PHYSICAL REVIEW B VOLUME 61, NUMBER 20 15 MAY 2000-II

Effects of interchain interactions, polarization anisotropy, and photo-oxidation on the ultrafast photoluminescence decay from a polyfluorene

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(Received 15 November 1999)

The ultrafast dynamics of excitons and excimers in an aligned film of poly(dioctylfluorene) (F8) have been studied by femtosecond time-resolved photoluminescence spectroscopy. The results indicate that the excimer formed in F8 involves only a small change in intermolecular separation upon excitation and has a limited, but nonzero, mobility. From changes in the photoluminescence decay upon photooxidation of F8 we deduce that the exciton diffusion constant is larger than the excimer diffusion constant by a factor of 21 ± 2, thereby explaining why the excitonic luminescence is more strongly affected by the presence of quenching sites than the excimer luminescence. The decay of excitonic photoluminescence exhibits a significant polarization anisotropy, consistent with migration of excitons between regions with different orientation of the polymer chains. In contrast, excimer migration between such domains is inhibited since the excimer experiences the domain borders as potential barriers.

I. INTRODUCTION

Light-emitting diodes incorporating conjugated polymers as the active layer have shown rapid improvement since the discovery of electroluminescence from poly(*p*-phenylenevinylene),[1] (PPV) with specifications now approaching industrial standards.[2] Moreover, the inherent anisotropy in these materials results in the emission of strongly polarized light from films in which polymer chains are oriented preferentially in a particular direction. Various methods have been developed to produce such aligned films, since they are promising candidates for use as backlights in liquid crystal displays (LCD's) which currently incorporate relatively bulky and expensive polarizers.[3] In this paper we address some of the properties of an oriented film of poly(dioctylfluorene) (F8), a high efficiency[4] blue-light-emitting conjugated polymer.

Interchain interactions in polyfluorene films have recently been found to result in the formation of excimers which give rise to an additional, redshifted band in the luminescence. Similar effects have been observed for a variety of conjugated polymer films.[5–8] Since interchain interactions lead to the formation of lower-energy excited states coupled only weakly to the ground state, they are generally considered to be detrimental to the luminescence efficiency. Another problem associated with F8 is that photo-oxidation affects the excitonic emission more strongly than the excimer emission, thereby causing an undesired color change in the luminescence.

In the following, we present results obtained from femtosecond up-conversion measurements on an oriented sample. We show that significant differences can be found between the properties of the excimer and those of the exciton, regarding the decay of the photoluminescence, its polarization anisotropy, and finally its changes upon photooxidation of the polymer chains.

II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Oriented films of poly(9,9dioctylfluorene) were produced by spin-casting F8 dissolved in *p*-xylene onto a glass substrate which had been coated with a polyimide film and rubbed with nylon cloth to provide an alignment layer. The F8 film was heated in vacuum to 200 °C, annealed for 100 h, cooled slowly to room temperature, then reheated to 205 °C and quenched to result in highly oriented films of about 100-nm thickness.[9]

We have performed time-resolved photoluminescence (PL) experiments on F8, employing the femtosecond up-conversion technique. The sample was excited with the frequency doubled output from a mode-locked Ti:sapphire laser supplying 200-fs pulses at an energy of 3.12 eV. To set the polarization of the exciting beam, it was passed through a $\lambda/2$ plate and a Glan-Thompson polarizing prism. Photoluminescence originating from the sample was up-converted in a β-barium-borate crystal using the fundamental laser beam at 1.56 eV as a gate. Sum-frequency photons were dispersed in a monochromator, and detected via single-photon counting. The overall temporal resolution of the system was about 400 fs. The average power on the sample was 0.5 mW on a spot of 107-μm diameter. A single pulse created an average excitation density of 5.0×10^{10} cm^{-2} (3.1×10^{10} cm^{-2}) for the exciting beam polarized parallel (perpendicular) to the alignment direction, the variation being due to the difference in reflection and absorption for the two excitation polarizations. Since only vertically polarized light could be up-converted, the sample was rotated to detect the luminescence emitted with polarization either parallel or perpendicular to the alignment direction. The sample was held in vacuum at a pressure of 10^{-5} mbar, and all experiments were conducted at room temperature. To measure time-integrated photoluminescence, the PL was diverted to a double-grating spectrometer (Spectramate 1680) and detected with a Si photodiode using a lock-in technique. Both time-resolved and time-integrated spectra were corrected for spectral response. To produce photo-oxidized samples, the pressure was increased by a factor of 1000 to $\approx10^{-2}$ mbar, and specific spots on the sample were irradiated with laser light at 3.12 eV and an intensity of 5.6 W cm^{-2}.

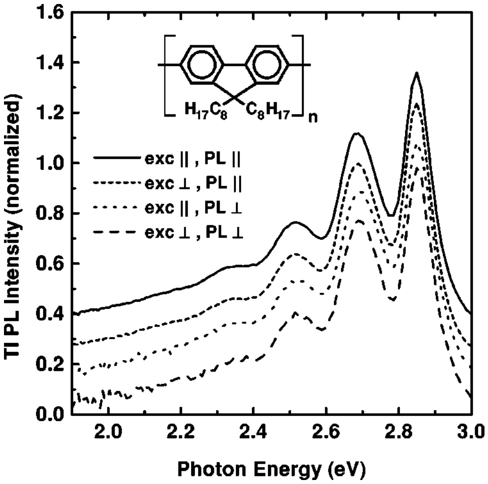

FIG. 1. Time-integrated photoluminescence spectra for the four combinations of excitation and photoluminescence polarization (normalized and offset); the inset shows the chemical structure of F8.

III. RESULTS AND DISCUSSION

In all experiments described below, the polarization of the exciting beam was set to be either parallel (exc ∥) or perpendicular (exc ⊥) to the sample's alignment direction. Similarly, the photoluminescence linear polarization components oriented either parallel (PL ∥) or perpendicular (PL ⊥) to the alignment direction were detected, resulting in four possible excitation and photoluminescence polarization combinations which we will denote in the following as (exc ∥, PL ∥), (exc ⊥, PL ∥), (exc ∥, PL ⊥), and (exc ⊥, PL ⊥). Figure 1 shows the time-integrated photoluminescence spectra of F8 for the four polarization combinations. The spectra are of approximately the same shape but differ in amplitude. The photon emission at 2.85 eV is due to the transition from the lowest vibrational level of the first excited electronic state to the lowest vibrational level of the ground electronic state (0-0 transition). Vibronic replicas exist at 2.69, 2.52, and 2.35 eV, corresponding to the (0-1), (0-2) and (0-3) vibronic transitions, respectively. Below $\approx$2.3 eV the photoluminescence spectrum displays a broad, featureless low-energy tail. This redshifted emission was reported previously for F8 (Ref. 10) and poly(dihexylfluorene).[11,12] Since these redshifted emission bands were not found for polyfluorene solutions,[12] and their relative intensity seems reduced when the film thickness is decreased below 10 nm,[11] the emission is likely to be caused by the interaction between polyfluorene chains in close proximity. The fact that no significant difference between the absorption in solution and in the solid film was found, as well as the observation of identical excitation spectra at the long-wavelength band and the excitonic band, led Bliznyuk *et al.* to the conclusion that the redshifted emission is due to the formation of excimers rather than physical dimers. In the following we will show that our results are compatible with the low-energy emission being caused by excimers that require only small changes in the intermolecular separation upon formation, resulting in a fast formation and a limited, but nonzero, excimer mobility.

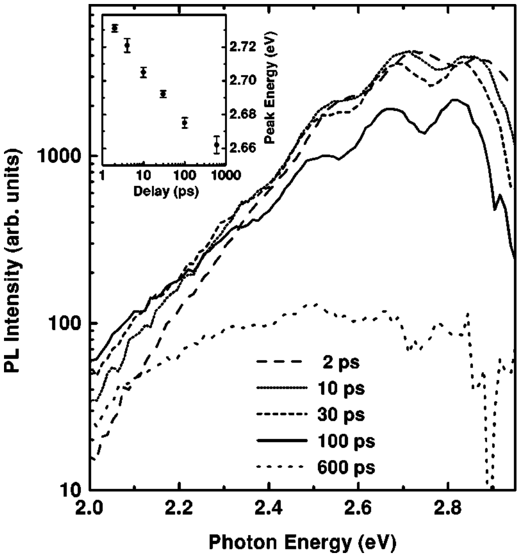

FIG. 2. Photoluminescence spectra at different times after excitation for (exc ∥, PL ∥). The inset shows the energy of the (0-1) transition peak vs time after excitation. (Zero delay corresponds to the onset of PL.)

Figures 2 and 3 show the photoluminescence spectra at various delays and the PL decay curves at numerous photon energies, respectively. As can be seen, the PL intensity at the three main vibronic peaks decays monoexponentially, accompanied by a redshift in the peak energy of the emission due to exciton migration to chains with longer conjugation lengths.[13] Fitting the sum of five Gaussians to the spectra at a variety of delays reveals that the vibronic peak energy shifts by 70 meV between 2 and 600 ps after excitation, which indicates the presence of a relatively wide range of conjugation lengths (see the inset in Fig. 2). Exciton migration is also responsible for the initial fast ($\tau \approx 3$ ps) decay of the photoluminescence at the high-energy tail (2.93 eV) of the (0-0) transition, and has been observed in a number of conjugated polymers other than F8.[13–15] Monoexponential fits to the decay curves measured at the three main vibronic peaks yield time constants between 120 and 130 ps depending on whether the curves were taken on the high- or low-energy sides of the vibronic peak.[16] All delay curves rise within the system resolution (400 fs), showing the strong

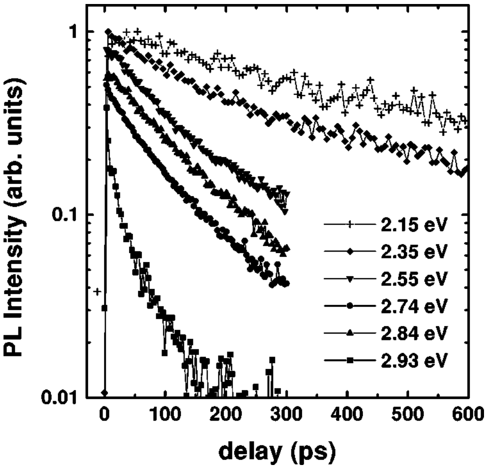

FIG. 3. Photoluminescence decay at various photon energies for (exc ∥, PL ∥).

electron-phonon coupling commonly observed in conjugated polymers.

At energies lower than 2.35 eV the temporal behavior of the photoluminescence changes significantly: The PL spectra at 100- and 600-ps delays (Fig. 2) converge with decreasing photon energy when plotted on a semilogarithmic scale, which indicates an increasing excimer lifetime with decreasing photon energy. These trends are supported by single-exponential fits to the photoluminescence decay curves: At 2.35 eV the photoluminescence decays with a time constant of 321 ± 8 ps, which increases to 511 ± 15 ps at 2.15 eV.

When the spatial separation between two monomers is reduced, the intermolecular interaction will result in a splitting of the exciton state into two nondegenerate states. It has been shown that in the case of parallel orientation of the molecules, the lowest of the two excited states is optically dipole forbidden due to like parity, and therefore acts as a trap.[17,18] However, recent theoretical calculations have revealed that the large electron-phonon coupling encountered in π-conjugated systems changes the symmetry of the excited-state wave functions, resulting in a finite transition probability for the lower of the two states.[19,20] Quantum-chemical calculations performed by Cornil *et al.*[19] indicated that geometrical changes due to lattice relaxations, which in π-conjugated systems occur within hundreds of femtoseconds after excitation, are located mostly on a single monomer. Excitation of one monomer therefore causes the dimer's geometry to be asymmetric with respect to the two chains, resulting in a relaxation of the optical selection rules and a transfer of oscillator strength to the lower of the two excited states. As the separation between the chains is decreased, the emission redshifts increasingly with respect to the emission of the isolated chain, and the amplitude of the transition dipole moment between the ground state and the lowest excited state decreases because the wave functions become more and more symmetric. These calculations therefore link the lifetime of the lowest excited state of two interacting conjugated polymer chains with the energy of the state: the lower the energy of the transition the longer the lifetime of the excited state will be, which is exactly what we observe in our measurements.

A second important aspect is the evolution of the photoluminescence at early times after excitation within the energy region of the redshifted band: We find that the photoluminescence shows an initial fast (<400 fs) rise followed by a slow increase, which peaks at a 25-ps delay for a photon energy of 2.15 eV (not shown). This secondary rise becomes slower with decreasing photon energy (the PL spectrum at 100 ps crosses the spectrum at 30-ps delay at ≈ 2.15 eV), and more dominant with respect to the initial fast rise. An excimer is a physical dimer which is associated in an excited electronic state and dissociated in its ground state.[21,22] That is, the formation of an excimer is a two-step process consisting of the excitation of one of the two molecules, followed by the reduction of the system's potential energy due to the attractive excimer interaction, accompanied by a change in the intermolecular separation. For this reason, the excimer photoluminescence should rise more slowly than the excitonic luminescence. However, if the intermolecular separation in the ground state of the two molecules is close to that in the excimer state, rapid excimer formation is possible, and has in fact been observed in pyrene crystals.[22] The rapid (<400 fs) initial rise we find in the excimer luminescence indicates that this is also the case for F8, at locations where the polymer chains are in close proximity. These findings are confirmed by the fact that the secondary rise becomes slower with decreasing photon energy: Mahrt *et al.* observed a similar delayed rise in the low-energy region of the photoluminescence from a poly-(para)-phenylene-type polymer (LPPP), and attributed it to the migration of excitons to sites with small interchain separation which support the formation of excited dimers.[5] However, the probability for an exciton to find a site where excimer formation can occur should not depend on the excimer transition energy at that site. This means that if the delayed rise was caused solely by exciton migration to excimer sites, the rise time should be independent of the excimer transition energy, which is not the case in our experiments. We therefore suggest that the excimers retain some mobility, enabling them to migrate to sites where the interchain separation is small and a lower-energy excimer can be formed. Since excimers are formed via a two-step process, in principle their migration would have to involve an energetically unfavorable dissociation, so excimers are generally expected to be trapped at the site of their formation. Fischer *et al.*, on the other hand, showed that excimer migration can occur if, at the intermolecular distance of the two molecules in their ground state, the excimer interaction is already strong enough to provide an overall attractive potential once the pair is excited.[23] In this case a relatively small amount of activation energy will be sufficient to transfer the excitation to adjacent molecules. The fact that we observe migration therefore confirms that the two molecules in their ground electronic state are at an interchain separation close to the equillibrium separation in the excimer state. Note that the possibility of excimer migration also means that excimers can to a limited extent be excited directly.[23] The distinction between a physical dimer, whose interchain separation does not vary upon excitation, and an excimer involving only small changes in the interchain separation is not always easy, and is sometimes avoided.[19,20] The excimer should show an almost negligible direct absorption and a limited amount of mobility, both of which should be dependent on temperature.[23]

The second part of this paper deals with anisotropy in the photoluminescence with excitation and emission polarization. Thin conjugated polymer films, in which all chains are aligned in one direction, have attracted interest because their polarized luminescence makes them a promissing replacement for the currently unpolarized backlights in LCD's. This would allow the removal of absorptive polarizers, resulting in the manufacture of thinner and cheaper LCD's with higher efficiencies. However, two factors limit the degree of anisotropy of luminescence polarization which can be achieved: disorder (or imperfect chain alignment), and the occurrence of an off-axis transition dipole moment with respect to the polymer backbone. While the former can be improved by the use of suitable processing techniques, the latter may provide a final limit to the obtainable degree of polarization. It is therefore important to be able to distinguish between these two effects. We will show in the following that disorder in an oriented sample leads to an anisotropy in the photoluminescence decay dynamics which can be easily identified.

The aligned F8 sample used for our experiments displays

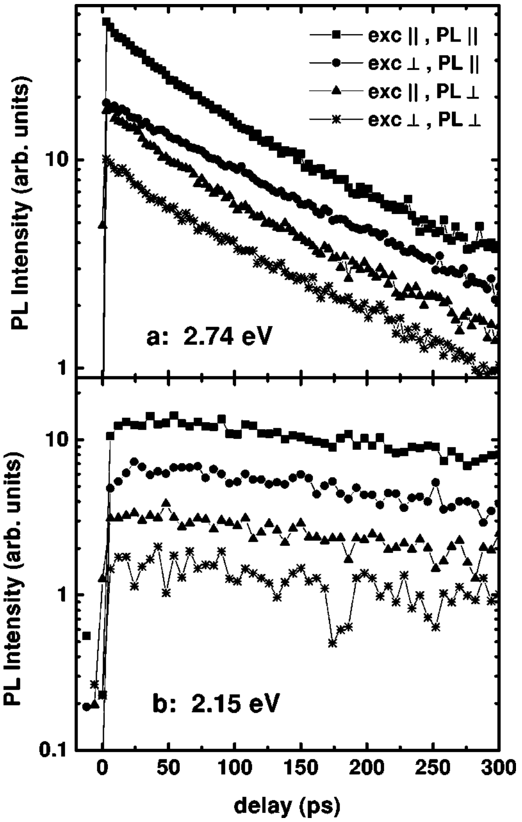

FIG. 4. Photoluminescence decay for the four excitation/photoluminescence polarization combinations at photon energies of (a) 2.74 eV and (b) 2.15 eV. The curves have been rescaled for better comparison.

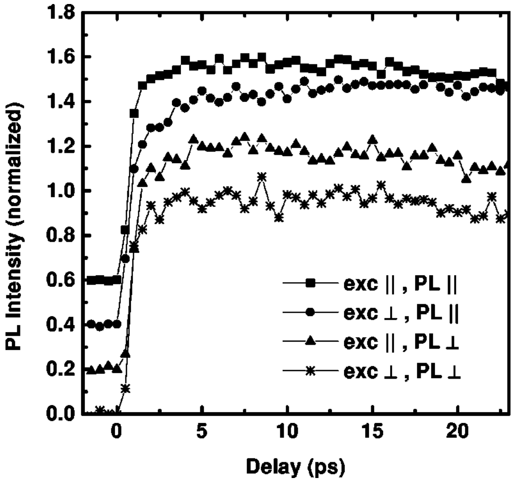

FIG. 5. Onset of the photoluminescence at 2.84 eV for the four excitation/photoluminescence polarization combinations. The curves have been rescaled and offset for clarity.

a dicroic ratio between the absorption coefficients of $\alpha_{\parallel}/\alpha_{\perp}=3.6\pm0.5$ at the excitation energy (3.12 eV). We define the polarization ratio as the ratio between the intensity of the photoluminescence emitted with the polarization parallel to the alignment direction and the intensity of the photoluminescence with polarization perpendicular to the alignment direction ($r_{pol}=PL_{\parallel}/PL_{\perp}$). The polarization ratio of the time-integrated photoluminescence varies with the polarization of the exciting light; for (exc $\parallel$), $r^{\parallel}_{pol}=4.1\pm0.5$, whereas in the case of (exc $\perp$) we find $r^{\perp}_{pol}=3.2\pm0.5$. This can be explained by assuming that some of the chains are not oriented parallel to the alignment direction: while parallel polarized light (exc $\parallel$) will predominantly excite chains oriented parallel to the alignment direction, light polarized perpendicular to the alignment direction is comparatively more likely to excite some of the unaligned chains, leading to a reduction of the polarization ratio in the case of (exc $\perp$). The fact that other groups have found higher dicroic absorbance ratios in aligned F8 samples[9,24] also shows that some amount of disorder is likely to be present in the samples used in our experiments.

The dependence of the photoluminescence decay on the polarization of the excitation and the luminescence is shown in Fig. 4. While in the region of the excitonic emission (2.74 eV) significant differences are found, the excimer luminescence (2.15 eV) exhibits an identical photoluminescence decay for the four excitation/luminescence polarization combinations. The changes in the decay of the excitonic PL start to occur immediately after excitation, as indicated in Fig. 5. These results can be explained by considering that exciton migration can take place between regions of the sample where the chains are parallel to the alignment direction, and regions where the chains form a reasonably large angle with respect to the alignment direction (unaligned regions).[25] Since the unaligned chains are in the minority, their nearest neighbors are likely to be chains oriented parallel to the alignment direction, meaning that exciton migration from unaligned polymer chains to aligned chains is more likely to occur than vice versa. For this reason, migration effects should be more dominant in the case of (exc $\perp$, PL $\parallel$) than in the case of (exc $\parallel$, PL $\perp$) which is what we observe. Figure 6 displays changes in polarization ratio with time after excitation for the two excitation polarizations. The curves were obtained by a division of the normalized decay curves taken at 2.74 eV. When the sample is excited with light polarized perpendicular to the alignment direction, the polarization ratio increases with time due to exciton migration to aligned regions, whereas exciton migration causes a reduction in the

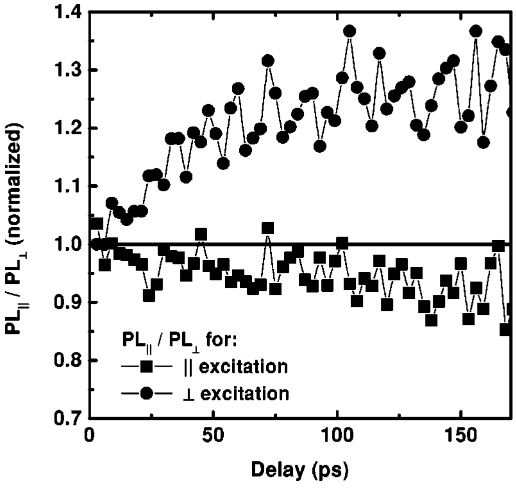

FIG. 6. Polarization ratio ($PL_{\parallel}/PL_{\perp}$) vs delay time for excitation polarization either parallel or perpendicular to the alignment direction. The decay curves were normalized at 3-ps delay prior to division.

polarization ratio with time in the case of excitation with parallel polarized light. Most of the changes occur within 100 ps after excitation, after which the polarization ratio assumes a constant value. Integration of the curves shown in Fig. 6 over time indicates that exciton migration leads to an increase in the overall PL polarization ratio of 25% in the case of (exc $\perp$) and a decrease of 8% in the case of (exc $\|$). Exciton migration therefore compensates in part, but not fully, for the variation in the polarization ratio of the time-integrated PL with the polarization of the exciting light (caused by preferential excitation of either aligned or unaligned regions of the sample, as mentioned earlier). For this reason, an accurate determination of order parameters solely from time-integrated photoluminescence measurements, as attempted by Schartel *et al.*,[26] is of limited validity even in highly oriented samples.

If all polymer chains were aligned perfectly, no anisotropy in the photoluminescence decay should be observed and the polarization ratio of the time-integrated photoluminescence should be independent of the excitation polarization. In this case any luminescence polarized perpendicular to the alignment direction will solely be due to an off-axis transition dipole moment, and the angle θ between the polymer backbone and the dipole moment can be taken directly from the polarization ratio as $\theta=\tan^{-1}(1/\sqrt{r_{pol}})$.[25]

Another aspect which needs clarification is why the luminescence decay is isotropic at 2.15 eV. As pointed out earlier, the excimer seems to retain some mobility, so that it is surprising to find that there are no signs of migration effects in the polarization dependence of the PL decay. On the other hand, calculations by Cornil *et al.*[19] showed that as the angle between the chain axes of two molecules sustaining an excimer is increased, the splitting between the lowest two optical transitions decreases because of the reduced overlap between the wave functions. For this reason, the lowest excited state of an excimer located on two chains which are not parallel is energetically higher than that for two parallel chains. If an excimer is to migrate from a sample domain where chains are oriented in a particular direction to a domain consisting of chains oriented in a significantly different direction, it will temporarily have to occupy a state of higher energy. For an excimer, domains of different chain orientation are therefore separated by a potential barrier inhibiting the migration between such domains.

Finally we wish to comment on the possibility of the generation of interchain excitons, or polaron pairs, where the electron is located on one chain and the hole on a neighboring chain. We find that throughout the whole spectral region the total number of photons emitted immediately after excitation per number of photons absorbed is independent of the polarization of the exciting light. These results take into account the changes in absorption and reflectivity $[(1-R_{\perp})/(1-R_{\|})=1.08\pm0.01]$, with the excitation polarization. It has been suggested that polaron pairs are created in greater quantity for excitation with light polarized orthogonally to the polymer axis.[27] Our results therefore indicate, in accordance with similar measurements performed on stretch-aligned PPV by Hayes *et al.*,[25] that in our case the primary excitations are not polaron pairs but polaron-excitons. This also holds in regions where the chains are close enough to support excimer formation.

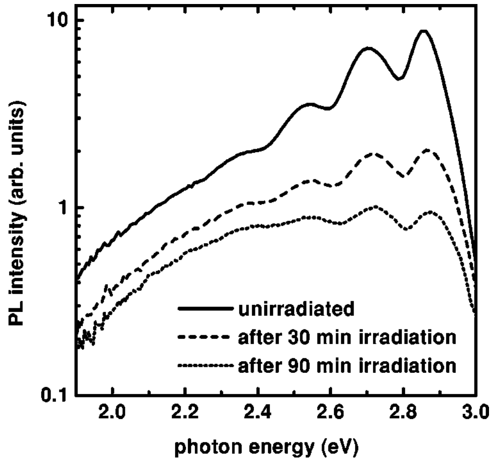

FIG. 7. Effect of UV irradiation in the presence of oxygen on the time-integrated photoluminescence of F8.

The third and final part of this paper is concerned with the effect of photooxidation on the photoluminescence of F8. It was observed previously that UV illumination of poly(dihexylflourene) in air results in a reduction of the photoluminescence intensity across the whole spectral region.[11] This degradation affects the excitonic luminescence more strongly than that originating from excimers, thereby causing an unwanted color change in the emission with illumination time. Bliznyuk *et al.*[11] confirmed that these changes originate from photooxidation of fluorene resulting in the creation of traps that act as quenching centers. We will show in the following that the reason why the excimer emission is less affected by sample oxidation than the excitonic emission can be related directly to the smaller diffusivity of the excimers.

Figure 7 displays the time-integrated photoluminescence spectra of F8 after different durations of UV irradiation in the presence of oxygen. The majority of the changes in the PL occur within the first 30 min of UV illumination, after which the degradation slows. These changes are most likely due to chain oxidation, since the degradation is reduced when either the air pressure is decreased or the irradiation is conducted through the substrate. Moreover, we observed a certain amount of photobleaching upon UV illumination, which was previously shown to accompany the photooxidation of PPV.[28,29] The photoluminescence decay curves at 2.74 and 2.15 eV after different UV illumination times are plotted in Fig. 8 for the case of (exc $\|$, PL $\|$). It can be seen that while the shape of the excitonic photoluminescence decay at 2.74 eV becomes strongly nonexponential with an initial fast decay, the excimer emission at 2.15 eV shows only a small reduction in the decay time upon increasing sample oxidation. In order to obain a quantitative analysis we have calculated fits to these data based on the model by Balagurov and Vaks[30] for the survival probability of an exciton on a one-dimensional walk with randomly situated traps. This model was used successfully by Yan *et al.* to describe the PL decay dynamics for PPV with varying degrees of photooxidation.[31] We have used the asymptotic fitting function

$$I=I_0\sqrt{\frac{t}{\tau_{diff}}}\exp\left(-\left[\frac{t}{\tau_{diff}}\right]^{1/3}\right)\exp\left(-\frac{t}{\tau_0}\right)+I_1\exp\left(-\frac{t}{\tau_0}\right), \tag{1}$$

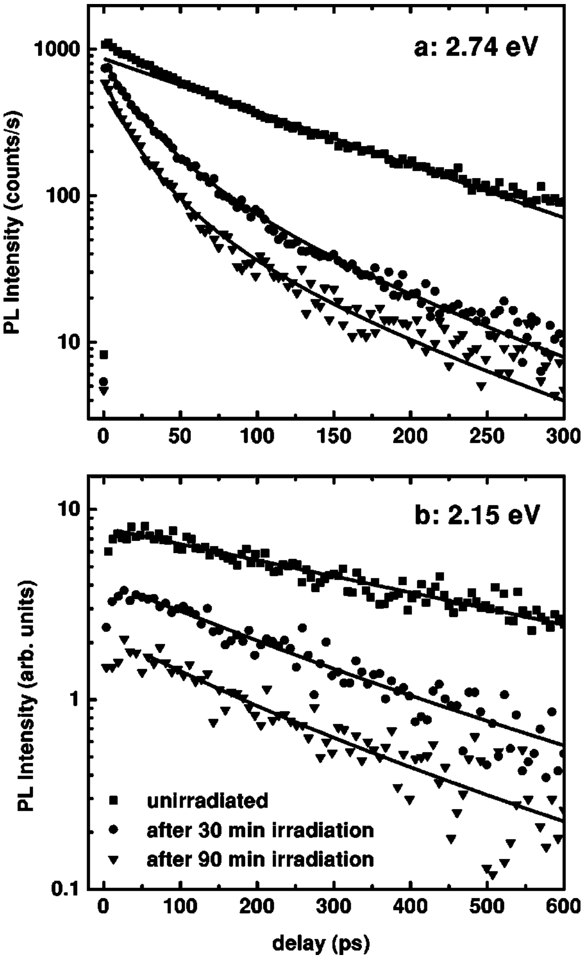

FIG. 8. Photoluminescence decay at (a) 2.74 eV and (b) 2.15 eV photon energy, before and after irradiation with UV light in the presence of oxygen. The solid lines represent fits to the data assuming a monoexponential decay in case of the unirradiated sample, and an additional loss due to carrier migration along a chain containing randomly situated traps in case of the UV irradiated sample. [Curves in (b) have been rescaled.]

where $\tau_{diff}=[2\pi^2(3/2)^3c^2D]^{-1}$ is the characteristic diffusion time, D the diffusion constant of the exciton or excimer in the absence of traps, and c the one-dimensional effective density of traps. The first part of Eq. (1) describes the diffusion of excitons or excimers to quenching centers, modified by the lifetime τ_0 of the excited state, while the second part represents the recombination from sample regions far from the surface which are largely unaffected by oxidation. The natural lifetime τ_0 was extracted from monoexponential fits to the PL decay from the unoxidized sample as 120 ps at 2.74 eV and 511 ps at 2.15 eV. For the curves taken at 2.74 eV, I_0, I_1, and τ_{diff} were varied, while for those at 2.15 eV only τ_{diff} and a scaling constant were adjustable, with the ratio I_0/I_1 taken from the previous fits to the curves at 2.74 eV. Table I contains the values obtained for τ_{diff} after different irradiation times both for the exciton and the excimer. The ratio between the characteristic diffusion times τ_{diff} and the ratio between the diffusion constants D are directly related via

$$\frac{\tau_{diff}(\text{excimer})}{\tau_{diff}(\text{exciton})}=\frac{D(\text{exciton})}{D(\text{excimer})}\equiv R_D. \tag{2}$$

TABLE I. Parameters extracted from fits to the decay curves based on the model of a one-dimensional exciton (excimer) diffusion.

Irradiation time (min)	τ_{diff} (exciton)	τ_{diff} (excimer)	$R_D=\frac{D(\text{exciton})}{D(\text{excimer})}$
30	0.61 ± 0.01	11.6 ± 1	19 ± 2
60	0.42 ± 0.01	9.8 ± 1	23 ± 2
90	0.41 ± 0.01	8.3 ± 1	20 ± 2

R_D is found to be independent of the degree of photooxidation, as should be expected. We can therefore extract an average value of $R_D=21\pm2$ for the ratio between the exciton diffusion constant $D(\text{exciton})$ and the excimer diffusion constant $D(\text{excimer})$. These results explain why the exciton is more strongly affected by chain photooxidation than the excimer: while the excitonic lifetime is only ≈4.3 times lower than the excimer lifetime (at 2.15 eV emission), the excitonic diffusion constant is larger by a factor of $R_D=21$ compared with that of the excimer. Therefore, an exciton is less likely to recombine radiatively before being trapped than an excimer. The value of R_D we obtain from the photooxidation measurements confirms the image of the excimer we have outlined earlier in this paper: While the excimer in F8 is not entirely stationary, its mobility is restricted, due to the activation energy needed to move an excimer, due to geometrical constraints (the excimer can only migrate to sites where chains are in close proximity), and finally by the borders between sample domains of different chain orientation representing potential barriers to the excimer.

IV. CONCLUSION

We have examined the time-resolved photoluminescence from poly(dioctylfluorene) (F8) and found distinct differences between the properties of the exciton and the excimer formed in F8. While the effective lifetime of the excitons is ≈120 ps and is independent of the transition energy, the excimer lifetime is generally longer and increases with decreasing energy. Both the short initial rise in the excimer luminescence and the slower, energy-dependent rise indicate that the excimer formed in F8 involves only a small change in interchain separation upon excitation, similar to the type of excimer found in pyrene crystals. The excimer therefore exhibits a small, but nonzero, mobility, in agreement with our measurements on photooxidized F8 which yield a ratio $R_d=21\pm2$ between the diffusion constants D of the exciton and the excimer. We show that while considerable exciton migration occurs between sample regions of different polymer chain orientations, the excimer is confined to its domain, since it experiences the domain borders as potential barriers. All our findings are consistent with quantum-chemical calculations performed by Cornil *et al.*[19] Our measurements of the polarization anisotropy in the PL decay dynamics exhibit a strong sensitivity to the amount of disorder in an oriented sample, and can therefore be used to probe the degree of order achieved. Suitable model calculations incorporating exciton migration in partly aligned polymer films provide an interesting topic for further research, since they could result in the determination of the angle the transition dipole moment forms with the polymer axis, as well as some order parameter, from the anisotropy found in the luminescence decay dynamics. Finally, we have shown that the changes in the spectral shape of the photoluminescence from F8 upon photo-oxidation are directly related to the smaller diffusivity of the excimer with respect to the excitonic diffusivity. Care has to be taken when the luminescence spectra of F8 films with different processing history are compared: since the inclusion of traps will reduce the excitonic luminescence more strongly than that originating from less mobile excimers, photoluminescence spectra from samples containing quenching centers will show a relative amount of excimer emission that is not representative of the degree of aggregation present in the sample.

ACKNOWLEDGMENTS

We would like to thank M. Grell from the University of Sheffield for supplying a substrate with an alignment layer, and Cambridge Display Technology for providing F8. We are grateful to M.A. Stevens for sample preparation and C. Silva for helpful discussions. This work was supported by the Engineering and Physical Sciences Research Council.

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