

Ultrafast Singlet Fission in a Push–Pull Low-Bandgap Polymer Film

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S Supporting Information

ABSTRACT: Excited-state dynamics in poly[4,6-(dodecyl-thieno[3,4-*b*]thiophene-2-carboxylate)-*alt*-2,6-(4,8-dioctylbenzo[1,2-*b*:4,5-*b'*]dithiophene)] (PTB1) was studied by transient absorption spectroscopy. Upon photoexcitation at 400 nm, an additional transient species is promptly generated along with singlet excitons and survives up to nanoseconds, while singlet excitons disappear completely. In order to assign the long-lived species, we measured transient absorption spectra over the wide spectral range from 900 to 2500 nm. As a result, we found that the long-lived species is ascribed not to polarons but to triplet excitons, which is formed through the ultrafast singlet fission (SF). We discuss the ultrafast SF mechanism in push–pull low-bandgap polymer PTB1 films on the basis of the excited-state dynamics under various excitation wavelengths and intensities.

Singlet fission (SF) is a spin-allowed process, in which one singlet exciton splits into two triplet excitons.^{1–3} Such multiple exciton generation from one photon can potentially improve the efficiency of organic photovoltaics (OPV).^{4,5} Therefore, a lot of experimental and theoretical studies have been reported particularly for small acene molecules in the last five years.^{6–15} In contrast, the SF in conjugated polymers has been reported only for limited materials to date.^{16–23} This is partly because the SF from the lowest singlet excited state S_1 is thermodynamically unfavorable in most of conjugated polymers: the lowest singlet excited-state energy E_{S1} is typically lower than twice the lowest triplet-state energy $2E_{T1}$ because the singlet–triplet energy gap ΔE_{ST} is smaller than that of small molecules such as pentacene.^{24,25} On the other hand, such a small ΔE_{ST} would be highly desirable for reducing the loss of open-circuit voltage in OPV.^{26,27}

The SF in conjugated polymers has been studied by several groups including ours.^{16–23} In most cases, the SF occurs from a higher singlet excited-state formed by the singlet–singlet exciton annihilation (SSA) in competition with the vibrational relaxation (singlet fusion followed by singlet fission).^{16,17,20,21} This is not multiple exciton generation because two singlet excitons are converted into two triplet excitons. Recently, the SF from one singlet exciton has been reported for poly(3-dodecylthienylenevinylene) (P3VT).²² However, photovoltaic performance of P3VT-based solar cells is generally very low.²⁸ Very recently, intrachain SF has been demonstrated for a push–pull low-bandgap polymer in solution.²³ However, triplet pairs generated by the intrachain SF should recombine geminately and hence cannot contribute to the photocurrent generation. As such, the

SF from one singlet exciton in push–pull low-bandgap polymer films is most possible candidate for effective improvement in the photovoltaic performance.

Push–pull low-bandgap polymers have attracted increasing attention in the past decade, because they can absorb many more photons and hence improve the photovoltaic performance significantly.^{29–35} In particular, thienothiophene-benzodithiophene-based polymers (PTBs, or PBDTTTs) have been intensively studied as benchmark low-bandgap polymers.^{33–39} Very recently, PTB7-based polymer solar cells exhibit a power conversion efficiency of more than 10%.^{33–35} Several groups have studied the excited-state dynamics of PTBs by transient absorption spectroscopy. They found ultrafast conversion of singlet excitons into long-lived species and ascribed the long-lived one to hot exciton dissociation into polarons.^{37–41}

Here, we study the excited-state dynamics in a push–pull low-bandgap polymer film, poly[4,6-(dodecyl-thieno[3,4-*b*]thiophene-2-carboxylate)-*alt*-2,6-(4,8-dioctylbenzo[1,2-*b*:4,5-*b'*]dithiophene)] (PTB1, the chemical structure is shown in Figure 1a) by transient absorption spectroscopy. In order to assign transient species carefully, we have measured transient absorption spectra over the wide spectral range from 900 to 2500

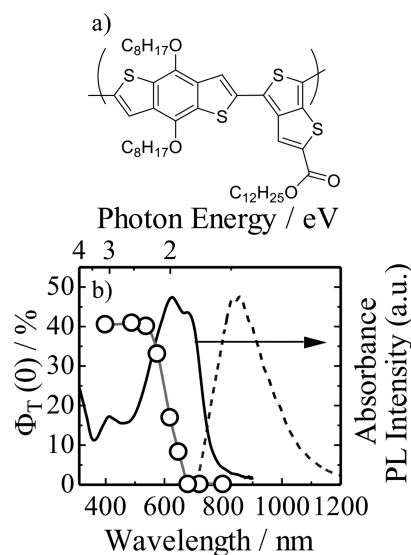


Figure 1. (a) Chemical structure of PTB1. (b) Absorption (solid line) and PL (broken line) spectra of a PTB1 film. The open circles represent the triplet formation yield at 0 ps for each pump photon energy.

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nm because triplet excitons and polarons exhibit similar absorption in the wavelength range from 900 to 1500 nm but different absorption from 1500 to 2500 nm. As a result, we found ultrafast triplet exciton formation in PTB1 films. We discuss the formation mechanism of triplet excitons on the basis of excitation wavelength and intensity dependence.

Figure 1b shows the steady-state absorption (solid line) and photoluminescence (PL) (broken line) spectra of a PTB1 pristine film prepared by spin-coating from a chloroform solution. As shown in the figure, a large absorption band and a small absorption band were observed at around 650 nm (1.9 eV) and 400 nm (3.1 eV), respectively, which are assigned to S_1 and S_2 absorption bands, respectively (see Supporting Information (SI)). From the intersection of the absorption and PL spectra, the E_{S_1} was estimated to be 1.65 eV.⁴² The lowest triplet-state energy E_{T_1} was roughly estimated to be ≥ 1 eV, because PTB1 triplet was quenched by O_2 (see SI). This is consistent with typical ΔE_{ST} of conjugated polymers (~ 0.7 eV) as discussed in previous reports.^{24,25} In other words, the threshold energy for the SF in PTB1, which is equivalent to twice the lowest triplet-state energy $2E_{T_1}$, is estimated to be ~ 2 eV. This estimate is rational as will be discussed later. In summary, the SF in PTB1 is thermodynamically unfavorable from the relaxed S_1 state but favorable from the S_2 state.

In order to assign absorption spectra of each transient species, we first measured the transient absorption spectra of the PTB1 film from 0 ps to 7 ns after the excitation at 800 nm (1.55 eV), where the SF is thermodynamically unfavorable as mentioned above. Immediately after the excitation, as shown by the black circles in Figure 2a, a large absorption band and a small absorption onset were observed at around 1400 and up to 2500 nm, respectively. These absorption bands are ascribed to PTB1 singlet excitons (detailed assignment is described in the SI), which is consistent with previous reports.^{37–41} The singlet exciton band decayed monotonically with a time constant of 160 ps on average. This decay dynamics was independent of the excitation intensity under low excitation conditions ($< 25 \mu\text{J cm}^{-2}$), which result in a low exciton density of $< 9.0 \times 10^{17} \text{ cm}^{-3}$. The intensity-independent decay is indicative of negligible bimolecular reaction such as SSA.^{43,44} At 7 ns, as shown by the blue circles in Figure 2a, the singlet exciton band completely disappeared, and instead a new absorption band was observed at around 1100 nm. This long-lived absorption is clearly different from PTB1 polaron absorption with a large absorption at around 2500 nm as shown by the green triangles in Figure 2c (see SI). We therefore ascribe the long-lived band at 1100 nm to triplet excitons generated through the intersystem crossing (ISC) from the S_1 state.^{45,46} The same assignments have been reported for PTB7 in a recent optical and magnetic study.⁴⁷ As shown in Figure 3, the ISC quantum efficiency was estimated to be $\sim 16\%$ from the ratio between the singlet exciton absorption at 0 ps and the triplet exciton absorption at 7 ns (detailed estimation is described in the SI).

We next measured the transient absorption spectra of the PTB1 film from 0 ps to 7 ns after the excitation at 400 nm (3.1 eV), where the SF is thermodynamically favorable. Here, the exciton density was estimated to be $< 5.2 \times 10^{18} \text{ cm}^{-3}$. Immediately after the excitation, as shown in Figure 2b, a small absorption shoulder was observed at around 1100 nm in addition to the singlet exciton band at around 1400 nm. For both bands, the transient signals at 0 ps linearly increased with increasing excitation intensity, suggesting that both transients are generated monomolecularly; no SSA is involved at the initial time stage.

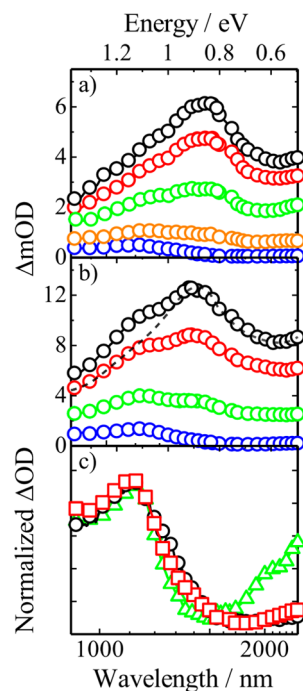


Figure 2. Transient absorption spectra of a PTB1 film measured at 0, 10, 100, 400, and 7000 ps after the laser excitation from top to bottom in each panel (a) and (b). The film was excited at (a) 800 nm with a fluence of $10 \mu\text{J cm}^{-2}$ and (b) 400 nm with a fluence of $20 \mu\text{J cm}^{-2}$. The broken line in panel (b) represents the transient absorption spectrum at 0 ps after the excitation at 680 nm. (c) Transient absorption spectra of the long-lived species after the excitation at 800 nm (black circles) and at 400 nm (red squares). The green triangles represent the absorption spectra of PTB1 polaron.

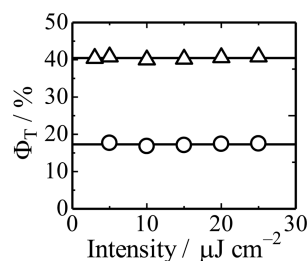


Figure 3. Excitation intensity dependence of triplet exciton generation yields from the ISC after the excitation at 800 nm (open circles) and from the ultrafast SF after the excitation at 400 nm (open triangles).

The singlet exciton band decayed with a time constant of ~ 120 ps on average. This is slightly shorter than but almost comparable to that upon the excitation at 800 nm (~ 160 ps), suggesting SSA is involved at a later time stage. We note that triplet formation via SF induced by SSA is negligibly small (see SI). On the other hand, the absorption at around 1100 nm decayed slowly and was still observed at 7 ns after the excitation. As shown in Figure 2c, the long-lived species exhibits a large absorption at around 1100 nm but negligible absorption at around 2000 nm. This is again different from PTB1 polaron but is rather in good agreement with PTB1 triplet excitons. We therefore conclude that both singlet and triplet excitons are generated immediately after the excitation at 400 nm. It is noteworthy that the long-lived species has been assigned to PTB1 polaron in previous reports.^{35–39} This different assignment is probably because there is no distinct spectral difference between PTB1 polaron and triplet exciton in

the wavelength range from 900 to 1500 nm. We thus emphasize that of particular importance is transient absorption measurements over the wide spectral range from 900 to 2500 nm in order to distinguish triplet excitons from polarons of low-bandgap polymers.

To discuss the formation dynamics of triplet excitons in more detail, we carefully analyzed the time evolution of transient species on the basis of spectral simulation by using absorption templates of singlet and triplet excitons. The transient absorption spectra observed can be well reproduced by the sum of these templates (some examples in the SI). As shown in Figure 3, triplet formation efficiency Φ_T at 0 ps after the excitation at 400 nm was estimated to be as high as 40% and was independent of the excitation intensity. These findings indicate that triplet excitons are promptly generated even at 0 ps through one photon excitation. Figure 4 shows the time evolution of triplet excitons

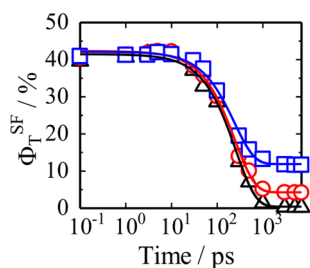


Figure 4. Time evolution of triplet excitons generated through the SF. The excitation wavelength was 400 nm (blue squares), 490 nm (red circles), and 540 nm (black triangles). Note that the triplet generation yield from the ISC is excluded.

obtained from the spectral simulation. Here, the triplet generation yield from the ISC is excluded (much slower triplet generation through the ISC is shown in the SI). As shown in the figure (blue squares), the ultrafast triplet formation observed in this study already completed within a short duration of the excitation pulse (~ 100 fs). This rapid triplet generation cannot be ascribed to charge recombination of polaron pairs, which typically proceeds on a time scale of nanoseconds.⁴⁹ Rather, such a rapid singlet–triplet conversion is indicative of strong spin mixing between singlet and triplet states. As mentioned before, SF is spin-conserving and hence spin-allowed process, and it can proceed on a short time scale of femto- to picoseconds.^{1–3} We therefore conclude that the ultrafast triplet exciton formation after the excitation at 400 nm is ascribed to the ultrafast SF from a hot singlet exciton in a push–pull low-bandgap polymer PTB1 film.

We move onto the decay dynamics of triplet excitons generated through the ultrafast SF after the excitation at 400 nm. As shown in Figure 4, about 70% of triplet excitons decayed with a lifetime of 250 ps. This decay constant is too short to be assigned to free triplet excitons with a lifetime of 4.1 μ s, as shown in the SI. Instead, such a rapid triplet decay has been attributed to geminate recombination of triplet pairs via the triplet–triplet exciton annihilation (TTA).^{20–23,49–52} A simple scheme for the SF is given by the following equation:



where (TT) is an intermediate triplet pair state.^{1–3} The reverse reaction of the SF, which is equivalent to the TTA, is also a spin-allowed fast process. Therefore, triplet pairs are likely to recombine to singlet states through the TTA before dissociating

into two of free triplet excitons. Indeed, the decay dynamics of the triplet exciton was independent of the excitation intensity (see SI). We therefore ascribe the fast decay of 70% triplets to geminate recombination of triplet pairs through the intensity-independent TTA. The rest of 30% triplets survive up to 7 ns, which are ascribable to “free” triplet excitons. As a result, the overall triplet yield via the SF was estimated to be $40\% \times 30\% = 12\%$. As we discussed in the previous report,²¹ the dissociation efficiency increases with increasing diffusion coefficient of triplet excitons. Therefore, the dissociation efficiency would be enhanced in crystalline low-bandgap polymer films. Interestingly, as shown in Figure 4, the dissociation efficiency was dependent upon the excitation wavelength: It was as high as 30% for the excitation at 400 nm, decreased to 10% for the excitation at 490 nm, and nearly 0% for the excitation at 540 nm. One possible explanation is that triplet pairs at higher energy sites in the density of states are selectively generated by the shorter excitation wavelength and hence can easily hop to more ordered and stable sites through the fast downhill energy relaxation toward lower energy sites.^{46,53} However, the limited data set presented herein is insufficient to provide unambiguous conclusion at this moment. Further experiments are currently in progress.

We further study the excitation wavelength dependence of the triplet formation. Transient absorption at 0 ps was measured under various excitation wavelengths from 800 to 400 nm (1.55 to 3.1 eV). The initial triplet formation efficiency $\Phi_T(0)$ can be estimated from the absorption ratio between singlet and triplet excitons at 0 ps (see SI). As shown by the open circles in Figure 1, the $\Phi_T(0)$ is negligible below 1.8 eV, while it steeply increases at ~ 2 eV and then is saturated to 40% above 2.3 eV. The saturated $\Phi_T(0)$ observed above 2.3 eV suggests that the ultrafast SF in PTB1 films is less sensitive to excess photon energy. This result is consistent with previous reports.^{18,19} On the other hand, the onset energy of ~ 2 eV is consistent with the SF threshold energy estimated before. This is again consistent with our assignment of the ultrafast SF from energetically hot singlet excitons competing with thermalization. This ultrafast SF may be competitive with ultrafast long-range charge separation in films blended with a fullerene derivative.⁵⁴

In conclusion, we have studied ultrafast excited-state dynamics in a push–pull low-bandgap polymer PTB1 film. We measured transient absorption over the wide wavelength range from 900 to 2500 nm. This is essential for correct assignment of triplet excitons and polarons with similar absorption spectra. Upon photoexcitation above the threshold photon energy, the ultrafast triplet formation was observed even at 0 ps, which is attributed to the ultrafast SF from energetically hot singlet excitons. Although the overall triplet yield via the SF is as low as 12% at best, this study has clearly demonstrated the free triplet generation from the SF in low-bandgap polymer PTB1 films. With more ordered film morphology, the overall triplet yield would be further improved. Our findings demonstrate that the ultrafast SF in low-bandgap polymers would be potentially beneficial for further improvements in photovoltaic performance of OPV.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b09361.

Experimental details, spectral assignments, spectral simulation, monomolecular singlet decay dynamics upon

the band-edge excitation, triplet formation dynamics, details of the estimation of Φ_T , TTA assignment, the transient absorption spectra at various excitation wavelengths, and pulse duration and determination of 0 ps for the transient absorption spectroscopy(PDF)

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Notes

The authors declare no competing financial interest.

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