Unique insight into phase separation in polymer solar cells from their electric characteristics†

Jian Wang, a Fujun Zhang,*a Qiaoshi An, a Qianqian Sun, a Jian Zhang b and Bin Hu*a c

A series of polymer solar cells (PSCs) were fabricated with indene-C60 bisadduct (ICBA) or [6,6]-phenyl-C61-butyric acid methyl ester (PC61BM) as an electron acceptor and with PBDT-TS1 as an electron donor. The donor/acceptor (D/A) phase separation was adjusted with different solution processing methods, consisting of cool (room temperature, 20 °C) solution, hot (70 °C) solution and the solutions with solvent additive 1,8-diododecan (DIO). The champion PCE of PSCs with ICBA or PC61BM as an electron acceptor is 4.32% or 5.97% for the active layers prepared from hot solution with DIO additive or cool solution with DIO additive, respectively. The improved PCEs should be attributed to the optimized D/A phase separation in the active layers by adjusting the redistribution of PC61BM or the ICBA among the PBDT-TS1 networks. The degree of phase separation of the active layers with different acceptors was evaluated according to the current density–voltage (J–V) curves of hole-only and electron-only devices. The distribution of PC61BM or ICBA molecules in the normal direction can be simply judged from the symmetry degree of J–V curves of electron-only devices measured under the forward and reverse bias.

1 Introduction

Polymer solar cells (PSCs) have attracted much attention due to the unique advantages such as low cost, flexibility and environmentally-friendly processes.1–3 To date, the power conversion efficiency (PCE) of bulk heterojunction PSCs has been improved to ~10% by different strategies from material synthesis or device physics.4,5 Among the approaches in increasing the PCE of PSCs, optimizing donor/acceptor (D/A) phase separation in the active layers plays a critical role. The gradual vertical D/A phase separation with acceptor-rich materials in the region near the cathode and donor-rich materials in the region near the anode is beneficial to improve charge collection and thus PCE of PSCs.6,7 In order to understand and better optimize the D/A phase separation, many technologies have been employed to investigate the active layers, including: (i) estimating the surface composition by energy dispersive spectrometry (EDS), X-ray photoelectron spectroscopy (XPS), peak force Kelvin ProbeForce microscopy (PF-KPFM) and water contact angle (WCA) characterization;6,8 (ii) characterizing the concentration-depth profiles with spectroscopic ellipsometry (SE), cross-sectional scanning tunneling microscopy (XSTM) and secondary ion mass spectroscopy (SIMS);9–12 and (iii) quantizing the degree of phase separation with resonant soft-X-ray scattering (R-SoXS).13 Though these technologies have unique superiority in investigating the D/A phase separation, the rigorous technology requirements and high cost limit their popular application. Hence, simple and effective methods are needed to clearly evaluate the degree of D/A phase separation dependence on the chemical structure of fullerene derivations and preparing conditions of active layers.

In 2010, Li et al. successfully reported the electron acceptor indene-C60 bisadduct (ICBA), which may increase the open-circuit voltage (VOC) and PCE of PSCs by replacing the widely used [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) or [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM).14,15 However, the PSCs based on narrow bandgap polymer/ICBA active layers usually show a rather low short circuit current (JSC) and a fill factor (FF).16,17 Li’s group and Yang’s group respectively pointed out that the PCE of PSCs based on narrow bandgap polymers and the ICBA may be mainly limited by large D/A phase separation in the active layers.18,19 It is known that the degree of D/A phase separation should be mainly determined by the distribution of the electron acceptor molecules among the polymer networks.6,20,21 It means that the degree of D/A phase separation can be evaluated from the electron transport behavior in the active layers. Recently, Hou et al. reported that the PC71BM molecules may diffuse towards the top surface of active layers along with the elevated volatilization of a solvent or a solvent additive.22 Zhang et al. reported that the low PCE of PSCs with ICBA as an electron acceptor may be attributed to the limited molecular distribution of the ICBA among donor
Hence, the improper vertical D/A phase separation in the active layers consisting of a narrow bandgap polymer donor and an ICBA acceptor may be the important factor for the low $J_{SC}$ and FF of the related PSCs.

In this work, a series of PSCs were prepared with narrow bandgap polymer PBDT-TS1 as an electron donor and with ICBA or PC$_{61}$BM as an electron acceptor. The degree of D/A phase separation can be adjusted by using different temperature solutions and solvent additives. For the PSCs with PBDT-TS1:ICBA (1:1.5, w/w) as an active layer, the PCE was increased from 3.25% to 4.32% by employing hot (70 °C) solution with DIO additive. For the PSCs with PBDT-TS1:PC$_{61}$BM (1:1.5, w/w) as an active layer, the PCE was increased from 5.56% to 5.97% by preparing the active layer from cool (room temperature) solution with DIO additive. The improved PCEs should be attributed to the optimization of D/A phase separation in the active layers, which can be evaluated from the $J$–$V$ curves of the corresponding electron-only devices. It is worth highlighting that the optimization of vertical D/A phase separation due to the migration of the ICBA or PC$_{61}$BM molecules towards the top surface of active layers can be evaluated from the symmetry degree of $J$–$V$ curves of electron-only devices under forward or reverse bias. Compared with the PSCs with PBDT-TS1:PC$_{61}$BM as an active layer, the lower performance of PSCs based on PBDT-TS1:ICBA mainly resulted from the discontinuous electron transport channels due to the aggregation of the ICBA. The electric character of active layers obtained from the $J$–$V$ curves of the hole-only and electron-only devices according to the PSCs may provide a unique insight into the relative D/A phase separation degree in the active layers with different acceptors.

2 Experimental details

2.1 Preparation of the samples

Patterned indium tin oxide (ITO) coated glass substrates (15 Ω $\square^{-1}$) were consecutively cleaned by glass lotion, de-ionized water and ethanol in ultrasonic baths, followed by the stoving-dried and UV-O$_3$ treatment for 6 minutes. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Clevios AI 4083) was spin-coated onto the ITO coated substrates at 5000 rounds per minute (rpm) for 40 s. Then the PEDOT:PSS coated ITO substrates were annealed at 120 °C for 10 minutes in an atmospheric air environment and transferred into a high purity nitrogen filled glove box. The electron donor PBDT-TS1 and electron acceptor ICBA or PC$_{61}$BM were dissolved in 1,2-dichlorobenzene (o-DCB) to prepare the blend solutions with a concentration of 25 mg mL$^{-1}$, the D/A weight ratio was kept constant at 1:1.5 for the solutions. Part of blend solutions were added 3% (v/v) solvent additive 1,8-diiodooctane (DIO) to adjust the electron acceptor aggregation extent in the blend films with continuous stirring. Then part of blend solutions were heated to 70 °C with continuous stirring to further increase the mixing degree of the electron donor and acceptor. The blend solutions were spin-coated onto the PEDOT:PSS coated substrates to prepare the active layers at 1000 RPM for 40 s. All blend films were placed under vacuum conditions (~1 Pa) for 10 minutes to accelerate the dry speed of the active layer and decrease the residual DIO in the active layers. The semiconducting conjugated polyelectrolyte poly[9,9-bis(3’-(N,N-dimethylamino)-propyl-2,7-fluorene)-alt-2,7-[9,9-dioctyfluorene]] (PFN) was dissolved in methanol to prepare a 0.2 mg mL$^{-1}$ solution with addition of 0.25 vol% acetic acid, and then PFN solutions were spin-coated on the top of active layers at 3000 rpm for 30 s to prepare an interfacial buffer layer. The aluminum (Al), silver (Ag), molybdenum oxide (MoO$_3$) or lithium fluoride (LiF) was deposited by thermal evaporation under 3 × 10$^{-4}$ Pa vacuum conditions. The thickness of the films was monitored by using a quartz crystal microbalance. The active area of each cell is about 3.8 mm$^2$, which is defined by the overlap of the ITO anode and the Al cathode. All the measurements were carried out under ambient conditions.

2.2 Characterization

The current density–voltage ($J$–$V$) characteristics of PSCs were measured using a Keithley 4200 semiconductor characterization system under dark and under light conditions. AM 1.5 illumination at 100 mW cm$^{-2}$ was provided using an ABET Sun 2000 solar simulator. The external quantum efficiency (EQE) spectra of PSCs were measured using a Zolix Solar Cell Scan 100. Absorption spectra of neat or blend films were measured using a Shimadzu UV-3101 PC spectrophotometer. Photoluminescence (PL) spectra of films were measured by using a HORIBA Fluorolog©-3 Spectrofluorometer. The morphology and phase images of active layers were investigated by using atomic force microscopy (AFM) with a multimode Nanoscope IIIa operated in the tapping mode. The chemical structure, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of used materials are shown in Fig. 1.

3 Results and discussion

The absorption spectra of PBDT-TS1, ICBA and PC$_{61}$BM films were measured and are shown in Fig. 2. The PBDT-TS1 film exhibits a relatively broad absorption range with an absorption peak at about 722 nm and a shoulder peak at about 657 nm. The HOMO and LUMO levels of PBDT-TS1 are about −5.29 eV and −3.40 eV, corresponding to a 1.89 eV bandgap. Both the
ICBA and PC_{61}BM exhibit very similar absorption intensity in the whole spectral range. It is envisaged that all the blend films should have the same absorption intensity and range, which is confirmed by the absorption spectra of the blend films prepared with different solutions, as shown in Fig. S1 (ESI†). It means that the photon harvesting ability should be the same for all PSCs with PBDT-TS1:ICBA or PBDT-TS1:PC_{61}BM as the active layer. Therefore, the effect of PC_{61}BM or the ICBA on the J_{SC} and FF should be mainly attributed to the different D/A phase separation degree in the active layers. It is known that the open circuit voltage (V_{OC}) is mainly determined by the energy offset between the HOMO level of the electron donor and the LUMO level of the electron acceptor for PSCs with the same interfacial layers and electrodes.\textsuperscript{24} The LUMO–LUMO offsets between PBDT-TS1 and the ICBA or PC_{61}BM are about 0.34 and 0.51 eV, which are larger than the typical value 0.3 eV for providing enough driving force for efficient exciton dissociation.\textsuperscript{25}

The variation of D/A phase separation should be mainly attributed to the ICBA or PC_{61}BM molecule redistribution in the polymer matrix during the film drying process. The blend solution conditions (temperature, DIO additive) should result in the different phase separation extent due to the different film drying process. The active layers prepared from hot (70 °C) solutions can be considered as the fast forming film process, D/A molecular distribution in solution states may be rapidly fixed in the solid films. The active layers prepared from cool solution and cool solution with DIO additive can be considered as the slow film drying processes, the ICBA or PC_{61}BM molecules may redistribute or migrate along with the volatilization of the solvent or the DIO additive from the wet films. Meanwhile, the chemical structure of the ICBA or PC_{61}BM may also influence its molecular redistribution during the film drying process.

For PSCs with ICBA as an electron acceptor, the J–V characteristic curves and EQE spectra of PSCs prepared from the different solutions were measured and are shown in Fig. 3. More than one hundred PSCs were prepared to confirm the solution processing methods on PSC performance, the detailed J–V curves are shown in Fig. S2 (ESI†). The key parameters of PSCs were summarized and are listed in Table 1. All the PSCs with ICBA as an electron acceptor exhibit a relatively large V_{OC} of 1.02 V, which can be well explained from the relatively high LUMO level of the ICBA. The PCEs of PSCs prepared from cool solution and cool solution with DIO additive can be considered as the slow film drying processes, the ICBA or PC_{61}BM molecules may redistribute or migrate along with the volatilization of the solvent or the DIO additive from the wet films. Meanwhile, the chemical structure of the ICBA or PC_{61}BM may also influence its molecular redistribution during the film drying process.

<table>
<thead>
<tr>
<th>Solutions</th>
<th>V_{OC} (V)</th>
<th>J_{SC} (mA cm(^{-2}))</th>
<th>FF (%)</th>
<th>Best PCE (%)</th>
<th>Ave PCE (%)</th>
<th>R_{S} (\Omega cm(^{-2}))</th>
<th>R_{SH} (\Omega cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cool</td>
<td>1.02</td>
<td>7.92</td>
<td>40.2</td>
<td>3.25</td>
<td>3.11 (±0.12)</td>
<td>45</td>
<td>586</td>
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<tr>
<td>70 °C</td>
<td>1.02</td>
<td>8.21</td>
<td>44.6</td>
<td>3.73</td>
<td>3.58 (±0.15)</td>
<td>32</td>
<td>712</td>
</tr>
<tr>
<td>DIO</td>
<td>1.02</td>
<td>9.05</td>
<td>45.1</td>
<td>4.16</td>
<td>3.90 (±0.25)</td>
<td>28</td>
<td>583</td>
</tr>
<tr>
<td>70 °C + DIO</td>
<td>1.02</td>
<td>8.76</td>
<td>48.3</td>
<td>4.32</td>
<td>4.20 (±0.10)</td>
<td>25</td>
<td>841</td>
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</table>

Average PCEs were calculated based on 20 cells.
solution were increased from 3.25% to 4.16% by doping the DIO additive, the PCE improvement should be attributed to the more ICBA diffusion to the top surface of active layers during the volatilization of the DIO additive, which can be further confirmed form the increased FF from 40.2% to 45.1%. The PSCs prepared from hot solution also exhibit a better performance compared with the PSCs prepared from cool solution, which should be attributed to more homogenous D/A distribution in the active layers due to the relatively fast film drying process. For the active layers prepared from cool solution without DIO additive, the ICBA may tend to aggregate in the active layers, rather than diffusing toward the top surface of active layers due to the absent driving force induced by the volatilization of the DIO additive. The champion PCE of PSCs arrived to 4.32% for the active layers prepared from the hot solution with DIO additive, the better vertical phase separation of PBDT-TS1:ICBA should be obtained because more ICBA can be elevated toward the top surface of active layers during the film drying process. The optimized PSCs exhibit the smallest $R_S$ of 25 $\Omega \text{cm}^2$ and the best FF of 48.3% for the active layers prepared from hot solutions with DIO additive. $R_S$ was decreased from 45 to 25 $\Omega \text{cm}^2$ and $R_{SH}$ was increased from 583 to 841 $\Omega \text{cm}^2$ by adjusting phase separation, resulting in the increased FF from 40.2% to 48.3%. This phenomenon further indicates that the vertical phase separation can be optimized by elevating the ICBA toward the top surface of active layers during the film drying process.

For the PSCs with PC$_{61}$BM as an electron acceptor, the $J$–$V$ characteristic curves and EQE spectra of PSCs were measured and are shown in Fig. 4. More than one hundred PSCs were prepared by using different solutions and the detailed $J$–$V$ curves of part cells are shown in Fig. S3 (ESI†). The key photovoltaic parameters of PSCs were summarized according to $J$–$V$ curves and are listed in Table 2. The champion PCE of PSCs with PC$_{61}$BM as an electron acceptor was 5.97% for the active layers prepared from cool solution with DIO additive, along with a relatively high $J_{SC}$ of 11.50 mA cm$^{-2}$ and a FF of 62.5% as well as a $V_{OC}$ of 0.83 eV. For the active layers prepared from cool solution with DIO additive, more PC$_{61}$BM can be elevated towards the top surface of active layers during the relatively slow drying process. The asymmetric structure of PC$_{61}$BM may be beneficial to molecular diffusion under the driving force induced by the volatilization of the solvent or the DIO additive. The PSCs with PC$_{61}$BM as an electron acceptor exhibit the smaller $R_S$ compared with PSCs with ICBA as an electron acceptor, indicating that the PC$_{61}$BM molecules can be easily elevated toward the top surface of active layers compared with ICBA molecules. The better FF and $J_{SC}$ of PSCs with PC$_{61}$BM as an electron acceptor indicate that the degree of vertical phase separation formed in the active layers is more beneficial to the exciton dissociation, charge carrier transport and collection.

For better understanding the effect of the phase separation degree on exciton dissociation, the photoluminescence (PL) spectra of the neat PBDT-TS1 film, PBDT-TS1:ICBA and PBDT-TS1:PC$_{61}$BM blend films prepared from different solutions were measured under the excitation of 680 nm light, as shown in Fig. S4 (ESI†). The typical PL spectra of neat PBDT-TS1 and

![Fig. 4](a) $J$–$V$ curves of PSCs under AM 1.5 illumination at 100 mW cm$^{-2}$ and (b) EQE spectra of the PSCs with PC$_{61}$BM as an electron acceptor.

<table>
<thead>
<tr>
<th>Solutions</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>Best PCE (%)</th>
<th>Ave PCE (%)</th>
<th>$R_S$ ($\Omega \text{cm}^2$)</th>
<th>$R_{SH}$ ($\Omega \text{cm}^2$)</th>
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</thead>
<tbody>
<tr>
<td>Cool</td>
<td>0.83</td>
<td>11.40</td>
<td>58.8</td>
<td>5.56</td>
<td>5.45 (±0.08)</td>
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<td>70 °C</td>
<td>0.83</td>
<td>10.62</td>
<td>60.1</td>
<td>5.30</td>
<td>5.26 (±0.03)</td>
<td>8.8</td>
<td>822</td>
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<tr>
<td>DIO</td>
<td>0.83</td>
<td>11.50</td>
<td>62.5</td>
<td>5.97</td>
<td>5.84 (±0.11)</td>
<td>7.4</td>
<td>1288</td>
</tr>
<tr>
<td>70 °C + DIO</td>
<td>0.83</td>
<td>10.75</td>
<td>62.8</td>
<td>5.60</td>
<td>5.48 (±0.10)</td>
<td>7.3</td>
<td>1318</td>
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</tbody>
</table>

Average PCEs were calculated based on 20 cells.
the corresponding blend films are shown in Fig. 5. It is apparent that neat PBDT-TS1 films exhibit strong PL emission with an emission peak at 790 nm. The PL emission of PBDT-TS1 is almost completely quenched in the all PBDT-TS1:PC61BM blend films, exhibiting the homogeneous D/A molecular distribution in the blend films. However, the PL emission of PBDT-TS1 is partly quenched in the PBDT-TS1:ICBA blend films prepared from cool solution, which may be due to the serious aggregation of the ICBA during the slow drying process of films. The emission of PBDT-TS1 was markedly quenched for the PBDT-TS1:ICBA blend films prepared from hot solution with DIO additive, exhibiting the limited ICBA aggregation during the rapid drying process. The PL spectra of active layers indicate that ICBA molecules may prefer to aggregate in the blend films resulting in the relatively strong PBDT-TS1 emission, which can effectively explain the performance of PSC dependence on the active layers prepared from different solution conditions.

To further investigate the effect of the phase separation degree on the exciton dissociation and charge carrier transport in the active layers, the photocurrent density ($J_{PH}$) versus effective voltage ($V_{EFF} = V_0 - V$) curves of PSCs were calculated according to the $J$–$V$ curves in dark and under AM 1.5 illumination at 100 mW cm$^{-2}$, as shown in Fig. 6. The $J_{PH}$ is defined as the difference between the current density under illumination ($J_L$) and the current density in the dark ($J_D$), thus $J_{PH} = J_L - J_D$. $V_0$ is the voltage at which $J_{PH} = 0$ and $V$ is the applied bias voltage.26 It is apparent that the $J_{PH}$ of PSCs based on PBDT-TS1:PC61BM as the active layer rapidly comes into the saturation state under relatively low $V_{EFF}$ compared with that of PSCs based on PBDT-TS1:ICBA as the active layer, which indicates the more efficient charge carrier transport channels formed in the PBDT-TS1:PC61BM blend films. The saturation current density ($J_{SAT}$) of PSCs with PC61BM as an electron acceptor is about 12 mA cm$^{-2}$ at $V_{EFF} \approx 2$ V, which is larger than that of 10 mA cm$^{-2}$ for the PSCs with ICBA as an electron acceptor. The exciton dissociation probability and charge carrier collection could be deduced from $J_{PH}/J_{SAT}$ under short circuit conditions and maximum power output conditions.27,28 Under short circuit conditions, $J_{PH}/J_{SAT}$ is about 94% or 88% for PSCs with PC61BM or ICBA as an electron acceptor, indicating high exciton dissociation efficiency which well accords with the PL emission quenching extent of the corresponding blend films. Under the maximum power output conditions, the $J_{PH}/J_{SAT}$ is about 75% or 62% for PSCs with PC61BM or ICBA as an electron acceptor, which indicates the lower charge carrier transport and collection ability in the
PBDT-TS1:ICBA active layer. It also well accords with the relative FF of corresponding PSCs with ICBA as an acceptor.

The hole-only ITO/PEDOT:PSS/active layers/MoO$_3$ (10 nm)/Ag (50 nm) and electron-only Al (100 nm)/LiF (1 nm)/active layers/LiF (1 nm)/Al (100 nm) devices were fabricated to investigate the charge carrier transport of active layers prepared under different solution conditions. The $J$–$V$ curves of the hole-only and electron-only devices were measured under dark conditions and are shown in Fig. 7. To provide more valuable information on the charge carrier transport ability in the PSCs, charge carrier transport characteristics of hole-only or electron-only devices were investigated under forward (hole collected by ITO cathode) or reverse (electron collected by top Al cathode) bias. It is apparent that hole and electron transport abilities of devices based on PBDT-TS1:PC$_{61}$BM as the active layer are larger than those of devices based on PBDT-TS1:ICBA as the active layer, which indicates that the better bicontinuous charge carrier transport channels have been formed in the devices with PBDT-TS1:PC$_{61}$BM as the active layer. It should be highlighted that hole transport ability of all devices is stronger than the corresponding electron transport ability, indicating that the performance of PSCs may be limited by the unbalanced charge transport due to the relatively low electron transport ability in the active layers. Hole transport ability of blend films is insensitive to the film drying process, as shown in Fig. 7a, indicating a relatively stable network of polymers. Meanwhile, hole transport ability in the PBDT-TS1:ICBA blend films was markedly decreased due to the aggregation of the ICBA. According to Fig. 7b, electron transport ability of active layers is more sensitive to the film drying process due to the easy redistribution of small molecules ICBA or PC$_{61}$BM in the active layers during the film drying process. The relatively large electron transport ability of PBDT-TS1:PC$_{61}$BM blend films should be beneficial to the more balanced charge transport in the active layer, resulting in the relatively high performance of the PSCs with PBDT-TS1:PC$_{61}$BM as the active layer. The relatively weak electron transport ability of PBDT-TS1:ICBA blend films may be due to discontinuous electron transport channels due to the aggregation of the ICBA. To further investigate ICBA or PC$_{61}$BM distribution in the active layers, $J$–$V$ curves of the electron-only devices (Al (100 nm)/LiF (1 nm)/active layers/LiF (1 nm)/Al (100 nm)) were measured under forward bias or reverse bias and the description is shown in Fig. 8a. Under the forward bias, electrons are injected from the bottom Al electrode. Under the reverse bias, electrons will be injected from the top Al electrode. According to the energy levels of used materials shown in Fig. 8b, the electron can be relatively easily injected from the Al electrode onto the LUMO of ICBA or PC$_{61}$BM if more ICBA or PC$_{61}$BM molecules enriched near the top surface of the active layers.

The double-logarithmic $J$–$V$ curves of the electron-only devices measured in dark are shown in Fig. 9a and b, as well as the single-logarithmic $J$–$V$ curves in the inset. It is apparent that the $J$–$V$ curves of devices with PBDT-TS1:PC$_{61}$BM as an active layer exhibit a similar characteristics under forward and reverse bias, it means that the distribution of the PC$_{61}$BM neat top or the bottom surface of the active layer should be the same. However, the $J$–$V$ curves of devices with PBDT-TS1:ICBA as an active layer exhibit a distinct deviation under forward and reverse bias, indicating that the distribution of the ICBA near the top or the bottom surface of the active layer should be obviously different. For the blend films, the redistribution of the ICBA and PC$_{71}$BM can be effectively optimized by using different solution conditions to form the better vertical phase separation in the active layers. The $J$–$V$ curves of the symmetric electron-only devices under forward or reverse bias were investigated, which may be a simple and effective method to evaluate the vertical phase separation in the active layers.
As we can envisage, the variation of phase separation may be slightly reflected by the surface morphology of the active layer. The morphology of all active layers with different electron acceptors or prepared from different solution conditions was characterized by atomic force microscopy (AFM), as shown in Fig. 10. The corresponding phase images of active layers are shown in Fig. S5 (ESI†). The surface root mean square (RMS) roughness of the PBDT-TS1:ICBA blend films is much larger than that of PBDT-TS1:PC61BM blend films, which may be due to the ICBA aggregation in the active layers. Meanwhile, the surface roughness of active layers strongly depends on the corresponding solution conditions, which also indirectly reflects the degree of phase separation in the active layers. To intuitively investigate the redistribution of the ICBA or PC61BM on the phase separation, a schematic image of the phase separation of the active layer with different film drying processes is shown in Fig. S6 (ESI†). The D/A phase separation strongly depends on the solution conditions, post treatment conditions on the active layer as well as the intrinsic factors of electron donor and electron acceptor molecular chemical structures.

4 Conclusions

In summary, the champion PCE values of PSCs arrived to 4.32% or 5.97% for the cells with ICBA or PC61BM as an electron acceptor and PBDT-TS1 as an electron donor, respectively. The PCE of PSCs based on PBDT-TS1:ICBA was increased from 3.25% to 4.32% by optimizing the D/A phase separation with hot solution and solvent additive DIO. The PCE of PSCs based on PBDT-TS1:PC61BM was increased from 5.56% to 5.97% by preparing the active layers with solvent additive DIO. The PL spectra show that the exciton dissociation efficiency in PBDT-TS1:ICBA can be increased by decreasing the ICBA aggregation level and optimizing the ICBA distribution in the active layer. The $J$–$V$ curves of the related hole-only and electron-only devices indicate that enhanced and more balanced charge transport ability can be obtained by optimizing D/A phase separation. The photovoltaic parameters of PSCs can be purposely optimized by adjusting the solution conditions according to the chemical structures of the electron donor and the electron acceptor. The investigation of $J$–$V$ curves of the symmetric electron-only devices under forward or reverse bias may provide a simple and effective method to evaluate the vertical phase separation in the active layers.

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Notes and references