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Enhancing the efficiency of PTB7-Th:CO*i*8DFIC-based ternary solar cells with versatile third components

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ABSTRACT:

Traditional single-junction binary organic solar cells suffer from narrow absorption windows, limiting their ability to harvest photons. One promising approach to avoid this issue is through the construction of a ternary system to enhance the spectral response and efficiency. However, the complex morphology and photophysical processes within ternary blends leave the criteria of an effective third component unclear and remain a challenge. In this work, we report the fabrication of PTB7-Th:CO*i*8DFIC based ternary solar cells with enhanced efficiency by employing either a polymer donor or a non-fullerene acceptor as the third component. We demonstrate that the third component is highly associated with the condensed state of the host acceptor and is the primary factor in determining efficiency improvement. The π-π stacking molecular packing of CO*i*8DFIC helps to maintain the optimal phase separation within the ternary blends and improves both the hole and electron charge mobilities, resulting in enhanced power conversion efficiency of over 14%, compared to 13.1% in binary devices. We also found an excessive amount of polymer donor or non-fullerene acceptor increases the phase separation and encourages lamellar crystallization with the hose acceptor domain, resulting in reduced light-harvesting and external quantum efficiencies at long wavelengths. Our results provide a rational guide to selecting the third component to fabricate

high-performance non-fullerene based ternary solar cells.

KEY WORDS: Organic solar cells, Ternary active layer, Non-fullerene acceptor, Morphology

INTRODUCTION

Over the past five years, organic solar cells (OSCs) have achieved significant progress benefiting from the continuous material development, especially from the design and synthesis of efficient non-fullerene electron acceptors (NFAs).[1-6] Compared to their conventional fullerene counterparts, NFAs not only possess merits of tunable optical properties and electronic energy levels, a smaller driving force is required for efficient exciton dissociation which features considerably reduced energy loss of NFA-based OSCs.[7-8] The state-of-the-art power conversion efficiency (PCE) of single-junction, binary OSCs is over 16% now, demonstrating a promising prospect of OSCs.[9-11] However, similar to the common organic semiconductors, non-fullerene acceptors also exhibit narrow absorption windows therefore limit the photon-harvesting ability of their OSCs.[12,13] Although integrating two single OSCs with different absorption windows to fabricate tandem device can utilize photons at different spectrum regions, the complicated and time-consuming manufacturing process limits the commercialization of this type of device.[14,15]

Constructing ternary photovoltaic devices has emerged as a promising strategy to enhance the device spectral response and efficiency by incorporating the third component with complementary absorption into the host binary system.[16-18] In addition to enhance the photon-harvesting property, the nanoscale morphology of the host system, e.g. the molecular ordering and orientation of each component, the phase separation between electrons and donors, can also be efficiently adjusted with the incorporation of the third component.[19,20] The choice of the third component therefore should be rationally made, otherwise the third component could easily alter the exciton dissociation, charge extraction and recombination processes, and finally impacts on device performance.[21,22] Consequently, besides the absorption window of the third components, their molecular ordering, energy levels, and compatibility with the host blend all should be taken into consideration in fabricating ternary OSCs.[23,24] Recently, a novel NFA named CO*i*8DFIC has been reported and demonstrated a record PCE of 13.8% in binary single-junction OSCs,[25,26] 14.6% in ternary single-junction OSCs,[27,28] and 17.3% in two-terminal tandem OSCs.[29] CO*i*8DFIC features an ultra-narrow bandgap and high crystallization ability to enable good light-harvesting ability and high electron mobility.[30,31] More interestingly, the molecular orientation of CO*i*8DFIC can be converted from edge-on and flat-on lamella to H- and J- type π-π stacking by the heating-induced aggregation effect that is executed through casting the photovoltaic blend on a hot substrate, and lead to a broadened absorption spectrum and finally enhanced photovoltaic performance.[26,31]

Aiming at further elevating the efficiency of PTB7-Th:CO*i*8DFIC binary OSC, a polymer electron donor PBDB-T-SF and a small molecular electron acceptor IT-4F with complementary absorption windows were selected as the third component to prepare ternary OSCs. We found that incorporating either PBDB-T-SF or IT-4F into the host blend can improve the spectral response at short wavelength. Importantly, they also can affect the molecular order of the host components, especially CO*i*8DFIC. The presence of a moderate content of PBDB-T-SF or IT-4F could enhance the π-π stacking of CO*i*8DFIC and maintain fine phase separation within the ternary active layer to enhance efficiency. The excessive amount of PBDB-T-SF or IT-4F in the host system increases the phase separation size, and encourages the conversion of CO*i*8DFIC molecular ordering from J-type π-π stacking into lamella, which results in reduced spectral response at long wavelength as evidenced from the absorption and external quantum efficiency (EQE) spectra of ternary OSCs.

RESULTS

The chemical structure, energy levels and absorption spectra of PTB7-Th, CO*i*8DFIC, PBDB-T-SF and IT-4F, as well as the device structure diagram of our solar cells are shown in **Fig. 1**.[2,26] It is apparent to found that the host components PTB7-Th and CO*i*8DFIC cover a broad absorption range from 350-1000 nm, however, their absorbance at short wavelength (350-550 nm) is not strong and a concave shape of absorption window from 700 to 800nm can be found. PBDB-T-SF and IT-4F possess a primary absorption window from 500 to 650 nm and 600 to 800 nm respectively, suggesting that either introducing PBDB-T-SF or IT-4F into the host blend can compensate the absorption window of the PTB7-Th:CO*i*8DFIC binary blend and has the potential to enhance the photovoltaic performance of PTB7-Th:CO*i*8DFIC OSCs.

The absorption spectra of the PTB7-Th:CO*i*8DFIC based ternary solar cells with different contents of PBDB-T-SF or IT-4F are shown in **Fig. 2(a) and 2(d).** Similar to our previous work, PTB7-Th:CO*i*8DFIC binary film exhibits three characteristic absorption peaks, in which the peak located at 710 nm comes from the absorption of PTB7-Th, the peak located at 830 nm can be attributed to the lamellar crystallization of CO*i*8DFIC, and the peak located around 950 nm is ascribed to the enhanced J-type π-π stacking of CO*i*8DFIC as induced by hot substrate casting.[26] When 15% of PBDB-T-SF or 10% of IT-4F was introduced as the third component, both ternary films exhibit enhanced absorption spectra at short wavelength from 350 to 800 nm, confirming that both PBDB-T-SF and IT-4F can improve the light-harvesting ability of host system with complementary absorbance. Meanwhile, we also found that the absorption at long wavelength was largely unchanged, implying that the molecular ordering of CO*i*8DFIC has not been affected with the presence of 15% of PBDB-T-SF or 10% of IT-4F. However, when the contents of PBDB-T-SF and IT-4F were increased to 30% and 20%, significant decrease of the J-type π-π stacking characteristic absorption peak of CO*i*8DFIC (from 900-1100 nm) can be found,[26] in despite of the continuously enhanced absorption intensity at the short wavelength. This suggests that the condensed state of the host acceptor component CO*i*8DFIC has be modified with the excessive incorporation of either PBDB-T-SF or IT-4F third component.[32-33]

TABLE 1. Photovoltaic parameters of PTB7-Th:CO*i*8DFIC ternary solar cells with different contents of IT-4F and PBDB-T-SF under the illumination of AM 1.5G at 100 mW cm^{-2}.

	FF [%]	J_{sc} [mA cm^{-2}]	Calculated J_{sc} [mA cm^{-2}]	V_{oc} [V]	PCE_{max} (PCE_{avg}) [%]
PTB7-Th:CO*i*8DFIC	68.4	27.6	26.5	0.69	13.1 (12.8±0.2)
With 15% PBDB-T-SF	70.6	28.8	27.4	0.69	14.1 (13.8±0.2)
With 30% PBDB-T-SF	65.4	26.9	26.1	0.69	12.2 (11.8±0.3)
With 10% IT-4F	71.2	28.9	27.3	0.69	14.2 (13.8±0.2)
With 20% IT-4F	70.4	26.0	25.3	0.69	12.5 (12.0±0.3)

The current density versus voltage (J–V) curves of PTB7-Th:CO*i*8DFIC based binary and ternary OSCs are shown in **Fig. 2 (b) and 2(e)**, and their corresponding device metric parameters are summarized in **Table 1**. The PTB7-Th:CO*i*8DFIC reference binary OSCs exhibited a maximum PCE (PCE_{max}) of 13.1%, with a J_{sc} of 26.5 mA cm^{-2}, V_{oc} of 0.69 V and FF of 68.4 %, this value is close to a PCE_{max} of 13.8% reported in our previous work which used a different batch of materials.[26] With the addition of 15% PBDB-T-SF or 10% IT-4F as the third component, the PCE_{max} was increased to 14.1% and 14.2% respectively, benefiting from the increased J_{sc} and FF values with their V_{oc} unchanged. On the contrary, when the contents of PBDB-T-SF and IT-4F were increased to 30% and 20% respectively, the J_{sc} and FF values of either PBDB-T-SF or IT-4F based OSCs decreased which led to a reduced PCE_{max} of 12.2% and 12.5%.

We further performed external quantum efficiency (EQE) measurements to gain a better insight into the photon response of these OSCs [shown in **Fig. 2(c)** and **2(f)].** The corresponding J_{cal} values integrated from the EQE spectra were listed in **Table 1**, which are only *ca.* 6% less than the J_{sc} values obtained from our J-V scans and demonstrate reliability of our J-V measurements. Compared to the PTB7-Th:CO*i*8DFIC binary device, ternary devices incorporating 15% PBDB-T-SF or 10% IT-4F exhibited enhanced photon response at the wavelength from 350 to 800 nm and 600 to 900 nm, consistent with their improved light-harvesting as confirmed by their absorption spectra. When the contents of PBDB-T-SF and IT-4F increased to 30% and 20%, their EQE spectra blue shifted with significant intensity reduction from 850 to 1000 nm. It is again consistent with their absorption spectra, and confirms that the excessive addition of PBDB-T-SF and IT-4F has affected the condensed state of CO*i*8DFIC remarkably. The photoluminescence (PL) spectra of PTB7-Th:CO*i*8DFIC films with the addition of different amounts of PBDB-T-SF and IT-4F were measured (see **Fig. S1** in the **supplementary material**). It can be found that PTB7-Th:CO*i*8DFIC binary film exhibits a weak peak at 970 nm, which is attributed to the characteristic PL peak of CO*i*8DFIC. With the addition of 15% PBDB-T-SF or 10% IT-4F in the ternary blends, the PL spectra of these samples exhibit marginal changes, which not only confirms that the addition of these third components did not alter the PL quenching of the active layer but also that the condensed state of CO*i*8DFIC did not change.[34] However, when the addition content of PBDB-T-SF and IT-4F increased to 30% and 20%, both ternary films exhibit increased PL intensity with a blue-shift from 970 to 925 nm. We link the blue-shift to the changed molecular ordering of the CO*i*8DFIC component, and the increased PL intensity to the increased phase separation size that reduces the PL quenching effect in the ternary photovoltaic blends[35], results that we will continue to present.

We firstly employed transmission electron microscopy (TEM) to study the effects of PBDB-T-SF and IT-4F content on the morphology of the active layer. The bright and dark regions in TEM images [shown in **Fig. 3(a)**] represent the polymer and non-fullerene domains respectively due to their different electron densities.[36] PTB7-Th:CO*i*8DFIC binary film exhibits a uniform and homogeneous distribution of polymer and non-fullerene domains, indicating fine phase separation in the film. With the incorporation of 15% PBDB-T-SF or 10% IT-4F in the host blend, fine phase separation can be maintained without the appearance of large aggregation domains, implying that exciton dissociation in these films could be efficient.[37,38] However, when the loading content of PBDB-T-SF and IT-4F increased to 30% and 20%, the dark areas, which is the phase separated CO*i*8DFIC domain, become pronounced. The excessive addition of either PBDB-T-SF or IT-4F therefore can disrupt the intimate mixing of PTB7-Th and CO*i*8DFIC, which would likely reduce the exciton dissociation in the ternary photoactive layer.

TABLE 2. Summary of fitting parameters of 1D GISAXS profiles of PTB7-Th:CO*i*8DFIC binary and ternary films containing different amounts of PBDB-T-SF or IT-4F.

	ζ_1 (nm)	ρ_1	ζ_2 (nm)	ρ_2
PTB7-Th:CO*i*8DFIC	27	36%	1.1	64%
With 15% PBDB-T-SF	25	47%	1.3	53%
With 30% PBDB-T-SF	25	72%	2.1	28%
With 10% IT-4F	29	55%	1.2	45%
With 20% IT-4F	21	76%	2.5	24%

Grazing-incidence small-angle X-ray scattering (GISAXS) measurements were employed to quantify the nanoscale phase separation of PTB7-Th:CO*i*8DFIC based binary and ternary films. **Fig. 3(b)** shows a representative 2D GISAXS image of PTB7-Th:CO*i*8DFIC binary film (with the rest shown in **Fig. S2** in the **supplementary material**). Herein, two Debye-Anderson-Brumberger (DAB) models were applied to fit the scattering intensity of various binary and ternary films. Parameters ρ_1 and ρ_2 are the relative volume fractions of the large-scale (with a correlation length ζ_1) and small-scale (with a correlation length ζ_2) structures. Whilst, ζ_1 can be roughly regarded as the size of the amorphous PTB7-Th:CO*i*8DFIC domain, and ζ_2 can be regarded as the distance between PTB7-Th and CO*i*8DFIC molecules in the amorphous PTB7-Th:CO*i*8DFIC domain.[26] Our GISAXS fitting results suggest that PTB7-Th:CO*i*8DFIC binary film comprises 36% large-scale structure with an amorphous domain of 27 nm, and 64% small-scale structures with a small average distance of 1.1 nm between donors and acceptors. With the addition of 15% PBDB-T-SF or 10% IT-4F, although the domain size of the amorphous region varied slightly and the distance between donors and acceptors largely unchanged, ρ_1 increased and ρ_2 decreased. This suggests that the moderate addition of PBDB-T-SF or IT-4F can tune the phase separated domain size, which could favor efficient charge transport.[39] However, when the ternary films contain 30% PBDB-T-SF or 20% IT-4F, the ρ_1 of both ternary films further increased to over 70%, and the ρ_2 decreased to about 25%, indicating that the excessive addition of PBDB-T-SF and IT-4F has induced a large fraction of large-scale domains in the films, character that is consistent with our TEM results. As a result, the average distance between polymer donors and NFA acceptors has increased to over 2 nm, which might reduce exciton dissociation of the device.

To gain deeper insight into the effect of PBDB-T-SF and IT-4F third component on the molecular ordering of the PTB7-Th:CO*i*8DFIC host blend, grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were performed. As shown in **Fig. 4**, the GIWAXS pattern of PTB7-Th:CO*i*8DFIC binary film exhibits a distinct diffraction signal q_{xy}=0.28 Å^{-1} in the in-plane direction and a distinct dispersion ring at q_z=1.7 Å^{-1} in the out-of-plane direction, the former is attributed to the alky chain stacking of PTB7-Th whilst the latter is ascribed to the overlapping of π-π stacking of PTB7-Th and CO*i*8DFIC. This GIWAXS feature is consistent with our previous work, with both PTB7-Th and CO*i*8DFIC feature face-on molecular orientation which could offer a short distance between donors and acceptors to promote exciton dissociation and charge generation.[26] When 15% of PBDB-T-SF or 10% of IT-4F were introduced into the host blend, the molecular packing and orientation of both PTB7-Th and CO*i*8DFIC are unchanged but enhanced alkyl chain stacking and π-π stacking are exhibited, a characteristic that has the possibility to facilitate charge transport in the film.[40] When the loading content of PBDB-T-SF and IT-4F increased to 30% and 20% respectively, the PTB7-Th alky chain stacking reduced significantly. However, a new intense diffraction peak at q_z=0.5 Å^{-1} appeared, which is associated with the edge-on lamellar crystal of CO*i*8DFIC.[26,31] This significantly increased molecular order of CO*i*8DFIC also leads to the increased correlation length of π–π stacking, therefore the crescent pattern at q_z=1.7 Å^{-1} became sharper. We believe that the increased phase separation domain size with the presence of excessive amount of PBDB-T-SF or IT-4F (see TEM and GISAXS results) account for this molecular order and orientation changes of the CO*i*8DFIC component. Without the interactions of PTB7-Th or third component in the relatively purer large domains, CO*i*8DFIC molecules can crystallize better and form more lamella instead of J-type π-π stacking, therefore show reduced light absorption in the long wavelength range. Comparing with literature reports on CO*i*8DFIC based ternary solar cells[27,41], our results not only suggest that the J-aggregation of

CO*i*8DFIC could be favored with the incorporation of the third components, but also suggest that the content of the third component would determine the phase separation size within the blend and impact on the crystallization of CO*i*8DFIC.

Finally to evaluate the exciton dissociation and charge collection in these PTB7-Th:CO*i*8DFIC based binary and ternary OSCs, their photocurrent density (J_{ph}) as a function of the effective voltage (V_{eff}) were studied (see **Fig. S3** in the **supplementary material**). It can be found that the J_{ph} of all OSCs saturates at large V_{eff}, and the ternary devices incorporating 15% PBDB-T-SF or 10% IT-4F obtained the highest saturated short-circuit current densities (J_{sat}), consistent with our absorption and EQE spectra.[42] Furthermore, the exciton dissociation efficiency (P_{diss}), charge transport and collection efficiency (P_{coll}), and hole (μ_h) and electron (μ_e) mobilities (see **Fig. S4** in the **supplementary material**) of these PTB7-Th:CO*i*8FIC based devices are summarized in **Table 3**[43-44]. The results suggest that although both hole and electron mobilities are increased with the increasing content of PBDB-T-SF and IT-4F, the P_{diss} and P_{coll} of these solar cells are decreased when the content of PBDB-T-SF and IT-4F increased to 30%. This implies that with the favorable morphology within the active layer (see in our morphological characterization part), ternary solar cells with the content of 15% PBDB-T-2F or 10% IT-4F could acquire efficient exciton dissociation, charge transport and collection processes. However, although incorporating 30% PBDB-T-SF or 20% IT-4F in the ternary solar cells could further enhance the charge transport, the large phase separation in the active layer hampers the exciton dissociation and charge collection processes, and finally reduces device performance.

TABLE 3 J_{sat}, P_{diss}, P_{coll}, electron and hole mobilities of PTB7-Th:CO*i*8DFIC OSCs with the addition of different amounts of PBDB-T-SF and IT-4F.

	J_{sat} [mA cm^{-2}]	P_{diss} [%]	P_{coll} [%]	Hole mobility (μ_h) cm^2 V^{-1} s^{-1}	Electron mobility (μ_e) cm^2 V^{-1} s^{-1}	μ_h /μ_e
PTB7-Th:CO*i*8DFIC	29.0	97.2	80.3	2.0×10^{-4}	7.0×10^{-5}	2.8
With 15% PBDB-T-SF	30.3	97.1	81.8	2.6×10^{-4}	1.0×10^{-4}	2.6
With 30% PBDB-T-SF	27.5	96.6	79.1	3.8×10^{-4}	1.2×10^{-4}	3.2
With 10% IT-4F	30.2	97.0	83.1	2.5×10^{-4}	1.6×10^{-4}	1.6
With 20% IT-4F	26.1	96.4	82.5	2.6×10^{-4}	2.3×10^{-4}	1.1

CONCLUSION

In summary, we have reported the versatile choice of a third component to prepare high-performance PTB7-Th:CO*i*8DFIC-based ternary solar cells, and demonstrated that either incorporating 15% PBBD-T-SF or 10% IT-4F into the host blend would compensate the absorption spectrum of the host blend, enhance π-π stacking in the active layer, maintain fine phase separation between donors and acceptors, facilitate charge transport, and consequently lead to enhanced PCEs over 14%. Moreover, our results also suggest that the content of the third component could significantly affect the molecular packing and orientation of CO*i*8DFIC acceptor, which critically determining the photon absorption and utilization at long wavelengths and ultimately the photovoltaic performance of ternary solar cells. Our results provide a rational guidance for the choice of the third component to make high-performance non-fullerene based ternary solar cells.

EXPERIMENTAL METHODS

A. Materials

CO*i*8DFIC was synthesized according to our previous work[25], PTB7-Th, IT-4F and PBDB-T-SF were purchased from Solarmer Materials (Beijing, China) Inc.

B. Device fabrication

All solar cells in this work were fabricated in an inverted structure (ITO/ZnO/Active layer/MoO_3/Ag). 30 nm of ZnO films were firstly spin-coated onto the clean ITO substrates (cleaned by sequential sonication in DI water, acetone and isopropyl alcohol) and thermally annealed following previous literature report.[45] Then PTB7-Th:CO*i*8DFIC:PBDB-T-SF or PTB7-Th:COi8DFIC:IT-4F blend solutions (14 mg/ml in chlorobenzene with 1 vol.% DIO as additive), with a fixed donor:acceptor ratio of 1:1.5, were spin-coated onto a pre-heated substrate (100 °C) as described in our previous work[26]. Finally, 10 nm MoO_3 and 100 nm Ag were thermally evaporated under high vacuum (10^{-6} Tor) as the anode.

C. Characterization

The J-V characterization of our solar cells was performed under AM 1.5G illumination (100 mW cm^{-2}) by a Newport 3A solar simulator (USA) with a J-V sweep software (Ossila Ltd, UK) and a Keithley 2612B (USA) source meter unit. A standard silicon reference solar cell certified by National Renewable Energy Laboratory was employed to calibrate the light intensity of the simulator. In order to eliminate the influence of stray and wave guided light, solar cells are measured with an aperture mask (size of 2.12 mm^2). An EQE system (Zolix, China) equipped with a standard Si diode was employed to measure the EQE of solar cells. Absorption and photoluminescence spectra of films were measured by a UV-Visible spectrophotometer (Lambda750, Perkin, USA) and PL microscopic spectrometer (Flex One, Zolix, China), respectively. A JEM-2100F Field Emission Electron Microscope were used to measure the morphology of PTB7-Th:COi8DFIC based binary and ternary films. GIWAXS measurements were conducted at Diamond Light Source (beamline of I07) in UK, and GISAXS were conducted at Shanghai Synchrotron Radiation Facility (beamline of BL16B1) in China.

SUPPLEMENTARY MATERIAL

See the supplementary material for the additional data on PL, 2D GISAXS patterns, and device performance.

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Figure captions

FIG. 1. (a) Chemical structures, (b) device structure diagram, (d) energy level alignment, and (d) absorption spectra of PTB7-Th, CO*i*8DFIC, PBDB-T-SF and IT-4F.

FIG. 2. (a, d) Absorption spectra of PTB7-Th:CO*i*8DFIC based ternary films. (b, e) J-V curves and (c, f) EQE curves of PTB7-Th:CO*i*8DFIC based ternary solar cells with different contents of PBDB-T-SF and IT-4F.

FIG. 3. (a) TEM images of PTB7-Th:CO*i*8DFIC binary and ternary films. (b) 2D GISAXS pattern of a PTB7-Th:CO*i*8DFIC binary film. 1D GISAXS profiles and their corresponding fitted curves of PTB7-Th:CO*i*8DFIC films with different amounts of (c) PBDB-T-SF and (d) IT-4F.

FIG. 4. 2D GIWAXS patterns and 1D GIWAXS profiles along q_{xy} or q_z axis for PTB7-Th:CO*i*8DFIC binary and ternary films with different amounts of PBDB-T-SF or IT-4F.