

Effectiveness of External Electric Field Treatment of Conjugated Polymers in Bulk-Heterojunction Solar Cells

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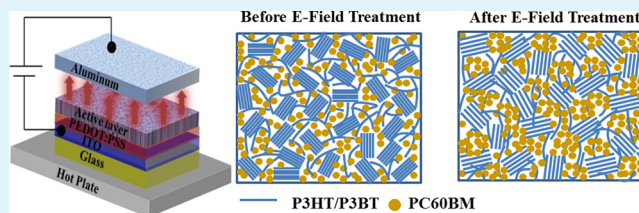
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Supporting Information

ABSTRACT: External electric field treatment (EFT) on P3HT:PCBM bulk heterojunction (BHJ) devices was recently found to be a viable approach for improving the power conversion efficiencies (PCEs) through modulating the blend nanomorphology. However, its effectiveness over the broad family of polymer–fullerene blends remains unclear. Herein, we investigate the effects of external EFT on various polymer–fullerene blends with distinct morphologies stemming from the difference in molecular structure of the polymers (i.e., semicrystalline vs amorphous) in a bid to establish a clear morphology–function–charge dynamics relationship to the photovoltaic performance. Our findings reveal that EFT promotes self-organization of the semicrystalline thiophene-based conjugated polymers (i.e., P3HT and P3BT) while it was ineffective for the amorphous polymers (i.e., PTB7 and PCPDTBT) even at the maximum applied E-field of 8 kV cm^{-1} . Transient absorption spectroscopy shows an improvement in the initial charge-carrier and polaron formation from delocalized excitons in the E-field treated semicrystalline blends compared to their untreated reference samples. Interfacial trap-assisted monomolecular and trap-free bimolecular recombination at nanosecond–microsecond time scale in the E-field treated P3BT:PC60BM devices are significantly suppressed. Importantly, our findings shed new light and provide guidelines on the effectiveness of utilizing external EFT to enhance the PCEs of a large family of conjugated polymer-based BHJ OSCs.

KEYWORDS: electric dipole moment, external electric field treatment, bulk heterojunction solar cell, morphology and transient absorption spectroscopy



INTRODUCTION

In the past decade, there have been increased interests in the field of organic solar cells (OSCs) due to their distinct advantages of easy processing, mechanical flexibility, low fabrication cost, and rapid energy payback time.^{1–5} Tuning the active layer morphology for optimal lamellar orientation and nanoscale structuring of the donor and acceptor materials has proven to be highly effective for optimizing the solar cell efficiency.^{6,7} Several approaches such as thermal annealing,^{8,9} solvent vapor annealing,¹⁰ ordered organization of blend,¹¹ and self-assembly with marginal solvents^{12,13} have been used to optimize the morphology to improve solar cell device performance. In particular, the processing of active layer with an external electric (E)-field has recently emerged as an attractive method to control the nanomorphology of the active layer to improve the photoabsorption and charge carrier

mobility.^{14,15} The basis of this approach arises from the concept of “dipole polarization” where polar molecules turn and orientate along the external applied E-field. E-field manipulation of liquid crystals orientation in liquid crystal display (LCD) is one good example. Researchers have also successfully used this approach to organize photoresists comprising block copolymer and carbon nanotubes.^{16–18} P. Goldberg Oppenheimer reported a three-orders improvement in electrical conductivity in a layer of block copolymer comprising donor and acceptor blocks with E-field treatment.¹⁹ H. L. Cheng²⁰ and A. M. Hiszpanski²¹ employed the same method to improve the in-plane charge carrier mobility by tuning the structural

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organization of organic molecules in thin-film transistor. Various research groups have also used this methodology at different stages of the OSCs processing to achieve the higher PCEs.^{9,14}

In this work, we investigate the influence of external electric field treatment (EFT) on polymer-based organic solar cells and establish its relationship with their optoelectronic properties, nanomorphology, molecular organization, and ultrafast charge dynamics. Our study seeks to provide new insights into the effects of the external electric field on OSCs fabricated using a broad family of donor:acceptor systems with different crystallization abilities and contrasting morphologies. It is important to highlight that the focus of our work is not on the absolute efficiencies, but rather on understanding the effectiveness of external EFT on the morphology–function–charge kinetics relationship for a broad family of polar polymers and on how such an understanding could help enhance their photovoltaic performance. To this end, two contrasting types of polar polymers (semicrystalline and amorphous) in the thiophene family were chosen to exemplify the diverse nanomorphology in active blend films. Poly(3-hexylthiophene) (P3HT) and poly(3-butylthiophene) (P3BT) were selected as the representatives of semicrystalline donor polymers which possess the intrinsic self-organization and crystallization property in active blend films.^{22,23} On the other hand, thieno[3,4-*b*]thiophene-*alt*-benzodithiophene (PTB7) and poly[2,6-(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]-dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) were opted as the amorphous counterparts, which are inherently unable to self-organize into any long-range order but show very fine intermixing with acceptor molecules to form small aggregate size (~ 10 nm) in the thin films.^{24,25} All four of these polymers are intrinsically polar, which can interact with external field through induced dipole polarization (Table S1).^{9,26} Density functional theory (DFT) simulations on their monomers were also performed to visualize the electrostatic potential distribution and molecular length. The BHJ solar cells based on semicrystalline polymers (i.e., P3HT:PC60BM and P3BT:PC60BM) showed improved PCEs when an optimum external electric field (E-field) was applied during the thermal annealing of the active layer before cathode deposition as shown in Figure S1. On the other hand, the performance of the active film containing amorphous donors (i.e., PTB7:PC70BM and PCPDTBT:PC60BM) remained almost invariant in the range of 2.0–8.0 kV·cm^{−1} EFT even though more effective dipole interaction could have been conjectured on account of their higher ground states dipole moments (Table S1). The origins of such phenomena were further investigated by examining the optical properties and nanoscale analysis of the active blends. The semicrystalline polymers showed better photoabsorption and charge transport as a result of the improved crystallinity ($\sim 16\%$ in P3HT:PC60BM and $\sim 35\%$ in P3BT:PC60BM) and ordering in the devices subjected to the EFT compared to their control films. However, the amorphous polymers did not show any significant optical/structural changes between EFT and control samples. Transient absorption spectroscopy measurements revealed a higher generation of excitons and polarons in E-field treated P3HT and P3BT blend samples compared to the standard samples (without EFT). The recombination dynamics at longer time scale (i.e., nanosecond to microsecond) showed reduced losses of the charge carriers through suppression of interfacial trap-assisted monomolecular (geminate) and trap-free bimolecular

(nongeminate) recombination as a result of a faster charge transfer mechanism in the E-field treated samples.

RESULTS AND DISCUSSION

Photovoltaic Characteristics. The current density–voltage (J – V) characteristics of the P3HT:PC60BM, P3BT:PC60BM, PTB7:PC70BM, and PCPDTBT:PC60BM solar cell devices (fabricated with and without EFT) measured under 100 mW cm^{−2} standard AM 1.5G illumination are shown in Figure 1 and S1 (Supporting Information). A blend of PTB7

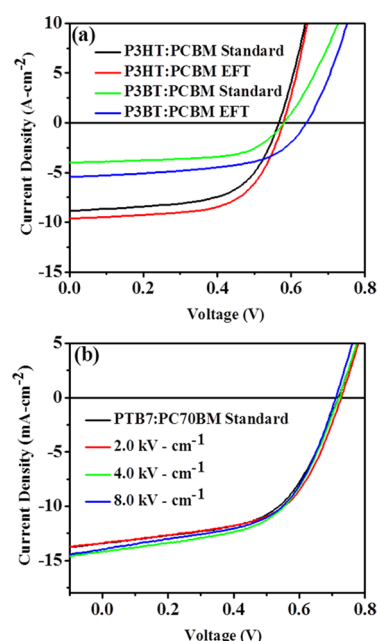


Figure 1. J – V characteristics of standard and E-field treated (a) P3HT:PC60BM, P3BT:PC60BM and (b) PTB7:PC70BM devices measured under 100 mW cm^{−2} illumination of AM1.5. The devices presented here as EFT P3HT and P3BT OSCs were treated under 4.0 kV cm^{−1}. (See Figure S2 for the details for the PCE vs E-field for PCPDTBT based solar cell devices.)

with PC70BM was chosen instead of with PC60BM because the former is considered to be one of the most efficient BHJ OSCs. The behavior of the PCPDTBT:PC60BM is very similar to that of PTB7:PC70BM; hence only the latter blend system will be discussed for amorphous polymers. Representative J – V data of the P3HT- and P3BT-based devices fabricated with their active layers treated with an optimum E-field of 4.0 kV cm^{−1} are shown in Figure 1a. Photovoltaic J – V parameters measured for the PTB7:PC70BM and PCPDTBT:PC60BM (Figure S2) in addition with the P3HT and P3BT BHJ devices fabricated with their respective active layers treated under different electric fields in addition to the pristine devices are given in Tables S2–S5 (Supporting Information). The effect of the polarity of the applied E-field was also investigated by Ma et al. on inverted solar cell devices and was found to drop in efficiency upon applying the reverse bias.²⁷ Therefore, we focus on the forward applied bias in this study to reveal the relationship between morphology–function–charge kinetics and the external EFT in a broad family of polar polymers.

Table 1 summarizes the relevant device parameters, e.g., short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factors (FF), power conversion efficiency (PCE), and series resistance (R_s) determined from the J – V characteristics of the

Table 1. Summary of the Performance of Different P3HT:PC60BM and P3BT:PC60BM Devices under Illumination

devices/parameters	PCE (%)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	R_s (Ω cm ²)
P3HT:PC60BM Standard	3.0 ± 0.2	8.8 ± 1.2	0.57 ± 0.01	0.61 ± 0.03	19.5 ± 2.4
P3HT:PC60BM EFT	3.5 ± 0.1	9.5 ± 0.8	0.58 ± 0.01	0.63 ± 0.02	17.4 ± 1.8
P3BT:PC60BM Standard	1.4 ± 0.1	4.00 ± 1.4	0.58 ± 0.01	0.61 ± 0.02	58.2 ± 3.9
P3BT:PC60BM EFT	1.8 ± 0.2	4.9 ± 1.5	0.64 ± 0.02	0.58 ± 0.01	45.9 ± 2.6

semicrystalline group of polymers with and without external electric field treatment. The BHJ devices fabricated using E-field treated blend films are termed “EFT” devices, while those prepared using active layers without any E-field treatment are termed “standard” devices. EFT solar cell devices based on P3HT:PC60BM and P3BT:PC60BM exhibit higher PCE as compared to standard devices as shown in Table 1.

In the EFT P3HT:PC60BM devices, PCE improvement was mainly contributed by J_{sc} enhancement, while for P3BT:PC60BM devices, it is a cumulative improvement from all the parameters. The lower series resistance and higher dark current (Figure S3) in both P3HT- and P3BT-based EFT devices indicate a more efficient charge transport. This could result from an improved organization of the polymers by dipole-E-field interaction, which leads to better connectivity inside the blend system.^{28,29} A significant V_{oc} improvement of 0.06 V in EFT P3BT solar cell devices is attributed to the reduced recombination sites in EFT system. In contrast to this group of polymers, PTB7:PC70BM and PCPDTBT:PC60BM based solar cells were found to be unresponsive to a range of applied external EFT (2.0–8.0 kV cm⁻¹) during the active layer drying process (Figure 1b and Figure S2). PTB7:PC70BM solar cell devices displayed 5.4 ± 0.3% PCE (J_{sc} = 13.3 ± 2.8 mA cm⁻², V_{oc} = 0.72 ± 0.02 V, FF = 0.56 ± 0.03) while PCPDTBT:PC60BM displayed 2.4 ± 0.2% PCE (J_{sc} = 9.6 ± 1.8 mA cm⁻², V_{oc} = 0.62 ± 0.03 V, FF = 0.41 ± 0.02) irrespective of the applied electric field (Tables S4 and S5, Supporting Information). These results are contrary to the expectations that polar molecule reordering should have taken place due to the dipole polarization under the influence of external E-field. This is a rather surprising observation since the amorphous polymers, such as PTB7, possessed higher dipole moments than P3HT and P3BT (Table S1).

To investigate the origin of such anomalous behavior, optical and structural characterizations were further performed on these blend films.

Linear Absorption. The linear absorption spectra of standard and EFT P3HT:PC60BM, P3BT:PC60BM, and PTB7:PC70BM blend films coated on ITO/glass substrates are shown in Figure 2 (refer to Figure S4 in Supporting Information for PCPDTBT:PC60BM). In P3HT:PC60BM, as shown in Figure 2a, the maximum absorption peak (λ_{max}) is observed at 513 nm and the other two vibronic “shoulders” are found to be at 550 and 600 nm in both standard films. The peak at the lower wavelength (λ = 513 nm) represents the π – π^* intrachain transition, while the vibronic features at longer wavelengths are correlated to the π – π^* stacking strength.

The spectral profile of P3BT:PC60BM blend films resemble that of P3HT:PC60BM due to the similar molecular structures of donor component in the blend films but the “vibronic shoulders” are more prominent in the latter blend. In addition, the absorption intensity in P3BT:PC60BM also maximizes at 488 nm, which is blue-shifted relative to the P3HT:PC60BM (λ_{max} = 500 nm)—indicating that in the blend system, P3BT molecules have weaker intermolecular interactions.³⁰ Thus, in

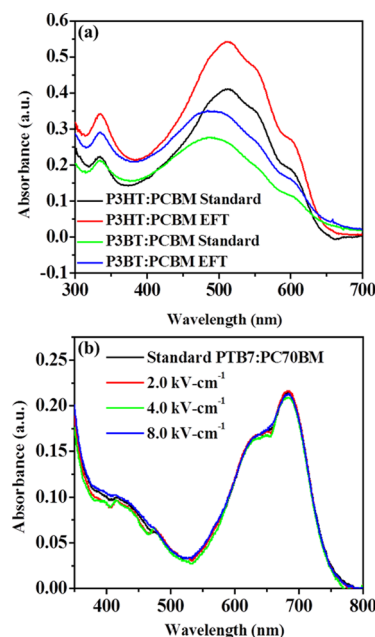


Figure 2. UV–vis absorbance in (a) standard and E-field treated (at 4.0 kV cm⁻¹) P3HT:PC60BM, P3BT:PC60BM and (b) PTB7:PC70BM blend films. The absorption features below 400 nm are due to the presence of PCBM in the blend (Figure S4 for PCPDTBT:PC60BM blend films).

the standard devices, the more organized P3HT molecules in the blend films result in higher absorption and improved charge transport that would eventually account for the better performance of the P3HT:PC60BM devices over the P3BT:PC60BM devices. The EFT on the polymer blends improves the photoabsorption compared to their respective standard blend films (Figure 2a).

A stronger absorption in the EFT blend films indicates further improvement of the molecular organization which enhances exciton and polaron generation. This is also consistent with the improved short-circuit current density in the EFT devices (Figure 1a). Thus, a combination of increased absorption and better charge transport (as the result of improved molecular organization) accounts for the performance improvement in these EFT devices. On the contrary, EFT blend films of PTB7:PC70BM (Figure 2b) and PCPDTBT:PC60BM display similar absorption spectra and device performances compared with those of their standard blend films (Figures S1 and S3, Supporting Information).

Grazing-Incidence X-ray Diffraction and Nanomorphology. Figure 3 shows the X-ray diffraction (XRD) patterns of both semicrystalline blend films coated on ITO/glass substrates. P3HT:PC60BM and P3BT:PC60BM show a clear single peak at 2θ ~5.48° (100) and ~6.78° (100), respectively. The diffraction patterns in P3HT and P3BT derive from the lamellar structure of these polymers which corresponds to a parallel edge-on π – π stacking among the thiophene chains with

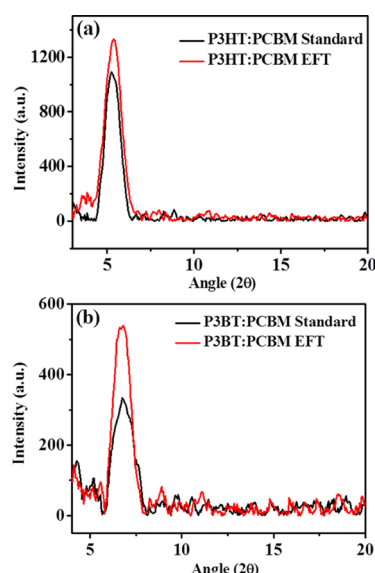


Figure 3. XRD patterns of standard and EFT (a) P3HT:PC60BM and (b) P3BT:PC60BM blend films. The samples were prepared on ITO coated glass substrates. (Figure S6 for XRD spectrum of PTB7:PC70BM and PCPDTBT:PC60BM).

respect to the substrate. The (100) peak intensity in the EFT films is stronger compared to that of the corresponding standard films, suggesting that the crystallinity of the both active layers is enhanced under the influence of E-field treatment. Table 2 shows the parameters (d -spacing, relative

Table 2. Summary of the XRD Parameters of Different P3HT:PC60BM and P3BT:PC60BM Blend Films

blend film/ parameters	FWHM (°)	crystallinity (a.u.)	(100) crystalline domain size D (nm)	$d(100)$ (nm)
P3HT:PC60BM Standard	1.13	1203	7.2	1.63
P3HT:PC60BM EFT	1.05	1393	7.8	1.78
P3BT:PC60BM Standard	1.35	448	6.1	1.29
P3BT:PC60BM EFT	1.14	605	7.2	1.31

crystallinity, and crystallite size) obtained by fitting the (100) reflections of both P3HT:PC60BM and P3BT:PC60BM blends. The processing of the blend films with E-field results in an increase in the $d(100)$ -spacing in the EFT blends. This increased lamellar spacing within the polymer crystallite is due to a more extended vertical ordering of the polymer chains by EFT, which leads to better inter- and intrachain transport.³¹ The relative crystallinity of the blends can be calculated by taking the dot product of the diffraction peak intensity and full-width half-maximum (FWHM). With EFT, the crystallinity improvement in P3HT:PC60BM and P3BT:PC60BM blend films is 15.8% and 35%, respectively. By employing the Debye–Scherrer’s equation ($D = k\lambda/\beta \cos \theta$, where $k = 0.9$ and β corresponds to the FWHM of the peak (in radians)), the mean polymer crystalline size (D) in the blends was also calculated and shown in Table 2. The increase in D in EFT blend films (from 7.2 to 7.8 nm in P3HT:PC60BM and 6.1 to 7.2 in P3BT:PC60BM) confirms the enhanced ordering of the blend films. The increased crystallite size and interlamellar spacing are

believed to be the result of improved ordering. Therefore, the polymer chains are better organized and result in more ordered structures with simultaneous external EFT during the thermal annealing of the systems. For small molecules used as replacements of semicrystalline polymers, thermal annealing and solvent additive approaches have also been used to enhance the crystallinity and organization of the active blend film.^{32–34}

XRD measurements were also performed on standard and EFT (4.0 kV cm^{−1}) PTB7 and PCPDTBT films as shown in Figure S6. It is important to note that fullerene is used in much higher amounts compared to the donor polymer to fabricate the devices (i.e., PTB7:PC70BM – 1:1.5 and PCPDTBT:PC60BM – 1:3). This is in contrast to the blend D:A ratio of 1:0.8 for both P3HT:PC60BM and P3BT:PC60BM. Therefore, to disregard the effect of fullerene organization (due to the higher PCBM loading in the former films), which could mask the effect of the EFT on the orientation of the amorphous polymers, we measured the XRD of the donor polymers only. No clear diffraction peaks corresponding to any crystallographic plane were observed from either of the amorphous polymer films. The invariance in the XRD profiles of the untreated and E-field treated films shows that E-field interaction with polymer dipoles is ineffective in promoting any structural reorientation in these polymers. This result also highlights an essential requirement for the donor polymers to undergo inherent structural self-organization for them to be effectively aligned under electric field.

The surface morphologies of P3HT:PC60BM and P3BT:PC60BM (standard and EFT) blend films were assessed using AFM. Figure S7 shows the $5 \times 5 \mu\text{m}^2$ topographical atomic force microscopy (AFM) images of the films in this study and their corresponding 3D projections. The surface topology of EFT films was found to be rougher than standard active layers in both polymer blends. The root-mean-square (RMS) surface roughness of the standard P3HT:PC60BM blend is 0.87 ± 0.02 nm (0.42 ± 0.03 nm for P3BT:PC60BM) while the EFT film shows 1.08 ± 0.04 nm (0.52 ± 0.04 nm for P3BT:PC60BM). The rougher surface is most likely a signature of self-organization of the polymer molecules which in turn enhances the formation of ordered structures in the blend film.³⁵ The E-field treatment might have induced vertical phase segregation, as shown by S. Y. Ma, resulting in PC60BM-rich top surface with higher nonuniformity.²⁷ No significant difference was observed in both standard and EFT amorphous polymer blends films (results not presented here). Thus, we conclude that the polymer chains of semicrystalline donors (P3HT and P3BT) are predominantly self-organized with lamellar stacking perpendicular to the substrate. As the E-field was applied concurrently during the thermal annealing, the lamellar stacking of donor polymer was promoted in the field direction with elongated lamellar spacing. We attribute this to the interaction of the electric dipole moment of the thiophene ring with E-field which enhances the vertical ordering of the donor molecule in the direction of the applied field.⁹ However, the E-field interaction with the molecular dipole moments was ineffective in the amorphous polymer blend systems due to the constraint imposed by the inability of the polymer molecules to form ordered phase. Hence, the respective EFT blends did not undergo any noticeable change in nanomorphologies, leading to indistinguishable optical and electrical properties, and expectedly similar solar cell device performance.

Investigation of Molecular Electrostatic Potential Distribution, Dipole Moment, and Molecular Orientation

tions. To uncover the origin for the different interaction behavior of these polymers with external EFT, the electrostatic charge distribution and orientation of the electric dipole at the molecular level for both groups of polymers were also visualized (Figure 4). The details of the calculations are given in Supporting Information.

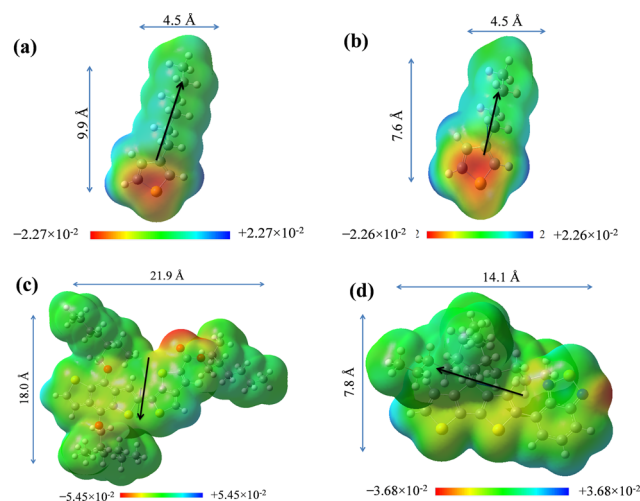


Figure 4. Electrostatic charge distribution and dipole direction (by black arrow) in the monomer of (a) P3HT, (b) P3BT, (c) PTB7, and (d) PCPDTBT.

Figure 4 represents the electrostatic potential (ESP) distribution in the monomer of these conjugated polymers. Red and blue regions in the ESP diagram of these monomers represent the negative and positive potentials, respectively. The negative charge mainly exists on the sulfur atom in the heterocycle of P3HT, P3BT and PTB7, while it is localized on the nitrogen atom (with lone pairs) in PCPDTBT. The electrons tend to be distributed around the sulfur atom more than hydrogen, carbon, and nitrogen atoms causing the sulfur to be negatively charged. This imbalance of the electronic charge distribution gives a polarity to the polymers. The black arrows in Figure 4 represent the direction of the ground-state dipole moments in each monomer, which are calculated to be 0.99, 0.97, 4.02 and 1.53 D for P3HT, P3BT, PTB7, and PCPDTBT, respectively. The monomer lengths were also examined using this model and found to be $L_{\text{P3HT}} = 0.99$ nm, $L_{\text{P3BT}} = 0.76$ nm, $L_{\text{PTB7}} = 2.19$ nm, and $L_{\text{PCPDTBT}} = 1.41$ nm. Figure 4a,b shows that the direction of the intrinsic dipole moment in P3HT and P3BT is along the polymer chain and these monomers are also smaller in size than the other polymers. When an external E-field is applied during thermal annealing of the films, thiophene molecules get polarized and the molecular dipoles in the amorphous region align themselves with E-field. This increases the vertical ordering in the system, which is beneficial for efficient charge transport in the device. On the other hand, our results suggest that the orientation and packing of the larger and more branched PTB7 and PCPDTBT monomers under EFT (at the largest applied E-field of 8 kV cm^{-1}) is still inhibited despite their higher dipole moment than the semicrystalline conjugated polymers. Therefore, the organization within the blends of amorphous polymers remains unaffected due to the steric constraints imposed by the inability of the polar molecules to orientate.

In summary, thermally annealed semicrystalline blend systems, P3HT and P3BT, are organized with lamellar stacking perpendicular to the substrate accompanied by surrounding amorphous phase.³⁶ When an external E-field is applied during the thermal annealing of these blend films, the lamellar stacking of polymers is further promoted in the field direction. The growth of the lamellar stacking in the P3HT and P3BT blend systems is confirmed by an increase of the (100) peak intensity in the XRD measurements. This results in the polarization of the polar polymer molecules in the system due to dipole-E-field interaction, which enhances the ordering of the blend in E-field direction. Higher crystallinity improves the photoabsorption and the ordering of the originally amorphous polymer phase also provides a more efficient charge transport, thus improving the PCE. On the other hand, PTB7 and PCPDTBT exhibit neither improvement in solar cell performance nor change in structural properties. Although PTB7 and PCPDTBT monomers have higher dipole moments than their P3HT and P3BT counterparts, the ineffectiveness of the EFT in the former is likely due to their larger and more complex monomers rendering them less responsive for reorientation and packing/stacking under external E-field for lamellar formation. In addition to this, molecular weight of the conjugated polymer can also be another parameter that affects the efficiency under the influence of external E-field treatment. Nevertheless, the contrasting response of P3HT and PCPDTBT (though both have similar molecular weights, i.e., $M_{\text{P3HT}} = 47 \text{ kg mol}^{-1}$, $M_{\text{PCPDTBT}} = 45 \text{ kg mol}^{-1}$; see Experimental Section) under the E-field treatment shows that the molecular structure of the polymer is more important for the effective interaction. Thus, the intrinsic dipole moment of a molecule is not the sole criteria to assess its suitability for EFT, but the intrinsic lamellar structure and molecular organization are also, and perhaps even more, essential. Hence, we infer that the EFT of the active layer in OSCs to improve the performance is best used only for molecules that have (i) electric dipole moment, (ii) intrinsic lamellar packing, and (iii) smaller linear monomer units.

On the other hand, the edge-on lamellar microstructures of P3HT and P3BT are more appropriate for lateral charge transport, e.g., in organic thin-film transistors (OTFTs). Hence, it is also desirable to fine-tune the orientation of the dipole moment within the molecules, which can be tailored via organic synthesis. Through proper selection of the conjugated backbones and side groups, it will be possible to prepare molecules that allow highly preferential face-on stacking under E-field, which is the ideal structure for high-performance OSC devices, as opposed to the edge-on orientation. Lastly, the effects of external electric field on the exciton/polaron formation and recombination mechanisms in P3HT:PC60BM and P3BT:PC60BM blend films are further investigated by time-resolved spectroscopy and correlated with their physical property characterizations and solar cell device performances.

Generation and Recombination Mechanisms in Femtosecond to Nanosecond (fs–ns) Temporal Regime.

To understand the influence of the EFT morphology on the generation and recombination mechanisms of the photoexcited species, transient absorption measurements were performed on standard and EFT active layers of P3HT:PC60BM and P3BT:PC60BM. The representative differential transmission (DT) spectra spanning from 520 to 1500 nm at varying delay times following 500 nm photoexcitation for all these active layers are shown in Figure S8 of Supporting Information and discussed in greater detail. Since E-field treatment is not

effective for the amorphous systems (as seen from the earlier structural and optoelectronic measurements), we have limited the charge dynamics study to semicrystalline systems only. Exciton peaks are found to be red-shifted ($\Delta\lambda_{\text{P3HT}} = 22$ nm, $\Delta\lambda_{\text{P3BT}} = 90$ nm) in the EFT films as compared to the standard films in both D/A systems, which suggests that singlet excitons in these EFT blend systems are not localized on single chains but delocalized over the crystalline phase.³⁷ Such delocalization of the excitons also confirms the better ordering and enhanced crystallinity in the E-field treated systems.³⁸ The longer peak shift of P3BT as compared to P3HT system indicates that excitons are more delocalized in the former EFT blend system.

To gain more insights into the mechanism of the exciton and polaron formation in the different blend films, singular value decomposition (SVD) and global fitting analysis for the transient absorption spectra were also performed. Figure 5 shows the separation of the features in the different blend films over the time range from 100 fs to 5 ns in NIR spectral range.

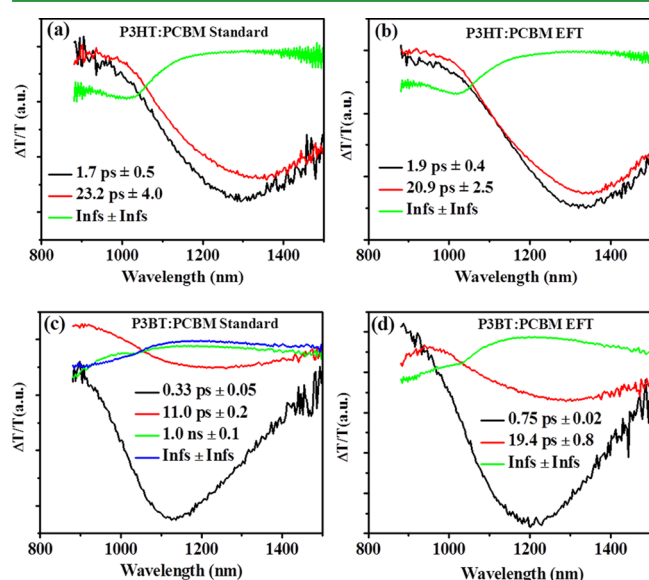


Figure 5. Pre-exponential coefficient spectrum obtained by SVD and global fitting analysis of (a) P3HT:PC60BM standard, (b) P3HT:PC60BM EFT, (c) P3BT:PC60BM standard, and (d) P3BT:PC60BM EFT blend films at $12 \mu\text{J cm}^{-2}$ pump fluence.

In P3HT:PC60BM, the first two most prominent decay time constants originate mainly from singlet excitons (dominant around 1300 nm); the first decay constant is due to the excitons present in the amorphous or intermixed phase of P3HT:PC60BM, while the second is assigned to the delayed exciton dissociation due to the migration in the larger P3HT crystallites. The prompt charge generation (<2 ps) indicates that no exciton diffusion is needed to reach PC60BM molecules to dissociate into free carriers. This is probably because PC60BM molecules are likely to be dispersed homogeneously in the amorphous region. The similar values of the decay time constants in both standard and EFT P3HT:PC60BM blend films indicate that the external E-field treatment does not make any significant difference to the exciton evolution in this time frame. On the other hand, the EFT P3BT:PC60BM blend film shows three different decay channels in contrast to the four decay channels in the standard blend film (Figure 5c,d). The first two decay constants in this system can also be assigned to the exciton dissociation similar to P3HT. The lengthening of

the first two decay processes in the EFT P3BT:PC60BM (from 0.33 to 0.75 ps and 11.0 to 19.4 ps) corresponds to the transformation of the intermixed phase of donor:acceptor to the crystalline phase and the expansion of the polymer crystallites (Figure 5). The additional decay channel ($1.0 \text{ ns} \pm 0.1$) in the standard P3BT blend film can be attributed to the strongly bound CT states which could not dissociate into free charge carriers. However, these states seem to be absent in the P3HT:PC60BM and EFT P3BT:PC60BM blend films. The last (longest) decay constant (i.e., Infs) in all four blend films is ascribed to the polarons and long-lived CT states, which decay outside this measurement time frame. The loss channel through strongly bound CT states in the P3BT blend system is thus suppressed by a faster charge transfer between the P3BT and PC60BM with the vertically organized morphology in the EFT samples. On comparing the decay dynamics in fs–ns time scale of all four blend films, the external E-field does not influence the dynamics significantly in P3HT:PC60BM, while exciton dissociation is delayed and strongly bound CT states are suppressed in the EFT P3BT:PC60BM. This occurs due to the improved crystallinity of the blend and self-organized P3BT lamellae in EFT blend system which assists a faster charge transfer and charge transport to the electrodes in the device. Thus, the higher charge transfer efficiency clearly demonstrates the effect of self-organization induced ordering in E-field treated blend films.

Modeling the Charge Carrier Recombination Dynamics. To investigate the slow decay transient of the remaining polarons band (at around 1000 nm) in these blend systems beyond 1 ns (Figure S8), we measured the decay dynamics in the nanosecond to microsecond (ns– μs) time scale when polarons and CT states population decay due to the recombination processes. The decay dynamics of these photoexcited species in standard and EFT blend films were investigated in region between 950 to 1050 nm as a function of the excitation pump fluence (from 35 to $140 \mu\text{J cm}^{-2}$). P3HT and P3BT are from the same thiophene family and show a resemblance of the steady state and transient absorption spectra. We assume that these dynamics in P3BT also arise from the same photoexcited species. Since the excitons are dissociated within the first nanosecond (Figure 5), the dynamics measured in this time frame therefore represent the bound CT states and free (delocalized or spatially separated) polarons as previously reported by I. A. Howard in the P3HT:PC60BM blend system.³⁹

The linear relationship between the rise of the DT signal and absorbed photon density in these blend films shows that the CT states and free polarons possess similar cross sections in this wavelength range (Figure S9, Supporting Information). Generally, CT states decay by monomolecular (geminate) recombination because they are generated from the same exciton while other polaron population decays by bimolecular mechanism.

Figure 6a,b shows that these decay dynamics are pump fluence dependent in P3HT:PC60BM blend films from first nanosecond onward, while Figure 6c displays the fluence independent dynamics within the first 8 ns in standard P3BT:PC60BM blend film. The fluence dependent dynamics in P3HT:PC60BM shows that these dynamics are dominated by free charge carriers, arising from the ultrafast dissociation of bound charges. On the other hand, the fluence independent decay in the standard P3BT:PC60BM shows dominance of the photoexcited species by strongly bound CT states which

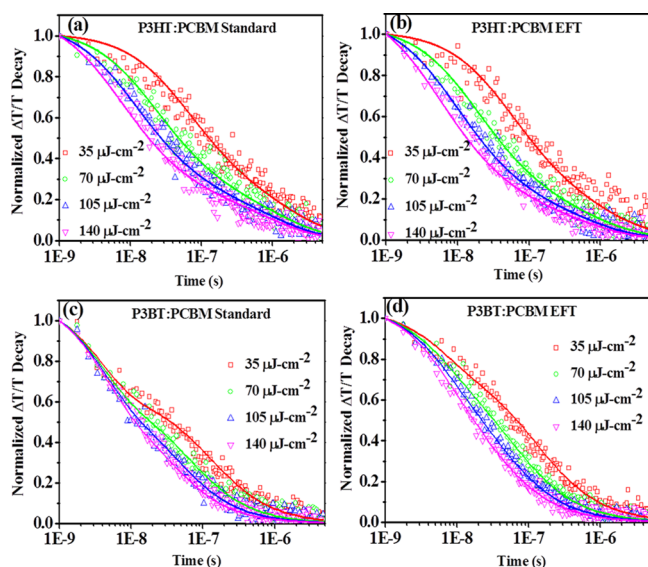


Figure 6. Global fitting of pump fluence dependent DT signal between 950 and 1000 nm in (a) P3HT:PC60BM standard, (b) P3HT:PC60BM EFT, (c) P3BT:PC60BM standard, and (d) P3BT:PC60BM EFT blend films.

survive for approximately 8 ns before dissociating or recombining to the ground state. This indicates that CT states act as interfacial traps for the charge carrier recombination. Such recombination is Shockley-Read-Hall (SRH)-type trap-assisted recombination, which is usually a monomolecular process. On the other hand, the dynamics in the EFT P3BT:PC60BM blend film exhibit shorter fluence independent dynamics (<2 ns), indicating that these CT states dissociate earlier (within 2 ns). This suggests that the Coulombic binding force within the CT states is weakened and interfacial bound charges are able to dissociate easily (Figure 6d). The change in Coulomb binding energy is a consequence of the improved crystallinity and organization of the blend components in the system.³⁷ C. Deibel had also observed a fall in Coulombic attraction and increase in dissociation efficiency in P3HT after the increase of crystallization in P3HT.⁴⁰ After 8 ns, the loss of free charges carriers in the polaron band of both systems are strongly intensity dependent and carriers recombine via Langevin type trap-free bimolecular (nongeminate) recombination.

For quantitative evaluation and to analyze the branching ratios of monomolecular versus bimolecular recombination, these normalized decay dynamics were fitted with a model developed previously.⁴¹ In our model, the recombination process comprises both monomolecular and bimolecular processes. As an approximation, a fraction (f) of the initially generated charges undergo bimolecular recombination while the rest ($1 - f$) undergo monomolecular recombination occurring in two independent processes.⁴² The expressions

describing the different recombination mechanism are derived as follows:

$$\frac{dN_{\text{mon}}}{dt} = -\gamma_1 N_{\text{mon}}^\alpha N_{\text{mon}}^1 \quad (1)$$

$$\frac{dN_{\text{bim}}}{dt} = -\gamma_2 N_{\text{bim}}^\alpha N_{\text{bim}}^2 \quad (2)$$

$$\frac{N}{N_0} = [(1-f)^{-\alpha} + \alpha\gamma_1 N_0^\alpha t]^{-1/\alpha} + [(1-f)^{-(\alpha+1)} + (\alpha+1)\gamma_2 N_0^{\alpha+1} t]^{-1/(\alpha+1)} \quad (3)$$

where N_{mon} and N_{bim} represent the population of charges recombining by monomolecular and bimolecular processes, respectively. N_0 stands for the total charge carrier population after photoexcitation. α is the population density dependent exponent while γ_1 and γ_2 are the recombination prefactors.

Figure 6 shows the global fitting of this model to the normalized decay dynamics of the different blend films as a function of pump fluence. The obtained values from the fitting of the model are given in Table 3. In the standard P3HT:PC60BM blend film, 83.96% (f) of the photoexcited species convert into free polarons, while the rest form strongly bound CT states which recombine geminately at the rate of $\gamma_1 = (1.1 \pm 0.1) \times 10^6 \text{ ns}^{-1}$. While in the EFT P3HT:PC60BM blend film, more photoexcited species ($89.07 \pm 1.0\%$) convert into the free polarons though these species decay at the similar rates. This shows that the improvement of PCE in EFT P3HT:PC60BM devices mainly result from the higher photoabsorption in the system while the recombination mechanism is not significantly affected by the improved ordering. On the other hand, standard P3BT:PC60BM blend film shows only $63.81 \pm 0.95\%$ of the excitons are available to convert into free charges as compared to $76.55 \pm 0.18\%$ in the EFT blend. In addition, the decay rate of these strongly bound states is also reduced drastically (from $\gamma_1 = (1.8 \pm 1.2) \times 10^8 \text{ s}^{-1}$ to $\gamma_1 = (4.0 \pm 2.7) \times 10^6 \text{ s}^{-1}$) in EFT blend films. The bimolecular recombination losses have also been reduced by approximately 1 order of magnitude (from $\gamma_2 = (8.2 \pm 2.3) \times 10^{-11}$ to $(2.3 \pm 1.1) \times 10^{-12}$), which is consistent with the higher charge carrier mobility and hence the efficient charge transport. The lower value of γ_1 in the EFT samples indicates the delocalization of the bound charge carriers and the suppression of the first-order interfacial trap-assisted recombination (monomolecular). From the observations of strong delocalization of the excitons in EFT P3BT:PC60BM blend film (Figure S8d), more delocalized polarons are likely to form, and are hence more efficiently dissociated into free carriers than in the standard P3BT:PC60BM.⁴³ The simulation of the hopping transport mechanism of bound charges performed by Deibel revealed that delocalization of the hole polarons along the polymer chains reduces the Coulombic attraction and enhances separation efficiency.⁴⁰ The effective charge separa-

Table 3. Summary of the Fitting Parameters Extracted from the ns-TAS Data

blend films/parameters	f (%)	$\alpha+1$	γ_1 (ns^{-1})	γ_2 (s^{-1})
P3HT:PC60BM Standard	83.96 ± 0.88	1.47 ± 0.02	$(1.1 \pm 0.1) \times 10^6$	$(1.8 \pm 0.9) \times 10^{-17}$
P3HT:PC60BM EFT	89.76 ± 0.93	1.49 ± 0.03	$(1.8 \pm 0.3) \times 10^6$	$(1.8 \pm 0.2) \times 10^{-17}$
P3BT:PC60BM Standard	63.81 ± 0.95	1.01 ± 0.02	$(1.8 \pm 1.2) \times 10^8$	$(8.2 \pm 2.3) \times 10^{-11}$
P3BT:PC60BM EFT	76.55 ± 0.18	1.09 ± 0.01	$(4.0 \pm 2.7) \times 10^6$	$(2.3 \pm 1.1) \times 10^{-12}$

tion in the charge transfer state would be further enhanced by such charge delocalization in more crystalline phases. Therefore, we propose that longer effective charge separation distance due to hole delocalization in crystalline phases in EFT P3BT:PC60BM would promote dissociation into free charge carriers while ordering of the amorphous phases (donor or intermixed) would promote efficient interconnecting pathways.

Though the crystallization of the donor has a crucial role in self-organization, PC60BM aggregation should not be ignored because crystallization of donor polymers could promote formation of PC60BM clusters which has been reported by several groups.^{44,45} As discussed above, electron delocalization in PC60BM aggregates would also prolong the effective electron–hole separation, hence promoting more effective charge dissociation. We therefore speculate that both hole and electron delocalizations could occur by the E-field treatment and therefore have a positive impact on charge dissociation. Thus, the crystallinity improvement of semicrystalline donors under E-field treatment may have two advantages for free charge generation: hole delocalization over the donor crystalline phase, and electron delocalization over PC60BM clusters stimulated by phase segregation. Thus, the external EFT suppresses the monomolecular recombination and bimolecular recombination losses in P3BT:PC60BM while the higher generation of the excitons and polarons population in EFT P3HT:PC60BM are the reasons for the improved performance of these solar cell devices.

CONCLUSIONS

In retrospect, the performance of solar cell devices based on semicrystalline conjugated polymers, i.e., P3HT:PC60BM and P3BT:PC60BM, could be improved with thermal annealing under simultaneous external electric field (E-field) treatment. The structural characterizations reveal an improved crystallinity and ordering by self-organization in the E-field treated blend films, which results in higher photoabsorption and more efficient charge transport. On the contrary, the performance of solar cell devices based on amorphous conjugated polymers, i.e., PTB7:PC70BM and PCPDTBT:PC60BM, is found to be unresponsive to the E-field treatment. The DFT calculations of the monomers indicate the higher dipole moment and larger size of PTB7 and PCPDTBT as compared to the semicrystalline polymers. The inherent capability of forming lamellar structure, smaller molecular size, and molecular dipole moment are essential requirements in conjugated polymers for an effective E-field induced molecular ordering. Transient absorption spectroscopy reveals higher photogeneration in both P3HT:PC60BM and P3BT:PC60BM EFT blend films with faster charge transfer mechanism as confirmed by global fitting analysis. The reduced interfacial trap-assisted monomolecular and trap-free bimolecular recombinations in the E-field treated P3BT:PC60BM blend also contribute to the higher short circuit density in these solar cell devices. Hence, our findings reveal that E-field treatment of semicrystalline polymers blends promotes self-organization that improves the ordering of the blend, resulting in reduced recombination losses and therefore enhanced photovoltaic performance.

EXPERIMENTAL DETAILS

Device Fabrication and Film Preparation for Electrical and Optical Characterizations. To prepare the different blend solutions, donors and acceptors were mixed in 1,2-dichlorobenzene in host solvent and stirred overnight. The D:A ratio and concentrations of

these blend solutions used were based on optimum performance of the devices, as reported in the literature, which were as follows: P3HT ($M_w = 47 \text{ kg mol}^{-1}$, Rieke Metals, Inc.):PC60BM (1:0.8, 18 mg/mL), P3BT ($M_w = 55 \text{ kg mol}^{-1}$, Rieke Metals, Inc.):PC60BM (1:0.8, 18 mg/mL), PTB7 ($M_w = 109 \text{ kg mol}^{-1}$, 1-material):PC70BM (1:1.5, 25 mg/mL), and PCPDTBT ($M_w = 45 \text{ kg mol}^{-1}$, 1-material):PC60BM (1:3, 28 mg/mL).⁴⁶ To fabricate the organic solar cell (OSC) devices, a thin film of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (CLEVIOS P VP Al 4083, HC Starck) layer of $\sim 30 \text{ nm}$ was deposited by spin-coating on cleaned ITO coated glass substrates (at 3000 rpm for 60 s), followed by annealing at 100°C for 15 min. Later these substrates were transferred to a N_2 -filled glovebox for further processing. Different blend solutions were then spin-coated on top of PEDOT:PSS layer. Solvent drying of these active layers was performed in two different sets for 30 min each. On the first set of the films, an external electric field was applied across the active layers by means of ITO and aluminum plate as the counter electrodes, i.e., the “electric field treated” film (EFT). Different magnitudes of constant electric field were applied during the thermal annealing (at 140°C) and natural drying (at room temperature) of semicrystalline (2.0, 4.0, and 6.0 kV cm^{-1}) and amorphous (2.0, 4.0, and 8.0 kV cm^{-1}) blend films, respectively. A schematic of the experimental setup used for E-field annealing is shown in Figure S1. Drying of the second set of devices of P3HT:PC60BM and P3BT:PC60BM was carried out at 140°C while PTB7:PC70BM and PCPDTBT:PC60BM blend films were dried naturally in a glovebox without any other treatment as standard or control films. The active layer drying conditions for different blend systems were based on previous literature reports to avoid any adverse effects such as lower crystallinity or polymer aggregation due to over-phase-separation. Finally, cathode contact of 100-nm-thick aluminum was deposited on the active layer through a shadow mask (with active area of 0.07 cm^2) in a vacuum of 10^{-6} Torr. For all optical measurements, different blend films were directly prepared on cleaned indium–tin oxide (ITO) coated glass substrates. Details of the setups used for the device and blend films characterizations are given in Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b08012.

Experimental setup details, dark I – V characteristics, absorption spectra, XRD data, AFM and PL spectra for different blend films (PDF)

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Notes

The authors declare no competing financial interest.

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