

An Easy and Effective Method to Modulate Molecular Energy Level of the Polymer Based on Benzodithiophene for the Application in Polymer Solar Cells

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Conjugated polymers constructed by the donor-acceptor (D-A) approach^[1,2] have attracted considerable attention for applications in polymer solar cells (PSCs), due to their easily tunable properties, like optical absorption band, molecular energy level and carrier mobility, and hence a lot of D-A polymers have been developed and applied in PSCs.^[3–22] Considering thousands of publications in the PSC field, the majority of important achievements made in the past few years are more or less related to the use of novel D-A polymers. Therefore, the molecular design of D-A polymers has become a very important topic with considerable further promise.

From the point of view of molecular design of D-A polymers, the modulation of molecular energy levels, i.e., the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level, is one of the most important issues, because the photovoltaic properties of D-A polymer are closely related to their HOMO and LUMO levels. For bulk heterojunction (BHJ) PSCs,^[23] the key physical processes during photoelectric conversion, including exciton generation and diffusion, charge separation, charge transport, and charge collection, correlate closely with HOMO and LUMO levels of the conjugated polymers in their active layers. For instance, from the perspective of polymers as electron donor materials in BHJ blends, optical absorption range, which is the key to realize efficient current generation, is determined by the gaps between their HOMO and LUMO levels.^[3] Furthermore, in order to assure efficient charge separation, the polymers should possess suitable HOMO and LUMO levels offset, but not excessively so, with the levels in electron acceptor materials in BHJ blend.^[4] In addition, it is essential to facilitate charge transport so that conjugated polymers should have well delocalized HOMO electron density distribution^[5] and also suitable

morphologies are needed to provide sufficient interfacial area and efficient channels to transport the carriers.^[24]

To date, two effective strategies have been successfully developed and employed to modulate molecular energy levels. One way is to construct D-A polymers with different donor and acceptor building blocks, and according to this method, various D-A polymers with different energy levels have been obtained.^[6–16] Recently, significant progress has been made in new D-A copolymers to enable PSC devices to show high PCEs (>8%) with this method.^[17] Another way is to introduce fluorine atoms onto the acceptor moieties in D-A polymers which could reduce the HOMO and LUMO levels of polymers simultaneously with only minor effect on the optical band-gap.^[18–20] Therefore, BHJ PSCs based on these fluorinated copolymers exhibited higher V_{oc} and PCE in comparison with the corresponding non-fluorinated derivatives. Although the use of fluorination has led to great successes, this method also causes a few drawbacks. For example, it is difficult to introduce the fluorine atoms to the polymers due to multi-step synthesis and low yield for the fluorination moieties,^[18b,c] and sometimes the introduction of fluorine atoms is not very efficient to improve the V_{oc} , i.e. when two fluorine atoms were introduced onto 2,1,3-benzodiazole, the HOMO levels of the corresponding copolymers can be reduced by 0.1 ~ 0.2 eV, but reflecting in photovoltaic behaviors, open circuit voltages (V_{oc}) of the PSCs can only be improved by 0 ~ 0.1 V.^[19] Therefore, to develop new method to modulate molecular energy levels through an easier and more efficient approach without sacrificing other properties is still of crucial importance to molecular design of D-A polymers.

In previous work, we designed and synthesized a series of benzo[1,2-b:4,5-b']dithiophene (BDT) derivatives with two-dimensional conjugated (2D) structure by introducing alkylthienyl groups to 4 and 8 positions of BDT, and by the use of this kind of 2D-building block, hole transport as well as photovoltaic properties of BDT-polymers can be improved distinctly.^[21] Based on the work by other research groups, this building block also shows improvements in photovoltaic properties of other polymers and small molecules.^[22] However, this building block has little positive influence on tuning molecular energy levels. As shown in **Scheme 1**, PBT-T has a typical D-A structure in which alkylthienyl-substituted BDT (**BDT-T**) units and fluorine-substituted thieno[3,4-b]thiophene (**TT**) are alternately linked with thiophene units which benefits for improving the FF of the corresponding device.^[21c] Although the TT moiety in this polymer is decorated with fluorine, this polymer still shows a high-lying HOMO level (−4.95 eV), so the PSC device

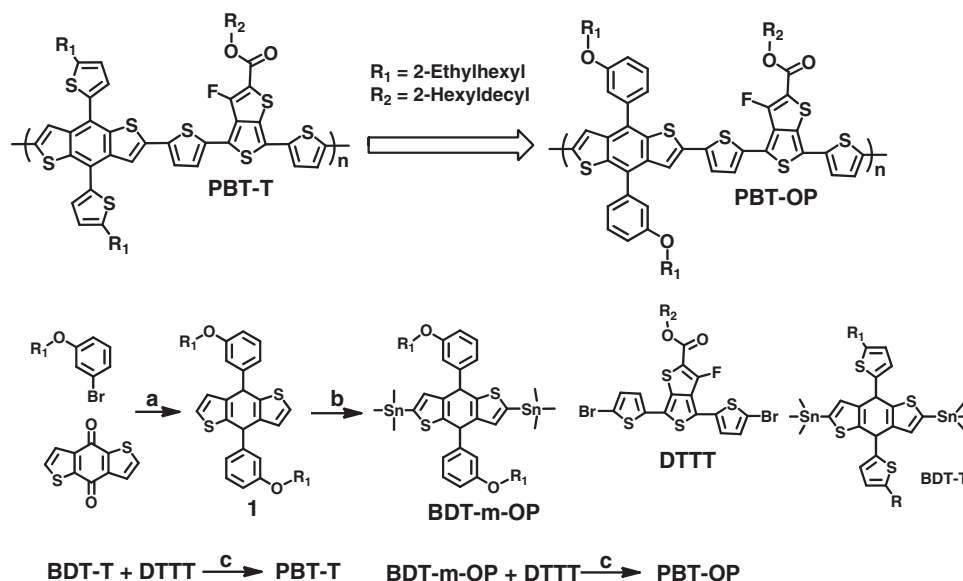
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Scheme 1. Structures and synthetic routes of **PBT-T** and **PBT-OP**. (a) Mg, THF; SnCl₂ · 2H₂O, 50 °C, overnight; (b) LDA, THF, –78 °C, Sn(CH₃)₃Cl, 2h; (c) Pd(PPh₃)₄, toluene, 110 °C, 12h.

based on this polymer showed a relatively low V_{oc} of 0.60 V in initial photovoltaic testing. Considering that the PSC device based on **PBT-T** showed a short circuit current density (J_{sc}) of 13.7 mA/cm² and a fill factor (FF) of 67.7%, both these two photovoltaic parameters are among promising values. If V_{oc} of the device can be enhanced effectively, there will be plenty of room for improvements in PCE. Therefore, this polymer was selected as the starting polymer. In order to extend the functionalities of the 2D structure, a *meta*-alkoxy-phenyl-substituted BDT (**BDT-*m*-OP**) building block was designed and employed in constructing D-A polymers. The results show that by replacing alkythienyl groups (**PBT-T**) with *meta*-alkoxy-phenyl groups (**PBT-OP**), optical absorption, molecular packing, and charge transport properties of the polymer are little changed, while the polymer's HOMO level can be reduced distinctly, so V_{oc} of the PSC device can be significantly enhanced from 0.60 V to 0.78 V, and consequently, the PCE of the corresponding PSC devices can be improved from 5.56% to 7.50%.

These two polymers were synthesized as shown as Scheme 1. The new monomer (**BDT-*m*-OP**) can be easily synthesized by modifying the method reported previously.^[21] The other two monomers are commercially available. **PBT-T** and **PBT-OP** were synthesized via a typical Stille-coupling reaction using toluene as solvent and Pd(PPh₃)₄ as catalyst. The number average molecular weight and polydispersity index (PDI) were 44.1k, 2.92 and 30.6k, 2.44 for **PBT-T** and **PBT-OP**, respectively, evaluated by high temperature gel permeation chromatography at 150 °C using 1, 2, 4-trichlorobenzene as the eluent. The thermogravimetric analysis measurements (TGA) showed that the onset temperatures with 5% weight-loss (T_d) of **PBT-T** and **PBT-OP** are all over 380 °C, respectively (see Figure S1 in Supporting Information, SI).

The optical properties of the polymers were investigated by ultraviolet–visible (UV–vis) absorption spectroscopy both in *o*-DCB solution (see Figure S2 in SI) and in thin films (see

Figure 1a). The detailed data obtained from these absorption spectra are summarized in Table 1. As shown in Figure S2 and Figure 1a, compared with **PBT-T**, **PBT-OP** exhibited slightly blue-shifted absorption spectra both in solution and in solid films; i.e. the films of **PBT-T** and **PBT-OP** show absorption peaks at 620 nm and 605 nm, respectively, implying that the replacement of **BDT-T** with **BDT-*m*-OP** only slightly increases the optical bandgap. The absorption edges (λ_{edge}) of the two polymer films are 750 nm for **PBT-T** and 730 nm for **PBT-OP**, from which the optical bandgaps (E_g^{opt}) of the polymers can be calculated according to $E_g^{opt} = 1240/\lambda_{edge}$. The E_g^{opt} values of **PBT-T** and **PBT-OP** are 1.67 and 1.70 eV, respectively.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the conjugated polymers can be determined by electrochemical cyclic voltammetry (CV).^[25] As shown in Figure 1b, the onset reduction potentials (ϕ_{red}) of **PBT-T** and **PBT-OP** are –1.59 and –1.57 V vs. Ag/Ag⁺, respectively, while the onset oxidation potentials (ϕ_{ox}) are 0.24, and 0.46 V vs. Ag/Ag⁺, respectively. Correspondingly, HOMO and LUMO levels of these two polymers were calculated according to the equations:^[26] HOMO = –e (ϕ_{ox} + 4.71) (eV); LUMO = –e (ϕ_{red} + 4.71) (eV) and listed in the Table 1. The HOMO levels of **PBT-T** and **PBT-OP** are –4.95 eV and –5.17 eV, and their LUMO levels are –3.12 eV and –3.14 eV, respectively. Obviously, when the alkythienyl groups were replaced by the *meta*-alkoxy-phenyl groups, HOMO level of the corresponding polymer can be significantly reduced by 0.22 eV due to the higher ionization potential of the functional groups.^[27] Since V_{oc} of BHJ PSCs is closely related to the gap between the LUMO of the acceptor material and the HOMO of the donor polymer in their active layers, higher V_{oc} can be realized in the PSCs based on **PBT-OP** compared to the PSCs based on **PBT-T**.

To investigate and compare the photovoltaic properties of these two polymers, BHJ PSC devices with a configuration of ITO/PEDOT: PSS/polymer: PC₇₁BM /Ca/Al were fabricated.

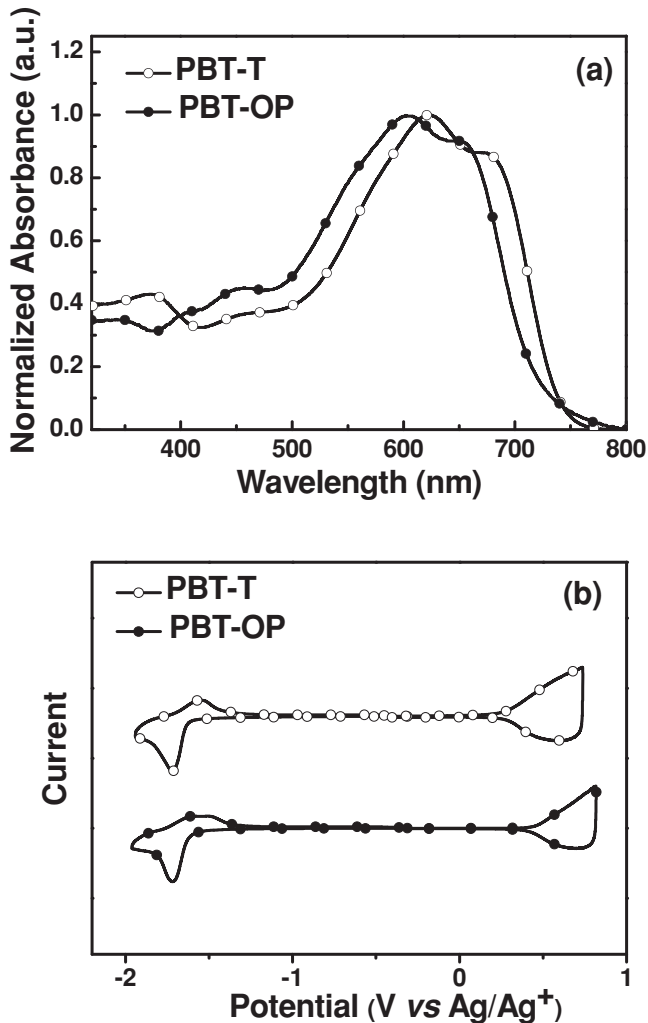


Figure 1. (a) Absorption spectra of polymers in films; (b) Cyclic voltammograms of polymers films on a platinum electrode measured in 0.1 mol/L Bu_4NPF_6 acetonitrile solutions at a scan rate of 50 mV/s.

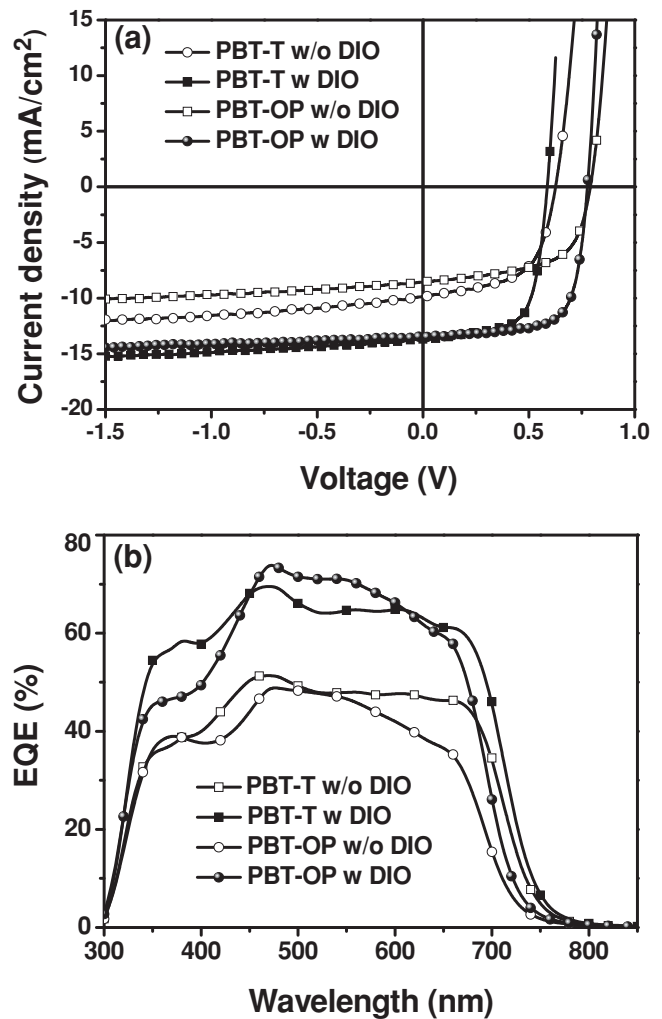


Figure 2. (a) The J - V curves of PSCs based on polymer: PC_{71}BM (1:1.5, w/w) without or with 3% DIO under the illumination of AM 1.5G, 100 mW/cm^2 . (2) EQE curves of the corresponding devices.

All active layers were spin-coated from the solutions in *o*-DCB. We found that for the devices based on these two polymers, the optimal D/A ratios (polymer/ PC_{71}BM) are 1:1.5 (as shown in Figure S3 and Table S1). In order to optimize morphologies of the blend films and thus to improve their photovoltaic properties, 3% (v/v) of 1, 8-diiodooctane (DIO) was used as additive.^[28] Figure 2a and 3b show the J - V curves of the PSCs based on polymer: PC_{71}BM (1:1.5, w/w) with 3% DIO under the illumination of AM 1.5G, 100 mW/cm^2 and the external quantum efficiency (EQE) curves of the corresponding devices, respec-

tively. Photovoltaic parameters of the corresponding J - V curves in Figure 2a are summarized in Table 2. As shown, **PBT-T** and **PBT-OP** exhibited improved photovoltaic performance after the addition of 3% DIO. For the PSC devices prepared by the optimal condition, the device of **PBT-OP** showed a V_{oc} of 0.78 V, which is 0.18 V higher than that of the device of **PBT-T**. The

Table 1. Optical and electrochemical properties of the polymers.

polymer	$\lambda_{\text{peak}}/\lambda_{\text{shoulder}}$ [nm]		λ_{edge} [nm]	$E_{\text{g}}^{\text{opt}}$ [eV]	HOMO [eV]	LUMO [eV]
	solution	film	film			
PBT-T	612/660	620/673	750	1.67	-4.95	-3.12
PBT-OP	605/652	605/655	730	1.70	-5.17	-3.14

Table 2. Photovoltaic performances of the PSCs based on polymer: PC_{71}BM under the illumination of AM1.5G, 100 mW/cm^2 .

Polymer: PC_{71}BM (1:1.5, w/w)	DIO	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE_{max} ($PCE_{\text{ave}}^{\text{a}}$) [%]	Thickness [nm]
PBT-T	w/o	0.63	9.9	58.2	3.63 (3.50)	95
	3%	0.60	13.7	67.7	5.56 (5.45)	96
PBT-OP	w/o	0.79	8.6	59.8	4.06 (3.96)	93
	3%	0.78	13.4	71.8	7.50 (7.41)	90

^{a)}The average PCE is obtained from over 20 devices.

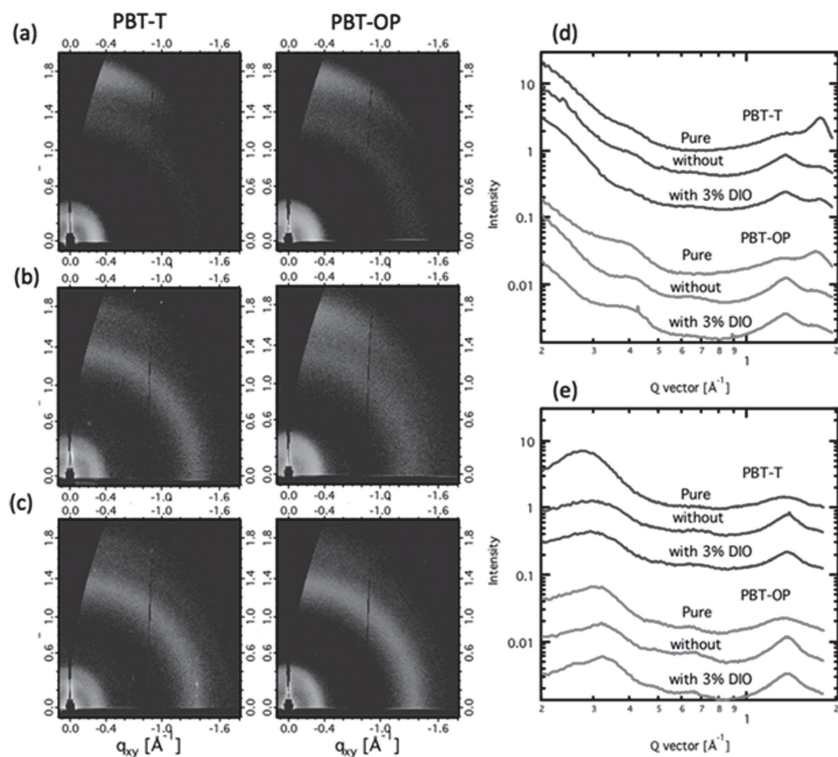


Figure 3. Two-dimensional grazing incidence X-ray diffraction (GIXD) images (a) neat polymer films, (b) polymer: PC₇₁BM blend films without DIO, (c) polymer: PC₇₁BM blend films with DIO. (d) Integrated out-of-plane scattering for neat polymer films, polymer: PC₇₁BM blend films without DIO and polymer: PC₇₁BM blend films with DIO. (e) Integrated in-plane scattering for neat polymer films, polymer: PC₇₁BM blend films without DIO and polymer: PC₇₁BM blend films with DIO.

improved V_{oc} of the device of **PBT-OP** can be ascribed to the deeper HOMO level of **PBT-OP** than **PBT-T**.

As shown in Figure 2b, these two kinds of devices processed by optimal conditions show EQE peak values of 70% and 75% for **PBT-T** and **PBT-OP** respectively at the same position (470 nm), while the response range of the device of **PBT-OP** at long wavelength direction is 20 nm blue-shifted compared to that of the device of **PBT-T**, which corresponds with the absorption spectra of the films of these two polymers as shown in Figure 1a, so the device of **PBT-OP** exhibited similar J_{sc} value compared to that of the device of **PBT-T**. In addition, w/o and with the use of DIO additive, FF values of the devices of **PBT-OP** are slightly higher than those of **PBT-T** in accordance with variation of the hole mobilities from **PBT-T** ($3.81 \times 10^{-3} \text{ cm}^2/\text{V s}$) to **PBT-OP** ($5.85 \times 10^{-3} \text{ cm}^2/\text{V s}$) measured by space-charge-limited current (SCLC) method. As a result, the overall efficiency of the device of **PBT-OP** processed by the use of 3% DIO reached 7.50%, which is 35% higher than that of the device of **PBT-T**. Obviously, the improved photovoltaic performance of **PBT-OP** is mainly contributed by the enhanced V_{oc} of the device, which benefits from its reduced HOMO level compared with that of **PBT-T**.

Grazing Incidence X-Ray Diffraction (GIXD) method was used to investigate the influence of the different BDT substituents (thienyl versus phenyl) and the processing additive (DIO) on morphological properties of the polymers and the polymer:

PC₇₁BM blends. As shown in Figure 3, the neat films of **PBT-T** and **PBT-OP** show very similar scattering patterns in GIXD analysis, i.e. both two neat films show (100) lamellar packing reflections at $\sim 0.3 \text{ \AA}^{-1}$ (corresponding to a d-spacing of $\sim 20.9 \text{ \AA}$) and (010) π - π stacking reflections at $\sim 1.6 \text{ \AA}^{-1}$ (corresponding to a d-spacing of 3.9 \AA), implying that the replacement of alkylthienyl with *meta*-alkoxy-phenyl has little influence on molecular packing of the neat films. Compared with the neat polymer films, the π - π stacking in the blend films is disrupted. An isotropic ring feature ($q = 1.4 \text{ \AA}^{-1}$, 4.5 \AA) is observed, corresponding to the Bragg diffraction of PC₇₁BM. Furthermore, as shown in Figure 3, there is no variation about the crystallite orientation relative to the electrodes in the blend films with 3% DIO as processing additive, indicating that the enhancement of the devices' performance with 3% DIO as processing additive is not resulted from the variation of the molecular packing, crystallinity, or orientation of the polymer's backbones.

Furthermore, atomic force microscope (AFM) and transmission electron microscope (TEM) methods were used to investigate the influence of the use of DIO on phase-separated morphologies of the polymer: PCBM blends. The TEM images of the blend films are provided in Figure 4, and the corresponding AFM images are

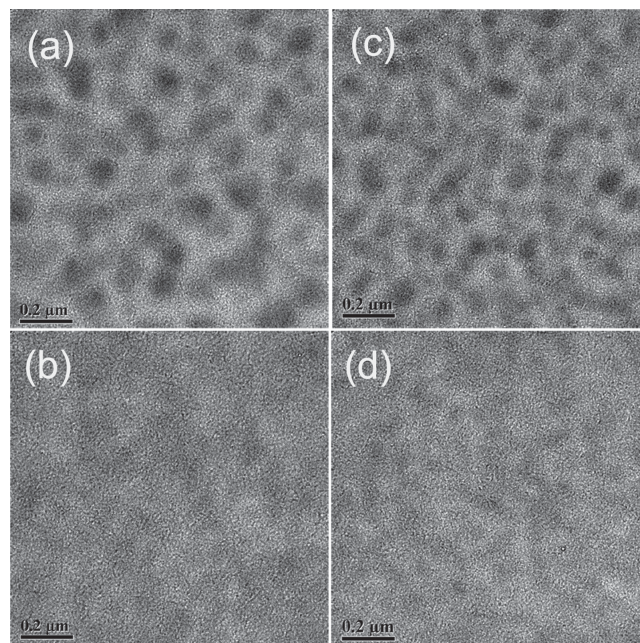


Figure 4. TEM images of polymer: PC₇₁BM blend films: (a) **PBT-T**: PC₇₁BM without DIO, (b) **PBT-T**: PC₇₁BM with 3% DIO, (c) **PBT-OP**: PC₇₁BM without DIO, (d) **PBT-OP**: PC₇₁BM with 3% DIO.

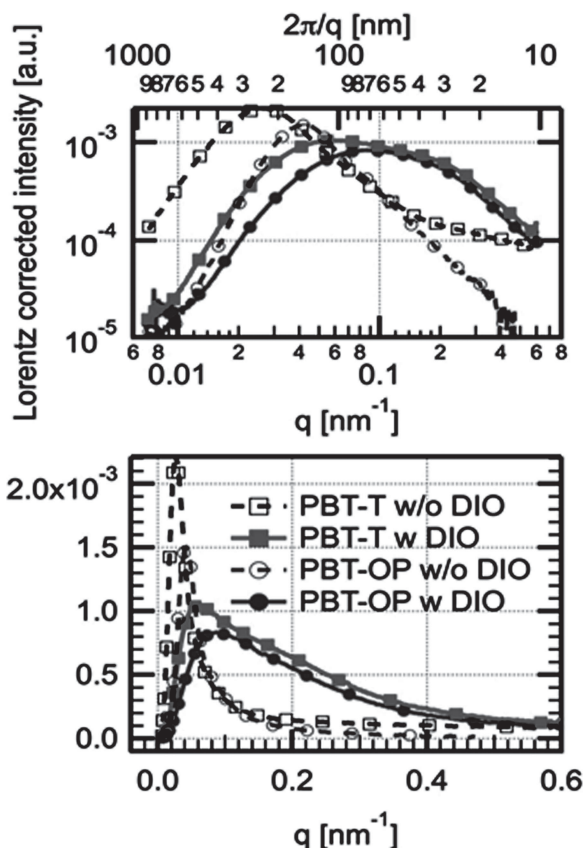


Figure 5. (a) Log-log RSoXS profiles for the polymer: PC₇₁BM blend films without DIO and with 3% DIO; (b) Lin-lin RSoXS profile, which emphasizes the high q peak of the spatial frequencies that characterized the sample morphology.

shown in Figure S4 (in SI). As shown, without the use of DIO, both two blend films of **PBT-T**/PC₇₁BM and **PBT-OP**/PC₇₁BM show severe phase separation, i.e. big size for light and dark domains, corresponding to the aggregations of polymer and PC₇₁BM respectively, can be observed in Figure 4a and 4c; after the use of 3% DIO, these big size aggregations of polymer and PC₇₁BM are diminished in Figure 4b and 4d. Moreover, the findings in TEM measurements can also be confirmed by AFM measurements (see Figure S4 in SI). These results demonstrate that nanoscale phase separation and interpenetrating network can be formed under the assistance of DIO, resulting in significant improvements of devices' J_{sc} and FF .

Although severe phase separation can be avoided by using 3% DIO as additive, the TEM images still shows phase separation at the length scale of ~ 100 nm (see Figure 4b and 4d), which can not fully explain the significantly improved J_{sc} . Hence, resonant soft X-ray scattering (R-SoXS) measurement was employed to provide additional information about the phase-separated morphologies of the blends.^[29] A photon energy of 284.2 eV was selected to provide high polymer/fullerene contrast while avoiding high absorption associated with the carbon 1s core level, which would produce background fluorescence and can lead to radiation damage.^[30] **Figure 5** shows the R-SoXS profiles for polymer: PC₇₁BM

(1:1.5, w/w) blend films cast from o-DCB w/o or with DIO as processing additive. The scattering profiles represent the distribution function of spatial frequency, s ($s = q/2\pi$), of the samples and are dominated by log-normal distributions that can be fitted by a set of Gaussians in lin-log space. The median of the distribution s_{median} corresponds to the characteristic median length scale, ξ , of the corresponding log-normal distribution in real space with $\xi = 1/s_{\text{median}}$, a model independent statistical quantity. From the profiles, we can find that without DIO, the **PBT-T**: PC₇₁BM blend showed bigger ξ (215 nm) than that of **PBT-OP**: PC₇₁BM blend (142 nm), which is consistent with the results investigated by TEM. Upon adding DIO, the ξ of these two blends were dramatically changed and all showed bimodal distribution which can be fitted very well with two log-normal distributions (see Figure S5). Well-defined peaks at low q with ξ of ~ 80 nm and ~ 60 nm for **PBT-T** and **PBT-OP** blends are observed in addition to a dominant log-normal distribution with a fractional total scattering intensity of 64% and 58%, respectively, at high q with ξ of 26 nm for both blends. Such a hierarchical phase separation is observed in other blends too and is considered to be favorable for charge separation and transport.^[31] Overall smaller domains are formed with the presence of DIO and the length scale of the smallest domains is close to the exciton diffusion length in polymer domains (ca. 10 nm).^[32] It is the development of the small length scale morphology that matters most. The impact of hierarchical nature remains unclear as the composition fluctuations between the larger domains may be within the window of overall D/A ratio for which the materials give good performance. Therefore, higher exciton dissociation efficiency and hence higher EQE can be realized in the PSC devices processed with DIO through control of the morphology, as previously observe in other systems.^[33] In addition, these results indicate that the replacing alkythienyl group with meta-alkoxy-phenyl group have little effect on the morphology of blend films processing with DIO, and the improvement of the PCE from **PBT-T** to **PBT-OP** mainly attributes to the effective modulation of molecular energy levels.

In conclusion, two polymers based on BDT with different conjugated side chains, **PBT-OP** and **PBT-T**, were synthesized and characterized. The results indicated that the variation of side chains from alkylthienyl groups to meta-alkoxy-phenyl groups has minimal effect on their optical absorption, molecular packing, device morphology and charge transport properties, but significant impact on the polymer's HOMO level. From **PBT-T** to **PBT-OP**, the V_{oc} of PSCs increased from 0.60 V to 0.78V while the J_{sc} and FF changed slightly, hence, PSCs based on **PBT-OP** showed a higher PCE of 7.50% which increased by $\sim 35\%$ compared with that of the devices based on **PBT-T**. Therefore, introducing the meta-alkoxy-phenyl groups as conjugated side chains is an effective way to modulate the molecular energy levels of D-A polymers for photovoltaic application.

Supporting Information

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

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