Panchromatic Ternary Organic Solar Cells with Porphyrin Dimers and Absorption-Complementary Benzodithiophene-based Small Molecules

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KEYWORDS

Porphyrin dimers, diketopyrrolopyrrole, absorption-complementary, panchromatic, ternary organic solar cells

ABSTRACT

Diketopyrrolopyrrole-ethynylene-bridged porphyrin dimers are capped with electron deficient 3-ethylrhodanine ($A_2$) via a π-bridge of phenylene ethynylene, affording two new acceptor-donor-acceptor structural porphyrin dimers (DPP-2TTP and DPP-2TP) with strong absorption in ranges of 400–550 (Soret bands) and 700–900 nm (Q bands). Their intrinsic absorption deficiency between the Soret and Q bands could be perfect compensated by a wide bandgap small molecule DR3TBDTTF (D*) with absorption in 500–700 nm. Impressively, the optimal ternary device based on the blend films of DPP-2TP, DR3TBDTTF (20 wt.%) and PC$_{71}$BM, shows a PCE of 11.15%, while the binary devices based on DPP-2TTP/PC$_{71}$BM and DPP-2TP/PC$_{71}$BM blend films exhibit PCEs of 9.30% and 8.23%, respectively. The high compatibility of the low bandgap porphyrin dimers with the wide bandgap small molecule provides a new threesome with PC$_{71}$BM for highly efficient panchromatic ternary organic solar cells.
**Introduction**

Solution processed organic solar cells (OSCs), as an extensive green technology for solar energy production due to their potential mass production flexibility, low cost fabrication of large area and lightweight devices by solution processing techniques. In the past decade, the power conversion efficiency (PCE) has improved gradually to 14% for fullerene and non-fullerene based systems, which can be either small molecule and polymer binary or ternary bulk heterojunction (BHJ) OSCs. Although tandem OSCs containing two or more organic solar cells with different absorption maximum and width was reported with a record efficiency of 17%. Whereas, ternary OSCs should be an advisable way to achieve notable PCE, which contain either three or more components (two donors and one acceptor or two acceptors and one donor system) in the active layer. Accordingly, a record efficiency of 14% has been achieved in ternary OSCs with significantly enhanced photon harvesting by using absorption or energy level complementary materials as the second donor or acceptor. Most of the reported ternary OSCs are dominated by polymer donors or acceptors, whereas small molecules ternary devices have been sporadically reported. Fabricating small molecule ternary devices play an essential contribution such as remarkable molecular design, synthesis, easy purification and no batch-to-batch variations. Nian et al. reported recently, for ternary OSCs containing two molecule donors and an acceptor device exhibited PCE of 11%. Previously, we and several other groups have continuously developed series of porphyrin small molecules as electron donors in OSCs with PCEs up to 10%. Porphyrin derivatives are characteristic of strong absorption in a range of 400–500 nm (Soret band) and 550–650 nm (Q bands), whereas there is a very weak absorption between the Soret and Q bands. Structural modification by extending the π-conjugation with push-pull configuration only shifted the Soret and Q bands to longer wavelength range, but could not compensate the absorption
deficiency between them. For example, we ever reported a porphyrin dimer with strong absorption in ranges of 450–550 nm and 650–900 nm, but still weak absorption in a range of 550–650 nm.\textsuperscript{45} Although its device performance in binary OSCs is not so impressive with PCE of 8.29\%, its strong absorption in the short wavelength and deep near-infrared region render the porphyrin dimer an ideal donor component in small molecules ternary OSCs.\textsuperscript{46} Particularly, a large pool of small molecules for highly efficient binary OSCs have been founded previously by chemists which could facilely provide an appropriate one with complementary absorption in the range of 550–650 nm.

\begin{center}
\includegraphics[width=\textwidth]{scheme1.png}
\end{center}

\textbf{Scheme 1}. Synthetic routes for DPP-2TTP and DPP-2TP. Reactions conditions: a) CuI, Pd(PPh\textsubscript{3})\textsubscript{4}, THF, trimethylamine; b) 3-ethylrhodanine, dry CHCl\textsubscript{3}, piperidine, reflux, overnight.
In this work, we synthesized two porphyrin dimers of DPP-2TTP and DPP-2TP (Scheme 1) with an optimal A_2-π-D-A_1-D-π-A_2 architecture, in which the two electron rich porphyrin units (D) were bridged by an electron deficient diketopyrrolopyrole (DPP) (A_1), endcapped with electron deficient 3-ethylrhodanine (A_2) via a π-bridge of phenylene ethynylene. The DPP-2TTP and DPP-2TP differ in the porphyrin units with alkylthiothiophene (TT) and alkylthiophene (T) as vertical meso-substitutions, respectively. As expected, the two porphyrin dimers exhibited a very strong absorption in ranges of 400–550 nm (Soret bands) and 700-900 nm (Q bands), whereas the weak absorption between the Soret and Q bands could be perfect compensated by a wide bandgap small molecule of DR3TBDTTF with absorption in a range of 550–650 nm. Subsequently, the two porphyrin dimers were used as electron donors with PC_{71}BM as electron acceptor in binary OSCs, resulting in impressive device performances with PCEs up to 9.30%. Next, using absorption and energy level complementary small molecule DR3TBDTTF at a weight ratio of 20% as the second donor, the ternary device based on DPP-2TTP:20%DR3TBDTTF: PC_{71}BM active layer showed a high PCE of 11.15 %, which was mainly ascribed to the enhanced photocurrent generation and high compatibility of the three components with an appropriate morphology.

**Results and discussion**

The synthetic routes of the intermediates of 1 2, 3, (4–8)A and (4–8)B and the targeting porphyrin dimers of DPP-2TTP and DPP-2TP are depicted in Scheme S1 and Scheme 1 with the details in Supporting Information (SI). The key intermediate 3, 7A, and 7B were prepared according to the modified methods in literatures. Then the Sonogashira coupling of 7A and 7B with 3 led to the precursor 8A and 8B, respectively. The subsequent Knoevenagel condensation of 8A and 8B with 3-ethylrhodanine, respectively, afforded the porphyrin dimers of DPP-2TTP and DPP-2TP in good yields. Both the DPP-2TTP and DPP-2TP are soluble in most organic solvents for solution-processed BHJ OSCs.
Figure 1. a) UV–vis-NIR absorption spectra of DPP-2TTP and DPP-2TP in chloroform solution (1x10⁻⁵ M), absorption spectra of DPP-2TTP (b) and DPP-2TP (c) in films, d) DPP-2TTP: xD* (x = 10%, 20%, and 30%): PC₇₁BM in films (insert: molecular structure of DR3TBDTTF).

The absorption spectra of DPP-2TTP and DPP-2TP were recorded in CHCl₃ solution. As shown in Figure 1a and compiled in Table 1, the broad and intense Soret band appears at 490 nm with molar extinction coefficient (ε) of 2.21 × 10⁵ M⁻¹ cm⁻¹ for DPP-2TTP and 480 nm with ε of 2.1 × 10⁵ M⁻¹ cm⁻¹ for DPP-2TP. The Q band attributes in the near-infrared region, which is 810 nm (ε = 2.16 × 10⁵ M⁻¹ cm⁻¹) with a weak shoulder of 762 nm for DPP-2TTP, similarly, 812 nm (ε = 2.04 × 10⁵ M⁻¹ cm⁻¹) and 760 nm for DPP-2TP. The wide and near-infrared absorption
of Q bands from 650 to 870 nm is ascribed to the efficient conjugation of the backbone structure of porphyrin dimer and intramolecular charge transfer (ICT) between the terminal acceptor units through the π-linker.\textsuperscript{50-52} The blend thin films DPP-2TTP (or DPP-2TP): PC\textsubscript{71}BM (1:1.5, w/w) were spin-coated from their chlorobenzene (CB) solutions and processed under solvent-vapor annealing (SVA) and thermal annealing (TA). The film spectra as shown in Figure 1(b, c) disclose significantly broad bathochromic absorption extended into NIR region over 1000 nm, which indicates stronger interelectronic π-π aggregations between the porphyrin dimers in the film. In addition, those films under SVA and TA processing show slightly increased intensity of absorption due to more orderly packed molecular interactions.\textsuperscript{53} Next, the blend films of DR3TBDTTF (D*) at a weight ratio of 10, 20, and 30%, respectively, with DPP-2TTP and PC\textsubscript{71}BM (DPP-2TTP:xD*:PCBM, x = 10\%, 20\%, and 30\%) were prepared similarly and recorded with full spectra in the visible-NIR region from 300 to 1000 nm (Figure 1d) because of the significant contribution of DR3TBDTTF component in a range of 550–700 nm. Moreover, the optical band gaps ($E_{\text{g opt}}$) were measured from the onset wavelength ($\lambda_{\text{onset}}$) of the absorption spectra of solution using $E_{\text{g opt}} = 1240 / \lambda_{\text{onset}}$ (eV), with low band gap values of 1.33 for DPP-2TTP and 1.34 eV for DPP-2TP.

Table 1. Photophysical and electrochemical properties of DPP-2TTP and DPP-2TP

<table>
<thead>
<tr>
<th>Comp</th>
<th>$\lambda_{\text{max}}$/nm ($\varepsilon/10^5\text{M}^{-1}\text{cm}^{-1}$)</th>
<th>$\lambda_{\text{max}}$/nm (Film)</th>
<th>$\lambda_{\text{onset}}$/nm (Solution)</th>
<th>$E_{\text{ox}}$ [V]</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
<th>$E_{\text{g}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPP-2TTP</td>
<td>490 (2.21), 752 (1.86), 810 (2.16)</td>
<td>485, 762, 831</td>
<td>932</td>
<td>0.38</td>
<td>−5.18</td>
<td>−3.77</td>
<td>1.33</td>
</tr>
<tr>
<td>DPP-2TP</td>
<td>480 (2.10), 755 (1.86), 812 (2.04)</td>
<td>475, 760, 830</td>
<td>923</td>
<td>0.36</td>
<td>−5.16</td>
<td>−3.76</td>
<td>1.34</td>
</tr>
</tbody>
</table>
Photoluminescence (PL) were performed to study the charge transfer process for the blend films. **Figure 2** (a) shows the PL spectra of the pristine and the binary blend films of D* and DPP-2TTP. When excited at 660 nm in an overlap absorption region of DPP-2TTP and D*, both the pristine films of D* and DPP-2TTP exhibits weak PL in the near-infrared region, whereas the blend film DPP-2TTP:20%D* exhibits a quenched PL of D* and intensity increased PL of DPP-2TTP. The result indicates efficient energy transfer (ET) from D* to DPP-2TTP, which is also supported by the large overlap between the emission spectrum of D* and the absorption spectrum of DPP-2TTP. Obviously, the efficient energy transfer between the two components is helpful to achieve high photocurrent in ternary OSCs. At the same time, the efficient energy transfer implies a good miscibility between D* and DPP-2TTP molecules, which is conducive to the formation of appropriate phase separation for high fill factor (FF) in ternary OSCs. Their sequential alignment of highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) (**Figure 2b**), also depicts that excitons could be efficient generated after light irradiation.
and undergo a considerable charge separation and transfer at the ternary blend interface of DPP-2TTP:D*:PC$_{71}$BM.$^{55}$

Cyclic voltammetry (CV) of two porphyrin dimers were recorded in CHCl$_3$ solution to estimate the energy levels and study the redox properties. As shown in Figure S1 (SI) and Table 1, the highest occupied molecular orbital (HOMO) energy levels were calculated from the onset of oxidation peaks to be $-5.18$ and $-5.16$ eV, and the corresponding lowest unoccupied molecular orbitals (LUMOs) were estimated to be $-3.77$ and $-3.76$ eV ($E_{LUMO} = E_{HOMO} + E_g$) for DPP-2TTP and DPP-2TP, respectively. The introduction of sulfur atoms in alkyl chains for DPP-2TTP does not effect on the band gap but slightly lowers its HOMO level due to the unique electron donating property of sulfur atom, which would lead to higher $V_{OC}$ (vide infra).$^{56}$ For consistence, the CV of D* was also recoded under the same conditions and its HOMO/LUMO energy levels were calculated to be $-5.15/-3.10$. As shown in Figure 2d, the perfect sequential alignment of their HOMO/LUMO energy levels indicated the electron at their interfaces could efficiently transfer from DR3TBDTTF (D*) to DPP-2TTP and then PC$_{71}$BM for the descending order of LUMOs, while hole transfers reversibly for the increasing order of HOMOs. In other words, DPP-2TTP might act as electron and hole transfer relay between the DR3TBDTTF and PC$_{71}$BM.

The photovoltaic studies were performed using DPP-2TTP and DPP-2TP as donors in the binary devices of ITO/PEDOT:PSS/Donor:PC$_{71}$BM/ZrAcac/Al under the simulated AM 1.5 G illumination at 100 mW cm$^{-2}$. After the systematic optimization (see Table S1, S2, and Figure S2 in SI), the optimal devices were screened out with a combination of chlorobenzene (CB): pyridine:1,8-diiodooctane (DIO) at 96:3:1 volume ratio (v%) and thermal annealing at 100 °C for 10 mins. The photovoltaic parameters of the optimal binary devices were summarized in Table 2. And the corresponding current density versus voltage ($J-V$) characteristics and the external
quantum efficiency (EQE) curves were illustrated in Figure 3 (a, b) respectively. The optimal binary devices exhibit a maximum PCE of 9.30% with an open circuit voltage ($V_{OC}$) of 0.80 V, a short circuit current ($J_{SC}$) of 16.35 mA cm$^{-2}$ and a fill factor (FF) of 71.1% for DPP-2TTP and similarly, a PCE of 8.23%, a $V_{OC}$ of 0.76 V, a $J_{SC}$ of 15.65 mA cm$^{-2}$ and a FF of 69.2% for DPP-2TP. Impressively, the two binary systems gained reliable low photon energy loss ($E_{loss}$) of 0.58 eV for DPP-2TTP and 0.6 eV for DPP-2TP, which is essential for the enhancement of $J_{sc}$ and PCE values. Peng et al. published DPP-porphyrin small molecule with a very low energy band gap of 1.37 eV and a high $V_{oc}$ of 0.78 V was achieved in BHJ OSCs and followed by a low energy loss of 0.59 eV. These results indicated a suitable alignment of the HOMO/LUMO energy levels of those components in the ternary blend active layer.

Figure 3. (a) Current density-voltage ($J$-$V$) curves and (b) the EQE curves for the devices under constant incident light intensity (AM 1.5G, 100 mW cm$^{-2}$) without and with SVA.

Table 2. Hole and electron mobilities and key parameters of device performances$^a$

<table>
<thead>
<tr>
<th>Device</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)$^b$</th>
<th>$\mu_h$ (cm$^2$/Vs)</th>
<th>$\mu_e$ (cm$^2$/Vs)</th>
<th>$\mu_e/\mu_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPP-2TTP: PC$_{71}$BM</td>
<td>16.35 ± 0.08 (16.02)$^b$</td>
<td>0.80 ± 0.01</td>
<td>71.1 ± 0.3</td>
<td>9.10 ± 0.20</td>
<td>1.25×10$^{-4}$</td>
<td>8.16×10$^{-5}$</td>
<td>0.65</td>
</tr>
<tr>
<td>Material</td>
<td>PCE (%)</td>
<td>$J_{SC}$ (mA cm$^{-2}$)</td>
<td>FF (%)</td>
<td>$V_{OC}$ (V)</td>
<td></td>
<td></td>
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<tr>
<td>DPP-2TP: PC$_{71}$BM</td>
<td>15.54 ± 0.09</td>
<td>0.76 ± 0.01</td>
<td>68.7 ± 0.3</td>
<td>8.00 ± 0.11</td>
<td></td>
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<tr>
<td>DPP-2TTP: 10%D*:PC$_{71}$BM</td>
<td>17.16 ± 0.13</td>
<td>0.81 ± 0.02</td>
<td>73.3 ± 0.6</td>
<td>10.03 ± 0.14</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>DPP-2TTP: 20%D*:PC$_{71}$BM</td>
<td>17.78 ± 0.11</td>
<td>0.82 ± 0.03</td>
<td>76.5 ± 0.6</td>
<td>11.01 ± 0.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPP-2TTP: 30%D*:PC$_{71}$BM</td>
<td>17.41 ± 0.19</td>
<td>0.83 ± 0.06</td>
<td>71.6 ± 0.2</td>
<td>10.16 ± 0.18</td>
<td></td>
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</tbody>
</table>

$^a$ Each value is averaged from 8 devices with standard deviation after ±. $^b$ Values in brackets are calculated from EQE.

Although the optimal binary devices showed a wide photocurrent response extending into 900 nm owing to the contribution of low bandgap porphyrin-based small molecules, the low EQE value of 27% at the bottom of the valley clearly reflected the intrinsic absorption deficiency between the Soret and Q bands in porphyrin-based small molecules. It is believed that ternary OSCs containing one more donor or acceptor have great potential to reduce the energy loss, enhance light-harvesting capability and improve device performance. Therefore, the wide bandgap small molecule electron donor DR3TBDTTF was selected as a third component for ternary OSCs for its complementary absorption spectrum and aligned energy levels regarding porphyrin-based small molecules. The blend films were fabricated from DPP-2TTP:D*:PC$_{71}$BM with different weight ratio (w/w) of D* at 10%, 20%, and 30% in 0.3 volume% of pyridine and chlorobenzene solution. Compared with the binary device DPP-2TTP: PC$_{71}$BM, the ternary devices based on the three active layers DPP-2TTP:xD*:PC$_{71}$BM (x = 10%, 20%, 30%, w/w) exhibit enhanced PCEs of 10.19%, 11.15% and 10.34% respectively. And the current density-voltage ($J$-$V$) characteristics are displayed in Figure 3a. For the ternary, the content of D* increased from 10 to 20 wt.%, led to progressively enhanced $J_{SC}$ from 17.29 to 17.89 mA cm$^{-2}$, FF from 73.4 to 77.1% 76.5%, and $V_{OC}$ from 0.83 to 0.85 V. This is mainly due to the improved light-harvesting capability in the range of 550–700 nm and favorable morphology for efficient charge dissociation and transfer in ternary devices with D*. 

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which is well consistent with PL experiments. Further increasing the content of DR3TBDTTF could continue to improve the light-harvesting in the range of 550–700 nm, but impair the light-harvesting in the Soret and Q regions of porphyrin-based small molecules. At the same time, high content of D* would lead to unfavorable morphology. As a result, the ternary device with 30% DR3TBDTTF exhibits a balanced \( J_{SC} \), slightly enhanced \( V_{OC} \), but significantly decreased FF, as a whole an inferior PCE of 10.34%. In addition, the integrated \( J_{SC} \) values are listed in Table 2 from EQE spectra for all the devices are consistent with \( J-V \) measurements with errors in 2%.

Further, we studied the exciton generation, dissociation and charge collection of the active layers through the charge photocurrent density \( (J_{sat}) \) and the effective voltage \( (V_{eff}) \). The binary DPP-2TTP:PC\(_{71}\)BM, DPP-2TP:PC\(_{71}\)BM and optimized ternary DPP-2TTP:20%D*:PC\(_{71}\)BM devices were carried under SVA conditions as shown in Figure S3a (SI). The photocurrent density \( (J_{ph}) \), as a function of the \( V_{eff} = V_0 - V_a \), where \( V_0 \) is voltage when \( J_{ph} = 0 \) and \( V_a \) is the applied voltage, is calculated by \( J_{ph} = J_L - J_D \), where \( J_L \) is the current density under illumination and \( J_D \) is the current density in the dark.\(^{57,58}\) Obviously, the \( J_{ph} \) increases rapidly with the increasing voltages within lower levels and becomes saturated when the effective voltage \( V_{eff} \) reaches 0.34 V, 0.32 V and 0.38 V for the devices based on the active layers of DPP-2TTP, DPP-2TP and DPP-2TTP:20%D*, respectively, which means that all the photo-generated excitons would be dissociated to free charge carriers and collected by the electrodes under high internal electric field. Moreover, the charge dissociation probabilities \( P(E,T) \) was conducted by normalizing of \( J_{ph} \) with \( J_{sat} \) under short circuit condition \( (J_{ph}/J_{sat}) \) to be 0.92% for DPP-2TTP: PC\(_{71}\)BM, 0.93% for DPP-2TP:PC\(_{71}\)BM and 0.95% for DPP-2TTP:20%D*:PC\(_{71}\)BM, as shown in Figure S3a. The higher \( P(E,T) \) value for ternary blend was correlated to the excellent \( J_{SC} \) of 17.78 mA cm\(^{-2}\), suggesting
that the contribution of 20% D* to the ternary blend is more capable for efficient charge collection than the binary devices.\textsuperscript{57,59-61}

To get more information about the effect of the involvement of D* on the charge recombination dynamics of the ternary devices, the variations of $J_{SC}$ and $V_{OC}$ versus light intensity were evaluated, respectively. As shown in Figure S3 (b, c) (SI) the slope ($\alpha$) of the ternary device was calculated to be 0.997 for DPP-2TTP:20%D*, which is slightly higher than that of the binary devices with values of 0.991 and 0.981 for DPP-2TTP and DPP-2TP, respectively. The $\alpha$ values close to 1 ($\alpha < 1$) implies that bimolecular recombination is not a crucial loss mechanism in both binary and ternary devices. On the other hand, the slope ($S = kT/q$, where $k$ is Boltzmann’s constant, $T$ is the temperature and $q$ is the elementary charge) of the $V_{OC}$ versus the natural logarithm of the light intensity, were predicted to be 1.19 (kT/q) for DPP-2TTP and 1.27 (kT/q) for DPP-2TP of the binary devices. As expected, the ternary blend of DPP-2TTP: 20%D* shows a lower slope of 1.10 (kT/q), implying a reduced trap-assisted recombination. As a result, the ternary device shows the highest FF of 76.5% and $V_{OC}$ of 0.85 V.\textsuperscript{62}

![Figure 4](image-url) Dark current-voltage characteristics of a) hole and b) electron only devices based on optimized devices Glass/ITO/PEDOT: PSS/active layer/MoO$_3$/Au and glass/Al/active layer/Al.
To further investigate the effect of D* on the performance of ternary solar cells, hole and electron mobilities of the optimal devices ITO/PEDOT: PSS/active layer/MoO$_3$/Au were measured by space charge limited current (SCLC) method as shown in Figure 4 (a, b) and the estimated values are displayed in Table 2. The hole mobilities of the binary films were calculated to be $1.25 \times 10^{-4}$ and cm$^2$/Vs for DPP-2TTP: PC$_{71}$BM, $8.83 \times 10^{-5}$ cm$^2$/Vs for DPP-2TP: PC$_{71}$BM, and $1.72 \times 10^{-4}$, $3.21 \times 10^{-4}$ and $2.36 \times 10^{-4}$ cm$^2$/Vs for the DPP-2TTP:xD*:PC$_{71}$BM ($x = 10, 20, 30$%), respectively. The electron mobilities are noted to be $8.16 \times 10^{-5}$ cm$^2$/Vs for DPP-2TTP:PC$_{71}$BM, $4.32 \times 10^{-5}$ cm$^2$/Vs for DPP-2TP:PC$_{71}$BM, and $1.28 \times 10^{-4}$, $2.84 \times 10^{-4}$ and $1.97 \times 10^{-4}$ cm$^2$/Vs for the DPP-2TTP:xD*:PC$_{71}$BM ($x = 10, 20, 30$%), respectively. The hole and electron mobilities were increased dramatically with the 20% weight ratio of D* in the ternary blend and then decreased with 30% of D*, this clearly suggesting that molecular arrangement could be adjusted by the contribution of D*. Moreover, electron to hole ($\mu_e/\mu_h$) ratio of DPP-2TTP:20%D*:PC$_{71}$BM shows a notable value of 0.88, which means the charge transport is more balanced on the 20% weight ratio of D* in the blend film. This process is applicable to increase the crystallinity and nanoscale morphology of the active layers. Whereas, the ternary blend of D* (30%) dropped from 0.88 to 0.83, which led to unbalanced hole and electron mobilities due to unfavorable morphology.
Figure 5. AFM height images (top) and phase images (bottom) of binary blend films of DPP-
2TTP:PC$_{71}$BM, DPP-2TP:PC$_{71}$BM and ternary blend films of DPP-2TTP:xD*:PC$_{71}$BM (x = 10%,
20%, 30%) from left to right. The scan size is 5 µm × 5 µm for all images.

At the same time, the morphology of the optimized binary and ternary blend films was analyzed
by trapping-mode atomic force microscopy (AFM). As shown in Figure 5, the height images (top)
from the corresponding binary devices DPP-2TTP:PC$_{71}$BM, DPP-2TP):PC$_{71}$BM and DPP-
2TTP:xD*:PC$_{71}$BM (x = 10%, 20%, 30%) are correlated to a root mean square roughness (RMS)
of 2.25 nm, 2.31 nm, 2.20 nm, 2.08 nm, and 2.35 nm, respectively. Obviously, a smoother surface
with an RMS of 2.08 nm was observed with 20% D* in the ternary blend, which should be
beneficial for more efficient exciton dissociation and charge transport to support for higher $J_{sc}$ and
PCE values. On the contrary, the doping of 30% D* led to unfavorable morphology with larger
phase separation. On the other side, the phase images (bottom) also indicate that the 20%D* in the
ternary blend is helpful to form bicontinuous interpenetrated heterojunction structure for efficient
charge dissociation and transfer.

Figure 6. a) GIWAXS 2D diffraction patterns, b) out-of-plane (solid line) and in-plane (dotted
line) line-cut profiles, and c) RSoXS profiles of DPP-2TTP:PC$_{71}$BM, DPP-2TP:PC$_{71}$BM binary
blend films and DPP-2TTP:xD*: PC$_{71}$BM ternary blend films (x = 10%, 20% and 30%).
Detailed molecular packing information was acquired by performing grazing incidence wide-angle X-ray scattering (GIWAXS) measurements. The 2D GIWAXS patterns and corresponding out-of-plane and in-plane line-cuts are shown in Figure 6 (a, b) When blending with PC$_{71}$BM in binary systems, both DPP-2TTP and DPP-2TP show sharp (100) diffraction peaks in both in-plane and out-of-plane directions, with $q \sim 0.27$ Å$^{-1}$ ($d$-spacing: 23.3 Å) for DPP-2TTP and $q \sim 0.28$ Å$^{-1}$ ($d$-spacing: 22.4 Å) for DPP-2TP respectively. DPP-2TTP shows preferential face-on orientation with stronger out-of-plane (010) π-π stacking peak at $q \sim 1.78$ Å$^{-1}$ ($d$-spacing: 3.53 Å), whereas DPP-2TP exhibits no preferential π-π stacking orientation judging from the almost isotropic scattering ring at $q \sim 1.78$ Å$^{-1}$. The coherence length of out-of-plane (010) π-π stacking peak was calculated to be 20.5 Å and 19.0 Å for DPP-2TTP and DPP-2TP respectively. Although DPP-2TP had a better lamellar packing than DPP-2TTP with a more pronounced (100) peak, preferential face-on π-π stacking of DPP-2TTP made it more beneficial for charge transport, which is shown in the enhancement of hole mobility and FF. When the third component D* was added to the DPP-2TTP:PC$_{71}$BM blend, the lamellar packing of DPP-2TTP was greatly depressed as evidenced by weakening and broadening of the (100) peaks in both in-plane and out-of-plane directions. The coherence length of DPP-2TTP lamellar packing decreased from 12.8 nm in binary film to 12.5, 9.6 and 7.1 nm with addition of 10%, 20% and 30% D*. Similarly, the coherence length of π-π stacking also shrank slightly from 2.6 nm to 2.5, 2.2 and 2.1 nm. Considering that no D* diffraction peak was observed in the ternary blend films, we concluded that DR3TBDTTF dissolve into the DPP-2TTP domain and disturb the molecular packing of DPP-2TTP inhibiting formation of big crystallites. However, the increased integrated intensity of (100) and (010) diffraction peaks indicated that the crystallinity of donor domain in ternary systems was improved with the addition of D*, resulting in the enhanced mobility and FF of the devices.
Resonant soft X-ray scattering (RSoXS) was used to investigate the phase separation of binary and ternary blend films. A photon energy of 284.2 eV was selected to enhance the contrast between PCBM and donor blends. As seen from Figure 6c, both DPP-2TTP:PC$_{71}$BM and DPP-2TP:PC$_{71}$BM binary blend films showed similar scattering profiles with main peak located at $q \sim 0.0032$ Å$^{-1}$, corresponding to a phase separation distance of $\sim 190$ nm, and shoulder peak at high $q$ which is caused by refined phase separation. There are also scattering peaks in the low $q$ region beyond the detection limits, which means larger phase separation in binary blends as confirmed by the AFM results. The addition of D* attenuated the scattering peak in the low $q$ and prevented the ternary blend films from forming larger phase separation which was detrimental for charge generation. Compared with the DPP-2TTP:PC$_{71}$BM film, the prime peak shifted to $\sim 0.0034$, 0.0042 and 0.0035 Å$^{-1}$ with smaller phase separation distance of 184, 150 and 180 nm in the ternary blend films with (10%, 20%, 30%)D* respectively. Although the phase separation distance reduced in ternary films, such phase separation distance was still too large for efficient charge separation since exciton diffusion length is generally considered to be $\sim 10$ nm. This indication clearly showed hierarchical morphology containing smaller domains had formed in the blend film.

Conclusions

In summary, two low bandgap porphyrin-based small molecules DPP-2TTP and DPP-2TP have been prepared and showed an intrinsic absorption range 400–550 (Soret bands) and 700–900 nm (Q bands). To overcome the absorption deficiency from 550 to 700 nm, a wide bandgap small molecule DR3TBDTTF has been contributed and optimized for the ternary devices. Such a combination performed synergically to improve the absorption range over 1000 nm and the key parameters as well. Especially, the device based ternary blend DPP-2TPP:20% DR3TBDTTF:PC$_{71}$BM showed a remarkable PCE of 11.15% with a significant FF of 77.1%,
which is highly considerable in comparison with the binary devices on DPP-2TTP:PC$_71$BM (9.30%) and DPP-2TP:PC$_71$BM (8.23%). The improved overall performance of the ternary devices could be attributed to complementary absorption of the two donors and favorable film morphology for the reduced recombination and enhanced charge extraction.

ASSOCIATED CONTENT

Supporting Information

The Supporting information is available free of charge on the http://pubs.acs.org/

The details of the synthesis and characterization of the targeting compounds DPP-2TTP and DPP-2TP, the intermediates 1–3, 4A–8A, and 4B–8B, device fabrication, photovoltaic performances and $J$-$V$ curves under various conditions, Variation of $J_{SC}$ and $V_{OC}$ with illumination intensity, $J_{ph}$-$V_{eff}$ characteristics, NMR spectra and MALDI-TOF mass spectra.

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ABBREVIATIONS
Nucleur magnetic resonance (NMR), Matrix-assisted laser desorption/ionization-time-of-flight (MALDI-TOF)

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Notes

The authors declare no competing financial interest.

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