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Performance Limitations in Thieno[3,4-*c*]pyrrole-4,6-dione-based Polymer:ITIC Solar Cells

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ABSTRACT

We report a systematic study of the efficiency limitations of non-fullerene organic solar cells that exhibit a small energy loss (E_{loss}) between the polymer donor and non-fullerene acceptor. To clarify the impact of E_{loss} on the performance of solar cells, three thieno[3,4-*c*]pyrrole-4,6-dione-based conjugated polymers (PTPD3T, PTPD2T and PTPDBDT) are employed as electron donor, which all have complementary absorption spectra compared to the ITIC acceptor. Corresponding photovoltaic devices show that low E_{loss} (0.54 eV) in PTPDBDT:ITIC leads to a high open-circuit voltage (V_{oc}) of 1.05 V, but also to a small quantum efficiency and in turn photocurrent. The high V_{oc} or small energy loss in PTPDBDT-based solar cells is a consequence of lesser non-radiative recombination, while the low quantum efficiency is attributed to the unfavorable micro-

phase separation, as confirmed by steady-state and time-resolved photoluminescence experiments, grazing-incidence wide-angle X-ray scattering and resonant soft X-ray scattering (R-SoXS) measurements. We conclude that to achieve high performance non-fullerene solar cells, it is essential to realize a large V_{oc} with small E_{loss} while simultaneously maintaining a high quantum efficiency by manipulating the molecular interaction in the bulk-heterojunction.

1. INTRODUCTION

Organic solar cells (OSCs) have received continuous attention in the last two decades due to their potential application in low-cost and flexible large-area devices.¹ Owing to the development of novel organic conjugated materials^{2, 3} and device architectures,^{4, 5} the power conversion efficiency (PCE), the key parameter in OSCs, has been continuously improving from 1%⁶ to 13%,⁷ now enabling commercialization. Conversion of photons into electrons in OSCs occurs in the bulk-heterojunction (BHJ) photoactive layer that typically consists of an electron donor and acceptor. Upon photon absorption, excitons are generated in both the donor and acceptor phase and successively dissociated into free charge carriers at the heterojunction interface driven by the energetic difference between the donor and the acceptor and the built-in electric field caused by the work function difference between the two device electrodes.^{8, 9} Both, the donor and the acceptor are important for light absorption and contribute to the photocurrent of the solar cell.¹⁰ However, the absorption coefficients of most donor materials are significantly larger than those of the acceptors, commonly fullerene derivatives.¹¹ Consequently, a lot of research addressing charge generation in organic solar cells focused on optimizing the alignment of the lowest unoccupied molecular orbital (LUMO) levels of the donor and acceptor. While this is important for the electron transfer from the donor to the acceptor,¹²⁻²⁰ studies concerning the physics of charge generation after excitation of the acceptor phase are rarely reported in literature.^{10, 21-25}

The development of novel non-fullerene acceptors in recent years now allows to achieve complementary absorption of the donor and acceptor phases in the BHJ photoactive layers, which ultimately leads to more efficient harvesting of photons from the sun.²⁶⁻³³ In particular, several conjugated small molecules³⁴⁻³⁹ and polymers⁴⁰⁻⁴⁶ have

been developed as electron acceptors absorbing in the near-infrared spectral region, and considerable contributions to the photocurrent generated from the acceptors were observed. In this case, free charge carriers are generated via dissociation of excitons created in the acceptor phase, when holes transfer from the acceptor molecules to the donor. This process, as also the electron transfer from the donor to the acceptor upon excitation of the donor, requires a sufficient thermodynamic driving force at the donor/acceptor interface in the BHJ, in part provided by the energetic offset between the highest occupied molecular orbital (HOMO) levels of the donor and acceptor molecules.⁴⁷

In fact, energetic differences between the donor and acceptor, namely HOMO and LUMO offsets, play an important role in charge generation in OSCs.^{48, 49} Although it has been widely reported that a LUMO offset of more than 0.3 eV is required for efficient charge separation,^{12, 50} some studies demonstrate that polymer/fullerene systems with lower LUMO offsets can perform equally well and achieve high performance.¹⁵⁻¹⁸ However, the role of the HOMO offset in charge generation is still debated. Recently, Janssen et al. reported that there was a dichotomous energy offset when exciting the polymer donor or the fullerene acceptor, in which a higher offset was required for efficient hole transfer from the acceptor to the donor. This could be a consequence of lower electronic coupling at the donor/fullerene acceptor interface, when exciting the fullerene acceptor.⁴⁷ Nevertheless, the recent high PCEs demonstrated in several OSCs with HOMO offsets less than 0.3 eV that use the non-fullerene acceptor ITIC developed by Zhan et al. are a promising contribution to field of organic solar cells.^{35, 34, 36, 51}

The different observations prompted us to investigate the charge generation process in non-fullerene OSCs with small energy offsets. Hence, we chose three conjugated polymers (PTPD3T, PTPD2T, and PTPDBDT) all based on the well-known electron-deficient thieno[3,4-*c*]pyrrole-4,6-dione (TPD) unit⁵² that exhibit different HOMO levels as the electron donor and the well-known ITIC as acceptor (Fig. 1). The donor polymers all absorb in the spectral range from 300 nm – 650 nm, while ITIC has a complementary absorption between 650 and 800 nm. We show that, despite the reduced voltage loss in the system, which exhibits the smallest energy loss (E_{loss}), the overall performance of the solar cells is less compared to those with larger E_{loss} , primarily due to significantly lesser

photocurrent generation. The voltage losses and reduced quantum efficiency in these solar cells were systematically studied by fourier-transform photocurrent spectroscopy (FTPS), steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectroscopy, and electroluminescence (EL) measurements. Furthermore, we investigated the micro-phase separation and conclude that low voltage losses and high quantum efficiency in non-fullerene solar cells with low E_{loss} could be realized simultaneously by optimization of the BHJ morphology.

Fig. 1 The chemical structures of (a) the conjugated polymers PTPD3T, PTPD2T, and PTPDBDT and (b) ITIC.

2. RESULTS AND DISCUSSION

2.1. Absorption and energy levels of TPD-based polymers

The TPD unit is a weak electron-deficient building block used to construct wide band-gap conjugated polymers with absorption in the visible spectral region.⁵²⁻⁵⁵ We synthesized three alternating conjugated polymers based on the TPD unit and terthiophene (PTPD3T),⁵⁶ bithiophene (PTPD2T)⁵⁷, and two-dimensional alkylthienylbenzodithiophene (PTPDBDT)⁵⁸ as electron-donating groups according to previously reported literature protocols.⁵⁶⁻⁵⁸ The molecular weights were determined by

high-temperature gel permeation chromatography (GPC) using *ortho*-dichlorobenzene (*o*-DCB) as eluent. PTPD3T has the highest number-average molecular weight (M_n) of 59.9 kg mol⁻¹ (Fig. S1 in Supporting Information, SI), while PTPD2T and PTPDBDT have relatively low M_n of 13.7 kg mol⁻¹ and 29.0 kg mol⁻¹, respectively. The three polymers show similar absorption spectra in thin films with optical band gaps (E_g s) of 1.79 eV–1.85 eV as determined from the absorption spectra. The electron acceptor ITIC displays a complementary absorption spectrum compared to the polymers (E_g = 1.59 eV) (Figure 2a). The absorption spectra of the polymer:ITIC (1:1) thin film blends are presented in Figure 2b, and show two distinct absorption bands, one from the polymer and the other from the ITIC. The three polymers were also tested as electron donors in fullerene-based solar cells and found to exhibit open-circuit voltages (V_{oc}) ranging from 0.79 V to 1.0 V.⁵⁶⁻⁵⁸ The difference in V_{oc} implies that the three polymers have different HOMO levels.

The energy levels of the polymers and ITIC were determined by cyclic voltammetry (CV) measurements and ultraviolet photoelectron spectroscopy (UPS), as shown in Fig. S2, Fig. S3 and summarized in Table 1. The three polymers show HOMO levels of -5.46, -5.50 and -5.60 eV as obtained from CV measurements (Fig. S2), while the HOMO levels are -5.05 eV, -5.09 eV and -5.14 eV as observed by UPS measurements (Table 1). The difference in HOMO levels originates from the different reference of the two experiments, as indicated in the literature.⁵⁹ The HOMO level of ITIC was found to be -5.61 eV and -5.74 eV from CV and UPS measurements, respectively. Hence, the HOMO offsets between the polymers and ITIC are 0.15, 0.11, and 0.01 eV, respectively, as concluded from CV measurements, similar to those reported for other ITIC-based solar cells.⁶⁰ However, the HOMO offsets observed by UPS measurements in these polymer:ITIC systems are significantly higher than 0.3 eV, a value, recognized as sufficient driving force for hole transfer (electron transfer) from the ITIC to the polymer (the polymer to ITIC).⁵⁰ For E_{loss} we used the difference between E_g and qV_{oc} as a measure to study the charge generation in these systems.

Table 1. Molecular Weight, Optical, and Electrochemical Properties of the three TPD-based Polymers and the Electron Acceptor ITIC.

Polymer	M_n^a	M_w^a	PDI	E_g^{film}	E_{HOMO}^b	E_{HOMO}^c
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	(kg/mol)	(kg/mol)	(eV)	(eV)		
PTPD3T	59.9	126.5	2.11	1.79	-5.46	-5.05
PTPD2T	13.7	24.6	1.80	1.79	-5.50	-5.09
PTPDBDT	29.0	55.9	1.93	1.85	-5.60	-5.14
ITIC	-	-	-	1.59	-5.61	-5.74

^a Determined by GPC at 140 °C using *o*-DCB as eluent. ^b Calculated by $-4.80 \text{ eV} - qE_{\text{ox}}$ from CV measurements. ^c Determined by UPS measurements.

Fig. 2 Absorption spectra of (a) neat PTPD3T, PTPD2T, PTPDBDT and ITIC thin films. (b) Absorption spectra of TPD-polymer:ITIC thin film blends with a weight ratio of 1:1.

2.2. Performance of polymer:ITIC solar cells

Inverted solar cells with ITO/ZnO cathodes and MoO₃/Ag anodes were fabricated and measured. The photoactive layers were processed from CHCl₃ solutions. Detailed information about the deposition conditions, including the use of solvent additives, the donor to acceptor ratio, and the thickness of the active layer are listed in Table S1-3, SI. The current-voltage characteristics of the optimized solar cells are shown in Fig. 3a and the corresponding photovoltaic parameters are summarized in Table 2. The average performance from eight optimized cells is summarized in Table S4-6, SI.

PTPD3T-based solar cells demonstrated the highest PCE of 8.4% with a short circuit current density (J_{sc}) of 13.5 mA cm^{-2} , V_{oc} of 0.91 V, and a FF of 0.68. PTPD2T-based solar cells showed a PCE of 7.0% with reduced J_{sc} of 12.3 mA cm^{-2} and enhanced V_{oc} of 0.96 V. PTPDBDT-based solar cells, with negligible HOMO offset, still exhibited a PCE of 5.4% with a J_{sc} of 8.5 mA cm^{-2} , and a high V_{oc} of 1.05 eV. The J_{sc} of the devices

matched the photocurrents as calculated from the external quantum efficiencies (EQE) of the devices, shown in Fig. 3b. All three photovoltaic systems showed virtually the same photoresponse from 300 nm to 800 nm, while PTPD3T-based solar cells had the highest EQE of up to 0.65. The maximum EQE was 0.60 and 0.40 for PTPD2T and PTPDBDT-based solar cells, respectively. We also calculated the energy loss (E_{loss}) between the optical band-gap of the thin films and V_{oc} , which showed that E_{loss} is gradually reduced from 0.68 eV for PTPD3T-based cells to 0.54 eV for PTPDBDT-based cells. From the photovoltaic performance, it seemed that when the HOMO levels of the donor polymers are closer to that of ITIC, the charge generation efficiency in solar cells was reduced. Hence, we performed further experiments to understand the charge generation process in these polymer:ITIC solar cells.

Table 2. Figures of Merit of Optimized Solar Cells using TPD Polymer Donors and ITIC Acceptor.

Polymer	J_{sc}^a (mA cm ⁻²)	V_{oc} (V)	FF	PCE	EQE _{max} ^b (%)	E_{loss} (eV)	EQE _{EL}
PTPD3T	13.5	0.91	0.68	8.4	0.65	0.68	3×10^{-4}
PTPD2T	12.3	0.96	0.60	7.0	0.60	0.63	4×10^{-4}
PTPDBDT	8.5	1.05	0.60	5.4	0.39	0.54	5×10^{-3}

^a J_{sc} was calculated by integrating the EQE with the AM1.5G spectrum. ^bThe maximum EQE at 685 nm. Weight ratio of the polymers to ITIC is 1:1. The active layers were spin-coated from CHCl₃/DIO (0.2%). The thickness of the active layers was 70 nm, 60 nm, and 85 nm for PTPD3T, PTPD2T, and PTPDBDT-based cells, respectively.

Fig. 3 (a) The J - V characteristics of optimized three TPD polymers:ITIC solar cells in dark (dashed lines) and under simulated AM1.5G illumination (solid lines). (b) EQE spectra of the corresponding devices.

2.3. Voltage losses

As shown in Table 2, the highest V_{oc} was obtained from the solar cell with PTPDBDT as donor, while the solar cell based on PTPD3T had the lowest V_{oc} . To further elucidate the reasons for the different V_{oc} in photovoltaic devices, we used a model based on Marcus theory that allows to determine the energy of the charge transfer state (E_{CT}) from the lower energy part of the EQE spectrum⁶¹:

$$EQE_{PV}(E) = \frac{f}{E\sqrt{4\pi\lambda kT}} \exp\left(\frac{-(E_{CT}+\lambda-E)^2}{4\lambda kT}\right) \text{ eq. 1,}$$

where EQE_{PV} is the photovoltaic external quantum efficiency, λ is the reorganization energy, k is the Boltzmann constant, T is the temperature, f is a factor proportional to the oscillator strength of the CT-state and the density of CT-states at the donor/acceptor interface, and E is the photon energy. The V_{oc} of the solar cells according to the detailed balance theory is then determined by the following equation⁶¹:

$$V_{oc} = \frac{E_{CT}}{q} + \frac{kT}{q} \ln\left(\frac{J_{sc}h^3c^2}{fq2\pi(E_{CT}-\lambda)}\right) + \frac{kT}{q} \ln(EQE_{EL}) \text{ eq. 2,}$$

Where h is Planck's constant, q is the elementary charge, c is the speed of light, and EQE_{EL} is the external quantum efficiency of electroluminescence of the device. This equation reveals that V_{oc} is directly related to E_{CT} and losses due to the rate of radiative (2nd term on the right side of eq. 2) and non-radiative recombination (3rd term on the right side of eq. 2).

Fig. 4 EQE_{EL} and FTPS- EQE_{PV} of the optimized solar cells. (a) PTPD3T:ITIC, (b) PTPD2T:ITIC, and (c) PTPDBDT:ITIC. The values correspond to the calculated values for E_{CT} , non-radiative losses, and radiative losses according to eq. 1 and eq. 2. (d) Normalized EL spectra of optimized solar cells.

From the EQE spectra measured with highly sensitive Fourier-transform photocurrent spectroscopy (FTPS), we obtained E_{CT} via eq. 1 for the solar cells based on PTPD3T (Fig. 4a). E_{CT} of the PTPD3T-based solar cell is about 0.07 eV lower compared to that of the PTPD2T (Fig. 4b). However, for the solar cell based on PTPDBDT (Fig. 4c), accurate determination of E_{CT} is not possible due to the absorption band of the CT-state being too close to that of ITIC. This is further confirmed by EL measurements (Fig. 4d), which showed that the emission spectra of the blend of PTPDBDT:ITIC and neat ITIC are virtually identical. Nevertheless, it is clear that the onset of the EQE of PTPDBDT-based solar cells is blue-shifted, compared to that of the other two donor polymers, which indicates a higher energy of the CT-state in the solar cell based on PTPDBDT.

We further investigated the origin of energy losses based on radiative and non-radiative recombination of charge carriers. Energy losses due to non-radiative recombination can be quantified by measuring the EQE of the CT-state's electroluminescence (EQE_{EL}). As shown in Fig. S4 and Table 2, we found that the

quantum efficiency is one order of magnitude higher in the system based on PTPDBDT, than those of the other two systems. This results in significantly lower non-radiative recombination losses, and it suggests that the reduction of the HOMO offset improves V_{oc} due to reduced energy losses during hole transfer and suppression of losses from fast non-radiative recombination.

The voltage losses due to radiative recombination of charge carriers are calculated using the fitting parameters for the CT state EQE, and they are found to be similar for the solar cells based on PTPD3T and PTPD2T (Fig. 4a and b). The radiative recombination losses are not expected to be very different in these OSCs since they depend logarithmically on the density of charge-transfer states and thus the degree of nano-scale phase separation between the donor and acceptor. It is therefore reasonable to assume a similar radiative recombination loss for the system based on PTPDBDT. This allows us to predict the V_{oc} for the different materials systems, using only the fitted E_{CT} and calculated losses coming from recombination. We found that the predicted values agree well with the measurement, as also indicated in Fig. 4.

It should be noted that for the solar cell based on PTPDBDT, the difference between qV_{oc} and the optical bandgap of the active layer (E_g of ITIC) is as small as 0.54 eV. To the best of our knowledge, this is among the smallest values reported so far. In fact, electroluminescence of the blend was found to be identical to that of neat ITIC, which suggests that the energy difference between the CT-state and ITIC singlet state is rather small (Fig. 4d). Nevertheless, generation and extraction of charge carriers are still quite efficient as indicated by the moderate J_{sc} (8.5 mA cm^{-2}) and FF of 0.6. In the next section, we will present and discuss the charge generation in these polymer:non-fullerene acceptor systems with different energy losses.

2.4. Quantum efficiency losses

Fig. 5 (a) Fraction of photons absorbed in the photoactive layers as calculated by optical transfer matrix simulations. (b) IQE of TPD-polymer:ITIC solar cells calculated from EQE and fraction of absorbed photons.

The optical properties of the polymer:ITIC systems that use different donors are similar, as indicated by the similar absorption of the photoactive layers of the solar cells obtained by an optical transfer matrix simulations (Fig. 5a). Therefore, the difference in J_{sc} of the three systems can only be explained by differences in the photon-to-electron conversion efficiency, namely the internal quantum efficiency (IQE). This is confirmed by IQE calculations shown in Fig. 5b. The difference in IQE is associated to either a difference in exciton quenching / dissociation efficiency of the singlet excitons generated in the neat donor/acceptor phases and/or recombination losses of photo-generated charge carriers. Dissociation of singlet excitons is controlled by the orbital energy offsets between donor and acceptor and the bulk-heterojunction morphology, while recombination losses depend on many parameters including charge carrier mobilities, energetic landscape at the donor-acceptor interface, as well as the internal electric field of the solar cell.

The exciton dissociation efficiency can be accessed from steady-state PL measurements, as shown in Fig. 6a. Compared to neat ITIC films, PL from PTPD3T:ITIC thin films was significantly quenched, while the PL quenching efficiency of PTPD2T:ITIC thin film was less. However, PTPDBDT:ITIC thin films showed almost identical PL intensity as observed from neat ITIC films, which is in line with our observation of similar CT-state energies as shown in Fig. 4d. The blends were further characterized by time-resolved photoluminescence (TRPL) spectroscopy. These

measurements were carried out by exciting into the ground state absorption of the ITIC acceptor and probing of the decay of the ITIC photoluminescence using a streak camera system. Fig. 6b shows the PL intensity decay of neat ITIC films in comparison to BHJ thin film blends using PTPD3T, PTPD2T, or PTPDBDT as donors. Bi-exponential fits were applied to parameterize the decays and to extract average exciton lifetimes, τ_{avg} ,

$$\tau_{avg} = \frac{(A_1 \times \tau_1) + (A_2 \times \tau_2)}{(A_1 + A_2)} \text{ eq.3,}$$

in order to allow a qualitative comparison of the exciton quenching. We note that the description by a bi-exponential decay is not based on a photophysical model and does not imply the presence of two separate exciton pools with different lifetimes, but rather a parameterization of the dynamics that yield average lifetimes (decay rates) to allow a qualitative comparison of the exciton quenching efficiency. We observed that singlet excitons created in the PTPD3T-based blend exhibited the shortest calculated average ITIC exciton lifetime of 18 ps, while the exciton lifetime increased to 26 ps in the PTPD2T-based blend. Clearly, the PTPDBDT-based blend showed the longest average exciton lifetime of 114 ps of all investigated polymer:ITIC systems. From the obtained lifetimes, the PL quenching efficiencies were determined (see Table 3), which are in qualitative agreement with the steady-state PL spectra. The average exciton lifetimes and obtained quenching efficiencies also correlate well with the observed quantum efficiencies, that is, the poor PL quenching will cause insufficient exciton dissociation, corresponding to the low EQE and IQE of the PTPDBDT:ITIC solar cells.

Fig. 6 (a) PL spectra and (b) PL decay dynamics of a neat ITIC film and the TPD-based conjugated polymers blended with ITIC. The decay dynamics were obtained by integrating the PL signal between 715 and 865 nm (filled dots) and fitted with a bi-exponential equation (solid lines). All films were excited into the ground state absorption of ITIC at 700 nm.

Table 3. TRPL Fit Parameters and Calculated Quenching Efficiency of the TPD-based Conjugated Polymers Blended with ITIC.

Polymer	A_1	τ_1 (ps)	A_2	τ_2 (ps)	τ_{avg} (ps)	Quenching Efficiency ^a
PTPD3T	0.47	6.95	0.56	27.5	18.1	0.93
PTPD2T	0.33	3.27	0.65	37.8	26.2	0.90
PTPDBDT	0.55	49.6	0.45	192.5	114	0.55

^aQuenching Efficiencies were calculated by using $1 - \frac{\tau_{avg,blend}}{\tau_{avg,ITIC}}$, where $\tau_{avg,blend}$ is the average exciton lifetime of the polymer blend and $\tau_{avg,ITIC}$ is the average exciton lifetime of the neat ITIC film.

2.5. Thin Film Morphology

Fig. 7 AFM height images ($3 \times 3 \mu\text{m}^2$) of the blended thin films spin-coated from CHCl_3/DIO (0.2%). (a) PTPD3T:ITIC (1:1). (b) PTPD2T:ITIC (1:1). (c) PTPDBDT:ITIC (1:1). The RMS roughness is also indicated in the images.

In this part, we provide insight into the micro-phase separation in order to elucidate the origin of quantum efficiency differences in these solar cells with different E_{loss} . The degree of donor/acceptor phase separation in the three different material systems was characterized by several techniques. AFM images indeed revealed differences in the topography of the photoactive layers (Fig. 7), in which PTPDBDT:ITIC blends showed higher roughness and larger domain size. Grazing-incidence wide-angle X-ray scattering (GIWAXS) revealed that PTPDBDT has smaller ‘crystal’ sizes than the other two polymers in blended thin films (Fig. 8 and Table 4), as indicated by the smaller π - π coherence length of PTPDBDT observed in PTPDBDT:ITIC systems.⁶² Resonant soft X-ray scattering (R-SoXS) was used to investigate the phase separation of the blend films and PTPDBDT showed considerably larger and less pure domains compared to the other two polymer:ITIC systems (Fig. 9).⁶³ This suggests that the exciton dissociation efficiency in PTPDBDT:ITIC blend is mainly limited by the large domain size, leading to inefficient exciton quenching, which in turn explains the low quantum efficiency in this system. From these studies, we conclude that poor micro-phase separation in PTPDBDT:ITIC blend is responsible for its low quantum efficiency. The results also imply that if the morphology of the BHJ system could be optimized, higher quantum efficiencies in combination with low energy losses can be achieved. We note that systems fulfilling these conditions have been reported recently.^{60, 64}

We provide some discussion about the large micro-phase separation in PTPDBDT:ITIC blend thin film. Phase separation in binary components is originally determined by chemical structures, such as the length of side chains,^{65, 66} crystallinity of conjugated backbone,⁶⁷ molecular weight^{68, 69} and solubility.⁷⁰ These properties are able to influence the miscibility between donor and acceptor, and the crystal growth during film formation, resulting in distinct morphology. It has been reported that conjugated polymers that have similar backbone with PTPDBDT show highly side chain dependent in solar cells,⁵⁴ indicating that PTPDBDT with varied side units will result in better phase

separation. In addition, From GIWAXS patterns (Fig. 8a-c), we note that PTPD3T and PTPD2T show highly ordered (*h*00) diffraction peaks, but PTPDBDT only shows (100) diffraction peak. This means that PTPDBDT has relatively poor lamellar stacking compared to the other two polymers. Therefore, we infer that by using short side chains and improving crystallinity, such as alkylthio units attached to BDT units, the micro-phase separation will be improved. The relative work is in progress in our lab.

Fig. 8 (a-g) GIWAXS images of the neat polymers, ITIC, and blended thin films. (h) the out-of-plane and in-plane cuts of the corresponding GIWAXS patterns. (a) PTPD3T, (b) PTPD2T, (c) PTPDBDT, (d) ITIC, (e) PTPD3T:ITIC, (f) PTPD2T:ITIC, and (g) PTPDBDT:ITIC.

Table 4. Crystallographic Parameters of the Neat Polymer and Blend Thin Films. OOP: out-of-plane. IP: in-plane. CL: coherence length.

	IP (100)		OOP (010)		Domain size (nm)	Domain purity
	<i>d</i> -spacing [nm]	CL [nm]	<i>d</i> -spacing [nm]	CL [nm]		
PTPD3T	2.62	10.0	0.37	3.1	-	-
PTPD2T	2.65	7.9	0.36	3.1	-	-
PTPDBDT	2.33	12.8	0.38	2.5	-	-
ITIC	1.91	6.5	0.35	2.4	-	-

PTPD3T:ITIC	2.60	10.0	0.36	2.4	17	1
PTPD2T:ITIC	2.60	10.0	0.36	2.7	19	0.83
PTPDBDT:ITIC	2.38	14.1	0.36	2.2	44	0.85

Figure 9. R-SoXS scattering profiles at 284.2 eV of the polymers blended with ITIC.

3. CONCLUSIONS

Three TPD-based wide bandgap conjugated polymers were used as donors in combination with the non-fullerene acceptor ITIC in organic solar cells, in which the ITIC substantially contributed to the photocurrent generation. We demonstrate that in principle by fine-tuning of the chemical structures, a high CT-state energy, low non-radiative recombination loss, and hence large open circuit voltage can be achieved. However, the overall performance of the solar cell with the lowest E_{loss} compared to the other two polymer blends with larger E_{loss} was reduced due to an overall lower internal quantum efficiency. The reason for the low quantum efficiency in the system with low E_{loss} was identified as insufficient exciton dissociation, revealed by reduced photoluminescence quenching and comparably long PL lifetime of the ITIC acceptor in blended thin films. We found that the reduced PL quenching is a consequence of donor-acceptor demixing and large-scale separation confirmed by GIWAXS and R-SoXS measurements, which demonstrated larger domain sizes and lesser phase purity in blended thin films, respectively. In conclusion, non-fullerene solar cells with small E_{loss}

can indeed lead to high photovoltages, however, an optimized micro-phase separation is essential to achieve high photovoltaic performance in these systems.

Supporting Information

Materials and measurements, GPC, UV and CV of the polymers and ITIC, solar cells and EQE_{EL} of the solar cells. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest

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TOC Picture and text

Three thieno[3,4-c]pyrrole-4,6-dione-based conjugated polymers were applied into non-fullerene solar cells, in which the polymer PTPDBDT provided a high photovoltage but a low quantum efficiency. This was caused by the large phase separation in bulk-heterojunction as confirmed by systematical studies.