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Simultaneous Improvement in Short Circuit Current, Open Circuit Voltage, and Fill Factor of Polymer Solar Cells through Ternary Strategy

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ABSTRACT: We present a smart strategy to simultaneously increase the short circuit current ($J_{sc}$), the open circuit voltage ($V_{oc}$) and the fill factor (FF) of polymer solar cells (PSCs). A two-dimensional conjugated small molecule material (SMPV1), as the second electron donor, was doped into the blend system of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C71-butyric acid methyl (PC$_{71}$BM) to form ternary PSCs. The ternary PSCs with 5 wt% SMPV1 doping ratio in donors achieve 4.06% champion power conversion efficiency (PCE), corresponding to about 21.2% enhancement compared with the 3.35% PCE of P3HT:PC$_{71}$BM-based PSCs. The underlying mechanism on performance improvement of ternary PSCs can be
summarized as (i) harvesting more photons in the longer wavelength region to increase $J_{sc}$; (ii) obtaining the lower mixed HOMO energy level by incorporating SMPV1 to increase $V_{oc}$; (iii) forming the better charge carrier transport channels through the cascade energy level structure, optimized phase separation of donor/acceptor materials to increase $J_{sc}$ and FF.

**KEYWORDS:** polymer solar cells, ternary strategy, energy transfer, charge carrier transfer, energy level

**INTRODUCTION**

Bulk heterojunction polymer solar cells (PSCs), as a promising photovoltaic technology, can be fabricated by solution processing and roll-to-roll manufacturing techniques with advantages of the better exciton dissociation efficiency and charge carrier transport due to the bicontinuous interpenetrating network in the active layers.\(^1\)\(^-\)\(^4\) In recent years, PSCs have achieved a considerable progress in power conversion efficiency (PCE) that has exceeded 10% with various strategies.\(^5\)\(^-\)\(^7\) It is generally believed that the PCE of PSCs is proportional to the product of short circuit current ($J_{sc}$), open circuit voltage ($V_{oc}$) and fill factor (FF).\(^8\)\(^-\)\(^9\) In order to improve the PCE, many effective strategies have been carried out to increase the $J_{sc}$, $V_{oc}$ and FF (three key photovoltaic parameters) by developing novel narrow bandgap material, adapting tandem device structure or active layer treatment methods.\(^10\)\(^-\)\(^13\) For instance, design and synthesis of narrow bandgap donor materials can harvest more photons from the solar light for $J_{sc}$ improvement.\(^14\)\(^-\)\(^16\) The tandem structure solar cells stack
two or more subcells can increase either the $J_{sc}$ or $V_{oc}$ for the subcells in parallel or
series, while the intricate production process is a serious challenge for large-area
fabrication.\textsuperscript{17-19} The surface morphology, phase separation and crystalline of active
layers can be optimized by incorporating additive or employing proper annealing
treatment for the $J_{sc}$ and FF improvement.\textsuperscript{20-23} Up to now, fewer strategies can
simultaneously improve the three key photovoltaic parameters for the performance
improvement of PSCs.\textsuperscript{24}

Recently, ternary strategy is expected to play an important role in achieving high
performance PSCs, which inherit the major benefit of incorporating multiple organic
materials in tandem cells while retaining the simple cell fabrication technology.\textsuperscript{25-30}
Ameri et al. reported that the $J_{sc}$ can be improved from 8.6 mA/cm$^2$ to 12 mA/cm$^2$ by
doping a low bandgap material into the system of poly(3-hexylthiophene) (P3HT) and
[6,6]-phenyl-C61-butyric acid methyl (PCBM), resulting in the PCE increased from
3.1% to 4%.\textsuperscript{31} Thompson et al. demonstrated that the $V_{oc}$ can be gradually increased
by only changing the doping weight ratios of two donors or two acceptors in ternary
PSCs.\textsuperscript{32-34} Chen et al. realized the FF improvement from 40.6% to 54.3% by
employing P3HT as an additive to adjust morphology of active layer.\textsuperscript{35} It is
reasonable to believe that the three key photovoltaic parameters of PSCs can be
simultaneously optimized through well-designed ternary strategy.

In ternary strategy, the active layers with polymer/polymer/fullerene system
generally have a strong tendency to undergo enthalpy-driven phase-separation, which
results in serious phase separation with domain sizes in the micrometer range\textsuperscript{36}. 

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Ruderer et al. reported that the ideal scale of the phase separation in active layer should be approximately equal to exciton diffusion length (~ 10nm), which is a crucial factor to affect exciton dissociation and charge carrier transport\textsuperscript{37}. The ternary strategies based on polymer/polymer/fullerene system are less effective than the polymer/small molecule/fullerene system due to the large scale of the phase separation. Recently, Liu et al. reported a high efficient two-dimensional conjugated small molecule photovoltaic material (SMPV1) which has excellent solubility in organic solvents and high absorption coefficient in the longer wavelength range\textsuperscript{38}. There is a larger absorption spectral complementary between P3HT and SMPV1, which provides the opportunity to fabricate high efficiency ternary PSCs based on P3HT and SMPV1 as the electron donors. In this research, the small molecule material SMPV1, as the second electron donor, was mixed with P3HT and [6,6]-phenyl-C71-butyric acid methyl (PC\textsubscript{71}BM) to fabricate ternary PSCs. The PCE values of PSCs were improved from 3.35% to 4.06% for the ternary cells with 5 wt% SMPV1 doping ratio in donors, which is attributed to a substantial improvement $J_{sc}$ and FF as well as a slight $V_{oc}$ increase.

**EXPERIMENTAL SECTION**

The patterned indium tin oxide (ITO) glass coated substrates (sheet resistance 15 $\Omega/\square$) were cleaned consecutively in ultrasonic baths containing acetone, detergent, de-ionized water and ethanol, respectively. The cleaned ITO substrates were blow-dried by high pure nitrogen gas and then treated by UV-ozone for 10 minutes in order to further increase the work function of ITO substrates. The
poly-(3,4-ethylenedioxythiophene):poly-(styrenesulphonicacid) (PEDOT:PSS)
(purchased from H.C. Starck co. Ltd.) thin films were fabricated on the cleaned ITO substrates by spin-coating method at 5000 round per minute (RPM) for 40 s, and then annealed at 150 °C for 10 minutes in air environment. The electron donor materials P3HT, SMPV1 and electron acceptor materials PC$_{71}$BM were purchased from Luminescence Technology Corp. The SMPV1 doping weight ratios are 0, 2.5 wt%, 5.0 wt%, 7.5 wt%, 15 wt% in electron donors (P3HT and SMPV1) and the weight ratio of donors to acceptor was kept constant as 1:1. The mixed materials (P3HT$_{1-x}$;SMPV1$_{x}$;PCBM$_{1}$) were dissolved in 1,2-dichlorobenzene to fabricate 40 mg/ml blend solutions, the subscript represents SMPV1 doping ratio in donors, $x=0$, 2.5%, 5%, 7.5%, 15%, respectively. The blend solutions were spin-coated on PEDOT:PSS films at 900 RPM for 20 s in a high purity nitrogen-filled glove box to fabricate the active layers. The thickness of the active layers is ~300 nm, which is measured by Ambios Technology XP-2 stylus Profiler. After that, the active layers were dried in a covered Petri dish for 1 hour (without annealing treatment on the active layer). The combined cathode of LiF/Al (0.9 nm/100nm) film was deposited on the active layer by thermal evaporation under $10^{-4}$ Pa and the thickness was monitored by a quartz crystal microbalance. The active area is about 3.8 mm$^2$, defined by the vertical overlap of ITO anode and Al cathode. The schematic configuration of the PSCs and the chemical structures of electron donor and acceptor materials are shown in Figure 1.
The ultraviolet-visible (UV-Vis) absorption spectra of films were obtained using a Shimadzu UV-3101 PC spectrometer. Ultraviolet photoemission spectroscopy (UPS) was measured by an ultrahigh vacuum system (10\(^{-9}\) Pa) with a hemispherical electron analyzer, a twin anode X-ray gun, a He discharge lamp. Photoluminescence (PL) spectra of films were measured by a Perkin Elmer LS-55 spectrophotometer. Time-resolved transient photoluminescence (TRTPL) spectra were obtained using a FluoroCube-01-NL and FluoroCub-NL from Jobin Yvon. The fabrication parameters of the above films for absorption, PL, TRTPL spectra and UPS measurements are described in the supporting information. The current density-voltage (J-V) curves of all PSCs were measured in air environment using a Keithley 2400 source meter. AM 1.5G irradiation at 100 mW/cm\(^2\) provided by an ABET Sun 2000 solar simulator. The external quantum efficiency (EQE) spectra of PSCs were measured by a Zolix Solar Cell Scan 100. The morphology of the blend films with different SMPV1 doping ratios in donors was investigated by atomic force microscopy (AFM) using a multimode Nanoscope IIIa operated in tapping mode. X-Ray diffraction (XRD) patterns of blend films were collected using a Bruker D8 Advance X-Ray diffractometer.
Figure 1. Schematic configuration of PSCs and the chemical structures of electron
donor and acceptor materials

RESULTS AND DISCUSSION

A series of PSCs with P3HT$_{1-x}$:SMPV1$_x$:PC$_{71}$BM$_1$ as the active layers were
fabricated under the same conditions to investigate the effect of SMPV1 doping ratios
in donors on the performance of PSCs (x= 0, 2.5%, 5%, 7.5%, 15%). The $J$-$V$ curves
and EQE spectra of all PSCs were measured under the same conditions and are shown
in Figure 2. According to the $J$-$V$ curves and EQE spectra of all PSCs, the key
photovoltaic parameters of PSCs are summarized in Table 1. The champion PCE of
4.06% was obtained from the ternary PSCs with 5 wt% SMPV1 doping ratio in
donors as the active layer, resulting from the simultaneous enhancement in $J_{sc}$ (10.06
mA/cm$^2$ vs. 9.32 mA/cm$^2$), $V_{oc}$ (0.61 V vs. 0.59 V) and FF (66.3% vs. 60.4%)
compared with the control PSCs based on P3HT:PC$_{71}$BM as the active layers. More
than two hundred PSCs were fabricated from different batches to further confirm the
effect of SPMV1 doping ratios in donors on the performance of PSCs, the typical $J$-$V$
curves of the optimized ternary PSCs with 5 wt% SMPV1 doping ratio are shown in
Figure S1 and the key photovoltaic parameters are listed in Table S1 (Supporting
Information). The average $J_{sc}$, $V_{oc}$, FF and PCE values of ternary PSCs with 5 wt%
SMPV1 doping ratio are 10.0 mA/cm$^2$, 0.607 V, 66.0% and 4.0% based on seven cells
prepared from different batches, respectively.
Figure 2. (a) J-V curves of PSCs with different SMPV1 doping ratios in donors under AM 1.5 G illumination at 100 mW/cm²; (b) EQE spectra of PSCs with different SMPV1 doping ratios in donors.

Table 1. Key photovoltaic parameters of PSCs with different SMPV1 doping ratios

<table>
<thead>
<tr>
<th>SMPV1 [wt%]</th>
<th>PCE [%]</th>
<th>Jsc [mA/cm²]</th>
<th>Cal. Jsc [mA/cm²]</th>
<th>Voc [V]</th>
<th>FF [%]</th>
<th>Rs [Ω cm²]</th>
<th>Rsh [Ω cm²]</th>
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<td>9.93</td>
<td>0.60</td>
<td>63.8</td>
<td>9.9</td>
</tr>
<tr>
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<td>4.06</td>
<td>3.95</td>
<td>10.06</td>
<td>10.10</td>
<td>0.61</td>
<td>66.3</td>
<td>8.5</td>
</tr>
<tr>
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<td>3.73</td>
<td>3.50</td>
<td>9.50</td>
<td>9.53</td>
<td>0.63</td>
<td>62.3</td>
<td>10.6</td>
</tr>
<tr>
<td>15</td>
<td>3.31</td>
<td>3.25</td>
<td>8.70</td>
<td>8.80</td>
<td>0.64</td>
<td>58.9</td>
<td>12.2</td>
</tr>
</tbody>
</table>

*Average PCE values are calculated based on 30 PSCs prepared from different batches

As described in Figure 2a, the Jsc of ternary PSCs is increased along with the increase of SMPV1 doping ratios (≤ 5 wt%) in donors and then decreased as SMPV1 doping ratios exceeds 5 wt% in donors. The calculated Jsc values from integration of the EQE spectra are close to the values obtained from J-V curves with the average error less than 2%, which indicates that the experimental results presented in this work are reliable. It is apparent that the EQE values of ternary PSCs are enhanced in the range from 600 to 700 nm along with the increase of SMPV1 doping ratios, as shown in Figure 2b. However, the EQE values of ternary PSCs begin to substantially
decline in the range from 400 to 600 nm when the SMPV1 doping ratios are larger than 5 wt% in donors. The trade-off of EQE values at different spectral range results in the increase and then decrease of $J_{sc}$ along with the increase of SMPV1 doping ratios. In order to clarify the effect of SMPV1 doping ratios in donors on $J_{sc}$ and EQE spectra of ternary PSCs, the normalized and un-normalized absorption spectra of neat P3HT, SMPV1 and PC$_{71}$BM films are shown in Figure 3a and Figure S2, respectively. The absorption spectra of P3HT and PC$_{71}$BM films show an apparent complementary absorption in the range from 300 nm to 600 nm. The SMPV1 has a broader absorption in visible light range with a strong absorption from 500 to 700 nm, which may be considered as an excellent second electron donor material to harvest more photons in longer wavelength region for P3HT:PC$_{71}$BM-based PSCs. The absorption spectra of ternary blend films with different SMPV1 doping ratios in donors are presented in Figure 3b. It is apparent that the absorption intensity of blend films is gradually enhanced in the spectral range from 600 nm to 700 nm along with the increase of SMPV1 doping ratios, which is beneficial to the $J_{sc}$ improvement. However, the absorption intensity of blend films is reduced in the range from 400 nm to 600 nm due to the relatively decreased P3HT content along with the increase of SMPV1 doping ratios, resulting in the decreased $J_{sc}$ of PSCs with relatively high SMPV1 doping ratios (> 5 wt%). The variation of $J_{sc}$ can be well explained from the absorption spectra of blend films and EQE spectra of ternary PSCs with different SMPV1 doping ratios in donors.
Figure 3. (a) Normalized UV–Vis absorption spectra of neat P3HT, SMPV1 and PC$_{71}$BM films; (b) absorption spectra of blend P3HT:SMPV1 films with different SMPV1 doping ratios and neat SMPV1 film.

Interestingly, the $V_{oc}$ of ternary PSCs is monotonically increased along with the increase of SMPV1 doping ratio. As we know, the $V_{oc}$ is mainly determined by the energy level difference between the highest occupied molecular orbital (HOMO) of electron donor and the lowest unoccupied molecular orbital (LUMO) of electron acceptor.$^{36,39-40}$ To clarify the effect of SMPV1 doping ratios on $V_{oc}$ of ternary PSCs, the HOMO energy levels of P3HT, SMPV1 and P3HT:SMPV1 films were investigated by ultraviolet photoemission spectroscopy (UPS)$^{41-42}$. It is known that the HOMO energy level is calculated according to the following equation,

$$E_{\text{HOMO}} = h\nu - (E_{\text{onset}} - E_{\text{cutoff}})$$

where $h\nu$ is the incident photon energy of 36 eV; $E_{\text{cutoff}}$ is defined as the lowest kinetic energy of the measured electrons and $E_{\text{onset}}$ is the HOMO energy onset, generally referred to as the high kinetic energy onset.$^{43-44}$ The $E_{\text{cutoff}}$ and $E_{\text{onset}}$ locations of P3HT, P3HT:SMPV1 (1:1), SMPV1 films are marked in Figure 4a and Figure 4b,
respectively. According to Figure 4 and the above equation, the calculated HOMO energy levels (summarized in Table S2) are -4.82 eV for P3HT, -4.97 eV for P3HT:SMPV1 and -5.26 for SMPV1. A series of PSCs with P3HT_{0.5}:SMPV1_{0.5}:PC_{71}BM_{1} (0.5:0.5:1) as the active layers were fabricated to further demonstrate the effect of mixed HOMO levels of donors on $V_{oc}$ of PSCs. The $J$-$V$ curves of PSCs under AM 1.5 G illumination at 100 mW/cm$^2$ are shown in Figure S3, and the key parameters are listed in Table S3. The $V_{oc}$ of the PSCs is increased from 0.59 V to 0.64 V for the cells with 15 wt% SMPV1 doping ratio and even to 0.73 V for the cells with 50 wt% SMPV1 doping ratio in donors. The monotonically increased $V_{oc}$ of ternary PSCs can be understood from the decreased HOMO levels of P3HT:SMPV1 along with the increase of SMPV1 doping ratios.

**Figure 4.** UPS spectra of the inelastic cutoff region (a) and HOMO region (b) of P3HT, P3HT:SMPV1 (1:1) and SMPV1 films (photon energy is 36 eV), measured in ultrahigh vacuum ($10^{-9}$ Pa) conditions.

According to the measured energy levels of P3HT and SMPV1 and reported energy levels of other materials, the energy level diagram of ternary PSCs is described in
Figure 5a. The HOMO (-5.26 eV) and LUMO (-3.51 eV) energy levels of SMPV1 properly locates between the corresponding energy levels of P3HT and PC71BM, respectively. The proper cascade energy level structure of P3HT, SMPV1 and PC71BM can provide several possible pathways for charge carrier transfer and transport among the electron donors and electron acceptor. The photogenerated excitons in P3HT or SMPV1 molecules can be directly dissociated into free charge carriers at the P3HT/PC71BM or SMPV1/PC71BM interfaces, respectively. The charge carrier transfer between P3HT and SMPV1 (electron transfer from P3HT to SMPV1 and hole transfer from SMPV1 to P3HT) may occur due to the suitable energy level alignment. As a consequence, charge carrier transfer is energetically allowed between P3HT and PC71BM, between SMPV1 and PC71BM, as well as between P3HT and SMPV1, which is beneficial to excitons dissociation, charge carrier transport and collection.

It is generally recognized that the FF strongly depends on the series resistances ($R_S$) and the shunt resistances ($R_{SH}$) of PSCs, which has tightly coupled relationships with exciton dissociation and charge carrier recombination in the active layer. The optimized excitons dissociation and charge carrier transport should contribute to suppress charge carrier recombination, resulting in the increase of FF. As seen from Table 2, it is apparent that the FF values of ternary PSCs are obviously higher than those of the control cells when SMPV1 doping ratio is lower than 7.5 wt% in donors. The optimized ternary PSCs (with 5% SMPV1 doping ratio) achieve the champion FF of 66.3% with the minimum $R_S$ of 8.5 $\Omega$ cm$^2$ and the maximum $R_{SH}$ of 850 $\Omega$ cm$^2$. To
the best of our knowledge, the FF of 66.3% should be among the highest reported values for ternary PSCs.\textsuperscript{50-51}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{(a) Energy level diagram of ternary PSCs highlighting possible pathways for charge transfer and charge transport; (b) PL spectra of P3HT:SMPV1 films with different SMPV1 doping ratios under 490nm wavelength light excitation. (c) $J-V$ curves of PSCs with P3HT, SMPV1 and P3HT:SMPV1 (1:1) as active layers (without PC\textsubscript{71}BM) under AM 1.5 G illumination at 100 mW/cm\textsuperscript{2}.

In order to further investigate the dynamic processes of charge carrier transfer or energy transfer between P3HT and SMPV1, PL spectra of P3HT:SMPV1 blend films with different SMPV1 doping ratios were measured under the excitation of 490 nm light and are shown in Figure 5b. It is apparent that neat P3HT and SMPV1 films show
strong emission peak at 660 nm and 720 nm, respectively. Generally, if energy transfer can be occurred from P3HT to SMPV1, one would expect a relatively increased SMPV1 emission intensity and decreased P3HT emission intensity for the blend P3HT:SMPV1 films along with increase of SMPV1 doping ratios, considering that the quantum yields of P3HT and SMPV1 are similar.\textsuperscript{45, 49} As seen from Figure 5b, both P3HT and SMPV1 emission intensity are substantially reduced along with the increase of SMPV1 doping ratios in donors due to charge carrier transfer between P3HT and SMPV1. Therefore, intermolecular energy transfer between P3HT and SMPV1 should be ignored. To further demonstrate charge carrier transfer process between P3HT and SMPV1, a series of PSCs with P3HT, SMPV1 or P3HT:SMPV1 (1:1) as active layers were fabricated, respectively. The $J$-$V$ curves of three kind PSCs under AM 1.5 G illumination at 100 mW/cm\textsuperscript{2} are shown in Figure 5c. The PSCs with P3HT:SMPV1(1:1) as the active layer display the largest $J_{sc}$ compared with that of P3HT-based and SMPV1-based cells, which should be attributed to the effective charge carrier transfer between P3HT and SMPV1 supported by their cascade energy levels.
Figure 6. (a) PL spectra of P3HT:SMPV1 solutions with different SMPV1 doping ratios (excitation wavelength 490 nm); (b) the photograph of different solutions (1-P3HT, 2-P3HT:SMPV1, 3-SMPV1, 4-P3HT:PC$_{71}$BM, 5-P3HT:SMPV1:PC$_{71}$BM, 6-SMPV1:PC$_{71}$BM) under UV-light excitation conditions; (c) TRTPL spectra of P3HT:SMPV1 solutions with different SMPV1 doping ratios (monitored at 670 nm).

The PL spectra of P3HT:SMPV1 solutions with different SMPV1 doping ratios were measured under the 490 nm light excitation to further confirm the charge carrier transfer dynamic process between P3HT and SMPV1, as shown in Figure 6a. Expectedly, the PL spectra of blend solutions exhibit a similar varying tendency compared with the PL spectra of blend films. The PL spectral changes of blend solutions can be further confirmed from the relative solutions emission color under UV-light excitation conditions, as shown in Figure 6b. Meanwhile, PL emission intensity of P3HT:SMPV1 blend solutions can be markedly quenched by doping a small amount of PC$_{71}$BM into blend solutions. Time-resolved transient photoluminescence (TRTPL) is a convenient tool to investigate the energy or charge
transfer between different molecules. The TRTPL spectra of P3HT:SMPV1 solutions with different SMPV1 doping ratios were measured by monitoring 670 nm emission under the light excitation of 460 nm pulse NanoLED source. As shown in Figure 5c, the emission lifetime of 670 nm for neat P3HT solution is ~0.62 ns and gradually increased to ~0.89 ns for the blend P3HT:SMPV1 solution with 15 wt% SMPV1 doping ratio in donors. The emission lifetime of 670 nm for neat SMPV1 solution (~0.91 ns) is slightly longer than that for neat P3HT and blend P3HT:SMPV1 solutions, indicating that the energy transfer between P3HT to SMPV1 molecules can be absent or negligible.\textsuperscript{52-53} The similar lifetime change trend is also observed from the TRTPL spectra for monitoring emission peak at 700 nm. The TRTPL spectra of blend solutions with different SMPV1 doping ratios were measured by monitoring 700 nm emission and are shown in Figure S4 and the emission lifetime values of 670 nm and 700 nm are summarized in Table S4. The decreased emission intensity of P3HT and SMPV1 should be due to the charge transfer rather than the energy transfer between P3HT and SMPV1 according to the PL spectra and TRTPL spectra of the blend solutions with different SMPV1 doping ratios.
Figure 7. Two-dimensional (2D) and three-dimensional (3D) images of AFM morphology of (a) P3HT:PC\textsubscript{71}BM film as cast, (b) P3HT:SMPV1:PC\textsubscript{71}BM film with 5 wt% SMPV1 doping ratio in donors, and (c) P3HT:SMPV1:PC\textsubscript{71}BM film with 15 wt% SMPV1 doping ratio in donors.

To further illustrate the effect of SMPV1 doping ratios on the performance of the PSCs, the surface morphology and phase images of blend films were investigated by atomic force microscopy (AFM). The films for AFM characterization were prepared under the same conditions compared with the active layers of PSCs. The morphology and phase images of blend films with different SMPV1 doping ratios are shown in Figure S5 and Figure S6. Here, the morphology and phase images of P3HT:PC\textsubscript{71}BM, P3HT\textsubscript{0.95}:SMPV1\textsubscript{0.5}:PC\textsubscript{71}BM\textsubscript{1} and P3HT\textsubscript{0.85}:SMPV1\textsubscript{0.15}:PC\textsubscript{71}BM\textsubscript{1} blend films are shown in Figure 7. The statistical average data root-mean-square (RMS) roughness of blend films are 9.6 nm, 8.3 nm and 19.5 nm along with the increase of SMPV1 doping ratios in donors. The optimized surface morphology and phase separation of the ternary films with 5 wt% SMPV1 doping ratio may be beneficial to exciton dissociation, charge carrier transport and collection, resulting in the improvement of $J_{sc}$ and FF of PSCs. The RMS roughness of blend films is increased when SMPV1 doping ratios in donors are larger than 5 wt% due to SMPV1 molecular aggregation. The more and more obvious islands can be observed from AFM images when SMPV1 doping ratio exceeds 5 wt%, as shown in Figure S5 and Figure S6. The bicontinuous interpenetrating network of P3HT:PC\textsubscript{71}BM may be disturbed by relatively high SMPV1 doping ratios, which can be further demonstrated from the X-ray diffraction
(XRD) pattern of blend films with different SMPV1 doping ratios and neat SMPV1 film.

![XRD pattern](image)

**Figure 8.** XRD patterns of P3HT$_{1-x}$:SMPV1$_x$:PC$_{71}$BM$_1$ films with different SMPV1 doping ratios in donors and neat SMPV1 film

Bearing in mind that the AFM investigation is only limited on the surface morphology and phase separation of films. In order to get better understandings of the effect of SMPV1 doping ratios on the performance of ternary PSCs, the molecular packing and crystalline structures of the ternary blend films are characterized by XRD, as shown in Figure 8. According to the XRD patterns, the key parameters are summarized in Table S5. The control P3HT:PC$_{71}$BM films exhibits a diffraction peak at $2\theta \approx 5.5^\circ$ of ordered P3HT molecular arrangement corresponding to a $d_{100}$-spacing value of 16.05 Å$^{39}$ The $2\theta \approx 5.5^\circ$ diffraction peak intensity is decreased along with the increase of SMPV1 doping ratios, which means that the ordered molecular arrangement of P3HT is disrupted by doping SMPV1.$^{54}$ A similar phenomenon has been already reported by Yu and co-workers in the system of P3HT:PC$_{71}$BM:SQ.$^{55}$ The neat SMPV1 films exhibit a strong diffraction peak at $2\theta \approx 4.2^\circ$ corresponding to a
d_{100}-spacing value of 20.97 Å. The blend films with 15 wt% SMPV1 doping ratio exhibits a strong diffraction peak at 2θ≈4.0° corresponding to a d_{100}-spacing value of 21.94 Å, which should be attributed to the ordered arrangement of SMPV1 molecules. The two diffraction peaks of blend films with 15 wt% SMPV1 doping ratio indicate that SMPV1 molecular aggregates in the blend films. The SMPV1 molecular aggregation in ternary films can disrupt the ordered molecular arrangement of P3HT, which may influence the exciton dissociation and charge carrier transport in the blend films. Therefore, the decreased performance of ternary PSCs with relatively high SMPV1 doping ratios in donors can be reasonably understood due to the serious aggregation of SMPV1 and the disrupted P3HT molecular arrangement in blend films.

**CONCLUSIONS**

In conclusion, three key parameters of ternary PSCs based P3HT:SMPV1:PC₇₁BM as the active layers can be simultaneously increased when SMPV1 doping ratios in donors are lower than 5 wt%. The champion PCE of 4.06 % is obtained based on ternary PSCs with 5 wt% SMPV1 doping ratio in donors, corresponding to about 21.2% improvement compared with that of 3.35% PCE for P3HT:PC₇₁BM-based cells. The PCE improvement of ternary PSCs should be attributed to the better balance among photon harvesting, exciton dissociation and charge carrier transport in blend films. The ternary strategy may open an effective way for high performance PSCs by retaining the major benefit of incorporating multiple organic materials in
tandem cells and the simple fabrication technology of single bulk heterojunction PSCs.

ASSOCIATED CONTENT

Supporting Information

Typical $J-V$ curves of the ternary PSCs with 5 wt% or 50 wt% SMPV1 doping ratio in donors; the parameters of energy levels of P3HT, SMPV1 and P3HT:SMPV1 with 1:1 weight ratio; TSTPL spectra of blend films with different SMPV1 doping ratios monitoring the emission peak at 700 nm; AFM surface morphology and phase 2D and 3D images of blend films with different SMPV1 doping ratios. These materials are available free of charge via the Internet at http://pubs.acs.org.

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Notes

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