Control of the active layer nanomorphology by using co-additives towards high-performance bulk heterojunction solar cells

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A B S T R A C T

In this work, two high boiling-point solvents (1-chloronaphthalene (CN) and 1,8-diiodooctane (DIO)) were utilized as co-additives in ortho-dichlorobenzene (ODCB) and chlorobenzene (CB) solutions to fine tune the donor and acceptor domains in the bulk heterojunction (BHJ) of poly(benzo[1,2-*b*:4,5-*b'*]dithiophene-*alt*-thieno[3,4-*c*]pyrrole-4,6-dione) (PBDTTPD) and fullerene derivatives. A power conversion efficiency of 7.1% and a fill factor up to 70% were obtained for solar cells with active area of 1 cm^2 when using [6,6]-phenyl C61-butyric acid methyl ester (PC$_{60}$BM) as acceptor, suggesting that an optimized morphology was achieved.

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1. Introduction

Polymer-based bulk heterojunction (BHJ) solar cells are one of the most promising solar cell technologies because of their low cost, simple device structures, and facile production scalability [1,2]. The control of the nano-scale morphology of the active layer is of paramount importance in achieving high-efficiency solar cells because it directly affects photocurrent and fill factor [3]. The morphology/sizes of the donor and acceptor domains in the active layer needs to be controlled and strikes a balance between efficient exciton dissociation and charge transport. The photogenerated excitons need to reach a donor/acceptor heterojunction to dissociate before it recombines. For the most efficient exciton dissociation, the donor/acceptor phase separation should be kept at minimum. A perfect mixing provides the best exciton quenching. However, the requirements for efficient charge transfer complex dissociation and charge transport are opposite in terms of domain

sizes: the coarser, the better. Therefore, the best device efficiencies are expected when the spatial dimensions of the domains correspond to twice the exciton diffusion length (∼20–40 nm). A number of approaches are widely used in the literature to control the bulk heterojunction (BHJ) morphology. One approach is the thermal annealing [4,5], it works well for crystalline materials such as P3HT. However, since P3HT is a quite unique conjugated polymer, this approach cannot be applied for all the materials used in bulk heterojunction (BHJ) solar cells, especially when those materials are mainly amorphous. Another approach used to control the nanomorphology of the blends is the so called slow drying or solvent annealing process, which controls the film drying process by increasing the partial vapour pressure around the sample or using high boiling temperature solvents so that the intrinsic driving force for self-organization in these materials can be used to form ordered structures during the quasi-equilibrium film drying process [6,7]. More recently, the additives approach has also attracted a lot of attention [8,9]. By incorporating a small amount of specific processing additives, such as 1-chloronaphthalene (CN) or 1,8-diiodooctane (DIO), into the host

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solvent, it is possible to control the phase separation in some BHJ systems and improve the performances of the devices [8–11]. Thus, by controlling the solvent quality of the additive for both the polymer and the fullerene derivative, both the polymer order and the degree of phase separation can be tuned. According to literature, 1,8-diiodooctane (DIO) is known to dramatically decrease aggregation and order within the polymer domains while avoiding excessive crystallization of the fullerene [9]. On the other hand, 1-chloronaphthalene (CN) is known to be a good solvent for aromatic polymers. The high boiling point and low vapor pressure of CN reduce the evaporation kinetics in the blend solvent and provide control over the morphology of the active layer [8].

We reported for the first time an alternating copolymer based on thieno[3,4-c]pyrrole-4,6-dione (TPD) for BHJ solar cells [12]. Poly(benzo[1,2-b:4,5-b']dithiophene-alt-thieno[3,4-c]pyrrole-4,6-dione) (PBDTTPD) was obtained using Stille cross-coupling polymerization. The molecular weights were determined using high temperature gel permeation chromatography (GPC) in trichlorobenzene at 140 °C (M_n = 13 kDa; M_w = 34 kDa; PDI = 2.6) since solubility issues have been noticed in chloroform or in tetrahydrofuran. In fact, aggregation was observed when GPC measurements were performed in both solvents which led to over-estimated molecular weights and wide polydispersity indexes. Power conversion efficiency (PCE) of 5.5% when PBDTTPD was blended with [6,6]-phenyl C_{71}-butyric acid methyl ester ($PC_{70}BM$) was reported [12]. It is worth noting that the active area of the device was 1 cm^2. A few weeks after, another group also reported BHJ solar cells using the same polymer (PBDTTPD). The molecular weights (determined by GPC in THF) were higher (M_n = 35 kDa; M_w = 94 kDa; PDI = 2.7). A power conversion efficiency up to 6.8% was reported with a short-circuit current (J_{sc}) of 11.5 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.85 V, and a fill factor (FF) of 0.68 for PBDTTPD:[6,6]-phenyl C_{61}-butyric acid methyl ester ($PC_{60}BM$) active layer on an area of 0.03 cm^2 [13].

Two interesting features of PBDTTPD, a low-lying HOMO energy level (−5.56 eV) and a relatively narrow bandgap (1.80 eV), make this material very attractive for BHJ solar cells and worth further investigation. Optimization of the polymerization procedure of PBDTTPD led to improve molecular weights (M_n = 20 kDa; M_w = 47 kDa; PDI = 2.4). The molecular weights of the p-type polymer are known to strongly influence the solar cell performances by directly affecting the nanostructure of the polymer film which control the charge carrier mobility, the π–π staking and the donor/acceptor organisation [14]. Heeger et al. reported that BHJ solar cells made from high molecular weight P3HT exhibited a higher performance due to the long conjugation length of the polymer chain and the excellent interconnections within the bicontinuous network [15]. Tao et al. have also clearly demonstrated the effect of the molecular weights over the power conversion efficiency for PDTSTPD, a promising materials for highly efficient BHJ polymeric solar cells [16]. All PBDTTPD batches obtained during these optimization processes were only fully soluble in ODCB and CB at high

temperature. Moreover, the active layer (blend of PBDTTPD:PCBM) had to be cast from hot solutions.

2. Results and discussion

In this work, we developed a new device fabrication process for high molecular weight PBDTTPD (Fig. 1(a)). We demonstrate that by using two processing additives (CN and DIO) of different functions, tuning and optimization of the nano-scale morphology is possible for the PBDTTPD:PCBM BHJ films. A power conversion efficiency of 7.1% was achieved for the PBDTTPD:$PC_{60}BM$ based photovoltaic (PV) devices with an active area of 1 cm^2. More importantly, a fill factor as high as 70% was obtained. These data are among the highest values reported so far for polymer PV devices with active area $\geqslant$1 cm^2 using the less expensive $PC_{60}BM$ as the electron acceptor.

Our first report on PBDTTPD (M_n = 13 kDa; M_w = 34 kDa; PDI = 2.6) showed a PCE of 5.5% with a short-circuit current (J_{sc}) of 9.81 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.85 V, and a fill factor (FF) of 66% when blended with $PC_{70}BM$ (1:2 by weight) and spin coated from hot ODCB solution (175 °C) with no processing additive [12]. However, when prepared using the same processing procedure, the devices based on another batch of PBDTTPD (M_n = 20 kDa; M_w = 47 kDa; PDI = 2.4) delivered a poorer performance with a J_{sc} of 7.8 mA/cm^2, a V_{oc} of 0.78 V, a FF of 44%, for an overall PCE of 2.7%. The absorption of the active layers in the visible region is very important for photovoltaic applications. Fig. 1(b) compares the UV–Vis absorption spectra of PBDTTPD:$PC_{70}BM$ and PBDTTPD:$PC_{60}BM$ films with a film thickness of 90 nm. As compared with PBDTTPD:$PC_{60}BM$, PBDTTPD:$PC_{70}BM$ has significantly higher absorption in the visible spectral range. It should be pointed out that the slightly higher absorption of PBDTTPD:$PC_{70}BM$ film in the 700–800 nm spectral range is also caused by the absorption of $PC_{70}BM$. Atomic force microscopy (AFM) studies revealed that the resulting blend film had a quite rough surface with a root-mean-square (rms) roughness of 23 nm, as shown in Fig. 2. As a comparison, the blend film composed of the low molecular weight PBDTTPD (M_n = 13 kDa; M_w = 34 kDa; PDI = 2.6) had fairly smooth surface with an rms roughness of only 1.7 nm. The higher surface roughness observed for PBDTTPD (M_n = 20 kDa) is probably due to poor solubility in ODCB. Adding 3% (v/v) DIO to the ODCB solution of high molecular weight PBDTTPD slightly improved the fill factor and PCE overall efficiency to 55% and 3.2%, respectively by controlling the fullerene domain sizes [9,17]. However, the film surface roughness remained high (22.9 nm) which was mainly caused by the limited solubility of PBDTTPD in ODCB. It is reported in the literature that using 1-chloronaphthalene (CN) as a processing additive can effectively suppress the formation of large polymer domains when the polymer has a strong tendency to form aggregates [6]. Therefore, we decided to use CN in the ODCB solution of PBDTTPD:$PC_{70}BM$ as an additive to solve the surface roughness and issues associated with the large polymer domains (Table 1). By using AFM analysis, it is possible to follow the
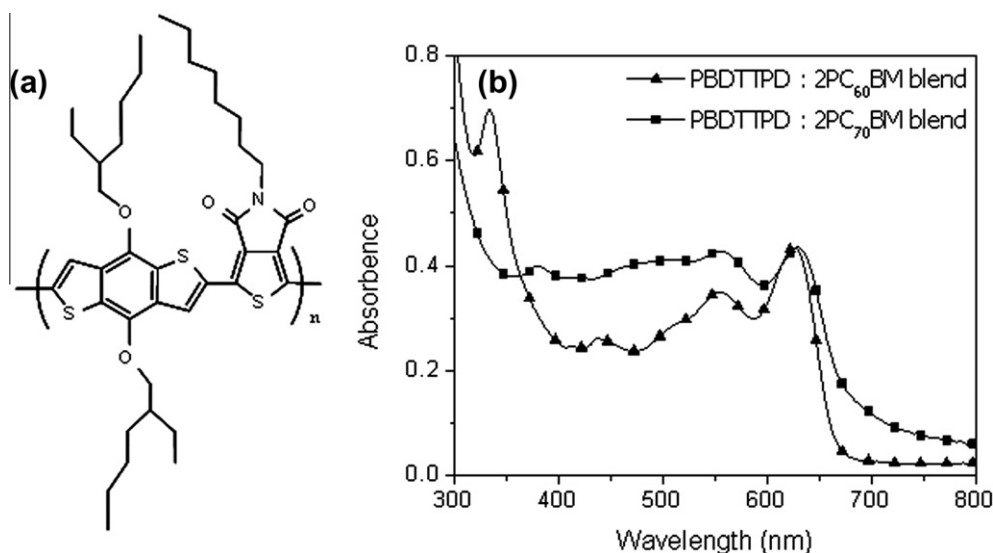
Fig. 1. (a) Chemical structure of PBDTTPD and (b) UV–Vis absorption spectra of the films (90 nm) of PBDTTPD:PC$_{70}$BM and PBDTTPD:PC$_{60}$BM blends.

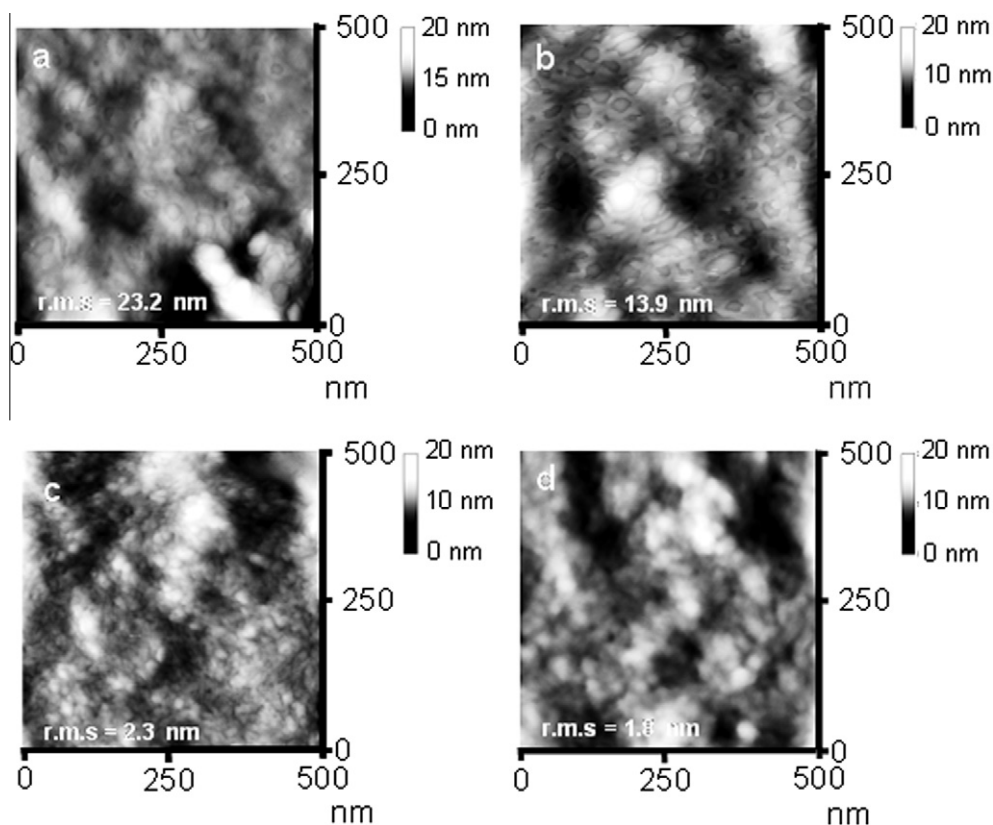**Fig. 2.** AFM images of active layers of (PBDTTPD:2PC$_{70}$BM) solubilized in ODCB containing different ratio of additives: (a) w/o additives; (b) w/2%CN; (c) w/ 4%CN; (d) w/10 CN and 1%DIO.

change in the surface roughness of the active layers (500 nm × 500 nm scan size) cast from different amount of CN. As shown in Fig. 2a–c (left column: height images; right column: phase images), the surface roughness of the PBDTTPD:PC$_{70}$BM blend films dramatically decreased from 23.2 to 2.3 nm when 4% (v/v) of CN was added to the dichlo-robenzene solution. The power conversion efficiency was also enhanced accordingly from 2.7% to 4.7%, and especially

Table 1
Summary of the PV performance for the high molecular weight PBDTTPD:PCBM based solar cells fabricated from different solutions.

	Active layers	Solvent	Additives	Rms (nm)	J_{sc} IV (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
Device 1	PBDTTPD/PC$_{70}$BM	ODCB	–	23.2	7.8	0.78	44	2.7
Device 2	PBDTTPD/PC$_{70}$BM	ODCB	3% DIO	22.9	6.6	0.87	55	3.2
Device 3	PBDTTPD/PC$_{70}$BM	ODCB	2% CN	13.9	9.1	0.85	59	4.4
Device 4	PBDTTPD/PC$_{70}$BM	ODCB	4% CN	2.3	9.4	0.85	59	4.7
Device 5	PBDTTPD/PC$_{70}$BM	ODCB	10% CN	4.2	8.8	0.85	59	4.4
Device 6	PBDTTPD/PC$_{70}$BM	ODCB	4% CN + 3% DIO	3.6	9.3	0.88	67	5.5
Device 7	PBDTTPD/PC$_{70}$BM	ODCB	4% CN + 1% DIO	2.4	10.7	0.87	65	6.0
Device 8	PBDTTPD/PC$_{70}$BM	ODCB	10% CN + 3% DIO	1.7	10.9	0.87	64	6.1
Device 9	PBDTTPD/PC$_{70}$BM	ODCB	10% CN + 1% DIO	1.8	11.0	0.87	67	6.4
Device 10	PBDTTPD/PC$_{60}$BM	CB	10% CN + 3% DIO	4.2	10.21	0.90	69	6.3
Device 11	PBDTTPD/PC$_{60}$BM	CB	10% CN + 1% DIO	3.4	10.77	0.89	67	6.4
Device 12	PBDTTPD/PC$_{60}$BM	CB	4% CN + 3% DIO	2.2	10.54	0.89	70	6.6
Device 13	PBDTTPD/PC$_{60}$BM	CB	4% CN + 1% DIO	1.8	10.89	0.93	70	7.1

the fill factor was increased from 44% to 59%. However, further increasing of the CN content to 10% (v/v) led to higher film roughness (4.2 nm) and thus, a slight reduction in the device efficiency. This phenomenon was already observed by Chen et al. High amount of CN can negatively affect active layer organization and thus decrease solar cells performances [18]. We suspect that is somehow related to the PCBM domain size control. These results prompted us to search for new additive systems.

For instance, DIO is a good solvent for PCBM and prevents the formation of large PCBM domains during spin coating. In addition, DIO is a poor solvent for the polymer, leading to the formation of a phase-separated morphology [9,19]. DIO can also provide enhanced wettability of the blend solution on the PEDOT:PSS layer, leading to the formation of a uniform active layer [20]. Therefore, we expected that by using CN and DIO simultaneously as co-additives in the ODCB solution of PBDTTPD and PCBM,
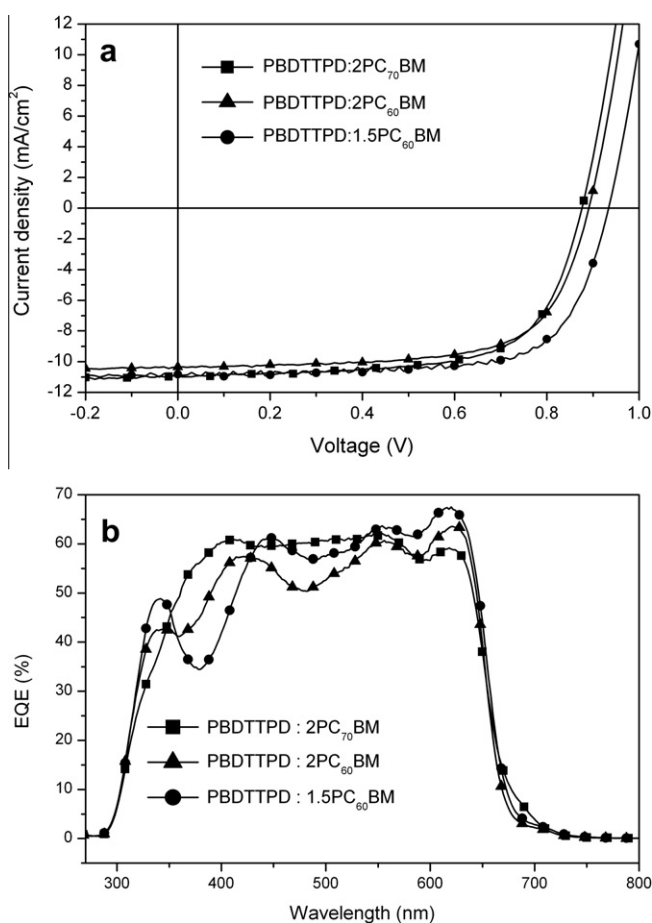
Fig. 3. (a) *I–V* characteristics and (b) EQE curves of the solar cells based on PBDTTPD:2PC$_{70}$BM, PBDTTPD:2PC$_{60}$BM, and PBDTTPD:1.5PC$_{60}$BM blends.

we may be able to control the active layer morphology for the high molecular weight PBDTTPD:PC$_{70}$BM blend. In order to achieve the morphology of interpenetrating PBDTTPD:PC$_{70}$BM networks with optimized domain sizes, different ratios of CN to DIO were tested. The performances of these solar cells are shown in Table 1. The device prepared using 4% CN and 1% (v/v) DIO (devices 7) additives showed a J_{sc} up to 10.7 mA/cm^2, which is already higher than the J_{sc} (9.81 mA/cm^2) obtained from the low molecular weight PBDTTPD [12]. The power conversion efficiency reached 6.0%. The PCE was further improved to 6.4% by increasing the CN content to 10% (v/v) while keeping the DIO content at 1% (v/v) (device 9). It is interesting to point out that the blend film spin-coated under this condition is very smooth with an rms roughness of 1.8 nm. As can be seen from its AFM phase image (Fig. 2d right), the film possesses an optimum phase-separated morphology which results in a high J_{sc} of (11.0 mA/cm^2) and a high FF of 67%. Our results clearly demonstrated that by using CN and DIO as co-additives, it is possible to control at the same time the PCBM domain and the active layer nano-scale morphology for low-solubility conjugated polymers.

We also applied this new additive system to the PBDTTPD:PC$_{60}$BM blend as PC$_{60}$BM has higher electron mobility and a much lower cost, as compared with PC$_{70}$BM [21]. In a preliminary test, the weight ratio of PBDTTPD to PC$_{60}$BM was fixed at 1:2, and the solvent used is dichlorobenzene containing 10% (v/v) CN and 1% (v/v) DIO (device 11). A PCE of 6.4% was obtained with a J_{sc} of 10.77 mA/cm^2, a V_{oc} of 0.89 V, and a FF of 67%. It is worth noting that although the PBDTTPD:PC$_{60}$BM blend has a lower absorption in the solar spectral range than the PBDTTPD:PC$_{70}$BM blend (see Fig. 1), the obtained short circuit current from the former blend (10.77 mA/cm^2) is close to the value from the latter blends (11.0 mA/cm^2). This means that the PBDTTPD:PC$_{60}$BM blend gives higher internal quantum efficiency. Optimizing the PBDTTPD:PC$_{60}$BM based solar cells by fine-tuning the PBDTTPD:PC$_{60}$BM weight ratio to 1:1.5, adjusting the additive contents to 4% (v/v) CN and 1% (v/v) DIO, and changing the solvent from dichlorobenzene to chlorobenzene (device 13) enhanced the device efficiency to 7.1% with a J_{sc} of 10.9 mA/cm^2, a V_{oc} of 0.93 V, and a FF of 70%, as shown in Fig. 3a. As can be seen from Fig. 3b, the maximum EQE reaches 68% at 620 nm. To the best of our knowledge, these data are among the highest values reported so far for the PV devices with an active area of 1 cm^2 using less expensive PC$_{60}$BM as the electron acceptor. The short circuit current calculated from the EQE data and the AM 1.5G solar spectrum is 10.4 mA/cm^2, within 5% error as compared with the J_{sc} obtained from the J–V measurements.

3. Conclusion

In summary, we have developed a new processing additive system consisting of two additives (CN and DIO) for the control of the active layer morphology of the solar cells based on low-solubility polymers. In this co-additive system, CN enhances the solubility of the polymer and suppresses the formation of large polymer domains, while

DIO acts as a PCBM crystallisation controller. Through fine-tuning the ratio between these two additives, it is possible to achieve optimized interpenetrating electron donor/acceptor morphology and thus significantly improve the solar cell performance. We believe that this new additive system can be applied to other low-solubility conjugated polymers.

4. Experimental section

4.1. General methods

Number-average (M_n) and weight-average (M_w) molecular weights of **PBDTTPD** were determined by gel permeation chromatography (GPC) using a high temperature Varian Polymer Laboratories GPC220 equipped with an RI detector and a PL BV400 HT Bridge Viscometer. The column set consists of 2 PLgel Mixed C (300 × 7.5 mm) columns and a PLgel Mixed C guard column. The flow rate was fixed at 1.0 ml/min using 1,2,4-trichlorobenzene (TCB) (with 0.0125% BHT w/v) as eluent. The temperature of the system was set to 140 °C. The sample was prepared at concentration of nominally 1.0 mg/ml in hot TCB. Dissolution was performed using a Varian Polymer Laboratories PL-SP 260VC sample preparation system. The sample vial was held at 160 °C with shaking for 1 h for complete dissolution. The solution was filtered through a 2 μm porous stainless steel filter used with the SP260 pipettor into a 2 ml chromatography vial. The calibration method used to generate the reported data was the classical polystyrene method using polystyrene narrow standards Easi-Vials PS-M from Varian Polymer Laboratories which were dissolved in TCB.

4.2. Synthesis and molecular weight of PBDTTPD

Systematic optimization of the polymerization procedure (temperature, time of polymerization, concentration of the comonomers, catalyst and ligands) have been performed in order to optimize the molecular weights (MW) of PBDTTPD. The following procedure led to consistent MW from batches to batches with $M_n \approx 20$ kDa and PDI ≈ 2.4. These MW results have been obtained using high temperature GPC in trichlorobenzene. 1,3-dibromo-5-octylthieno[3,4-c]pyrrole-4,6-dione (1 equiv.) and 2,6-bis(trimethyltin)-4,8-di(2-ethylhexyloxyl)benzo[1,2-b:3,4-b]dithiophene (1 equiv.) were dissolved in toluene ([ ] = 0.1M). The solution was flushed with argon for 10 min, and then Pd$_2$dba$_3$ (2% mol) and AsPh$_3$ (8%) were added into the flask. The flask was purged three times with successive vacuum and argon filling cycles. The polymerization reaction was heated to 110 °C, and the mixture was stirred for 72 h under argon atmosphere. 1-Bromobenzene was added to the reaction and reacted for 1 h. Then trimethyltin phenyl was added and reacted for one hour to complete the end capping process. The mixture was cooled to room temperature and poured slowly in methanol (400 ml). The solid was filtered through 0.45 μm nylon filter. The crude polymer was washed with acetone and hexanes in a soxhlet apparatus to remove the oligomers and catalyst residue. Finally the

polymer was extracted with chloroform. The polymer solution was condensed to about 20 ml and slowly poured in methanol (200 ml). The solid was filtered through 0.45 μm nylon filter. The polymer was treated to remove residual metals and a dark purple solid was obtained.

The MW were determined using GPC in hot TCB. It is worth noting that we replicated exactly the same GPC set-up reported in literature for the determination of the MW of PBDTTPD in THF [13]. Unfortunately, we found out that our PBDTTPD batches were slightly soluble in THF. The MW obtained using the reported setup were low since the majority of the polymer remained in the syringe filter prior to injection in the GPC apparatus.

4.3. Devices fabrication and characterization

The PV device structure employed in this study is ITO/PEDOT:PSS (30 nm)/PBDTTPD:PC$_{60}$BM or PC$_{70}$BM (90–100 nm)/BCP (6 nm)/Al (120 nm), where BCP stands for bathocuproine and functions as a hole/exciton blocking layer [15]. The active area of each fabricated solar cell is 100 mm^2. Poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS) (Clevios P, purchased from H.C. Starck) was spin coated at 7000 rpm for 60 s and then baked at 140 °C for 15 min. After cooling down the PEDOT:PSS coated substrate to room temperature, a hot solution of the PBDTTPD:PCBM blend in ortho-dichlorobenzene (ODCB, 175 °C) or in chlorobenzene (CB, 130 °C) with and without processing additives was spin coated on top of the PEDOT:PSS layers. Finally, a cathode consisting of 6 nm of bathocuproine (BCP) and 120 nm of aluminium (Al) was thermally evaporated through a shadow mask at a pressure of 2.0×10^{-7} Torr. The photovoltaic performances of these solar cells were tested under simulated AM 1.5G irradiation of 100 mW cm^{-2}, which was calibrated using a KG5 filter covered silicon photovoltaic solar cell traceable to the National Renewable Energy Laboratory (NREL). The external quantum efficiency (EQE) measurement was performed using a Jobin-Yvon Tariax 180 spectrometer, a Xenon light source, a Merlin lock-in amplifier, a calibrated Si UV detector, and an SR570 low noise current amplifier.

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