Efficient Polymer Solar Cells Based on Benzothiadiazole and Alkylphenyl Substituted Benzodithiophene with a Power Conversion Efficiency over 8%

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In the past decades, polymer solar cells (PSCs) have attracted considerable attention for applications in renewable energy due to their low cost, easy fabrication, light weight, and the capability to fabricate flexible large-area devices.[1–7] The key factors that determine the power conversion efficiency (PCE) of the PSCs are the open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), and fill factor (*FF*). From the point of view of active layer materials, V_{oc} is directly proportional to the offset between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor.[8] So, many approaches that can enlarge the offset and, thus, improve the V_{oc} of PSCs have been developed and used in active layer materials design.[9,10] Since a broad absorption band and balanced hole and electron mobilities of bulk heterojunction (BHJ) layers of PSCs are desirable to realize good J_{sc} and *FF*, conjugated polymers with low band gap as well as high hole mobility were designed and synthesized for high efficiency PSCs.[11–20]

Exciton diffusion and the charge transport in conjugated polymers are not as efficient as in inorganic counterparts. Therefore, it is of great importance for the molecular design of highly efficient photovoltaic polymers to facilitate the intermolecular electron transport. In conjugated polymers, the π-electrons are transported along the backbone with intra-molecular transport or through the overlapped π-electron wave functions between adjacent backbones for inter-molecular transport. Since intermolecular electron transmission occurs by a hopping mode,[21] which limits exciton diffusion and charge transport in PSC devices, methods that can enhance inter-molecular π–π interactions can be beneficial in improving the photovoltaic properties of conjugated polymers. For example, two dimensional (2-D) conjugated structures have been used to enhance intermolecular π–π interactions by extending the conjugating surface of benzodithiophene (BDT)-based polymers.[22] Consequently, the replacement of the alkoxy moiety with an alkylthienyl has been utilized to improve photovoltaic properties of the BDT-polymers.[22c,22d] Although a higher J_{sc} can be realized by using polymers with a 2-D conjugated structure, this structure has little influence on the V_{oc} of PSCs. Therefore, if the HOMO and LUMO levels of BDT-based polymers can be effectively reduced simultaneously by employing the 2D conjugated structure, new polymers with efficient photovoltaic performance will emerge.

Recently, alkylphenyl substituted BDT (BDTP) has attracted much attention as a weak electron-donating unit with large π-conjugated area and good planarity. Dou et al reported a series of copolymers based on BDTP for photovoltaic application.[18a] It was found that BDTP based polymers exhibited similar photovoltaic performance (PCE of >6% for single cells and >8% for tandem cells) and relatively higher V_{oc} in comparison with BDTT based polymers which indicated that BDTP should be a promising candidate unit for highly efficient photovoltaic materials. However, the BDTP Unit has not been explored in other conjugated polymer system. Herein, we copolymerized the BDTP unit with the well-known classic building block, 4,7-di(4-(2-ethylhexyl)-2-thienyl)-2,1,3-benzothiadiazole) (DTBT), to generate a new polymer, poly{4,8-bis(4-(2-ethylhexyl)-phenyl)-benzo[1,2-b:4,5-b′]dithiophene-alt-[4,7-di(4-(2-ethylhexyl)-2-thienyl)-2,1,3-benzothiadiazole)-5, 5′-diyl]} (**PBDTP-DTBT**), which is shown in **Scheme 1**). The optical, electrochemical and photovoltaic properties and the evolution of morphology of the blend films with different content 1,8-diiodooctane (DIO) as processing additive were investigated. The polymer exhibited a strong absorption in the range of 300 ~ 700 nm, a low-lying HOMO energy level of −5.35 eV and a high hole mobility of 8.89×10^{-2} cm^2/V s. The best PSC device based on **PBDTP-DTBT**: PC$_{71}$BM (1:1.5, w/w) showed a PCE of 8.07% with a V_{oc} = 0.88 V, a J_{sc} = 12.94 mA/cm^2 and a *FF* = 70.9%. Furthermore, We found that when the active layer was processed with DIO, the crystallinity of the polymer was enhanced and multi-length scale morphology was formed that was beneficial for exciton dissociation and charge carried transport which contributed to the high efficiency of the PSCs. These results indicate that **PBDTP-DTBT** will be a promising material for photovoltaic application.

As shown in Scheme 1, **PBDTP-DTBT** was easily synthesized by a three-step synthetic route starting with commercially available chemicals. A Pd-catalyzed Stille-coupling reaction,

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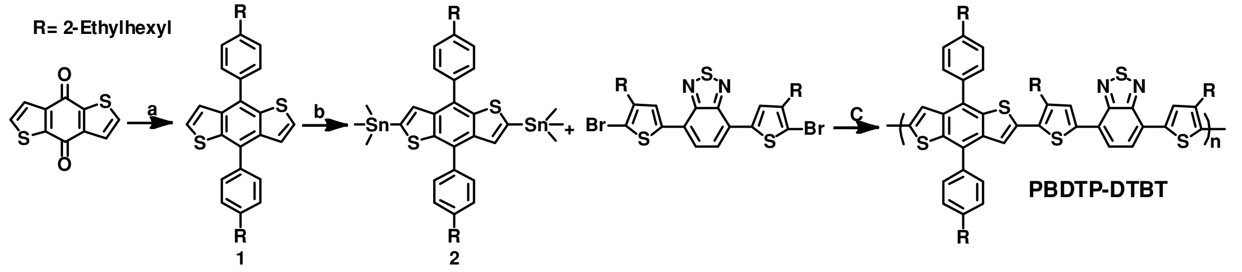

Scheme 1. The synthetic route and molecular structure of the polymer **PBDTP-DTBT**. (a) n-BuLi, THF, –78 °C, 4-(2-ethylhexyl)bromobenzene, 1h; benzo[1,2-b:4,5-b′]dithiophene-4,8-dione, 55 °C, 2h; then, $SnCl_2 \cdot 2H_2O$, HCl, 60 °C, overnight. (b) LDA, –78 °C, 1h, $Sn(CH_3)_3Cl$, room temperature, 2h. (c) $[Pd(PPh_3)_4]$, toluene, reflux, 12h.

with a yield of 80%, was used for the polymerization reaction. The polymer shows good solubility in chlorinated solvents such as chloroform, chlorobenzene and *o*-dichlorobenzene (*o*-DCB). The number average molecular weight (M_n) and polydispersity index (PDI) of the polymer are 32.2 K and 2.0, respectively, which were estimated by gel permeation chromatography (GPC) using chloroform as the solvent and polystyrene with narrow molecular weight distribution as a standard. The thermogravimetric analysis (TGA) shows that **PBDTP-DTBT** has good thermal stability with an onset of decomposition temperature of ca. 350 °C (See Figure S1 in Supporting Information, SI). From the DSC thermograms of **PBDTP-DTBT** (Figure S2), no obvious exotherms or endotherms were observed from 40 to 250 °C, at a heating rate of 10 °C/min.

UV-vis absorption spectra of the polymer in *o*-DCB and as a solid film are shown in **Figure 1**a. **PBDTP-DTBT** shows three absorption bands in the range 300–730 nm both in solution and in the solid state (film). The absorption maximum of **PBDTP-DTBT** is located at ca. 550 nm in solution. In the solid film, the absorption maximum is red-shifted to 610 nm and a weak shoulder at ca. 640 nm can be observed. The absorption edge (λ_{edge}) of the polymer film is at ca. 730 nm, corresponding to an optical bandgap (E_g^{opt}) of 1.70 eV. Electrochemical cyclic voltammetry (CV) was performed to determine the HOMO and LUMO levels of the polymer. The onset reduction potential (ϕ_{red}) and the onset oxidation potential (ϕ_{ox}) are –1.36 V *vs.* Ag/Ag$^+$ and 0.65 V *vs.* Ag/Ag$^+$, respectively, corresponding to a LUMO level of –3.34 eV and a HOMO level of –5.35 eV. In comparison to other polymers with similar backbone structures but different side groups (the alternative copolymers based on BDT and DTBT), **PBDTP-DTBT** shows similar E_g^{opt} and a deeper HOMO level.[23] The hole mobility of the polymer was measured by the space-charge-limited-current (SCLC) method (see SI) and the hole mobility of **PBDTP-DTBT** is 8.89×10^{-2} cm^2/V s, which is a relatively high value for copolymers based on DTBT and BDT derivatives,[23] resulting from the extended π-conjugation system due to the using of BDTP as building block.

PSC devices were fabricated and characterized to investigate the photovoltaic properties of the polymer. The device structure used in this work is ITO/PEDOT: PSS/**PBDTP-DTBT**:PC$_{71}$BM/Ca/Al. Detailed information of device fabrication and characterization are provided in SI part. Initially, PSC devices with different D/A ratios (**PBDTP-DTBT**/PC$_{71}$BM, w/w) were fabricated to optimize the D/A ratio of the blend. Figure S3 (see SI) shows the current density–voltage curves (*J–V*) of the devices under the illumination of AM 1.5G (100 mW/cm^2) and the external quantum efficiency (*EQE*) spectra of devices with different D/A ratios (1:1, 1:1.5 and 1:2). It is clear that the optimal D/A ratio of the blend is 1:1.5, and a *PCE* of 5.09% was obtained with V_{oc} = 0.922 V, J_{sc} = 11.46 mA/cm^2, and *FF* = 44.60%.

To further improve the photovoltaic performance of the device, 1,8-diiodooctane (DIO) was added to the solutions prior to the spin-coating process.[24] We found that photovoltaic performance of the blend can be improved significantly by adding a small amount of DIO, while when too much DIO was added,

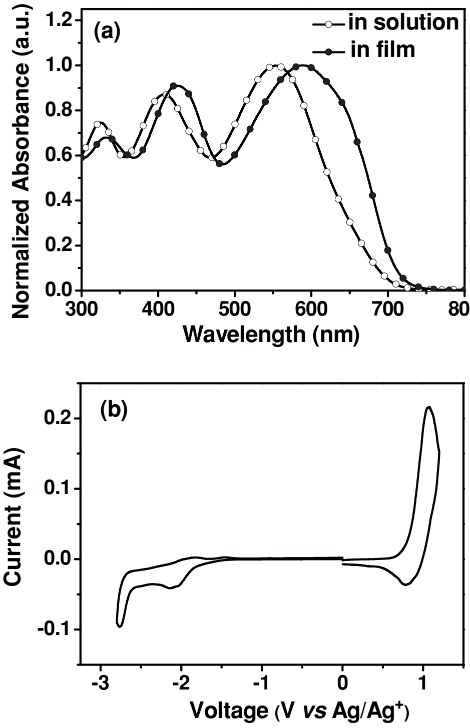

Figure 1. (a) The absorption spectra of the polymer in dichlorobenzene and in solid film. (b) Cyclic voltammogram of polymer film on a glassy carbon electrode measured in 0.1 mol L^{-1} Bu$_4$NPF$_6$ acetonitrile solution at a scan rate of 50 mV s^{-1}.

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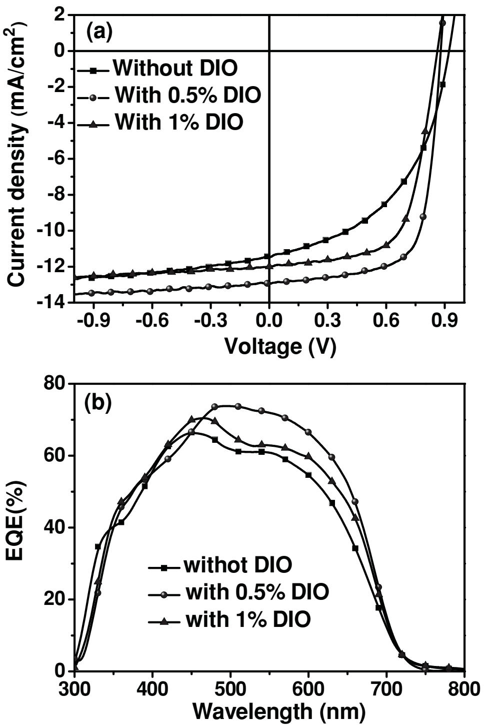

Figure 2. (a) *J–V* characteristics and (b) *EQE* curves of solar cells based on the **PBDTP-DTBT**/PC$_{71}$BM (1:1.5, w/w) blend without and with 0.5% or 1% DIO as additive.

the device performance dropped dramatically. **Figure 2** shows *J–V* characteristics and *EQE* curves of solar cells based on the **PBDTP-DTBT**/PC$_{71}$BM (1:1.5, w/w) blend spin-coated without additive and with 0.5% and 1% DIO (DIO/o-DCB, v/v). The photovoltaic parameters of the devices fabricated under the optimal conditions are summarized in **Table 1**. Compared to the devices processed without additive, the devices processed with DIO showed a slightly lower V_{oc}, a slightly higher J_{sc}, and a remarkably improved *FF* (from 48.2% to 70.9%). Overall, the best result was obtained when 0.5% DIO was used, and a maximum $PCE = 8.07\%$ was found with a $V_{oc} = 0.880$ V, $J_{sc} = 12.94$ mA/cm^2 and $FF = 70.9\%$. Compared with the other copolymers based on DTBT and BDT derivatives for polymer solar cells,[23] the optimal devices based on **PBDTP-DTBT** exhibited slight change of V_{oc} in correspondence with the HOMO levels of polymers, but significantly increased J_{sc} and FF probably caused by the relatively high hole mobility due to the extended π-conjugation of BDTP. From Figure 2b, it can be seen that, after adding 0.5% DIO, the quantum efficiency of the device, from 500 nm to 700 nm, increased significantly and a maximum *EQE* of 74% at 500 nm was recorded. Considering that more than 20% sunlight is lost, due to the reflection and absorption of light by the ITO glass substrate and the PEDOT:PSS buffer layer, >70% *EQE* is close to the threshold of a PSC device which implies that geminate recombination in the blend is very low. According to the *J–V* curve of the best device, it is quite clear that the current density is almost independent of the bias, from −1.0 V to 0.6 V, so that the device shows a high *FF* of 70.9%, indicating that bimolecular recombination in the blend should also very low. The V_{oc} of 0.880 V is also among the top values for the PSC devices based on polymers with E_g^{opt} of 1.70 eV,[25] suggesting that the energy loss during the charge separation process is quite low. Therefore, it can be concluded that the **PBDTP-DTBT**/PC$_{71}$BM blend is a highly efficient photovoltaic system.

Table 1. Photovoltaic properties of the PSCs based on **PBDTP-DTBT** and PC$_{71}$BM (1:1.5, w/w) under illumination of AM 1.5G, 100 mW/cm^2

PBDTP-DTBT/PC$_{71}$BM (1:1.5, w/w)	Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	*FF* [%]	PCE_{max}($PCE_{ave}$$^{a)}$) [%]
without DIO	108	0.922	11.46	48.2	5.09 (4.95)
0.5% DIO	102	0.880	12.94	70.9	8.07 (7.92)
1% DIO	100	0.862	12.00	64.8	6.70 (6.51)

[a)] The average PCE is obtained from over 20 devices.

Grazing incidence X-Ray diffraction (GIXD) method is used in this work to characterize the morphology evolution of the blend films processed without or with different amount of DIO. **Figure 3**a and 3b shows in-plane (IP) and the out-of-plane (OOP) and GIXD profiles of the samples, including the thin films for pure polymer or **PBDTP-DTBT**: PC$_{71}$BM blend (1:1.5, w/w) cast from pure o-DCB, DIO(0.5%)/*o*-DCB and DIO(1%)/*o*-DCB, respectively. The IP profile of the pure polymer film processed without DIO showed a pronounced (100) diffraction peak at 0.30 Å^{-1}, arising from the alkyl chain packing with the d-spacing of ~21 Å. And the OOP profile of this film showed only one broad peak at ~1.67 Å^{-1}, which corresponds to the (010) π–π stacking. This indicates that the polymer chains took the face-on orientation, if processed without DIO. Interestingly, when the pure polymer film was cast from a mixture of DIO(0.5%)/o-DCB, a weak OOP (100) peak at 0.30 Å^{-1} was seen, suggesting the formation of the edge-on structure. Once the concentration of DIO increased to 1%, the OOP (100) peak from the resultant film became more obvious and the intensities of OOP (010) and IP (100) peaks increased slightly, indicating that the crystallinity of PBDTP-DTBT was enhanced. A similar trend was observed for the blend films as well. As shown in Figure 3, for the blend films, the OOP or IP (100) reflections were seen at almost the same position as that for the pure polymer film. The crystals composed of pure polymer had formed; no PC$_{71}$BM molecule was intercalated between the polymer chains. The broad peak at q ~ 1.35 Å^{-1} is attributed to the form factor of PC$_{71}$BM, which obscured the observation of the (010) peaks. If the blend film was processed without DIO, the weak OOP (100) could almost be ignored and the IP (100) peak was evident, indicating the face-on structure was dominant. When DIO was used and its concentration was increased, the OOP (100) reflection became increasingly intense, but the IP (100) peak changed little. The introduction of additives, therefore, enhanced the edge-on orientation and packing of the PBDTP-DTBT without disrupting the crystallinity of face-on direction. Hence, the overall degree of crystallinity of **PBDTP-DTBT** was enhanced, which benefits the exciton diffusion and charge carrier transport, resulting in the improved device performance.

The bulk morphology of the blends prepared by the different conditions was further investigated by resonant soft x-ray scattering (RSoXS).[26]X-rays with a photon energy of 284.2 eV

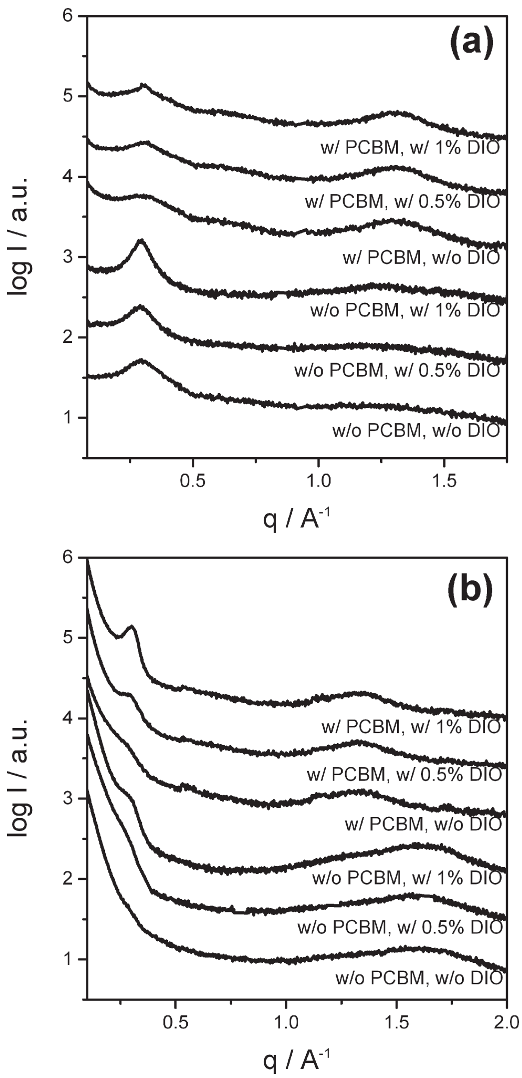

Figure 3. In plane (a) and out-of-plane (b) GIXD profiles for the pure films of **PBDTP-DTBT** and the blend of **PBDTP-DTBT**: $PC_{71}BM$ (1:1.5, w/w) with different amount of DIO.

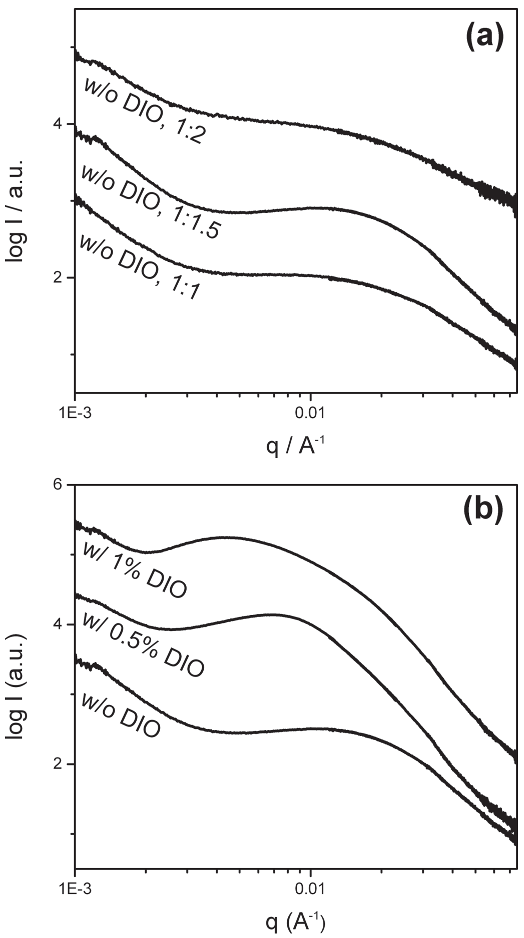

Figure 4. RSoXS profiles for (a) **PBDTP-DTBT**: $PC_{71}BM$ blends processed by o-DCB with different D/A ratios and (b) **PBDTP-DTBT**: $PC_{71}BM$ (1:1.5, w/w) blends processed by o-DCB, DIO(0.5%)/o-DCB or DIO(1%)/o-DCB, respectively.

were utilized to enhance the contrast between **PBDTP-DTBT** and $PC_{71}BM$. The measurements were performed in the transmission geometry with the diffraction vector being in the plane of the film. **Figure 4**a shows the RSoXS profiles for **PBDTP-DTBT**: $PC_{71}BM$ blends cast from o-DCB with different D/A ratios and Figure 4b shows the RSoXS profiles for **PBDTP-DTBT**: $PC_{71}BM$ (1:1.5, w/w) blends cast from o-DCB, DIO(0.5%)/o-DCB or DIO(1%)/o-DCB, respectively. In the RSoXS profiles, the diffuse scattering maximum represents an average center-to-center distance between the domains. As shown in Figure 4a, the blend with non-optimized D/A ratio shows a weak scattering, indicating the small degree of phase separation. While the scattering maximum for the optimized ratio, 1:1.5 w/w, was more evident, with a shoulder in the scattering corresponding to a spacing of ~35 nm. In addition, it is clear that the location of scattering maximum is sensitive to the amount of DIO added in the solution. For the blend films processed by DIO(0.5%)/o-DCB or DIO(1%)/o-DCB, the scattering peaks became more intense, indicating that the degree of phase separation was enhanced. Meanwhile, the dominant domain spacing increased to ~80 nm or 130 nm respectively, while the d-spacing at ~35 nm still remained, as indicated by the shoulder in the scattering profiles. The broad distribution of the peak locations suggested the existence of the multi-length scale morphology. These results are consistent with the formation of **PBDTP-DTBT** fibrils that form a continuous network-type of morphology, where the center-to-center distance between the fibrils or, in other word, the length scale of the mesh of the network being many tens of nanometers. Within this network, a phase separated morphology on the tens of nanometer level forms. This multi-length scale morphology enhances exciton dissociation is one of the key factors affecting the performance of the polymer solar cells.[27]

Furthermore, the real space morphologies on the surface and in the bulk of the blend films were studied by atomic force microscopy (AFM) and transmission electron microscopy (TEM). According to the height images of the blend films, as shown in Figure S4, the root-mean-square (RMS) values are 0.33 nm, 0.48 nm and 1.87 nm, for the blends processed without additive, with 0.5% DIO and 1% DIO respectively. Consequently increasing the amount of DIO results in an enhanced phase separation (see Figure S4). As seen in TEM images (see Figure S5), the blend film processed by o-DCB looks uniform; when 0.5% DIO was used as additive, dark and light domains can be clearly distinguished, the network of the fibrils is also evident; when 1% DIO was used, the phase separation became much stronger and the mesh size between the fibrils became larger. It should be noted that the mesh size observed in the TEM images seems smaller than that observed by RSoXS which can be a result of the projection of a 3D morphology onto a plane. In conclusion, the results from AFM and TEM images agree well with that from GIXD and RSoXS measurements.

According to the photovoltaic and morphological results, it can be concluded that after adding DIO, the dominant domain spacing, as well as the polymer crystallinity along with molecular orientation in the **PBDTP-DTBT**/PC$_{71}$BM blend, can be tuned. It is well known that the excitons and the free charges in polymer domains are transported by intra-molecular and inter-molecular modes. HOMO orbital surfaces of polymer donors are distributed evenly along the conjugated backbone; and the π-electrons can be easily delocalized along the backbone. Therefore, the intra-molecular charge transport in polymer domain is very efficient. On the other hand, the inter-molecular charge transport occurs by a hopping mode through the overlapped π-orbits between the adjacent molecules, which needs to overcome the Coulombic force and, thus, is more inefficient when compared to the intra-molecular transport. Once the processing additive was used, the increased crystallinity of **PBDTP-DTBT** was associated with the formation of continuous networks of fibrils, where the direction of π–π stacking is along the long axis of the fibrils. Consequently, the inter-molecular transport along the π–π stacking had been facilitated, resulting in the better overall charge transport of the blend in PSCs.

In conclusion, a new copolymer based on BDTP as donor and DTBT as acceptor, **PBDTP-DTBT**, was designed and synthesized for photovoltaic application. The polymer exhibited a suitable bandgap of 1.70 eV and a deeper HOMO energy level of –5.35 eV. The PSCs based on **PBDTP-DTBT**: PC$_{71}$BM (1:1.5, w/w) with 0.5% DIO showed a PCE of 8.07% with V_{oc} = 0.88 V, J_{sc} = 12.94 mA/cm^2, and FF = 70.9%, under the illumination of AM 1.5G, 100 mW/cm^2. The morphological study on the blend of **PBDTP-DTBT**/PC$_{71}$BM by AFM, TEM, GIXD and RSoXS, revealed that the introduction of the additives during the processing effectively enhanced the crystallinity of the polymer and induced the formation of a multi-length scale morphology that was favorable for exciton dissociation and charge carrier transport, resulting in the high efficiency of the polymer solar cells. Hence, the **PBDTP-DTBT** was proven to be a promising donor material for high efficiency polymer solar cells.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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