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Optimization of charge carrier transport balance for performance improvement of PDPP3T-based polymer solar cells prepared from hot solution

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Polymer solar cells (PSCs) with poly(diketopyrrolopyrrole-terthiophene) (PDPP3T): [6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) as active layers were fabricated from different temperature solutions. The champion power conversion efficiency (PCE) of PSCs prepared from hot solution is about 6.22%, which is better than that of 5.54% for PSCs prepared from cool (room temperature) solution and 5.85% for PSCs prepared from cool solution with 1,8-diiodooctane (DIO) solvent additive. The underlying reasons on PCE improvement of PSCs prepared from hot solution should be attributed to the more dispersive donor and acceptor distribution in the active layer, resulting in the better bi-continuous interpenetrating network for exciton dissociation and charge carrier transport. The enhanced and more balanced charge carrier transport in the active layer is obtained for the PSCs prepared from hot solution, which can be demonstrated from the *J-V* curves of the related hole-only and electron-only devices.

1 Introduction

Polymer solar cells (PSCs) have attracted more and more interest due to their low-cost, roll-to-roll manufacturing, environmentally friendly process, lightweight and mechanical flexibility [1, 2]. Recently, low bandgap conjugated polymer donors are preferred for achieving high efficiency PSCs due to the expanded light absorption range, which can increase the photogenerated carrier densities in the active layer of PSCs [3-5]. The key essential condition for high performance PSCs is that the photogenerated carriers in the active layer must be swept-out by the internal field prior to their recombination [6]. Therefore, some effective strategies have been carried out to promote the sweep-out of charge carriers, such as: i) increasing the charge carrier transport by optimizing the molecules structure or weight of polymer donors [7, 8], ii) increasing the charge carrier collection on the electrodes by employing appropriate interfacial engineering [9-11], iii) increasing the excitons dissociation and charge carrier transport by tuning the donor/acceptor (D/A) phase separation in the active layer [12, 13]. Among the approaches, optimizing D/A phase separation has been one pillar to improve power conversion efficiency (PCE) of solution-processed PSCs. For example, Kim et al. reported that the PCE of PSCs was improved from 3.94% to 7.08% by optimizing the D/A phase separation in the active layer with 5% (v/v) solvent additive 1-chloronaphthalene (CN) [14]. However, the doping ratio and processing time of solvent additive should be accurately controlled during the preparation of blend solutions [15]. In addition, the residual of solvent additives in the active layer may lead to the instability of device performance [16].

The performance of PSCs can be seriously limited by the charge carrier recombination or formation of space charges in the active layer due to the various D/A domain sizes, especially to the unbalanced charge carrier transport in the active layer [17, 18]. Hence, a simple solution processing approach of active layer is required which can form homogeneous dispersive of D/A domains with moderate domain size for efficient and balanced charge carrier transport [19]. Adhikary et al. reported that the solubility of polymer poly(diketopyrrolopyrrole-terthiophene) (PDPP3T) in chlorobenzene (CB) was increased at 70 ℃ compared that at room temperature, and the PDPP3T:[6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) blend films prepared by spin-coating the 70 ^{o}C solution had an improved D/A phase separation due to decreased domain size [20]. It can be inferred that the D/A blend materials have a more dispersive distribution in hot solution and the D/A distribution can be well inherited in the active layer spin-coated from hot solution. Therefore, the active layer prepared from hot solution is an attractive approach to prepare high performance PSCs, especially the PSCs based on polymer donor that insoluble at room temperature. However, no further investigation on hot solution for performance improvement of PSCs has been reported from physical mechanism.

In this work, the PDPP3T:[6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) (1:2, Wt/Wt) hybrid were dissolved in 1,2-dichlorobenzene (*o*-DCB) solvent and then the mixed solution was heated to 70 ^{o}C in a sealed bottle under continuous stirring for better dissolution. The prepared hot solution was used to prepare the active layers of PSCs. The short circuit current density (J_{sc}), fill factor (FF), and the balance of charge carrier transport of PSCs prepared from hot solution were simultaneously improved compared with those of PSCs prepared from cool solution or cool solution with DIO additive. The optimized PCE of PSCs prepared from hot solution is about 6.22%, which is larger than 5.54.% for the PSCs prepared from cool solution and 5.85% for PSCs prepared from cool solution with DIO additive.

2 Experimental details

2.1 Preparation of the samples

Patterned indium tin oxide (ITO) coated glass substrates (15 Ω/□) were consecutively cleaned in ultrasonic baths containing glass lotion, de-ionized water, ethanol and then blow-dried by high pure N_2. All pre-cleaned ITO substrates were treated by UV-O_3 for 6 minutes for improving the work function of ITO and cleaning the surface of ITO coated substrates. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Clevios AI 4083) was filtered through a 0.22 μm syringe filter and spin-coated onto the ITO coated substrates at 5000 rounds per minute (rpm) with 40 s. Then the PEDOT:PSS coated ITO substrates were annealed at 120 °C for 10 minutes in atmospheric air and transferred into a N_2 glove box. Electron donor PDPP3T (purchased from Organtec Materials Inc., Mn > 240 k) and electron acceptor $PC_{71}BM$ (purchased from Luminescence Technology Corp.) hybrid was dissolved in *o*-DCB at a concentration of 15 mg/mL with D/A weight ratio of 1:2 at 70 °C. Part of the blend solution was kept at 70 °C for fabrication of PSCs with hot solution, and the rest of blend solution was cooled to room temperature. Then solvent additive DIO was added into part of the room temperature solution with 5 % volume. The PDPP3T:$PC_{71}BM$ solutions were spin-coated on top of the PEDOT:PSS layer to prepare the active layers. All the prepared PDPP3T:$PC_{71}BM$ blends films were treated under *o*-DCB vapor annealing for 2 hours. The lithium fluoride (LiF), molybdenum trioxide (MoO_3), aluminium or silver thin films was deposited by thermal evaporation under 3×10^{-4} Pa vacuum conditions, the thickness of film was monitored by a quartz crystal microbalance. The active area of PSCs was defined about 3.8 mm^2 by the vertical overlap area of ITO and Al electrodes. All the measurements were carried out in the room conditions.

2.2 Characterizations

The absorption spectra of films were measured with a Shimadzu UV-3101 PC spectrometer. The morphology of films was characterized by atomic force microscopy (AFM) using a multimode Nanoscope IIIa operated in tapping mode. The current-voltage (*I-V*) characteristics curves were measured by using a Keithley 4200 semiconductor characterization system. The AM 1.5 light at one Sun intensity 100 mW/cm^2 was provided by an ABET Sun 2000 solar simulator. The external quantum efficiency (EQE) spectra were measured by a Zolix Solar Cell Scan 100. The chemical structure of used materials and PSCs energy level diagram are shown in Fig. 1.

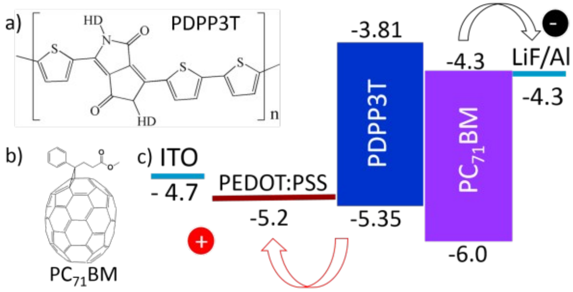

Fig. 1 The chemical structures of PDPP3T and $PC_{71}BM$, the energy level diagram of PSCs.

3 Results and discussion

Three series of PDPP3T:$PC_{71}BM$-based PSCs were prepared to investigate the evolution of charge carrier transport dynamics in the active layers prepared from different solutions. The competition between charge carrier transport and their recombination can be reflected by the FF values of PSCs [21]. The PDPP3T:$PC_{71}BM$ active layers were prepared from cool solution (Cool), cool solution with DIO additive (DIO) and hot solution (70 °C, Hot), respectively. The thickness of PDPP3T:$PC_{71}BM$ blend films was adjusted by changing spin-coating speed to obtain the optimized PCE of each kind of PSCs. The *J-V* characteristics curves and EQE spectra of all PSCs are shown in Fig. S1. According to the *J-V* curves, the key photovoltaic parameters of PSCs are shown in Table S1. The evolution of key photovoltaic parameters of PSCs along with the variation of active layers thicknesses are shown in Fig. 2, where the active layers thicknesses are represented by the spin-coating speeds of the related solutions. The optimized thicknesses are 137 nm (Cool, 1000 rpm), 123 nm (DIO, 1500 rpm) and 140 nm (Hot, 800 rpm), which corresponds to the optimized performance of PSCs prepared from different solutions. It is apparent that the open-circuit voltage (V_{oc}) is kept about from 0.64 V to 0.68 V for all PSCs prepared from different solution and spin-coating speeds. The J_{sc} of all PSCs shows a strong dependence on the thickness of active layers. The optimized active layer thickness is a result of the tradeoff between light absorption and charge carrier collection due to the limited charge carrier transport ability in the blend films [22-24]. The optimized FF and PCE of PSCs prepared from hot solution are larger than those of other PSCs, it means that the charge carrier transport ability and their balance have been improved in the active layer prepared from hot solution.

The *J-V* characteristics curves of each kind of optimized PSCs are shown in the Fig. 3a. The key photovoltaic parameters of PSCs according to the *J-V* curves were summarized and are listed in Table 1. The V_{oc} of all PSCs is kept almost constant about 0.67 V with 0.01 V indeterminacy. The optimized PSCs prepared from cool solution show a PCE of 5.54% along with a J_{sc} of 13.32 mA/cm^2 and a FF of 62.0%. The optimized PSCs prepared from cool solution with DIO additive show a relatively high PCE of 5.85% along with a J_{sc} of 14.27 mA/cm^2 and a FF of 61.2%. The positive effect of DIO additive on the performance of PSCs have been widely demonstrated and can be attributed to the improved D/A phase separation for better exciton dissociation and charge carrier transport, with less charge carrier recombination loss in active layer [25-27]. Here, it is worthwhile to be highlighted that the optimized PSCs prepared from the hot solution show the best PCE of 6.22% along with a relative high J_{sc} of 13.65 mA/cm^2 and a FF of 69.0%. In order to confirm the effect of active layer prepared from hot solution on the performance of PSCs, the EQE spectra of the optimized PSCs were measured and are shown in Fig. 3b.

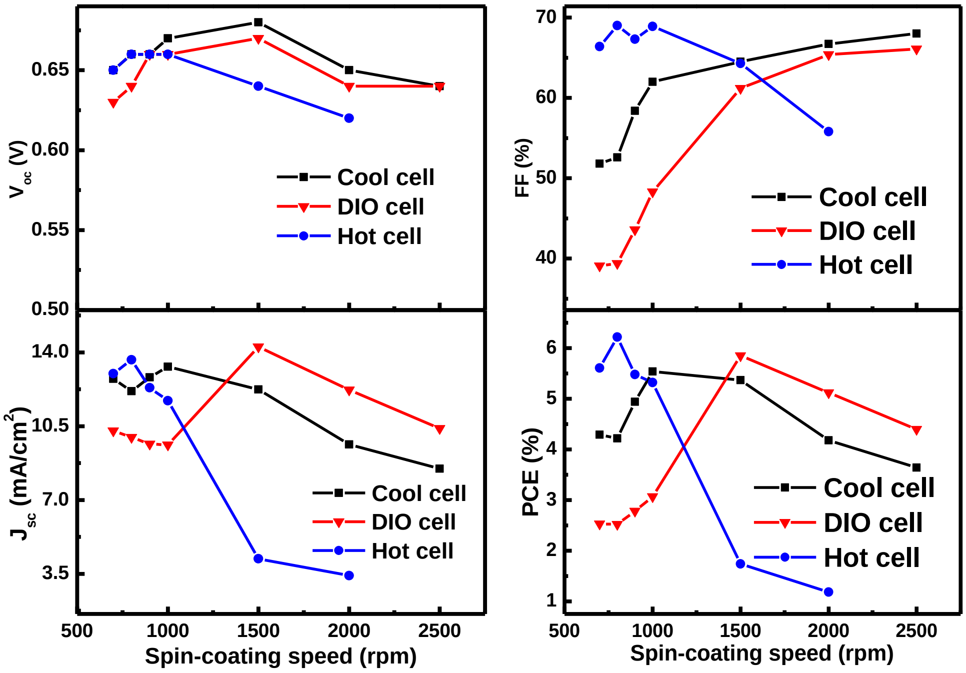

Fig.2 The evolution of key photovoltaic parameters of PSCs prepared from different solutions and different spin-coating speeds

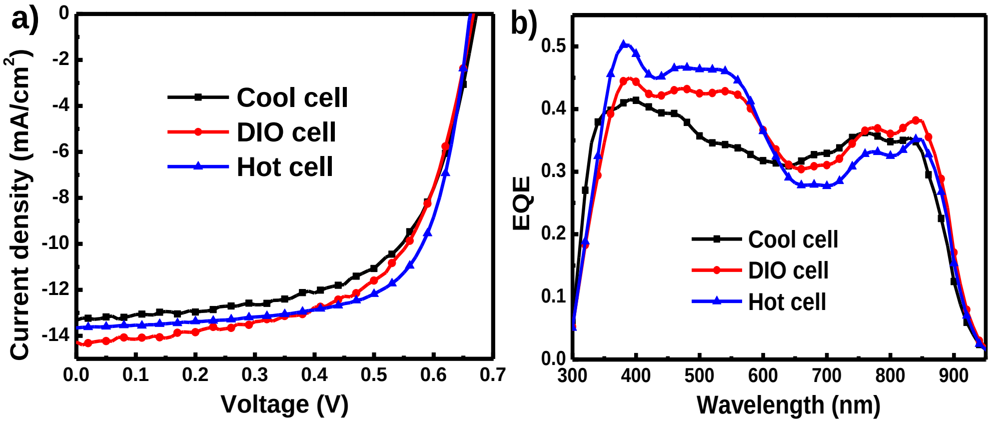

Fig.3 a) *J-V* curves and b) EQE spectra of the optimized PSCs prepared from different solutions.

Table 1 Performance of optimized PSCs prepared from different solutions

Solution	**V_{oc} (V)**	**J_{sc} (mA/cm^2)**	***FF* (%)**	**PCE (%)**	**PCE* (%)**
Cool	**0.67**	**13.32**	**62.0**	**5.54**	**4.74** [12]
DIO	**0.67**	**14.27**	**61.2**	**5.85**	**5.75** [12]
Hot	**0.66**	**13.65**	**69.0**	**6.22**	**4.02**^{a} [20]

* The PCE of PSCs based on PDPP3T:PCBM as the active layer reported by other group, ^{a} the acceptor is PC$_{61}$BM.

According to the EQE spectra of the optimized PSCs in the range from 350 nm to 600 nm, it is apparent that the EQE values are increased for the cells prepared from cool solution with DIO additive and the values are the maximum for the PSCs prepared from hot solution, which should be attributed to the more dispersive PC$_{71}$BM distribution for effective exciton dissociation and charge carrier transport [28]. In the longer wavelength from 650 nm to 900 nm, the PSCs prepared from cool solution with DIO additive show a negligible change. However, the PSCs prepared from hot solution show a slightly decreased EQE values in the same wavelength region, which plays a negative effect on the J_{sc}. As we might envisage, molecular arrangement of polymer PDPP3T in the active layer can be influenced by the solution processing ways. The molecular arrangement in the blend films may affect charge carrier transport ability and photon harvesting ability [29]. It means that the prominent FF values of PSCs prepared from hot solution may be originated from the enhanced charge carrier transport ability in the active layer.

The absorption spectra were measured to further clarify the underlying reason of active layer fabrication conditions on the performance of PSCs and are shown in Fig. 4. The light absorption in the range from 300 nm to 650 nm is mainly absorbed by $PC_{71}BM$ domains, and that in the range from 650 nm to 900 nm is mainly attributed to the PDPP3T domains [30]. It is apparent that absorption intensity of blend films prepared from cool solution with DIO additive and hot solution is decreased in the whole spectral range compared with the blend films prepared cool solution. It is worth noting that the thickest blend films (140 nm) prepared hot solution show lower absorption intensity compared with blend films prepared from cool solution (137 nm). The decreased absorption intensity in the range from 300 nm to 650 nm should be attributed to the more dispersive $PC_{71}BM$ domains in the blend films [31-33]. In the range from 650 to 900 nm, the decreased absorption intensity may be resulted from the change of PDPP3T molecular arrangement [34, 35]. The photon harvesting ability of polymer can be decreased due to the separated chains and decreased conjugation length induced by solvent treatment or adding solvent additive [35, 36]. The more dispersive $PC_{71}BM$ domains indicated that the charge carrier transport ability can be improved in the blend films prepared from cool solution with DIO additive and hot solution. In addition, the PDPP3T molecular arrangement inherited from the homogenous distribution in hot solution can lead to an improved charge carrier transport balance in the active layer prepared from hot solution.

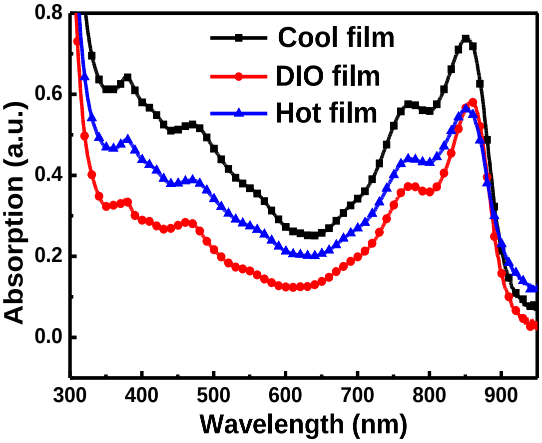

Fig.4 UV-vis absorption spectra of $PDPP3T:PC_{71}BM$ films prepared from different solutions, the fabrication conditions of films are same with the active layers of optimized PSCs.

In order to clarify the charge carrier transport ability and their balance on the performance improvement of PSCs, the hole-only ITO/PEDOT:PSS/active layers/MoO_3 (10 nm)/Ag (50 nm) and electron-only ITO/Al (10 nm)/LiF (1 nm)/active layers/LiF (1 nm)/Al (100 nm) devices were fabricated according to the related PSCs. The *J-V* curves of hole-only and electron-only devices were measured in dark conditions and are shown in Fig. 5a. To provide more valuable information on charge carrier transport ability of active layers prepared different conditions, the *J-V* characteristics of hole-only and electron-only devices were measured under low bias (less than 1 V). It is apparent that hole transport ability is larger than electron transport ability for all active layers prepared from different solutions. It means that the performance of PSCs was restricted by the relative weak electron transport ability. Compared with the device prepared from cool solution, the hole current density of hole-only devices prepared from hot solution was only moderately increased under the same applied voltage. According to the *J-V* curves of electron-only devices, the electron-only devices prepared from hot solution show the largest current density under the same applied voltage, which means that the electron transport channels can be well formed in the active layers prepared from hot solution. For the PSCs prepared from hot solution, the increased hole and electron transport ability is important reason for the performance improvement of PSCs. The current density ratios of electron to hole were calculated and are shown in the Fig. 5b. It is apparent the hole and electron transport balance in active layer prepared from hot solution is improved significantly compared with the other active layers. The simultaneously improved charge carrier transport and their balance lead to the largest PCE of 6.22% in the PSCs prepared from hot solution. For the PSCs prepared from cool solution with DIO additive, the performance improvement is limited due to the unbalanced charge transport, although both hole and electron transport ability are increased.

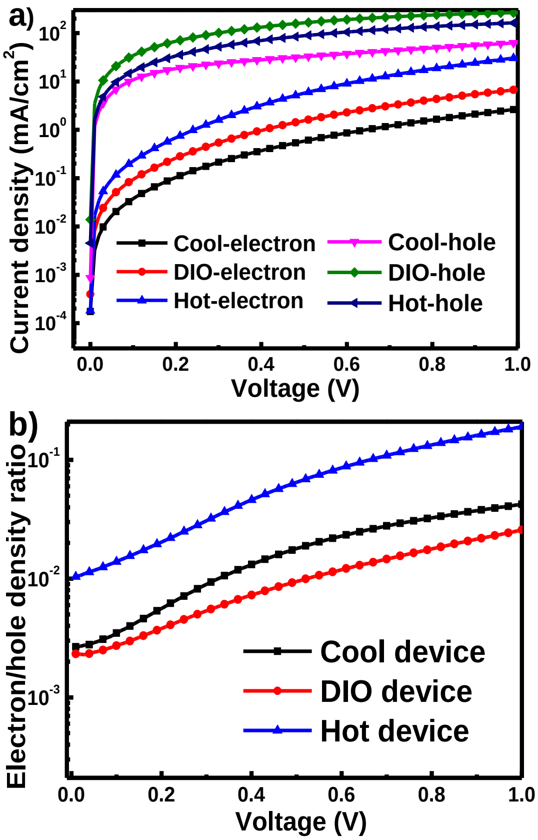

Fig. 5 a) The *J-V* characteristic curves of hole-only and electron-only devices, b) the calculated current density ratios of electron to hole of devices.

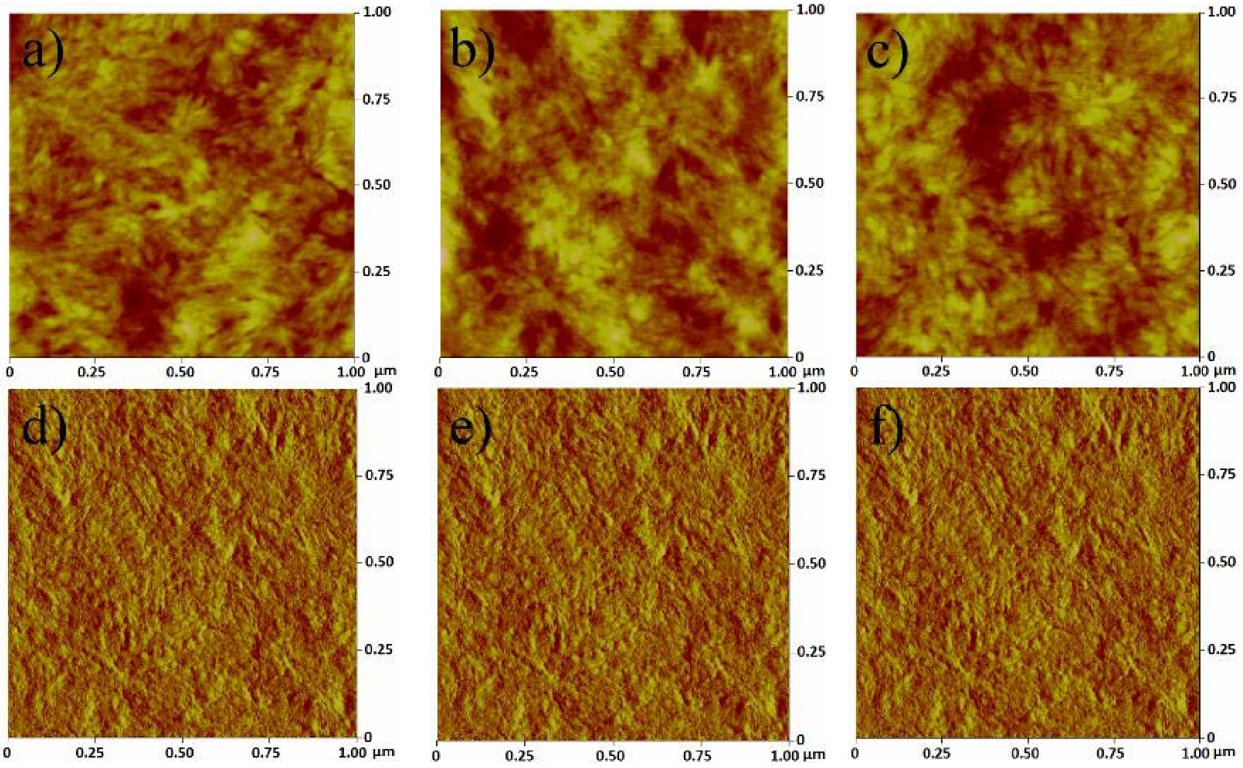

Fig.6 Morphology and phase images of PDPP3T:PC$_{71}$BM blend films prepared from different solutions, a and d) films prepared from cool solution, b and e) films prepared from cool solution with DIO additive, c and f) films prepared from hot solution (height scale: 12.0 nm, phase scale: 15°)

In order to further demonstrate that the simultaneously improved charge carrier transport ability and their balance in the active layer prepared from hot solution was resulted by the more homogenous D/A distribution, the surface morphology of PDPP3T:PC$_{71}$BM blend films prepared from different solutions were measured with tapping mode AFM, as shown in Fig. 6. The root mean square surface roughness (RMS) of the blend films prepared cool solution and cool solution with DIO additive are 10.4 nm and 10.3 nm, respectively. The decreased RMS should be attributed to the more dispersive PC$_{71}$BM domains induced by the DIO additive. The RMS in the film prepared from hot solution was decreased to 9.0 nm, meaning that the aggregation levels of PDPP3T domains was decreased. The more homogenous D/A distribution in the active layer is beneficial to exciton dissociation and the charge carrier transport as well as their balance in the active layers prepared from hot solution.

3 Conclusions

In summary, the champion PCE of PSCs based on PDPP3T:PC$_{71}$BM as active layer prepared from 70 °C solution arrives to 6.22%, which is better than that of 5.54% for PSCs prepared from cool solution (room temperature) and 5.85% for PSCs prepared from cool solution with DIO additive. The performance improvement of PSCs prepared from hot solution can be attributed to the better bi-continuous interpenetrating network for excitons dissociation and charge carrier transport. The balance between hole and electron transport in the active layer prepared from hot solution is optimized, resulting in the largest FF among the PSCs. This strategy may provide a simple and effective method to adjust phase separation of donor and acceptor materials for improving the performance of PSCs.

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Notes and references

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