

Alkyl Side-Chain Engineering in Wide-Bandgap Copolymers Leading to Power Conversion Efficiencies over 10%

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Extensive studies have been recently focused on polymer:fullerene bulk-heterojunction solar cells. The combination of material development and device engineering leads to a significant boost in the power conversion efficiencies (PCEs).^[1–14] PCEs over 10% have been achieved for several representative medium-bandgap (MBG) ($1.6 < E_g^{\text{opt}} < 1.8$ eV) polymers, such as fluorinated benzothiadiazole-based copolymer PffBT4T-2OD,^[1] and well-known benzodithiophene-based copolymer PTB7-Th.^[4,5] Compared with MBG polymers, wide-bandgap (WBG) ($E_g^{\text{opt}} > 1.8$ eV) polymers received much less attention. Only few classic materials, such as poly(3-hexylthiophene) (P3HT), poly(p-phenylenevinylene) derivative MDMO-PPV, and poly(2,7-carbazole) copolymer PCDTBT, have been extensively studied in the past, but they suffer from low PCEs.^[15,16] The development of WBG copolymers is crucially important. It was realized that the performance of organic photovoltaic devices like tandem/ternary/nonfullerene organic solar cells are strongly dependent on the choice of WBG materials.^[16–27] Although steady improvements in PCEs have been achieved in recent years, their overall performance is still much lower than those of MBG polymer counterparts.^[28–34]

Basically, from the viewpoint of fundamental polymer design, three key constituting components, including polymeric backbones, conjugated functional substituents, and alkyl side chains should be taken into account. Much effort has been devoted to modifying polymeric backbones and functional substituents in comparison with alkyl side chains.^[35] In most cases, alkyl side chains have been used to tune the solubility of copolymers. In fact, the impact of alkyl side chains on photovoltaic properties of conjugated polymers remains complicated since the position, length, and bulkiness of alkyl side chains will largely influence aggregation behavior including intermolecular interactions and related stacking/packing in the solid state.^[36–39] Therefore, systematic studies of the influence of alkyl side chains on the properties of conjugated polymers are important, which will provide insight into structure-property relationships, adding rational design of new materials for polymer solar cells.

In this contribution, we designed a series of novel WBG copolymers (**PBT1-MP**, **PBT1-EH**, and **PBT1-BO**, see **Scheme 1** for their chemical structures). The copolymers consist of identical polymeric backbones with benzodithiophene (BDT) as the electron-rich unit and benzodithiophene-4,8-dione (BDTDO) as the electron-deficient unit, in which alkyl side chains having 40 carbon atoms in total were employed. The effect of alkyl side chains on both BDT donor and BDTDO acceptor units on the electronic structures, molecular packing, charge transport, photovoltaic properties of WBG copolymers have been systematically studied. It was found that **PBT1-EH** with the moderate bulky side chains exhibited the best photovoltaic performance. When paired with PC₇₁BM, **PBT1-EH**-based solar cells showed a high PCE of 10.3%, the highest values reported in the literature so far for WBG polymer:fullerene solar cells. Furthermore, a high PCE of 10.6% has been achieved when it was blended with a deep absorbing nonfullerene acceptor (ITIC-Th),^[24] indicating that **PBT1-EH** is a good candidate for incorporation in various types of organic photovoltaic devices. The results suggest that the alkyl side-chain engineering is an effective strategy to further tuning the optoelectronic properties of WBG polymers.

The synthetic route of WBG polymers is shown in Scheme 1. Dialkylthieno-2-yl flanked benzo[1,2-b:4,5-b']dithiophene subunits (D1, D2, and D3) and 3-bis(thiophen-2-yl)-benzo-[1,2-c:4,5-c']-dithiophene-4,8-dione subunits (A1, A2, and A3) were prepared according to previously reported approach (Scheme S1, Supporting Information).^[40,41] Various bulky side chains of R1 (R1 = 2-methylpropyl (MP), 2-ethylhexyl (EH), and 2-butyloctyl (BO)) and R2 (R2 = 2-hexyldecyl, 2-butyloctyl, and 2-ethylhexyl) were introduced to BDT and BDTDO units. Subsequently, the

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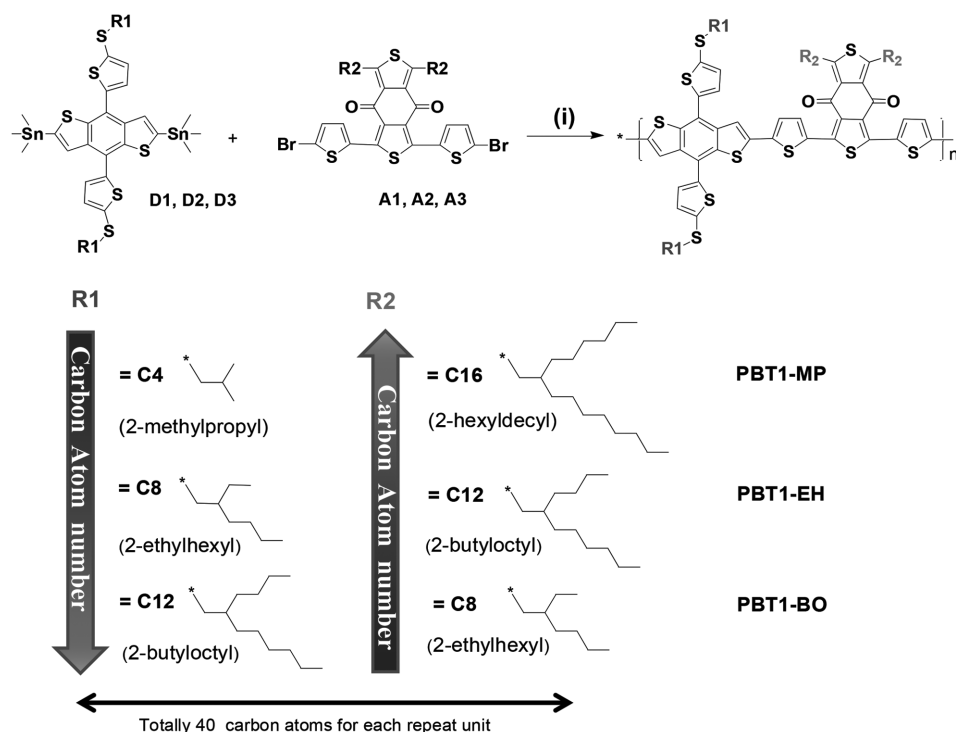
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Scheme 1. Synthetic routes of WBG copolymers: (i) Toluene, Pd(PPh₃)₄, 110 °C, 12 h.

copolymers were prepared by a classic Stille cross-coupling polymerization reaction. The general polymerization reaction was conducted in toluene at 110 °C under inert atmosphere for 12 h. The copolymers were purified by precipitation into methanol, then subjected to soxhlet extraction with methane, hexane, and chloroform consecutively to obtain **PBT1-MP**, **PBT1-EH**, and **PBT1-BO**.

Thermogravimetric analysis with Fourier transform infrared (FTIR) spectroscopy was performed to study the thermal stability of the copolymers. As shown in Figure S1 (Supporting Information), these copolymers are thermally stable with a decomposition temperature beyond 305 °C under nitrogen. FTIR results indicate that **PBT1-EH** and **PBT1-BO** are stable below 150 °C and no degradation step has been observed since the peaks positioned between 2800 and 3000 cm⁻¹ (C–H stretching) and between 2250 and 2400 cm⁻¹ (O=C=O stretching) are not obviously increased. In contrast, **PBT1-MP** exhibits a small degradation step with ≈0.2% weight loss at ≈150 °C and the peak in the 3000–2850 cm⁻¹ region is attributed to the C–H stretch of the methyl group.

Density functional theory (DFT) calculations were performed to study the effect of alkyl side chain length on the molecular geometry and electronic structure of **PBT1-MP**, **PBT1-EH**, and **PBT1-BO**. DFT calculations are based on 6 repeat units. As shown in Figure 1, **PBT1-MP** bearing the longest alkyl side chain on the acceptor unit resulted in a twisted molecular geometry, which is mainly ascribed to the large steric hindrances caused by the bulkier side chains on BDTDO unit. In contrast, **PBT1-EH** and **PBT1-BO** both have nearly planar molecular geometry.

The temperature-dependent UV–vis absorption spectra of **PBT1-MP**, **PBT1-EH**, and **PBT1-BO** were measured to

investigate the aggregation behavior of the copolymers in dilute solutions. As shown in Figure S2 (Supporting Information), even at elevated temperatures (e.g., 70 °C), all copolymer solutions showed obvious shoulder peak at longer wavelength, indicating strong aggregation of the polymer chains in dilute solutions. In the solid state, slightly redshifted absorptions are observed for all copolymers due to enhanced π – π stacking. In detail, a larger redshift (≈12 nm) was observed for **PBT1-BO**, while a smaller redshift was found for **PBT1-MP**. This suggests that the bulky alkyl chains especially on BDTDO motif can cause larger steric hindrance and subsequently decrease the planarity of the main backbone and lead to decreased π – π stacking interactions. E_g^{opt} values of these polymers calculated from the absorption edge are 1.86 eV (**PBT1-MP**), 1.84 eV (**PBT1-EH**), and 1.81 eV (**PBT1-BO**), respectively.

In evaluating their electrochemical properties, cyclic voltammetry was performed to determine the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels. As displayed in Figure S3 (Supporting Information), both p- and n-doping processes are reversible for all copolymers. The corresponding HOMO/LUMO levels of **PBT1-MP**, **PBT1-EH**, and **PBT1-BO** are –5.49/–3.46 eV, –5.43/–3.43 eV, and –5.40/–3.41 eV, respectively. One can find that increasing the length of alkyl chain substituents on BDTDO motif leads to a deeper HOMO level, agreeing well with the DFT simulated results (Figures S4–S6, Supporting Information).

To assess the photovoltaic performance of these copolymers, organic solar cells have been fabricated using PC₇₁BM as the acceptor and 1, 8-diiodooctane (DIO) as the solvent additive

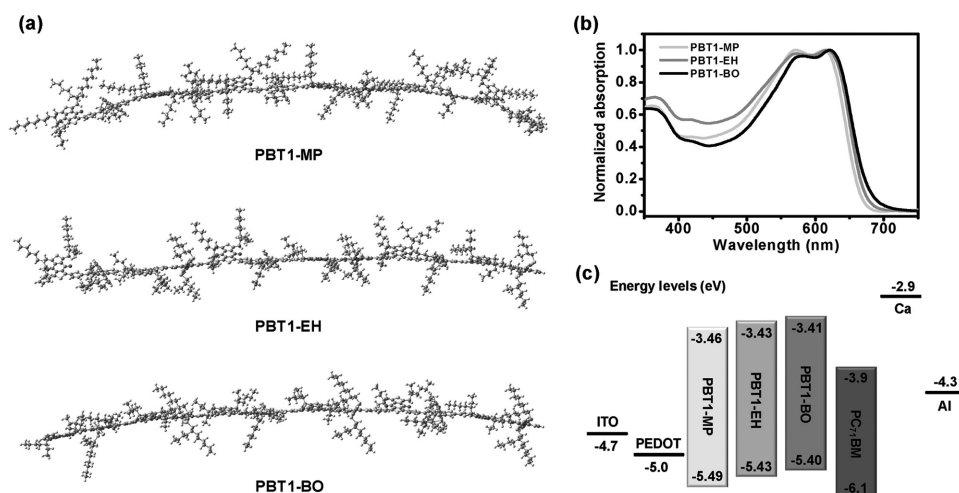


Figure 1. a) Optimized molecular geometries (6 repeat units) of **PBT1-MP**, **PBT1-EH**, and **PBT1-BO** (side view). b) Absorption spectra of **PBT1-MP**, **PBT1-EH**, and **PBT1-BO** in the solid state. c) Schematic energy diagram of the components in the fabrication of solar cells.

to optimize the active layer morphology. Typical current density–voltage (J – V) curves of solar cells are shown in **Figure 2** and the corresponding device performance is summarized in **Table 1**. It was found that the DIO concentration has pronounced effects on the device performance. Without using DIO, all devices incorporating these three copolymers show rather low PCEs (<4%), but with quite impressive high V_{oc} values of ≈ 1.0 eV. Dramatic increases in the device performance were observed upon addition of a small amount of DIO (see **Table 1** and **Figure 2**). The optimal DIO concentration was found to be 0.5% for all the blend films. Under this condition, the **PBT1-EH**:PC₇₁BM solar cell showed a short-circuit current (J_{sc}) of 14.22 mA cm^{-2} , an open-circuit voltage (V_{oc}) of 0.97 V, and a fill factor (FF) of 75.1%, producing an overall efficiency of 10.3%. To our best knowledge, the efficiency of 10.3% represents the highest value reported in the literature so far for WBG polymer:fullerene solar cells. 100 cells from different batch runs were fabricated in total (**Figure S8**, Supporting

Information) and the average PCE from 20 best cells is 10.1%, indicating good reproducibility. The efficiency versus the active layer thickness has been investigated (**Figure S10**, Supporting Information). At the active layer thickness of 130 nm, solar cells showed the best photovoltaic performance. When the thickness was increased to 160 nm, the PCE was decreased to 9.3%. Further increasing the thickness up to 210 nm, the PCE dropped to 7.6% due to the dramatically reduced FF. **PBT1-MP**:PC₇₁BM solar cells showed a PCE of 9.1%, with a J_{sc} of 12.87 mA cm^{-2} , a V_{oc} of 0.98 V, and a FF of 72.5%. Among the three polymers, **PBT1-BO**-based solar cells show the lowest V_{oc} (0.93 V), and FF (66.7%) values, which contributed to a low PCE (8.1%). The lowest V_{oc} obtained in **PBT1-BO**-based solar cells is mainly due to its higher HOMO level. The hole and electron mobilities of **PBT1-EH**:PC₇₁BM films were measured as 1.94×10^{-3} and $2.87 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (**Figure S11** and **Table S1**, Supporting Information), which are higher than those of **PBT1-MP**:PC₇₁BM and **PBT1-BO**:PC₇₁BM films. The high and balanced

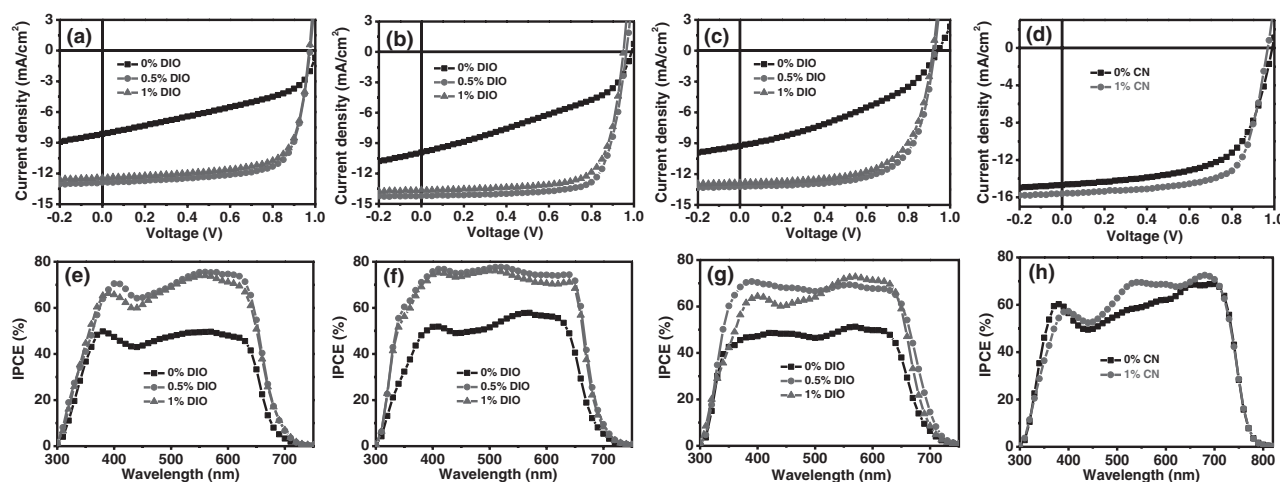


Figure 2. J – V characteristics and the corresponding IPCE spectra of a, e) **PBT1-MP**:PC₇₁BM, b, f) **PBT1-EH**:PC₇₁BM, c, g) **PBT1-BO**:PC₇₁BM, and d, h) **PBT1-EH**:ITIC-Th solar cells with different solvent additives under the illumination of AM1.5G, 100 mW cm^{-2} , respectively.

Table 1. Summary of device parameters of **PBT1-MP**:PC₇₁BM, **PBT1-EH**:PC₇₁BM, **PBT1-BO**:PC₇₁BM, and **PBT1-EH**:ITIC-Th solar cells with different solvent additives under the illumination of AM1.5G, 100 mW cm⁻².

Active layer	Additive [%]	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF [%]	PCE ^{a)} [%]	PCE _{max} [%]
PBT1-MP : PC ₇₁ BM (DIO)	0	1.00 ± 0.01	8.08 ± 0.06	43.4 ± 0.7	3.5 ± 0.1	3.6
	0.5	0.97 ± 0.01	12.81 ± 0.09	72.2 ± 0.3	9.0 ± 0.1	9.1
	1.0	0.97 ± 0.01	12.32 ± 0.09	71.5 ± 0.2	8.5 ± 0.2	8.7
PBT1-EH : PC ₇₁ BM (DIO)	0	0.99 ± 0.01	9.85 ± 0.11	39.3 ± 0.2	3.7 ± 0.1	3.8
	0.5	0.96 ± 0.01	14.14 ± 0.07	74.7 ± 0.3	10.1 ± 0.2	10.3
	1.0	0.95 ± 0.01	13.68 ± 0.08	72.6 ± 1.0	9.4 ± 0.1	9.5
PBT1-BO : PC ₇₁ BM (DIO)	0	0.95 ± 0.01	8.94 ± 0.26	38.4 ± 0.2	3.2 ± 0.1	3.3
	0.5	0.92 ± 0.01	12.97 ± 0.16	67.2 ± 0.3	8.0 ± 0.1	8.1
	1.0	0.92 ± 0.01	12.76 ± 0.09	64.1 ± 0.6	7.5 ± 0.2	7.7
PBT1-EH : ITIC-Th (CN)	0	0.99 ± 0.01	14.64 ± 0.11	61.4 ± 0.5	8.9 ± 0.2	9.1
	1.0	0.97 ± 0.01	15.52 ± 0.21	68.1 ± 1.1	10.3 ± 0.2	10.6

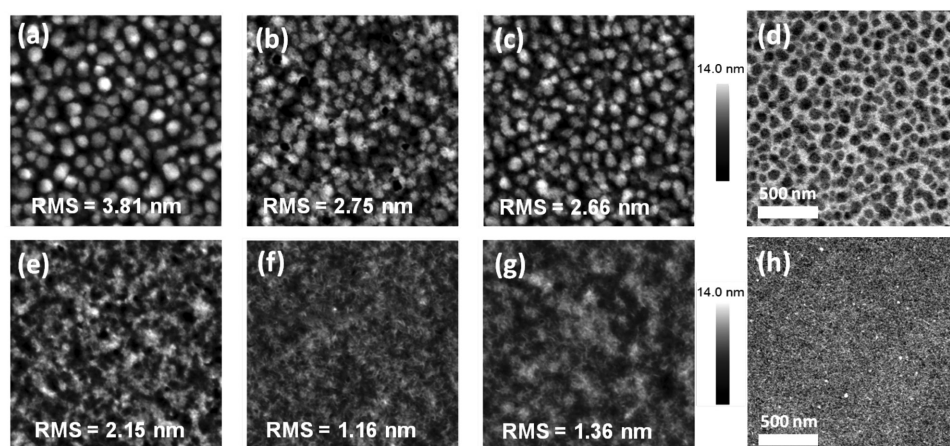
^{a)}The values in parentheses are average PCEs from 20 devices.

hole and electron mobility helps to explain the high J_{sc} and FF achieved in **PBT1-EH**:PC₇₁BM devices. The corresponding incident photon conversion efficiency (IPCE) spectra are shown in Figure 2. The IPCE curves exhibited a broad photoresponse in the range of 300–700 nm for all the cells. Especially for **PBT1-EH**:PC₇₁BM device, IPCE exceeds 70% from 380 to 650 nm, with a peak of 78% at 520 nm. Therefore, **PBT1-EH**-based device yielded the highest J_{sc} . The calculated J_{sc} from the IPCE spectra is 13.97 mA cm⁻², in good agreement with the value obtained from J - V measurements.

Atomic force microscopy (AFM) and transmission electron microscopy (TEM) were performed to study the active layer morphology. As illustrated in Figure 3, rather coarse surfaces with high root-mean-square roughness (R_q) of 3.81, 2.75, and 2.66 nm were observed for **PBT1-MP**:PC₇₁BM, **PBT1-EH**:PC₇₁BM, and **PBT1-BO**:PC₇₁BM films, respectively. The addition of DIO additive suppressed the large aggregation of PC₇₁BM in blends. The blend films thus became quite smooth with no obvious density fluctuations. We see from TEM image

that fibrillar type of topology showed up, which came from the aggregated chain of polymers.

The influence of alkyl side chain length on the local molecular packing and orientation of the neat films was investigated using grazing incidence wide angle X-ray scattering (GIWAXS). The 2D GIWAXS patterns and the corresponding out-of-plane and in-plane line cuts are shown in Figure 4. The (100) lamellar diffraction peaks for **PBT1-MP**, **PBT1-EH**, and **PBT1-BO** neat films were observed at $q_{xy} \approx 0.267$, 0.266, and 0.258 Å⁻¹, corresponding to lamellar packing distances of ≈ 23.55 , 23.64, and 24.40 Å, respectively, which suggests that the bulky alkyl chains on BDT unit lead to an increase in interchain distance of copolymers. Very weak lamellar diffraction peaks and strong π - π stacking peaks were observed in the out-of plane direction, indicating that a preferred face-on molecular orientation in all neat films. The (010) π - π stacking peaks were located at $q_z \approx 1.69$, 1.70, and 1.70 Å⁻¹ for **PBT1-MP**, **PBT1-EH**, and **PBT1-BO** neat films, which corresponds to π - π stacking distances of ≈ 3.72 , 3.69, and 3.69 Å, respectively. The crystal

**Figure 3.** AFM topography images (2 × 2 μm) of **PBT1-MP**:PC₇₁BM blend films a) without and e) with 0.5% DIO additive; **PBT1-EH**:PC₇₁BM blend films b) without and f) with 0.5% DIO additive; **PBT1-BO**:PC₇₁BM blend films c) without and g) with 0.5% DIO; TEM images of **PBT1-EH**:PC₇₁BM blend films d) without and h) with 0.5% DIO additive.

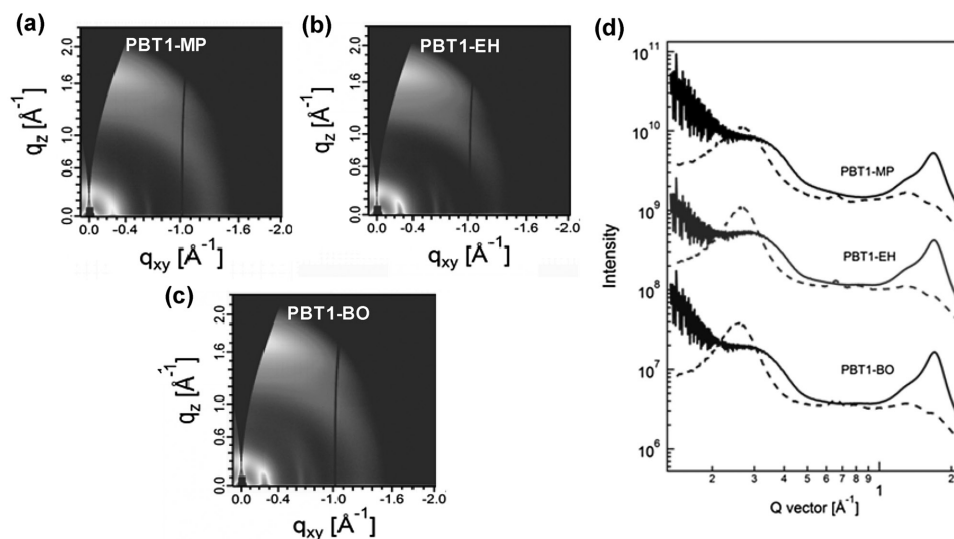


Figure 4. a–c) 2D GIWAXS images of **PBT1-MP**, **PBT1-EH**, **PBT1-BO**, and d) the corresponding out-of-plane (solid lines) and in-plane (dash lines) line cuts.

size of the neat films were further studied by calculating the coherence lengths of the (100) lamellar packing in the in-plane direction for the neat films using the Scherrer equation.^[42] The values are 5.8, 7.9, and 7.6 nm for **PBT1-MP**, **PBT1-EH**, and **PBT1-BO**, respectively. The results suggest that the longest alkyl chain length on BDTDO led to reduced polymer crystallinity. When mixed with PC₇₁BM, the π – π stacking peaks of all active layers were almost disappeared. When DIO was used, both the lamellar packing and π – π stacking of blend films were enhanced (Figure S13, Supporting Information). As a result, higher photovoltaic performance has been achieved.

Nonfullerene acceptor-based organic solar cell has recently attracted a lot of attention.^[15,43,44] As aforementioned, WBG polymers play a critical role in determining the overall performance of nonfullerene organic solar cells. Therefore, **PBT1-EH** and a well established nonfullerene acceptor, ITIC-Th,^[22] have been

used to fabricate the devices. Without any treatments, a high PCE of 9.1% has been achieved with a J_{sc} of 14.70 mA cm^{-2} , a V_{oc} of 0.99 V, a FF of 62.1%. With the addition of 1% chloronaphthalene (CN) additive, the PCE was improved to 10.6%, with a J_{sc} of 15.62 mA cm^{-2} , a V_{oc} of 0.97, and a FF of 69.8%, which is among the best PCE values for nonfullerene systems reported in the literature. It was found that the addition of CN additive into the blend films led to a rough surface and enhanced π – π stacking of ITIC-Th (Figure S14, Supporting Information). Furthermore, resonant soft X-ray scattering was carried out to study the phase separation of **PBT1-EH**:ITIC-Th films (Figure 5e). The domain size in the **PBT1-EH**:ITIC-Th films with CN additive is 35 nm, which is much smaller than that (145 nm) in **PBT1-EH**:ITIC-Th films without CN additive. It has been well known that the small domain size would be favorable for exciton dissociation and lead to high

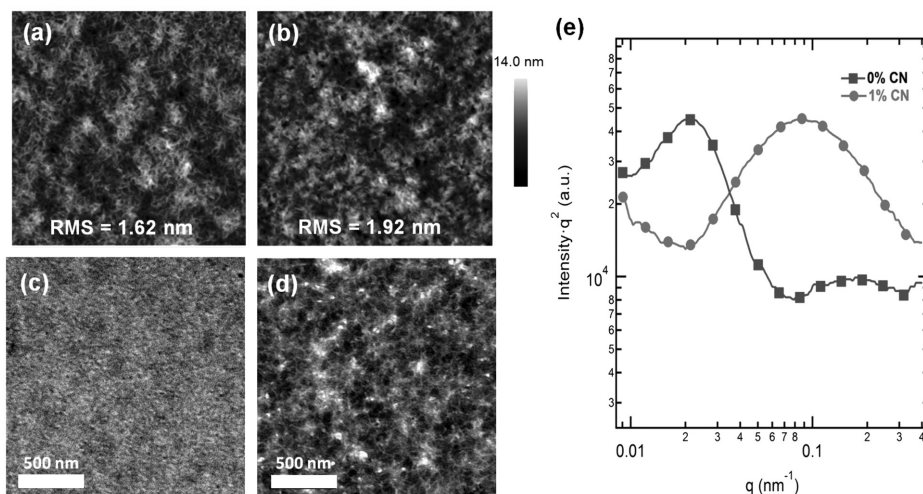


Figure 5. AFM topography images (2 × 2 μm) of **PBT1-EH**:ITIC-Th blend films a) without and b) with 1% CN additive; TEM images of **PBT1-EH**:ITIC-Th blend films c) without and d) with 1% CN additive. e) Resonant soft X-ray scattering of **PBT1-EH**:ITIC-Th blend films without and with 1% CN additive. A photon energy of 284.8 eV was selected to provide the high contrast between the donor and acceptor.

photovoltaic performance. The relative domain purity can also be acquired by calculating the total scattering intensity.^[45] The relative domain purity is 0.78 for **PBT1-EH:ITIC-Th** films while the purity of blend films processed with CN additive is 1. The purer domain may reduce the recombination of electron and hole, and leads to a higher FF.^[46] The hole and electron mobility are 1.63×10^{-3} and $2.45 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, which ensures effective charge carrier transport to the electrodes, resulting in such high PCEs (Figure S15, Supporting Information).

In summary, a series of WBG copolymers with different alkyl side chains on BDT donor and BDTDO acceptor units were synthesized and characterized. The results clearly show that the alkyl side chains have obvious impacts on optical, electrical, and photovoltaic properties, as well as on the molecular packing and crystallinity of polymers. We observed that the longest alkyl substituents on BDTDO unit can cause large steric hindrance and lead to a twisted molecular geometry. Consequently, **PBT1-EH** with the moderate bulky side chain on BDTDO unit showed the best photovoltaic performance with high PCEs over 10% in both fullerene and nonfullerene acceptor-based organic solar cells. Our results provided new insights into the structural and photovoltaic properties of WBG copolymers and are helpful for rationally designing high-performance organic photovoltaic materials via alkyl side-chain engineering.

Experimental Section

Solar Cell Fabrication and Characterization: Polymer solar cells were fabricated with a conventional architecture of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene): (PEDOT):poly(styrenesulfonate) (PSS)/active layer/Ca/Al. After cleaning, the ITO-coated glass substrates were ready for use. In terms of the device fabrication, a 40 nm thick PEDOT:PSS (Heraeus Clevis P VP A 4083) layer was spin-cast on top of the ITO substrates and then annealed on a hotplate at 150 °C for 10 min in air. The polymers were mixed with PC₇₁BM at various blending ratio in CHCl₃. The polymer concentration was fixed at 8 mg mL⁻¹. The mixed solution was spin-cast on top of PEDOT:PSS substrate to form the active layer. The optimal thickness of the active layers were measured as 130 nm using an Ambios Technology XP-2 surface profilometer. For **PBT1-EH:ITIC-Th** active layer, the concentration of the mixed solutions is 8 mg mL⁻¹ in CHCl₃ and the optimal thickness of the active layer is 110 nm. Finally, a 10 nm thick Ca layer and a 100 nm Al electrode were successively deposited on top of the active layers by thermal evaporation. The active area of devices is 4.5 mm². During measurements, an aperture with the area of 3.14 mm² was used. Current density–voltage (*J*–*V*) characteristics were measured using a Keithley 2400 source measure unit. Solar cell performance used an Air Mass 1.5 Global (AM 1.5 G) solar simulator (Class AAA solar simulator, Model 94063A, Oriel) with an irradiation intensity of 100 mW cm⁻², which was measured by a calibrated silicon solar cell and a readout meter (Model 91150V, Newport). IPCE spectra were measured by using a QEX10 solar cell IPCE measurement system (PV measurements, Inc.).

Supporting Information

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

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