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Morphology-Limited Free Carrier Generation in Donor/Acceptor Polymer Blend Solar Cells Composed of Poly(3-hexylthiophene) and Fluorene-Based Copolymer

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Abstract:

The charge generation and recombination dynamics of a poly(3-hexylthiophene) (P3HT)/poly[2,7-(9,9-didodecylfluorene)-*alt*-5,5-(4',7'-bis(2-thienyl)-2',1',3'-benzothiadiazole)] (PF12TBT) donor/acceptor polymer blend solar cell are studied by transient absorption measurements. In the unannealed blend film, charge carriers are efficiently generated from polymer excitons but some of them recombine geminately. In the blend annealed at 160 °C, on the other hand, the geminate recombination loss is suppressed and hence free carrier generation efficiency increases up to 74%. These findings suggest that PF12TBT and P3HT are intermixed within a few nanometers, resulting in impure PF12TBT and disordered P3HT domains. The geminate recombination is likely due to charge carriers generated on isolated polymer chains in the matrix of the other polymer and at the domain interface with disordered P3HT, which are reduced by both the purification of the PF12TBT-rich domain and crystallization of the P3HT chains. These results show that efficient free carrier generation is not inherent to the polymer/fullerene domain interface, but is possible with polymer/polymer systems composed of crystalline donor and amorphous acceptor polymers, opening up a new potential method for the improvement of solar cell materials.

1. Introduction

Conjugated polymer-based solar cells have gained increasing attention as an inexpensive source of renewable energy because of their advantages including high throughput and large-area production with low-cost printing processes.^[1] The most widely studied polymer-based solar cells have a bulk-heterojunction (BHJ) structure, in which a polymer acting as an electron donor is mixed with an electron acceptor, specifically a low-molecular-weight fullerene derivative such as [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM).^[2,3] On the other hand, polymer/polymer BHJ solar cells, which consist of a polymer donor and a polymer acceptor, have been increasingly researched given the potential advantages they could have over conventional polymer/fullerene devices.^[4–6] The added flexibility in molecular design introduced by polymer acceptors is particularly important, as it helps to improve short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and the fill factor (FF) through fine tuning optical, electronic, and morphological properties. However, despite these attractive features, the development of polymer/polymer BHJ solar cells still lags far behind that of their polymer/fullerene counterparts,^[7,8] with power conversion efficiencies (PCEs) around 2% until recently.^[9–11]

Owing to considerable efforts in synthesizing polymer acceptors and optimizing the blend morphology, the PCEs of polymer/polymer BHJ solar cells have been improved up to more than 5% in the last few years.^[4,6,12–18] Fluorene and benzothiadiazole-based copolymers are among the most promising of these acceptor alternatives^[9,10,19–21] because of their large absorption coefficients in the visible region and higher energy levels for the lowest unoccupied molecular orbital (LUMO); these features in turn increase light absorption and V_{oc} , respectively. Recently, we reported a polymer/polymer BHJ solar cell containing poly(3-hexylthiophene) (P3HT) as the donor and poly[2,7-(9,9-didodecylfluorene)-*alt*-5,5-(4',7'-bis(2-thienyl)-2',1',3'-benzothiadiazole)] (PF12TBT) as the acceptor (**Figure 1a**).^[9,10] This system gave an energy difference of more than 1 eV between the highest occupied

molecular orbital (HOMO) of the donor and the LUMO of the acceptor, retaining the 0.8 eV offset between the two LUMOs needed for efficient electron transfer (Figure 1). As expected, much higher V_{OC} of 1.26 V was yielded when compared to P3HT/PCBM devices, which typically yield values of only about 0.6 V.^[9,10] In addition, thermal annealing improved both the J_{SC} and the FF, resulting in a PCE of 2.7%.^[10] However, the maximum external quantum efficiency (EQE) of the device was just 30%, far below the 70 – 80% values reported for P3HT/PCBM devices. This means that, the high V_{OC} of this device could give PCE values exceeding 7% if the EQE could be brought up to standard P3HT/PCBM levels.

This relatively poor EQE is not specific to our P3HT/PF12TBT blend, but is rather common for other donor/acceptor polymer combinations.^[19–25] The origin of such a low EQE is not well understood, but is likely due to substantial charge loss by geminate recombination, which might be inherent to the electronic structure at the polymer/polymer domain interface^[26] and/or the result of non-optimized blend morphology.^[22–25] Therefore, it is necessary to gain a better understanding of the photovoltaic processes that occur in the nanoscale phase-separated films. In this study, femtosecond to submicrosecond transient absorption (TA) measurements are used to probe the efficiency and kinetics of charge generation and recombination. Our TA study shows that free carrier generation efficiencies depend on the nanoscale morphology of phase separation and that they are improved by thermal annealing, which purifies and extends the phase-separated domains.

2. Results

2.1. Influence of Thermal Annealing on EQE

Figure 2a and **b** show the EQE spectra of the P3HT/PF12TBT BHJ solar cells and the corresponding values at 400 nm for various annealing temperatures. PF12TBT is the primary source that contributes to photocurrent generation at this wavelength, accounting for 73% of absorption overall.^[27] Annealing showed a significant effect on EQE; the 8% value observed for the unannealed (as-spun) device increased to about 27% for those devices annealed at 80 – 120 °C. However, increasing temperature beyond this point had a detrimental effect, with a drop to 18% for annealing at 160 °C.

2.2. Temperature Dependence of Photoluminescence (PL) Quenching Efficiency

Figure 3a shows the PL spectra of both PF12TBT neat and the P3HT/PF12TBT blend films for excitation at 392 nm; PF12TBT was mainly responsible for excitation, accounting for 75% of all excitation observed in the blend film as a whole. PF12TBT neat film showed a strong PL (solid line in **Figure 3a**), with a peak centered at 695 nm. The significant decrease in emission of the unannealed blend film in comparison indicates efficient charge generation from PF12TBT excitons. The PL intensity recovered, however, as annealing was applied and as the temperature increased. The temperature dependence of PL quenching efficiency (Φ_q) is shown in **Figure 3b**. Φ_q reached values as high as 85 – 90% for both the unannealed film and those films that had been annealed at 60 and 80 °C; however, it monotonically decreased with increasing temperature to as low as 50% at 160 °C.

2.3. Temperature Dependence of Charge-Carrier Mobility

Charge-carrier mobilities for both the neat and blend films were measured. The electron mobility (μ_e) was decreased by a factor of 4 by blending with P3HT, dropping from the value

of $2.9 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ observed for PF12TBT neat film to $6.6 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. On the other hand, the hole mobility (μ_h) of $2.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ observed for P3HT neat film dropped by a factor of more than 20, to $1.2 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. **Figure 4** shows the temperature dependence of charge-carrier mobility. The value of μ_e increased with temperature, reaching $1.8 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ by 120 °C; this is close to the value of μ_e for the PF12TBT neat film. However, μ_h was insensitive to thermal annealing for temperatures up to 80 °C, but did show an increase above 80 °C. The blend film annealed at 120 °C showed an improved μ_h almost 10 times greater than the unannealed one.

2.4. TA Spectra

2.4.1. Neat Films

Figure 5 shows the TA spectra of the P3HT and PF12TBT neat films, measured at 0.5, 10, 100, and 3000 ps after excitation at 400 nm. P3HT (Figure 5a) showed negative TA spectrum below 650 nm, with distinct vibronic peaks at 560 and 610 nm. This TA signal is attributed to the transient ground-state bleach (GSB), which was determined by comparing the data with the steady-state absorption spectrum (Figure 1c). Meanwhile, the weak negative signal in the PL region (650 – 800 nm) is due to stimulated emission (SE) from the P3HT singlet excitons. The broad positive TA signal that ranges from 800 – 1500 nm and peaks at 1200 nm has been assigned to P3HT singlet excitons.^[28,29]

PF12TBT (Figure 5b) also gave a negative signal at wavelengths shorter than 650 nm, corresponding to the GSB. Likewise, the negative signal at 650 – 800 nm is the result of SE from PF12TBT singlet excitons. The bimodal positive TA signal with peaks at 900 nm and around 1200 – 1300 nm is assigned to PF12TBT singlet excitons; this was evident due to the fact that the TA signal showed the same decay lifetime as the SE signal (see Supporting Information). The change in the relative TA intensity (ΔOD) between these two peaks

observed within the first 10 ps is ascribed to the relaxation of the singlet exciton population from higher energy excitonic states to lower energy intramolecular charge transfer states^[30] (see Supporting Information).

2.4.2. TA Spectra of the Blend Films

Figure 6a shows the simulated TA spectra of a P3HT/PF12TBT blend film. This was constructed by adding the TA spectra of the two neat films, taken at the same observation time; the intensities of both spectra were corrected by the excitation fractions. These spectra would be observed if excited states in blend films deactivate to the ground state without any other relaxations such as charge generation. In contrast, different spectral change should be observed if there are any other relaxation pathways in blend films as described below.

Figure 6b shows the TA spectra for the unannealed blend film. They show spectral features that are clearly different from the simulated spectra. Even 0.5 ps after excitation, the positive TA signal is observed at 650 – 800 nm, while the simulated spectra predict a slightly negative SE signal. The positive signal increases in intensity until 100 ps after excitation, while the singlet exciton signal at around 1200 – 1300 nm decreases over the same time scale. After 3000 ps, the new transient species is clearly distinguished from the polymer singlet excitons, with the long-lived signal observed from 650 – 1200 nm resulting from absorption by both the P3HT hole and the PF12TBT electron polarons. The spectral assignment for these polarons is shown in the Supporting Information. In summary, singlet excitons and polymer polarons are both generated immediately after the laser excitation. Subsequently, singlet excitons decrease while polymer polarons increase on a time scale of subnanoseconds as the conversion of singlet excitons to charges proceeds; the TA charge feature becomes dominant in the wavelength range of 650 – 1200 nm at longer delay times.

The TA spectra of the blend film annealed at 140 °C (Figure 6c) matches the simulated spectra initially, yet slowly evolves into a long-lived TA signal. On the other hand, the TA

spectra for the blend film annealed at 200 °C (Figure 6d) are almost identical to the simulated spectra throughout the time range, indicating that most of the polymer singlet excitons decay to the ground state without being converted into charges. We note that the spectral shape of the GSB changed due to annealing; the unannealed blend film showed structureless GSB spectra, while the annealed blend films contained more pronounced vibronic structures due to π -stacking of the P3HT chains.^[28,31,32]

2.5. Charge Generation and Recombination

2.5.1 Unannealed Blend Film

Note that the simulated spectra in Figure 6a show a TA intensity of effectively zero for a wavelength of 760 nm over the whole time range, which happens because of negligible contributions from both constituent polymers. Therefore, the generation and recombination kinetics of the transient species that are additionally generated in the blend films can be extracted by tracking the time evolution of the TA signal at this wavelength.

The corresponding time evolutions for the unannealed blend film are shown in **Figure 7** as open circles. To begin, note that charge generation kinetics are highlighted for time domains shorter than 150 ps. In this case, 64% of charges were generated within the first 0.5 ps, with virtually all remaining charges generated within 50 ps. The charge generation dynamics can be fitted to Equation (1), given a rise time (τ_R) of 11 ps;

$$\Delta OD(t) = A [1 - \exp(-t/\tau_R)] + B \quad (1)$$

On the other hand, the TA signal from polymer singlet excitons, monitored at 1200 nm, showed two exponential decay lifetimes (Figure 7, open triangles); one was 11 ps, the same as τ_R , while the other was 190 ps. The longer lifetime matches the lifetime of the PF12TBT singlet excitons of the neat film measured under identical excitation fluence (Figure 7, closed circles). Meanwhile, the TA intensity from GSB, measured at 550 nm (Figure 7, open

squares), recovered slightly over the 190 ps lifetime, while the corresponding TA charge intensity remained constant. These data suggest that some fraction of the PF12TBT excitons decay to the ground state without dissociating into charges, which agrees with the incomplete PF12TBT PL quenching of Φ_q approximately 85% as mentioned above.

Studying charge recombination kinetics requires analyzing over a longer range of delay times, from 150 to 3000 ps. The decay dynamics monitored at 760 nm can be fitted by Equation (2), with a lifetime (τ_D) of 2500 ps (64 %) and a constant (36%);

$$\Delta OD(t) = G \exp(-t/\tau_D) + C \quad (2)$$

On the other hand, the kinetics for the corresponding GSB recovery are described by two exponential functions (72%) and a constant (28%). The major component of the recovery has a lifetime of 2500 ps (61%), while the minor component has a lifetime of 190 ps (11%), which correspond well to the charge and PF12TBT singlet exciton decay lifetimes, respectively. Subtracting the contribution of the 190-ps minor component from the total GSB recovery gives a value of 68% for the 2500-ps major component and 31% for the constant; these values are in turn very close to the decay (64%) and constant (36%) charge recombination fractions calculated above. Therefore, we conclude that charges are not transformed into triplet excitons, but rather drop back to the ground state. In addition, the TA signals observed in the microsecond time domain were not quenched in an oxygen atmosphere, suggesting that no triplet excitons were generated through recombination of the charge carriers (see Supporting Information).

Recombination dynamics were further investigated by examining the dependence of τ_D on excitation fluence. Monomolecular recombination occurs at the same rate irrespective of charge density ($n(t)$); however, $n(t)$ does play a role if recombination is predominantly bimolecular. **Figure 8** shows the decay dynamics for varying $n(t)$ values, as measured for excitation fluences ranging from 1.5, 2.0, and 3.8 $\mu\text{J cm}^{-2}$ ($n(t)$ was calculated as described in

the Supporting Information). Overall, $n(t)$ varied linearly with excitation fluences. However, the decay dynamics were independent of $n(t)$, and charges decayed monoexponentially with an inverse rate of 2500 ps, even at fluences as low as $1.5 \mu\text{J cm}^{-2}$. Therefore, monomolecular charge recombination occurs predominantly in the subnanosecond to several nanosecond range. Meanwhile, the charges represented by C in Equation (2) began to decay after tens of nanoseconds; these are assigned to bimolecular recombination, as described in the next section.

2.5.2 Annealed Blend Films

Figure 9 shows the kinetics of charge generation for the annealed blend films, as monitored at 760 nm. As mentioned before, all samples showed both immediate and delayed charge generation, which can be described using Equation (1). The fitting parameters are summarized in **Table 1**, which shows influence from annealing. As temperature increased, τ_R increased, while the maximum value for ΔOD decreased. The fraction of promptly generated charges, defined as $B/(A+B)$, decreased as well, meaning that charge generation became increasingly dominated by the delayed process.

Figure 10 shows the decay dynamics for the formed charges. These were also influenced by thermal annealing, and were fitted to Equation (2), as shown by the solid lines; fitting parameters are summarized in **Table 2**. The fraction of monomolecular recombination decreases from 64% for the unannealed blend film to 26% for the blend film annealed at 160 °C; however, the decay lifetime of τ_D is insensitive to the annealing. Therefore, thermal annealing increases the dominance of the long-lived charges.

Therefore, we further tracked the long-lived charges, represented by C in Equation (2), by measuring the dynamics over a wider time domain of several tens of nanoseconds, and showed that they decayed in this time frame. Moreover, the decay dynamics were dependent

on the excitation fluence (see Supporting Information). Therefore, the non-decaying charges can be assigned to the spatially separated free charges.^[33] On the basis of these assignments, the generation efficiency for the free charges (η_{free}) can be estimated from fraction C; this value is defined as $C/(G+C)$. η_{free} increased by thermal annealing from 36% for the unannealed blend film to 74% for the blend film annealed at 160 °C.

3. Discussion

3.1. Development of Nanoscale Phase Separation by Thermal Annealing

All P3HT/PF12TBT blend films show charge generation dynamics characterized by immediate charge generation on a time scale of less than 0.5 ps and subsequent delayed charge generation that ends from tens to hundreds of picoseconds, depending on the annealing temperature. The immediate charge generation is likely the result of excitons formed directly on the polymer chains adjacent to the donor/acceptor domain interfaces and/or on the isolated polymer chains in the matrix of the other polymer, both of which does not require the exciton diffusion to the heterojunctions. The existence of this phenomenon for all the blend films demonstrates that charge transfer (exciton dissociation) between PF12TBT and P3HT occurs so quickly that it does not limit the overall charge generation rate, as has been reported for polymer/PCBM blend films.^[29,33,34] This efficient charge transfer is consistent with sufficient LUMO–LUMO and/or HOMO–HOMO energy offsets of 0.8 eV as shown in Figure 1(b).

On the other hand, delayed charge generation is attributed to a diffusion controlled process, which should be influenced by the film morphologies. Assuming that charge generation is diffusion limited, τ_R represents the time it takes the polymer singlet excitons to reach the distributed heterojunction interface. The mean distance that polymer excitons must diffuse is calculated from the equation $r = \sqrt{6D\tau_R}$,^[35] where D is the diffusion coefficient of polymer singlet excitons. The r values calculated using the known D value of PF12TBT ($D = 9.8 \times$

$10^{-4} \text{ cm}^2 \text{ s}^{-1}$)^[36] were plotted as a function of annealing temperature in **Figure 11a**. Before thermal annealing, r is estimated to be about 3 nm. Therefore, in the unannealed film, P3HT and PF12TBT are well mixed with each other on a length scale shorter than the typical exciton diffusion length of polymers.^[35–38] r shows a weak dependence on thermal annealing at temperatures below 80 °C, yet increases steeply above 80 °C, representing that domain growth is accelerated at temperatures above this point. This coarsening of phase separation is in agreement with the glass transition temperature (T_g) of PF12TBT (76 °C).^[9,10] Above the T_g of at least one of the polymers in a blend film, the polymer chain becomes more mobile and can redistribute to decrease the free energy of the system, resulting in demixing.^[39] As reported previously,^[9] no distinct change in atomic force microscopy (AFM) images was observed before and after the thermal annealing, suggesting that the demixing in the polymer blend proceeds on a length scale shorter than tens of nanometers.

The electron and hole mobilities of the blend films provide additional information regarding the morphological changes that occur in the samples. The fact that μ_e increases steadily even at temperatures below 80 °C suggests that the PF12TBT-rich domains increase in purity, even if domain coarsening is frozen. The electron transport will be improved by the exclusion of the isolated P3HT chains from the PF12TBT domains. Meanwhile, the significant decrease in μ_h in the unannealed blend film suggests that the ordering of the P3HT chains is disturbed, a conclusion confirmed by the structureless GSB spectra in Figure 6b. In turn, annealing improves the ordering of the P3HT chains, as revealed by the pronounced vibronic structures of the resulting GSB spectra (Figure 6c and d). Furthermore, the increase in μ_h at temperatures above 80 °C correlates to the growth of adjacent P3HT domains, resulting in an interconnected P3HT crystalline phase.

3.2. Morphology-Limited Free Carrier Generation

In general, the monomolecular decay of charges on a subnanosecond to several nanosecond timescale has been assigned to the geminate recombination of strongly bound interfacial radical pairs (charge-transfer states) and/or electron–hole pairs that are spatially confined by the physical size of their respective domains.^[33,34] The generation of spatially confined pairs is believed to arise from charge transfer at the interface of closely mixed donor and acceptor polymer chains, or else on isolated polymer chains inside another polymer domain. In other words, geminate recombination is not inherent just to the molecular electronic nature of the particular donor/acceptor interface, but to the blend morphology as well.^[40,41] As for the molecular electronic nature at the domain interface, the observed ordering of P3HT chains that results from thermal annealing plays an important role in circumventing charge pair recombination, because it not only delocalizes polarons within the π -stacking P3HT chains but also increases local hole mobility, both of which are thought to facilitate free carrier generation.^[41–43] On the other hand, as listed in Table 1, many charges are generated from the excitons that diffuse long distances to the preferred domain interface; for example, for the blend film annealed at 160 °C, as much as 69% of overall charge generation process arises from the exciton diffusion, and still considerable 36% even in the unannealed blend film. Therefore, domain purification is also critically important for suppressing undesired geminate charge recombination, because confinement of charges on isolated polymer chains in the matrix of the other polymer hinders the separation of the interfacial electron–hole pairs into free charges. The importance of domain purity is not limited to just P3HT/PF12TBT but rather all polymer/polymer blends, which are more likely to phase-separate on a larger scale than of the polymer/fullerene blends are.^[4,5,9]

3.3. Relevance to Device Performance

Only free carriers can be extracted as photocurrent from a device. Therefore, geminate charge recombination reduces the photocurrent, thereby reducing the EQE. The dominant geminate

recombination of 64% of total charges observed in the unannealed blend film is responsible for the poor EQE of this device, though a well mixed blend structure results in high conversion of polymer excitons into charges. The degree of PL quenching provides information on the charge generation efficiency from the PF12TBT excitons. Therefore, the parameter $\Phi_q \times \eta_{\text{free}}$ can help to approximate overall generation yield of free carriers from excitons. Figure 11b shows the temperature dependence of $\Phi_q \times \eta_{\text{free}}$, which is in good agreement with the EQE dependence provided in Figure 2b. This suggests that free carrier generation yield is a major factor that limits the EQE in this system. The EQE increases with annealing temperatures up to 80 °C because η_{free} increases without suffering from a reduction in Φ_q . However, while greater temperatures increase η_{free} , they also reduce Φ_q due to domain coarsening. Consequently, EQE reaches a maximum at 80 – 120 °C, then decreases above that point. Thermal annealing of the films without domain coarsening is therefore required to achieve larger EQE values.

Our TA measurements revealed that η_{free} approaches 74% for the blend film annealed at 160 °C. This finding indicates that efficient free carrier generation is not an inherent advantage of the polymer/fullerene domain interface, but that it can be achieved at the polymer/polymer domain interface as well. This conclusion is reinforced by the EQE values of current, state-of-the-art polymer/polymer solar cells, which exceed 50%.^[16–18] In addition, the efficient free carrier generation observed in these films indicates that crystalline polymer acceptors are not necessarily required for free carrier generation, opening up further possibilities for the development of polymer/polymer BHJ solar cells.

4. Conclusions

We found that charge generation and recombination dynamics are significantly affected by thermal annealing. Polymer excitons were efficiently converted into charges in the unannealed blend film because the P3HT and PF12TBT were mixed to within their exciton diffusion range. However, the incomplete demixing of polymer phases and the disordered nature of the P3HT chains primarily resulted in geminate recombination of charges because confinement of charges on isolated chains in the matrix of the other polymer and at finely-mixed disordered domain interfaces impede further spatial separation of the electron-hole pairs, and consequently limit the production of free charges. On the other hand, thermal annealing promoted demixing of the polymers, forming relatively pure domains and ordering the P3HT chains. As a result, the geminate recombination loss was suppressed and η_{free} increased with increasing temperature. However, increasing temperature also caused the reduction in Φ_q , meaning that the charge generation efficiency is reduced owing to domain bloating beyond the exciton diffusion length of polymers. The good correlation between the temperature dependence of $\Phi_q \times \eta_{\text{free}}$ and EQE revealed that overall free carrier generation yield from excitons is a major factor that limits EQE, even when η_{free} itself is improved by annealing. The P3HT/PF12TBT domain interface is therefore a promising site for efficient free carrier generation. Restricting domain coarsening during annealing is key to further improving EQE and overall device performance. The ideal blend morphology may be achieved by using high-molecular-weight PF12TBT. In a device with high-molecular-weight PF12TBT, efficient charge generation (large Φ_q values) is maintained even at high annealing temperatures because the rate of domain bloating decelerates owing to the reduced diffusional mobility of the PF12TBT chains. In addition, η_{free} increases as well during the annealing through both domain purification of PF12TBT and ordering of P3HT chains.

5. Experimental Section

Materials: P3HT was purchased from Aldrich Chemical Co. (Lot MKBD3325). The head-to-tail regioregularity, weight-average molecular weight (M_w), and polydispersity index (PDI, given by M_w/M_n , where M_n is the number-average molecular weight) provided on the Certificate of Analysis were 90.0%, 42300 g mol⁻¹, and 1.9, respectively. PF12TBT was synthesized and characterized by Sumitomo Chemical Co., Ltd. The M_w , PDI, and T_g were reported as 20000 g mol⁻¹, 2.0, and 76 °C, respectively. Poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) was purchased from H. C. Stark (PH-500).

Film Fabrication: Sapphire substrates were washed by ultrasonication with toluene, then acetone, and finally ethanol for 15 min each, and then dried under N₂ flow. The washed substrates were further treated with a UV–O₃ cleaner (Nippon Laser & Electronics Lab., NL-UV253S) for 30 min. P3HT and PF12TBT neat films were spin-coated onto the cleaned sapphire substrates from chloroform (CF) solution with concentrations of 16 mg mL⁻¹ and 18 mg mL⁻¹, respectively. Meanwhile, the P3HT/PF12TBT blend films were spin-coated from CF solution with a total concentration of 18 mg mL⁻¹, and then annealed at different temperatures, ranging from 60 to 200 °C, for 10 min in a N₂-filled glove box. The spinning rate was kept at 3000 rpm for all films.

Solar Cell Fabrication and Characterization: Indium–tin-oxide-coated (ITO-coated) glass substrates (10 Ω per square) were washed by ultrasonication with toluene, then acetone, and finally ethanol for 15 min each, and then dried under N₂ flow. The washed substrates were further treated with a UV–O₃ cleaner for 30 min. Next, a 40-nm-thick layer of PEDOT:PSS was spin-coated onto the ITO substrate at a spinning rate of 3000 rpm for 99 s and then dried in air at 140 °C for 10 min. A 65-nm-thick blend layer of P3HT/PF12TBT was then spin-

coated onto the PEDOT:PSS film at 3000 rpm for 60 s from CF solutions. The blend solution was prepared by mixing P3HT and PF12TBT in a weight ratio of 1:1 in CF: P3HT (6.5 mg) and PF12TBT (6.5 mg) were dissolved in 1 mL of CF. After film deposition, thermal annealing was conducted at temperatures ranging from 60 to 200 °C for 10 min in a N₂-filled glove box. Finally, a calcium interlayer (Ca, 10 nm) and an aluminum electrode (Al, 70 nm) were vacuum-deposited through a shadow mask at 2.5×10^{-4} Pa. The active area of the device was 0.07 cm², which was determined from the area of the top Ca/Al electrode. EQE spectra were measured using an ECT-250D integrated system made by Bunko-Keiki Co., under the illumination of monochromatic light from a 300 W xenon lamp with optical cut filters and a double monochromator. The power of the incident monochromatic light was kept under 0.05 mW cm⁻², as measured by a calibrated silicon reference cell.

PL Quenching Measurements: PL spectra were measured for both the PF12TBT neat film and P3HT/PF12TBT blend films spin-coated on quartz substrates using a calibrated fluorescence spectrophotometer (Hitachi, F-4500). Excitation was performed at 392 nm in order to mainly excite the PF12TBT component (the excitation fraction of PF12TBT was 75% while that of P3HT was 25%), and at an incident angle of 30° normal to the substrate. Emission was collected normal to the excitation light. The PF12TBT PL quenching efficiency in the blend film was evaluated from the ratio of the PL intensity for the P3HT/PF12TBT blend films to that of the PF12TBT neat film after each PL intensity was corrected for variations in the PF12TBT absorption at 392 nm.

Fabrication of Single Carrier Devices and Mobility Measurement: Single carrier devices for charge carrier mobility measurements were fabricated as follows: for hole-only devices, a 90-nm-thick P3HT/PF12TBT blend layer was spin-coated on ITO substrates covered with 40-nm-thick PEDOT:PSS. The blend films were then annealed at various temperatures in a N₂-

filled glove box. Finally, a gold electrode (Au, 50 nm) was vacuum-deposited on each layer (ITO|PEDOT:PSS|P3HT/PF12TBT|Au).

For electron-only devices, a 50-nm-thick Al layer was vacuum-deposited on a glass substrate covered with 20-nm-thick poly(sodium 4-styrenesulfonate) ($M_w = 70000 \text{ g mol}^{-1}$). A 90-nm-thick P3HT/PF12TBT blend layer was spin-coated onto the Al electrodes, and then annealed at various temperatures in a N₂-filled glove box. Finally, a Ca interlayer (10 nm) and an Al (70 nm) layer were vacuum-deposited (Al|P3HT/PF12TBT|Ca|Al). The Ca layer was used to enhance the efficiency of electron injection.

The dark J - V characteristics of the devices were measured under a N₂ atmosphere by using a direct-current voltage and a current source/monitor (Advantest, R6243). The P3HT/PF12TBT blend layer was spin-coated under the same conditions used for the solar cell fabrication, as described above.

TA Measurements: TA data were collected using a femtosecond pump and probe transient absorption spectroscopy system. This system consists of a transient absorption spectrometer (Ultrafast Systems, Helios) and a regenerative amplified Ti:sapphire laser (Spectra-Physics, Hurricane) that provided 800-nm fundamental pulses at a repetition rate of 1 kHz, with an energy of 0.8 mJ and a pulse width of 100 fs (full width at half maximum); the pulses were split into two optical beams with a beam splitter to generate pump and probe pulses. One fundamental beam was converted to pump pulses at 400 nm with a second harmonic generator (Spectra-Physics, TP-F). The other fundamental beam was converted into white light continuum pulses with a wavelength range of 400 to 1500 nm, for use as probe pulses. The pump pulses were modulated mechanically at a repetition rate of 500 Hz. The temporal evolution of the probe intensity was recorded with a Si CCD-array photodetector (Ocean Optics, S2000) in the visible range and with an InGaAs digital line scan camera (Sensors Unlimited, SU-LDV) in the near-IR measurement. The excitation fluence was varied from

7.5 to 1.5 $\mu\text{J cm}^{-2}$, as measured by a calibrated photodiode (OPHIR, PD300-UV) connected to an energy meter (OPHIR, Nova). TA spectra were obtained over a time range of -5 ps to 8 ns. Typically, 2500–5000 laser shots were averaged for each delay time. This gave a detectable absorbance change ΔOD as small as $10^{-5} - 10^{-3}$, depending on the monitor wavelength range and the excitation fluence. In order to cancel out orientation effects on the dynamics, the polarization direction of the linearly polarized probe pulse was set to a magic angle of 54.7° with respect to that of the pump pulse. The sample films were sealed in a N_2 -filled quartz cuvette.

Nanosecond TA data were collected with a pump and probe TA system (Ultrafast Systems, EOS). An identical excitation source was used. The probe pulse (0.5 ns pulse width, 20 kHz repetition rate) was generated by focusing a Nd:YAG laser pulse at a photonic crystal fiber. The probe pulses were synchronized with the femtosecond amplifier, while the delay time was electronically controlled by a digital delay generator (CNT-90, Pendulum Instruments). The sample films were sealed in a N_2 -filled quartz cuvette.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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Figures and Figure Captions

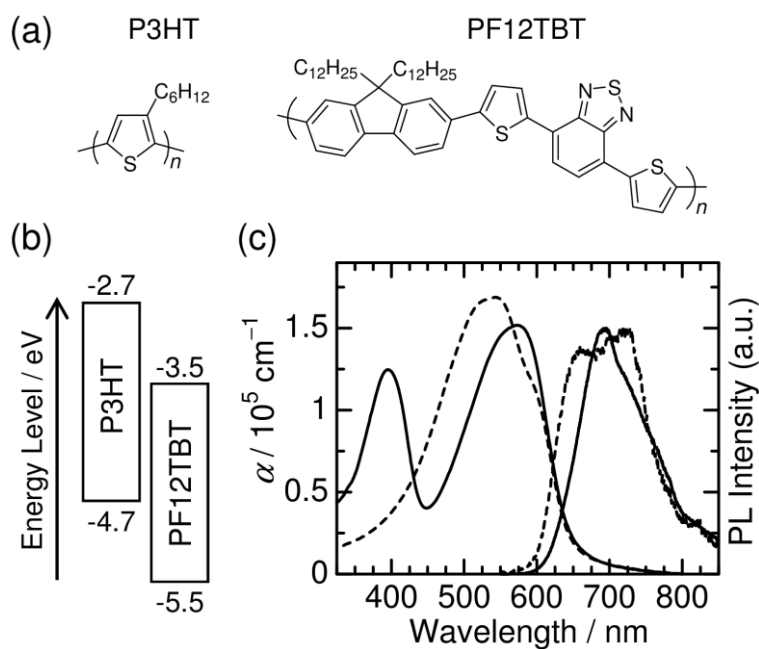


Figure 1. (a) The chemical structures of P3HT and PF12TBT. (b) Energy level diagrams for neat films of P3HT and PF12TBT. HOMO levels were determined by photoelectron yield spectroscopy, while the LUMO levels were estimated by adding the optical bandgap energy, calculated from the 0–0 transition, to the HOMO energy. (c) Absorption coefficients (α) and PL spectra of neat films of P3HT (broken line) and PF12TBT (solid line).

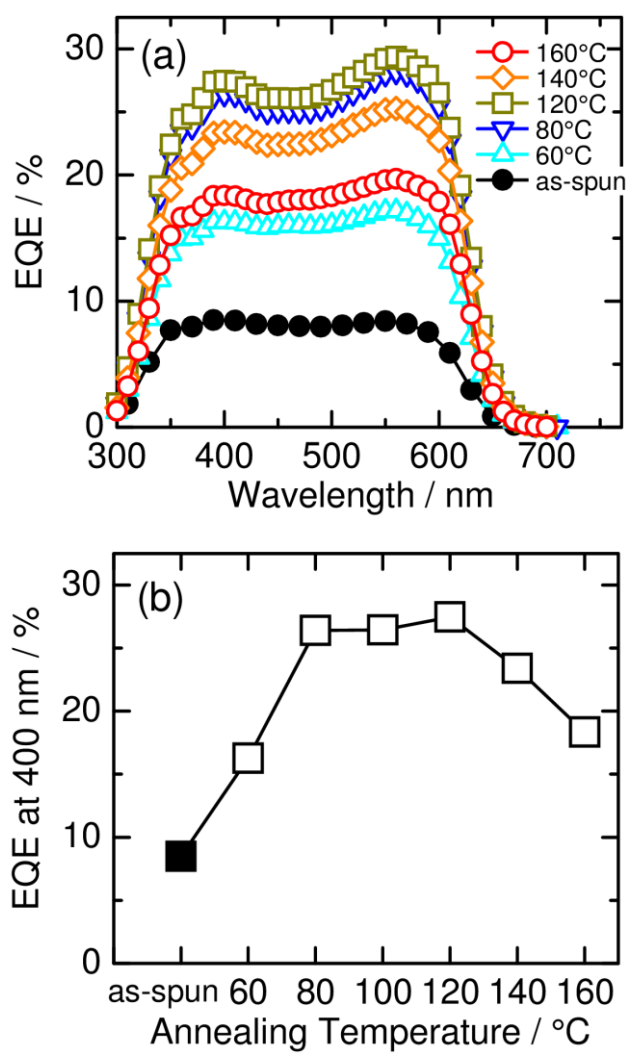


Figure 2. (a) EQE spectra of P3HT/PF12TBT BHJ solar cells annealed at various temperatures. (b) The annealing temperature dependence of EQE at 400 nm.

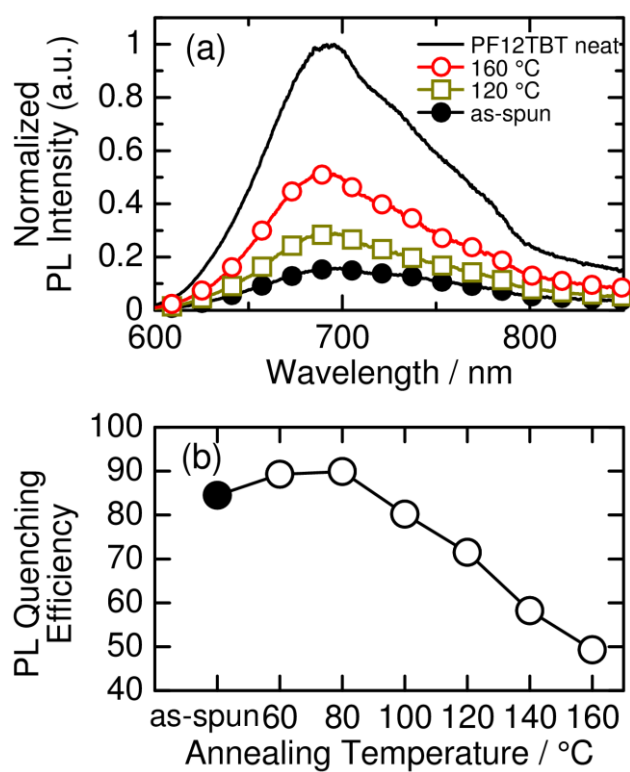


Figure 3. (a) The PL spectra of PF12TBT neat and the P3HT/PF12TBT blend films, excited at 392 nm. (b) The annealing temperature dependence of PL quenching efficiency for the blend films.

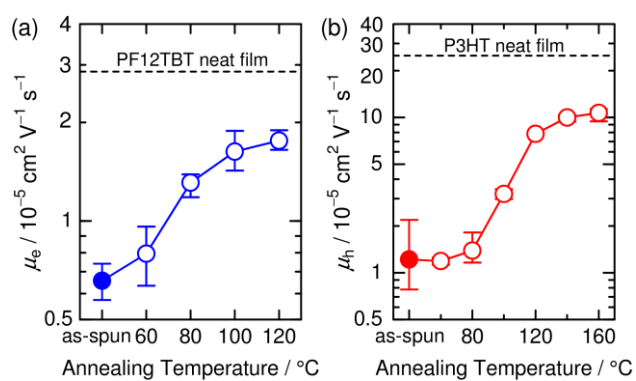


Figure 4. (a) Electron and (b) hole mobilities of the P3HT/PF12TBT blend films with respect to annealing temperature. Dotted lines in each figure indicate mobility values of the PF12TBT and P3HT neat films.

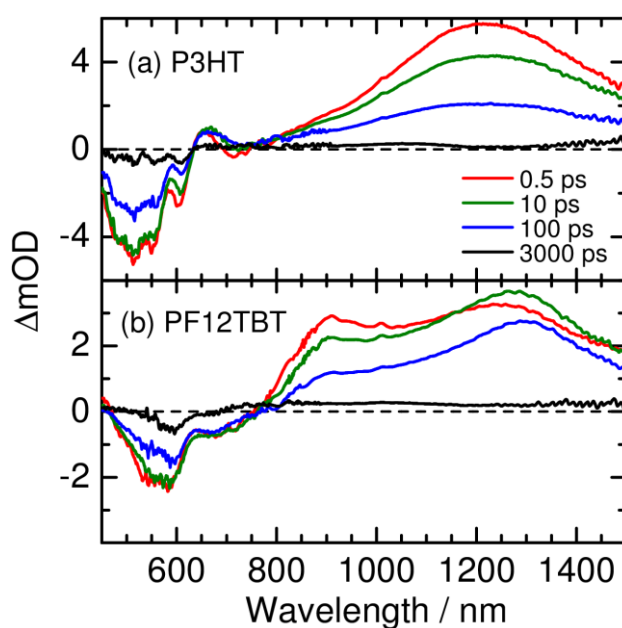


Figure 5. TA spectra for the (a) P3HT and (b) PF12TBT neat films, measured at delay times of 0.5 ps (red lines), 10 ps (green lines), 100 ps (blue lines), and 3000 ps (black lines) after excitation. The excitation wavelength was 400 nm and the fluence was $7.5 \mu\text{J cm}^{-2}$. The ΔOD values were corrected for variations in absorption at 400 nm of each neat film. The black dashed line indicates $\Delta\text{OD} = 0$.

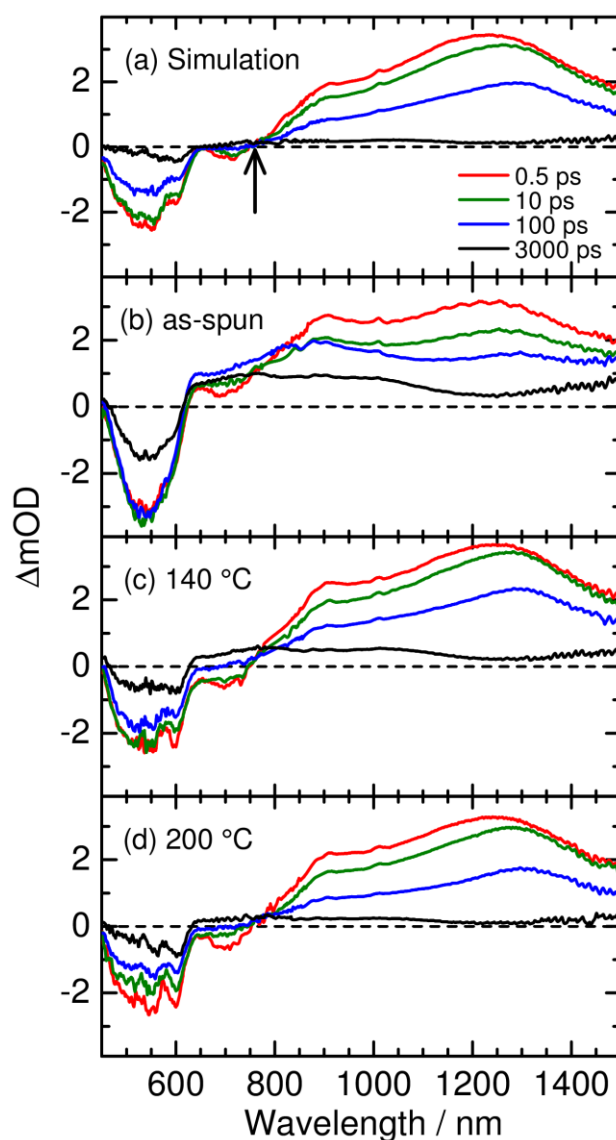


Figure 6. (a) Simulated TA spectra for the P3HT/PF12TBT blend film calculated by adding the weighted TA spectra of the P3HT and PF12TBT neat films. The arrow indicates a wavelength of 760 nm. TA spectra of P3HT/PF12TBT blend films that were (b) unannealed or annealed at (c) 140 or (d) 200 °C. All presented samples are provided for delay times of 0.5 ps (red lines), 10 ps (green lines), 100 ps (blue lines), and 3000 ps (black lines) after excitation. The excitation wavelength was 400 nm and the excitation pulse intensity was $7.5 \mu\text{J cm}^{-2}$. The ΔOD values were corrected for variations in absorption at 400 nm of each film. The black dashed line indicates $\Delta OD = 0$.

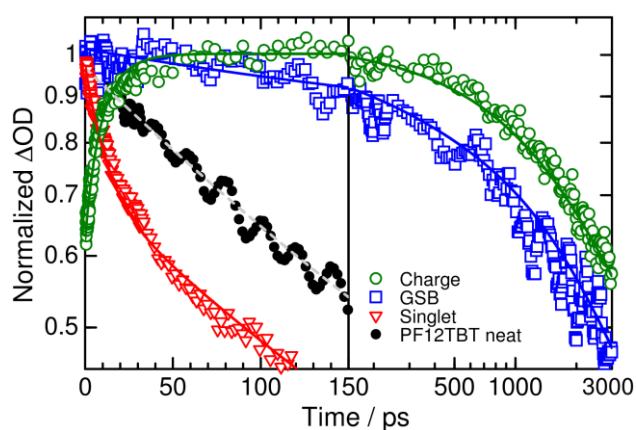


Figure 7. Normalized TA signals of the unannealed blend films for charge induced absorption (open circles), singlet excitons (open triangle), and the GSB (open square), observed at 760 nm, 1200 nm, and 550 nm, respectively. Closed circles show the TA signal for singlet excitons in the PF12TBT neat films and were recorded at 1200 nm. The ΔOD was normalized, with the maximum peak intensities set be 1. The solid lines represent the best fitting curves, while the dashed line tracks exponential decay for a lifetime of 190 ps. The excitation wavelength was 400 nm and the excitation fluence was $7.5 \mu\text{J cm}^{-2}$.

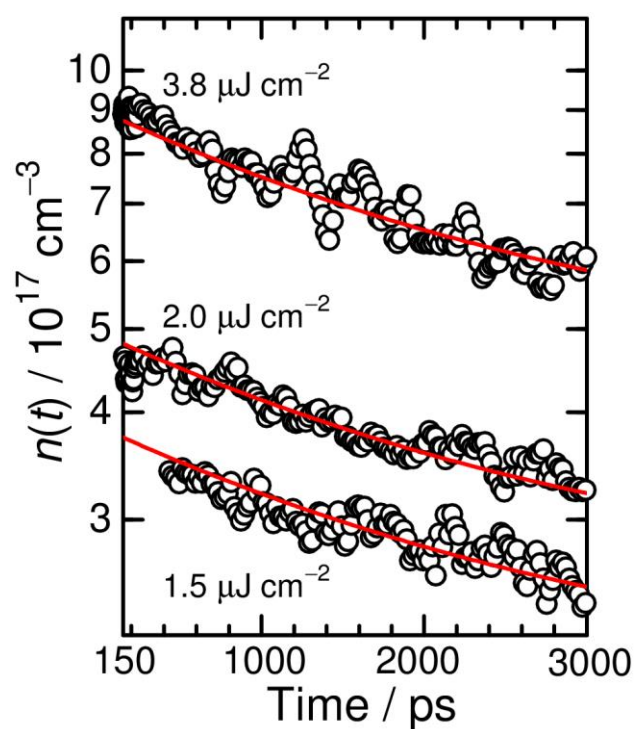


Figure 8. The dependence of charge recombination dynamics on fluence for the unannealed P3HT/PF12TBT blend film, observed at a wavelength of 760 nm. The solid lines represent single exponential fits with an inverse rate of 2500 ps. The excitation wavelength was 400 nm, with excitation fluences of 1.5, 2.0, and 3.8 $\mu\text{J cm}^{-2}$.

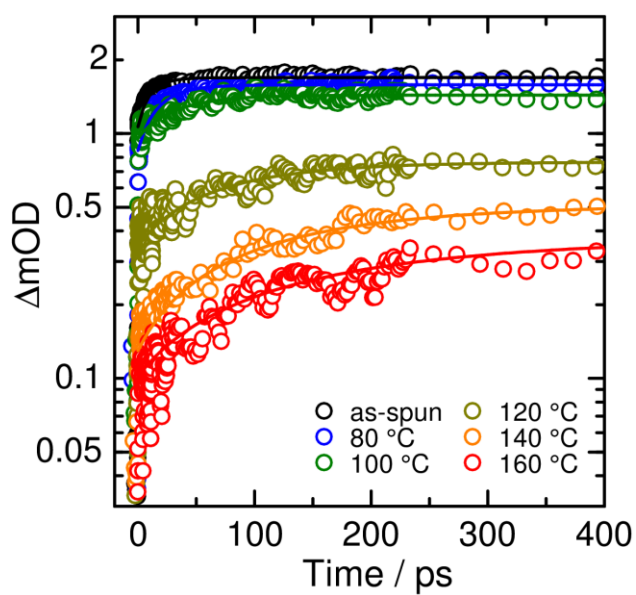


Figure 9. The dependence of charge generation dynamics on annealing temperature, observed at a wavelength of 760 nm. The solid lines represent the best fitting curves. The excitation wavelength was 400 nm and the excitation fluence was $7.5 \mu\text{J cm}^{-2}$. The ΔOD values were corrected for variations in absorption at 400 nm of each film.

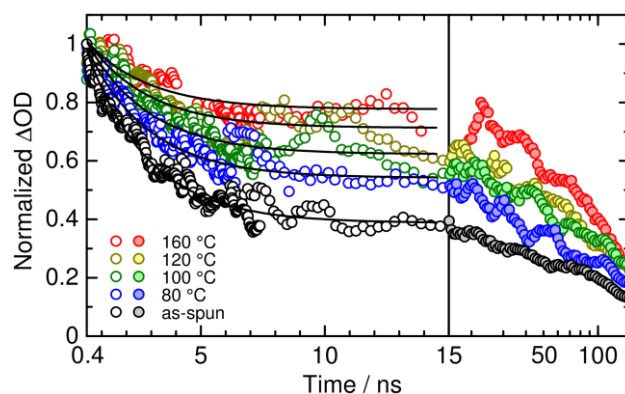


Figure 10. The dependence of charge recombination dynamics on annealing temperature, observed at a wavelength of 760 nm. The solid lines represent the best fitting curves. The excitation wavelength was 400 nm and the excitation fluence was $3.8 \mu\text{J cm}^{-2}$.

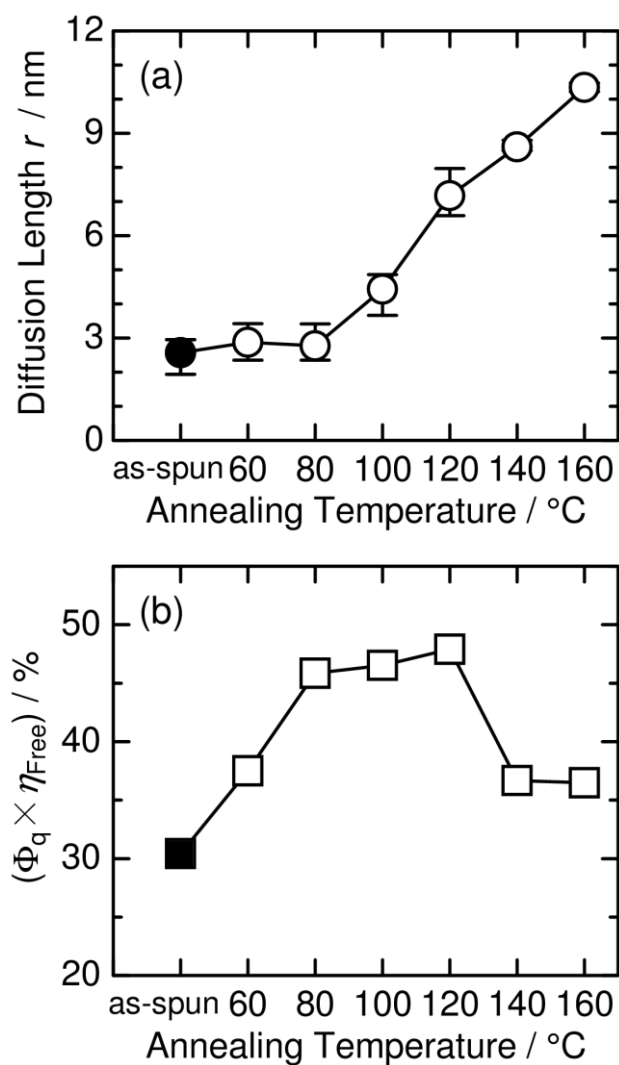


Figure 11. (a) Diffusion length r for polymer singlet excitons and (b) overall generation yield of free carriers ($\Phi_q \times \eta_{\text{free}}$) in the P3HT/PF12TBT blend films as a function of annealing temperature.

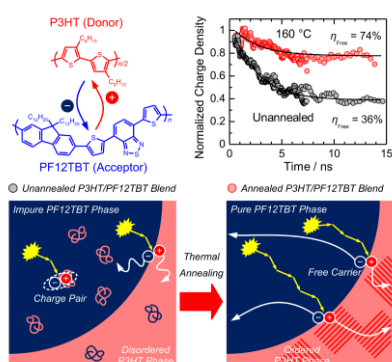
Table 1. Fitting parameters of the charge generation dynamics shown in Figure 9, obtained using Equation (1).

Annealing Temp. [°C]	as-spun	60	80	100	120	140	160
τ_R [ps]	11	14	13	33	87	126	182
A/(A+B) [%]	36	38	40	42	49	63	69
B/(A+B) [%]	64	62	60	58	51	37	31

Table 2. Fitting parameters of the geminate recombination shown in Figure 10, obtained using Equation (2).

Annealing Temp. [°C]	as-spun	60	80	100	120	140	160
G/(G+C) [%]	64	58	49	42	33	37	26
C/(G+C) [%]	36	42	51	58	67	63	74

The table of contents entry



Charge generation and recombination dynamics in donor/acceptor polymer blend solar cells composed of poly(3-hexylthiophene) (P3HT) and fluorene-based copolymer (PF12TBT) are examined by transient absorption spectroscopy. Thermal annealing improves both the purity of the PF12TBT domains and the ordering of the P3HT chains. These morphological changes suppress the monomolecular recombination of charge pairs, increasing the free carrier generation efficiency up to 74%.

Keywords: polymer solar cells, conjugated polymer blends, poly(3-hexylthiophene), fluorene-based copolymer, transient absorption spectroscopy

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Morphology-Limited Free Carrier Generation in Donor/Acceptor Polymer Blend Solar Cells Composed of Poly(3-hexylthiophene) and Fluorene-Based Copolymer

ToC figure ((Please choose one size: 55 mm broad × 50 mm high **or** 110 mm broad × 20 mm high. Please do not use any other dimensions))

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Supporting Information

Morphology-Limited Free Carrier Generation in Donor/Acceptor Polymer Blend Solar Cells Composed of Poly(3-hexylthiophene) and Fluorene-Based Copolymer

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1. TA dynamics from singlet excitons and SE for the PF12TBT Neat Film

To confirm the assignment of the TA spectra to the PF12TBT singlet excitons, we compared the dynamics of singlet excitons probed at 1200 nm with those of SE recorded at 650 nm (Figure S1). These two dynamics coincide with each other. We therefore attribute the broad absorption band at 800 – 1500 nm to the absorption of PF12TBT singlet excitons.

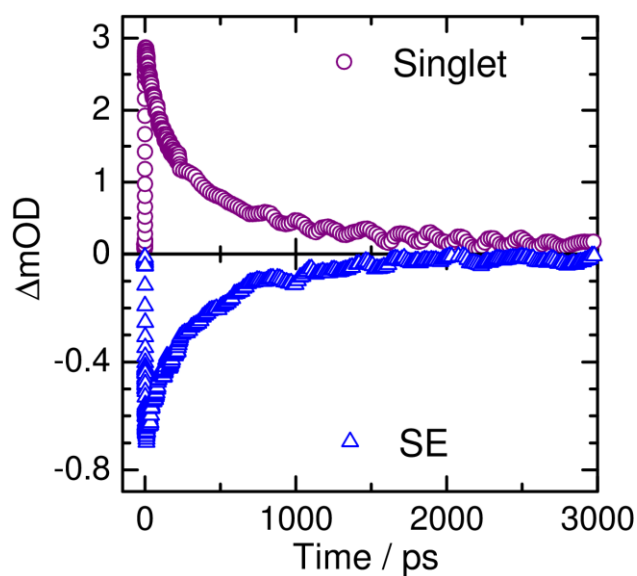


Figure S1. TA signals from singlet excitons (circles) and SE (triangles) in a PF12TBT neat film, recorded at 1200 nm and 650 nm, respectively. The excitation wavelength was 400 nm and the excitation fluence was $7.5 \mu\text{J cm}^{-2}$.

2. TA spectra of the PF12TBT neat film

To address the origin of the spectral change in Figure 5b, we measured the TA spectra of the PF12TBT neat film by changing the excitation wavelength (energy). Figure S2 shows the TA spectra of the PF12TBT neat film, recorded at an excitation of 560 nm. Little changes in the spectral shape with time were observed differently from the spectra obtained at an excitation of 400 nm, as shown in Figure 5b. In general, copolymers based on fluorene and 4,7-dithiophene-2-yl-benzo[1,2,5]thiadiazole (TBT) units have two distinct absorption bands: a blue band below 450 nm attributed to a fully-delocalized excitonic $\pi-\pi^*$ transition, and a red band at around 580 nm ascribed to a localized charge transfer state, with the excited electron confined to the TBT unit.^[S1] Singlet excitons are generated in the charge transfer state immediately after excitation at 560 nm. We therefore attribute the spectral change within 10 ps after excitation at 400 nm (Figure 5b) to the relaxation of singlet excitons from higher energy excitonic states to lower energy charge transfer states.

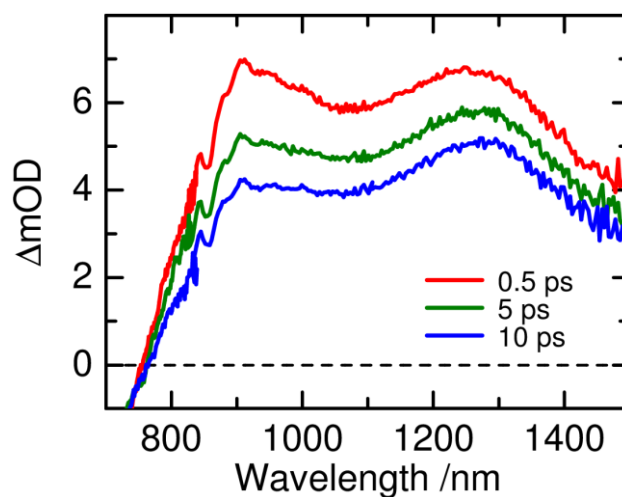


Figure S2. TA spectra of the PF12TBT neat film excited at a wavelength of 560 nm at delay times of 0.5 ps (red solid line), 5 ps (green solid line), and 10 ps (blue solid line). The excitation fluence was $10 \mu\text{J cm}^{-2}$.

3. Assignment of Charge Induced Absorption

To confirm the assignment of the long-lived transient species observed at 3 ns, we measured the TA spectra of the unannealed blend film in the microsecond time range. Figure S3 shows the microsecond TA spectra and accompanying decays. The long-lived transient species also exists in the microsecond time range and has the the same spectral shape. Furthermore, the decay rate of the TA signal did not change under O₂ atmosphere. We therefore conclude that the long-lived species observed in the blend films is the P3HT and PF12TBT polarons.

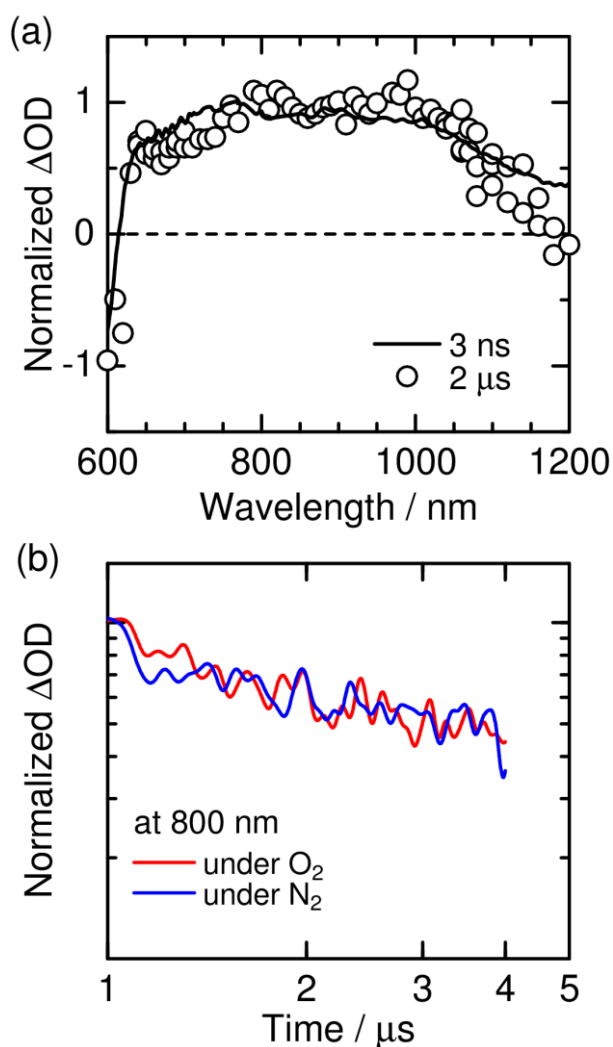


Figure S3. (a) Normalized TA spectra of the unannealed blend film measured at delay times of 3 ns (solid line) and 2 μs (open circles). (b) TA decay signals recorded at 800 nm under N₂ (blue line) and O₂ (red line) atmosphere. The excitation wavelength was 400 nm and the excitation fluence of the microsecond TA measurements was 20 μJ cm⁻².

4. Estimation of the Molar Absorption Coefficient (ϵ) of the Charge Induced Absorption

To estimate molar absorption coefficient (ϵ) of the charge induced absorption observed in the P3HT/PF12TBT blend films, we estimated the spectral shape of the PF12TBT electron polarons. The absorption spectra of the PF12TBT anion was obtained by spectroelectrochemical measurements of a PF12TBT neat film coated on a conductive substrate. The TA spectra of the P3HT hole polarons have already been reported by Guo *et al.*^[S2,S3] This report described both delocalized and localized polarons. The spectral shape of the charge induced absorption was constructed by adding these three absorption spectra; ϵ was then estimated based on the corresponding value of the P3HT localized polaron reported in the literature.^[S3]

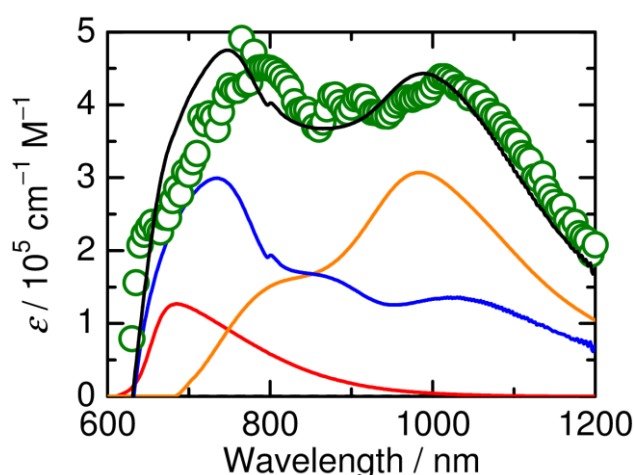


Figure S4. Molar absorption coefficient (ϵ) of the charge induced absorption of the blend film (green circles). The black solid line represents the absorption spectrum calculated by adding the P3HT delocalized hole polaron spectrum (red line), the P3HT localized hole polaron spectrum (orange line), and the PF12TBT electron polaron spectrum (blue line). The PF12TBT electron polaron spectrum was obtained by spectroelectrochemical measurements.

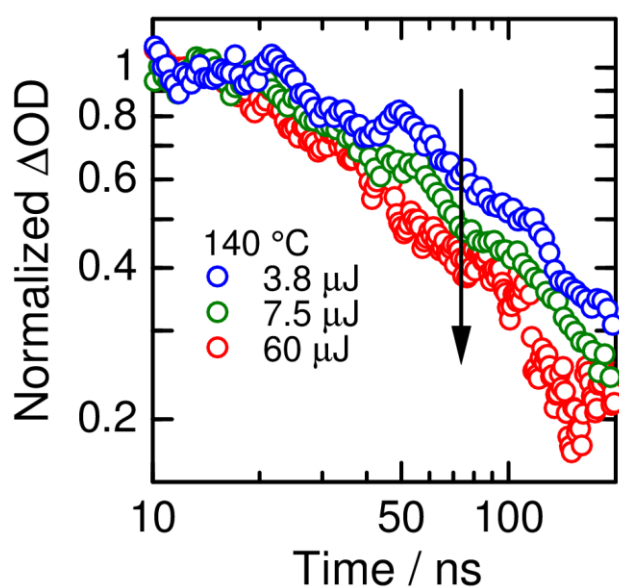


Figure S5. The fluence dependence of the charge recombination dynamics for the blend film annealed at 140 °C, observed at a wavelength of 760 nm and over a submicrosecond time range. The excitation wavelength was 400 nm and the excitation fluence was 3.8, 7.5, and 60 $\mu\text{J cm}^{-2}$.

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