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Enhanced performance of polymer solar cells by employing ternary cascade energy structure

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We present a route to successfully tackle two main limitations, low open circuit voltage (V_{oc}) and limited short circuit-density (J_{sc}), of polymer solar cells (PSCs) based on poly(3-hexylthiophene) (P3HT) as electron-donor. The indene-C60 bisadduct (ICBA) was selected as electron acceptor to improve open circuit voltage (V_{oc}). Narrow band gap polymer poly[(4,8-bis-(2-ethylhexyloxy)-benzo[1,2-b:4,5-b′]dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thieno [3,4-b]thiophene)-2,6-diyl] (PBDTTT-C) as the complementary electron-donor material was doped into the host system of P3HT:ICBA to compose ternary cascade energy structure PSCs for increasing J_{sc}. The power conversion efficiency (PCE) of P3HT:ICBA-based cells was improved from 3.32% to 4.38% by doping 3 wt% PBDTTT-C and 1 minute 150℃ annealing treatment. The 4.38% PCE of ternary PSCs is still larger than that 3.79% of the PSCs based P3HT:ICBA with 10 minutes 150℃ annealing treatment.

1 Introduction

The excessive development and consumption of mineral materials have brought a series of problems to the society progress, such as energy shortage, greenhouse effect, acid rain as well as haze. The polymer solar cells (PSCs) as inexpensive renewable energy source have attracted enormous attention because of their easy fabrication, light weight, flexibility, and abundant raw materials.[1-3] One of the most accessible electron-donor materials is poly(3-hexylthiophene) (P3HT), which has relatively good charge transport properties and high crystallinity among the different conjugated polymers.[4, 5] In addition, compared with narrow band gap electron-donor materials, polymer P3HT has a relative good stability during thermal treatment on the blend films with fullerene derivatives. The system of P3HT and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) was the mostly studied for the PSCs in the past ten years, obtaining power conversion efficiencies (PCEs) of 3-5%.[6-8] However, further improvement PCE of PSCs based on P3HT:PCBM as the active layer may be limited by following factors: i) low open circuit voltage (V_{oc}) ~0.6V results from the low lowest unoccupied molecular orbital (LUMO) energy level of PCBM; ii) low short-circuit current (J_{sc}) is mainly due to the limited photon harvesting (only 22% of the total photons in solar light) induced by the wide band gap ~2 eV of P3HT.[9, 10]

It is well known that V_{oc} of PSCs is mainly determined by the difference between the LUMO energy level of electron-acceptor material and the highest occupied molecular orbital (HOMO) of electron-donor material.[11] To improve the V_{oc} of PSCs, a series of fullerene derivatives with high LUMO energy levels have been synthesized as electron-acceptors.[12, 13] Blom et al. reported that a novel type of fullerene (bisPCBM) as electron-acceptor and P3HT as electron-donor achieved a relative high V_{oc} of 0.73V.[14] Hou et al. reported an excellent electron-acceptor material, indene-C60 bisadduct (ICBA), with

a LUMO level 0.17 eV higher than that of PCBM.[15, 16] The PSCs based on P3HT:ICBA matrix achieved the higher V_{oc} of 0.84 V compared with that of P3HT:PCBM cells. Furthermore, ICBA has more facile synthesis, higher solubility in common organic solvents, and stronger visible absorption for better photon harvesting in the photovoltaic process.[17, 18]

In order to extend absorption range of the active layer for achieving high performance PSCs, different strategies have been extensively carried out, such as design and synthesis of narrow band gap polymer or adopting tandem structure. However, both synthesizing new materials and fabricating tandem PSCs have serious technical challenges as well as high cost.[4] Recently, ternary cascade energy structure as a promising alternative strategy has been realized to extend the spectral response of wide band gap polymers into the near infrared (NIR) region, resulting in J_{sc} and PCE improvement.[19-22] In addition, the exciton dissociation and charge carriers transfer in blend films could be effectively optimized by the ternary cascade energy structure.[23, 24] Chen et al. reported that design of the complementary materials for ideal ternary PSCs is required to achieve suitable energy-level offset, optimal panchromatic absorption, more balanced charge carriers transport and collection, as well as high photon harvest efficiency.[25]

In this research, we present an effective strategy to simultaneously improve V_{oc} and J_{sc} of PSCs based on P3HT as electron-donor material. A narrow band gap polymer poly[(4,8-bis-(2-ethylhexyloxy)-benzo[1,2-b:4,5-b′]dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thieno[3,4-b]thiophene)-2,6-diyl] (PBDTTT-C) as complementary electron-donor material was blended into the host system of P3HT:ICBA to compose ternary cascade energy structure PSCs. The power conversion efficiency (PCE) of P3HT:ICBA based PSCs was improved from 3.32% to 4.38% by doping 3 wt% PBDTTT-C and 1 minute 150℃ annealing treatment, which corresponds to about 32% PCE improvement. The optimized PCE of ternary PSCs

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with 1 minute 150℃ annealing treatment also shows a superior performance compared with binary PSCs with 10 minutes 150℃ annealing treatment.

2 Experimental

2.1 Preparation of the samples

The indium tin oxide (ITO) glass substrates (sheet resistance 15 Ω/□) 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 clean substrates and 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 4000 round per minute (RPM) for 40 s, and then annealed at 120 ℃ for 10 minutes in room conditions. The electron-donors, P3HT (purchased from Luminescence Technology Corp) and PBDTTT-C (purchased from Luminescence Technology Corp), were dissolved in 1,2-dichlorobenzene to generate 36 mg/ml blend solutions. The doping concentrations of PBDTTT-C in donors are 0, 1 wt%, 3 wt%, 5 wt%, 30 wt% and 100 wt%. The electron-acceptor, ICBA (purchased from Luminescence Technology Corp), was individually prepared in 1,2-dichlorobenzene at a concentration of 36 mg/ml and then mixed with the blend solutions of donors. The weight ratio of electron-donors to electron-acceptor was kept constant at 1:1. The ternary mixed solutions were spin-coated on PEDOT:PSS layer at 800 RPM in a high purity nitrogen-filled glove box to fabricate the active layers. The thicknesses of active layers are about 160 nm, which was measured by Ambios Technology XP-2 stylus Profiler. The cathode of LiF/Al (0.9 nm/100nm) was deposited 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. Thermal treatment on active layers was carried out at 150℃ for various time in high-purity nitrogen-filled glove box after evaporation LiF/Al cathode. A series of ternary and binary PSCs were fabricated under the same conditions to investigate the effect of PBDTTT-C doping concentrations on performance of ternary PSCs. The schematic configuration of the PSCs and chemical structures of used materials are shown in Fig. 1.

2.2 Characterizations

The thickness of the active layers was measured by an Ambios Technology XP-2 stylus Profiler. Photoluminescence (PL) spectra of films were measured by a Perkin Elmer LS-55 spectrophotometer. The absorption spectra of films were obtained using a Shimadzu UV-3101 PC spectrometer. The current density-voltage (*J-V*) characteristics of PSCs were measured using a Keithley 4200 semiconductor characterization system and ABET Sun 2000 solar simulator. The external quantum efficiency (EQE) spectra of PSCs were measured by a Zolix Solar Cell Scan 100. X-Ray diffraction (XRD) patterns were collected using a Bruker D8 Advance X-Ray diffractometer. The morphology of films was investigated by atomic force microscopy (AFM) using a multimode Nanoscope IIIa operated in tapping mode.
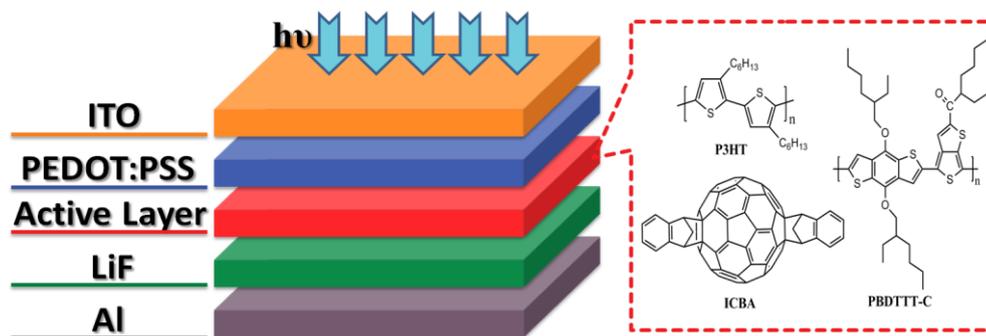
Fig. 1 Schematic configuration of the PSCs and chemical structures of used materials in active layer.

3 Results and discussion

The absorption spectra of pure P3HT and PBDTTT-C films as well as the PL spectra of P3HT films are shown in Fig. 2(a). It is apparent that the absorption spectra of the two electron-donor materials show an apparent complementary in the range from 400 nm to 800 nm, which is beneficial for the solar light photon harvesting in the ternary PSCs. The main absorption peaks of P3HT and PBDTTT-C films locate at 518 nm and 685 nm, respectively. The emission spectrum of P3HT films shows a wide emission range from 600 to 800 nm with an emission peak at 700 nm. The well spectral overlap between PBDTTT-C absorption spectrum and PL spectrum of P3HT indicates that Förster resonance energy transfer (FRET) certainly occurs between P3HT and PBDTTT-C molecules.[22] The FRET of P3HT and PBDTTT-C may provide an additional route to improve exciton dissociation efficiency at interfaces between two electron-donor materials and ICBA. The energy levels diagram of used materials and cathodes is shown in insert of Fig. 2(a), which outlines the possible charge carriers transfer pathways in blend system. The excitons formed on P3HT and PBDTTT-C may be directly dissociated into free charge

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carriers at their interfaces between ICBA or may have a FRET process before dissociation. The HOMOs of P3HT and PBDTTT-C are very similar, which is beneficial to holes intermolecular transfer between P3HT and PBDTTT-C. Therefore, the narrow band gap polymer PBDTTT-C is an ideal complementary electron-donor material to P3HT for the widened photon harvesting range, meanwhile the matched energy levels is beneficial to charge carrier transfer or transport in the ternary blend thin films. The charge carrier transport

should be influenced by the intermolecular charge transfer between P3HT and PBDTTT-C. Therefore, the performance of PSCs should be codetermined by the balance between photon harvesting and charge carrier collection. In order to confirm the influence of PBDTTT-C doping concentrations on the photon harvesting of ternary blend thin films, the absorption spectra of ternary blend films were measured and are shown in the Fig. 2(b).
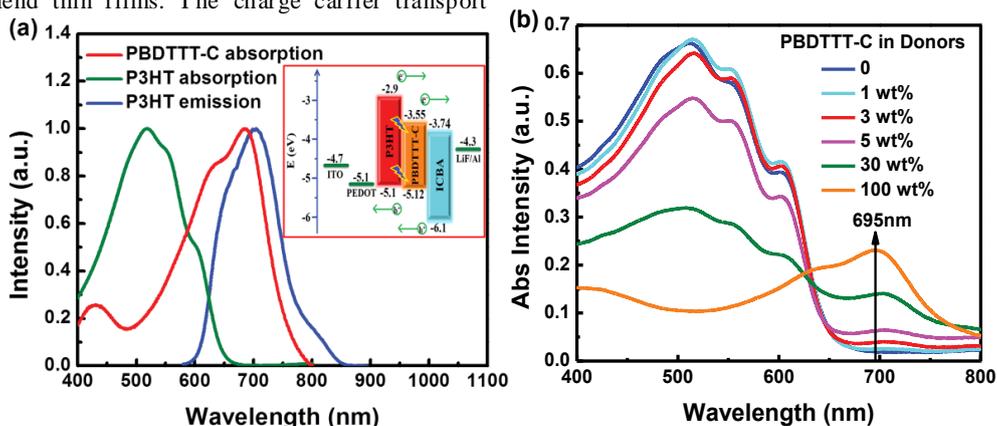
Fig. 2 (a) Normalized absorption spectra of P3HT and PBDTTT-C films, and emission spectrum of P3HT film. Inset: energy levels diagram of used materials and cathodes, curved arrows indicate the pathways of charge carriers transfer in the ternary blend and the lightning bolt indicate the potential energy transfer pathway; (b) absorption spectra of P3HT:PBDTTT-C:ICBA films with various PBDTTT-C doping concentrations.

It is obvious that the binary blend P3HT:ICBA films present a relative strong absorption in the range of 400 nm to 650 nm. The PBDTTT-C:ICBA films have a broad absorption in the longer wavelength range with an absorption peak at 695 nm. The relative absorption intensity from 650 nm to 800 nm of the ternary blend films could be regularly enhanced along with the increase of PBDTTT-C doping concentrations, which indicates that more low energy photons have been harvested by PBDTTT-C molecules. The absorption intensity of ternary blend films shows a slightly decrease in the visible light range when PBDTTT-C doping concentrations are less than 3 wt%, it means that the π-π stacking of P3HT may be not disrupted under the lower PBDTTT-C doping concentrations.[23] However, absorption intensity of ternary blend films was distinctly decreased along with the increase of PBDTTT-C doping concentration, which may be due to the distorted P3HT molecular arrangement induced by doping more PBDTTT-C molecules.
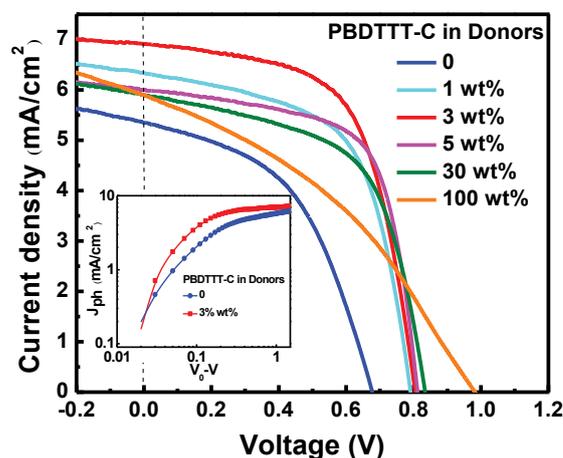
Fig. 3 *J-V* characteristics of PSCs with various PBDTTT-C doping concentrations under 100 mW/cm^2 illuminations intensity, inset: photocurrent density dependence on the effective voltage.

Table 1 Key photovoltaic parameters of PSCs with various PBDTTT-C doping concentrations

PBDTTT-C in Donors	J_{sc}	V_{oc}	FF	PCE [%]	
[wt%]	[mA:cm^2]	[V]	[%]	Best	Average*
0	5.33	0.68	48	1.74	1.65
1	6.34	0.79	60	3.00	2.90
3	6.91	0.80	62	3.43	3.35
5	6.02	0.81	65	3.18	3.07
30	5.89	0.83	59	2.88	2.77
100	5.90	0.98	37	2.15	2.09

*Average PCE: more than 50 PSCs without annealing treatment were evaluated

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The *J-V* characteristics of PSCs were measured under 100 mW/cm^2 illuminations intensity and are shown in Fig. 3. According to the *J-V* curves, the corresponding photovoltaic parameters of PSCs are summarized in Table 1. The PCE of ternary PSCs with 3 wt% PBDTTT-C arrived to 3.43%, with a J_{sc} of 6.91 mA/cm^2, a V_{oc} of 0.8V, and a fill factor (FF) of 62%. However, the PCE of PSCs based on P3HT:ICBA (control cells) is only 1.74% for the cells without annealing treatment, which is due to the serious horizontal phase separation in the active layers results from highly symmetric molecule ICBA.[26-28] We analysed the effect of PBDTTT-C doping concentration on the performance of PSCs without annealing treatment. The maximum PCE of ternary PSCs was obtained for the cells with 3 wt% PBDTTT-C as the complementary electron-donor and then was decreased along with the increase of PBDTTT-C doping concentrations. According to the absorption spectra of binary and ternary blend films, the ordered P3HT molecular arrangement was disrupted by the more PBDTTT-C doping, resulting in the absorption intensity decrease in the visible light range. As we known, the disordered P3HT molecular arrangement may also decrease the charge carrier transport in the ternary blend films, which results in the decrease of J_{sc} along with the increase of PBDTTT-C doping concentrations. Therefore, there is a balance between photon harvesting and charge carrier collection induced by doping PBDTTT-C. The performance of ternary PSCs was decreased when PBDTTT-C

doping concentration exceed 3 wt%, which may be attributed to more exciton from P3HT transfer to PBDTTT-C or the limited charge carrier transport in the ternary blend films. It is known that the PSCs based on PBDTTT-C:ICBA matrix showed a much lower PCEs than that of PBDTTT-C:PCBM cells, which is due to the weak driving force for exciton dissociation due to the small difference LUMOs barrier between PBDTTT-C and ICBA.[29, 30] The J_{sc} and FF of PSCs were decreased due to the more PBDTTT-C doping, which may be attributed to the disrupted interpenetrated network of P3HT:ICBA matrix, resulting in the limit of charge carrier transport in the ternary blend films.[31] In order to further confirm the effect of PBDTTT-C doping concentrations on the charge carrier transport in the blend films, the photocurrent density (J_{ph}) dependence on the effective voltage of control cells and ternary cells (3 wt% PBDTTT-C doping concentration) were investigated (inset of Fig. 3(a)). The J_{ph} is defined as the difference between the current density under illumination (J_L) and the current density in dark (J_D), thus $J_{ph} = J_L$-J_D. The J_{ph} of the ternary PSCs could rapidly come into the saturation status than that of control cells along with the increase of reverse bias, it means that the ternary blend films with 3 wt% doping concentration may provide an effective charge carrier transport compared with the P3HT:ICBA films without annealing treatment.[32]
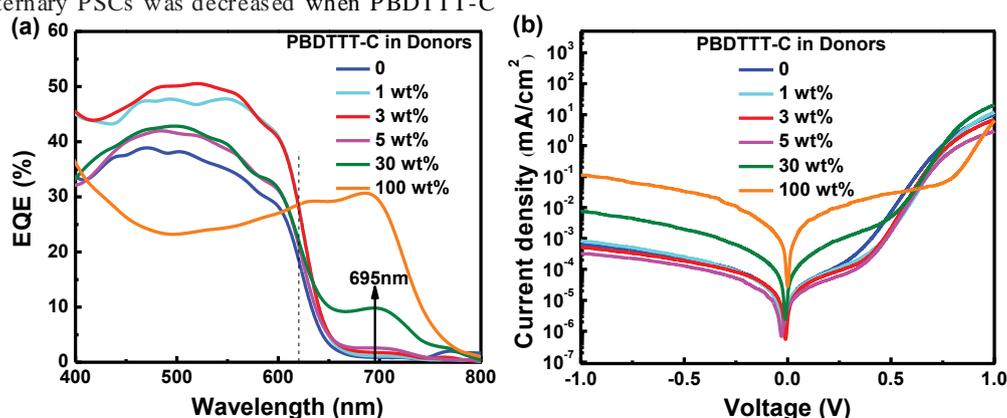
Fig. 4 (a) EQE spectra of PSCs with various PBDTTT-C doping concentrations; (b) dark *J-V* characteristics of PSCs with various PBDTTT-C doping concentrations.

Fig. 4(a) shows the EQE spectra of PSCs with various PBDTTT-C doping concentrations. The EQE spectra of PSCs with 3 wt% PBDTTT-C doping concentrations are the best among the PSCs, which accords with the observed performance from *J-V* characteristics. The EQE spectra of PSCs are increased more than 10% in the region from 400 nm to 620 nm

by doping 3 wt% PBDTTT-C concentration. The change of absorption spectrum of the film is not obvious in this region, which indicates that the EQE enhancement of PSCs should be attributed to the additional exciton dissociation and charge carriers paths.[33] Meanwhile, the EQE spectra of ternary PSCs in the range of 620 nm to 800 nm were continually improved

along with the increase of PBDTTT-C doping concentrations. However, the EQE spectra of ternary PSCs from 400 nm to 620 nm were significantly decreased when the PBDTTT-C doping concentrations exceed 3 wt%. These results are in good agreement with the absorption spectra of ternary blend films with different PBDTTT-C doping concentrations, as shown in Fig. 2(b). The enhancement of EQE spectra is not distinct in the range of 620 nm to 800 nm when the doping concentrations of PBDTTT-C are lower than 5 wt%. As seen from Fig. 4(b), it is very interesting that the dark current densities of ternary PSCs (less than 5 wt% PBDTTT-C doping concentration) have the similar trend and values compared with that of the control cells. There is a relative large leak current for the ternary PSCs with high PBDTTT-C doping concentrations, especially to the cells with 30 wt% and 100 wt% PBDTTT-C doping concentrations. It may be concluded that the higher PBDTTT-C doping concentrations in active layers may have a negative influence on charge transport and collection in the ternary PSCs, resulting in the distinctly decreased FF.[34]

It is known that the crystallinity and nanomorphology of P3HT-based films could be improved by annealing treatment, resulting in the improved performance of the PSCs.[17, 35, 36] Li et al. reported that the interpenetrating network of P3HT:ICBA matrix was enhanced by annealing treatment, which is beneficial to the exciton dissociation and charge transport.[15] In order to study the influence of annealing treatment on the performance of ternary PSCs, a series of control cells and ternary cells were annealed at 150 ℃ with different time. The *J-V* characteristic curves of PSCs after annealing treatment are shown in ESI. The typical *J-V* characteristic curves of PSCs with different annealing treatment time are shown in Fig. 5(a) and the key parameters of PSCs are summarized in the Table 2. As shown in Fig. 5(b), the diffraction peak intensity of both control and ternary (3 wt% PBDTTT-C doping concentration) films is increased by annealing treatment, which indicates that the crystalline fibrils consisting of a more ordered packing of P3HT chains could be formed during annealing treatment.
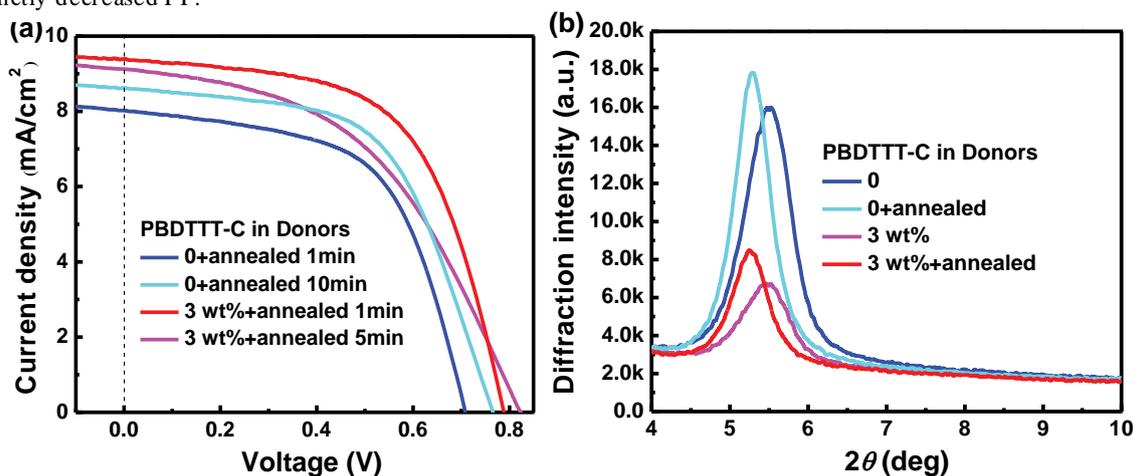
Fig. 5 (a) *J-V* characteristics of PSCs with 150 ℃ annealing treatment for different time under 100 mW/cm² illumination, (b) XRD patterns of control and ternary (3 wt% PBDTTT-C doping concentration) films with or without annealing treatment.

Table 2 Key photovoltaic parameters of PSCs with different annealing treatment time.

PBDTTT-C in Donors [wt%]	J_{sc} [mA:cm²]	V_{oc} [V]	FF [%]	PCE[%]	
				Best	Average*
0 + annealed (1 minute)	8.03	0.71	55	3.32	3.21
0 + annealed (10 minutes)	8.63	0.77	57	3.79	3.65
3+ annealed (1 minute)	9.41	0.79	60	4.38	4.30
3+ annealed (5 minutes)	9.13	0.82	47	3.55	3.42

*Average PCE: more than 50 annealed cells were evaluated

The PCE of control cells with 1 minute 150℃ annealing treatment was improved to 3.32% from 1.74% for the PSCs without annealing treatment, resulting from the improvement of J_{sc}, V_{oc} and FF. The PCE of the control cells could be improved to 3.79% by 10 minutes 150℃ annealing treatment. It should be mentioned that the ternary PSCs with 1 minute annealing treatment arrives to the champion performance with J_{sc} of 9.41 mA/cm², V_{oc} of 0.79 V, FF of 60%, and PCE of 4.38%.

However, , the PCE of ternary PSCs was decreased to 3.55% due to further increasing annealing treatment time up to 5 minutes. The decreased performance of ternary PSCs may be due to the degradation of PBDTTT-C induced by the prolonged annealing treatment time. Commonly, annealing treatment also results in the decreased performance of PSCs based on narrow band gap materials.[37, 38] The short time annealing treatment on ternary blend PSCs maybe adjust the molecular arrangement

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and optimize morphology of the active layer film for the better exciton dissociation.
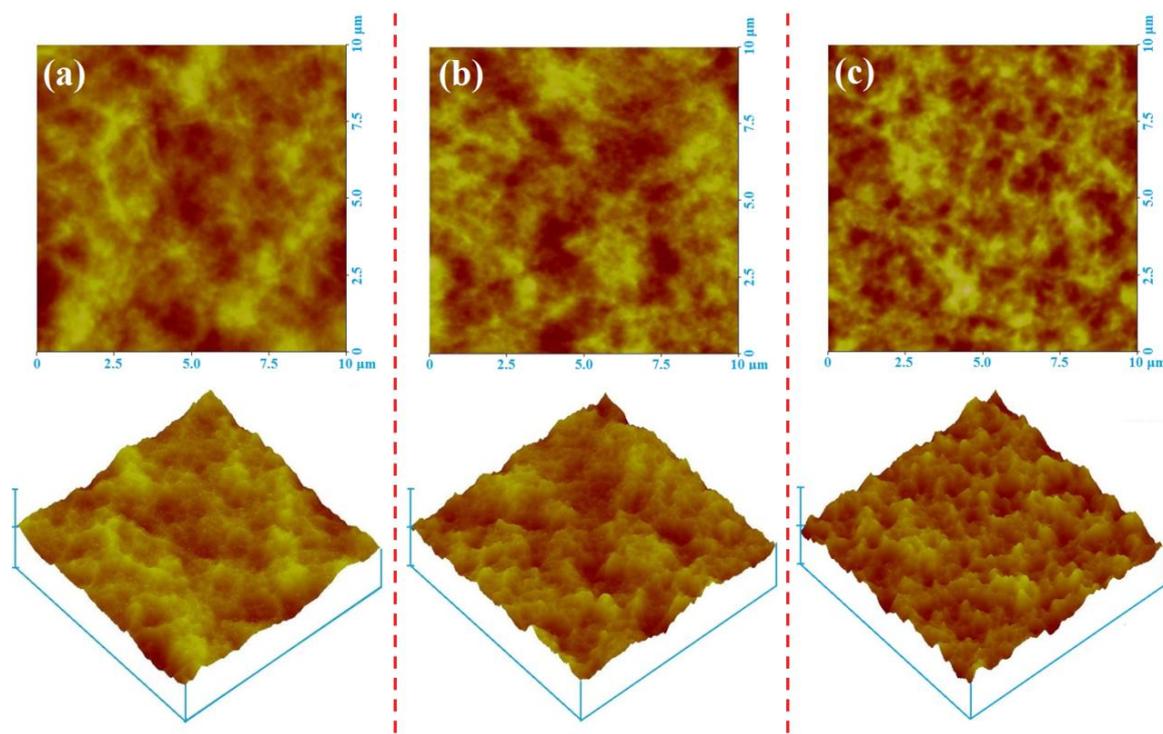
Fig. 6 AFM morphology images of films of (a) P3HT:ICBA as cast, (b) P3HT:ICBA films with annealing treatment at 150 ℃ for 1 minute, and (c) P3HT:PBDTTT-C:ICBA (3 wt% PBDTTT-C doping concentration in donors) films with annealing treatment at 150 ℃ for 1 minute.

In order to further clarify the effect of annealing treatment and PBDTTT-C doping concentrations on the performance of PSCs, the morphology of the P3HT:ICBA films and the ternary films (3 wt% PBDTTT-C doping concentration) with or without annealing treatment were measured by atomic force microscopy (AFM). The preparation conditions of the films for AFM measurement were kept constant compared with those for fabricating cells. As clearly show in Fig. 6(a), the surface morphology of the P3HT:ICBA film without annealing treatment is quite rough and root-mean-square (RMS) roughness is about 27.5 nm, resulting a relative low PCE of 1.74%. Lin et al. reported that the highly symmetric molecule ICBA could result in serious horizontal phase separation of the incompatible organic-inorganic interface and then render asymmetrical the blending of the acceptor/donor morphology, which have negative influences on the performance of PSCs.[28] According to the Fig. 6(b), the morphology of control films becomes more smoother with RMS of 21.5 nm after annealing treatment at 150 ℃ for 1 minute, which is beneficial to exciton dissociation and charge carriers transfer.[39, 40] It is interesting to note from Fig. 6(c) that the surface roughness of the ternary blend film with 1 minute 150 ℃ annealing treatment is about 12.7 nm. The noticeable change in the morphology can be explained by the fact that the addition of proper PBDTTT-C into P3HT:ICBA allows tailoring of the miscibility between P3HT and ICBA leading to more homogeneous films and optimal domain sizes with smooth surface.[41] The optimized surface morphology and nanometer-scale phase separation of the films could provide large interface area for exciton dissociation as well as continuous percolating path for hole and electron transport to respective electrodes.

4 Conclusions

In conclusion, the performance of P3HT:ICBA-based cells was effectively improved by doping the proper concentration of narrow band gap material PBDTTT-C. With such a simple strategy of ternary cascade energy structure, the PCE of PSCs was improved from 1.74% to 3.43% by doping 3 wt% PBDTTT-C as the complementary electron-donor material. Moreover, the PCE of the ternary cell was further enhanced to 4.38% with 1 minute 150 ℃ annealing treatment on cells. The performance improvement of ternary PSCs should be predominantly attributed to the better exciton dissociation, charge carriers transport and collection. The strategy of this ternary blend films can be expanded to other low band gap conducting polymers for high efficiency bulk heterojunction PSCs, which has a far-reaching impact on the industrialization of PSCs due to the effortless cells fabrication process.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [*J-V* characteristic curves of control and ternary PSCs annealed at 150 ℃ for various time]. See DOI: 10.1039/b000000x/

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Ternary cascade energy structure was demonstrated an effective strategy for improving the performance of polymer solar cells.