PHYSICAL REVIEW B **71**, 125212 (2005)

Enhanced triplet exciton generation in polyfluorene blends

T. A. Ford,[1] I. Avilov,[2,3] D. Beljonne,[2] and N. C. Greenham[1]
[1]*Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom*
[2]*Laboratory for Chemistry of Novel Materials, Center for Research in Molecular Electronics and Photonics,*
University of Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium
[3]*Institute of Molecular and Atomic Physics, National Academy of Sciences of Belarus, F. Skaryna Ave. 70, 220072 Minsk, Belarus*

(Received 26 October 2004; published 29 March 2005)

Photoinduced absorption spectroscopy is used to study the intersystem crossing in a blend consisting of the fluorene-based conjugated polymers poly(9,9′-dioctylfluorene-*co*-benzothiadiazole) (F8BT) and poly**(**9,9′-dioctylfluorene-*co*-bis-*N*,*N*′-(4-butylphenyl)-bis-*N*,*N*′-phenyl-1,4-phenylene-diamine**)** (PFB). The intersystem crossing efficiency is found to be ~10 times higher in F8BT:PFB than in F8BT alone. We attribute this effect to enhanced increased intersystem crossing in the charge-separated states formed at the polymer/polymer heterojunctions in the blend. Applying an electric field dissociates these states and thus reduces the rate of triplet state formation. We also perform time-dependent density functional theory quantum chemical calculations to determine the $T_1 \rightarrow T_n$ absorption cross section and to estimate the triplet yield.

DOI: 10.1103/PhysRevB.71.125212 PACS number(s): 78.66.Qn, 78.30.Jw

I. INTRODUCTION

Polyfluorene materials are a class of conjugated polymers that have received recent attention due to their attractive properties for use as the active layer in thin-film devices such as light-emitting diodes[1] (LEDs) and transistors.[2] Furthermore, depositing binary mixtures (blends) of polyfluorene materials from common solution has proved to produce systems with good operating characteristics both in photovoltaic applications[3,4] and in LEDs.[5]

Recent work[5,6] has highlighted the importance of interfacial states in polyfluorene blends, including blends of poly(9,9′-dioctylfluorene-*co*-benzothiadiazole) (F8BT) and poly**(**9,9′-dioctylfluorene-*co*-bis-*N*,*N*′-(4-butylphenyl)-bis-*N*,*N*′-phenyl-1,4-phenylene-diamine**)** (PFB). It was shown that photoexcited singlet excitons will diffuse to a F8BT:PFB polymer interface and undergo interfacial electron transfer to form a geminate electron-hole pair. This geminate pair may either relax to an exciplex state or may undergo charge separation. Exciplexes are neutral excited states with a significant charge-transfer character and are much longer-lived than singlet excitons. Thermally excited energy transfer to reform the F8BT singlet exciton is an important decay channel for exciplexes.[6]

Triplet excitons represent another important class of excitations in conjugated polymers. Photoexcitation produces predominantly singlet excitons, and typically only a small fraction of these undergo intersystem crossing (ISC) to form the lower-energy triplet exciton. In systems which contain heavy atoms (either deliberately[7] or accidentally[8]), ISC may proceed directly via spin-orbit coupling. In most conjugated polymers, however, spin-orbit coupling is very weak, and the mechanisms for ISC are not well established. One possibility is that the formation of charge-separated states may be necessary before ISC can occur. In LEDs, however, triplet excitons may be formed directly by electron-hole recombination, and triplet exciton formation can represent an important limit to device efficiency. Recent work suggests that the probability of triplet exciton formation in polymer LEDs may be significantly less than the statistical value of 75%.[7,9,10] The mechanism of exciton formation via charge-separated states is therefore of intense interest.

In this paper we examine the formation and decay of triplet excitons in blends of F8BT and PFB using photoinduced absorption spectroscopy. We will show that the yield of triplet excitons is significantly increased in the blend system as compared with the constituent polymers. Furthermore, we perform theoretical calculations of the F8BT $T_1 \rightarrow T_n$ absorption cross section in order to estimate the ISC efficiency. Finally we will discuss this result in the context of the charge-separated states which are known to form at the polymer/polymer heterojunctions in these blends.

II. EXPERIMENTAL METHODS

Photoinduced absorption spectroscopy (PIA) detects long-lived excited states formed after photoexcitation. These states are detected by measuring the small changes in infrared optical absorptions in response to modulated laser excitation above the energy gap. Triplet excitons show a characteristic absorption to a higher-lying triplet state $(T_1 \rightarrow T_n)$, typically around 1.5 eV. Additional absorptions due to charges produced as a result of charge separation at the interface may also be present. Singlet excitons, exciplexes, and other fast-decaying states are too short-lived to be detected in this quasi-steady-state technique.

Our experimental setup has been described elsewhere.[11] Excitation was provided by an argon-ion laser at 488 nm, modulated with a mechanical chopper wheel at 63 Hz and attenuated with a continuous optical density wheel. A 150-W halogen lamp produced a wideband probe beam. Detection was provided by a monochromator and Si (visible) and cooled InSb (IR) photodiodes. Changes in transmission were detected by a lock-in amplifier referenced to the modulation frequency and were normalized to the unmodulated transmission at each wavelength. All samples were measured in a continuous flow helium cryostat under a low-pressure helium atmosphere.

Blend films were prepared by spinning from common chloroform solution onto Spectrosil IR quartz substrates. All preparation was carried out under an anhydrous nitrogen atmosphere. Films spin coated from chloroform have a fine scale of phase separation, and exciton diffusion to internal interfaces is therefore efficient.[12]

In order to investigate the effect of an electric field on triplet exciton formation in blend films, PIA measurements were also performed on planar device structures with a blend film sandwiched between electrodes. Semitransparent blend devices were prepared as reported by Dhoot *et al.*[9] The active polymer layer (approximately 200 nm thick) was spun on a glass substrate with a thin gold layer acting as the anode. A thin calcium electrode was subsequently evaporated onto the polymer layer and capped with a thin layer of gold. The electrodes were approximately 20 nm in thickness.

Triplet excitons have no dipole-allowed transition to the ground state and hence decay nonradiatively. In conjugated polymers, triplets have been shown to undergo both monomolecular and bimolecular decay processes,[13] the bimolecular decay being attributed to triplet-triplet annihilation. These recombination processes may be probed by studying the dependence of the induced absorption on the excitation intensity.

We consider the rate equation for the population of triplet excitons,

$$\frac{dn}{dt} = g(t) - \frac{n}{\tau} - \beta n^2, \tag{1}$$

where $g(t)$ is the triplet generation rate, n is the number density of triplet excitons, τ is the monomolecular lifetime, and β the bimolecular recombination constant.

In our experiment the pump beam was modulated with a mechanical chopper. Adapting the treatment of Westerling *et al.*,[14] we model this approximately by the first two terms of a Fourier series,

$$g(t) = \frac{\gamma G}{2}[1 + \cos(\omega t)], \tag{2}$$

where $(\pi/4)G$ represents the unmodulated rate of photon absorption per unit volume and γ is the quantum efficiency of triplet production via ISC. In this treatment we neglect any contribution to triplet generation from bimolecular process such as recombination of nongeminate charges. The assumption that bimolecular triplet generation processes are unimportant is justified by the good fit of our experimental data to this model.

Assuming that n is a constant throughout the film, the fractional change in transmission of the probe beam is given by

$$\frac{\Delta T}{T} = -n\sigma d, \tag{3}$$

where d is the film thickness and σ is the $T_1 \rightarrow T_n$ absorption cross section. Expressions for the in-phase (X) and out-of-phase (Y) signal recorded on the lock-in amplifier may be found by solving Eqs. (1) and (2) for the Fourier terms oscillating at frequency ω,

$$\left(\frac{\Delta T}{T}\right)_X = -\left(\frac{\gamma G\tau}{2}\right)\left(\frac{\omega_1\tau}{(\omega_1\tau)^2 + (\omega\tau)^2}\right)\sigma d, \tag{4}$$

$$\left(\frac{\Delta T}{T}\right)_Y = \left(\frac{\gamma G\tau}{2}\right)\left(\frac{\omega\tau}{(\omega_1\tau)^2 + (\omega\tau)^2}\right)\sigma d, \tag{5}$$

where

$$\omega_1\tau = \left(\frac{\tau}{\tau_B}\right)\sqrt{-\frac{1}{2}[(\omega\tau_B)^2 - (\tau_B/\tau)^2 - 2] + \frac{1}{2}\sqrt{[(\omega\tau_B)^2 + (\tau_B/\tau)^2 + 2]^2 - 2}}$$

and

$$\tau_B = \frac{1}{\sqrt{\gamma G\beta}}.$$

At high laser intensities the Y-channel signal saturates.[14] This saturation allows a straightforward determination of the bimolecular recombination constant β, provided the absorption cross section σ is known:

$$\beta = \frac{\omega\sigma d}{(\Delta T/T)_{Y,sat}(2 + \sqrt{2})}. \tag{6}$$

The remaining parameters τ and γ may be fitted from a plot of induced absorption against the absorbed laser intensity. In this treatment we have neglected the spatial variation of n within the film; however, we still obtain good fits to our data.

Theoretical calculation of the $T_1 \rightarrow T_n$ absorption cross section in PPV and F8BT was carried out as follows: DFT calculations of the lowest triplet state T_1 were performed using Becke's three-parameter hybrid functional B3LYP (Refs. 15 and 16) within the unrestricted formalism and a 6-31G basis set.[17,18] The calculation of the $T_1 \rightarrow T_n$ absorption spectra was carried out at the time-dependent density functional theory (TD-DFT) level.[19,20] All calculations were performed using the GAUSSIAN 98 (revision A.11) suite of programs.[21]

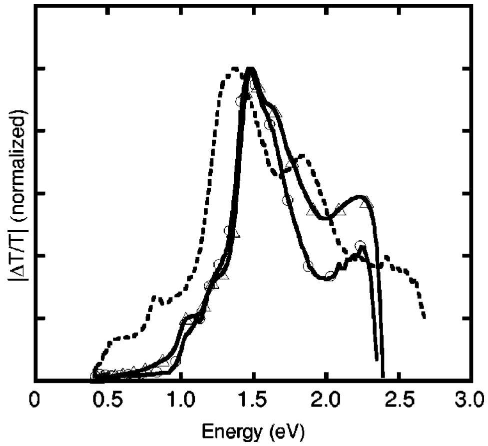

FIG. 1. Photoinduced absorption spectra of films of F8BT (circles), PFB (dotted line), and a 1:1 blend of F8BT:PFB (triangles) at 10 K. The spectra have been normalized to their central absorption peaks. Excitation for the F8BT and F8BT:PFB materials was 75 mW cm^{-2} at 488 nm and for PFB was 280 mW cm^{-2} multiline UV excitation (351 nm and 364 nm).

III. RESULTS AND DISCUSSION

Figure 1 shows the PIA spectra for films of pristine F8BT and PFB and a 1:1 blend of F8BT:PFB measured at 10 K. The spectra have been normalized for ease of comparison but it should be noted that the F8BT:PFB blend showed an absorption approximately 10 times stronger than either of the pristine polymers.

All the materials show a broad absorption, F8BT and F8BT:PFB peaking close to 1.5 eV and PFB at 1.35 eV. $T_1 \rightarrow T_n$ transitions in this energy range are typical for conjugated polymers, and hence we assign these absorptions to the triplet state. We also note that the spectrum presented here for F8BT is the same as that of Dhoot *et al.*[10] for F8BT spin-coated from xylene solution and is also spectrally similar to that recorded for poly(9,9′-dihexylfluorene-*co*-benzothiadiazole) (F6BT) by Westerling *et al.*[14] The triplet absorption in PFB shows two peaks, at 1.35 eV and 1.83 eV. These show identical recombination kinetics as determined from frequency and intensity dependences of the absorption signal (not shown). They therefore appear to arise from the same triplet exciton species. Similarly, the shoulders at 2.25 eV and 1 eV in the F8BT and F8BT:PFB spectra show identical recombination kinetics to the main peak. If any absorptions due to photogenerated charges are present in the F8BT:PFB spectrum, they are obscured by the much stronger triplet absorption.

The triplet absorption in F8BT:PFB is spectrally very similar to that in F8BT and is unchanged if the excitation wavelength is changed to the UV so as to excite the PFB in addition to the F8BT. This suggests that efficient energy transfer from PFB to F8BT takes place in the blend. This is consistent with a lower triplet energy in F8BT, as expected from the lower energy gap in F8BT (2.32 eV compared with 2.84 eV in PFB) given that the exchange energy in conjugated polymers is usually insensitive to their chemical structure.[22]

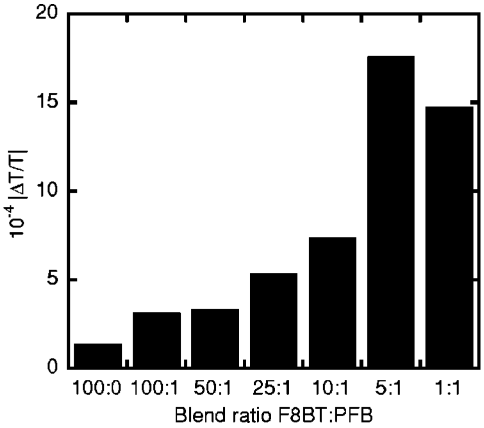

FIG. 2. Magnitude of the triplet induced absorption at 1.5 eV under 25 mW cm^{-2} of laser excitation for various blend ratios F8BT:PFB.

Figure 2 shows the strength of the induced absorption measured at the triplet peak of 1.5 eV for films with blend ratios of 1:1, 5:1, 10:1, 25:1, 50:1, 100:1, and 100:0 F8BT:PFB. The absorbed excitation intensity is 25 mW cm^{-2} in each case. It is clearly seen that addition of PFB to the polymer blend strongly increases the magnitude of the triplet absorption. All the films show similar spectral shapes.

In order to assess whether the increased triplet absorption in the blend films is due to a change in the ISC efficiency or due to a change in triplet lifetime, the X- and Y-channel absorptions at 1.5 eV were measured as a function of the absorbed intensity, as shown for several illustrative blend ratios in Fig. 3. The solid lines are logarithmic least-squares fits using Eqs. (4) and (5). Figure 3 shows a reduction in the gradient of the X-channel absorption and a saturation of the Y-channel absorption at around 75 mW cm^{-2} of absorbed intensity, as the system moves into a regime dominated by bimolecular kinetics. The fits to Eqs. (4) and (5) are good, but not perfect; the X-channel saturates more strongly than predicted, and the Y-channel saturation is not complete. We believe that this deviation may be due to the approximations made in deriving Eqs. (4) and (5), in particular the neglect of higher Fourier components in the square-wave excitation and the neglect of variation of the excitation intensity through the thickness of the film. Both these effects may play a role at higher excitation intensities when the system is in a nonlinear regime.

In order to extract the intersystem crossing efficiency γ for the blend films we require knowledge of the $T_1 \rightarrow T_n$ absorption cross section. The value for F8BT is not well established but we note that in previous work cross sections between 10^{-16} cm^2 and 1.5×10^{-15} cm^2 have been estimated for other conjugated polymers.[9,23,24] To resolve this uncertainty we performed quantum chemical calculations to determine the absorption cross section.

The $T_1 \rightarrow T_n$ absorption spectra of F8BT oligomers ranging in size from one to four units were simulated on the basis of the excitation energies and transition dipole moments, as computed at the TD-DFT level on the basis of the relaxed T_1 geometries. The dynamical polarizability α was calculated

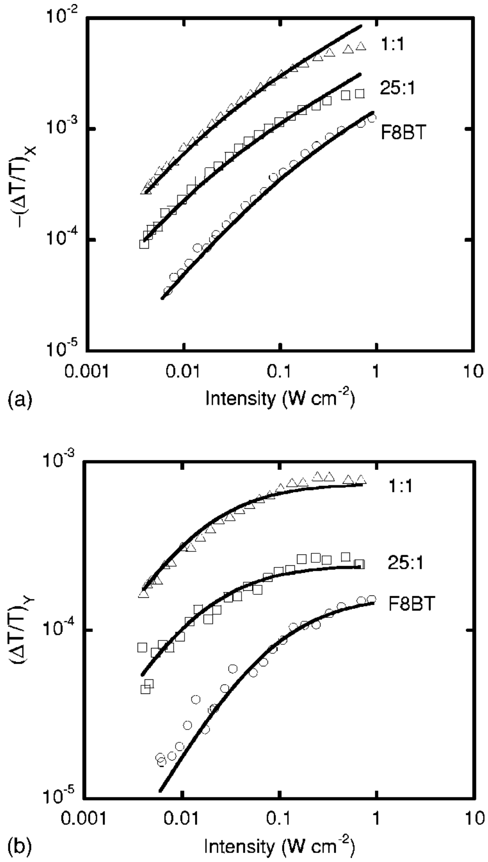

FIG. 3. Intensity dependence of the induced absorption at 1.5 eV for F8BT (circles), F8BT:PFB 25:1 (squares), and 1:1 (triangles). The X channel is shown in (a) and the Y channel in (b). Solid lines are fits to Eqs. (4) and (5). The blends show a crossover from monomolecular kinetics to bimolecular kinetics at around 75 mW cm^{-2}, indicated by a square root dependence of the X channel and saturation of the Y channel.

assuming Lorentzian line shapes with half width at half maximum (HWHM or α_L) values of 0.125 eV (which best fits the experimental line width). Absorption cross sections σ were then calculated from

$$\sigma = \frac{\omega}{c\varepsilon_0}\langle \mathrm{Im}(\alpha)\rangle, \tag{7}$$

where ω is the incoming frequency, c the speed of light, ε_0 the permittivity of vacuum (local field factors are neglected), and $\langle \mathrm{Im}(\alpha)\rangle$ is the imaginary part of the dynamical polarizability averaged over the three spatial directions.

As an example, the simulated transient absorption spectrum for a triplet exciton on a representative F8BT oligomer, $(\mathrm{F8BT})_3$, is compared to that for a phenylenevinylene oligomer of similar physical length, $(\mathrm{OPV})_5$, in Fig. 4. ($T_1 \rightarrow T_n$ absorption spectra for PV oligomers, which were previously reported,[25] were kindly provided by Dr. A. Pogantsch.) Figure 4 shows that while $(\mathrm{OPV})_5$ has a single strong resonance located at ~1.6 eV, at least three optical features (referred to as I, II, and III in Fig. 4) can be identified for $(\mathrm{F8BT})_3$. Importantly, the cross section for the main $T_1 \rightarrow T_n$ absorption peak for $(\mathrm{OPV})_5$ greatly exceeds that of any of the $(\mathrm{F8BT})_3$ triplet-state absorptions. The inset to Fig. 4 shows that the cross section of band II in F8BT oligomers exhibits a weak chain-length dependence in comparison to the main transient absorption in oligophenylenevinylenes.

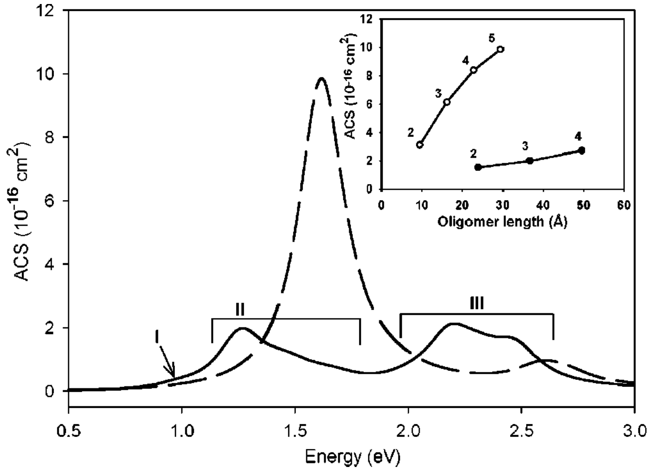

FIG. 4. Simulated theoretical $T_1 \rightarrow T_n$ absorption spectra of $(\mathrm{F8BT})_3$ (solid line) and $(\mathrm{OPV})_3$ (dashed line) oligomers. The inset shows the evolution of the absorption cross section (ACS) depending upon the oligomers' physical length (band II in the case of F8BT oligomers); the numbers beside the calculated points indicate the number of subunits.

These results can be rationalized from a detailed analysis of the triplet excited-state wave functions. In the case of the F8BT oligomers, this analysis indicates that (a) the lowest triplet state T_1 is mostly localized on a single BT subunit, (b) the final triplet state reached upon excitation into band I is formed by one-electron excitations between molecular orbitals (MO's) that are almost completely localized on BT subunits, (c) band II arises from excitations involving occupied and unoccupied MO's that extend over neighboring F8 and BT subunits, and (d) band III is formed by charge-transfer excitations from delocalized occupied MO's with large contributions on F8 units to empty MO's confined on BT units. It thus appears that the relatively small cross sections calculated for representative F8BT oligomers result from the weaker electronic interactions between monomers in the F8BT copolymer (compared to the interunit interactions in OPV). This leads to molecular orbitals and excited-state wave functions that are *less delocalized* and a *redistribution* of the T_1 absorption cross section among several higher-lying triplet excited states with different nature and localization.

The simulated triplet spectrum in Fig. 4 compares well to the measured spectrum in Fig. 1. In particular, the experimental spectrum shows a weak shoulder at ~1 eV, a main band at ~1.5 eV, and an additional feature superimposed on ground-state bleaching at ~2.5 eV, which we assign to the calculated bands I, II, and III, respectively. The calculated cross section amounts to $\sim 2 \times 10^{-16}$ cm^2 at ~1.3 eV (band II) for $(\mathrm{F8BT})_3$ [compared to $\sim 10^{-15}$ cm^2 at ~1.6 eV for $(\mathrm{OPV})_5$]. Note that (i) because of the weak chain-length

TABLE I. γ (intersystem crossing quantum efficiency), τ (monomolecular lifetime), and β (bimolecular recombination constant) for F8BT, PFB, and a range of F8BT:PFB blend films. These parameters were obtained from fitting Eqs. (4) and (5) to the intensity dependence of the triplet induced absorption.

Material	γ	τ (ms)	β (cm^3 s^{-1})
F8BT	0.019	0.981	1.72×10^{-15}
F8BT:PFB 100:1	0.047	1.30	7.74×10^{-16}
F8BT:PFB 50:1	0.053	1.58	7.24×10^{-16}
F8BT:PFB 25:1	0.082	1.68	4.34×10^{-16}
F8BT:PFB 10:1	0.124	2.75	2.28×10^{-16}
F8BT:PFB 5:1	0.240	3.75	4.00×10^{-16}
F8BT:PFB 1:1	0.200	2.07	3.60×10^{-16}
PFB	0.034	8.35	7.93×10^{-16}

dependence, the cross section obtained for the F8BT trimer should be close to the polymer value and (ii) the results reported here for oligophenylenevinylenes are consistent with those reported previously from a combined experimental and theoretical investigation of alkoxy-substituted PPV derivatives [of order 10^{-15} cm^2 (Ref. 9)].

Most importantly, our calculations indicate that the $T_1 \rightarrow T_n$ absorption cross sections are *significantly smaller* in F8BT compared to PPV. Since σ has not yet been experimentally measured in F8BT, we adopt the theoretical value of 2×10^{-16} cm^2 as the cross section for the 1.5-eV peak in the experimental system.

With the theoretical value for the cross section established, the ISC efficiency γ, triplet monomolecular lifetime τ, and bimolecular recombination constant β may be extracted from the intensity dependences for each blend ratio. These are listed in Table I. For comparison, the PFB triplet absorption, measured at its peak (1.35 eV), is also included (assuming a similar cross section to F8BT). We additionally note that we have used the same value of the cross section for each blend ratio. This is justified by the lack of large spectral changes as the blend ratio is changed, suggesting that the same absorbing species is present in each blend.

Table I shows that the ISC efficiency γ increases strongly as the ratio of PFB is increased in the F8BT:PFB blend. γ increases from 0.019 in pure F8BT to a maximum of 0.24 in the 5:1 blend. We note that the absolute value of γ which we extract is inversely proportional to the value of σ used. Hence, if the true value of σ is larger than the predicted value of 2×10^{-16} cm^2, our value of γ will be an overestimate. However, any error in the cross section will affect each blend equally, and hence our results unambiguously demonstrate a strong increase in ISC efficiency in the F8BT:PFB blend as compared to the pristine polymer.

Table I additionally shows that as PFB is added to the blend, the monomolecular lifetime τ increases from around 1 ms in pure F8BT to a maximum of 3.75 ms in the 5:1 blend. The bimolecular recombination constant β drops from 1.72×10^{-15} cm^3 s^{-1} in F8BT to a minimum of 2.28×10^{-16} cm^3 s^{-1} in the 10:1 blend. In the blends, the F8BT chains on which the triplet exciton resides are increasingly separated from each other. Triplet interchain movement is therefore impeded and the triplet mobility decreased, thus decreasing the rate of triplet-triplet annihilation β. Reduced triplet mobility also explains the observed increase in monomolecular lifetime τ, due to the decrease in the rate of exciton quenching at impurity or defect sites.

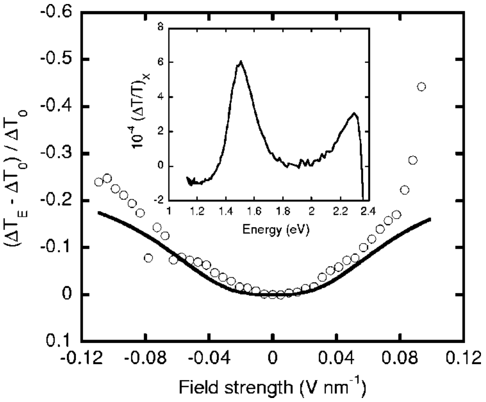

FIG. 5. Field-induced quenching of the photoinduced triplet absorption at 1.5 eV in an F8BT:PFB device at 150 K (circles). The data are plotted as the relative change in absorption at each applied field. The solid line is a fit to an Onsager recombination process, as described in the text. The inset shows the field-modulated-induced absorption spectrum, under an applied field of -0.1 V nm^{-1} and laser intensity of $\sim$300 mW cm^{-2}.

We hypothesize that the enhanced ISC seen in the blends is mediated by the interfacial species which are known to be formed on photoexcitation in these systems. The populations and dynamics of these states are highly sensitive to electric fields,[6] and we have therefore measured PIA in semitransparent device structures under applied electric fields. Figure 5 shows the field dependence of the magnitude of the PIA peak at 1.5 eV in a F8BT:PFB 1:1 blend device. The device was operated at 150 K and excited with an intensity of $\sim$300 mW cm^{-2} at 488 nm. The data are plotted as the fractional change in triplet absorption at an applied field E as compared to that under no applied field $[(\Delta T_E - \Delta T_0)/\Delta T_0]$. The effect of the electrical field on the PIA spectrum was measured by exciting the device with an unmodulated laser and modulating the field between zero and -0.1 V nm^{-1}. The change in transmission measured by the lock-in amplifier was then normalized by the unmodulated transmission at each wavelength, to produce the spectrum shown in the inset to Fig. 5.

Figure 5 shows that the effect of the field is to reduce the intensity of the triplet absorption. At fields less than 0.08 V nm^{-1} this effect is symmetric about zero bias, despite the fact that the current through the device was highly asymmetric, being very much higher under forward bias. There is an asymmetry at very high forward biases where the current through the device was very high ($>$5 mA). This indicates that any quenching of the triplet by interaction with charges is only significant at high forward biases. No reduction in the intensity of triplet absorption is seen in control devices fabricated with F8BT alone, indicating that the field has no effect on the tightly bound triplet excitons once formed.

Morteani *et al.* have shown that the effect of an electric field in F8BT:PFB blends is to dissociate the geminate charge pairs formed after charge transfer at the heterojunction.[6] Exciplexes are formed by relaxation of these charge pairs, and hence the electric field suppresses the formation of exciplexes. The reduction in triplet population seen in Fig. 5 follows a similar field dependence to that seen for exciplexes. At low fields it fits well to an Onsager model for charge pair separation with a permittivity of 3.4 and an initial geminate charge separation of 3.0 nm, similar to the values reported by Morteani *et al.*[6] The inset to Fig. 5 shows a quenching of the PIA signal across most of the spectrum, but a small enhancement below about 1.4 eV. This is consistent with an absorption at low energies due to long-lived charges which are produced on dissociation of geminate charge pairs.

We propose that the enhanced ISC seen in the blends takes place in the charge-separated states formed after photoinduced charge transfer, either in the geminate charge pair or in the exciplex itself. Both these states have much smaller electron-hole wave function overlap than the intrachain singlet exciton and hence have a small exchange energy, consistent with more rapid ISC. After ISC takes place, the excited state then has the opportunity to relax further to form an intrachain triplet exciton by an exothermic process. Since the charge-separated state can in principle also undergo further ISC back to the singlet state, the yield of triplet excitons depends on the ISC rate and on the relaxation rates for singlet and triplet charge-separated states to form singlet and triplet excitons, respectively.

As the amount of PFB in the F8BT:PFB blend increases, the probability that a singlet exciton reaches an interface and therefore can undergo interface-mediated ISC increases, leading to an overall enhanced ISC efficiency as observed. An electric field acts to dissociate the geminate charge pairs, thus reducing the probability that ISC will take place.

The high value of γ recorded in the F8BT:PFB blend would imply that triplet formation is a significant nonradiative loss mechanism for the decay of photoexcited singlet excitons and that the low photoluminescence efficiency of F8BT:PFB [16% compared to 55% in pure F8BT (Ref. 4)] is in part due to enhanced ISC, in addition to charge separation at the polymer interfaces. However, further experimental work is required to confirm the value of σ in these systems before a fully quantitative picture can be obtained. We note that triplet formation provides a possible loss mechanism in polymer photovoltaic devices, since tightly bound intrachain triplet excitons are not likely to be dissociated into charges. F8BT:PFB blends show promising performance in photovoltaic devices, with short-circuit quantum efficiencies in excess of 20%,[26] but to improve these efficiencies further, triplet formation is a loss mechanism which must be taken into account.

Exciplex-moderated ISC has been previously studied in several organic exciplex systems in nonpolar solvents. These include anthracene/anilines,[27,28] *trans*-stilbene/trialkylamine,[29] 1,4-dicyanonaphthalene/methoxy- and methyl-substituted benzenes,[30] and pyrene/tertiary amines.[31]

Another polymer system which exhibits exciplex formation is the blend of F8BT with poly**(**9,9-dioctylfuorene-*co*-N-(4-butylphenyl)diphenylamine**)** (F8BT:TFB). Unlike F8BT:PFB, this system produces highly efficient LEDs.[5] We have performed PIA measurements on a 1:1 F8BT:TFB blend as a function of incident intensity, and this system also yielded an enhanced ISC efficiency γ of 0.09 at 10 K, again using $\sigma = 2 \times 10^{-16}$ cm^2. This value of γ, which is considerably smaller than that in F8BT:PFB, places an absolute upper limit of 91% on the singlet fraction in F8BT:TFB LEDs. This value is certainly consistent with the high LED efficiencies which are observed (however, a direct comparison is not possible due to the very different temperatures involved). The singlet fraction in the LED may in fact be lower due to direct formation of triplet charge-separated states by recombination; however, we note that it has proved difficult to detect triplet excitons from their absorptions in F8BT:TFB LEDs.[10]

Since our measurements rely on photoexcitation, they do not provide direct information about the population of triplet excitons in working LEDs. However, they do provide useful information about the spin dynamics of the charge-separated states which are a precursor to exciton formation in LEDs. Two criteria are required to achieve a singlet fraction of more than 25% in an LED. First, the rate of formation of singlet excitons from charge pairs must be larger than the rate of formation of triplet excitons. Second, the spin state of the charge pairs must be efficiently mixed in order to provide a steady supply of charge pairs able to form singlet excitons. Our measurements provide evidence for a measurable ISC rate in the charge-separated states which are a precursor to exciton formation in polymer blend LEDs. They therefore show that mixing of the spin state of coulombically bound charge pairs is possible, consistent with high singlet fractions.

IV. CONCLUSION

We have shown that ISC in F8BT:PFB blends is approximately 10 times more efficient than that in F8BT alone, leading to an increased triplet exciton population after photoexcitation in the blend system. Furthermore, we have calculated the $T_1 \rightarrow T_n$ absorption cross section to establish an estimate of the ISC efficiency. We attribute the enhanced efficiency to enhanced ISC in the charge-separated states formed at the F8BT:PFB interface. Application of an electric field acts to dissociate these charge-separated states before ISC can occur, thus reducing the population of triplet excitons. Intersystem crossing within charge-separated pairs is an important process determining LED efficiency but further experimental work is required to clarify the effect in a device architecture.

ACKNOWLEDGMENTS

We are grateful to Professor R. H. Friend, A. C. Morteani, Dr. W. Barford, and Dr. C. Silva at the Cavendish Laboratory for many useful discussions. We would like to thank Dr. A. Pogantsch for providing the results of the TD-DFT triplet calculations on the oligophenylenevinylenes. The work in Cambridge was funded by the Engineering and Physical Sciences Research Council, UK. The work in Mons is partly supported by the Belgian Federal Services for Scientific, Technical, and Cultural Affairs (InterUniversity Attraction Pole 5/3) and the Belgian National Science Foundation (FNRS). The research of I. Avilov was funded by European Commission Contract No. IST-2001-37375 (STEPLED).

---

[1] A. W. Grice, D. D. C. Bradley, M. T. Bernius, M. Inbasekaran, W. W. Wu, and E. P. Woo, Appl. Phys. Lett. **73**, 629 (1998).

[2] N. Stutzmann, R. H. Friend, and H. Sirringhaus, Science **299**, 1881 (2003).

[3] J. J. M. Halls, A. C. Arias, J. D. Mackenzie, W. S. Wu, M. Inbasekaran, E. P. Woo, and R. H. Friend, Adv. Mater. (Weinheim, Ger.) **12**, 498 (2000).

[4] H. J. Snaith, A. C. Arias, A. C. Morteani, C. Silva, and R. H. Friend, Nano Lett. **2**, 1353 (2002).

[5] A. C. Morteani *et al.*, Adv. Mater. (Weinheim, Ger.) **15**, 1708 (2003).

[6] A. C. Morteani, P. Sreearunothai, L. M. Herz, R. H. Friend, and C. Silva, Phys. Rev. Lett. **92**, 247402 (2004).

[7] J. S. Wilson, A. S. Dhoot, A. J. A. B. Seeley, M. S. Khan, A. Köhler, and R. H. Friend, Nature (London) **413**, 828 (2001).

[8] J. M. Lupton, A. Pogantsch, T. Piok, E. J. W. List, S. Patil, and U. Scherf, Phys. Rev. Lett. **89**, 167401 (2002).

[9] A. S. Dhoot, D. S. Ginger, D. Beljonne, Z. Shuai, and N. C. Greenham, Chem. Phys. Lett. **360**, 195 (2002).

[10] A. S. Dhoot and N. C. Greenham, Adv. Mater. (Weinheim, Ger.) **14**, 1834 (2002).

[11] D. S. Ginger and N. C. Greenham, Phys. Rev. B **59**, 10 622 (1999).

[12] A. C. Arias, J. D. MacKenzie, R. Stevenson, J. J. M. Halls, M. Inbasekaran, E. P. Woo, D. Richards, and R. H. Friend, Macromolecules **34**, 6005 (2001).

[13] M. Westerling, C. Vijila, R. Osterbacka, and H. Stubb, Chem. Phys. Lett. **286**, 315 (2003).

[14] M. Westerling, C. Vijila, R. Osterbacka, and H. Stubb, Phys. Rev. B **67**, 195201 (2003).

[15] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[16] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[17] R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys. **54**, 724 (1971).

[18] W. J. Hehre, R. Ditchfield, and J. A. Pople, J. Chem. Phys. **56**, 2257 (1972).

[19] R. Bauernschmitt and R. Ahlrichs, Chem. Phys. Lett. **256**, 454 (1996).

[20] M. E. Casida, C. Jamorski, K. C. Casida, and D. R. Salahub, J. Chem. Phys. **108**, 4439 (1998).

[21] Computer code GAUSSIAN 98, revision A.11, Gaussian Inc, Pittsburgh, PA, 2002.

[22] A. Köhler and D. Beljonne, Adv. Funct. Mater. **14**, 11 (2004).

[23] A. P. Monkman, H. D. Burrows, M. D. Miguel, I. Hamblett, and S. Navaratnam, Chem. Phys. Lett. **307**, 303 (1999).

[24] L. P. Candeias, J. Wildeman, G. Hadziioannou, and J. M. Warman, J. Phys. Chem. B **104**, 8366 (2000).

[25] A. Pogantsch, G. Heimel, and E. Zojer, J. Chem. Phys. **117**, 5921 (2002).

[26] A. C. Arias, N. Corcoran, M. Banach, R. H. Friend, J. D. MacKenzie, and W. T. S. Huck, Appl. Phys. Lett. **80**, 1695 (2002).

[27] N. Orbach, J. Novros, and M. Ottolenghi, J. Phys. Chem. **77**, 2831 (1973).

[28] T. Nishimura, N. Nakashima, and N. Mataga, Chem. Phys. Lett. **46**, 334 (1977).

[29] W. Hub, S. Schneider, F. Dorr, J. D. Oxman, and F. D. Lewis, J. Phys. Chem. **87**, 4351 (1983).

[30] H. F. Davis, S. K. Chattopadhyay, and P. K. Das, J. Phys. Chem. **88**, 2798 (1984).

[31] P. van Haver, N. Helsen, S. Depaemelaere, M. Vanderauweraer, and F. C. Deschryver, J. Am. Chem. Soc. **113**, 6849 (1991).