

Monomolecular triplet decay dynamics in fluorene-based conjugated polymer films studied by transient absorption spectroscopy

H. Ohkita^{a,*}, S. Cook^a, T.A. Ford^b, N.C. Greenham^b, J.R. Durrant^{a,**}

^a Department of Chemistry, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom

^b Cavendish Laboratory, University of Cambridge, J.J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom

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Abstract

Monomolecular decay dynamics of triplet excited states formed in fluorene-based conjugated polymer pristine and blend films were studied by transient absorption spectroscopy over the temperature range 77–300 K. The decay rate was temperature independent below 150 K and steeply increased above 150 K. The temperature dependence from 150 to 300 K was expressed by the Arrhenius equation with an activation energy of 0.12 eV. The thermal activation process was assigned to the temperature-dependent non-radiative decay of triplet excitons, which might result from the spin–orbit coupling enhanced by vibrational motions in F8BT. The same tendency was observed for blend films, although with slightly faster decay dynamics, suggesting that the thermal activation process reflects an intrinsic photophysical property of the fluorene-based polymer.

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1. Introduction

Fluorene-based conjugated polymers have attracted considerable attention owing to their remarkable properties such as high efficient photoluminescence, high charge-carrier mobility, good processability, and thermal stability [1–3]. These properties have been finely tuned by chemical modifications such as substitutions and copolymerization of various combinations of monomeric units. Among them, poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) (F8BT) is distinguished for its high electron mobility while most other fluorene-based polymers exhibit high-mobility hole transport but relatively poor electron transport [4,5]. Focusing on these different properties, organic photovoltaic (PV) cells and light-emitting diodes (LEDs) have been recently fabricated using a combination of two fluorene-based polymers: F8BT and poly(9,9-dioctylfluorene-*alt*-bis-*N,N'*-(4-butylphenyl)-bis-*N,N'*-phenyl-1,4-phenylenediamine) (PFB) blends exhibit 4% photocurrent external quantum efficiency [6,7] and F8BT and poly(9,9-dioctylfluorene-*alt*-bis-*N*-(4-

butylphenyl)diphenylamine) (TFB) blends display high electroluminescence efficiencies (up to 19.4 lm W^{-1}) [8].

The formation and decay of triplet excitons in conjugated polymers is currently receiving significant attention, since triplet exciton formation is a potential loss mechanism in polymer LEDs and PVs. Recently, we reported that triplet excitons play an important role in the F8BT/PFB blend films employed in polymer PV devices [9–11]. In most conjugated polymers, such as poly(*p*-phenylene vinylene) and polyfluorene derivatives, intersystem crossing (ISC) from singlet to triplet excitons occurs with only a low efficiency due to weak spin–orbit coupling; consequently optical excitation typically results in triplet formation quantum yields of only a few percent [9,12,13]. Nevertheless, bimolecular quenching of singlet excitons by triplet excitons has been suggested to be a significant deactivation process [13] because of the long lifetime of triplet excitons. Triplet migration in poly(9,9-di(ethylhexyl)fluorene) (PF2/6) films has been analyzed employing the concept of dispersive hopping in a Gaussian distribution of states [14–16]. The bimolecular recombination in poly(9,9-dihexylfluorene-*alt*-benzothiadiazole) (F6BT) films has been also discussed in terms of a non-Arrhenius temperature dependence of triplet diffusion dynamics [17,18]. On the other hand, there are few reports on the monomolecular decay dynamics of triplet excitons formed in conjugated polymer films. This is partly because it is difficult to detect triplet excitons separately owing to the low ISC efficiency and the highly efficient

* Corresponding author at: Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo, Kyoto 615-8510, Japan. Tel.: +80 75 383 2613; fax: +80 75 383 2617.

** Corresponding author. Tel.: +44 20 7594 5321; fax: +44 20 7594 5801.

E-mail addresses: h.ohkita@imperial.ac.uk (H. Ohkita), j.durrant@imperial.ac.uk (J.R. Durrant).

triplet–triplet (T–T) annihilation observed under high excitation densities typically employed in such dynamic studies.

Herein we report the monomolecular triplet dynamics in an F8BT pristine film and an F8BT/PFB blend film studied by transient absorption spectroscopy over the wide temperature range from 77 to 300 K. To exclude the contribution of T–T annihilation to the triplet decay dynamics, we measured the transient absorption decay under weak excitation intensities ($\sim 1 \mu\text{J cm}^{-2}$), one to two order magnitudes less than those employed in previous literature studies [14–18]. Under low excitation conditions, it has been reported that not only the fluorescence but also the phosphorescence intensities of fluorene-based polymers are proportional to the pump excitation energy [13,19], indicating that the triplet decay dynamics should be primarily monomolecular under such excitation condition. Due to the high sensitivity of our transient absorption system ($\Delta\text{OD} \sim 10^{-4}$ to 10^{-6}) [20], we are able to detect transient signals of triplet excitons formed in the F8BT pristine and F8BT/PFB films under low excitation conditions over the whole temperature range. The monomolecular decay dynamics of these F8BT triplet excitons are discussed in terms of thermally activated non-radiative decay.

2. Experimental

2.1. Sample preparation

The F8BT and PFB polymers were separately dissolved in chloroform solution at a concentration of 16 mg mL^{-1} . The chemical structure of the polymers are shown in Fig. 1. For the F8BT/PFB blend films, both solutions were mixed in equal concentration. Polymer films were prepared by the spincoating from chloroform solution of F8BT or F8BT and PFB at a spin rate of 1750 rpm for 60 s. The film thickness was approximately 200 nm.

2.2. Measurements

Steady-state absorption spectra were measured with a UV–vis spectrophotometer (Shimadzu, UV-1601) at room temperature. Transient absorption decays were measured by the “laser photolysis” technique. The sample film was excited with a dye laser (Photon Technology International Inc., GL-301) pumped by a nitrogen laser (Photon Technology International Inc., GL-3300). The excitation wavelength was 490 nm, the pulse width was 0.6 ns, the fluence was $\sim 1 \mu\text{J cm}^{-2}$, and the repetition frequency was 4 Hz. For micro- to millisecond measurements, a 100-W quartz halogen lamp (Bentham, IL1) with a stabilized power supply (Bentham, 605) was used as a probe light source. The probe light passing through the sample was detected with a silicon photodiode (Hamamatsu Photonics, S1722-01). The signal from the photodiode was pre-amplified and sent to the main amplification system with an electronic band-pass filter to improve the signal to noise ratio (Costronics Electronics). The amplified signal was collected with a digital oscilloscope (Tektronics, TDS220), which was synchronized with a trigger signal of the laser pulse from a photodiode (Thorlabs Inc., DET210). To

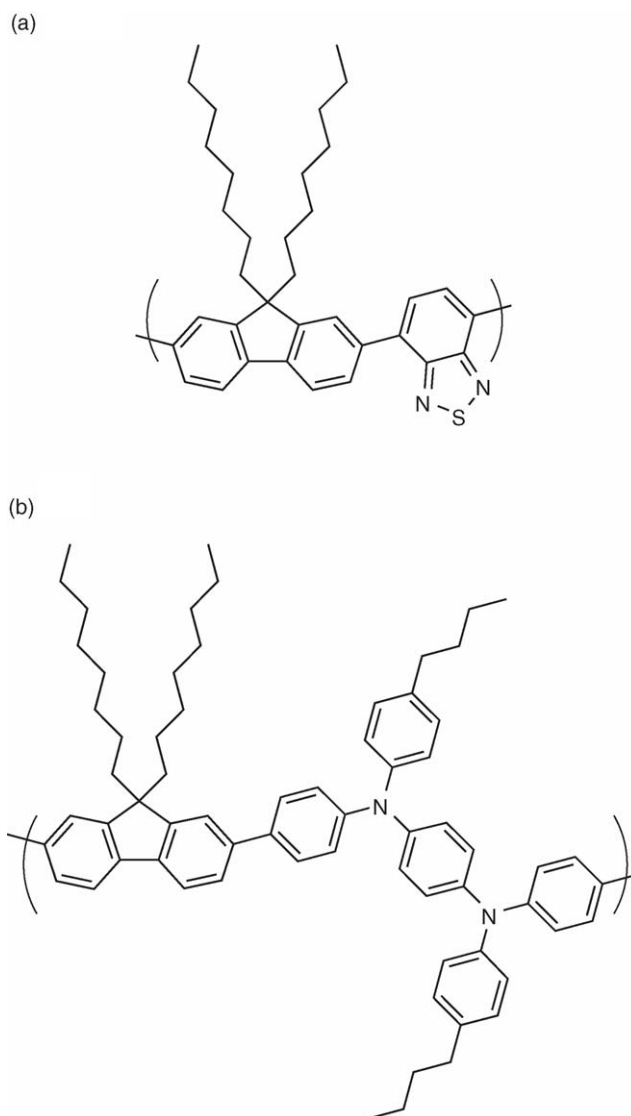


Fig. 1. Chemical structures of the fluorene-based polymers used in this study: (a) F8BT and (b) PFB.

reduce stray light, scattered light, and emission from the sample, two monochromators and appropriate optical cut-off filters were placed before and after the sample film. Owing to the amplification and noise reduction system, the detectable absorbance change ΔOD was as small as 10^{-5} to 10^{-6} . For sub-microsecond measurements, a fast response silicon photodiode (EG&G, FFD-100) was used as a detector, and a CW diode laser (Thorlabs Inc., DL7032-001; 830 nm, 100 mW) was used as a probe light system without a monochromator. In this system, the detector with an optical band-pass filter (Thorlabs Inc., FB830-10) was located as far away from the sample as possible to minimize the unfavourable detection of scattered light and the sample emission.

For the measurements from 77 to 300 K, the sample was placed in a cryostat (Oxford instruments, Optistat DN-V) and its temperature was regulated under vacuum conditions with a temperature control unit (Oxford instruments, ITC502). For the

measurements at room temperature, the sample film was placed in a quartz cuvette purged with argon or oxygen gas.

3. Results

Fig. 2 shows absorption spectra of an F8BT pristine film (solid line) and an F8BT/PFB blend film (broken line) at room temperature. The F8BT polymer has two absorption bands at 320 and 460 nm while PFB has an absorption band at 390 nm. From the absorption and emission spectra, the energy level of the lowest singlet excited state S_1 was evaluated to be 2.4 eV for F8BT and 2.9 eV for PFB, which are the same as those reported in the literature [6,7]. Here the excitation wavelength was set at 490 nm (2.53 eV) to excite F8BT selectively even in the blend film. Thus, we can safely focus our attention on the F8BT excited states in this study.

In general, most fluorene-based conjugated polymers have low ISC rates as mentioned above. In the case of F8BT, the ISC quantum efficiency is reported to be as low as $\sim 2\%$ [9]. Therefore, it is difficult to detect transient signals of triplet excitons formed in such conjugated polymer thin films. Nevertheless, a transient absorption decay was observed at 830 nm for the F8BT pristine film under argon atmosphere at room temperature as shown in Fig. 3. Transient spectra for this decay showed a peak around 820 nm, characteristic of the $T-T^*$ absorption of the F8BT polymer as has already been reported [9,10,21]. To confirm this assignment, we performed an oxygen quenching experiment, as also shown in Fig. 3. As expected, the transient signal decayed much faster under the oxygen atmosphere. Thus, the transient absorption observed at 830 nm was ascribed to the F8BT triplet state. The inset to Fig. 3 shows the transient decays at 830 nm under different excitation conditions from 0.3 to $1.3 \mu\text{J cm}^{-2}$. All the transient signals decayed monoexponen-

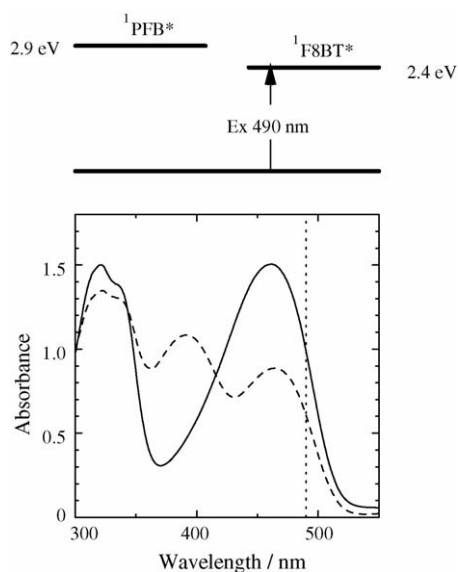


Fig. 2. Schematic energy diagram for S_1 of F8BT and PFB, evaluated from the absorption and emission spectra. The arrow represents the selective excitation of F8BT by the 490-nm dye laser (upper). Absorption spectra of F8BT pristine film (solid line) and F8BT/PFB blend film (broken line) at room temperature. The dotted line shows the excitation wavelength (bottom).

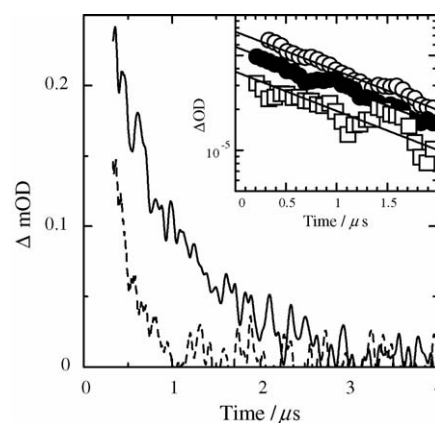


Fig. 3. Transient absorption decays at 830 nm of the F8BT pristine film at room temperature under argon (solid line) and oxygen (broken line) atmospheres. The laser intensity was around $20 \mu\text{J cm}^{-2}$. The inset shows transient absorption decays at 830 nm of the F8BT pristine film at room temperature under argon atmosphere. The laser intensity was varied with neutral density filters: 0.3, 0.7, and $1.3 \mu\text{J cm}^{-2}$ from the bottom to top.

tially with the same lifetime, consistent with a monomolecular decay pathway. If a bimolecular process such as $T-T$ annihilation were dominant, non-exponential dynamics should be observed with a half lifetime increasing by a factor of four with the decrease in the intensity from 1.3 to $0.3 \mu\text{J cm}^{-2}$. As shown in the inset to Fig. 3, this is not the case. Thus these findings clearly indicate that the transient decays observed here primarily reflect monomolecular decay of triplet excitons formed in the F8BT pristine film, an issue we discuss in more detail below.

To address the monomolecular triplet dynamics in F8BT, we measured transient absorption decay over the wide temperature range from 77 to 300 K at a laser intensity of $\sim 1 \mu\text{J cm}^{-2}$. Fig. 4 shows the transient absorption decays at several temperatures. All the decays were well fitted with a single exponential function, strongly suggesting monomolecular decay of triplet excitons over the whole temperature range measured. The fitting parameters are summarized in Table 1. As shown in Fig. 4, the initial absorbance change ΔOD_0 was much the same over

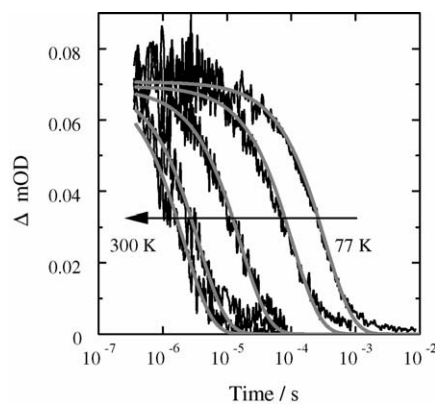


Fig. 4. Transient absorption decays at 830 nm of the F8BT pristine film at several temperatures under vacuum: 77, 150, 200, 250, and 300 K from right to left. The laser intensity was around $1 \mu\text{J cm}^{-2}$. The thick gray lines are fitting curves with a single exponential function.

Table 1
Fitting parameters for the transient absorption decays of the F8BT pristine film over the temperature range from 77 to 300 K

Temperature (K)	ΔOD_0	τ (s)
77	7.1×10^{-5}	3.4×10^{-4}
100	7.2×10^{-5}	2.6×10^{-4}
150	7.0×10^{-5}	1.1×10^{-4}
200	6.9×10^{-5}	1.6×10^{-5}
250	7.0×10^{-5}	3.6×10^{-6}
300	7.0×10^{-5}	2.1×10^{-6}

the whole temperature range and the transient signal decayed faster with increasing temperature. This finding shows that there is a temperature-dependent monomolecular deactivation pathway from the lowest triplet excited state T_1 to the ground state S_0 .

For the F8BT/PFB blend system, we observed that the triplet formation yield was much enhanced compared with the F8BT pristine film. The increase in triplet yield is attributed to ISC in long-lived charge-separated states formed in the blend, as we discuss in detail elsewhere [9,10]. Here, we focus our attention on the decay dynamics of triplet excitons formed in the F8BT/PFB blend films. Fig. 5 shows transient absorption decays at 830 nm of the blend film over a temperature range of 77–300 K. Similarly to the temperature dependence observed for the F8BT pristine film, the decay rate k was independent of temperature below 150 K and steeply increased above 150 K. The decay in long time domains was roughly fitted with a single exponential function. Deviations from single-exponential behaviour at early times most probably arise from a contribution from T–T annihilation due to the high triplet exciton yields and/or the formation of long-lived charged species in the F8BT/PFB blend film. The decay rates obtained are summarized in Table 2. These decay rates showed essentially the same temperature dependence as observed for the pristine F8BT film, as we discuss in more detail below, although the absolute decay rate was slightly larger for the F8BT/PFB blend film over the whole temperatures range measured.

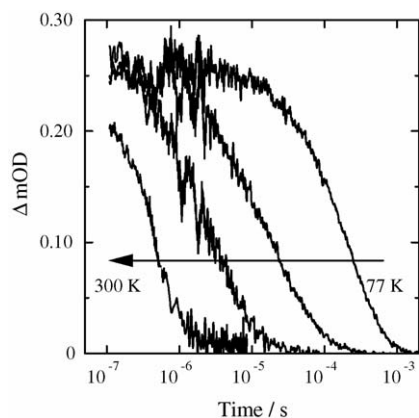


Fig. 5. Transient absorption decays at 830 nm of the F8BT/PFB blend film at several temperatures under vacuum: 77, 150, 200, 250, and 300 K from right to left. The laser intensity was around $1 \mu\text{J cm}^{-2}$.

Table 2
Comparison of the monomolecular decay rate between the F8BT pristine film and the F8BT/PFB blend film over the temperature range from 77 to 300 K

Temperature (K)	k (s^{-1})	
	F8BT	F8BT/PFB
77	3.3×10^3	4.3×10^3
150	9.1×10^3	3.4×10^4
200	6.3×10^4	2.2×10^5
250	2.8×10^5	6.7×10^5
300	4.8×10^5	1.6×10^6

4. Discussion

The rate equation for the triplet exciton states in conjugated polymers may be expressed by Eq. (1)

$$\frac{d[T]}{dt} = G(t) - k[T] - \gamma[T]^2 \quad (1)$$

where $G(t)$ is the triplet generation rate, $[T]$ the concentration of triplet state, k the monomolecular decay rate, and γ is the bimolecular decay rate [14]. Dispersive effects may in general lead to the rate constants being time-dependent. Here, $G(t)$ can be assumed to be instantaneous because the triplet generation was already completed in the time domain measured. Under low excitation conditions the last term, bimolecular decay, is negligible whilst it is expected to become dominant under high excitation conditions. In other words, the rate equation can be simplified as follows:

$$\frac{d[T]}{dt} = -k[T], \quad k \gg \gamma[T] \quad (2a)$$

$$\frac{d[T]}{dt} = -\gamma[T]^2, \quad k \ll \gamma[T] \quad (2b)$$

As described above, however, the triplet exciton decay dynamics reported here exhibit monoexponential, excitation density independent dynamics indicating that they should be assigned to monomolecular decay processes, Eq. (2a), above. In contrast, previous studies of triplet exciton decay dynamics, employing relatively high excitation densities, have focused on bimolecular quenching assigned to T–T annihilation [14–18] (Eq. (2b)). Westerling et al. studied the bimolecular recombination kinetics in F6BT and found that the recombination rate has a very strong non-Arrhenius temperature dependence described by $\beta = \beta_0 \exp[(T/T_0)^2]$ with $\beta_0 = 1.0 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ and $T_0 = 82 \text{ K}$ [17,18]. We employed these literature data to estimate whether our excitation conditions are indeed consistent with negligible contributions from bimolecular decay. The initial concentration of triplet states formed in the F8BT pristine film $[T]_0$ was evaluated to be $\sim 3 \times 10^{16} \text{ cm}^{-3}$ from the initial absorbance change of $\Delta OD_0 \sim 7 \times 10^{-5}$ in the transient absorption decays. We assume a T–T* absorption cross-section of $\sigma = 2 \times 10^{-16} \text{ cm}^2$, as suggested by quantum-chemical calculations [9]. As such, the monomolecular decay rates k ($= \tau^{-1}$) obtained from the fitting were at least one order of magnitude larger than the calculated $\gamma[T]_0$, consistent with

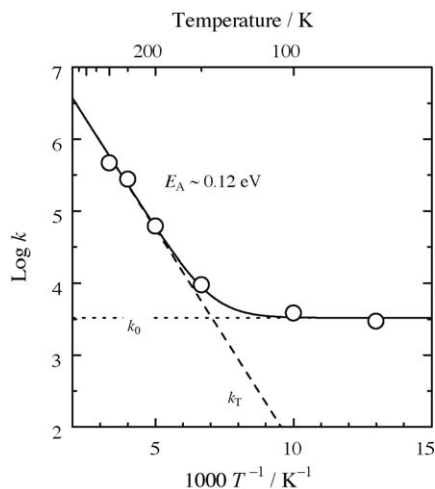


Fig. 6. Arrhenius plots for the monomolecular decay rate k over the temperature range from 77 to 300 K. The solid line is a fitting curve with $k = k_0 + k_T \exp(-E_A/k_B T)$. The dotted line is the temperature-independent deactivation rate of the triplet state k_0 . The broken line is the temperature-dependent deactivation rate of the triplet state $k_T = k_{T_0} \exp(-E_A/k_B T)$.

$k \gg \gamma[T]$ and therefore with our observation of monomolecular decay dynamics, Eq. (2a) above.¹

Thus, this evaluation clearly supports our conclusion that the temperature dependence of τ observed here is attributable to not the bimolecular dynamics but monomolecular kinetics observed under low excitation conditions. Our observation is also consistent with the intensity dependence studies reported in the literature. Stevens et al. reported that the time-integrated photoluminescence intensity of F8BT films is linearly proportional to the pump pulse intensities below a few $\mu\text{J cm}^{-2}$ [19]. Scherf and co-workers reported that the phosphorescence intensity of poly(9,9-di(ethylhexyl)fluorene) (PF2/6) films is linearly proportional to the pump intensity below $20 \mu\text{J cm}^{-2}$ [13,14]. In other words, bimolecular annihilation is not major process in the triplet exciton dynamics in PF2/6 films under low excitation conditions of a few $\mu\text{J cm}^{-2}$. We thus conclude that our observation of the monomolecular decay dynamics under low excitation densities is consistent with previous literature data.

As illustrated in Fig. 6, the monomolecular decay rate k was independent of temperature below 150 K while it steeply increased above 150 K. This finding suggests that the monomolecular decay has at least two deactivation channels: temperature-dependent and independent pathways. Thus, the temperature dependence of the monomolecular decay rate k can be described by the following equation:

$$k = k_0 + k_T = k_0 + k_{T_0} \exp\left(-\frac{E_A}{k_B T}\right) \quad (3)$$

where k_0 is the temperature-independent deactivation rate, k_T the temperature-dependent deactivation rate, and E_A is the

activation energy for the temperature-dependent deactivation process. As shown as the solid line in Fig. 6, the temperature dependence of k was well reproduced by Eq. (3). The temperature-independent deactivation rate k_0 was $3.3 \times 10^3 \text{ s}^{-1}$, which is of the same order as that measured around 10 K reported previously [9,21]. The activation energy E_A was $0.12 \pm 0.01 \text{ eV}$.

The thermal activation energy for this process, E_A , is much smaller than the S_1 - T_1 energy gap, which is estimated to be 0.8 eV from theoretical calculations of F8BT oligomers [22]. We can therefore safely rule out thermal regeneration of singlet excitons from triplet excitons as the temperature-dependent deactivation process of triplet excitons. Quenching by residual oxygen (or other impurities) in the film is also a possible temperature-dependent deactivation process. Since triplet excitons are much more mobile than impurities, the temperature-dependent decay rate would arise from the temperature dependence of the triplet diffusion coefficient. The temperature dependence of the quenching rate k_q should thus be the same as that of the bimolecular recombination rate β of triplet excitons. As described above, the bimolecular recombination rate β shows a strong non-Arrhenius temperature dependence owing to the energetic disorder [16–18]. Dispersive hopping can be modelled by employing a Monte Carlo simulation for an energetically random system with a Gaussian distribution of the density of states (DOS) [16]. The width of the DOS of triplet excitons was evaluated to be 40 meV for PF2/6 [14,15]. However, the relatively large activation energy we report here (0.12 eV), and our observation of Arrhenius behaviour, both indicate that the temperature dependence we report here most probably does not result from quenching by the residual oxygen or other impurities in the film.

An alternative explanation for the observed behaviour is a temperature-dependent non-radiative decay rate k_{nr} . In most aromatic molecules, the ISC rate from T_1 to S_0 is independent of temperature [23,24]. For example, a recent study using single-molecule spectroscopy of poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV) revealed the absence of any strong temperature dependence for the reverse ISC of MEH-PPV single polymer molecules [25]. However, Jones and Siegel reported that the triplet lifetimes of several aromatic molecules in a rigid matrix of poly(methyl methacrylate) (PMMA) exhibit small but real temperature dependences [26] and evaluated the activation energy for thermally activated non-radiative decay to be $0.06 \pm 0.01 \text{ eV}$. They speculated that the temperature dependence of k_{nr} results from the lower-frequency intramolecular vibrations (out-of-plane bending modes) associated with vibrations or rotations of the polymer segments enabled by a sub-transition in PMMA at $\sim 140 \text{ K}$. Although our activation energy is slightly higher, the same could be true of our results because the higher activation energy can be explained by "proximity effect", which is common for nitrogen-heterocyclic compounds with closely spaced, lowest energy, $n\pi^*$ and $\pi\pi^*$ states [27]. The activation energy of the triplet decay rate of pyrazine, which has two nitrogen atoms in the aromatic ring like the benzothiadiazole (BT) unit in F8BT, was reported to be 0.16–0.32 eV dependent upon the solvent employed [28], comparable to our observed activation energy. In pyrazine, the $T_1(n\pi^*)$ state could mix with the higher $T_2(\pi\pi^*)$ state through

¹ At 300 K, our calculations indicate $k > \gamma[T]_0$, however, at this temperature this calculation probably overestimates $\gamma[T]$ because $[T]$ is less than half $[T]_0$ in the time range measured, consistent with the monomolecular decay still primarily contributing to the triplet deactivation even at room temperature.

low-frequency out-of-plane vibrations [28]. A semi-empirical quantum-chemical calculation for fluorene-based conjugated oligomers demonstrated that the triplet state formed in F8BT is localized on the BT unit [22]. Another theoretical calculation for conjugated oligomers revealed that the spin–orbit coupling for the S_1 – T_1 channel is generally small due to symmetry considerations, but that it could be enhanced by molecular distortions such as twists of the aromatic rings along the conjugated path leading to σ – π mixing [29]. Thus, we speculate that the temperature-dependent non-radiative process results from the spin–orbit coupling enhanced by vibrational motions in F8BT.

The larger decay rates observed for the F8BT/PFB film suggests that there might be another decay channel in the triplet excited state formed in the F8BT/PFB blend film. Thermal re-excitation of some intermediate excited state is a possible decay channel for the triplet state. One such intermediate excited state is the exciplex, which also acts as a precursor to triplet formation [8–10,30]. However, the energy gap between the exciplex formed in the F8BT/PFB blend films and T_1 of F8BT can be estimated to be 0.6 eV, because the S_1 – T_1 gap and the energy gap between S_1 and the exciplex were reported to be 0.8 eV [22] and 0.20 eV [8,30], respectively. This energy gap \sim 0.6 eV is too large for the thermal regeneration of the exciplex from T_1 with an activation energy of 0.12 eV. Thus, thermal regeneration can be ruled out. Consequently, the same scenario as in the F8BT pristine film would be true in the F8BT/PFB blend system, with the temperature dependent acceleration of the F8BT dynamics again being assigned to internal vibrational dynamics of the F8BT polymer.

5. Conclusions

Monomolecular decay of triplet excitons formed in F8BT pristine films or F8BT/PFB blend films was directly observed by transient absorption spectroscopy. The decay dynamics were independent of temperature below 150 K and became thermally activated above 150 K. The temperature-dependent deactivation rate can be well expressed by the Arrhenius equation with an activation energy of 0.12 eV. This is significantly different from that observed for the bimolecular recombination, which has a strong non-Arrhenius temperature dependence. The deactivation process is assigned to the temperature-dependent non-radiative decay of triplet excitons, which might result from the spin–orbit coupling enhanced by vibrational motions in F8BT.

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