Delayed Fluorescence and Phosphorescence from Polyphenylquinoxalines

A. Hayer,[†] H. Bässler,*[,†] B. Falk,[‡] and S. Schrader[§]

Institut für Physikalische-, Kern- und Makromolekulare Chemie und Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität Marburg, Hans-Meerwein-Strasse, 35032 Marburg, Germany, and Institut für Dünnschichttechnologie und Mikrosensorik Teltow, Kantstrasse 55, D-14513 Teltow, Germany, and Institut für Physik, Lehrstuhl Physik kondensierter Materie, Universität Potsdam, Am Neuen Palais 10, 14469 Potsdam, Germany

Received: June 12, 2002

We report on phosphorescence and delayed fluorescence from polyphenylquinoxalines in frozen solution and in the film at 77 K. Upon pulsed optical excitation, the following types of experiments have been carried out: (a) optical spectra detected by means of a gated optical multichannel analyzer, (b)-transient measurements employing a single photon counting setup, and (c) photoluminescence excitation spectra. We will argue that in a polymer in which the quinoxaline units are directly linked together via C−C-bonds, the delayed fluorescence is due to the recombination of Coulombically bound electron−hole pairs, which on their part are generated by direct optical excitation. This is deduced from the facts that (a) the intensities of delayed fluorescence, phosphorescence and prompt fluorescence all vary linearly with the pump intensity; that (b) both delayed fluorescence and phosphorescence decay according to a power law up to 1 s, i.e., at times exceeding the triplet lifetime; and that (c) the photoluminescence excitation spectrum of the delayed fluorescence shows an onset at 0.4 eV above the absorption edge. In an oxygen-bridged polyphenylquinoxaline, on the other hand, both geminate pair recombination and triplet−triplet annihilation play a role in the generation of delayed fluorescence.

I. Introduction

It was for a long time that π-conjugated polymers were considered as nonphosphorescent. The apparent lack of interest in this subject was partly due to the anticipated absence of an energy gap between singlet and triplet states implied by the application of the semiconductor band model to those materials.[1] However, since then many authors have reported on indirect evidence for the existence of triplet excitations in π-conjugated polymers.[2−6] Meanwhile there is unambiguous evidence that not only polymers containing heavy atoms in the backbone,[7] but π-conjugated polymers in general do phosphoresce, at least dispensed in a glassy matrix.[8−10] The singlet−triplet gap is about 0.7−0.8 eV[11] and the lifetime can be as long as 1 s. In other words, spectroscopically π-conjugated polymers do not behave different from conventional π-bonded molecules. It has been recognized, though, that in films of π-conjugated polymers phosphorescence is heavily quenched, probably due to impurities. This problem is already known from organic molecular crystals where the trapping of triplets can become dominant due to their long lifetimes, thus complicating the detection of phosphorescence.

Another aspect of the photophysics of triplet excitations besides phosphorescence is delayed fluorescence generated by the bimolecular recombination of two triplets.[12] At high pump intensities their concentration can be sufficiently large so that their mutual interaction dominates over their monomolecular decay. However, triplet−triplet fusion is not the only mechanism by which an emitting singlet excitation can be generated after some delay time. A metastable Coulombically bound electron−hole pair can act similarly provided that its energy exceeds the singlet energy. Analoguously, the bimolecular recombination of electrons and holes injected from its electrodes into a light emitting diode also leads to retarded emission once the applied electric voltage is turned off.[13] Delayed fluorescence from triplet−triplet fusion has, in fact, been detected in a polyfluorene derivative in the form of a spin-coated film and in frozen solution,[9] while a ladder-type poly-*para*-phenylene (MeLPPP) is an example of delayed geminate electron−hole pair recombination in the film.[14] To disentangle both cases is not at all trivial, though, as became evident when revisiting delayed fluorescence from the "classic" fluorescent polymer poly(vinylcarbazole).[15]

The purpose of this work was to distinguish both generation mechanisms for delayed fluorescence in a π-conjugated polymer in which triplet excitations must play a major role by virtue of a large intersystem crossing rate in the repeat unit of the polymer backbone. The test system were two types of polyphenylquinoxalines in which the repeat units are linked together either directly or via an oxygen bridge. These polymers have already proven to be promising candidates for the use as electron-transporting materials in bilayer polymer LEDs.[16,17] It turns out that they do emit delayed fluorescence as well as phosphorescence and the complexities of the underlying triplet processes can, in fact, be unraveled by combined stationary and transient experiments including photoluminescence excitation spectroscopy.

II. Experimental Section

The chemical structures of the polyphenylquinoxalines PPQ1A (with direct linkage of the quinoxaline units) and PPQ2B

[†] Institut für Physikalische-, Kern- und Makromolekulare Chemie und Wissenschaftliches Zentrum für Materialwissenschaften.
[‡] Institut für Dünnschichttechnologie und Mikrosensorik Teltow.
[§] Institut für Physik.

10.1021/jp0214110 CCC: $22.00
Published on Web 10/19/2002

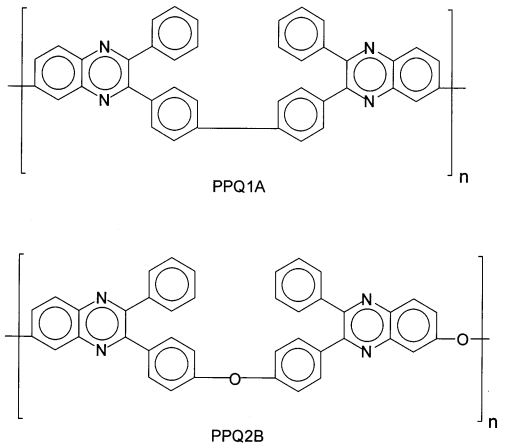

Figure 1. Structures of the investigated polyphenylquinoxalines.

(oxygen-bridged polymer) are displayed in Figure 1. The synthesis of these polymers that were used without additional purification is discussed elsewhere.[17] High optical quality films have been prepared by spin-coating of a solution of the polymer in chloroform on a quartz substrate. Liquid samples were obtained by dissolving PPQ2B in 2-methyl-tetrahydrofuran and PPQ1A in a mixture of toluene/cyclohexane (1:1). The samples were attached to the sample holder of a liquid nitrogen cryostat, providing a sample temperature of 77 K.

Two different laser systems were used for optical excitation. High intensities at a fixed excitation wavelength of 355 nm were provided by the third harmonic of a Q-switched Nd:YAG laser (Spectra Physics Quanta Ray GCR 100) with a repetition rate of 10 Hz and a pulse duration of 7 ns. Other excitation wavelengths were obtained from a tunable dye laser (Lambda Physics FL 2001) pumped by a XeCl excimer laser (Lambda Physics COMPex) with a variable repetition rate in the range of 1−10 Hz and a pulse duration of 15 ns. Spectra were recorded by an optical multichannel analyzer (PAR model 1460, EG&G Parc) after dispersing the luminescence by a monochromator with a resolution of 2 nm. The gateable intensified diode array detector provides gate widths of 100 ns−10 ms (variable delay with respect to the excitation pulse: 0 ns−13 ms). Spectra with a gate width of 100 ns and without delay are referred to as prompt fluorescence spectra. Delayed emission spectra were recorded with a gate width of 10 ms and a delay of 1 μs unless otherwise noted. For time dependent measurements a single photon counting setup was employed. The luminescence was filtered by an interference filter, thus allowing for the analysis of only one emission band, and recorded by a multichannel detection unit (SR 430 Multichannel Scaler) after preamplification (Stanford Research Systems SR 445). Absorption spectra were recorded with a Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer.

III. Results

A. Spectral Characterization. Figure 2 shows the prompt and delayed emission spectra of PPQ1A at 77 K in the film and in dilute frozen solution ($c \leq 10^{-4}$ mol/L referred to the repeat unit as shown in Figure 1) after excitation at 3.49 eV as well as the absorption spectrum of the film at room temperature. The absorption maximum is at 3.12 eV. Due to increased inhomogeneous broadening at high temperatures vibronic features are unresolved. The prompt fluorescence of PPQ1A in the film is characterized by the $S_1 \rightarrow S_0$ (0−0)-transition at 2.74 eV, followed by a second band at 2.62 eV and a shoulder at approximately 2.45 eV. The spectral position of the high energy

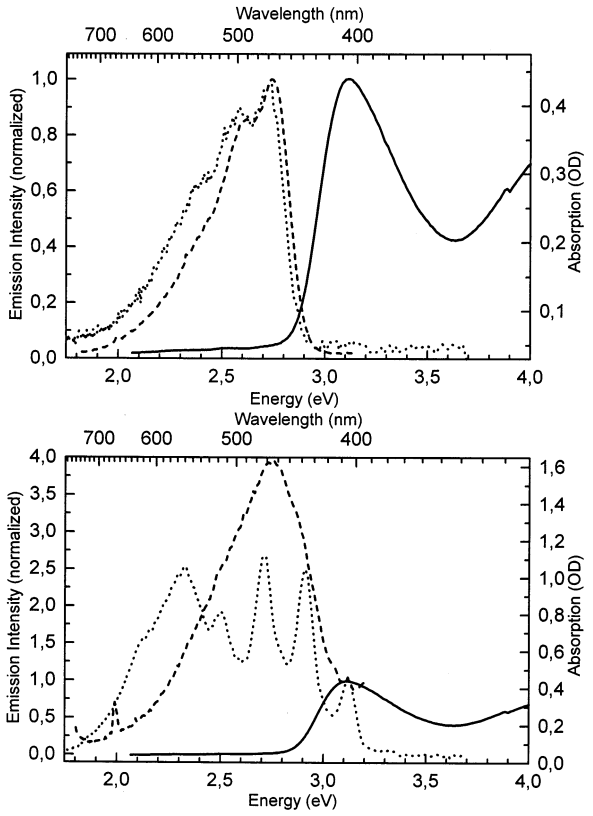

Figure 2. Prompt (- −) and delayed emission spectrum (• •) of PPQ1A in the film (upper part) and in dilute ($c \leq 10^{-4}$ mol/l) solution (lower part) at 77 K compared to the room-temperature absorption spectrum of the corresponding film (—).

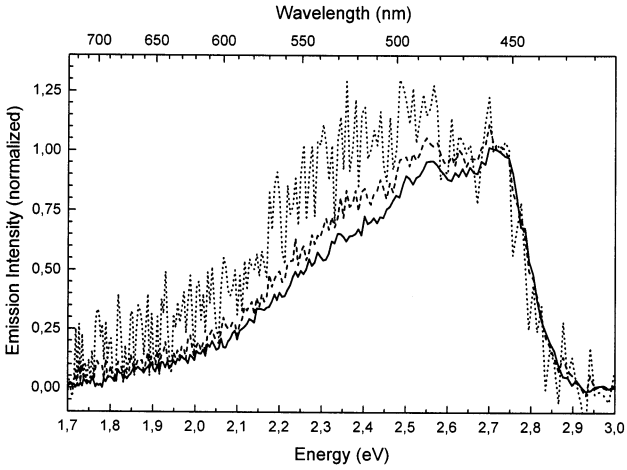

Figure 3. Emission spectra of a PPQ1A film with different delay times: 1 μs (—), 10 μs (- −), and 100 μs (• •).

part of the delayed emission in the film coincides with the prompt fluorescence. From this it follows that the former is due to delayed fluorescence (DF) from the S_1 state of PPQ1A. In the delayed emission spectrum in the film phosphorescence is not resolved as an individual band. Nevertheless, from an increased intensity of the low energy part of the spectrum as compared to the prompt fluorescence one can conclude on a weak delayed emission in this spectral region. Spectra recorded with increasing delay with respect to the excitation pulse (see Figure 3) are in agreement with this conclusion. The phosphorescence maximum lies at approximately 2.35 eV.

The behavior in frozen solution is more complicated. The prompt fluorescence band is extremely broad and can be explained as the superposition of the emission of two different

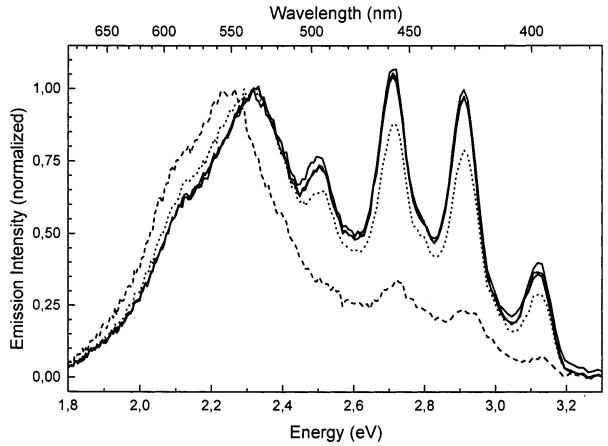

Figure 4. Emission spectra of a PPQ1A solution ($c \leq 10^{-4}$ mol/l) with different delay times: 1 μs, 10 μs, and 100 μs (—), 1 ms (• •), and 10 ms (- —).

singlet species. One of them is the species causing the prompt fluorescence in the film. The other species is the one from which the delayed fluorescence in frozen solution occurs. The latter has its $S_1 \rightarrow S_0$ (0−0)-transition at 3.12 eV and shows a distinct vibronic progression with a splitting of 200 meV and a rather weak inhomogeneous broadening ($\sigma \approx 40$ meV). The vibronic splitting reflects stretch modes in the heteroaromatic quinoxaline ring: C═C stretch modes in phenyl rings require 185−200 meV, C═N stretch modes 200−210 meV.

The position of the delayed fluorescence (0−0)-transition in frozen solution suggests perfectly resonant emission when compared to the absorption spectrum of the film which also exhibits a maximum at 3.12 eV. However, this is not entirely true: The intensity distribution of the vibronic bands of a transition is identical in absorption and emission, so that the absorption maximum coincides with the (0,1)- rather than with the (0−0)-transition. Consequently, the absorption spectrum of the solution has to be blue-shifted with respect to the film, as the emission cannot occur at higher energy than the absorption. This is in agreement with the photoluminescence excitation spectrum of phosphorescence in frozen solution being slightly blue shifted with respect to the absorption spectrum in the film (cf. Figure 7 and section IV). Consequently, it is impossible to deduce an exact Stokes shift from these spectra, but it can be concluded that the shift has to be rather small.

Phosphorescence is more intense in frozen solution than in the film. It is resolved as an extra band at 2.31 meV with an additional shoulder at 2.14 meV. From this it follows that the singlet−triplet energy gap is of the order of $\Delta E_{ST} \approx 0.8$ eV. While the delayed fluorescence occurs at the same spectral position irrespective of the delay relative to the excitation pulse, the phosphorescence emission is subject to a slow spectral relaxation process (see Figure 4): Whereas for delays up to 100 μs the phosphorescence spectra coincide, the intensity of the low energy part increases after 1 ms and a considerable bathochromic shift to a maximum at 2.25 eV is observed after 10 ms.

Because triplet excitons are very mobile and therefore easily quenched by impurities, delayed luminescence at room temperature is neither observed in the film nor in dilute solution. Prompt fluorescence in the film occurs at the same spectral position at both room temperature and 77 K, but the vibronic finestructure vanishes at room temperature. As a consequence of more efficient energetical relaxation the prompt fluorescence in solution is red-shifted by about 50 meV at room temperature.

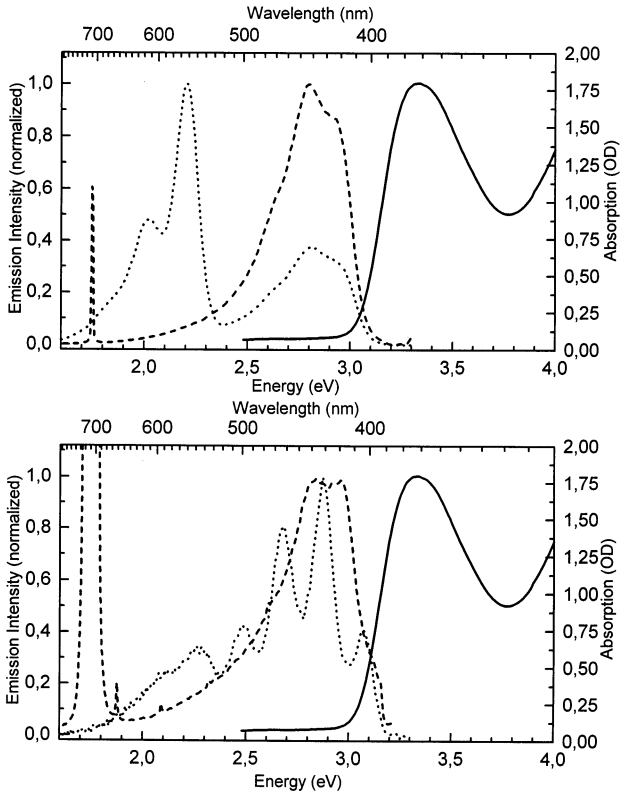

Figure 5. Prompt (- —) and delayed emission spectrum (• •) of PPQ2B in the film (upper part) and in dilute ($c = 10^{-4}$ mol/L) solution (lower part) at 77 K compared to the room-temperature absorption spectrum of the corresponding film (—). The sharp peak at 1.75 eV in the prompt emission spectra is due to the second harmonic of the laser.

The oxygen-bridged polymer PPQ2B exhibits the same emission behavior as PPQ1A (see Figure 5). Especially the occurrence of two different singlet species in dilute frozen solutions is a common feature of both materials. The absorption in PPQ2B films at room temperature has its maximum at 3.36 eV. The (0−0)-transition of prompt and delayed fluorescence in the film lies at 2.92 eV, followed by a second band at 2.80 eV and a shoulder at 2.66 eV. In contrast to PPQ1A, phosphorescence in PPQ2B films is more intense than delayed fluorescence. The singlet−triplet energy gap amounts to $\Delta E_{ST} = 0.72$ eV, the $T_1 \rightarrow S_0$ (0−0)-transition occurring at 2.20 eV. A second phosphorescence band lies at 2.03 eV. Delayed fluorescence in frozen solution ($c = 10^{-4}$ mol/L) occurs from a well-defined state with low inhomogeneous broadening ($\sigma \approx 50$ meV) and a vibronic splitting of 190 meV. The $S_1 \rightarrow S_0$ emission is characterized by a (0−0)-transition at 3.06 eV. The relative intensity of phosphorescence is lower than in the film, but phosphorescence is still resolved as an individual band at 2.28 eV.

Both polymers exhibit absorption and emission bands that are red-shifted by several hundred meV with respect to monomeric quinoxaline. The latter has (0−0)-transitions at 3.93 eV in absorption and at 2,62 eV in phosphorescence emission. Furthermore, the absorption spectrum of monomeric quinoxaline differs from the spectra of the polymers by showing an additional weak transition around 3.6 eV, presumably a (n−π*)-transition. The red-shift of the polymer spectra implies that the effective conjugation lengths have to be considerably longer than the structural repeat unit. The hypsochromic shift of the absorption of the oxygen-bridged PPQ2B with respect to PPQ1A analoguously indicates a higher degree of delocalization in the latter. Continuing this line of reasoning, the weak (n−π*)-

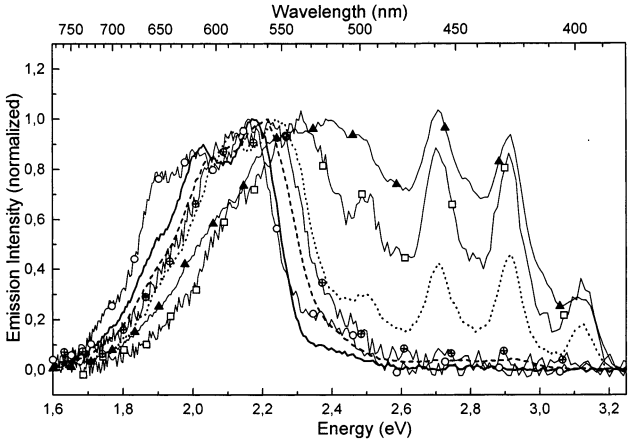

Figure 6. Delayed emission spectra of PPQ1A in dilute solution ($c \leq 10^{-4}$ mol/L) at various excitation energies: 4.03 eV/308 nm (▲), 3.49 eV/355 nm (□), 3.35 eV/370 nm (• •), 3.26 eV/380 nm (⊕), 3.18 eV/390 nm (- −), 3.05 eV/406 nm (—), 3.01 eV/412 nm (○).

transition observed in the monomer absorption spectrum should exhibit a smaller red shift upon increasing the conjugation length due to its more localized character. Its absence in the polymer spectra is thus explained by a superposition of the weak forbidden and the allowed transition. While the absorption of the polymers is shifted by about 800 meV with respect to monomeric quinoxaline, phosphorescence is shifted only by about 350 meV. This is probably due to a stronger localization of triplet excitons with respect to singlet excitons as observed in the case of poly-*para*-phenylene- and poly-*para*-phenylene-vinylene derivatives.[21]

B. Site-Selective Measurements and Photoluminescence Excitation Spectra. Prompt emission spectra of dilute frozen solutions of PPQ1A at 77 K do not change upon varying the excitation energy in the range of 4.03−2.92 eV. Even at the absorption edge, no energetic localization (see section V and Figure 11a) is observed. However, this is not the case for the delayed emission spectra of the same sample (see Figure 6). Phosphorescence shows all the characteristics of localization: The $T_1 \rightarrow S_0$ (0−0)-transition is shifted linearly with decreasing excitation energy at the tail of the absorption, while the relative intensities of the lower energy bands increase and the inhomogeneous broadening decreases. Delayed fluorescence, on the other hand, occurs always at the same spectral position if it occurs at all. It is already localized at high excitation energies showing narrow, unshifted bands (for a detailed explanation, see section IV). The extremely broad, unstructured low energy bands appearing upon excitation at 4.03 and 3.49 eV are interpreted not as phosphorescence but as excimer emission due to the complete lack of resemblance to the phosphorescence spectra at low excitation energies.

The fact that delayed fluorescence in frozen PPQ1A solutions occurs at high excitation energies only is again illustrated in the upper half of Figure 7: The photoluminescence excitation (PLE) spectrum, i.e., spectrally integrated emission intensity versus excitation energy, of the delayed fluorescence does not follow the absorption spectrum, but shows an onset of delayed fluorescence at about 0.4 eV above the absorption edge. The PLE spectrum of the phosphorescence in frozen PPQ1A solutions, as well as the PLE spectra of both phosphorescence and delayed fluorescence in frozen PPQ2B solutions (see lower half of Figure 7), on the other hand, do follow the absorption spectrum. In the case of delayed fluorescence, this behavior is characteristic for a generation via triplet−triplet annihilation (see section IV). Nevertheless, the relative intensity of delayed

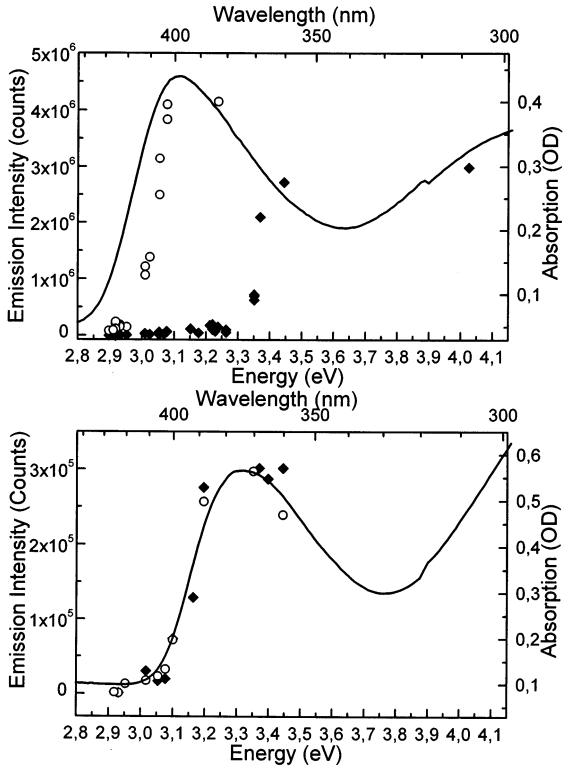

Figure 7. Photoluminescence excitation spectra of delayed fluorescence (♦) and phosphorescence (○) in PPQ1A (upper half) and in PPQ2B (lower half) solutions at 77 K compared to the corresponding room-temperature absorption spectra (—).

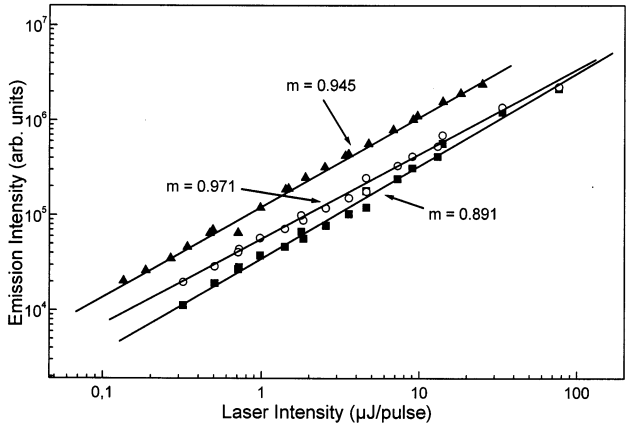

Figure 8. Dependence of fluorescence (▲), phosphorescence (○), and delayed fluorescence (■) intensity of PPQ1A in dilute solution ($c \leq 10^{-4}$ mol/L) on excitation intensity at 77 K. *The time delay for measurements of delayed fluorescence and phosphorescence was 1 μs.* Excitation was at 3.49 eV.

fluorescence compared to phosphorescence in PPQ2B increases at higher excitation energy, indicating that a second generation process plays a role at high energies. Neither in prompt fluorescence nor in phosphorescence localization was observed for PPQ2B.

C. Intensity Dependence. Figure 8 shows the dependence of emission intensity upon laser excitation intensity for the different types of luminescence in frozen solutions of PPQ1A at 77 K. Prompt fluorescence and phosphorescence as well as delayed fluorescence increase linearly with laser intensity. Neither quadratic behavior for the delayed fluorescence at low intensities nor square-root behavior of the phosphorescence at high intensities, which both are signatures of triplet−triplet annihilation, is observed. Consequently, the ratio of delayed

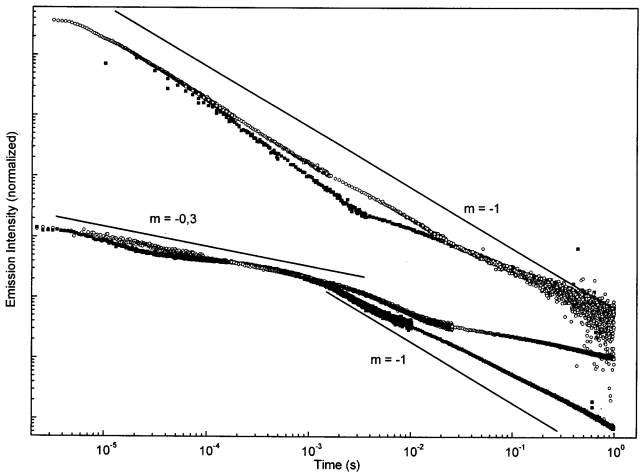

Figure 9. Time dependence of the phosphorescence (○) and delayed fluorescence (■) intensity in PPQ1A in the film (upper part) and in dilute solution (lower part) at 77 K. Excitation was at 4.03 eV with 40 μJ/pulse.

TABLE 1: Slopes Derived from Logarithmic Plots of the Prompt Fluorescence (PF), Delayed Fluorescence (DF), and Phosphorescence (Ph) Intensities versus the Excitation Intensity for Different PPQ1A Samples

	PF	DF	Ph	DF/Ph
thick film	1.232	1.177	0.980	1.200
thin film	0.955	1.251	1.113	1.124
solution	0.945	0.971	0.891	1.090

TABLE 2: Slopes Derived from Logarithmic Plots of the Prompt Fluorescence (PF), Delayed Fluorescence (DF), and Phosphorescence (Ph) Intensities versus the Excitation Intensity for Different PPQ2B Samples.

	PF	DF	Ph	DF/Ph
thick film	0.848	1.707	0.888	1.922
thin film	0.844	1.212	0.729	1.663
concentrated solution (10^{-3} mol/l)	0.939	1.346	0.881	1.528
dilute solution (10^{-4} mol/l)	0.926	1.058	0.91	1.163

fluorescence to phosphorescence is nearly constant all over the investigated intensity range. Furthermore, these results prove that singlet−singlet annihilation does not occur. Table 1 lists the slopes derived from logarithmic plots of the intensities of different luminescence types versus the excitation intensity for different PPQ1A samples. The ratio of the slopes for delayed fluorescence and phosphorescence is always near to 1, regardless of whether a frozen solution or films of varying thicknesses were investigated.

In this respect PPQ2B behaves differently (see Table 2): In the series thick film > thin film > concentrated solution > dilute solution the ratio of the slopes for delayed fluorescence and phosphorescence varies from 2 to 1. Moreover, the intensity dependences in the thick film show a turnover at high intensities to linear behavior for the delayed fluorescence and square-root behavior for the phosphorescence.

D. Time-Resolved Measurements. Figure 9 shows the time dependence of phosphorescence and delayed fluorescence intensity in films (upper part) and frozen solutions (lower part) of PPQ1A. In the film the phosphorescence decay follows a power law $I_P \propto t^{-1}$ up to 1 s. Exponential decay is not observed, not even at times exceeding the triplet lifetime of monomeric quinoxaline[22] which at 80 K in dilute frozen solution is $\tau = 0.25$ s. Delayed fluorescence decay matches this behavior except for small deviations at intermediate times. In dilute frozen solution the delayed fluorescence decay changes from a $I_{DF} \propto t^{-0.3}$ law at initial stage to a $I_{DF} \propto t^{-1}$ law as observed in the film after 1 ms. Phosphorescence intensity exhibits analogous behavior up to 1 ms. The long time region of the phosphorescence curve no longer reflects the true kinetics of the sample because the emission leaves the detection window set by the interference filter due to spectral diffusion.

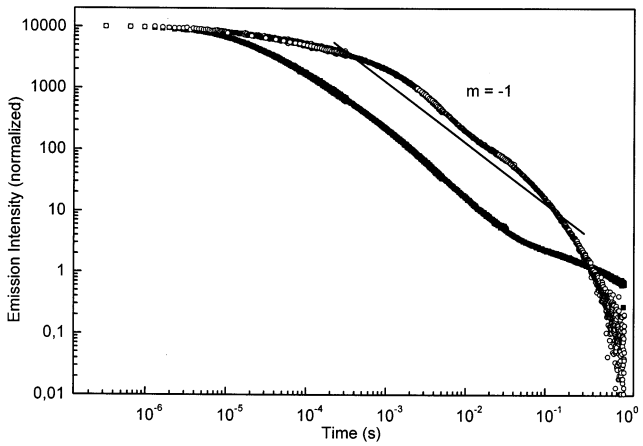

Figure 10. Time dependence of the phosphorescence (○) and delayed fluorescence (■) intensity in a PPQ2B film at 77 K. Excitation was at 4.03 eV with 40 μJ/pulse.

The delayed luminescence kinetics of PPQ2B films are shown in Figure 10. The phosphorescence decay follows a power law $I_P \propto t^{-1}$ at intermediate times. In the long time limit exponential decay with a lifetime $\tau = 0.183$ s comparable to that of monomeric quinoxaline is reached (see inset in Figure 10). Delayed fluorescence starts to obey a power law dependence $I_{DF} \propto t^{-1}$ at slightly shorter times than phosphorescence. Exponential decay is not observed. The change in the decay curve at about 0.05 s is presumably accidental, caused by normalizing the intensities of delayed fluorescence and phosphorescence. The absolute value of the delayed fluorescence intensity is considerably smaller than that of phosphorescence and consequently the detection limit is reached earlier. Without going into detail, one can say that time-resolved measurements in frozen PPQ2B solutions yield curves whose complexity can only be explained by a superposition of both geminate pair recombination and triplet−triplet annihilation.

IV. Discussion

A. Emission from Singlet States. In conjugated polymers the energy of the chromophores is distributed randomly following a density of states function (DOS). Conformational breaks give rise to a distribution of effective conjugation lengths. Furthermore, the energetic stabilization of the chromophores due to their interaction with the polarizable environment is a local quantity like in any other disordered solid. Upon excitation in the higher region of the DOS, a relaxation within the DOS takes place via energy transfer between neighboring chromophores and the exciton mobility is relatively high. The resulting emission is red-shifted with respect to the absorption. It maps the occupied density of states (ODOS) after relaxation and is subject to inhomogeneous broadening. At the absorption tail, on the other hand, the density of states is so small that within the intrinsic lifetime of an excited state, no lower lying site may be reached. The consequence is energetic localization that leads to quasi-resonant emission with reduced line widths (see Figure 11a).

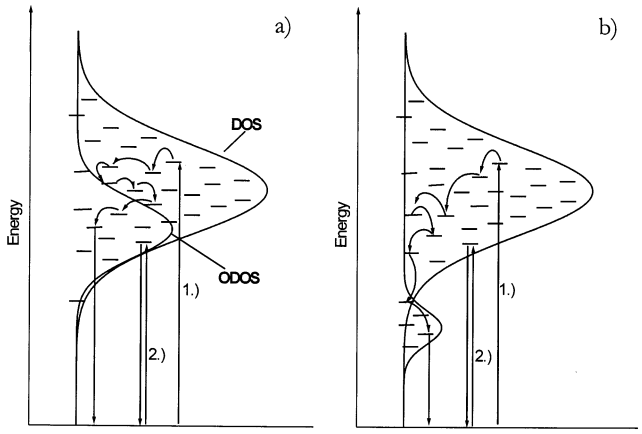

Figure 11. (a) Schematic representation of the Density of States (DOS) of conjugated polymers and the occupied density of states (ODOS). (1) describes the optical excitation with subsequent spectral relaxation and emission, whereas (2) describes the excitation at low energies where relaxation is impossible and resonant emission occurs. (b) Schematic representation of the DOS of the intrinsic states of a conjugated polymer and its overlap with the DOS of trapping sites. (1) Describes the optical excitation with subsequent spectral relaxation and emission from the trapping sites, whereas (2) describes the excitation at low energies where relaxation is impossible and resonant emission occurs

In dilute frozen solutions of the investigated polyphenylquinoxalines, two different singlet species were observed. In delayed emission spectra, the emission occurs from a well-defined state with narrow line widths and distinct vibronic coupling. In prompt emission spectra, an additional, more intense second species was observed that showed inhomogeneously broadened, poorly structured bands at lower energy than the first species. The occurrence of these two different singlet species in dilute frozen solution can be explained in terms of a hopping process involving trap sites, due to, for example, π-stacking, beneath the intrinsic DOS (see Figure 11b). If excitation occurs at high energies, exciton migration and therefore energetic relaxation are efficient. Singlet excitons that avoid intersystem crossing before reaching the traps emit prompt fluorescence from there. Such an emission is characterized by broad, poorly structured bands at relatively low energies. Triplet excitons formed after intersystem crossing may relax in an analoguous process and emit phosphorescence from trap sites. On the other hand, these triplet excitons may also recombine bimolecularly on their way to the lowest lying triplet states. As collisions and triplet−triplet annihilation occur only after a certain migration time in which spectral relaxation takes place, the singlet excitons formed upon recombination are already localized in energy. Delayed fluorescence consequently occurs from a well-defined intrinsic molecular state. This localization implies that trap sites may not be reached from the lowest lying molecular states, even if they are more stable in energy. If the localization cannot have a thermodynamic reason, it has to be due to a kinetic inhibition. The DOSs of the polymer itself and the trap sites have an overlap. In principle an energy transfer to the trap sites is possible, as seen in the emission characteristics of the prompt fluorescence. Still, two isoenergetic states are not neccessarily neighboring in space and molecular geometry. If that is not the case, migration of an exciton from one of these sites to the other can only occur via intermediate population of a neighboring third site that may lie considerably higher in energy, i.e., the migration would involve the population of a high-lying transition state. It has to be concluded that triplet−triplet annihilation occurs after localization of one of the triplets within the intrinsic DOS of the polymer. An analoguous explanation holds if the delayed fluorescence originates from geminate pair recombination rather than from triplet−triplet annihilation. Under these circumstances, the two excited species that collide and recombine only after a certain migration time and consequently after a certain relaxation are the parts of a Coulombically bound electron−hole-pair rather than two triplet excitons. In any case, recombination occurs only on a site that is a local energy minimum, implying that one of the partners has to be trapped beforehand.

The different behavior in films of the same materials can be explained by the higher exciton mobility in the bulk: Due to close packing of the chromophores in condensed phase, interchain energy transfer is possible as a second relaxation pathway in addition to on-chain energy transfer. Consequently, even singlet excitons formed upon recombination can relax to the trap sites and delayed fluorescence as well as prompt emission occurs from trap sites only. This difference in exciton mobility is also reflected in the fact that in dilute frozen solution, even the prompt fluorescence shows some amount of intrinsic polymer emission, whereas in the film, only trap emission is detected.

B. Generation Mechanisms of Delayed Fluorescence. Delayed fluorescence from triplet−triplet annihilation and from geminate pair recombination can be distinguished by both the decay pattern of phosphorescence and delayed fluorescence and the dependence of their intensity on the pump intensity.

Triplet−triplet annihilation gives rise to the luminescence characteristics described in the following paragraph.[23] The rate equation for the triplet excitons is given by

$$\frac{\mathrm{d}[\mathrm{T}]}{\mathrm{d}t} = G_\mathrm{t} - \beta[\mathrm{T}] - \gamma_{\mathrm{TT}}[\mathrm{T}]^2 \qquad (1)$$

where t is the time, [T] is the concentration of populated triplet states, G_t represents the generation of triplet states, β is the sum of the radiative and nonradiative rate constants, and γ_{TT} refers to the bimolecular annihilation constant. After the end of the laser pulse, two different cases can be discerned, depending on which of the desactivation mechanisms is dominant. Dominant phosphorescence ($\beta[\mathrm{T}] \gg \gamma_{\mathrm{TT}}[\mathrm{T}]^2$) leads to an exponential decay

$$[\mathrm{T}(t)] = [\mathrm{T}_0] \exp(-\beta t) \qquad (2)$$

The intensities of phosphorescence and delayed fluorescence in this case are

$$I_{\mathrm{Ph}}(t) = k_\mathrm{r}[\mathrm{T}(t)] = k_\mathrm{r}[\mathrm{T}_0] \exp(-\beta t) \qquad (3)$$

and

$$I_{\mathrm{DF}}(t) = \frac{1}{2} f \gamma_{\mathrm{TT}}[\mathrm{T}(t)]^2 = \frac{1}{2} f \gamma_{\mathrm{TT}}[\mathrm{T}_0]^2 \exp(-2\beta t) \qquad (4)$$

where k_r is the radiative rate constant, f is the fraction of recombination events that lead to singlet excitons, and the factor of $^1/_2$ occurs because the recombination of two triplet excitons yields only one singlet exciton. If phosphorescence is dominant, delayed fluorescence decays exponentially with twice the rate constant of phosphorescence. Its intensity increases quadratically with the initial triplet concentration, which itself behaves linearly with the pump intensity.

Dominant delayed fluorescence ($\gamma_{\mathrm{TT}}[\mathrm{T}]^2 \gg \beta[\mathrm{T}]$) on the other hand leads to a power law for the phosphorescence decay:

$$[\mathrm{T}(t)] = \frac{[\mathrm{T}_0]}{1 + \gamma_{\mathrm{TT}} t [\mathrm{T}_0]} \qquad (5)$$

The resulting phosphorescence and delayed fluorescence intensities are

$$I_{Ph}(t) = k_r[T(t)] = \frac{k_r[T_0]}{1 + \gamma_{TT} t[T_0]} \quad (6)$$

and

$$I_{DF}(t) = \frac{1}{2} f \gamma_{TT} [T(t)]^2 = \frac{1}{2} f \gamma_{TT} \frac{[T_0]^2}{(1 + \gamma_{TT} t[T_0])^2} \quad (7)$$

respectively. It follows that at moderately short times ($\gamma_{TT} t[T_0] \ll 1$), delayed fluorescence is constant

$$I_{DF}(t) \approx \frac{1}{2} f \gamma_{TT} [T_0]^2 \quad (8)$$

whereas in the long time limit ($\gamma_{TT} t[T_0] \gg 1$) a power law $\propto t^{-2}$ is reached:

$$I_{DF}(t) \approx \frac{f}{2\gamma_{TT} t^2} \quad (9)$$

If delayed fluorescence is dominant, the intensity dependences change as well. Applying a steady-state approximation to eq 1 and assuming $\gamma_{TT}[T]^2 \gg \beta[T]$ leads to

$$G_t = \gamma_{TT}[T]^2 \quad (10)$$

Equation 10 shows that delayed fluorescence in this case behaves linearly with the triplet generation and therefore with the pump intensity as virtually every triplet is lost via a bimolecular process. The intensity of the remaining phosphorescence consequently shows a square root behavior with pump intensity as it increases with the triplet concentration and not with its square.

Whereas in organic molecular crystals such as anthracene, the diffusivity and consequently also the bimolecular recombination constant γ_{TT} are time-independent, this does not hold for disordered solids such as π-conjugated polymers. Because of energetic relaxation within the DOS, energy transport at short and intermediate times is dispersive. The time dependence of γ_{TT} should be reflected directly in the delayed fluorescence kinetics at intermediate times according to eqs 8 and 9. Only in the long time limit, γ_{TT} should reach saturation and I_{DF} should approach a t^{-2} law. This has been verified by theoretical and experimental methods: In Monte Carlo simulations[24] on a system of point sites with random energy one percent of which were occupied by triplet excitations, a turnover from a decay behavior $I_{DF} \propto t^{-m}$ with $m = 1$ to 1.3 at short times to $I_{DF} \propto t^{-2}$ in the long time limit was found. This turnover from $I_{DF} \propto t^{-1.3}$ to $I_{DF} \propto t^{-2}$ has been confirmed experimentally on a polyfluorene derivative.[9]

There is an alternative process which can give rise to delayed fluorescence. This is recombination of geminately bound electron−hole pairs generated via singlet excitation. The kinetics of this type of luminescence do not feature an exponential decay as the rate determining step is not the radiative return of a chromophore to its ground state with an intrinsic lifetime. Monte Carlo simulations[25] predict a time dependence $I \propto t^{-1}$ for both delayed fluorescence and phosphorescence. Their kinetics are necessarily identical as long as charge carrier recombination (leading to triplet as well as to singlet excitons) plays a dominant role. Furthermore, if Coulombically bound electron−hole pairs are generated in a monomolecular reaction (via dissociation of a singlet exciton, for example), the intensity dependence of both delayed fluorescence and phosphorescence on the pump intensity is linear. If the geminate pair generation is due to singlet−singlet annihilation,[26] the delayed fluorescence intensity features a turnover from linear to quadratic increase with the excitation intensity as in the triplet−triplet annihilation case, but it is the prompt fluorescence (and not the phosphorescence) intensity that changes from square-root to linear behavior. Those two cases can still be discerned by the combined intensity dependences of all three types of luminescence.

We will argue that in the polyphenylquinoxaline PPQ1A with directly linked quinoxaline units, the delayed fluorescence is due to geminate pair recombination. The first evidence for this notion is the dependence of the emission intensity on the pump intensity: Both types of delayed luminescence increase linearly with the pump intensity. Over the entire range of laser intensities, the delayed fluorescence thus behaves linearly with the phosphorescence rather than quadratically as it should if triplet−triplet annihilation would prevail. This behavior is observed in the film as well as in dilute frozen solution(see Table 1), indicating that interchain topology plays no major role.

Second, the decay of delayed fluorescence and phosphorescence in the film is virtually identical and follows a power law $I \propto t^{-1}$ as predicted for the recombination of geminate electron−hole pairs (see Figure 9). Whereas at short times such a decay could also be explained by dominant triplet−triplet annihilation and triplet exciton relaxation still in progress, a $I_{DF} \propto t^{-2}$ law at intermediate times and an exponential decay at times exceeding the intrinsic triplet lifetime would necessarily have to be observed for delayed fluorescence due to triplet−triplet annihilation.

The time dependent measurements on a dilute frozen solution of PPQ1A (see Figure 9) can also be explained by geminate pair recombination. At times exceeding 1 ms, delayed fluorescence exhibits the expected $I_{DF} \propto t^{-1}$ behavior. The decay $I_{DF} \propto t^{-0.3}$ at short times can be explained as follows: It is assumed that the recombination of electron−hole-pairs occurs between one charge carrier that is already trapped and its counterpart that reaches the same site after a certain number of random walk-steps within the Coulombic potential of the first charge carrier. The crucial step in recombination is thus very similar to the trapping of a single charge carrier. From experiments on photoconductivity[27] it is known that the trapping of charge carriers migrating through a disordered material follows an exponential law $\exp[-t/\tau]$ with time-independent rate constant only under the condition that the mobility of the charge carriers is isotropic. In the one-dimensional case, the decay at short and intermediate times is slower, following an exponential law $\exp[-(t/\tau)^{1/3}]$. A qualitative reason is that the trapping probability of a charge carrier increases linearly with the number of new sites visited during the random walk. In the bulk, most of the sites are visited only once, so that the number of new sites visited increases linearly with the number of jumps and consequently with time. In the one-dimensional case, on the other hand, excitons can only migrate forward and backward on the same polymer chain, so that the number of new sites visited, and consequently, the trapping probability, increases sublinearly with the number of jumps. In the long-time limit, the behavior known from the three-dimensional case is approached as the exciton reaches entangled polymer chains that allow for migration in three dimensions. Qualitatively, the slow decay behavior of the delayed fluorescence in frozen PPQ1A solutions at short and intermediate times can be explained analoguously, whereas triplet−triplet annihilation could not lead

to this effect. The fact that phosphorescence and delayed fluorescence exhibit very similar kinetics is also at variance with triplet−triplet annihilation being the dominant generation mechanism of delayed fluorescence.

The attribution of delayed fluorescence to geminate pair recombination is also confirmed by the PLE spectrum in frozen solution (see Figure 7). If triplet−triplet annihilation was at the origin of delayed fluorescence, the latter would necessarily occur every time that triplet excitons are formed in sufficiently high concentrations as no excess energy is needed to yield recombination. Then the PLE spectrum would have to follow the absorption spectrum. This is the case for the delayed fluorescence in PPQ2B, as well as for the phosphorescence in both materials, but not for the delayed fluorescence in PPQ1A. In PPQ1A, the onset of delayed fluorescence lies approximately 0.4 eV above the absorption edge. This value is of the order of magnitude of the energy difference between the first excited singlet state and the lowest lying charge-transfer state in organic molecular crystals such as anthracene ($\sim$ 0.5 eV),[28] i.e., the energy that is needed to transfer an electron from an excited singlet chromophore to an adjacent chromophore, so to generate an electron−hole pair. It is remarkable that this delayed fluorescence predominantly due to geminate-pair recombination occurs in dilute frozen solution. This indicates that the primary step of the dissociation of an singlet exciton into a Coulombically bound electron−hole pair is an *intra*chain process, as postulated by Vissenberg et al.,[26] rather than an *inter*chain transition.[27]

Unlike the findings for the fully conjugated PPQ1A, the delayed fluorescence of the oxygen-bridged polyphenylquinoxaline PPQ2B cannot be attributed to either triplet−triplet annihilation or geminate pair recombination alone. According to the results of the intensity dependences (see Table 2), one has to conclude that in thick films of PPQ2B, only triplet−triplet annihilation contributes to the delayed fluorescence, as a dependence $I_{DF} \propto I_P^2$ is observed over the entire range of excitation intensities. On the other hand, geminate pair recombination is by far the most important process in dilute frozen solutions ($I_{DF} \propto I_P \propto I_{PF}$). The other samples represent intermediate cases between these extremes. This influence of interchain topology can be explained by the higher exciton mobility in the three-dimensional case due to interchain energy transfer. Triplet excitons may return radiatively to the ground state if they do not meet a recombination partner within their intrinsic lifetime. Consequently, the lower their mobility, the lower their contribution to delayed fluorescence. Geminate pairs, on the other hand, can only return to the ground state via recombination as there is no competing desactivation process. Moreover, these charge carriers appear in pairs, so that they can always find a recombination partner irrespective of their mobility. Consequently, their contribution to delayed fluorescence is largely uninfluenced by sample aggregation.

The results of the time-resolved measurements on PPQ2B films (see Figure 10) are in agreement with the intensity dependences and suggest that triplet−triplet annihilation is the dominant generation process for the delayed fluorescence. The phosphorescence decay follows a power law $I_P \propto t^{-1}$ at intermediate times as expected in the case of dominant triplet−triplet annihilation and, in contrast to PPQ1A, features a turnover to an exponential decay with an intrinsic lifetime of $\tau = 0.183$ s in the long-time limit, when unimolecular decay necessarily prevails over bimolecular desactivation. The delayed fluorescence shows a $I_{DF} \propto t^{-1}$ decay at intermediate times rather than a $I_{DF} \propto t^{-2}$ decay, which is due to the triplet excitons still undergoing energetical relaxation. The delayed fluorescence decay $\propto t^{-1}$ sets on earlier than the phosphorescence decay $\propto t^{-1}$; both behaviors do not map each other, which is another evidence against geminate pair recombination.

In the case of frozen PPQ2B solutions, there is conflicting experimental evidence. Whereas the results of the intensity dependence experiments suggest that delayed fluorescence in this sample is predominantly due to geminate pair recombination, the PLE spectrum (see Figure 7) following the absorption spectrum is a strong evidence for dominant triplet−triplet annihilation. Nevertheless, the increase of the relative intensity of delayed fluorescence compared to phosphorescence with increasing excitation energy indicates that some amount of geminate pair recombination occurs at high energies in addition to triplet−triplet annihilation. As already mentioned in the results section, neither geminate pair recombination nor triplet−triplet annihilation alone can account for the observed complexity of the temporal decay behavior in frozen PPQ2B solutions.

V. Conclusion

The combination of various experimental results leads to the conclusion that in the polymer in which the quinoxaline units are directly linked together via a C−C-bond, delayed fluorescence is predominantly caused by the monomolecular recombination of Coulombically bound electron−hole pairs. A particularly noteworthy recognition, inferred from the excitation spectrum of the delayed fluorescence in the matrix-isolated polymer, is that geminate pairs can be directly excited on a given chain if an excess energy of 0.4 eV as compared to the $S_1 \leftarrow S_0$ transition is supplied, not requiring the fusion of two singlet excitations. Since delayed fluorescence probes metastable geminate pairs, that energy has to be less than the exciton binding energy required to dissociate a geminate electron−hole pair into an unbound one. Continuing this line of reasoning suggests that off-chain geminate pairs are primarily generated from on-chain precursors rather than directly.

Since the direct excitation of on-chain geminate pairs does not, or only with small yield, occur in the more localized oxygen-bridged polymer (cf. absorption spectra), one has to conclude that the degree of π-conjugation between the repeat units is crucial. This implies that on-chain π-bonding favors splitting a "hot" singlet state into a geminate electron−hole pair. The origin of delayed fluorescence in organic molecular crystals, a polyfluorene derivative and a ladder-type poly-*para*-phenylene is in agreement with the implication that geminate pairs are not formed if the degree of π-conjugation is low. In organic molecular crystals where π-conjugation between the molecules is absent, only triplet−triplet annihilation plays a role in the generation of delayed fluorescence.[20] This is also true for a polyfluorene derivative[9] with relatively low conjugation lengths. In films of a ladder-type poly-*para*-phenylene[14] that is planarized due to its chemical structure and therefore shows high conjugation lengths; on the other hand, delayed fluorescence is caused by geminate pair recombination. While at high excitation intensities where bimolecular processes dominate, these geminate pairs are formed via singlet−singlet annihilation, recent experimental findings[28] show that at low excitation intensities the dissociation of singlet excitons into geminate pairs does take place. The polyphenylquinoxalines studied in this work thus represent cases of intermediate π-conjugation where a turnover from triplet−triplet annihilation to geminate pair recombination as the dominant process in the generation of delayed fluorescence is observed.

Acknowledgment. We would like to thank A. Gerhard for help with experimental details and for valuable discussions. Financial support by the Stiftung Volkswagenwerk and by the Fonds der Chemischen Industrie is gratefully acknowledged.

References and Notes

(1) Heeger, A. J. In *Primary Photoexcitations in Conjugated Polymers: Molecular Exciton versus Semiconductor Band Model*; Sariciftci, N. S., Ed.; World Scientific: Singapore, 1997

(2) Wohlgenannt, M.; Graupner, W.; Leising, G.; Vardeny, Z. V. *Phys. Rev. B* **1999**, 60, 5321.

(3) Colaneri, N. F.; Bradley, D. D. C.; Friend, R. H.; Burn, P. L.; Spangler; A. B. *Phys. Rev. B* **1990**, *42*, 11670

(4) Dyakonov, V.; Rösler, G.; Schwoerer, M.; Frankevich, E. L. *Phys. Rev. B* **1997**, *56*, 3852

(5) Swanson, L. S.; Shinar, J.; Yoshino, K. *Phys. Rev. Lett.* **1990**, *65*, 1140

(6) Wei, X.; Hess, B. C.; Vardeny, Z. V.; Wudl, F. *Phys. Rev. Lett*. **1992**, *68*, 666

(7) Chawdhury, N.; Köhler, A.; Friend, R. H.; Wong, W.-Y.; Lewis, J.; Younus, M.; Raithby, P. R.; Corcoran, T. C.; Al-Mandhary, M. R. A.; Khan, M. S. *J. Chem. Phys*. **1999**, *110*, 4963

(8) Romanovskii, Yu. V.; Gerhard, A.; Schweitzer, B.; Scherf, U.; Personov, R. I.; Bässler, H. *Phys. Rev. Lett*. **2000**, *84*, 1027

(9) Hertel, D.; Bässler, H.; Guentner, R.; Scherf, U. *J. Chem. Phys* **2001**, *115*, 10007

(10) Romanovskii, Yu. V.; Bässler, H. *Chem. Phys. Lett*. **2000**, *326*, 51

(11) Monkman, A. P.; Burrows, H. D.; Hartwell, L. J.; Horsburgh, L. E.; Hamblett, I.; Navaratnam, S. *Phys. Rev. Lett.* **2001**, *86*, 1358

(12) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals and Polymers*; Oxford University Press: New York 1999

(13) Karg, S.; Dyakonov, V.; Meier, M.; Riess, W.; Paasch, G. *Synth. Met.* **1994**, *67*, 165

(14) Romanovskii, Yu. V.; Gerhard, A.; Schweitzer, B.; Personov, R. I.; Bässler, H. *Chem. Phys.* **1999**, *249*, 29

(15) Stolzenburg, F.; Bässler, H. *Mol. Cryst. Liq. Cryst*. **1989**, *75*, 147

(16) Schrader, S.; Riess, W.; Vestweber, H.; Koch, N. *Proc. SPIE* **1998**, *3476*, 188

(17) Schrader, S.; Imperia, P.; Koch, N.; Leising, G.; Falk, B. *Proc. SPIE* **1999**, *3797*, 209

(18) Hertel, D. Dissertation, Marburg, 2000.

(19) Richert, R. Habilitation, Marburg, 1991.

(20) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals and Polymers*; Oxford University Press: New York, 1999; p 134

(21) Scheidler, M.; Cleve, B.; Bässler, H.; Thomas, P. *Chem. Phys. Lett*. **1994**, *225*, 431

(22) Ries, B.; Bässler, H. *J. Mol. Electron*. **1987**, *3*, 15

(23) Hertel, D.; Romanovskii, Yu. V.; Schweitzer, B.; Scherf, U.; Bässler, H. *Synth. Met.* **2001**, *116*, 139

(24) Seiferheld, U.; Bässler, H.; Movaghar, B. *Phys. Rev. Lett.* **1983**, *51*, 813

(25) Hensel, K.; Bässler, H. *Adv. Mater. Opt. Electron.* **1992**, *1*, 179

(26) Vissenberg, M. C. J. M.; de Jong, M. J. M. *Phys. Rev. Lett.* **1996**, *77*, 4820

(27) Arkhipov, V. I.; Bässler, H.; Deussen, M.; Göbel, E. O.; Kersting, R.; Kurz, H.; Lemmer, U.; Mahrt, R. F. *Phys. Rev. B* **1995**, *52*, 4932

(28) Müller, J. G.; Lemmer, U.; Feldmann, J.; Scherf, U. *Phys. Rev. Lett.* **2002**, *88*, 147401