

Highly Efficient Ternary-Blend Polymer Solar Cells Enabled by a Nonfullerene Acceptor and Two Polymer Donors with a Broad Composition Tolerance

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In this work, highly efficient ternary-blend organic solar cells (TB-OSCs) are reported based on a low-bandgap copolymer of PTB7-Th, a medium-bandgap copolymer of PBDB-T, and a wide-bandgap small molecule of SFBCRN. The ternary-blend layer exhibits a good complementary absorption in the range of 300–800 nm, in which PTB7-Th and PBDB-T have excellent miscibility with each other and a desirable phase separation with SFBCRN. In such devices, there exist multiple energy transfer pathways from PBDB-T to PTB7-Th, and from SFBCRN to the above two polymer donors. The hole-back transfer from PTB7-Th to PBDB-T and multiple electron transfers between the acceptor and the donor materials are also observed for elevating the whole device performance. After systematically optimizing the weight ratio of PBDB-T:PTB7-Th:SFBCRN, a champion power conversion efficiency (PCE) of 12.27% is finally achieved with an open-circuit voltage (V_{oc}) of 0.93 V, a short-circuit current density (J_{sc}) of 17.86 mA cm⁻², and a fill factor of 73.9%, which is the highest value for the ternary OSCs reported so far. Importantly, the TB-OSCs exhibit a broad composition tolerance with a high PCE over 10% throughout the whole blend ratios.

Extensive efforts were devoted to improving the power conversion efficiency (PCE) of OSCs, which involved photosensitive material development,^[2–8] interfacial modification,^[9,10] and device structure design.^[11–13] At present, PCEs over 12% have realized for both single junction and multijunction OSCs.^[13–18]

In search for more efficient OSCs, a wide but also strong absorption window of the used active layer is prerequisite to make the best possible utilization of solar irradiation. However, due to the narrow molecular orbital energy level, it is difficult to obtain panchromatic absorption coverage from a single organic or polymeric semiconductor.^[19] Therefore, using multiple materials with complementary absorptions is an effective way to overcome the absorption bottleneck and boost the promising PCEs. In the past decade, tandem cell concept,^[13] sequential-casting ternary method,^[11] and bicontinuous

Bulk-heterojunction (BHJ) organic solar cells (OSCs) have received academic and industrial interests due to the advantages of low cost, light weight, flexibility, and solution processability.^[1,2]

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BHJ layers,^[12] which stacked two or more active blends with different absorption bands, were employed to achieve desirable light absorption and high device performance. In those cases, the interfacial contact and/or the processing complexity of multilayer deposition should not be ignored. As an alternative method, TB-OSCs have attracted a tremendous attention recently,^[14,19–26] where the active layer typically consists of either two donors and one acceptor (D1:D2:A) or one donor and two acceptors (D:A1:A2). The TB-OSCs strategy could not only afford the enhanced absorption coverage by using different materials with different absorption bands, but also preserve the processing simplicity of a single junction device. In addition, the introduction of a third component may interact synergistically with the host active material, forming the so-called “alloy model”^[21,27–29] or “parallel model” mechanisms,^[30,31] and resulting in the composition dependence of open-circuit voltage (V_{oc}) variations. Furthermore, the “alloy model” can also provide a cascade energy structure and more channels for efficient charge carrier transfer, thus improving the short-circuit current density (J_{sc}). Due to above mentioned superiorities, TB-OSCs have experienced a rapid progress with the PCEs over 12.0%.^[14,15]

Historically, fullerene derivatives are often used in TB-OSCs as the primary acceptors.^[24] But they have many intrinsic

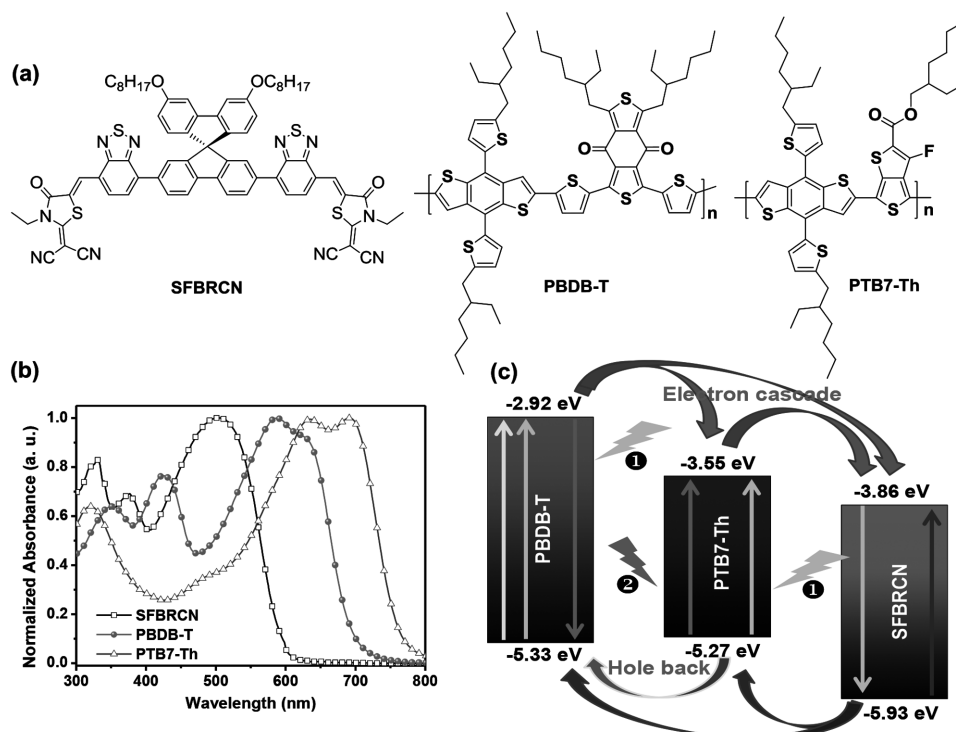


Figure 1. Molecular structures (a) and UV–vis absorptions (b) of SFBRCN, PBDB-T, and PTB7-Th. c) The proposal working mechanism of the non-fullerene ternary system in this work; ① and ② represent the energy transfers from SFBRCN and PBDB-T, respectively; the upward arrows represent the excitation by the solar irradiation or PL light; the downward arrows represent PL emission; the banding arrows represent the possible charge transfer pathways.

limitations, such as difficult synthesis and purification, weak absorption in the visible region and limited energy level tunability.^[32] As a result, the nonfullerene acceptors (NFAs) have emerged to overcome above shortcomings. In fact, the most efficient nonfullerene OSCs (NF-OSCs) were based on the low bandgap NFAs, such as 3,9-bis[2-(3-oxo-2-vinyl-2,3-dihydroinden-1-ylidene)-malononitrile]-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-sindaceno[1,2-b:5,6-b']dithiophene (ITIC) and the similar structural derivatives.^[16,17,32,33] Only few highly efficient NF-OSCs (PCE > 10%) were reported using the large bandgap NFAs.^[34,35] Most recently, we reported a small molecular acceptor (SFBRCN; **Figure 1**),^[35] which exhibited a wide optical bandgap of 2.03 eV with deep energy levels and matched well with those excellent low or medium bandgap copolymer donors. When poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b'] dithiophene-co-3-fluorothieno[3,4-b]thiophene-2-carboxylate] (PTB7-Th)^[36] was used as the donor material, a high PCE of 10.26% was achieved. To further elevate the PCEs, the TB-OSCs based on such large bandgap NFA are highly desirable for understanding the mechanism of non-fullerene ternary blend devices.

Herein, we report the fabrication and investigation of nonfullerene TB-OSCs, which comprise a wide bandgap NFA of SFBRCN, a medium bandgap copolymer donor of poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5'-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione))] (PBDB-T)^[37] and a low bandgap copolymer donor of PTB7-Th (**Figure 1a**). Such ternary blends displayed a broad composition tolerance over

the whole D1:D2 weight ratios (from 1:0 to 0:1), indicating the good miscibility of the two donor materials and desirable morphology when blending with the acceptor. By adding 30% (weight ratio in donors) of PBDB-T as the third component, the resulting devices exhibited synergistically improved V_{oc} of 0.93 V, J_{sc} of 17.86 mA cm⁻² and fill factor (FF) of 73.9%, delivering a champion PCE of 12.27%. To our best knowledge, this is the best value for TB-OSCs at present (Table S1, Supporting Information). Apart from the complimentary absorption (**Figure 1b**), the hole-back transfer from PTB7-Th to PBDB-T, multiple electron charge transfer, and nonradiative Förster resonance energy transfer (FRET) between the acceptor and the donor materials should also be responsible for the improvement of the whole device performance (**Figure 1c**).

The normalized UV–vis absorption profiles of PTB7-Th, PBDB-T, and SFBRCN in film state are shown in **Figure 1c**. These materials have different absorption bands with the effective absorption in the ranges of 400–550 nm for SFBRCN, 500–650 nm for PBDB-T, and 550–750 nm for PTB7-Th, respectively, which finally forms a complementary absorption within the visible region. The absorptions of the blend films with different weight ratios of PTB7-Th were further examined in detail, in which the weight ratios of (D1 + D2): A were fixed at 1:0.8 (**Figure S1**, Supporting Information). With increasing the amount of PTB7-Th from 0 to 1, the absorption would decrease gradually below 620 nm, while increase beyond that range. Therefore, there should be a balance between the absorption range and the strength for generating the highest device performance (vide infra). The highest occupied

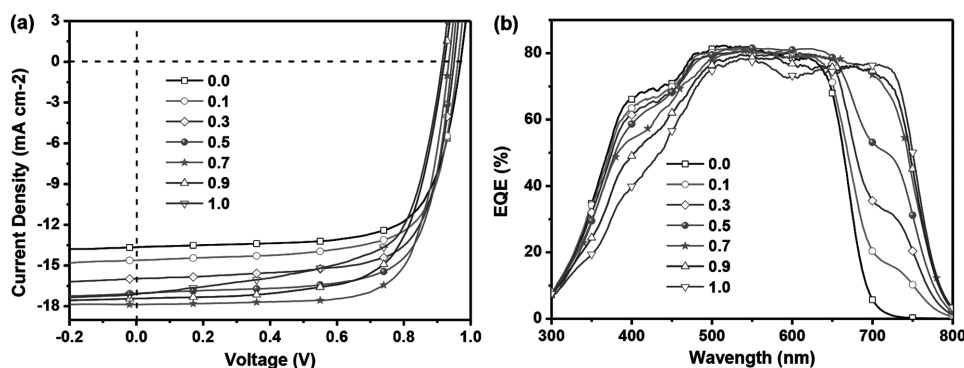


Figure 2. J - V curves (a) and EQE curves (b) of the optimized binary and ternary devices.

molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of these materials are $-5.93/-3.86$ eV for SFBCRCN,^[35] $-5.33/-2.92$ eV for PBDB-T,^[37] and $-5.27/-3.55$ eV for PTB7-Th,^[35] respectively (Figure 1c). Due to the lower-lying HOMO level of PBDB-T, a higher V_{oc} is expected by using PBDB-T as the host donor material.

The photovoltaic performance of TB-OSCs with different PTB7-Th contents were fabricated and evaluated, in which the total D:A weight ratios were kept constant at 1:0.8. As shown in Figure 2a, the binary device based on PBDB-T:SFBCRCN exhibited a high V_{oc} of 0.97 V and FF of 70.9%, delivering a high PCE of 9.39%. The relatively low J_{sc} of 13.65 mA cm^{-2} limited further improvement of the device performance, caused by the limited absorption range. In addition, PTB7-Th:SFBCRCN-based binary devices had a higher PCE of 10.11% with a larger J_{sc} of 17.11 mA cm^{-2} because of the relatively broader absorption range. However, the lower V_{oc} of 0.91 V and FF of 64.9% were observed, which resulted from the higher HOMO level and weak crystallinity of PTB7-Th.^[35] By varying the amount of PTB7-Th in ternary blends, the V_{oc} of the related devices would decrease while the J_{sc} and FF increase first and then decrease gradually (Table 1). When the ratio of PTB7-Th was kept at 0.7, the highest PCE of 12.27% was obtained with a V_{oc} of 0.93 V, J_{sc} of 17.86 mA cm^{-2} , and FF of 73.9%, which is the best efficiency for the reported TB-OSCs at present. It is interesting that the PCEs would remain over 9% throughout the whole

blend ratios, which showed that our TB-OSCs exhibited a broad composition tolerance.

The J_{sc} improvements were confirmed by external quantum efficiency (EQE) measurements (Figure 2b). PBDB-T:SFBCRCN-based binary devices showed a high EQE response in the shorter wavelength region of 400–650 nm (calculated J_{sc} : 13.61 mA cm^{-2}), while PTB7-Th:SFBCRCN-based devices exhibited a dominant EQE response in the longer wavelength range of 450–800 nm (calculated J_{sc} : 17.00 mA cm^{-2}). If reducing the PTB7-Th content while increasing the PBDB-T ratio, the related EQE response would decrease gradually in longer wavelength but increase gradually in shorter wavelength, which should be originated from the optical absorption variations (Figure S1, Supporting Information). When the weight ratio of PTB7-Th was changed to 0.7, a wide and strong EQE response was optimized from 400 to 800 nm, giving rise to the highest calculated J_{sc} value of 17.82 mA cm^{-2} , which was in consistent with the results from J - V measurements.

The morphology of the active blends was studied by grazing-incidence wide-angle scattering (GIWAXS), resonant soft X-ray scattering (R-SoXS) and atomic force microscopy (AFM) measurements. GIWAXS patterns of the ternary blend films were first studied (Figure 3a–f). These blends showed almost the same (100) diffraction positions located around $q_{xy} = 0.27 \text{ Å}^{-1}$, corresponding to a similar lamellar distance (d_l) of 23.3 Å. The reason is that PBDB-T and PTB7-Th have the comparable side chains. The (010) diffractions were located at out-of-plane direction with q_z ranged from 1.66 to 1.69 Å^{-1} , corresponding to their π - π distances ($d_{\pi\pi}$) of 3.78–3.72 Å (Table 2). The blend films exhibited gradually increased (100) diffractions in the in-plane direction while first increased and then decreased (010) diffractions in the out-of-plane direction. To further analyze the molecular packing behavior, the Herman's orientation parameter of (100) diffraction peak (S_{100}) was calculated.^[38,39] The S ranged from -0.5 to 1, where -0.5 represented a perfect face-on orientation on the substrate and 1 corresponded to a perfect edge-on orientation, while 0 indicated no preferential alignment of the (100) plane.^[38,39] The calculated S values were gradually decreased from -0.014 to -0.055 with the increase of PTB7-Th content

Table 1. Photovoltaic parameters of the nonfullerene ternary OSCs under AM 1.5G 100 mW cm^{-2} illumination.

PTB7-Th content	V_{oc} [V]	J_{sc} [mA cm^{-2}]	J_{cal}^a [mA cm^{-2}]	FF [%]	$\text{PCE}_{\text{max/ave}}^b$ [%]	Hole/electron mobility μ_h/μ_e [$\times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$]
0.0	0.97	13.65	13.61	70.9	9.39/9.17	1.62/2.06
0.1	0.96	14.61	14.48	71.1	9.97/9.69	1.75/2.15
0.3	0.95	15.96	15.77	71.5	10.84/10.21	1.91/2.22
0.5	0.94	17.05	16.81	72.3	11.59/11.19	2.01/2.30
0.7	0.93	17.86	17.82	73.9	12.27/11.89	2.25/2.41
0.9	0.92	17.42	17.28	68.8	11.03/10.81	1.71/2.33
1.0	0.91	17.11	17.00	64.9	10.10/9.87	1.51/2.25

^{a)}The J_{cal} values were determined from the integration of the related EQE curves; ^{b)}The PCE values are average values from at least 20 devices.

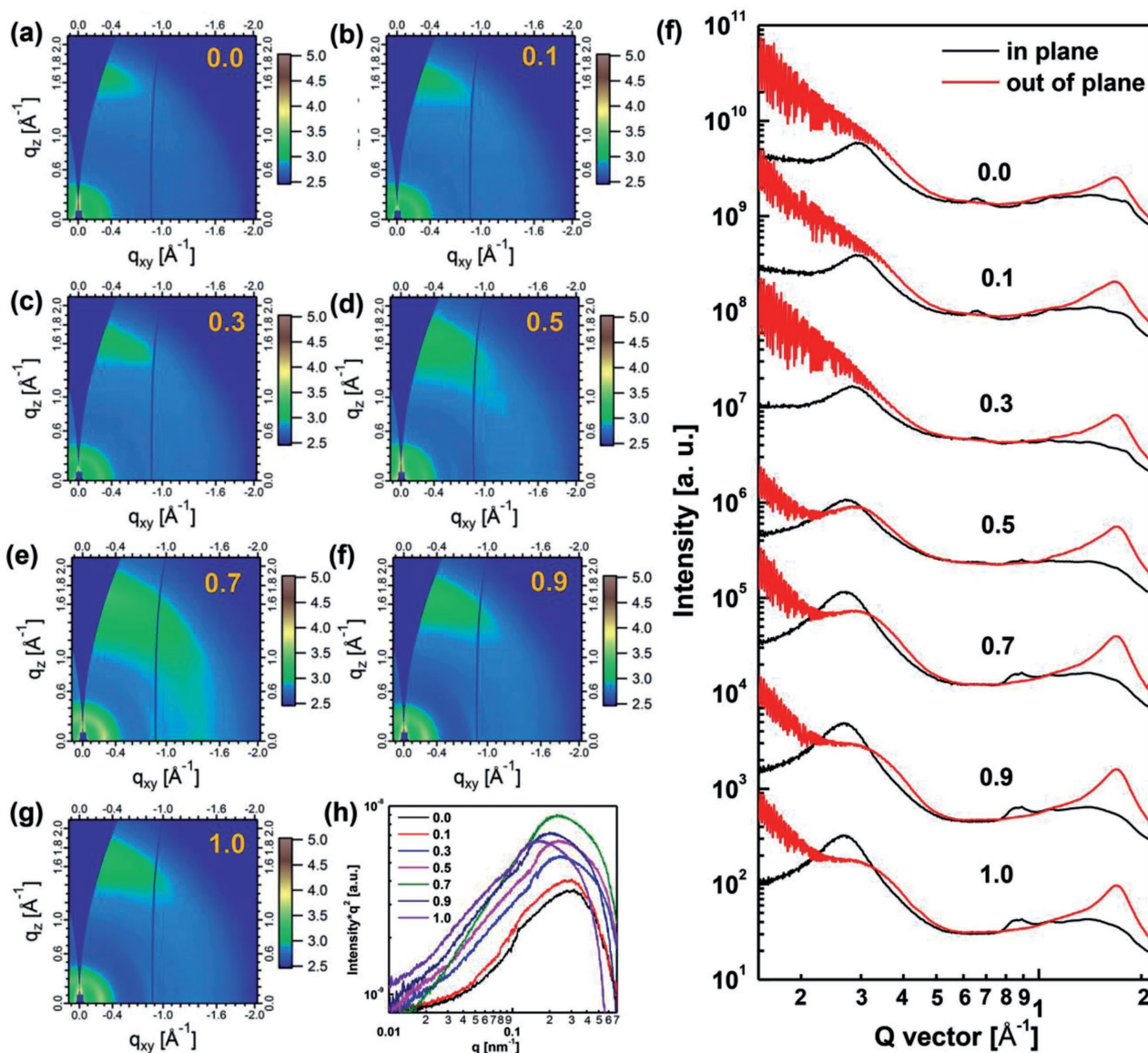


Figure 3. a–e) GIWAXS patterns of the binary- and ternary-blend films with different PTB7-Th contents. f) The in-plane (black line) and out-of-plane (red line) profiles of GIWAXS patterns. g) R-SoXS profiles of the binary and optimal ternary-blend films.

(Table 2), showing that such ternary blend system possessed a preferential face-on packing behavior and improved by adding more and more PTB7-Th. Obviously, the ternary blend with 0.7 ratio of PTB7-Th exhibited reasonably highest face-on orientation and crystallinity, which should be expected to obtain the largest charge mobility in OSCs.

Resonant R-SoXS was further employed to provide detailed phase separation information of the active blends. A photon energy of 284.2 eV was utilized to probe the material contrast. The distribution of scattering profiles can be fitted by log-normal functions and represents the distribution function of spatial frequency (s , $s = q/2\pi$). Therefore, the distribution mode (s_{mode}) corresponds to the characteristic mode length scale (domain spacing, $\xi = 1/s_{\text{mode}}$) and the mode domain size ($\xi/2$). From the R-SoXS profiles of the active blends with increasing

the weight ratios of PTB7-Th (Figure 3g), the ξ values were increased from 22 to 38 nm, corresponding to their domain sizes from 11 to 19 nm on account of two-phase separation (Table 2). Although the ternary blend with 0.7 ratio of PTB7-Th had the moderate domain size, it exhibited the highest domain purity, which could be responsible for the highest J_{sc} and FF values among the fabricated TB-OSCs.

The AFM images of the ternary blends exhibited rather smooth with a well-defined nanophase separation (Figure S2, Supporting Information). PBDB-T:SFBCN-based binary blend exhibited the smallest root-mean-square roughness (RMS) of 0.70 nm. By increasing the PTB7-Th amount, the RMS values enlarged gradually to 1.13 nm for the ternary blends with increasing the PTB7-Th content (Table 2), which could be attributed to the increased domain size. The AFM images

Table 2. The summarized morphology energy transfer efficiency and recombination parameters of the ternary blends.

PTB7-Th content	$d_l^{a)}$ [Å]	$d_{\pi}^{a)}$ [Å]	$S_{100}^{b)}$	$\xi^{c)}$ [nm]	Domain size ^{c)} [nm]	RMS ^{d)} [nm]	$E^e)$ (%)	$S^f)$ [Kt/e]	$\alpha^g)$	$P_{(E,T)}^{h)}$ [%]
0.0	23.3	3.78	−0.014	22	11	0.70	82.2	1.34	0.996	0.92
0.1	23.3	3.78	−0.023	23	11.5	0.71	82.3	1.33	0.973	0.93
0.3	23.3	3.76	−0.024	25	12.5	0.73	82.4	1.30	0.986	0.95
0.5	23.3	3.74	−0.030	28	14	0.81	83.8	1.26	0.993	0.96
0.7	23.3	3.72	−0.048	30	15	0.87	85.7	1.18	0.995	0.97
0.9	23.3	3.72	−0.053	36	18	1.05	82.7	1.28	0.970	0.93
1.0	23.3	3.72	−0.055	38	19	1.10	76.5	1.35	0.946	0.91

^{a)}The lamellar (d_l) and π - π staking (d_{π}) distances are calculated from the GIWAXS profiles; ^{b)}The Herman's parameters are calculated by using the literature reported method^[37,38]; ^{c)} ξ values and domain sizes are obtained from the R-SoXS profiles; ^{d)}RMS values are obtained from the AFM measurements; ^{e)}The energy transfer efficiency (E) results are obtained from fitting the TPL curves; ^{f)}The S values are the slopes of V_{oc} -Light intensity curves in semilogarithmic plots; ^{g)} α values are the slopes of J_{sc} -light intensity curves in logarithmic plots; ^{h)} $P(E, T)$ are calculated from the J_{ph} - V_{eff} curves in logarithmic plots.

showed clearly that PBDB-T:SFBCN binary blend exhibited the smoothest surface and smallest domain size, however, PTB7-Th:SFBCN binary blend showed the roughest surface with largest domain size. Obviously, the ternary blend with 0.7 ratio of PTB7-Th had a well-controlled phase separation without destroying the smooth surface, which was positive for improving the related exciton dissociation and charge transfer in OSCs. More than that, the morphology of this ternary blend system exhibited a small change under the whole ternary conditions, implying the good miscibility of these two donor materials and desirable phase separation with SFBCN. Such small morphology variations should responsible for the high device performance with broad composition tolerance.

To investigate the blend ratio effect on the charge transfer properties, hole and electron mobilities of the binary and ternary blends were measured (Figure S3, Supporting Information). The calculated hole and electron mobilities were summarized in Table 1 and Figure S3c in the Supporting Information. All the blends with different ratios of PTB7-Th exhibited high electron mobilities over $2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a very small variation. In contrast, the hole mobilities depended on the component of the blends, which increased first but decreased dramatically with increasing the content of PTB7-Th. The unbalanced charge mobilities of binary blend devices should be originated from the relatively poor morphologies, thus resulting in the low FF values. The ternary blend with 0.7 ratio of PTB7-Th possessed the highest but the most balanced hole ($2.25 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and electron mobilities ($2.41 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), contributing to the best FF value of 73.9%.

To further explore the improvement of device performance enabled by the ternary blend strategy, photoluminescence (PL) and transient PL (TPL) were then performed. PL and TPL can be used to detect the possible energy transfer pathways and evaluate the energy transfer efficiency.^[40,41] As shown in Figure S4 in the Supporting Information, the PL spectrum of SFBCN exhibited an apparent overlap with the absorption spectra of these two copolymer donors. Also the PL spectrum of PBDB-T displayed some extent overlap with the absorption of PTB7-Th. The results implied that energy transfer from SFBCN to these two copolymers and from PBDB-T to

PTB7-Th might occur, according to the FRET theory.^[42,43] As shown in Figure 4a, the maximum PL peaks of PBDB-T and PTB7-Th were located at different positions. But the PBDB-T:PTB7-Th (1:1, w/w) blend film only appeared one maximum PL peak at the position similar to PTB7-Th, which demonstrated that the efficient nonradiative FRET process from PBDB-T to PTB7-Th. The energy transfer efficiency (E) could be estimated by the Equation (1)^[42,43]

$$E = 1 - \frac{\tau_{\text{blend}}}{\tau_{\text{pristine}}} \quad (1)$$

where τ_{pristine} and τ_{blend} are the fluorescence lifetimes of the pristine and blend films, respectively. The average fluorescence lifetime was estimated by TPL measurement (Figure 4b), which was 165.9 ps for PBDB-T and 59.5 ps for PBDB-T:PTB7-Th, delivering a high energy transfer efficiency of 64.1%. Furthermore, the fluorescence of SFBCN was quenched by adding the donor materials with different content of PTB7-Th (Figure 4c). The efficiency of fluorescence quenching was over 99.8% for all the blend films, which was elevated to the highest value (99.99%) for the ternary blend film with 0.7 ratio of PTB7-Th. On the other side, the energy transfer efficiencies could be also evaluated by TPL measurements (Figure 4d), which were increased from 82.2% to 85.7% and then decreased to 76.5% with increasing the ratio of PTB7-Th (Table 2). Among them, the ternary blend with 0.7 ratio of PTB7-Th exhibited the highest fluorescence quenching efficiency and energy transfer efficiency, thus contributing to the best device performance as mentioned above.

Apart from the energy transfer, charge transfer also plays an important role in ternary blend devices. To study the possible charge transfer pathways, hole-only and electron-only devices based on single layer and double layers of copolymers were fabricated (Figure S5, Supporting Information).^[20,25] As shown in Figure S5 in the Supporting Information, the J - V curves of both type of devices with single layer of pristine copolymer exhibited a highly symmetric feature, regardless of the device structures. On the other side, the hole-only device based on PBDB-T/PTB7-Th exhibited a symmetric J - V curve, indicating the bidirectional charge transfer, while the related electron-only

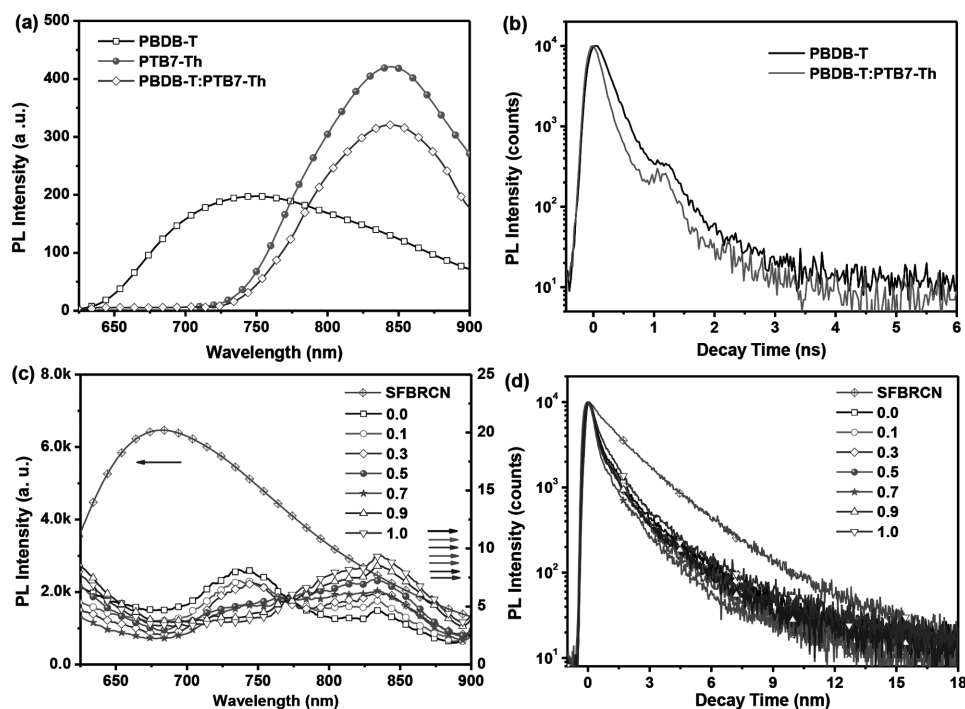


Figure 4. PL spectra (a) and TPL spectra (b) of the pristine polymer films and PBDB-T:PTB7-Th blend (1:1, w/w). PL spectra (c) and TPL spectra (d) of SFBCRN and the active blend films with different weight ratios of PTB7-Th.

device appeared an asymmetric curve, implying the unilateral charge transfer. These results confirmed that the electrons could only transfer from PBDB-T to PTB7-Th due to the large LUMO offset, but the holes could transfer easily between these two copolymers because of the small HOMO variations. The energy and charge transfer mechanisms in our ternary blend system were graphically illustrated in Figure 1c. Beside the light absorption, the nonradiative FRET from SFBCRN to the copolymer donors and from PBDB-T to PTB7-Th were exactly existed (proved by PL measurements), which were helpful for enhancing the energy conversion efficiency. At the same time, the hole-back charge transfer from PTB7-Th to PBDB-T and the present cascade electron transfer among the blend components would provide multiple charge transfer channels, which were also favorable for promoting the exciton dissociations.

To get a deep insight of the effect of ternary blend strategy on charge recombination dynamics, the V_{oc} and J_{sc} as a function versus light intensity (P_{light}) for PBDB-T:SFBCRN, PTB7-Th:SFBCRN, and the corresponding ternary blend with 0.7 ratio of PTB7-Th were examined (Figure 5a,b). From the curves of $V_{oc}-P_{light}$, the slopes decreased first from 1.34 kT/e to 1.18 kT/e and then increased to 1.35 kT/e with increasing the content of PTB7-Th (Table 2). The smallest slope for the ternary blend with 0.7 ratio of PTB7-Th was mostly close to kT/e , implying that the Shockley–Read–Hall or trap-assisted recombination was efficiently suppressed.^[5,44,45] The correlation between J_{sc} and P_{light} can be expressed as a power-law equation of $J_{sc} \propto P_{light}^{\alpha}$. The slopes (α) increased gradually from 0.966 to 0.995 and then decreased to 0.946 with increasing the content of PTB7-Th (Table 2), suggesting the reduced bimolecular recombination enabled by the ternary

blend strategy. The suppressed charge carrier recombination should be beneficial for more efficient exciton dissociation, which could also be confirmed by the $J_{ph}-V_{eff}$ plots (Figure 5c).^[5,44] The J_{ph} is defined as $J_L - J_D$, where J_L and J_D are the current densities under AM 1.5G illumination and dark, and V_{eff} is defined as $V_0 - V$, where V_0 is the voltage at which $J_L = J_D$ and V is the applied voltage. At high reverse voltages ($V_{eff} > 2$ V), J_{ph} reached saturation (J_{sat}), that is all the dissociated and charge carriers were swept out due to the high internal electric field. The charge dissociation probability ($P(E, T)$) can be defined as J_{ph}/J_{sat} under the short-circuit condition. The calculated $P(E, T)$ values were over 0.9 for all the conditions and 0.97 for the ternary blend with 0.7 ratio of PTB7-Th, indicating that the ternary blend exhibited a higher exciton dissociation rate, and thus giving rise to the larger J_{sc} and FF values in OSCs.

Ternary blend strategy showed a positive role to improve the device stability, which was critical for commercialization of OSCs.^[26] To explore the ternary composition effect on the device stability, the OSCs were treated thermally from room temperature to 140 °C (10 min for each point). As shown in Figure 5d, PBDB-T:SFBCRN devices showed better thermal stability than PTB7-Th:SFBCRN devices (0.8 vs 0.38 at 100 °C and 0.6 vs 0.24 at 140 °C), which was due to the relatively lower stability of PTB7-Th.^[26] However, the stability of both binary blend devices could be improved by using the ternary blends, which was ascribed from a locked nanophase morphology induced by the molecular interactions of the two copolymer donors.^[26] From the results, OSCs based on the ternary blend with 0.5 ratio of PTB7-Th showed the best thermal stability (over 0.8 at 140 °C). The best devices based on the ternary blend with 0.7 ratio of

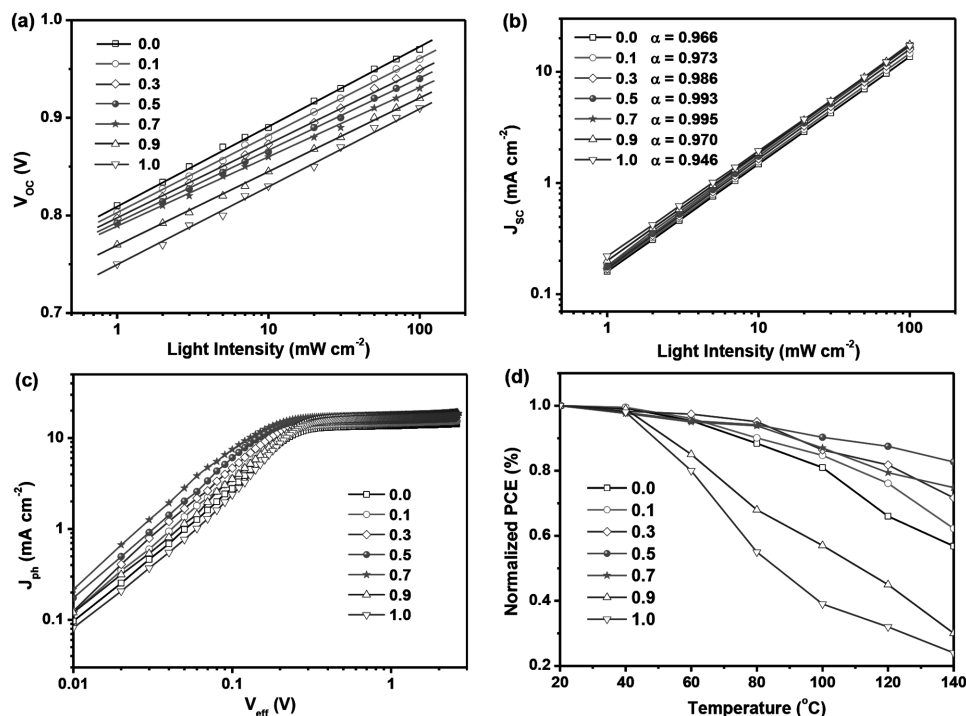


Figure 5. Open-circuit voltage (a) and short-circuit density (b) versus light-intensity plots of the ternary-blend OSCs. c) Photocurrent against effective voltage of the ternary-blend OSCs. d) Normalized PCEs of the ternary-blend OSCs heated in N_2 filled glove box for 10 min.

PTB7-Th also showed relatively high thermal stability (0.76 at 140°C) at the same condition.

In summary, we demonstrate here the highly efficient TB-OSCs based on one wide bandgap nonfullerene small molecular acceptor (SFBCRN) and two copolymer donors (PBDB-T and PTB7-Th) with the desirable complementary absorption coverage. The used two copolymers exhibited excellent miscibility with each other and good phase separation with the corresponding NFA. Our studies indicated that the multiple nonradiative FRET pathways existed from PBDB-T to PTB7-Th and from SFBCRN to the copolymer donors. Beside the electron cascade charge transfer among the ternary components, the hole transfer exhibited a hole-back phenomenon due to the small HOMO offset of PBDB-T and PTB7-Th. Such energy and charge transfer mechanisms played an important role for improving the energy conversion, charge dissociation, and collection efficiencies in devices, thus reducing the charge recombination probability. The optimized weight ratio was found to be 0.3:0.7:0.8 for PBDB-T:PTB7-Th:SFBCRN-based ternary blend, delivering a champion PCE of 12.27% with a high V_{oc} of 0.93 V, J_{sc} of 17.86 mA cm^{-2} and FF of 73.9%. To our best knowledge, the efficiency is the best record for TB-OSCs reported so far. Furthermore, the TB-OSCs in this work exhibited a broad composition tolerance, which was originated not only from the good miscibility and similar molecular packing behavior of PBDB-T and PTB7-Th but also from the desirable nanophase morphology with different ternary components. Our work would give a deep insight into the working mechanism of nonfullerene ternary blend OSCs, which could be used to direct highly efficient OSCs in the future.

Experimental Section

Materials: PTB7-Th was purchased from 1-Material Chemscitech. PBDB-T and SFBCRN were synthesized according to previously reported procedures.^[35,46] Other materials were commercially available and used without further purification.

Device Fabrication and Measurements: The device structure is ITO/PBDB-T_{1-x}:PTB7-Th_x:SFBCRN/MoO₃/Ag. Prepatterned ITO substrates (sheet resistance = $15 \Omega \text{ sq}^{-1}$) were sequentially ultrasonicated in detergent, deionized water, acetone, and isopropanol, and then UV-cleaned in a UV-ozone chamber for 20 min. The ZnO solution (2 M in toluene, diluted by tetrahydrofuran) was first spin-coated onto the surface of the ITO substrates at a rate of 5000 rpm for 30 s in the condition of 20 L min^{-1} dry airflow, and then baked on a hot plate at 100°C for 20 min to form a thin layer of about 30 nm. Ternary blend films with the fixed D:A ratio of 1:0.8 and the total concentration of 18 mg mL^{-1} in chlorobenzene (adding 0.75% v/v of 1,8-diiodooctane, DIO) were prepared by spin-coating method at 2000 rpm for 60 s. A molybdenum trioxide interlayer (MoO₃, 10 nm) and an aluminum anode (Al 100 nm) were finally deposited onto the surface of the active layer in an evaporation chamber under high vacuum ($\leq 10^{-6}$ mbar). Hole-only and electron-only devices were fabricated similar to the typical fabrication condition of ternary blend devices with the architectures of ITO/PEDOT:PSS/active layer/MoO₃/Au and glass/Al/active layer/Al, respectively. The thickness of the each layer was screened by using a Dektak 6 M surface profilometer. The device area was fixed at 4.0 mm^2 . The J - V characterization of the devices was carried out on a computer-controlled Keithley 2400 source meter with an Air Mass 1.5 Global (AM 1.5 G) solar simulator (XES-70S1, SAN EI Co., Ltd.) as the light source with an irradiation intensity of 100 mW cm^{-2} , which was calibrated by using a standard silicon solar cell. The EQE values were tested with a Newport Model 77890 (Newport Co. Ltd.) during the illumination with a monochromatic light from a xenon lamp. All fabrication and characterization processes, except for the EQE measurements, were conducted in a glove box filled with argon atmosphere ($<0.1 \text{ ppm O}_2$ and H_2O).

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

broad composition tolerance, charge transfer, energy transfer, nonfullerene acceptors, ternary blend polymer solar cells

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