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Morphology dependence of the triplet excited state formation and absorption in polyfluorene

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Poly(9,9-dioctylfluorene) (PFO) is widely used as a highly efficient blue-emitting polymer for light-emitting diode applications. Films of PFO are known to contain a planar β-phase or a disordered glassy phase that affects the emission characteristics. We have studied the morphology dependence of the photoinduced absorption in such PFO films and find that the T_1-T_n absorption signal differs between the two phases in energy, linewidth, and intensity. The lower intensity we observe in the β-phase as compared to the glassy phase is evidence for a lower T_1 population in the former. We attribute this to firstly, reduced intersystem crossing and secondly, increased charge generation due to both more extended conjugation along the chains and higher interchain interactions in the planar, well-ordered β-phase. The reduced energy and smaller linewidth of the triplet absorption in the β-phase as compared to the glassy phase are indicative of a more delocalized T_n state and a higher degree of order in the β-phase, respectively.

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Polyfluorenes have emerged as a promising class of organic semiconductors for efficient blue luminescence in light-emitting applications.[1,2] The strong morphology dependence of their photophysical properties, particularly in poly(9,9-dioctylfluorene) (PFO), has been studied intensely in recent years.[3–8] Among its applications is, for example, the fabrication of polymer light-emitting devices (LEDs) with highly polarized emission from aligned chains.[9–11] In PFO, distinct phases have been identified; mainly a disordered glassy phase and a crystalline β phase consisting of more planar chains.[4,12] The fraction of each phase present in a film can be influenced by thermal[4–6,12] and vapor[3,6] treatment of as-cast films or by spinning films from solvents with different boiling points and solubility parameters.[3,7,8] Besides being a material of strong interest for application purposes, PFO, through its morphological diversity, offers a unique possibility to study structure-property relationships without the need for chemical modification. In the present study, we focus on the morphology dependent properties of triplet excited states in PFO. Detailed knowledge about triplet states is of importance for both a thorough understanding of the fundamental photophysics of conjugated polymers and for their technological application in electronic devices such as LEDs. We perform photoinduced absorption measurements to study the effect of chain planarization and interchain order on the formation probability of triplet excited states and the energy of the triplet-induced absorption.

Polymer solutions at 10 mg/ml in either chloroform or cyclopentanone were prepared from PFO as obtained from CDT Ltd. 100-nm-thick films were spun onto quartz substrates using a conventional photoresist spin coater. A Hewlett-Packard ultraviolet-visible spectrometer was used to take absorption spectra. Photoluminescence (PL) measurements were carried out at room temperature in a Cary Eclipse Fluorescence Spectrophotometer. Photoinduced absorption measurements were taken at 90 K in a continuous flow cryostat with excitation provided by a continuous wave 405 nm laser diode at 45 mW. The pump beam was modulated mechanically. The probe beam was generated by a 150 W tungsten halogen lamp and the probe wavelength selected with a Chromex 250SM scanning monochromator. The transmitted probe beam was monochromated using a second Chromex 250SM and its intensity detected by a Si photodiode coupled to a SR830 dual phase lock-in amplifier. Measurement of the lock-in signal after closing the first monochromator slit allowed any background PL signal to be subtracted from the total signal.

We prepared PFO films with different β-phase contents by spin coating from different solvents as detailed in Ref. 8. A film containing pure disordered glassy phase was spun from chloroform, a low boiling point solvent with a solubility parameter matching that of PFO. Cyclopentanone, a high boiling point solvent with a solubility parameter dissimilar to that of PFO, is used to induce the formation of a high amount of planar β-phase embedded in the disordered glassy phase. The amount of β-phase was further increased by exposing the sample to a saturated atmosphere of toluene vapor for 4 h.

The absorption and photoluminescence spectra of the samples obtained are shown in Fig. 1. The glassy phase is typically characterized[1] by a broad, unresolved absorption spectrum with an onset at around 2.95 eV and a photoluminescence with a 0-0 transition at 2.93 eV and a linewidth of about 160 meV. The absorption of the planar β-phase occurs

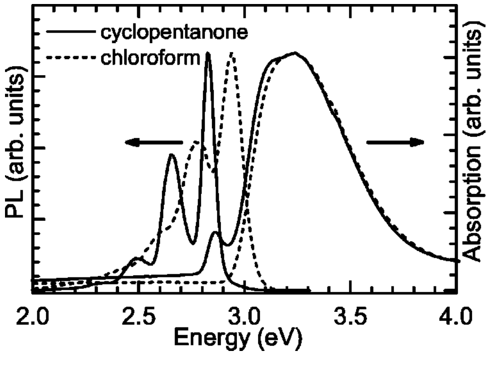

FIG. 1. Absorption and photoluminescence of PFO films spun from chloroform (dashed lines) and cyclopentanone (solid lines).

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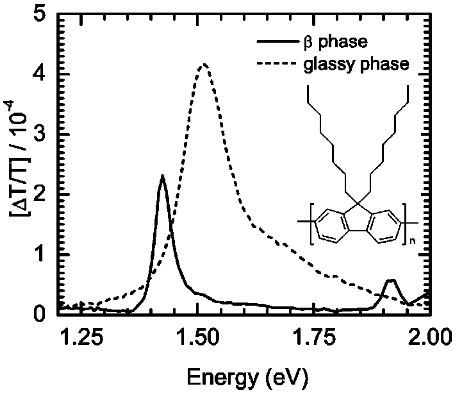

FIG. 2. Photoinduced absorption of PFO films spun from chloroform (dashed lines) and cyclopentanone (solid lines) at 90 K and 36 Hz. Inset: Chemical structure of PFO.

at lower energy with well-resolved 0-0 and 0-1 transitions at 2.83 and 3.10 eV, respectively. The emission with its 0-0 transition at 2.82 eV is similarly redshifted with respect to the glassy phase and exhibits a narrower linewidth of about 65 meV. From the absorption spectra of our samples and the pure β-phase absorption spectrum, we calculate that the chloroform-spun film studied here does not contain any detectable amount of β-phase (less than 1%) while the cyclopentanone-spun film contains about 16% of β-phase. Nevertheless, we note that the emission in the cyclopentanone-spun film stems exclusively from planar β-phase chromophores. This is due to the ultrafast, very efficient energy transfer between the two closely intermixed phases which is facilitated by the remarkably high Förster radius of the planar β-phase.[8]

The photoinduced absorption (PA) spectra of the films studied in absorption and PL are shown in Fig. 2. Both samples show a strong T_1-T_n transition for which we find firstly, two different spectral positions and secondly, a different spectral width in the two samples. We attribute the transition in the chloroform-spun sample to the glassy phase (*vide infra*). It has a transition energy of 1.51 eV and a full width at half maximum of 120 meV. In the cyclopentanone-spun sample, we assign the transition to the β-phase (*vide infra*). It occurs at 1.43 eV and has a much smaller full width at half maximum of 45 meV, indicative of a narrower density of states and thus a higher degree of ordering in the β-phase. The energy and width we find for the β-phase T_1-T_n transition is consistent with the signals attributed by Cadby *et al.*[5] to both β-phase and glassy phase PFO (*vide infra*). Under 36 Hz modulation, the intensity of the T_1-T_n absorption signal in the β-phase is lower than the intensity in the glassy phase by a factor of 2. In addition to this, the cyclopentanone-spun sample shows a small polaron absorption peak at 1.93 eV, which is in agreement with Cadby *et al.*'s[5] findings of a PFO polaron signal at this position.

We attribute the triplet-state-induced absorption signal at 1.51 eV in the chloroform-spun sample to the glassy phase and the corresponding signal at 1.43 eV in the cyclopentanone-spun sample to the β-phase due to the following reasons: The chloroform-spun sample shows only evidence for the presence of glassy phase in both absorption and singlet emission (Fig. 1). Thus we conclude that this sample contains pure glassy phase, and consequently we attribute its T_1-T_n absorption signal to the glassy phase.

The cyclopentanone-spun sample, on the other hand, shows only β-phase emission although a large amount of the sample is constituted of glassy phase. This is due to the aforementioned picosecond complete energy transfer between the closely intermixed phases.[8] After photoexcitation, triplet formation occurs through intersystem crossing (ISC) on the order of nanoseconds in aromatic hydrocarbons,[13,14] which is slower than the picosecond energy transfer between the two phases. ISC thus takes place on β-phase chromophores. In addition, the T_1 state in planar β-phase PFO is expected to be lower in energy than that in the glassy phase as the T_1 energy of poly-para-phenylene-type polymers decreases with increasing planarization.[15] Accordingly, we expect that if a small, undetected fraction of singlet excitons did still remain on the glassy phase in our cyclopentanone-spun sample and some ISC took place there, this would be followed by rapid triplet energy transfer to the β-phase as triplet excitons are highly mobile. Furthermore, the fact that the linewidth found in our cyclopentanone-spun sample is narrower than in the chloroform-spun sample by a factor of 3 can be attributed to a much narrower density of states and thus a higher degree of interchain ordering in the former sample. In fact, the singlet exciton emission linewidth is similarly decreased from 160 to 65 meV between the glassy phase and the β-phase. We consequently attribute the T_1-T_n transition detected in the cyclopentanone-spun sample to the planar β-phase.

The energy shift of 80 meV between the two phases is consistent with a larger conjugation length in the planar phase which seems to stabilize the delocalized T_n state more strongly than the rather localized T_1 state,[16,17] particularly for high band-gap materials.[18] A similar energy shift between glassy and β-phase PFO from 1.7 to 1.6 eV was observed in the $(S_1$-$S_\mathrm{n})$ singlet excited-state absorption.[22]

We now consider the relative intensity of the T_1-T_n absorption signals in both phases. The intensity of the photoinduced absorption signal is given by

$$\Delta T/T = n_T \sigma d, \tag{1}$$

where n_T is the population density, σ the excited state absorption cross section, and d the thickness of the film. We presume that the absorption cross section in the highly conjugated planar β-phase is likely to be similar or even higher than in the disordered glassy phase. We therefore argue that the smaller signal in the planar β-phase as compared to the disordered glassy phase reflects a lower triplet state population density in the former.

For steady-state conditions, the triplet generation rate g_T is connected to the population density n_T via

$$n_T = g_T \tau / A d, \tag{2}$$

so that

$$\Delta T/T = g_T \tau \sigma / A, \tag{3}$$

where τ is the triplet lifetime and A the sample area. Thus, for identical sample areas and absorption cross sections, a

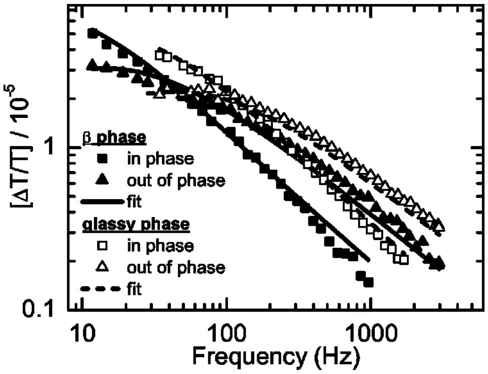

FIG. 3. Modulation frequency dependence (data and fit) of the triplet-exciton-induced absorption band in PFO films at 90 K: at 1.43 eV in the cyclopentanone-spun sample (solid symbols) and at 1.51 eV in the chloroform-spun sample (open symbols).

stronger induced absorption signal is connected to either a longer triplet lifetime or a larger triplet generation.

The triplet lifetimes can be obtained by measuring the dependence of the induced absorption intensity on the chopping frequency. In the case of a monomolecular dispersive process where a distribution of lifetimes governs the dynamics of the photoexcitations, the instrument response $R(\omega)$ in an induced absorption measurement can be modeled as a complex function[19]

$$R(\omega) = \frac{R_0}{1 + (i\omega\tau_0)^{\alpha}}, \tag{4}$$

where R_0 is the steady-state response, τ_0 is a "mean" lifetime, and $\alpha < 1$ is connected to the lifetime distribution function that can be realized once this parameter has been obtained experimentally. The real (imaginary) part of this complex function is the in-phase (out-of-phase) component. By fitting the frequency dependence at 90 K of the triplet-induced absorption band accordingly we obtain triplet lifetimes of 3.1 and 14.5 ms for the glassy phase and β-phase, respectively (Fig. 3) with very similar values for α of 0.74 and 0.68.

According to (4), the long triplet lifetime in the β-phase implies that the intensity of the photoinduced absorption signal in Fig. 2 may be somewhat reduced by overmodulation. In fact, when considering the frequency dependence of the absolute signal intensity, the glassy phase and the β-phase have almost identical intensities at 10 Hz, where overmodulation is not an issue. Considering the much longer lifetime of the β-phase signal, however, Eq. (3) suggests that the associated weaker induced absorption signal in the β-phase is due to a lower triplet generation rate. We consider that the reduced triplet generation is due to several differences that we are now going to discuss.

Triplet exciton formation occurs either by intersystem crossing from a singlet state or through the recombination of polarons.

(i) The intersystem crossing rate increases with increasing amount of spin-orbit coupling. For symmetry reasons, spin-orbit coupling is low in highly symmetrical, planar conjugated compounds[20] so that intersystem crossing is expected to be lower in the β-phase as compared to the glassy phase.

(ii) Triplet generation also depends on the population density of the singlet state from which intersystem crossing occurs. The amount of singlet excitons created in the first instance is identical between both samples presented here as their optical density at the excitation wavelength is identical. However, the singlet exciton population density is considerably reduced if dissociation into electron-hole pairs occurs. This dissociation is significantly enhanced by an increasing degree of conjugation between the repeat units[21] as well as by increased interchain interactions.[22,23] In fact, the former appears to assist the separation into geminate polaron pairs,[21] while the latter seems to stabilize the final separation into nongeminate polaron pairs.[22,23] Both conjugation length and interchain interactions are indeed increased upon β-phase formation. Consequently, the rate constant of charge separation is expected to be higher in the β-phase. Korovyanko *et al.*[22] find indeed an increasing polaron generation in PFO samples with increasing content of planar β-phase. Silva *et al.*[23] show that in polyindenofluorenes, a class of semiconducting polymers that is very similar to polyfluorenes in both structure and photophysical behavior, substitution of the polymer with bulky sidechains preventing interchain interactions not only decreases the polaron formation, but also increases the magnitude of the triplet signal detected in steady-state PA.

In the present study, experimental evidence for singlet exciton dissociation in the planar β-phase is the appearance of a small photogenerated polaron absorption peak at 1.93 eV in the cyclopentanone-spun sample (Fig. 2). Such a signal is absent in the chloroform-spun sample, indicating that exciton dissociation does not take place in the glassy phase. One might argue that exciton dissociation in the glassy phase simply does not occur under excitation at 405 nm at the glassy phase absorption edge (as presented here) because not enough excess energy is supplied to overcome the exciton binding energy. However, even under excitation at 351 and 364 nm, we did not observe any polaron absorption feature in the glassy phase. These results are in agreement with Cadby *et al.*'s[5] findings of a polaron peak at 1.95 eV in their thermally treated (high β-phase) sample but none in their as-spun sample.

(iii) In addition to triplet formation via ISC, the triplet level may be populated through recombination of some of the polarons generated by exciton dissociation. The spin dependence of this recombination mechanism has been intensely researched in recent years.[24,25] A large fraction of singlets (57%) (Refs. 26 and 27) is already formed in glassy phase PFO. The conjugation length in β-phase PFO is longer than in glassy phase PFO; this will further reduce the likelihood of recombination into a triplet state[26] and thus the contribution of polaron recombination to the (low) triplet generation in β-phase PFO.

To sum this discussion up, triplet formation in the β-phase may be less efficient than in the glassy phase due to weaker intersystem crossing, higher exciton dissociation, and stronger spin dependence of polaron recombination.

It is interesting to note that we find different spectral positions and widths for the T_1-T_n absorption signals of the glassy and the β-phase while Cadby *et al.*[5] find the same spectral feature for both their samples, albeit with different intensities. This apparent contradiction requires a more detailed analysis. We therefore take a closer look at the absorption and PL spectra reported by Cadby *et al.*[5] for their samples. A careful inspection of the emission spectrum for their as-spun PFO film, assigned to pure glassy phase, shows a small shoulder at the position of the β-phase peak, that is at 2.82 eV. A similar spectral shape has been seen in other spin-coated films,[8] and a Franck-Condon analysis has shown that the shoulder is indeed indicative of a small amount of planar β-phase embedded in a large amount of glassy phase. Furthermore, in our sample containing pure glassy phase, the 0-0 transition is stronger than the 0-1 transition (Fig. 1), while the opposite is the case in Cadby *et al.*'s[5] spectra, which also indicates the presence of a small amount of β-phase hidden under this spectral feature. We note that such a fraction may be less than 1%, yet it can still contribute by 10% to the emission[8] and hence to the singlet population in the β phase. Moreover, triplet excitons are very mobile due to their long lifetime. It is therefore probable that additional energy transfer from the glassy phase to the β-phase occurs after ISC, resulting in a higher β-phase percentage in the triplet exciton population than in the singlet exciton population. We therefore attribute the T_1-T_n transition observed by Cadby *et al.*[5] in their as-spun sample exclusively to β-phase chromophores.

In conclusion, we have performed a photoinduced absorption study on poly(9,9-dioctylfluorene) (PFO) spun from different solvents, yielding films containing once pure disordered glassy phase and once a high fraction of planar β-phase embedded in the glassy phase. We were able to demonstrate that the longer conjugation length and higher degree of order and interchain interaction in the planar β-phase compared to the glassy phase leads to a T_1-T_n absorption signal of lower energy, narrower linewidth, and smaller intensity. The reduced triplet state formation in the β-phase is attributed to a combination of lower intersystem crossing and higher exciton dissociation into polaron pairs.

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