, and excited-state absorptions, some of which may be intensity dependent, can complicate the interpretation of these measurements.^{5,18-20} The data at 400 nm, in Fig. 5, show a much stronger intensity dependence which is well-fit using Eq. (4) and a $\gamma = 2 \times 10^{-8}$ cm³/s. But in this wavelength range there is an induced absorption in addition to the bimolecular decay which leads to a faster apparent decay of the induced transmission, as can be seen in the highest intensity trace. The best experiment to compare the data with is the fluorescence decay itself, which is free of artifacts resulting from excited-state absorption. This data is shown in Fig. 6, along with calculated curves using both $\gamma = 6 \times 10^{-9}$ cm³/s and $\gamma = 3 \times 10^{-9}$ cm³/s. It is clear that the γ used to describe the total fluorescence saturation overestimates the intensity dependence of the fluorescence decay, as has been observed previously.¹⁷ Although the γ 's derived from our time domain data and from our integrated fluorescence data differ only by a factor of 2, it does indicate that a quantitative description

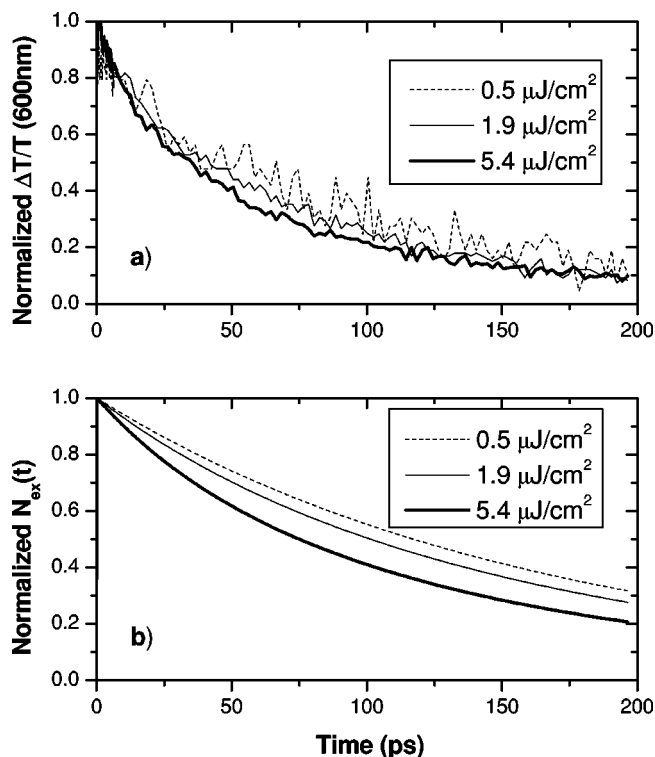


FIG. 4. (a) Normalized pump (400 nm)-probe (600 nm) data from PPV using pump fluences of 0.5, 1.9, and $5.4 \mu\text{J}/\text{cm}^2$. (b) Calculated decays using Eq. (4) with $k_{fl}^{-1} = 180$ ps and $\gamma = 6 \times 10^{-9}$ cm³/s. Note that no adjustable parameters are used to calculate these curves: k_{fl}^{-1} and γ are obtained from the measured fluorescence decay and fluence dependence of the fluorescence, respectively.

of EEA in PPV must be more complicated than the simplest approach embodied in Eq. (3).

In addition to excitons quenching each other at fluences below the level where it is discernible in the pump-probe or fluorescence decay, we also observe a long-lived quenching effect, due to an unidentified dark state. In Paper I, we analyzed the formation of this dark state using a very simple three-level kinetic model. A more realistic, quantitative description of dark state formation and decay in PPV is difficult because there are many possible dark states (polarons, excimers, etc.) whose formation rates and yields are largely unknown. The assumptions underlying the analysis in Paper I are clearly not valid, and rather than try to extend that analysis, we simply assert that the long-lived dark states are formed within the lifetime of the luminescent exciton, but after it has decayed they undergo no further dynamics, either relaxation or formation, on the 6 ns time scale of the experiment. This is clearly the case from the data shown in Fig. 1. The observed long-time bleaching is then due to two unknown quantities, γ_d , the bleaching rate constant, and N_d , the unchanging density of dark states. A simple way to illustrate this is if we assume that the probe pulse is weak enough that EEA between its own excitons can be neglected, in which case the exciton population due to the delayed probe pulse evolves according to

$$\frac{dN_{ex}^{pr}}{dt} = -(k_{fl} + \gamma_d N_d^{pu}) N_{ex}^{pr}, \quad (7)$$

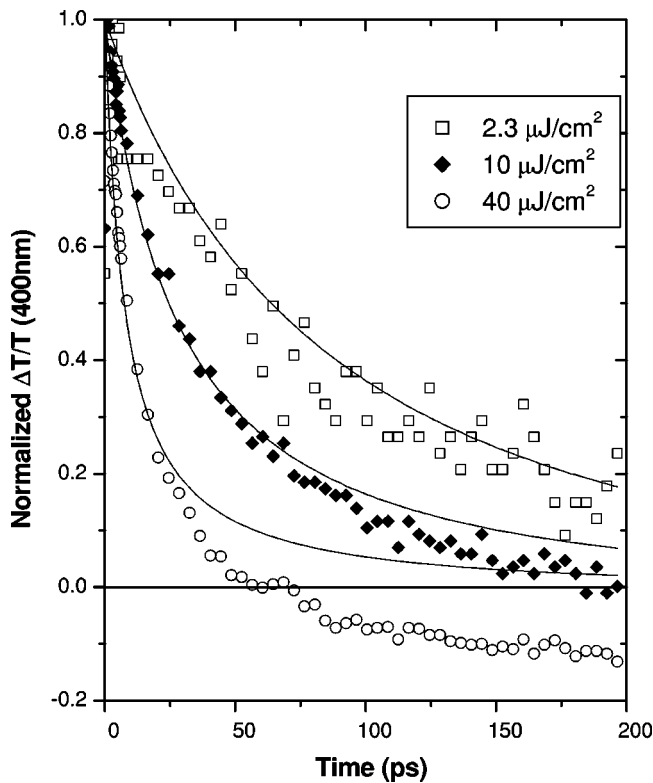


FIG. 5. Degenerate 400–400 nm pump–probe data from PPV using pump fluences of 2.3, 10, and 40 $\mu\text{J}/\text{cm}^2$. Symbols are experimental data and the solid lines are calculated using Eq. (4) and values of $k_{\text{fl}}^{-1} = 180$ ps and $\gamma = 2 \times 10^{-8}$ cm^3/s .

where N_d^{pu} is the population of dark states left after the earlier pump pulse. The change in fluorescence of the probe beam is then

$$\frac{\Delta \text{Fl}}{\text{Fl}} = \frac{\gamma_d N_d^{\text{pu}}}{k_{\text{fl}} + \gamma_d N_d^{\text{pu}}} \quad (8)$$

In these expressions, only k_{fl} is known from the fluorescence decay. We need a new experiment to estimate N_d , the number of initially excited species that end up in quenching dark states. We use the recovery of the 400 nm absorption at long delays as a way to estimate the fraction of initially excited chromophores that remain trapped in dark states after the luminescent singlet excitons have disappeared. If we follow the nanosecond decay of the low power 400–400 nm pump–probe signal at room temperature, whose early-time behavior is shown in Fig. 5, we find that the signal decays almost completely by 3 ns. By averaging the signal from 3 to 5 ns, we find that at most 2% of the initially excited chromophores remain trapped in a dark state in this period. It is these species that cause the 10% fluorescence bleaching at long delays seen in Fig. 1. The noise in this estimate is due to the very low residual absorption at these long delays and low fluence levels. As mentioned earlier, it is also possible that excited-state absorption masks part of the bleach, making it appear smaller than it should and causing us to underestimate the percentage of chromophores remaining trapped in the dark states. Neglecting such complications for the time being, we can use Eq. (8) to estimate the value of γ_d . Assuming an

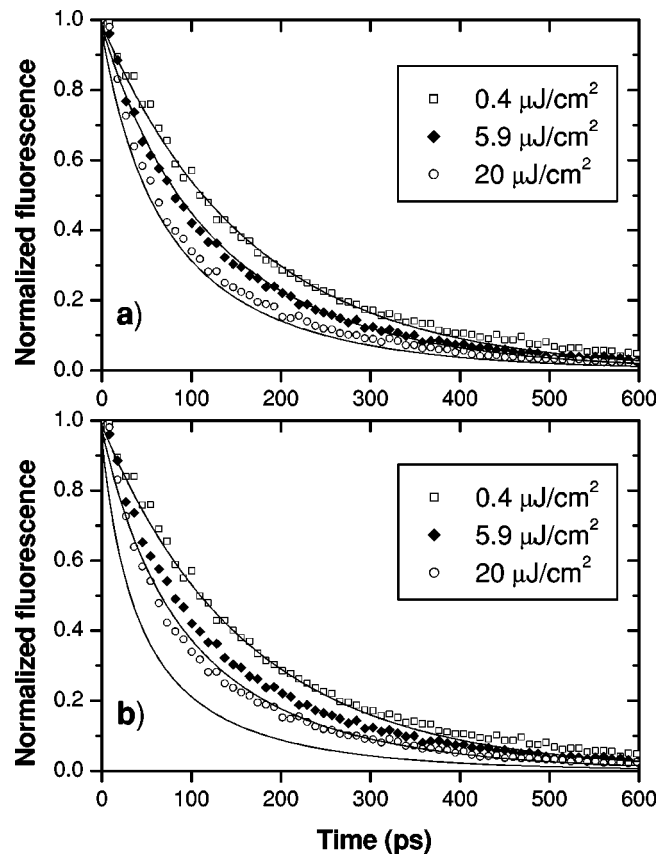


FIG. 6. Fluorescence decay traces of PPV measured with a streak camera using excitation fluences of 0.4, 5.9, and 20 $\mu\text{J}/\text{cm}^2$. Symbols are experiments and the solid lines are calculated using Eq. (4) and values of (a) $k_{\text{fl}}^{-1} = 180$ ps and $\gamma = 3 \times 10^{-9}$ cm^3/s and (b) $k_{\text{fl}}^{-1} = 180$ ps and $\gamma = 6 \times 10^{-9}$ cm^3/s .

initial density of excitons of $6.6 \times 10^{17}/\text{cm}^3$, $N_d = 1.3 \times 10^{16}/\text{cm}^3$ and k_{fl}^{-1} of 180 ps, we find that $\gamma_d = 1.2 \times 10^{-8}$ cm^3/s .

IV. DISCUSSION

The experiments in this paper demonstrate that the fluorescence bleaching in PPV is due to intermolecular interactions and quenching as opposed to true saturation behavior. Concerning the short-time quenching, which is due to EEA, the most striking observation is that even though time-resolved measurements like pump–probe and the fluorescence decay are not fluence-dependent at the 10 $\mu\text{J}/\text{cm}^2$ level, measurements that detect the integrated fluorescence, like the single and double pulse bleaching experiments, indicate that EEA is occurring to an appreciable extent. By taking into account errors in beam size measurements and noise in the fitting, we estimate the error in our calculated values of γ and γ_d to be on the order of 30%, less than the observed variation. This variation may help explain why the γ 's obtained from different measurements can vary so widely, although there may also be a dependence on differences in sample preparation between different groups as well.²¹ Using more complicated models for exciton–exciton annihilation, as discussed above, did not improve agreement between the two types of measurements. The physical origin of this dis-

crepancy is unclear, but it is possible that there is a fluence-dependent decay in the time-resolved experiments that is unresolved within our time resolution (100 fs). Such a decay could be the result of small domains within the material, within which excitons could annihilate each other very rapidly, or it could be the result of the instantaneous creation of quenching species along with the luminescent excitons. There is evidence that in addition to luminescent excitons, polarons can also be directly created upon photoexcitation of PPV,^{22,23} and polarons are expected to be quenching species (see below).

In our previous work, we discussed the physical origin and kinetics of the dark state. Briefly, we found no evidence for a large, rapid dark state formation time, but only for a slower process whose yield follows the temperature dependence of the singlet exciton lifetime. In this paper, we revise the actual numbers in the previous paper downward, so that the yield is approximately a factor of 10 lower than in Paper I. Furthermore, we can obtain an estimate, probably a lower bound, for the fluorescence quenching rate of the dark states, namely 1.2×10^{-8} cm³/s, which is comparable to or larger than the EEA rate of 6×10^{-9} cm³/s. Although we can estimate a luminescence quenching rate for the dark states, these experiments do not establish their identity. Possibilities include charge-transfer excimer states, polarons, and triplet states. All these species have been identified in PPV using photo-induced absorption and optical magnetic resonance.^{19,24}

Of these possibilities, quenching by charged polarons has received the most attention in the literature.²⁵ Early work by Friend and co-workers showed that long-lived photoexcitations could efficiently quench luminescence in partially converted PPV, where one would expect many defect centers to be present.²⁶ The most detailed studies of polaron–exciton interactions in fully conjugated polymers have concentrated on poly(phenylene) ladder polymers.^{27–29} These workers found a polaron quenching rate of 9×10^{-10} cm³/s, almost a factor of 10 lower than what we obtain for PPV. Other studies by the Vardeny and Barbara groups have identified efficient luminescent quenching by polarons in PPV derivatives like DOO-PPV,³⁰ aggregates of a porphyrin derivative³¹ and MEH-PPV.^{32,33} In the latter case,³² a Stern–Volmer quenching constant of 7×10^{-19} cm³ was obtained, which implied that a single charge could quench over a thousand surrounding chromophores. Our quenching constant γ_d is related to the Stern–Volmer constant K via

$$K = \frac{\gamma_d}{k_{\text{fl}}}, \quad (9)$$

and we find an even larger Stern–Volmer quenching constant of 2.2×10^{-18} cm³ for PPV. In both cases, quenching in PPV appears to be stronger than in these other polymers. This may be a consequence of the fact that the other polymers are functionalized with alkyl sidechains, while PPV has no sidechains and has significant crystallinity. In PPV the chromophores are more closely packed and polarizable, and this may make them more susceptible to quenching interactions like charge transfer. Alternatively, it may be that the singlet emission of PPV and the absorption spectrum of its radical

cationic or anionic polarons have better spectral overlap, leading to more efficient Forster energy transfer. Finally, our estimate of the dark state yield based on the 400 nm absorption recovery, is $\sim 2\%$, which is less than the 10% yield of polarons estimated by Miranda *et al.* based on transient infrared absorption.²² This estimate was based on the peak signal of an absorption that quickly decayed: After 20 ps, only about one-third of the original charges remained (Fig. 3 of Ref. 22). This decay leads to an effective yield of long-lived polarons on the order of 3%–4%, similar to what we observe in this paper.

There are two observations which provide indirect evidence that charged polarons are the dark states responsible for the long-time fluorescence quenching. First, from our previous work, we know that the probability of generating the dark state increases as the excitation wavelength decreases. This wavelength dependence among 300, 400, and 500 nm excitation is similar to that observed for photoconductivity in PPV, where the greater photon energy increases the exciton dissociation probability, although the exact amount of enhancement is still under debate.^{34–36} This is not conclusive evidence, however, since the triplet yield in PPV has also been found to be wavelength-dependent due to singlet exciton fission.³⁷ Second, the amount of quenching depends on the introduction of oxygen defects in a manner consistent with polaron generation. PPV samples exposed to oxygen and light are known to develop carbonyl defects that provide locations for enhanced charge separation, as measured by photoconductivity.³⁸ In samples which are deliberately photo-oxidized under air and room lights, we see a decrease in the fluorescence lifetime and a corresponding increase in the amount of long-time quenching. Both observations are consistent with an increase in the dark state formation rate at the expense of the excitons, suggesting that it is related to the charge separation which such defects enhance. A quantitative comparison of how the photoconductivity and the fluorescence quenching depend on the degree of photo-oxidation would help cement this connection.

The existence of EEA in our bleaching data, even at very low pump fluences, raises the possibility that the dark state may be generated by EEA itself, as opposed to being an intrinsic characteristic of the polymer. Experiments by several groups have interpreted large, power dependent absorptions in the near infrared as being due to charge creation and recombination after EEA.^{16,18} We have seen similar dynamics and power dependence in 400 nm pump–800 nm probe experiments. Such a mechanism would lead to a nonlinear dependence of the long-time bleach on pump fluence, however, which we do not observe. The relation of the induced absorption to polarons in conjugated polymers is also not absolutely clear. Recently, Gulbinas and co-workers shows that part (but not all) of the photo-induced absorption (PA) of ladder-type polymer at 1.9 and 2.1 eV are due to polarons.³⁹ Experiments on MEH-PPV under charge injection conditions, on the other hand, have resulted in the conclusion that polarons have no absorption in the range 0.5–1.8 eV.⁴⁰ Transient experiments on DOO-PPV by Vardeny and co-workers have led to the conclusion that the 800 nm induced absorption is due to in large part to the excitons.⁴¹ In Paper I, we

discussed the relation of the 800 nm induced absorption to the quenching states, and concluded that there was no easy way to relate the two observables, since the 800 nm absorption did have an appreciable decay on the 6 ns time scale, while the dark quenching state did not.

If the connection between the long-lived fluorescence quenching species and the polarons in PPV can be definitely established, then it opens up the possibility of using fluorescence to detect the dynamics of charged states in polymer samples in the absence of external fields, which can also quench the exciton fluorescence through field-induced dissociation in the absence of any charges.^{42,43} For example, the charge recombination rate in PPV is unknown, but is related to the nanoscopic charge mobility in the material. If the amount of fluorescence quenching is directly related to the amount of charged polarons in the sample, then this provides a highly sensitive way to follow the disappearance of those charges due to recombination or trapping.³² As the charges recombine, the quenching disappears and the fluorescence excited by the delayed probe pulse would recover to its initial value. A second point is that if the long-lived dark state does turn out to be a charged polaron, it has implications for electrically pumped luminescent organic devices like LED's and lasers. One of the goals in organic electronics is to increase carrier mobility and thus charge density in devices to obtain high brightness and possibly stimulated emission and lasing. As the charge density increases, however, the luminescence quenching may also increase, preventing large gains in fluorescence output. The role of charges in reducing the luminescence efficiency of small molecule devices has already been investigated to some degree,⁴⁴ and it is very possible that similar effects will limit polymer devices as well.

V. CONCLUSION

The main goal of Paper I was to describe the role of long-lived dark states in PPV, whose fraction we estimated using the amount of long-time fluorescence bleach, which was assumed to be due to ground-state depletion. In this paper the absorption cross section of PPV at 400 nm is measured directly and is found to be 6×10^{-17} cm², which is a factor of 100 smaller than that required to deplete the ground state by the amount observed in our experiments. We have reanalyzed our transient fluorescence bleaching data in Paper I and have found that the magnitude of the signal is consistent with EEA rather than ground-state depletion. The early-time bleaching signal is consistent with EEA, while the long-time behavior is due to a dark state with a quenching constant on the order of 1.2×10^{-8} cm³/s. Although our data alone is insufficient to conclusively determine the identity of the dark quenching states, the dependence of the bleach magnitude on sample preparation and on excitation wavelength are qualitatively similar to what is expected for polaron formation. This new analysis requires us to revise downward the value reported in Paper I for the dark state yield, but also provides new insights into the interactions between those dark states and the luminescent excitons in PPV and related polymers. The very effective luminescence quenching of this dark state, even at very low densities, suggests that it may be

a useful tool for the detection of such states. Unfortunately, this quenching may also limit the ultimate brightness of organic electroluminescent devices based on conjugated polymers.

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