Miscibility Tuning for Optimizing Phase Separation and Vertical Distribution toward Highly Efficient Organic Solar Cells

Lifu Zhang, Nan Yi, Weihua Zhou,* Zoukangning Yu, Feng Liu,* and Yiwang Chen*

Blending multidonor or multiacceptor organic materials as ternary devices has been recognized as an efficient and potential method to improve the power conversion efficiency of bulk heterojunction devices or single-junction components in tandem design. In this work, a highly crystalline molecule, DRCN5T, is involved into a PTB7-Th:PC70BM system to fabricate large-area organic solar cells (OSCs) whose blend film thickness is up to 270 nm, achieving an impressive performance of 11.1%. The significant improvement of OSCs after adding DRCN5T is due to the formation of an interconnected fibrous network with decreased π-π stacking and enhanced domain purity, in addition to the optimized vertical distribution of PTB7-Th and PC70BM, producing more effective charge separation, transport, and collection. The optimized morphology and performance are actually determined by the miscibility in different components, which can be quantitatively described by the Flory–Huggins interaction parameter of 0.80 and 2.94 in DRCN5T:PTB7-Th and DRCN5T:PC70BM blends, respectively. The findings in this work can potentially guide the selection of an appropriate third additive for high-performance OSCs for the sake of large-area printing and roll-to-roll fabrication from the view of miscibility.

1. Introduction

Organic solar cells (OSCs) play an important role over the past two decades, which have grown rapidly with interpenetrating network structure of active layer, and this structure is also known as bulk heterojunction (BHJ).[1–3] It has been recognized as a great promising substitute for silicon-based photovoltaic with advantages of lightweight, inexpensive cost, and large-area flexible preparation with roll-to-roll (R2R) process. Besides understanding the internal mechanism of binary OSCs deeply, more and more efforts were paid to improve the performance of OSCs via tuning absorption and energy level of novel donor[4–12] and acceptor[13–15] materials, optimizing processing methods,[16–19] interfacial engineering,[20] and innovative device architectures.[21–27]

As an efficient and new type of device structure, ternary OSCs generally consist of multidonor and one acceptor or one donor and multiacceptor. The third component is usually combined with the host single-junction system to provide complementary absorption, tune recombination behavior, and optimize the morphology of active layer.[28–30] Up to now, the best performance of ternary OSCs has been reported to be over 14%.[13] What is more, another novel device, tandem OSC,[24] consisting of two or more sub-cells has achieved a record-breaking efficiency of 17.3%.[25] Although both ternary OSCs and tandem OSCs could improve the power conversion efficiency (PCE) value to about 15%, the ternary strategy possessing simplicity of processing active layer exhibits great potential in R2R technology.[31] And the ternary OSCS literatures have been widely published in recent years including fullerene and non-fullerene systems.[6,32–34] Unfortunately, most of the research work about how to select appropriate third additive is based on the trial and error strategy, which is a process of labor and time consumption. The light absorption, energy level alignment, energy transfer, crystallization as well as miscibility should be taken into consideration during the fabrication of ternary OSCs.[29] Especially, many researchers have realized the importance of miscibility in ternary OSCs,[30,35–37] such as the appearance of Förster resonance energy transfer,[38] distribution of third additive on the interfaces of donor and acceptor,[39] formation of alloy with donor or acceptor,[36,37,40] etc. However,
the effect of miscibility on the fabrication of thick blend films ternary OSCs, in addition to the vertical distribution of donor and acceptor remains to be explored.\cite{31,44} The relative research work about how to quantitatively describe the miscibility in ternary systems has scarcely been reported.

For example, it is crucial to increase the active layer thickness of ternary OSCs without damaging the parameters of devices, which is contributive to the fabrication of large area OSCs via printing techniques. Nevertheless, the majority of ternary components show their highest performance at the appropriate blend films thickness (about 100 nm), further increasing the film thickness eventually would bring about the sharp reduction in PCE values.\cite{42} There are multiple reasons for the poor performance of ternary OSCs with thicker active layer. When the crystallization of donor or acceptor is disturbed for the poor performance of ternary OSCs with thicker active layer. When the crystallization of donor or acceptor is disturbed for the poor performance of ternary OSCs with thicker active layer, the Flory–Huggins interaction parameter measured by DSC and the chemical structure, energy levels as well as the absorption spectrums of pristine PTB7-Th, DRCN5T, and PC70BM are distributed on the blend film superficially. The optimized distance between third additive and donor or acceptor should all be taken into consideration to predict the effect of miscibility on the morphological evolution in the horizontal and vertical direction of the blend film.

In this article, the widely studied PTB7-Th and PC70BM are chosen as the host system due to the high reproducibility and performance.\cite{32} The small molecule DRCN5T was selected as the extra additive attributing to the well-matched energy level alignment and high crystallinity. It is founded that the involvement of DRCN5T in PTB7-Th:PC70BM binary system could enhance the absorption, which is helpful for the preparation of thick active layer of 270 nm whose maximal PCE value is of 11.1%, comparing with the binary system of 7.9% (250 nm) and 8.8% (100 nm). Surprisingly, the larger area ternary devices with efficient area up to 18 mm² could still retain PCE above 10% in contrast to the traditional devices with efficient area of 4 mm². The excellent PCE of the ternary active layer system is demonstrated to be related with the miscibility of different components. The Flory–Huggins interaction parameter measured by DSC is calculated to be −0.80 and 2.94 in DRCN5T:PTB7-Th and DRCN5T:PC70BM blends, respectively. The good miscibility between DRCN5T and PTB7-Th facilitates the crystallization of PTB7-Th to form the interconnected fibrous network, showing more face-on crystals with higher domain purity. The aggregation of PC70BM molecules separates from PTB7-Th phase because of the bad miscibility between DRCN5T and PC70BM, while more PTB7-Th polymers with lower surface energy could distribute on the blend film superficially. The optimized distribution of PTB7-Th and PC70BM in vertical and horizontal direction is beneficial to the large-area, thick, and high performance OSCs. The investigation of the miscibility between different components could provide knowledge for modulating the active layer morphology effectively and precisely so as to achieve higher efficiency of OSCs.

2. Results and Discussions

The chemical structure, energy levels as well as the absorption spectrums of pristine PTB7-Th, DRCN5T, and PC70BM are displayed in Figure 1a–c. The highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital level of DRCN5T are −5.32 and −3.64 eV, respectively,\cite{51} which forms an energy cascade with PTB7-Th and PC70BM benefiting for charge separation and collection.\cite{29} It is observed that DRCN5T displays complementary absorption with PTB7-Th
and PC70BM from 450 to 700 nm. Hoping to investigate the impact of DRCN5T on the absorption behaviors, the binary PTB7-Th:DRCN5T and ternary PTB7-Th:DRCN5T:PC70BM blend films with different DRCN5T ratio are analyzed, as shown in Figure 1d and Figure S1 in the Supporting Information. With the increment of DRCN5T ratio in PTB7-Th, the intensity of absorption increased gradually in the wavelength of 350–650 nm. In the PTB7-Th:DRCN5T blend film (Figure 1d), the incorporation of DRCN5T leads to an obvious absorption peak shifting from 709.9 to 724.6 nm, demonstrating a significantly increased molecular ordering of PTB7-Th, due to the specific interaction between them. Therefore, it is speculated that the crystallization of PTB7-Th could be enhanced by the incorporation of DRCN5T.[31] In addition, the enhancement of absorption is eventually beneficial to the increase of current density.[14]

The photovoltaic performance of both binary and ternary devices fabricating in the inverted structure of indium tin oxide (ITO)/ZnO/BHJ films/MoO3/Ag is shown in Figure S2a in the Supporting Information. For the purpose of systematically investigating the impact of DRCN5T ratio on the performance of devices, the weight ratio of donor to PC70BM is first kept constant at 1:2, and the thickness of the active layer is maintained at about 100 nm. As observed from Figure 2 and Table 1, the PTB7-Th:PC70BM presented a PCE value of 8.8%, a $V_{oc}$ of 0.782 V, $J_{sc}$ of 16.54 mA cm$^{-2}$, and FF of 67.2%, respectively. After the incorporation of 0, 10, 20, 30, and 40 wt% DRCN5T into the binary PTB7-Th:PC70BM system, the $J_{sc}$ value first increased from 16.53 to 18.63 mA cm$^{-2}$, and then reduced to 17.84, 17.13, and 16.99 mA cm$^{-2}$, respectively. A similar trend of FF change versus DRCN5T ratio was also observed. It was noteworthy that the $V_{oc}$ values of devices increased slightly with the increase of DRCN5T content, which was probably on account of the lower HOMO level of DRCN5T than that of PTB7-Th.[52] The ternary blending device with 10 wt% DRCN5T showed the highest PCE value of 10.9% with an FF of 73.2%, $V_{oc}$ of 0.782 V, and $J_{sc}$ of 18.88 mA cm$^{-2}$, which is a remarkable achievement in the PTB7-Th:PC70BM ternary systems.[53]

To further demonstrate the possibility that the incorporation of DRCN5T could induce the crystallization of PTB7-Th for fabrication of devices with thick blend film, the binary and ternary OSCs incorporating 10 wt% DRCN5T with the blend film thickness changing from 180 to 350 nm were prepared, and the corresponding results are summarized in Table S1 and Figure S2c,d in the Supporting Information. 270 nm was observed to be the optimal ternary blend film thickness, exhibiting the highest PCE value at 11.1% (Table 1). The high device performance was mainly owing to the significant increase of $J_{sc}$ value from 18.63 to 20.10 mA cm$^{-2}$, although the FF decreased from 73.5% to 69.8%. Increasing the blend film thickness to 350 nm reduced FF to 60.7% and $J_{sc}$ to 18.75 mA cm$^{-2}$, achieving an acceptable PCE value of 8.94%. In contrast, in the PTB7-Th:PC70BM binary system, when the blend film thickness was 250 nm, the $J_{sc}$ increased to 17.16 mA cm$^{-2}$ while the FF dropped to 57.4%, resulting in a low PCE value of 7.78%. Further increasing to 350 nm eventually leads to the sharply reduced $J_{sc}$, FF, and PCE values of 9.25 mA cm$^{-2}$, 49.6%, 3.69%, respectively. In comparison to the binary systems, the ternary system containing 10 wt% DRCN5T exhibited an improvement of PCE by 29.1% at blend film thickness of 100 nm and 42.7%
at blend film thickness of 250 nm, respectively. These results are similar to those reported by other research groups,[31,40,54] suggesting that the incorporation of crystalline molecule could facilitate the fabrication of PTB7-Th:PC70BM-based devices with thick active layer suitable for large-area printing. The optimal devices with different area of 6, 8, and 18 mm² were prepared to explore the impact of efficient area on the corresponding performance, the detailed results are summarized in Figure 3 and Table 2. Both of the devices containing 10 wt% DRCN5T with blend film thickness of 100 and 270 nm exhibited an excellent PCE value over 10% as the efficient area was increased from 6 to 18 mm².

The external quantum efficiency (EQE) spectra of these OSCs were exhibited in Figure S2b in the Supporting Information. The integrating current density provided by EQE curves are illustrated in Table 1 and Table S1 in the Supporting Information, all these values are conformed to the $J_{sc}$ obtained from the $J$–$V$ curves with errors less than 3%. For the binary blend systems, the EQE values were improved between 500 and 650 nm as blend film thickness was increased from 100 to 250 nm, which corresponds with the absorption spectra in Figure S1b in the Supporting Information. Unfortunately, the EQE value obviously reduced between 650 and 750 nm, leading to the poor $J_{sc}$. For the ternary blend systems with blend film thickness increasing from 100 to 270 nm, the absorption enhancement from 500 to 800 nm plays a great role in the improvement of EQE value, which is contributed by DRCN5T and PTB7-Th. These results might be originating from the change of vertical

![Figure 2](image-url)

*Figure 2. a) PCE and FF values of ternary OSCs with thin active layers versus different ratios of DRCN5T. b) PCE and FF of binary and ternary OSCs versus active layer thickness, c) $J$–$V$ and d) EQE curves of PTB7-Th:PC70BM binary and PTB7-Th:DRCN5T:PC70BM ternary devices with active layers of different thickness.*

| PTB7Th:DRCN5T:PC70BM | Thickness [nm] | $V_{oc}$ [V] | $J_{sc}$ [mA cm⁻²] | $J_{calc}$ [mA cm⁻²] | FF [%] | $PCE_{ave}$ [%] | $PCE_{max}$ [%] |
|-----------------------|----------------|-------------|-------------------|---------------------|-------|----------------|----------------|
| 1:0:2                 | 100            | 0.782 ± 0.02| 16.53 ± 0.11     | 16.2                | 66.7 ± 0.5 | 8.6 ± 0.2  | 8.8            |
| 1:0:2                 | 250            | 0.78 ± 0.002| 17.16 ± 0.04     | 16.4                | 57.4 ± 0.3 | 7.8 ± 0.2  | 7.9            |
| 0.9:0.1:2             | 100            | 0.787 ± 0.01| 18.63 ± 0.25     | 18.3                | 73.1 ± 0.5 | 10.7 ± 0.2 | 10.9           |
| 0.9:0.1:2             | 250            | 0.78 ± 0.002| 18.86 ± 0.07     | 17.95               | 68.6 ± 0.5 | 10.1 ± 0.1 | 10.2           |
| 0.9:0.1:2             | 270            | 0.78 ± 0.002| 20.10 ± 0.07     | 19.05               | 69.8 ± 0.2 | 10.7 ± 0.4 | 11.1           |
| 0.8:0.2:2             | 100            | 0.788 ± 0.01| 17.84 ± 0.32     | 17.2                | 71.2 ± 0.3 | 10.2 ± 0.2 | 10.4           |
| 0.7:0.3:2             | 100            | 0.790 ± 0.02| 17.13 ± 0.46     | 16.7                | 70.0 ± 0.1 | 9.6 ± 0.1  | 9.7            |
| 0.6:0.4:2             | 100            | 0.798 ± 0.02| 16.10 ± 0.20     | 16.4                | 68.7 ± 0.1 | 9.3 ± 0.2  | 9.5            |

$a)$ $J_{sc}$ integrated from the EQE spectrum; $b)$ All average PCE values are obtained from ten devices.
gradient distribution of different components in the blend film,[21] which will be explained in the later section.

Hoping to further explore the function of DRCN5T ratio on the performance of ternary OSCs, density of photocurrent versus voltage ($J_{ph}$–$V_{oc}$) curves of all OSCs are carried out and displayed in Figure 4a and Figure S3 in the Supporting Information. Here, the detail definitions of $J_{ph}$ and $V_{oc}$ are discussed in Electronic Supporting Information. For PTB7-Th:PC$_{70}$BM binary devices, the $J_{sat}$ values were 17.82 mA cm$^{-2}$ for 100 nm thick active layer and 18.92 mA cm$^{-2}$ for 250 nm thick active layer. For ternary devices, the $J_{sat}$ were 19.42 mA cm$^{-2}$ (10 wt% DRCN5T, 100 nm), 20.93 mA cm$^{-2}$ (10 wt% DRCN5T, 270 nm), 18.85 mA cm$^{-2}$ (20 wt% DRCN5T, 100 nm), 18.37 mA cm$^{-2}$ (30 wt% DRCN5T, 100 nm), and 18.26 mA cm$^{-2}$ (40 wt% DRCN5T, 100 nm), respectively. It was obvious that the ternary systems with both of thin and thick active layers show prominent enhancement of $J_{sat}$ as compared with PTB7-Th:PC$_{70}$BM system. Moreover, the $J_{sat}$ of ternary system (10 wt% DRCN5T) exhibited prominent improvement when the blend film thickness was increased to 270 nm and is 17.5% higher than that of the PTB7-Th:PC$_{70}$BM binary system with thin active layer. The result indicated that the usage of thick active layer is one of the efficient methods to improve the $J_{sat}$ by enhancing light harvesting. The $J_{ph}^c/J_{sat}$ and $J_{ph}^d/J_{sat}$ expound the differences of these devices.[34,56] Here, the $J_{ph}^c$ and $J_{ph}^d$ refer to the current density at short circuit and maximum power output conditions, respectively. The exciton dissociation efficiency ($\eta_d$) and charge collection efficiency ($\eta_c$) can be assessed by $J_{ph}^d/J_{sat}$ and $J_{ph}^c/J_{sat}$.

To elucidate charge transport dynamics in blend films, the $J$–$V$ curves of these OSCs are measured under different illumination intensity from 1 to 100 mW cm$^{-2}$, as shown in Figure 4b and Figure S4 in the Supporting Information. The relationship between $J_{sc}$ and light intensity could be expressed by the power-law formula of $J_{sc} \propto P_{light}^\alpha$, where $\alpha$ is the exponential factor.[57] Generally, the $\alpha$ value is approximately equal to 1, indicating the fewest bimolecular recombination of active layer. The $\alpha$ value was 0.982 for PTB7-Th:PC$_{70}$BM system, which was lower than that of the ternary systems with different DRCN5T content. For the optimized ternary OSCs, the highest $\alpha$ value of 0.998 was calculated, which was very close to 1, suggesting the weakest bimolecular recombination.[57] Moreover, the $V_{oc}$ dependence on light intensity could be assessed by $V_{oc} \propto n (kT/q)\ln (P_{light})$, $n$ value is generally ranging from 1 to 2. The $n$ value close to 1 indicates the insignificant trap-assisted recombination in blend film. The $n$ value reaching to 2 suggests the serious trap-assisted recombination causing by impurities or defects in blend films.[6,34] The $n$ values were 1.15 (10 wt% DRCN5T), 1.28 (20 wt% DRCN5T), 1.30 (30 wt% DRCN5T), and 1.45 (40 wt% DRCN5T) for the ternary OSCs, which is smaller than the $n$ value of 1.46 for the binary PTB7-Th:PC$_{70}$BM system. The $n$ value was close to 1 of the optimized ternary OSCs, suggesting the negligible trap-assisted recombination in this system.[38] Both of these two recombinations can be effectively suppressed for more charge transport and then collected in the ternary OSCs after the incorporation of 10 wt% DRCN5T into

### Table 2. Photovoltaic performance of optimal thin and thick ternary blend films with different active layer areas.

| PTB7-Th:DRCN5T:PC$_{70}$BM (0.9:0.1:2) | Area [nm$^2$] | $V_{oc}$ [V] | $J_{sc}$ [mA cm$^{-2}$] | FF [%] | PCE$_{max}$ [%] |
|--------------------------------------|----------------|----------------|-----------------|--------|----------------|
| 100 nm                               | 6              | 0.785          | 18.12           | 72.8   | 10.4           |
| 8                                     | 0.785          | 17.98          | 72.3            | 10.2   |
| 18                                    | 0.783          | 17.89          | 71.9            | 10.1   |
| 8                                     | 0.779          | 19.53          | 69.6            | 10.6   |
| 270 nm                               | 8              | 0.777          | 19.19           | 69.2   | 10.3           |
| 18                                    | 0.776          | 18.93          | 68.8            | 10.1   |

Figure 3. $J$–$V$ curves of PTB7-Th:DRCN5T:PC$_{70}$BM devices with active layer thickness of a) 100 nm and b) 270 nm at different efficient area.
PTB7-Th:PC70BM system, which could be further verified by the larger $\eta_c$ of 85% and FF of 73.6% for the optimal ternary OSCs.

As is known, it has already been reported that balanced charge transport and high charge mobility strongly affect the performance of OSCs, especially for thick film devices. To further study the performance of OSCs with both thin and thick blend films, the charge mobilities were measured by utilizing space charge–limited current method. The curves of single-charge devices under dark mode are revealed in Figure 4d and Figure S3a–c in the Supporting Information. The calculated hole mobility ($\mu_h$) and electron mobility ($\mu_e$) were shown in Table S4 in the Supporting Information. First, for the binary and ternary OSCs with active layer thickness of about 100 nm, the $\mu_h$ and $\mu_e$ of PTB7-Th:PC 70BM binary devices were $8.31 \times 10^{-4}$ and $6.18 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. When DRCN5T was added into PTB7-Th:PC70BM, the $\mu_h$ and $\mu_e$ values of all the ternary devices are greater than those in binary devices. Furthermore, both of the $\mu_h$ and $\mu_e$ values reached to the maximum up to $3.32 \times 10^{-3}$ and $2.85 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ when the DRCN5T content was 10 wt%. The value of $\mu_h/\mu_e$ was calculated to be 1.16, indicating the more balanced charge transport, which is beneficial to the higher FF and PCE. As compared with binary blend systems, the more excellent charge transfer of ternary blend systems is due to the optimized morphology upon the incorporation of DRCN5T. Furthermore, the mobility of PTB7-Th:PC70BM and PTB7-Th:DRCN5T:PCBM (0.9:0.1:2)-based devices with the blend film thickness of 250 and 270 nm was determined. It was observed that the $\mu_h$ value of binary blend systems apparently reduces to $6.51 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ as the active layer thickness increases to 250 nm. However, in the ternary blend systems, a decrease in hole mobility from $3.32 \times 10^{-3}$ to $2.20 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ is noticed. The variation in FF of the OSCs mentioned above is consistent with the mobility change of holes and electrons. The higher mobility of charges and more balanced $\mu_h/\mu_e$ value facilitate to improve charge extraction and restrain charge recombination, which could well explain the fact that binary OSCs with thicker films showed a lower PCE than the thinner ones while the ternary OSCs (10 wt% DRCN5T) with thicker films exhibiting a higher PCE.

Based on the above analysis, the significant improvement of photovoltaic performance of PTB7-Th:PC70BM system upon incorporation of DRCN5T should be related to the optimized morphology of blend films including the beneficial phase separation in horizontal and vertical directions, as well as the crystallization of polymers. Thus, atomic force microscopy (AFM) and transmission electron microscopy (TEM) techniques were performed to investigate the surface and internal morphology of the blend films,[50] and the corresponding images are displayed in Figure 5 and Figure S5 in the Supporting Information. From the AFM images, the ternary blend films (100 nm) showed a more uniform morphology and smoother surface than the PTB7-Th:PC70BM film (100 nm), exhibiting root mean square (RMS) surface roughness of 1.01 nm (10 wt% DRCN5T), 1.53 nm (20 wt% DRCN5T), 1.89 nm (30 wt% DRCN5T), and 2.06 nm (40 wt% DRCN5T), respectively. In contrast, the binary blend films showed of a rougher surface (RMS = 2.83 nm for 100 nm, RMS = 3.44 nm for 250 nm, respectively).
for 180 nm, RMS = 1.36 nm for 270 nm, respectively), which is slightly larger than the above 100 nm thick ternary blend film (10 wt% DRCN5T). It is suggested that the difference of RMS value in binary and ternary blend films might be relevant to the dissimilar surface behavior causing by the change in vertical composition and miscibility between different components.

In the TEM images, it was observed that the obvious nanofibrous structure appears after incorporation of DRCN5T into PTB7-Th:PC70BM, providing more channels for charge generation and transport, which is beneficial to improving the photovoltaic performance. The appearance of nanofibers induced by DRCN5T also demonstrated the more ordered structure of PTB7-Th, contributing to the shift of absorption from 709.9 to 724.6 nm, which was in accordance with UV spectra. With the increase of DRCN5T content, the density of the nanofibers increased, accompanied by the appearance of notable phase separation at DRCN5T ratio above 30 wt%. Further increasing the thickness of blend films from 100 to 270 nm leads to the gradual morphology evolution in PTB7-Th:PC70BM binary blend films, showing discernable phase separation structure, which is consistent with the sharp depression in Jsc and FF. In ternary active layers (10 wt% DRCN5T), the morphology of film at 180 and 270 nm seems to be the same, exhibiting discernable fibrous structure. It is suggested that the DRCN5T could act as nucleating agent to induce the crystallization of PTB7-Th and stabilize the morphology as the thickness of the films increases.

Then, the crystalline structure of the films with various DRCN5T contents was investigated by GIWAXS, and the corresponding 2D patterns and 1D cuts in the in-plane and out-of-plane directions are shown in Figure S6 in the Supporting Information and Figure 6a, and the corresponding parameters are displayed in Table S5 in the Supporting Information. Generally, the (100) lamellar peak of PTB7-Th at 0.34 Å−1 in the out-of-plane curve. By the incorporation of 10 and 20 wt% DRCN5T into the binary system, the (100) peaks slightly shift to lower q values, and the lamellar distance between alkyl chains became larger. Moreover, the coherence length of ternary blend system significantly increased in contrast to the binary PTB7-Th:PC70BM blend, indicating that DRCN5T could promote the crystallization of PTB7-Th, in accordance with the UV and TEM result. Similarly, the (010) peak at 1.61 Å−1 is less obvious in the PTB7-Th:PC70BM blend, and the d-spacing is determined to be 3.90 Å. Upon the addition of DRCN5T, the d-spacing of (010) peak significantly reduced, suggesting of stronger π–π stacking. The corresponding coherence length of the ternary blend film is larger than that in binary active layer, indicating that the addition of DRCN5T could induce the crystallization of PTB7-Th and formation of more face-on crystals, which is consistent with the appearance of interconnected fibrous structure and obviously improved hole mobility. Additionally, the aggregation size of PC70BM slightly increased upon the incorporation of DRCN5T, which is probably due to the bad miscibility between DRCN5T and PC70BM molecules.

Resonant soft X-ray scattering (R-SoXS) was also implemented on investigating the domain size of these different active layer films, and the Lorentz-corrected R-SoXS scattering profiles of various DRCN5T ratios active layer films are shown in Figure 6b. The domain size (Table S5, Supporting Information) of 17.0 nm (q = 0.018 Å−1) is observed for PTB7-Th:PC70BM blend film, which was increased to 19.8 nm as the DRCN5T weight ratio increases from 10 to 40 wt%. Moreover, the scattering intensity gradually increased with the incorporation of small molecules, showing that the enhanced crystallinity correlates with the higher domain purity. The larger domain size demonstrates that the incorporation of DRCN5T could drive the PC70BM molecules into larger aggregates.

As discussed previously, the incorporation of DRCN5T to improve the photovoltaic performance of PTB7-Th:PC70BM-based devices originates from two aspects, including facilitating the crystallization of PTB7-Th to form interconnected fibrous structures.
structure and optimizing donor and acceptor distribution in vertical direction. Therefore, a water contact angle (WCA) test of pristine and blending films of PTB7-Th, PC70BM, DRCN5T, PTB7-Th:PC70BM (100 and 250 nm), PTB7-Th:DRCN5T:PC70BM (0.9:0.1:2) (100 and 270 nm), PTB7-Th:DRCN5T:PC70BM (0.7:0.3:2) (100 nm) was performed to explore the effect of small molecules on the surface behaviors of active layer, and the corresponding results are appeared in Figure 7. Due to the different surface energies of PTB7-Th and PC70BM, the WCAs test can visually reflect the distribution of donor or acceptor in the blend film. The WCAs are determined to be 103.28°, 92.48°, 98.04° of PTB7-Th, PC70BM, and DRCN5T, respectively. It is indicated that PTB7-Th donor has a lower surface energy, and it is more intense hydrophobic than PC70BM and DRCN5T. As the blending films are concerned, only one component should be distributed on the film.

Figure 6. a) Out-of-plane and in-plane curves and b) R-SoXS profiles for PTB7-Th:DRCN5T:PC70BM ternary blend films.

Figure 7. WCA images of pristine a) PTB7-Th, b) PC70BM, c) DRCN5T films, in addition to the thin d) binary and ternary blend films with e) 10% and f) 30% DRCN5T, the thick g) binary and h) ternary blend films with 10% DRCN5T.
surface if the WCA value is close to the single-component pure film. In Figure 7, it is found that the WCA value is 99.44° of PTB7-Th:PC70BM, which is close to the pure film of PTB7-Th (103.28°), indicating that more PTB7-Th gather on the blend film superficially, in addition to the small amount of PC70BM molecules. For the ternary thick blend films, the WCA values increased gradually after the incorporation of DRCN5T. The WCA values are 102.04° of ternary films containing 10 wt% DRCN5T and 103.22° of ternary films containing 30 wt% DRCN5T, which are very close to the pure PTB7-Th film of 103.28°. As the thick films are concerned, the WCA values exhibit distinct changes, showing a WCA value of 96.66° for binary blend film and 102.17° for ternary blend film (10 wt% DRCN5T), respectively. In contrast to the thin PTB7-Th:PC70BM film (100 nm), the thick binary blend film (250 nm) shows a much smaller WCA, attributing to the enrichment of more PC70BM molecules on the surface of films. As the ternary PTB7-Th:DRCN5T:PC70BM (0:9:0.1:2) film is concerned, the WCA value of the thick film (270 nm) is very close to that of the thin film (100 nm). These results indicate that more PC70BM enriched on the surface of the thick binary blend film while more PTB7-Th enriched on the surface of thin binary film and ternary films, which well correlates with the EQE result in Figure 2a. Based on these data, it is included that the incorporation of DRCN5T into PTB7-Th:PC70BM could alter the vertical distribution of PTB7-Th and PC70BM, which is vital in the charge collection as well as the eventual photovoltaic performance. Moreover, the vertical distribution of donor or acceptor influencing by the DRCN5T should be due to the difference in miscibility between DRCN5T and donor/acceptor, which has never been reported previously.[28,44] The miscibility between the different components is recognized as the key factor in determining the vertical and horizontal phase separation, and eventually the performance of solar cells. Anyway, how miscible between DRCN5T and PC70BM is actually unknown.[31]

The interaction parameter $\chi$ from the melting point depression method based on the DSC equipment could be calculated by Equation (1)

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{-\frac{R}{\Delta H_f}}{\nu_1 (m_2 - 1) + \frac{1}{m_2}} \ln \phi_2 + \chi (1 - \phi_2)^2$$

where subscript 1 is identified with the weaker crystalline material and 2 with the stronger crystalline material, respectively. $T_m$ and $T_m^0$ are the melting points of mixture and pure crystalline material. $R$ is the ideal gas constant. $\Delta H_f$ is the heat fusion of crystalline material. $\nu$ is the molar volumes. The $m$ is the degree of polymerization. $\Phi$ is the volume fraction. For the PTB7-Th:DRCN5T blends, the subscript 1 represents the weakly crystalline polymer PTB7-Th and 2 identifies the highly crystalline DRCN5T. $m_1$ is very large compared to 1 and $m_2$ is 1. Then, the above equation reduces to Equation (2)

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{-\frac{R}{\Delta H_f}}{\nu_1} \ln \phi_2 + (1 - \phi_2) + \chi (1 - \phi_2)^2$$

For the DRCN5T:PC70BM blends, the subscript 1 identifies with the less crystalline molecule PCBM and 2 with the highly crystalline molecule DRC5T, both of $m_1$ and $m_2$ are 1, the above equation is thus reduced to Equation (3)

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{-\frac{R}{\Delta H_f}}{\nu_1} \ln \phi_2 + \chi (1 - \phi_2)^2$$

By neglecting the effects of entropy and $\Phi_2$, the $\chi$ can have the following form

$$\chi = \frac{B \nu_1}{RT}$$

where $B$ is the interaction energy density characteristic of the organic material pair.

Substituting Equation (4) into the above equations, the $\chi$ can be extracted by the slope of the linear fit straight line.

The DSC heating and cooling curves of DRCN5T:PTB7-Th and DRCN5T:PC70BM blends are exhibited in Figure S7 in the Supporting Information, the corresponding melting temperatures are listed in Table 3. In the PTB7-Th:DRCN5T blends, the $\chi$ value is calculated to be about -0.80. In contrast, the $\chi$ value in DRCN5T:PC70BM blends is determined to be about 2.94, as listed in Table 4. The negativeness of $\chi$ for the PTB7-Th:DRCN5T blend indicates that they can form a thermodynamically stable and compatible mixture at temperatures above the melting point. Additionally, the DRCN5T and PC70BM are totally immiscible.

Therefore, the incorporation of the DRCN5T serves several roles to optimize the morphology for eventual increase of photovoltaic performance. One is the nucleating agent, the crystalline DRCN5T could induce the crystallization of PTB7-Th polymers to form the interconnected fibrous network, facilitating the transport of charges. Second, based on the surface energy and the interaction parameters, DCRN5T molecules should be well blended in the PTB7-Th phase, residing in the interface between PTB7-Th and PC70BM. The bad miscibility between DRCN5T and PC70BM eventually drives PC70BM to separate from PTB7-Th phase, leading to the enrichment of PTB7-Th on the active layer surface. In other words, the DRCN5T molecules could optimize the vertical phase separation, leading to enrichment of PTB7-Th at the anode and PC70BM at the cathode.

3. Conclusions

In summary, high-efficient ternary OSCs have been designed and prepared. As compared with binary system, the ternary device with 10 wt% DRCN5T displayed a highest PCE of 11.1% whose blend film thickness is 270 nm. Encouragingly, the high-performance ternary devices with both of thin and thick films showing active layer area of 18 mm² could still achieve PCE above 10%. The superior performance is mainly due to improved charge collection and separation, attributing to the formation of obvious interpenetrating network morphology. Another important reason is that DRCN5T could optimize the vertical distribution of PTB7-Th and PC70BM because of different miscibility with donor or acceptor. The miscibility could be quantitatively described by Flory–Huggins interaction parameter, which were calculated to be -0.80 and 2.94 in...
Table 3. The melting temperatures of DRCNST with the increase of PTB7-Th or PC70BM ratio.

| Blends          | \(T_m^{\text{DRCNST}}[^{°}\text{C}])\) | \(\Delta H_m[^{\text{DRCNST}}][\text{J g}^{-1}]\) |
|-----------------|----------------------------------------|-----------------------------------------------|
| DRCNST:PTB7-Th  | 219.6                                  | 44.89                                         |
| DRCNST:PC70BM   | 219.6                                  | 44.89                                         |

\(\Delta H_m^{\text{DRCNST}} = -44.89 \text{ J g}^{-1}\)

DRCNST:PTB7-Th and DRCNST:PC70BM blends, demonstrating that DRCNST and PTB7-Th are miscible and DRCNST and PC70BM are immiscible. The poor miscibility between DRCNST and PC70BM eventually led to the enrichment of DRCNST:PTB7-Th on the active layer surface. The finding in this work provides novel guideline to select appropriate third additive based on the miscibility between different components.

4. Experimental Section

Materials: DRCNST, PTB7-Th, and PC70BM were acquired from Solarmer Materials Inc. Chlorobenzene and other solvent were purchased from Sigma Co. Ag, Al, and MoO3 were purchased from Zhong Nuo Advanced Materials Co. In order to ensure the accuracy of experimental results, all the materials employed in the experiment were purchased from the same batch.

Device Fabrication: Both binary and ternary active layers were fabricated with inverted device structures to evaluate the performance of PTB7-Th:PC70BM host binary system and PTB7-Th:DRCNST:PC70BM ternary system with various DRCNST contents. The concentration of the solution was 20 mg mL\(^{-1}\) and the donor and acceptor weight ratio is maintained at 1:2, in addition to the volume ratio of solvent (CB) and additive (1, 4-butanediol, BT) keeping at 97:3. The solutions were stirred at 70 °C overnight. The ITO glass substrates (≤15 Ω sq\(^{-1}\)) were cleaned successively via acetone, ultrasonication in liquid detergent, deionized water, and isopropanol for 30 min of each step. ZnO precursor solution was prepared by dissolving 0.5 g of zinc acetate (Zn(CH\(_3\)COO)\(_2\) \(\cdot\) 2H\(_2\)O, 99%) in 5 mL of 2-methoxyethanol (CH\(_3\)OCH\(_2\)CH\(_2\)OH, 98%) and 0.138 mL of ethanolamine (NH\(_2\)CH\(_2\)CH\(_2\)OH, 98%), and stirring overnight at room temperature.[10] The cleaned ITO glass substrates were dried by nitrogen flow and then treated by UV-Ozone for 18 min. Then, the ZnO precursor solution was spun at 4000 rpm for 1 min and annealed at 200 °C for 60 min in air atmosphere to afford 30 nm thick layer, followed by transferring the substrates into the N\(_2\) glove box for spinning the active layers. The thickness of active layer was kept at around 100 nm. For the thicker film, the concentration of solution was increased to 35 mg mL\(^{-1}\) and the spin rate was ranging from 600 to 1800 rpm to afford films with different thickness. After thermal evaporation of 7 nm MoO\(_3\) and 90 nm Ag under a pressure of 2 \(\times\) 10\(^{-4}\) Pa, the devices were then used for further characterization. For the common devices, the active area was kept at 4 mm\(^2\). For the devices with larger area, the ITO width was increased from 2 to 9 mm with the same shadow mask.

Device and Film Characterization: The solar simulator (SS-FS-AAA, Enli technology Co., Ltd.) with an AM 1.5 G (100 mW cm\(^{-2}\)) spectra was used to perform the J–V measurements. The intensity of spectra was calibrated by the certified standard silicon solar cell (SRC-2020, Enli technology Co., Ltd.). The EQE data were obtained by using solar cell spectral-response measurement (QE-R, Enli technology Co., Ltd.). The UV-vis absorption spectra were obtained by Hitachi UV-3010 spectrophotometer. The morphology of blend films was measured by AFM (Nanoscope III A scanning probe microscope) and TEM (JSM-7100F).

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

crystallization, interaction parameter, morphology, ternary devices, vertical phase separation

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