The role of long-lived dark states in the photoluminescence dynamics of phenylene vinylene conjugated polymers

Sang-Hyun Lim, Thomas G. Bjorklund, Kevin M. Gaab, and Christopher J. Bardeen
Department of Chemistry, University of Illinois, Urbana, Illinois 61801

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The role of intermediate nonluminescent states in the relaxation of singlet excitons in the conjugated polymer poly(phenylene vinylene) (PPV) and its soluble derivative poly[(2-methoxy-5-hexyloxy-p-phenylene) vinylene] (MH-PPV) is investigated. Time-resolved luminescence and absorption measurements provide evidence for a long-lived, weakly emissive species in PPV at 17 K, in addition to the luminescent singlet state. Ground state recovery times at this temperature provide evidence that up to 40% of the initially excited chromophores end up in a state that does not relax back to the ground state on the 5 ns time scale of the experiment. As the temperature is raised from 17 K to 290 K, the redshifted emission disappears, the fluorescence decay becomes more rapid, and the magnitude of the long-time bleach decreases. These results can be understood in terms of a three-level model where the initially excited singlet state decays nonradiatively via two separate channels: thermally-activated direct relaxation to the ground state, and nanosecond relaxation into a third, long-lived dark state. As the temperature increases, the thermally-activated process increases at the expense of both the fluorescence and the intermediate dark state population. Using this model, a temperature-independent dark state formation time of 1.8 ns was found for PPV, and 1.1 ns for MH-PPV. Our data and modeling provide no evidence for a subpicosecond relaxation channel in the decay of the luminescent excitons in these phenylene vinylene polymers. © 2002 American Institute of Physics.

I. INTRODUCTION

Conjugated organic polymers are of interest both because of their practical applications and because of their novel electronic and optical properties. Since many potential applications of these materials involve their ability to convert electrical current into light and vice versa,1 the dynamics of the optically accessible states are of particular interest. The exact nature of these states, however, is still a subject of active debate.2 Poly(phenylene-vinylene) (PPV) is a prototypical conjugated polymer, and as such has been the subject of intensive study. The primary excited state in this polymer is a singlet exciton whose binding energy has been estimated to range from 0.06 eV3 to 0.3–1.0 eV.4–6 Once created, the luminescent exciton can either relax radiatively or undergo nonradiative quenching via thermally-activated exciton diffusion. This scenario is supported by measurements of the temperature-dependent fluorescence; as the temperature is lowered, the fluorescent lifetime and quantum yield both increase, consistent with activated exciton diffusion to quenching sites.7–9 But while the time-resolved fluorescence experiments tell us how quickly the luminescent exciton disappears, they do not reveal its subsequent fate. Possible pathways include direct relaxation back to the original ground state and/or relaxation into an intermediate state, with delayed ground state recovery. Such an intermediate would involve nonluminescent species like free charges, triplets, and excimers, all of which are expected to have much longer lifetimes than the singlet excitons. Observations of long tails in the fluorescence decay10 and delayed luminescence11,12 provide ample evidence for the existence of long-lived charge carriers and triplet excitons in PPV, although their relative importance in the overall luminescence yield is not well established. The simplest three level system that takes both direct relaxation to the ground state and relaxation through an intermediate state into account is illustrated in Fig. 1, where the luminescent S state can relax either to the ground state G or to the intermediate dark state D. The key to unraveling the dynamics of such a system is to measure both the dynamics and populations in two of the three states shown in the figure. Since some types of intermediate states, for instance free charge carriers, may limit the electroluminescence efficiency in actual organic light emitting diodes (OLEDs),13 this question is of practical interest as well.

The detection and quantification of dark states in condensed phase chemical systems is a challenging problem. Although these states should have unique transient absorption spectra, the assignment of the photoinduced absorption in PPV is not necessarily straightforward, and the oscillator strengths of these species are generally unknown. In this paper, we take a different approach to the study of such states in PPV and the related, soluble polymer poly[(2-methoxy-5-hexyloxy-p-phenylene) vinylene], abbreviated MH-PPV. Our experimental approach is to use a combination of time-resolved luminescence, absorption, and fluorescence bleaching recovery to measure the time-dependent populations in the luminescent singlet state S and the ground state G. The fluorescence bleach recovery experiment provides a straightforward way to detect the ground state dynamics of the luminescent molecules. While this combination of measurements cannot determine the identi-
ties of different types of nonluminescent intermediate states, it can assess the relative magnitude of their role in the photodynamics of the luminescent exciton, which is critical for OLED applications. We also study the dynamics as a function of temperature in order to examine the mechanisms of dark state formation and relaxation, and compare these dynamics to those observed for the singlet exciton probed by time-resolved fluorescence experiments.

Our results demonstrate that at low temperature, the early, intense emission due to singlet exciton states is followed by a weak, long-lived component, suggesting the existence of excimerlike states. The existence of long-lived, nonemissive states is confirmed by both the absence of a full recovery of the fluorescence bleach on a nanosecond timescale and the presence of a long-lived induced absorption in the near infrared. As the temperature increases, a decrease in the singlet state lifetime is accompanied by a drop in the fluorescence yield. The long-lived redshifted emission also disappears, while the amount of long-lived bleach in the fluorescence yield. The long-lived redshifted emission also decreases as well. The main nonradiative relaxation pathway for luminescent photoexcitations in room temperature PPV is not the formation of long-lived dark states, but rather direct relaxation to the ground state. Our results can be interpreted in terms of the three-level model in Fig. 1, where the temperature-dependent relaxation of the singlet exciton to the ground state determines both the luminescence yield and that of the dark states as well. From this data, we infer a dark state formation time of 1.8 ns in PPV and 1.1 ns in MH-PPV, where the formation of excimers is expected to be more favored due to packing considerations. An important result of this work is that direct relaxation of the luminescent exciton to the ground state is the dominant relaxation pathway in room temperature PPV. As the lifetime of the exciton increases at lower temperatures, it has more time both to emit fluorescence and to find other avenues of relaxation into long-lived dark states such as excimers and triplets. This mechanism is the simplest way to explain the combination of fluorescence and bleach recovery data and may help explain why these materials work reasonably well at elevated temperatures even though the exciton is subject to rapid nonradiative decay. Since this decay leads directly to the singlet ground state, as opposed to long-lived trapping states, there is less accumulation of species that would degrade device performance under steady-state excitation conditions.

II. EXPERIMENT

The PPV samples are prepared via the precursor polymer route described previously. The precursor polymer with a tetrahydrothiophenium leaving group is synthesized and dissolved in water. Films are spin cast on a 0.5 mm thin sapphire substrate and thermally converted under vacuum (<30 mTorr) at 300 °C for 3 h. The resulting films have optical densities of around 0.6 at 400 nm. The poly[(2-methoxy-5-hexyloxy-p-phenylene) vinylene] (MH-PPV) samples are synthesized via a Gilch polymerization procedure. In the latter case, continuum seed pulses are generated by focusing the 800 nm beam in a 2 mm sapphire plate and amplified in a 3 mm BBO (31°, Type I phasematching) pumped by the 400 nm pumping beam. The wavelength can then be tuned from 480 nm to 650 nm by changing the BBO crystal angle and the angle between the seed and the pump beams. In this experiment we generate 500 nm and 600 nm pulses, which are passed through interference filters (10 nm FWHM, Andover). For 300 nm excitation, the filtered 600 nm NOPA output is frequency doubled using 0.1 mm BBO.

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. A calcite polarizer is used to purify the polarization of the excitation beam. The fluorescence is collected using a second calcite polarizer at the magic angle (54.7°) polarization to avoid unwanted rotational effects. 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 excitation fluence is kept below 1 J/cm² at all the wavelengths to avoid high fluence effects such as the amplified spontaneous emission. The instrumental response time of this measurement is about 50 ps in a 5 ns sweep window.

Wavelengths of 300, 400, 500, and 600 nm are used for the bleach recovery pump pulses. A small fraction of the 400 nm beam is split from the original beam and used as a fluorescence excitation probe pulse. This probe pulse is delayed using a retroreflector mounted in a homemade 1 m travel motorized delay stage controlled by a personal computer. Both the bleaching and probe beams are focused onto the sample with a 15 cm lens. The spot sizes of bleaching and

![Figure 1](https://example.com/image1.png)

FIG. 1. Schematic of the 3-level model assumed in this paper. S is the singlet exciton state, D is the intermediate dark state, and G is the ground state. ke and km are rate constants for radiative and nonradiative decays from S to G. kd and k′d are relaxation rates from S to D and D to G, respectively.
probe beams are 40 and 20 μm FWHM, respectively. To test the reliability of the optical delay stage, a CCD camera is placed at the sample position to measure the deviation of the probe beam as the delay is scanned. When the probe is scanned over its entire 1 m travel range, the focal spot moves ~10 μm, well within the diameter of the pump spot. The fluences of the bleaching and probe beams are kept below 10 μJ/cm² to avoid high fluence effects. Even at these low powers, the pump pulse could deplete the probe fluorescence by up to 50% at short delay times. The 400 nm probe beam is chopped with a mechanical chopper, and the fluorescence by the probe is collected with a 5 cm lens from the front side of the sample at an angle of about 45° from the sample surface normal. It is then detected with a photomultiplier tube and the signal is fed into a lock-in amplifier.

In this way the ground state population by the probe fluorescence is measured after the bleaching occurs. To determine if thermal effects are distorting the bleach recovery experiment, we ran the experiment at a 5 kHz repetition rate with no observable change in the time-dependent shape of the signal. Changing the pulse energy by a factor of 4 in either direction also had no observable effect on the signal shape.

Transient pump–probe experiments are performed using the 1 m travel stage to delay the probe beam. Silicon photodiodes are used to detect both the probing and reference 800 nm pulses. Standard lock-in detection and subtraction techniques are used to improve the signal-to-noise ratios. The same 400 nm pump fluence (<10 μJ/cm²) is used as in the bleaching experiment, while the probe fluences are below 5 μJ/cm². At these fluence levels, the pump–probe traces do not have the rapid initial decay in the first 10 ps which is observed with higher pump fluences.

III. RESULTS

In earlier work, we examined the temperature dependence of PPV’s fluorescence decay, concentrating mainly on the first two nanoseconds of the decay. This early time decay was found to be thermally activated and was interpreted in terms of activated hopping to quenching sites. Over the first two nanoseconds, we found that the spectral shape of the emission was unchanged, in contrast to that of MH-PPV, which showed clear evidence of excimer formation during the same time interval. Further examination of the low temperature, longer-time PPV emission also shows an evolution in the spectral shape, from the sharp exciton emission to a redshifted, broadened spectrum similar to that observed in MH-PPV. Figure 2 shows the evolution of the spectrum at 17 K after excitation at 400 nm. Note that the long-lived excimer-type emission is <1% of the total emission at this temperature, and so makes a negligible contribution to the steady state luminescence. As the temperature is increased, the main fluorescence decay rate increases and the shapeless long-time emission component disappears completely, leaving only a very weak exciton emission at these long times, as seen in Fig. 3. The temperature dependence of the long time emission suggests that formation of the excimer (sometimes referred to as a self-trapped state) does not increase with temperature, contrary to what has been observed in some organic molecular crystals. These data confirm that at least one other state besides the luminescent exciton is accessible by photoexcitation in PPV.

In order to investigate the importance of long-lived, weakly emissive states in the luminescence dynamics of PPV, we performed a second type of time-resolved experiment to measure the ground state recovery in parallel with the fluorescence decay. The ground state recovery time is measured using a two pulse bleach recovery experiment, where the ground state depletion due to a “pump” pulse is manifested as a decrease in the amount of fluorescence excited by a trailing “probe” pulse. In many ways this experiment resembles a normal transient absorption experiment, except that by detecting only the integrated
fluorescence due to the probe, we are sensitive only to absorption events that result in fluorescence, i.e., from the ground to excited state. Complicating factors like excited state absorption do not affect the experimental observable, and the measurement is similar in this respect to a fluorescence depletion experiment.

In a simple system with two electronic states, the ground state recovery and the excited state decay rates should match each other. To check this, we performed a bleach recovery experiment on a fluorescent dye molecule, Coumarin 307, in methanol. The recovery time trace exactly matched the fluorescence decay time trace over a 7 ns time range, thereby confirming the reliability of our experiment.

PPV is a more complicated system than Coumarin 307 because it has at least two accessible excited states. The simplest possible analysis of the kinetics involves three states, as outlined in Fig. 1, whose rate equations are as follows:

\[
\frac{dN_s}{dt} = -(k_{nr} + k_e)N_s, \tag{1}
\]

\[
\frac{dN_g}{dt} = (k_{nr} + k_e)N_s + k_dN_d = (k_{nr} + k_e)N_s, \tag{2}
\]

\[
\frac{dN_d}{dt} = k_eN_s - k_dN_d = k_eN_s, \tag{3}
\]

where \(N_s\), \(N_g\), and \(N_d\) are populations of the singlet exciton state, the ground state and the dark state, respectively. \(k_{nr}\) and \(k_e\) are rate constants for nonradiative and radiative decays from the singlet exciton state to the ground state. \(k_{nr}\) and \(k_d\) are relaxation rates from the exciton state to the dark state and the dark state to the ground state. From the data below, we find that the lifetime of the dark state is longer than our experimental time scale, so we assume \(k_d \approx k_{nr}\). This leads to the approximate rate Eqs. (2) and (3). Using this condition, the time-dependent populations can be expressed as

\[
N_s(t) = N_s(0) \exp\left[ - (k_{nr} + k_e) t \right], \tag{4}
\]

\[
N_d(t) = \frac{k_e N_s(0)}{k_{nr} + k_e + k_e} \left( 1 - \exp\left[ - (k_{nr} + k_e) t \right] \right) = \frac{k_e N_s(0)}{k_{nr} + k_e + k_e} \left( 1 - \exp\left[ - (k_{nr} + k_e) t \right] \right), \tag{5}
\]

\[
N_g(t) = N_g(0) + \frac{(k_{nr} + k_e) N_s(0)}{k_{nr} + k_e + k_e} \left( 1 - \exp\left[ - (k_{nr} + k_e) t \right] \right), \tag{6}
\]

where \(N_g(0)\) is the population of each state just after the pump pulse and it is assumed that the dark state is not directly populated by the light pulse. Note that \(N_s(t)\) does not fully recover due to the above assumption of the long dark state lifetime. The normalized recovery time trace, \(S_{rec}(t)\), can be expressed as

\[
S_{rec}(t) = \frac{N_g(t) - N_g(0)}{N_s(0)} = \frac{k_{nr} + k_e}{k_{nr} + k_e + k_e} \left( 1 - \exp\left[ - (k_{nr} + k_e) t \right] \right). \tag{7}
\]

This function increases from zero to some fraction of unity and measures the fraction of initially excited chromophores that have returned to the ground state. At time \(t = 0\), the recovery function will be zero and the probe fluorescence will experience the greatest depletion, while at long times the probe fluorescence will see only a decrease due to the chromophores left in the long-lived dark states. It is straightforward to write \(S_{rec}(t)\) in terms of the normalized fluorescence decay, \(S(t)\),

\[
S_{rec}(t) = \frac{1}{1 - \frac{k_e}{(k_{nr} + k_e + k_e)} \left( 1 - S(t) \right)}, \tag{8}
\]

where \(S(t) = \exp\left[ - (k_{nr} + k_e + k_e) t \right]\). Within this model, we can simulate the bleaching recovery experiments with fluorescence decay data and a single parameter \(k_e\), which can be obtained from any single set of a bleaching recovery and a fluorescence decay data. After \(S_n\) decays to a negligible level (about 5 ns in our experiment), we find that

\[
S_{rec}(t \rightarrow \infty) = \frac{1}{1 - \frac{k_e}{(k_{nr} + k_e + k_e)}} \tag{9}
\]

where \(k_{nr} + k_e + k_e\) is the total fluorescence decay rate which can be measured from the streak camera data. We rearrange Eq. (9) and solve for \(k_e\), the relaxation time into state \(D\),

\[
\frac{1}{k_e} \equiv \frac{1}{(k_{nr} + k_e + k_e)} (1 - S_{rec}(t \rightarrow \infty)). \tag{10}
\]

Figure 4 shows a series of bleach recovery experiments on PPV using 400 nm pump and probe pulses over the temperature range 17–290 K. The pump–probe fluorescence signal is subtracted from the probe-only signal and the resulting trace is normalized and subtracted from 1.0 to generate the \(S_{rec}(t)\) curves. All the PPV data traces show three main features. First, there is a fast initial ground state recovery in

FIG. 4. Normalized recovery time traces of the ground state population, \(S_{rec}(t) = \left[N_g(t) - N_g(0)\right]/N_s(0)\), of PPV with 400 nm excitation at the temperatures from 17 K to 290 K.
<2 ns. This initial recovery should overlap the fluorescence decay measured with the streak camera, offset by a constant [see Eq. (7)]. Figure 5 shows the overlapped data, which proves that the initial recovery of the bleach is due to direct relaxation from the excited state to the ground state. Note that we have made no assumption as to whether the decays are exponential in this comparison. Second, even after most of the fluorescence has decayed, there exists a large bleach component which does not recover within our experimental time scale ~5 ns!. Even though the excimer-type emission spectra can be seen at these later times ~Fig. 2!, it should be pointed out that this emission still shows a slow decay that is not observed in bleach recovery experiments. So the longer-lived bleached states are likely composed of several different types of dark states in addition to the states observed directly through emission. After 5 ns at 17 K the emission decayed to <1% of its initial value, while only 60% of the initially excited ground state population has recovered. The remaining 40% of the excitations are left in states whose lifetimes are long relative to the 5 ns observation time of the experiment. The fraction of the long-lived dark states decreases by a factor of 2, from 40% at 17 K to 20% at 290 K. This parallels a factor of 4 decrease in the integrated fluorescence yield over the same temperature range. Using Eq. (10) and the temperature dependent fluorescence lifetime obtained from the streak camera measurements, we obtain the data in Table I. The dark state formation time is found to be 1.8 ns in PPV and is independent of temperature.

To further investigate the nature of these dark states, we have performed bleach recovery experiments at three different pump wavelengths while using 400 nm as the fluorescence probe. The data at 17 K is shown in Fig. 6. With 400 nm and 500 nm bleaching pulses, there is no difference in the $S_{\text{rec}}(t)$ dynamics, but with 300 nm the relative population of dark states increases significantly, from 40% to 70% of the initial excitations. One caveat is that the 300 nm bleaching pulse also photodamages the sample slightly in these experiments, leading to a 5% decrease in the total fluorescence over the course of a single experiment. It does appear, however, that high energy photons result in a larger population of nonemissive states, a conclusion also reached by previous fluorescence excitation and photoconductivity experiments.27,28 This wavelength dependence is not observed in the fluorescence decays. We perform the fluorescence decay experiment with 3 different wavelength excitation beams ~300 nm, 400 nm, and 500 nm!, but there is no discernible change in their decay time traces. Over the entire temperature range from 17 K to 290 K, all three fluorescence decays show identical decay traces.

![Table I. Rate constants from the modeling.](http://jcp.aip.org/jcp/copyright.jsp)
To examine whether the existence of long-lived dark states is unique to PPV, we also examined a soluble derivative of PPV, MH-PPV, where alkoxy groups have been placed at the 2 and 5 positions of the phenyl ring. PPV and MH-PPV have different microscopic morphologies. PPV tends to form a microcrystalline structure, whereas the alkoxy sidechains of MH-PPV prevent the formation of significant long-range order. The bleach-recovery dynamics of MH-PPV shown in Fig. 7 are similar to those observed for PPV, but the resulting $1/k_e$ formation time for the dark state is 1.1 ns as opposed to 1.8 ns. The data in Fig. 7 also show no discernible temperature dependence, which is the case for the fluorescence decay dynamics of this polymer as well.

As mentioned in the Introduction, the long-lived states whose existence is inferred from the bleach-recovery experiments should also give rise to induced absorptions. We have made measurements of the transient absorption in the near infrared, since earlier work has suggested that this spectral region reflects dark state dynamics. Transient absorption experiments in PPV polymers have variously assigned induced absorption at 800 nm to singlet exciton states, polarons, and charge-transfer excitons, and triplet excitons. It is worth noting that this experiment is highly sensitive to pump fluence, and even at the level of 10 $\mu$J/cm$^2$, where the initial $\Delta T/T$ is about $10^{-4}$, the initial decay rate will increase rapidly as the fluence rises. After 1 ns, however, the decay trace has virtually the same rate for pump fluences below 20 $\mu$J/cm$^2$ and its lifetime is $>5$ ns. After 400 nm excitation, our data at 800 nm, shown in Fig. 8, does not have the same rapid decay or temperature dependence seen in the fluorescence. At low fluence, the life time is extremely long ($>5$ ns), and it is possible that these transient 800 nm absorbing states are related to the dark states whose existence is inferred from the bleach-recovery experiments. The 800 nm absorption does not exhibit a 1.8 ns formation time, however, and has a measurable decay on this timescale, preventing us from directly linking it to the long-lived dark states inferred from the bleach-recovery experiments. One final point is that the long-time $\Delta T/T$ signal level at 800 nm decreases by about 50% as temperature increases from 17 K to 290 K, following the same trend as the dark state yield.

IV. DISCUSSION

A comparison of the fluorescence decay dynamics with the ground state recovery dynamics in PPV confirms the existence of at least one long-lived dark state in this material. The existence of such states has been inferred from a variety of other measurements and is not a surprise. What is perhaps surprising is that the formation of this dark state, whether due to intersystem crossing or charge separation, is not necessarily the dominant relaxation pathway for the luminescent exciton. At low temperatures, the 1.8 ns formation time is competitive with both the radiative and ground state recovery times of the singlet exciton, and a large proportion of the initially excited chromophores end up in a dark state whose lifetime is $>5$ ns. As the temperature is increased, it appears that the dark state formation rate does not change nearly as much as the decay rate directly to the ground state ($k_{nr}$). This accelerated decay to the ground state leads to the observed faster ground state recovery and lower total dark state yield. Once formed, however, the dark states appear to have a temperature-independent lifetime on the time scale of this experiment. Referring back to the two extreme cases for a 3-level system discussed in the Introduction, we appear to go from an intermediate situation at low temperature, where all
the relaxation rates are comparable, to a situation where the dominant relaxation channel is direct repopulation of the ground state at high temperature. Results from MH-PPV yield a slightly faster dark state formation time, 1.1 ns, which is expected based on emission measurements and its greater tendency to form excimers.\textsuperscript{10}

Our results show that once a stable luminescent exciton is created, its lifetime (and thus its fluorescence probability) is most strongly effected by a relaxation channel that puts it into the ground state. The fact that this thermally-activated diffusion-quenching of the exciton puts the chromophore back into the ground state (rather than an intermediate charge-separated state) has consequences for the mechanism of relaxation. Rothberg \textit{et al.} have shown that photo-oxidation of PPV films leads to more rapid fluorescence decays and increased photoconductivity.\textsuperscript{27} Care was taken to avoid exposure of the samples used in this experiment to air and light, and furthermore there was no measurable effect of different preparations and solvent used on the temperature-dependent decays seen in PPV. Although chemical defects are certainly important in determining the luminescence properties of PPV, it is also possible that structural defects, for example surface states in the polycrystalline material, also play a role. Such states would not involve an oxygen atom that lowers the barrier to charge separation, but would instead allow for a fast internal conversion back to the ground state. At higher excitation energies, charge separation likely plays a greater role, as suggested by our data at 300 nm, where the amount of long-lived dark states almost doubles. At these energies, previous measurements have shown that the photoconductivity yield increases while the fluorescence yield drops, consistent with this observation.\textsuperscript{10}

The specific identity of the intermediate dark state $D$ inferred from our experiment is an open question. The most likely species are associated polaron pairs,\textsuperscript{10} effectively excimers,\textsuperscript{34,35} which have also been observed in model compounds.\textsuperscript{36} These species can then go on to produce even longer-lived species like triplet excitons and spatially-separated polaron pairs, and there is abundant evidence for the existence of such species on the microsecond to millisecond time scale in PPV and its derivatives.\textsuperscript{31,37,38} While there are several possibilities for the identity of this dark state, it is clear that the time scale of its formation is fairly slow. It is possible that there is an ultrafast relaxation pathway to a dark state in addition to the slower one we directly measure.\textsuperscript{26} The question then is whether this channel is of comparable importance to the nanosecond channel identified in this work. Data from our group and others\textsuperscript{7,8} show that the decrease in fluorescence lifetime with increased temperature largely explains the temperature-dependent decrease in quantum yield as well. Therefore, if there is an ultrafast relaxation in addition to these slow dynamics, it must be temperature independent. A significant subpicosecond contribution to the dark state yield would lead to a temperature-independent offset in the long time ground state bleach. This does not appear to be the case in our data: a single, relatively slow decay into the long-lived dark state does a satisfactory job of fitting all our data. In short, there is nothing to suggest that a significant portion of the initially excited excitons undergo a subpicosecond decay to a nonemissive state, unless those excitons correspond to different sites that can never contribute significantly to the luminescence under any circumstances. Another way to explain the decrease in dark state yield with temperature is to assume the existence of a subpopulation of dark states which possess a temperature-dependent relaxation time. In this case, both the probability of reaching the dark state and the lifetime of the dark state decrease as temperature increases. We see no evidence for a transition from slow to fast relaxation in the long-time bleach data or in the absorption data, however. While the lifetimes of triplet excitons and polarons probably do depend on temperature, the time scale of our experiments is 5 ns, which is short enough that such relaxations will still appear negligible during the measurement.

The assumption that all absorptions have the same probability to reach a fluorescent state is implicit in the model used to analyze our data. PPV is a heterogeneous material,\textsuperscript{15,39} however, and it is possible that some absorbing species only emit with low probability, leading to a case where our experiment preferentially detects those sites which contribute significantly to the fluorescence. There is some evidence that this is the case in related polymers like MEH-PPV.\textsuperscript{40} Other sites may absorb a photon and never luminesce, instead undergoing rapid dissociation into free charges, or internal conversion. Such sites, which may include a substantial fraction of the absorbers in PPV, would not effect our experimental observables. For example, both transient absorption and transient photocurrent experiments indicate that free charges can be created in these materials on the femtosecond to picosecond time scale.\textsuperscript{31,42} Such events would not be resolved in our measurements, which rely on luminescent states for detection. Once a luminescent exciton has been created, we can follow its trajectory, either back to the ground state or to a long-lived dark state. But if an initial photoexcitation always goes to a dark state, it would never effect our measurement. In other words, luminescent detection methods like those utilized in this paper cannot measure the dynamics of absorbing species which never luminesce, or that do so with very low quantum yield.

Our results have implications for the photogeneration of charge carriers in PPV and related polymers. Two possible mechanisms for charge generation are direct polaron generation and dissociation of luminescent excitons. In this work we have shown that no significant portion of the luminescent excitons decay to dark states on a subpicosecond timescale, and the simple three-level model does a good job in fitting the experimental data. The yield of dark states we observe resulting from the nanosecond exciton relaxation decreases with increasing temperature, in contrast to what has been observed for photogenerated charges in PPV and related polymers.\textsuperscript{43,44} These two facts, along with recent experimental results showing virtually instantaneous creation of charge carriers upon visible photoexcitation,\textsuperscript{41} suggest that the excition dissociation mechanism may not be the dominant channel for polaron formation in pristine PPV. As discussed above, our results suggest that there may exist a variety of photoexcited species, some of which fluoresce, while others
probably go directly to a charge separated state that never contributes to the overall luminescence.

Finally, our results also suggest that high repetition rate laser experiments conducted on PPV should be interpreted with care, since there are clearly species which can live for tens of nanoseconds after the initial excitation. The possibility that one could build up a significant population of dark states at low temperatures with 100 MHz laser pulse repetition rates needs to be taken into account when one assumes that the sample is actually equilibrated at a given temperature. In our experiments at 40 kHz, such “pile-up” effects are not important, as evidenced by the lack of signal dependence on repetition rate and average pump power in the fluorescence regime where this data was taken.

V. CONCLUSION

To briefly summarize, we have shown that the relaxation of the luminescent excitons in PPV occurs via two channels: a thermally activated process leading to internal conversion back to the ground state, and a slower, temperature-independent conversion to a long-lived dark state. As the temperature increases, direct relaxation to the ground state becomes dominant and both the fluorescence quantum yield and the dark state yield decrease. Measurements on MH-PPV confirm a similar situation in this soluble PPV derivative; at room temperature, the dominant relaxation pathway is back to the ground state and not to a long-lived dark state. In neither polymer do we find evidence for a decay channel to the dark state other than the nanosecond process in our three-level model. The fact that the dominant relaxation pathway at high temperature does not involve a long-lived intermediate state may have implications for the overall electroluminescence efficiency of this material.

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