

Delocalisation boosts charge separation in organic solar cells

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Abstract

Organic solar cells (OSCs) utilising π -conjugated polymers have attracted widespread interest over the past three decades because of their potential advantages, including light weight, thin film flexibility, and low-cost manufacturing. However, their power conversion efficiency (PCE) has been far below that of inorganic analogues. Geminate recombination of charge transfer excitons is a major loss process in OSCs. This paper reviews our recent progress in using transient absorption spectroscopy to understand geminate recombination in bulk heterojunction OSCs, including the impact of polymer crystallinity on charge generation, and charge dissociation mechanisms in nonfullerene acceptor-based OSCs. The first example of high PCE with small photon energy loss is also given. The importance of delocalisation of the charge wave function to suppress geminate recombination is highlighted by this focus review.

Introduction

Over the past three decades, organic solar cells (OSCs) utilising π -conjugated polymers have attracted widespread interest because of their potential advantages, including light weight, thin film flexibility, and low-cost manufacturing [1-4]. When a light is shined on semiconducting polymers, singlet excitons, i.e. Coulombically bound electron-hole (e^- -

h) pairs instead of free charge carriers, are promptly generated because of their small dielectric constants. This is in sharp contrast to inorganic semiconductors such as silicon, in which light absorption directly results in the generation of free electrons and holes in the conduction and valence bands, respectively. OSCs require a donor-acceptor (DA) heterojunction to ionize singlet excitons, where, as a result of the offset in the lowest unoccupied molecular orbital (LUMO) or highest occupied molecular orbital (HOMO) energy at the DA interface, singlet excitons separate into holes on the donor and electrons on the acceptor. If the electron and hole separate further, they become free from Coulombic attraction, and hence survive up to nano- or microseconds, long enough to be transported to each electrode. Otherwise, the geminate e–h pairs are likely to recombine to the ground state (Figure 1).

<<< Figure 1>>>

Historically, geminate recombination has been one of the most detrimental processes for OSCs. Singlet excitons in blends of regiorandom poly(3-hexylthiophene) (RRa-P3HT) and a fullerene derivative PCBM undergo efficient charge transfer (CT) at the DA interface (the quantum efficiency of CT at the DA interface is nearly unity); however, CT

excitons then experience strong geminate recombination within ~ 2 ns ($\sim 70\%$ of CT excitons geminately decay to the ground state) [5]. Higher performing OSCs have generally consisted of crystalline donor polymers such as regioregular P3HT (RR-P3HT) blended with either PCBM or its C70 analogue PC₇₁BM. For example, in blends of RR-P3HT and PCBM, $>90\%$ of CT excitons dissociate into free charge carriers [5]. Therefore, it is important to understand how polymer crystallisation impacts charge dissociation efficiency.

Nonfullerene acceptors (NFAs) have been considered as an alternative to fullerenes. They provide stronger optical absorption in the visible to near-IR region, allowing easier optimisation of the molecular orbital energy. Until recently, however, NFA-based OSCs routinely lagged in charge generation efficiency, and hence power conversion efficiency (PCE), behind their fullerene-based analogues [6-8]. One reason for the lower device efficiency of NFA-based OSCs is that most NFA-based OSCs suffer from terrible geminate recombination loss [9-14]. For example, blends of PBDTTT-C and a perylene diimide (PDI) monomer lost more than half of the CT excitons through geminate recombination on the sub-nanosecond time scale [14]. As a result, fullerenes were considered “*special*” electron acceptors for a long time. Thanks to development of new NFAs, the PCEs for NFA-based OSCs have improved very rapidly [4,15,16], and

currently some NFA-based OSCs have a far superior PCE to conventional fullerene-based OSCs [17-19]. In contrast to the rapid improvement of device efficiency, the fundamental mechanisms for charge generation and recombination in NFA-based OSCs are still being debated. It is important to understand whether the models developed for fullerene acceptor systems are also applicable to efficient NFA systems.

Another remaining challenge in this field is to reduce photon energy loss (E_{loss}) in OSCs, which is defined as the difference between the optical bandgap (E_g) of the materials and the open-circuit voltage (V_{OC}) ($E_{\text{loss}} = E_g - qV_{\text{OC}}$ where q is an elementary charge). It is well known that the E_{loss} in OSCs is typically more than 0.7 eV [20], which is much larger than that in the silicon-based solar cell (E_{loss} is only ~ 0.4 eV). This is partly because OSCs require a DA heterojunction to ionize the excitons as mentioned above, resulting in a reduction of energy from E_g to the CT state energy E_{CT} . Historically, it has been considered that a LUMO (or HOMO) energy offset of more than 0.3 eV is necessary for efficient charge generation. For example, Li et al. found a strong correlation between the LUMO energy offset and the external quantum efficiency (EQE) [21]. The energy offset was varied by using various donor polymers with fullerene acceptors, and it was found that the EQE drops sharply when the E_{loss} is less than 0.6 eV. This is rationalised by an insufficient driving force for charge generation as a result of the small LUMO energy

offset. OSCs that exhibit efficient charge generation despite a small energy offset are therefore strongly required.

We have tackled above mentioned challenges by using transient absorption (TA) spectroscopy. TA spectroscopy is one of the most powerful and useful tools for tracking the time evolution of transient species in OSCs, such as excitons and charges, with high temporal resolution [22-31]. In this focus review, our recent findings regarding the dissociation of CT excitons into free charge carriers are summarised. The impacts of polymer crystallisation on charge dissociation efficiency [24] and mechanisms of charge dissociation in an efficient NFA-based OSCs [31] are discussed. Finally, an example of efficient charge generation with small LUMO energy offset is introduced [28].

Impacts of polymer crystallisation on charge dissociation efficiency

Many previous studies have pointed out that crystallisation or aggregation of materials promotes charge dissociation in OSCs [5,32-37]. However, exactly how polymer crystallinity impacts charge dissociation is still unclear. Herein, we discuss the impact of polymer crystallisation on charge dissociation in blends of various donor polymers with PCBM [24]. Figure 2a shows the TA spectra of a PSBTBT/PCBM blend film as an example. A positive signal around 1500 nm observed immediately after photoexcitation

is attributable to a photoinduced absorption (PIA) band of PSBTBT singlet excitons. Even just after the photoexcitation ($t = 0$ ps), the TA amplitude of the singlet exciton band is reduced compared with that of the PSBTBT pristine film, indicating that some excitons dissociate to charge pairs within the time resolution of our TA system (~ 130 fs, full width at half maximum). Instead, another PIA band ascribable to polymer hole polarons was observed, ranging from 800 to 1300 nm for the blend film. Note that the PCBM anion has a PIA band centred at 1020 nm [5], but this band was not observed because of its small absorption cross-section. The singlet excitons decayed with a time constant of 0.8 ps, and the polaron band became more pronounced at the same time. At 10 ps after photoexcitation, singlet excitons completely disappeared, and a broad polaron band with peaks at 1000 and 1300 nm was clearly observed. Interestingly, decay kinetics monitored at 1000 nm were faster than those monitored at 1300 nm, indicating that there are at least two distinct charged states in the PSBTBT domains. We found that the band at 1000 nm could be assigned to polarons generated in the PSBTBT disordered phase, and the band at 1300 nm to the PSBTBT crystalline phase. Figure 2b shows the decay kinetics of those two polarons after 10 ps. Interestingly, the population of polarons in the crystalline phase still increased with a time constant of ~ 24 ps, even though singlet excitons had completely disappeared at this point. We found that the increase of polarons in the crystalline phase

was accompanied by a decrease of polarons in the disordered phase, indicating that some of the polarons in the disordered phase were transferred to the crystalline phase. Within a nanosecond time scale, about a half the polarons in the disordered phase decayed geminately, whilst geminate recombination was negligible in the crystalline phase.

<<< Figure 2 >>>

Charge dissociation efficiencies for other blends are summarised in Table 1 [5,37-44]. We first focus on the impacts of hole transfer from the disorder phase to the crystalline phase observed in PSBTBT/PCBM blends. A similar hole transfer has been reported for RR-P3HT/PCBM blends [5]. Owing to the hole transfer from the disordered phase to the crystalline phase, charge dissociation efficiency in the disordered phase ($\eta_{\text{CD}}^{\text{dis}}$) in blends of crystalline donor polymers is higher than that in amorphous RRa-P3HT blends. The driving force for the hole transfer is believed to be potential energy cascades between the crystalline and interfacial disordered phases. Previous studies have established that most OSCs consist of nanoscale domains of pure polymers, pure fullerenes, and the intermixed regions in between [45-48]. Thus, the three-phase morphology introduced by polymer crystallisation would be a key driver for efficient charge dissociation through the hole

transfer [34] because the ionization potential of conjugated polymers, in general, is reduced with increasing polymer crystallinity, resulting in a HOMO energy cascade between the intermixed disordered phase and the pure polymer crystalline phase [49].

<<<Table 1>>>

The charge dissociation efficiency is clearly dependent on the blend morphology. Quantum efficiencies of charge dissociation in crystalline phases ($\eta_{\text{CD}}^{\text{cry}}$) are nearly unity, which is surprisingly high according to the conventional charge dissociation model based on the Braun-Onsager framework [1]. According to the Braun-Onsager framework, an electron and a hole are tightly bound at the DA interface by strong Coulombic attraction because the dielectric constants of organic materials are low, and hence efficient charge dissociation requires a strong electric field ($>10^8$ V m) and/or a high temperature. However, this is not true for most OSCs, wherein electric field and temperature independent charge dissociation has been observed [32,50]. We found a positive correlation between dissociation efficiency and crystalline coherent length in the π -stacking direction L_{010} , suggesting that delocalisation of hole polarons in the crystalline phase plays a key role in the charge dissociation. As shown in Table 1, high charge

dissociation efficiencies are observed for crystalline polymers with a correlation length of $L_{010} > 4$ nm, which is comparable to the effective Coulombic capture radius at the DA interface, taking into account the entropic contribution to the Gibbs free energy [1]. We therefore conclude that large delocalisation of hole wave functions in polymer crystalline phases promotes charge dissociation. Our findings would be consistent with spectroscopic studies reported by Friend and co-workers, wherein ultrafast long-range charge separation occurs through access to band-like electron states in fullerene aggregates [35].

Ultrafast charge dissociation in nonfullerene acceptor-based solar cells

The charge dissociation mechanisms in NFA-based OSCs are exemplified in blends of a benchmark donor polymer, PTB7-Th, and an efficient NFA, bay-di-PDI [31]. Figure 3a shows the femtosecond TA spectra for the PTB7-Th/bay-di-PDI blend under the selective excitation of PTB7-Th. The large positive band in the visible region is ascribed to ground-state bleaching (GSB), and a broad PIA tail observed around 1400 nm is attributable to polymer singlet excitons. Singlet excitons rapidly decayed with a lifetime of 1.3 ps. Because the intrinsic exciton lifetime of PTB7-Th is ~220 ps, this indicates that almost all excitons were converted into charged species. The PIA centred at 1150 nm became

dominant within 10 ps, which can be ascribed to hole polarons on the donor polymer. Note that PIA band of bay-di-PDI radical anion was not observed because it fully overlaps with the large GSB band [51]. Hole polarons, then, remained almost unchanged until the nanosecond time scale. For comparison, Figure 3b shows the TA spectra for the PTB7-Th/PC₇₁BM blend film. As in the PDI blend, the polaron band remain unchanged until 1 ns. Note that an additional PIA band was observed at 1300 nm at later times only for the PC₇₁BM blend, which we attribute to polymer triplet absorption formed through bimolecular charge recombination [52-54].

<<< Figure 3 >>>

Figure 4a,b shows the normalised TA spectra in the visible region. We found that both the peak position and onset of the main GSB band blue-shift even after singlet excitons have been fully quenched. This indicates that a small PIA overlaps this region, with dynamics different to both singlet excitons and charges. In line with previous results [35], we attribute this to the electroabsorption (EA) of PTB7-Th. When an exciton dissociates into an e-h pair, a dipole-like local electric field is generated in its surroundings. This results in a Stark shift for surrounding molecules, adding a first-derivative-like spectrum

component to the TA data. As the amplitude of the EA signal is a function of the local electric field, i.e. a function of separation distance of the e–h pair, we can directly quantify the separation distance of the e–h pair. Figure 4c shows the time evolution of the EA amplitude. For the PC₇₁BM blend, the EA amplitude is already large at 200 fs, and reaches its maximum by 400–500 fs. As shown in the right axis of Figure 4c, the EA amplitude was converted into electrostatic energy stored in the field per an e–h pair, which was calculated as $\frac{1}{2} \epsilon_0 \epsilon_r \int |E|^2 dV$ and calibrated against quasi steady-state EA measurements on diode structures. During this short duration, electrostatic energy of ~200 meV was stored in the field, which is well above the thermal energy at room temperature and on the same order of the CT state binding energy. This indicates that the e–h pair undergoes rapid spatial separation, despite the opposing Coulombic attraction. This picture is again inconsistent with the Braun-Onsager framework, but is consistent with ballistic charge separation through delocalised wave function [35]. Interestingly, the EA amplitude of the PDI blend is as large as that of the PC₇₁BM blend, indicating that charge separation mechanisms for the PDI blend can be rationalised by the ballistic charge separation model. Before our study, ballistic charge separation was only observed in blends that consist of relatively large fullerene aggregates. However, we provided clear experimental evidence that ballistic charge separation can also take place in NFA-based blends, and hence the

model that charges separate coherently through delocalised states can be more widely applied to various types of OSCs.

<<< Figure 4 >>>

Figure 5a shows the time evolution of polaron signals in the PDI and PC₇₁BM blends on the nanosecond time scale. We found no apparent difference in the charge dynamics between the PDI and PC₇₁BM blends, indicating that there is no intrinsic disadvantage for NFAs in terms of charge generation, i.e. fullerenes are not so “*special*”. Figure 5b shows the excitation wavelength dependence of charge dynamics in the PDI blend. As clearly seen in the figure, the charge dynamics are independent of the excitation wavelength, indicating that both electron transfer from PTB7-Th to bay-di-PDI (excited at 650 nm) and hole transfer from bay-di-PDI to PTB7-Th result in efficient charge generation. This is consistent with the EQE spectra for this blend which follows the absorption spectra. It is interesting to investigate the separate roles of electrons and holes in the charge dissociation process. We do find that the charge dissociation process is strongly dependent on the morphology of both donor and acceptor, indicating that both the donor and acceptor do play an important role in the charge dissociation process.

<<< Figure 5 >>>

Efficient charge separation with small driving force

We have demonstrated the first efficient charge generation with small photon energy loss [28]. We used a high-efficient donor polymer, PNTz4T or PNOz4T, blended with PC₇₁BM. The PNTz4T-based device had an E_g of 1.56 eV (based on absorption onset) and showed a PCE of 10.1% with a high short-circuit current density (J_{SC}) of 19.4 mA cm⁻² [55]. However, the E_{loss} was as large as 0.85 eV, resulting in a V_{OC} of only 0.71 V. Such a large E_{loss} is partly because of a large LUMO energy offset between PNTz4T and PC₇₁BM. In contrast, the PNOz4T-based device showed an E_g of 1.52 eV [56], which is almost the same as the PNTz4T-based device, and a V_{OC} of 0.96 V, resulting in an E_{loss} of 0.56 eV [28]. Surprisingly, the J_{SC} and PCE were as high as 14.6 mA cm⁻² and 8.9%, respectively. This results in our system having the highest known PCE among OSCs with an E_{loss} less than 0.6 eV (at least in 2015).

We expected that the origin of the small E_{loss} in the PNOz4T-based device is a small LUMO energy offset. To confirm this, we measured the temperature dependence of the V_{OC} as shown in Figure 6. The V_{OC} increased linearly with decreasing temperature. It is

well known that the effective bandgap (E_g^{eff}) obtained from the intersection at 0 K is a good indicator for E_{CT} because the E_g^{eff} is identical with the E_{CT} at 0 K [57,58]. Note that the E_{CT} at room temperature is typically 0.1–0.2 eV above the E_g^{eff} . The E_g^{eff} for the PNOz4T- and PNTz4T-based devices were 1.38 and 1.07 eV, respectively. Thus, the difference between the E_g and E_{CT} in the PNOz4T-based device at room temperature would be less than 0.14 eV, whilst it is as large as 0.4–0.5 eV in the PNTz4T-based device. This is consistent with the observation that the electroluminescence (EL) spectrum of the PNOz4T/PC₇₁BM device is almost the same as that of the PNOz4T pristine device. This indicates that charge generation in the PNOz4T-based device is efficient even though the LUMO energy offset is smaller than the empirical threshold of 0.3 eV.

<<< Figure 6 >>>

Figure 7a,b shows the TA spectra for the PNTz4T/PC₇₁BM and PNOz4T/PC₇₁BM blend films. Immediately after photoexcitation, PIA bands attributable to singlet excitons were observed at 1100–1400 nm in both blends. In the PNTz4T blend, singlet excitons had almost disappeared within 10 ps, which is a sign of fine morphology. Instead, another PIA band ascribable to PNTz4T polarons was observed centred at 1100 nm, which then

slightly decayed on the nanosecond time scale through geminate recombination, probably as a result of the well-mixed disordered morphology. In contrast, singlet excitons decayed slowly in the PNOz4T blend, which implies large phase-separated domains or slow CT at the interface. Interestingly, a contribution from polaron absorption was observed for the TA data even at 0 ps, which indicates immediate CT of some excitons that generated very close to the interface. This suggests that CT itself is still fast and efficient even in the PNOz4T blend, and hence the slow exciton decay kinetics is attributable to a large domain size. This is consistent with the difference in morphology of the two blends observed in the transmission electron micrography images. What is important in our findings is that no polaron decay was observed in the PNOz4T blend up to 3 ns, which is clear evidence of efficient charge dissociation. We therefore conclude that, in the PNOz4T-based device, excitons dissociate into charges very efficiently without a large driving force. Although the mechanism of efficient charge dissociation without a large offset is still unclear, probably the highly crystalline nature of PNOz4T is essential for the charge dissociation, and this study clearly demonstrates the potential advantages of utilising small offset systems.

<<< Figure 7>>>

Conclusion

This focus review highlights our recent studies using TA spectroscopy to investigate charge generation and recombination dynamics in OSCs. The impacts of polymer crystallinity on charge dissociation efficiency, mechanisms of charge dissociation in NFA-based OSCs, and efficient charge dissociation with a small LUMO energy offset were described. It was shown that the crystallisation or aggregation of materials promotes charge dissociation, which is rationalised by the delocalisation of charge wave functions in the crystalline or aggregate domains. State-of-the-art OSCs consist of wide-bandgap donor polymers and low-bandgap NFAs with a small HOMO energy offset, but understanding charge generation mechanisms with a small energy offset remains a challenge. Further spectroscopic studies will provide comprehensive understanding and clear design concepts for materials and devices.

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Notes

The authors declare no competing financial interest.

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Titles and Legends to Figures

Figure 1. (a) Photocurrent conversion processes in OSCs: (1) photon absorption to generate singlet excitons, (2) exciton diffusion to the DA interface, (3) charge transfer to generate CT excitons, (4) dissociation of CT excitons into free carriers, and (5) charge collection to each electrode. (b) Exciton diffusion followed by charge transfer at the interface. (c) Geminate recombination and charge dissociation of CT excitons.

Figure 2. (a) TA spectra of the PSBTBT/PCBM blend film excited at 800 nm with a fluence of $11 \mu\text{J cm}^{-2}$. The broken line represents the PIA band of PSBTBT singlet excitons observed for a PSBTBT pristine film. (b) Time evolution of polarons in the disordered phase (open triangles), and polarons in the crystalline phase (open squares) in the PSBTBT/PCBM blend film. The closed circles represent the total polaron density.

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Figure 3. TA spectra of the (a) PTB7-Th/bay-di-PDI blend, and (b) PTB7-Th/PC₇₁BM blend, excited at 650 nm with a fluence of $1.6 \mu\text{J cm}^{-2}$. The spectra in the near-IR region (850–1050 nm) were rescaled to that of the IR region (1050–1400 nm) owing to a small change in the pump–probe overlap. Reprinted with permission from ref. [31]. Copyright

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Figure 4. (a,b) Normalised TA spectra in the visible region. Broken lines represent the TA spectra of the pristine PTB7-Th film as a reference. (c) Time evolution of the EA amplitude per unit charge obtained by dividing the EA amplitude by the charge signal. The right axis shows total electrostatic energy stored in the field per electron–hole pair. The energy is obtained assuming that half of the field is in the donor phase as $\frac{1}{2}\epsilon_0\epsilon_r \int |E|^2 dV$ and a taking a value of 3 for ϵ_r . The spatially integrated square of the electric field was converted from the diode-based EA amplitude. Reprinted with permission from ref. [31]. Copyright 2017 American Chemical Society.

Figure 5. (a) Normalised time evolution of the polaron band in the PDI (red) and PC₇₁BM (black) blends. (b) Excitation wavelength dependence of polaron dynamics in the PDI blend. Reprinted with permission from ref. [31]. Copyright 2017 American Chemical Society.

Figure 6. Temperature dependence of the V_{OC} for the PNOz4T and PNTz4T-based devices. Adapted from ref. [28]. Copyright 2015 Springer Nature.

Figure 7. (a,b) TA spectra of the PNTz4T/PC₇₁BM and PNOz4T/PC₇₁BM blend films. (c,d) Normalised time evolution of the singlet excitons (blue) and polaron (red) bands in the PNTz4T/PC₇₁BM and PNOz4T/PC₇₁BM blend films. Green squares represent total density of singlet excitons and polarons. Adapted from ref. [28]. Copyright 2015 Springer Nature.

Table 1. Photovoltaic conversion efficiency of OSCs.

Display Items

Figure 1

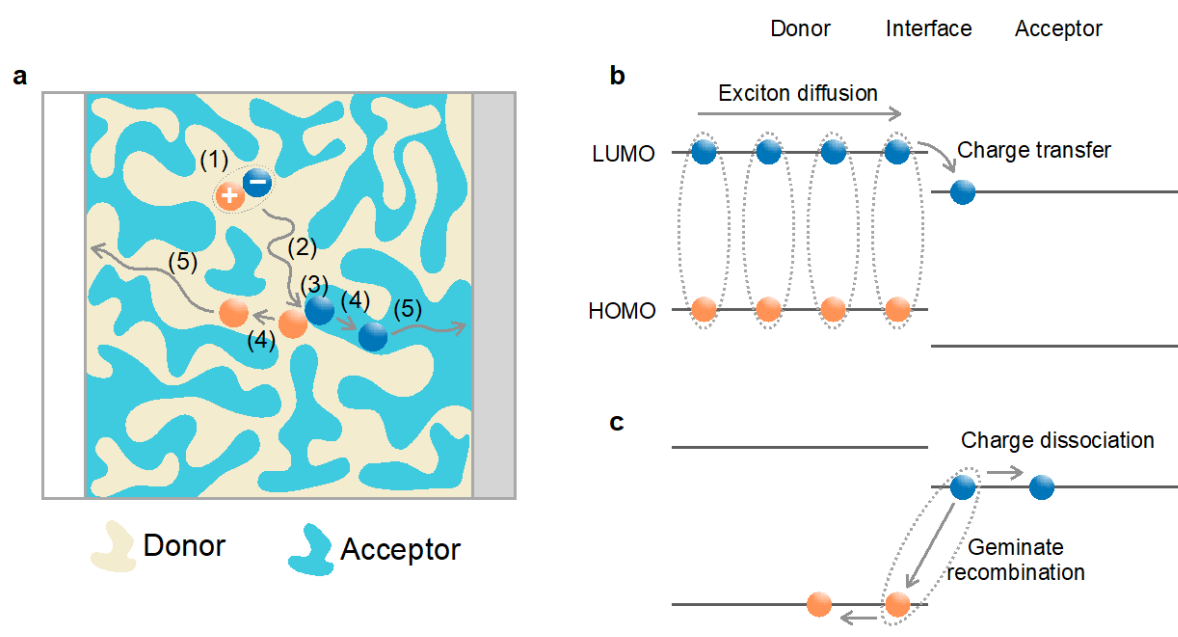


Figure 2

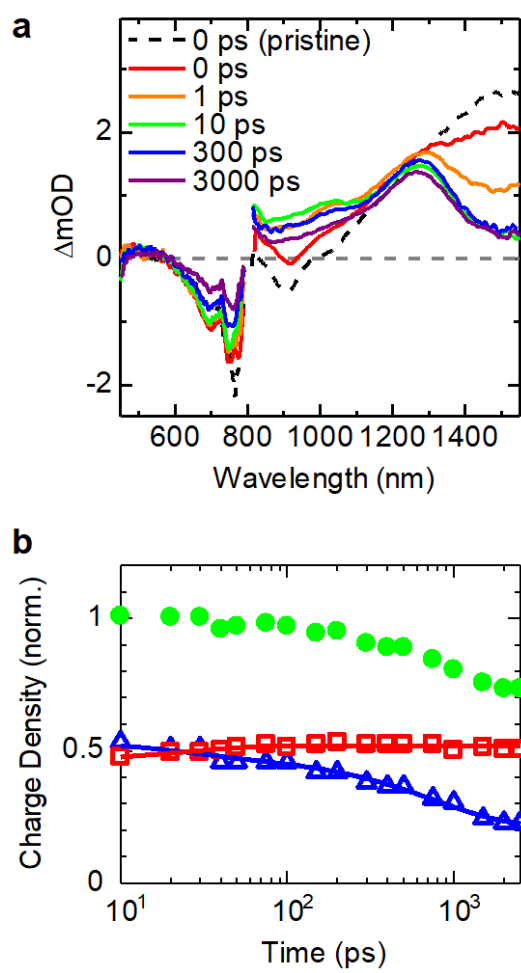


Figure 3

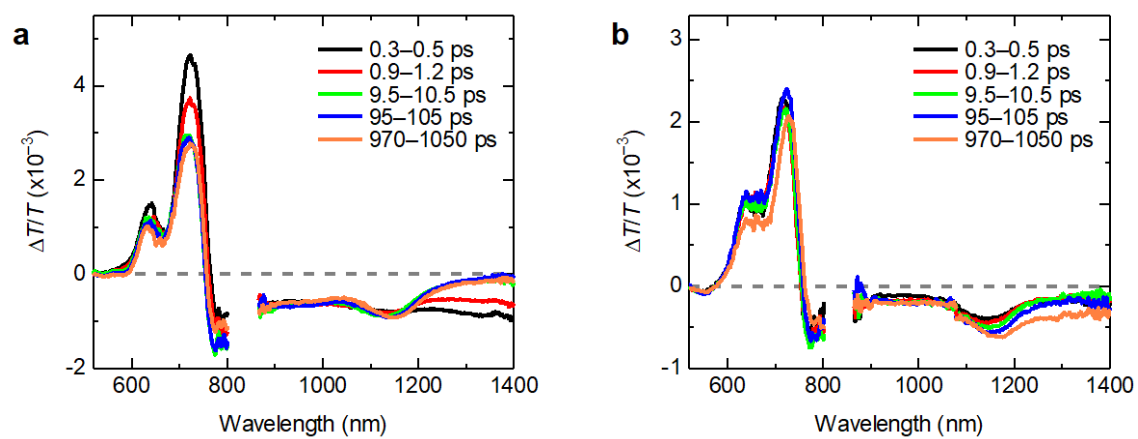


Figure 4

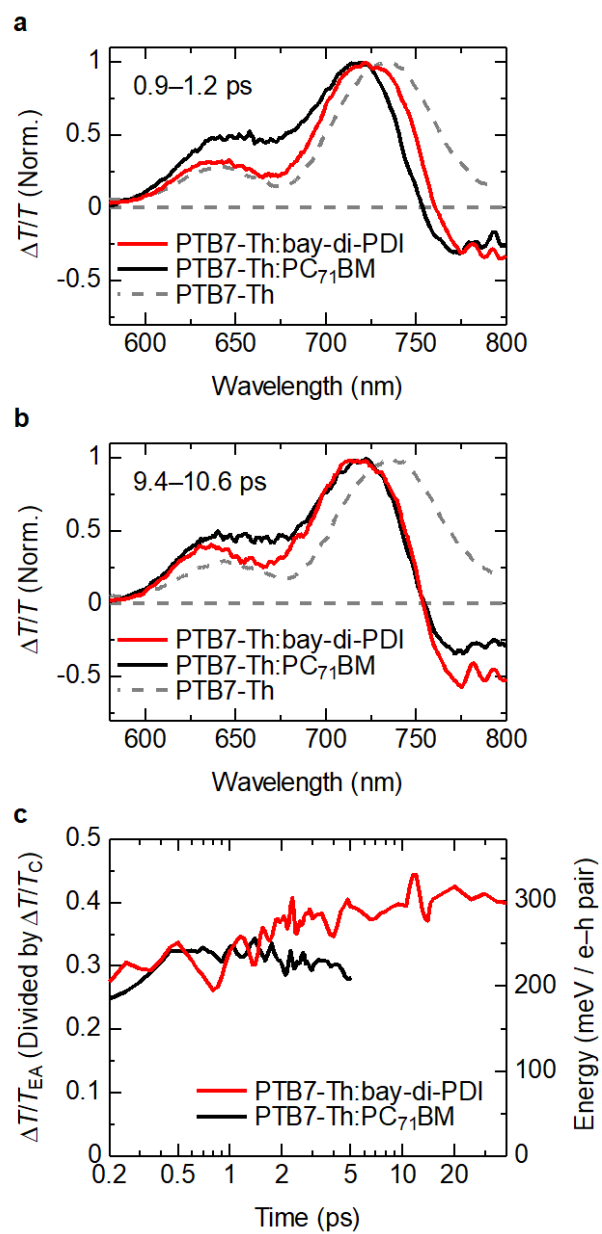


Figure 5

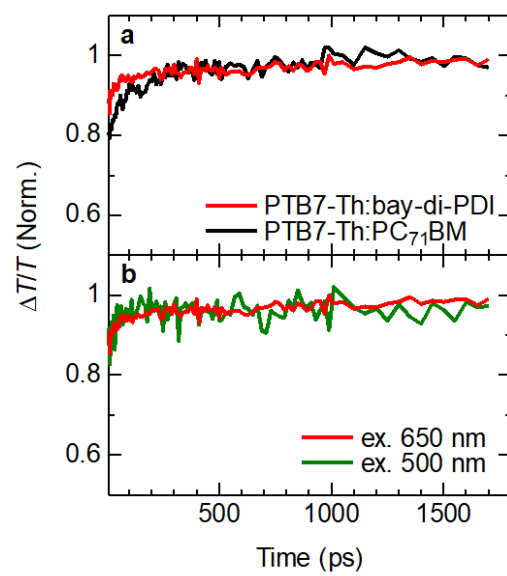


Figure 6

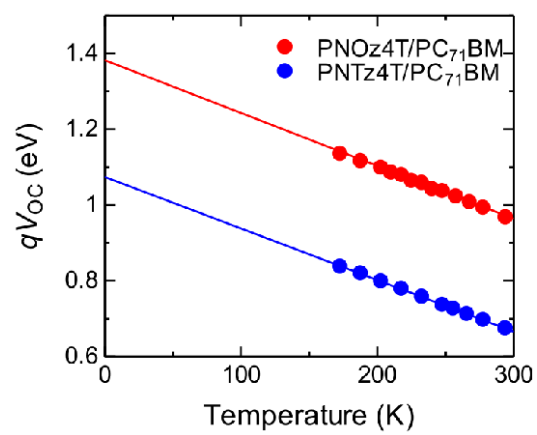


Figure 7

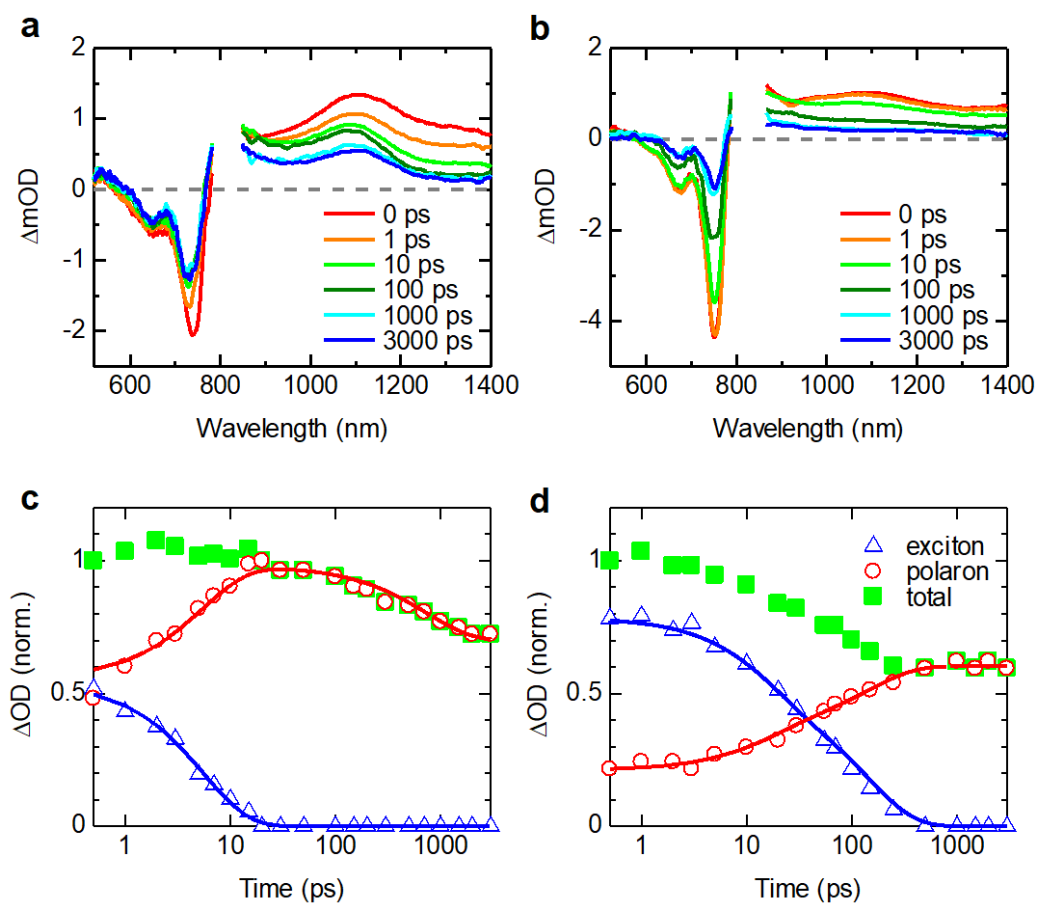


Table 1

Polymers	phase	$\eta_{\text{CD}}^{\text{cry}}$	$\eta_{\text{CD}}^{\text{dis},a}$	$\eta_{\text{CD}}^{\text{total}}$	L_{010} (nm) ^b	d (Å) ^b
RR-P3HT w anneal	Highly crystalline	1 ^[5]	(0.69) ^[5]	0.93 ^[5]	~12 ^[41]	3.8 ^[39]
RR-P3HT w/o anneal	Modest crystalline	1 ^[5]	(0.38) ^[5]	0.8 ^[5]	~5.7 ^[38]	3.8 ^[38]
PSBTBT	Small crystalline	1 ^[24]	0.51 (0.12) ^[24]	0.75 ^[24]	~4.6 ^[44]	3.5 ^[40,44]
PCPDTBT w additives	Slightly ordered	—	—	0.7 ^[37,43]	(~1.1) ^[42]	(3.8) ^[42]
PCPDTBT w/o additives	Less ordered	—	—	0.5 ^[37]	(~0.5) ^[42]	(3.9) ^[42]
RRa-P3HT	Amorphous	—	0.3 ^[5]	0.3 ^[5]	—	—

$\eta_{\text{CD}}^{\text{cry}}$, $\eta_{\text{CD}}^{\text{dis}}$, and $\eta_{\text{CD}}^{\text{total}}$ are charge dissociation efficiency in the crystalline phase, in the disordered phase, and overall, respectively.

^a The value in parenthesis is the charge dissociation efficiency via the hole transfer.

^b The value in parenthesis is obtained from PCPDTBT pristine films. No clear diffraction peaks have been reported for PCPDTBT in the blend films, suggesting that PCPDTBT forms less ordered aggregates in the blend films.

Graphical Abstract

