# Crystalline and Active Additive for Optimization Morphology and Absorption of Narrow Bandgap Polymer Solar Cells

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**ABSTRACT:** The morphology of active layer with an interpenetrating network structure and appropriate phase separation is of great significance to improve the photovoltaic performance for polymer solar cells. A highly crystalline small molecule named DPP-TP6 was synthesized and incorporated into the narrow bandgap polymer solar cells to optimize the morphology of PTB7:PC<sub>71</sub>BM active layer. The DPP-TP6 small molecule was demonstrated to enhance the light absorbance of active layer and play the role of energy cascade to increase the exciton separation and charge transfer. What's more, DPP-TP6 facilitated forming interpenetrating network structure and increasing the phase separation size of ternary blends. These phenomena lead to a higher hole mobility and a more balanced carrier mobility, so as to increase the power conversion efficiency to 7.85% at DPP-TP6 weight ratio of 8 wt %, comparing to the pristine PTB7:PC<sub>71</sub>BM system of 6.50%. © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *00*, 000–000

**KEYWORDS**: additives; conjugated polymers; morphology; polymer solar cells

**INTRODUCTION** Polymer solar cells have drawn significant attention in past decades due to their light weight, low-temperature solution-processing, good flexibility and large area manufacturing.<sup>1,2</sup> The power conversion efficiency (PCE) based on bulk heterojunction (BHJ) has reached above 10%, through designing new materials,<sup>3</sup> optimizing device structure,<sup>4</sup> applying new preparation technology, as well as optimizing morphology of active layer.<sup>5</sup>

The morphology of active layer is of great significance for device performance, especially for the formation of bicontinuous interpenetrating network structure with appropriate phase separation.<sup>6,7</sup> As a result of the exciton diffusion distance is only 10 nm, the phase separation size between the donor domain and the acceptor domain should be 10-20 nm to ensure more exciton be separated into electron-hole pair in the interface between donor domain and acceptor domain. In addition, the formed electron should transmit into the cathode along the acceptor domain, and the formed hole should transmit into the anode along the donor domain. Therefore, except for the phase separation size at 10–20 nm,

the film also requires to form bicontinuous interpenetrating network structure.<sup>8</sup> Meanwhile, crystallization is one of the most important driving force for the formation of interpenetrating network structure and phase separation, especially for crystallization of donor material.9 The active material with high crystallinity is easy to form crystalline phase during process of solvent evaporation. It can be considered that polymer donor is extracted from the blending system and form polymer crystalline region. Then, the rest of fullerene acceptor form fullerene aggregates. Hence, most active layer with highly crystalline donor could form a large phase separation. In addition, molecular interaction is another driving force, such as miscibility of donor and acceptor.<sup>10,11</sup> If the miscibility of donor and acceptor is very good, that is the interaction between them is large, the blend will be easy to form homogeneous phase, resulting in a small phase separation size. On the contrary, if the miscibility is very weak, that is the interaction is small, the blend will form independent phases with a big phase separation size. In a consequence, optimizing morphology of active layer to form bicontinuous

Dedication to the celebration of Prof. Ben-Zhong Tang's 60th birthday

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interpenetrating network structure is of great significance to improve device performance of polymer solar cell.<sup>12,13</sup>

In recent years, many scholars have made a lot of research on optimizing morphology of active layer for organic solar cell.<sup>14-18</sup> Generally speaking, the pristine and untreated active layer deposited by spin coating does not reach the thermodynamically equilibrium state. Thus, during process of fabricating active layer, the films need some special methods to achieve the optimized morphology. It has been reported that many physical methods, such as thermal annealing, solvent annealing, solvent additive, adding a third component, and so on could be applied to modulate morphology of active layer to realize higher photovoltaic performance.<sup>19–22</sup> Among them, adding a third component not only is an effective method to optimize morphology of active layer, but also is an easier and more simple method to achieve high performance in contrast of the tandem solar cell. The organic solar cell with a third component is also called ternary organic solar cell. Most ternary solar cells possess three crucial advantages, which are enhancing light absorption, playing the role of energy cascade and optimizing morphology of active layer.<sup>23–29</sup>

The polymer solar cell based on a narrow gap polymer with thieno[3,4-b]thiophene and benzodithiophene (PTB7) and PC<sub>71</sub>BM exhibits an excellent photovoltaic performance.<sup>30-33</sup> It possesses a high charge carrier mobility about  $10^{-4}-10^{-3}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, and high light absorption. But the phase separation size of PTB7:PC<sub>71</sub>BM film deposited from chlorobenzene (CB) is very large.<sup>13,15</sup> So, 1,8-diiodoctane (DIO) is a common solvent additive for the PTB7:PC<sub>71</sub>BM system to optimize morphology and reduce phase separation size.<sup>34</sup> Even so, DIO additive is of no effect on crystallization of polymer and interpenetrating network structure. In PTB7:PC<sub>71</sub>BM system, it is difficult to achieve an interpenetrating network structure and relative research is very infrequent, especially for the method of adding a third component.

Based on our previous study,<sup>35</sup> the liquid crystalline molecules such as 5CT could induce the crystallization of P3HT, in addition to the induction of aggregation of PCBM molecules, leading to eventual improvement of morphological stability of active layer. As reported previously, the donor of 3,6-bis{5-(4-alkylphenyl)thiophen-2-yl}-2,5-di(2-ethylhexyl)pyrrolo[3,4-c]-pyrrole-1,4-diones (DPP-TP6) exhibited the liquid crystalline behavior, showing of excellent PCE of 4.3% after blending with PC<sub>71</sub>BM.<sup>36</sup> By analyzing the energy levels of components, the DPP-TP6 liquid crystalline molecule might be useful in PTB7:PC<sub>71</sub>BM system by forming the cascade energy level alignment. Anyway, adding liquid crystalline molecules into the PTB7:PC<sub>71</sub>BM system has not been reported previously.

In this article, we are aimed to optimize morphology and facilitate formation of interpenetrate network structure for  $PTB7:PC_{71}BM$  active layer by simple solution blending method. The diketopyrrolopyrrole (DPP) based small molecule

3,6-bis{5-(4-alkylphenyl)thiophen-2-yl}-2,5-di(2-ethylhexyl)pyrrolo[3,4-c]-pyrrole-1,4-diones (DPP-TP6) possessing a high crystallinity was synthesized and incorporated into PTB7:PC<sub>71</sub>BM system to improve photovoltaic performance. The influence of DPP-TP6 weight ratio on light absorption, interpenetrating network structure of active layer, and photovoltaic performance was investigated. It is observed that adding of 8 wt % DPP-TP6 small molecule into PTB7:PC<sub>71</sub>BM solar cell could increase PCE value from 6.50 to 7.85%.

## **EXPERIMENTAL**

#### Materials

PTB7 was purchased from Rieke Metals, and  $PC_{71}BM$  (99.5% purity) was purchased from Nano-C. MoO<sub>3</sub> (99.99% purity) and Pd(PPh<sub>3</sub>)<sub>4</sub> was obtained from Alfa Aesar. Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH, K<sub>2</sub>CO<sub>3</sub>, CB, and 4-hexylphenylboronic acid were purchased from Sigma Aldrich, whereas indium tin oxide (ITO) glass was purchased from Delta Technologies Limited. All the reagents were used directly as received without further purification.

#### Synthesis of DPP-TP6

The 3,6-bis(5-bromothiophen-2-yl)-2,5-di(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4-diones(0.75 g, 1.10 mmol) and 4hexylphenylboronic acid (0.62 g, 3.00 mmol) were added into 30 mL dry toluene under stirring, followed by the addition of  $Pd(PPh_3)_4$  (0.075 g, 0.064 mmol) and aqueous  $K_2CO_3$ (2.0 M, 5 mL; N<sub>2</sub> bubbled before use). The mixture was vigorously stirred at 80 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into water, and then extracted with CHCl<sub>3</sub>. The combined organic layer was washed with water, and dried over anhydrous MgSO<sub>4</sub>. After filtration and evaporation, the crude product was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> as the eluent), recrystallized from CHCl<sub>3</sub>/methanol, and dried under vacuum to afford a dark violet solid. (yield = 0.71 g, 56%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.97 (d, 2H), 7.56 (d, 4H), 7.41 (d, 2H), 7.21 (d, 4H), 4.06 (m, 4H), 2.63 (t, 4H), 1.94 (m, 2H), 1.63 (m, 4H), 1.41-1.26 (m, 28H), 0.92-0.85 (m, 18H).

# **Fabrication of Inverted Devices**

The desired geometric configuration of ITO coated glass substrates were patterned by etching. The ITO glass substrates were cleaned by detergent, deionized water and isopropyl alcohol sequentially with ultrasound treating and dried by nitrogen flow, followed by UV treatment for 20 min. The cleaned ITO substrates were covered by spin-coating with a layer of ZnO through preparing ZnO precursor (in the Supporting Information) to form an electron transport layer, thermal annealing at 200 °C for 1 h, and transferring into nitrogen-filled glove box. The PTB7:PC71BM blends with different weight percentage of DPP-TP6 were spin-coated onto the top of ZnO layer producing about a 120 nm thick active layer. The ternary blend solution contains DIO additive with the volume ratio of DIO and CB of 3:97. After drying and driving off the residual solvent, 7 nm MoO<sub>3</sub> and 90 nm Ag were deposited on top of active layer by thermal evaporation

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with a mask at a pressure of  ${\sim}10^{-6}$  Torr as an anode. The detailed information of preparing PTB7:DPP-TP6:PC\_{71}BM ternary blends was shown in the Supporting Information.

# Characterization

The ultraviolet-visible (UV) spectra of the specimens were recorded by a PerkinElmer Lambda 750 spectrophotometer. Fluorescence measurement was carried out on a Hitachi F-7000 PC spectrofluorophotometer. To study the phase transition temperature and the crystallization behavior, differential scanning calorimetry (DSC) curves were obtained by TA DSC Q2000 differential scanning calorimeter with an invariable heating/cooling rate of 10°C/min. X-ray diffraction (XRD) study were recorded on a Bruker D8 Focus X-ray diffractometer with a copper target ( $\lambda = 1.54$  Å). Photocurrent/voltage (I/V) curves were recorded by using a Keithley 2400 Source Meter under 100 mW/cm<sup>2</sup> simulated AM 1.5 G irradiation (Abet Solar Simulator Sun 2000) and in the dark. The current-voltage characterization was recorded by using a Keithley 2400 Source Meter. The atomic force microscopy (AFM) images were gauged by nanoscope III A scanning probe microscope. The morphology of active layerwas conducted by employing transmission electron microscopy (TEM; JEM-2010 HR). The polarizing optical microscope (POM) images were obtained with a NIKON E600 POL equipped with a camera to investigate the morphology of the films.

#### **RESULTS AND DISCUSSION**

The DPP-TP6 small molecule was synthesized as described previously.<sup>36</sup> The molecular structure of DPP-TP6 is shown in Figure 1 and the corresponding <sup>1</sup>HNMR spectra is shown in Supporting Information Figure S1. The crystallization behavior of DPP-TP6 was investigated by differential scanning calorimetry (DSC) with the heating and cooling rate of 10 °C/min. The DPP-TP6 exhibits a conspicuous melting peak at 168.5 °C on the heating curve. In addition, a crystallization peak with the crystallization temperature of 134.6 °C could be noticed on the cooling curve. It is revealed that DPP-TP6 small molecule is crystalline, possessing of a high crystallinity.

The UV-vis absorption spectra of DPP-TP6 films from CB solution with or without thermal annealing were shown in Figure 1(b). The as-cast film exhibits two distinct peaks and an unconspicuous peak at 638, 584, and 543, respectively. The maximum absorption peak at 638 nm is corresponding to the  $\pi$ - $\pi^*$  [highest occupied molecular orbital (HOMO)lowest unoccupied molecular orbital (LUMO)] transition. The structured absorption is likely intrinsic to a single molecule with restricted intramolecular motion. The lowest vibronic band with the maximum absorption in the film originates from J-type aggregation, owing to excitonic coupling between the transition dipoles of adjacent molecules. It is worth noting that the absorption peak of J-aggregation band at 638 nm observed for as cast DPP-TP6 film steadily decreases and at the same time a new absorption band centered around 550 nm emerges upon thermal annealing at 140 °C 10 min. This variety of absorption is defining for



**FIGURE 1** (a) DSC cooling and heating curves of DPP-TP6 at a rate of  $10^{\circ}$ C/min, and the corresponding chemical structure of DPP-TP6. (b) UV-vis spectra of DPP-TP6 films without and with thermal annealing at 140°C.

characteristic of *H*-type aggregation. Therefore, upon thermal annealing, *J*-aggregation of the DPP-TP6 molecules transform into the thermodynamically favored *H*-aggregates with the specific stacking changes in film. The thermoresponsive reorganization behavior for DPP-TP6 is in accordance with the appearance of liquid crystalline state upon heating, in which the DPP-TP6 molecules retain at least some mobility. The DPP-TP6 small molecule is sensitive to thermal annealing within the transformation of aggregation state.

The polarizing microscope images of DPP-TP6 films with or without thermal annealing are shown in Figure 2. The ascast film exhibits some fascicular fibers that distributed in the whole film. However, upon the thermal annealing at 140 °C, the DPP-TP6 film presents spherulites as shown in Figure 2(b). The different crystalline morphology should correspond to the previous UV-vis absorption with two different aggregation states as shown in Figure 1(b). Corresponding XRD spectra in Supporting Information Figure S2 illustrates that the crystal form of DPP-TP6 is different before and after thermal annealing at 140 °C, with the  $2\theta$  value changing from





FIGURE 2 POM images of DPP-TP6 film (a) without and (b) with thermal annealing at 140 °C.

 $5.96^{\circ}$  to  $6.71^{\circ}$ . The interplanar distance is calculated to be 0.148 and 0.131 nm, respectively.

The molecular structure of PTB7 and PC71BM are shown in Figure 3(a). Figure 3(b) exhibits the UV-vis absorption of DPP-TP6, PTB7, and PC71BM in CB solution. The PTB7 specimen shows a strong absorption between 550 and 750 nm, with a shoulder peak at 622 nm and a maximum peak at 680 nm. The maximum absorption of  $PC_{71}BM$  stands on the short wavelength (300-500 nm). However, the DPP-TP6 specimen possesses a strong absorption between 500 and 650 nm. It reveals that the absorption of these three specimens is complementary on account of the different absorption in different wavelength. It could enhance the light absorption when these three components are blended together, to increase the current intensity. The ternary blends based on PTB7:DPP-TP6:PC71BM with different weight percentage of DPP-TP6 (0, 4, 8, 12, 16, and 100 wt %, the weight ratio of donor and acceptor was maintained to be 1:0.8) were prepared and the UV-vis absorption are shown in Figure 3(c). The pristine PTB7:PC<sub>71</sub>BM specimen exhibits an obvious absorption between 300 and 750 nm. As the content of DPP-TP6 increases, the light absorption of ternary blends increases and the enhanced absorption between 500 nm and 650 nm is attributed to DPP-TP6. As DPP-TP6 content increasing to 8 wt %, the absorption of ternary

blend reaches to the highest. It is believed that addition of DPP-TP6 could enhance the light absorption of ternary blends. The photoluminescence (PL) spectra (Supporting Information Figure S3) of PTB7:PC<sub>71</sub>BM specimen shows a strong PL emission peak at 480 nm assigned to radiative decay of excitons to ground state. Incorporation of DPP-TP6 into the active layer could decrease PL emission intensity. In addition, the specimen of PTB7:DPP-TP6:PC<sub>71</sub>BM with 8 wt % DPP-TP6 exhibits the weakest PL emission peak, indicating that the radiative decay to ground state decreases and the exciton dissociation efficiency increases.

The BHJ solar cells based on PTB7:DPP-TP6:PC $_{71}$ BM with different weight percentage of DPP-TP6 were fabricated. Device



**FIGURE 3** (a) Molecular structure of PTB7 and  $PC_{71}BM$ . (b) UVvis absorption profiles of PTB7,  $PC_{71}BM$ , and DPP-TP6 in CB solution. (c) UV-vis spectra of PTB7: $PC_{71}BM$  blend films containing different weight ratios of DPP-TP6.



**FIGURE 4** (a) The device structure of the inverted polymer solar cell, (b) energy-level diagram of the inverted structure used in ternary blend, (c) current-voltage (*J-V*) characteristics, and (d) EQE spectra of solar cells based on PTB7:PC<sub>71</sub>BM blends containing different weight ratios of DPP-TP6.

structure of ITO/ZnO/PTB7:DPP-TP6:PC<sub>71</sub>BM/MoO<sub>3</sub>/Ag and the energy-level diagram of inverted structure is shown in Figure 4(a,b), respectively. The LUMO and HOMO of DPP-TP6 are -3.7 and -5.5 eV, which lie between the values of PTB7 and PC<sub>71</sub>BM. It indicates that DPP-TP6 plays the role of a hole relay between PC<sub>71</sub>BM and PTB7 via its HOMO energy orbital. It could reduce the charge transfer barrier within active layer by decreasing recombination of photogenerated electrons and holes, according to the theory of cascade energy level alignment. This energy cascade provided a suitable prerequisite for good charge collection. Given that the energy levels of three components were well-matched, the open-circuit voltage did not significantly decrease in the present ternary system.

Figure 4(c) shows the current-voltage (*J-V*) characteristics of BHJ solar cell based on PTB7:DPP-TP6:PC<sub>71</sub>BM system at different weight percentage of DPP-TP6 that were measured under AM 1.5G (100 mW/cm<sup>2</sup>) light intensity illumination. A summary of photovoltaic performance parameters is given in Table 1. The device based on PTB7:PC<sub>71</sub>BM blends exhibits a PCE value of 6.5%, with a short-circuit current ( $J_{sc}$ ) of 13.45 mA cm<sup>-2</sup>, an open circuit voltage ( $V_{oc}$ ) of 0.726 V, and a fill factor (FF) of 66.3%, respectively. With increase of DPP-TP6

content to 8 wt %, the PCE reaches to the highest value of 7.85% for the corresponding solar cell device. As is expected, both of  $J_{\rm sc}$  and FF reach to the maximal value of 15.54 mA  $\text{cm}^{-2}$  and 69.2%, respectively. The series resistance ( $R_s$ ) decreases from 4.933 to 1.023  $\Omega \cdot \text{cm}^2$  and the shut resistance  $(R_{sh})$  possesses a little change, in contrast to pristine PTB7:PC<sub>71</sub>BM device. Consequently, the reduced  $R_s$  contribute to the enhanced device performance by increasing  $J_{sc}$ and FF that has to do with the morphology of active layer. As the DPP-TP6 content increases continuously,  $J_{sc}$  and FF begin to decrease. The  $V_{\rm oc}$  of ternary system exhibits a little change possessing to the increasing trend with increase of DPP-TP6 content. It can be concluded that adding a small amount of DPP-TP6 into PTB7:PC71BM system could improve  $J_{\rm sc}$ , FF, and  $V_{\rm oc}$  of device, resulting in a higher photovoltaic performance. In addition, the increased  $J_{sc}$  and PCE value have been determined by external quantum efficiency (EQE) shown in Figure 4(d). The enhanced EQE value could further interpret improvement of  $J_{\rm sc}$  and PCE.

All values represented averages from  $0.04 \text{ cm}^2$  devices on a single chip. And all data of devices had been tested from more than five substrates (15 chips) to ensure reproducibility.

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DPP-TP6 content (wt %)	J <sub>sc</sub> (mA/cm²)	V <sub>oc</sub> (V)	FF (%)	PCE (%)	$R_{ m s}~(\Omega~{ m cm}^2)$	$R_{ m sh}~(\Omega~{ m cm}^2)$
0	$13.45\pm0.3$	$\textbf{0.726} \pm \textbf{0.02}$	$66.3 \pm 1$	$\textbf{6.50} \pm \textbf{0.1}$	4.933	385.9
4	$14.37\pm0.2$	$\textbf{0.729} \pm \textbf{0.02}$	$68.4 \pm 1$	$\textbf{7.17} \pm \textbf{0.1}$	3.006	799.9
8	$15.54\pm0.3$	$\textbf{0.730} \pm \textbf{0.03}$	$69.2 \pm 1$	$\textbf{7.85} \pm \textbf{0.2}$	1.023	330.2
12	$14.01\pm0.2$	$\textbf{0.729} \pm \textbf{0.03}$	$69.0 \pm 2$	$\textbf{7.04} \pm \textbf{0.2}$	3.012	352.5
16	$13.82\pm0.2$	$\textbf{0.733} \pm \textbf{0.03}$	$\textbf{63.1}\pm\textbf{1}$	$\textbf{6.40} \pm \textbf{0.1}$	6.363	1833

**TABLE 1** Summary of the Photovoltaic Performance of PTB7:PC71BM Solar Cells Containing Different Weight Ratios of DPP-TP6under AM 1.5G Solar Illumination

To evaluate the apparent charge carrier mobility in the active layer,  $J^{0.5}$ -V characteristics of single charge carrier devices were measured using the space charge-limited-current (SCLC) model according to the Mott-Gurney equation:

$$J = (9/8)\mu\varepsilon_0\varepsilon_r (V^2/L^3)$$
 (1)

where *J* is the current density,  $\mu$  is the charge carrier mobility,  $\varepsilon_0$  is the permittivity of free space (8.85 × 10<sup>-12</sup> F·m<sup>-1</sup>),  $\varepsilon_r$  is the dielectric constant of PTB7 or PC<sub>71</sub>BM (assumed



**FIGURE 5**  $J^{0.5}$ -*V* characteristics of (a) hole-only and (b) electrononly devices containing different weight ratios of DPP-TP6.

to 3),  $\mu$  is carrier mobility, *V* is the applied voltage, and *L* is the film thickness.

The thickness of BHJ blend for SCLC measurement was about 120 nm. The J<sup>0.5</sup>-Vcharacteristics of hole-only and electrononly devices are shown in Figure 5. The summary of hole mobility and electron mobility that were fitted with SCLC model is shown in Table 2. The hole mobility and electron mobility of PTB7:PC<sub>71</sub>BM specimen are  $1.66 \times 10^{-4}$  $\mathrm{cm}^2 \cdot \mathrm{V}^{-1} \cdot \mathrm{s}^{-1}$  and 2.84  $\times$  10<sup>-4</sup>  $\mathrm{cm}^2 \cdot \mathrm{V}^{-1} \cdot \mathrm{s}^{-1}$ , respectively. As the DPP-TP6 content increases to 8 wt%, the specimen possesses a more balanced carrier mobility with hole mobility of 2.16  $\times$  10  $^{-4}$  cm  $^{2}$  V  $^{-1}$  s  $^{-1}$  and electron mobility of 2.30  $\times$  $10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ . When the DPP-TP6 content increases to 16 wt %, the carrier mobility shows of a decrease. The enhancement of hole mobility is mainly contributed to increased light absorbance and effect of energy cascade which have been mentioned above. In addition, the morphology of BHJ could be another factor resulting in the improvement of device performance.

To explore the internal morphology of thin films and to understand effect of morphology on device performance, the corresponding TEM images are shown in Figure 6. The specimen of PTB7:PC<sub>71</sub>BM blend shows of almost no discernable structure, attributing to a largely homogenous morphology without serious phase separation. The PTB7 and PC<sub>71</sub>BM could mix well after casting from CB containing 3% DIO solvent. However, the DPP-TP6:PC<sub>71</sub>BM specimen shows a

**TABLE 2** Hole Mobility and Electron Mobility of PTB7:PC71BM

 Solar Cells Containing Different Weight Ratios of DPP-TP6

 under AM 1.5G Solar Illumination

DPP-TP6 content (wt %)	Hole mobility (cm²/V·s)ª	Electron mobility (cm²/V·s) <sup>b</sup>
0	$1.66 imes10^{-4}$	$2.84 imes10^{-4}$
4	$1.83  imes 10^{-4}$	$2.74 imes10^{-4}$
8	$2.16 imes10^{-4}$	$2.30  imes 10^{-4}$
12	$1.96  imes 10^{-4}$	$2.62  imes 10^{-4}$
16	$1.53 imes10^{-4}$	$2.12  imes 10^{-4}$

 $^{\rm a}$  Hole-only device configuration: ITO/PEDOT:PSS/PTB7:DPP-TP6: PC\_{71}BM/MoO\_3/Ag.

<sup>b</sup> Electron-only device configuration: ITO/ZnO/PTB7:DPP-TP6:PC<sub>71</sub>BM/AI.

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FIGURE 6 TEM graphs of the PTB7:PC71BM films containing (a) 0, (b) 4, (c) 8, 12, 16, and (d) 100 wt % DPP-TP6, respectively.

remarkably different morphology, presenting a lot of black interpenetrating network structures throughout whole film. The black structures could be considered to be DPP-TP6 crystals and phase separation is more obvious. When 4 wt % DPP-TP6 was added into PTB7:PC71BM blend, the specimen presents a lot of unconspicuous interpenetrating network structures with a bigger phase separation, in contrast to the pristine PTB7:PC71BM specimen. As DPP-TP6 content increases to 8 wt %, the interpenetrating network structures could be observed obviously, and the size of separated phase becomes larger than that of PTB7:4 wt % DPP-TP6:PC71BM specimen. As DPP-TP6 content increases to 16 wt %, the interpenetrating network structures becomes more discernible, the phase separation is serious, resulting in decrease of charge separation efficiency. In other words, addition of DPP-TP6 into PTB7:PC71BM system could facilitate formation of interpenetrating network structures with a proper phase separation, leading to enhanced charge separation efficiency and charge transport efficiency.

To further investigate the morphology evolution of blend films after blending with DPP-TP6, AFM images are shown in Supporting Information Figure S4. The pristine PTB7:PC<sub>71</sub>BM film shows a small surface roughness with the root-meansquare value of 2.31 nm. As DPP-TP6 content increasing, the RMS value of corresponding specimen increases gradually. The variation of surface roughness should be corresponding to change of separated phase size in TEM images. Consequently, the addition of highly crystalline DPP-TP6 into PTB7:PC<sub>71</sub>BM blends could increase the surface roughness, resulting in a better contact between buffer layer and active layer.

In addition, in PTB7:DPP-TP6:PC<sub>71</sub>BM ternary blend films in Supporting Information Figure S5, no discernible diffraction peak ascribing to DPP-TP6 could be observed, indicating that the DPP-TP6 could not crystallize after incorporation into

PTB7:PC<sub>71</sub>BM blends. Moreover, the DPP-TP6 shows of no beneficial contribution to the thermal stability of PTB7:PC<sub>71</sub>BM. In Supporting Information Figure S6, the photovoltaic performance of PTB7:PC<sub>71</sub>BM devices deteriorate after thermal annealing at 150 °C for 30 min, especially for the specimens at high DPP-TP6 content. The corresponding parameters are shown in Supporting Information Table S2, the PCE value of PTB7:PC<sub>71</sub>BM system decreases to 2.0% after thermal annealing, which further reduces to 1.3% at DPP-TP6 content of 16 wt %. The reduction is mainly contributing to the depressed  $J_{sc}$  value, showing that DPP-TP6 is not beneficial to the improvement of thermal stability of PTB7:PC<sub>71</sub>BM due to the lack of supramolecular interactions between DPP-TP6 and PTB7 and PC<sub>71</sub>BM.<sup>37</sup>

# CONCLUSIONS

Highly crystalline small molecule DPP-TP6 was synthesized and the DPP-TP6 small molecule was easy to form nanofibroid structure due to its high crystallinity. The incorporation of DPP-TP6 into PTB7:PC71BM system was demonstrated to increase the PCE value to 7.85% at DPP-TP6 weight ratio of 8 wt %, in contrast to pristine PTB7:PC<sub>71</sub>BM system of 6.50%. The DPP-TP6 could make up the range of light absorbance, as to enhance light absorbance, as well as play the role of energy cascade to promote exciton separation and charge transfer. In addition, the addition of highly crystalline small molecule into PTB7:PC71BM blends could facilitate the formation of interpenetrating network structure for the active layer and increase phase separation size and surface roughness. The improved device performance was contributed to the enhanced light absorption of active layer, as well as higher and more balanced carrier mobility. The addition of third additive such as liquid crystalline molecules into the narrow bandgap polymer solar cells should be a versatile strategy to improve photovoltaic performance of corresponding devices. Anyway, the thermal stability may deteriorate upon incorporation of DPP-TP6, due



to the lack of supramolecular interactions between DPP-TP6 and other components.

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