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Side-chains Engineering of Conjugated Polymers toward Additive-free Non-fullerene Organic Solar Cells

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Electronic Supplementary Information

Abstract Side-chain engineering plays a significant role in the design of conjugated materials. In this work, a series of conjugated polymers PBDB-T-R with functionalized groups at the end of side units were developed as electron donor for organic solar cells (OSCs). The donor polymers PBDB-T-I and PBDB-T-OAc with iodine and acetate end groups exhibited similar absorption and energy levels, but showed much improved PCEs in OSCs compared to the polymer PBDB-T-H without substitutions at the end groups. Additionally, we found that PBDB-T-I and PBDB-T-OAc based cells exhibited optimized performance when using chloroform as solution-processed solvent without any additives. These results indicate that these conjugated polymers can act as self-additive to fabricate photoactive layers via solution process in OSCs.

Keywords Organic solar cells; Non-fullerene; End group; Additive; Crystallinity

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INTRODUCTION

Non-fullerene organic solar cells (NFOSCs) have attracted much attention due to their advantages of high performance, low-cost, easy processing and thus potential large-area application.^[1–10] Recently, Zou *et al.* developed a ladder-type acceptor Y6 with strong absorption in the near-infrared region (NIR).^[11] NFOSCs based on Y6 as electron acceptor and wide-bandgap benzodithiophenedione (BDT)-based donor polymers (such as PM6 and PM7) provided excellent PCEs (15%–18%).^[12–18] It is important to put continuous efforts into material design and device engineering in order to further enhance the PCEs of NFOSCs.

Besides the conjugated backbone engineering, side-chain engineering plays a significant role in the material design. Side chains of conjugated polymers can influence the solubility, aggregation and crystalline properties, and charge transport properties.^[19–22] Many works have focused on modifying side chains, such as *via* introducing fluorine and chlorine atoms,^[23,24] alkyloxy and alkylthio units,^[25] thienyl and phenyl side units,^[26] *etc.* In addition, the device engineering, for instance, through using high boiling point additive during solution-processing for photoactive layers, is

an efficient route to the optimization of microphase separation in the bulk-heterojunction blends.^[27,28] 1,8-Diiodooctane (DIO),^[29–31] phenyl ether^[32,33] and 1-chloronaphthalene^[34–36] have been widely used as additive for this purpose. However, the addition of these solvents can also increase the complexity of fabrication process. Moreover, some reports also revealed that these additives with high boiling point had the difficulty to be removed, so that these additives coexisted with the photoactive layers. This would lower the photovoltaic performance and also reduce the device stability.

Recently, we designed a series of donor polymers with different end groups on the alkyl side chains, including bromine (Br), alkyloxy unit (OMe) and alkyl thiophene (T). These extra groups helped the polymers to form optimized morphology in the blends and hence provided high PCEs over 13%.^[37] Inspired by this work, herein, we further developed two conjugated polymers with different end groups on the side chains, including iodine (I) and acetate (OAc) units, as shown in Fig. 1(a). Interestingly, we found that when using Y6 as electron acceptor, NFOSCs based on the two polymers as donor exhibited the best PCEs by using chloroform (CF) as solution-processed solvent, which is higher than those of the solar cells by using CF with DIO as the additive. The results indicate that rational design of end groups on the side units can afford conjugated polymers for additive-free NFOSCs.

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EXPERIMENTAL

Materials and Measurements

The synthetic procedures were performed under argon atmosphere. Commercial chemicals (from Sigma-Aldrich, JK Chemical and TCI) were used as received. Compound 2,6-dibromo-4,8-bis(5-(12-bromododecyl)-4-chlorothiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (**M-Br**) was prepared according to literature procedure.^[38]

¹H-NMR and ¹³C-NMR spectra of intermediate products and monomers were recorded at 400 MHz on a Bruker AVANCE spectrometer with tetramethylsilane (TMS) as the internal standard. The molecular weight was determined with GPC at 140 °C on a PL-GPC 220 system using a PL-GEL 13 μm Olexis column and *o*-DCB as the eluent against polystyrene standards. Optical absorption spectra were recorded on a JASCO V-570 spectrometer with a slit width of 2.0 nm and a scan speed of 1000 nm·min⁻¹. Cyclic voltammetry was performed under an inert atmosphere at a scan rate of 0.1 V·s⁻¹ and 1 mol·L⁻¹ tetrabutylammonium hexafluorophosphate in acetonitrile as the electrolyte, a glassy-carbon working electrode coated with samples, a platinum-wire auxiliary electrode, and an Ag/AgCl as a reference electrode. Thermogravimetric analysis data were obtained from a TGA8000 thermogravimetric analyzer (PerkinElmer). DSC measurement was performed on a DSC-250 apparatus.

The two-dimensional (2D) grazing incidence wide angle X-ray scattering (GIWAXS) experiments were carried out on a GANESHA 300XL+ system from JJ X-ray in the X-ray lab at DSM Materials Sciences Center (DMSC). The instrument is equipped with a Pilatus 300K detector, with pixel size of 172 μm × 172 μm. The X-ray source is a Genix 3D Microfocus Sealed Tube X-Ray Cu-source with integrated Monochromator (multilayer optic “3D version” optimized for SAXS) (30 W). The wavelength used is λ=1.5418 Å. The detector moves in a vacuum chamber with sample-to-detector distance varied between 0.115 and 1.47 m depending on the configuration used, as calibrated using silver behenate (*d*₀₀₁=58.380 Å). The minimized background scattering plus high-performance detector allows for a detectable *q*-range varying from 3 E⁻³ to 3 Å⁻¹ (0.2 nm to 210 nm). The sample was placed vertically on the goniometer and tilted to a glancing angle of 0.2° with respect to the incoming beam. A small beam was used to gain a good resolution. The primary slits have a size of 0.3 mm × 0.5 mm (horizontal × vertical), and the guard slits have a size of 0.1 mm × 0.3 mm (horizontal × vertical). The accumulation time was 6 h for each measurement. The line cuts were conducted using SAXSGUI program.

Photovoltaic devices with inverted configuration were made by spin-coating a ZnO sol-gel at 4000 r·min⁻¹ for 40 s onto pre-cleaned, patterned ITO substrates. The photoactive layer was deposited by spin coating CF solution containing the polymer and the appropriate amount of DIO as processing additive. The thin films were then transferred into the N₂-filled glove box. MoO₃ (10 nm) and Al (100 nm) were deposited by vacuum evaporation at *ca.* 4×10⁻⁵ Pa as the back electrode.

The active area of the cells was defined as 0.04 cm² by using an aperture. The *J*-*V* characteristics were measured by a

Keithley 2400 source meter unit under AM1.5G spectrum from a solar simulator (Enlitech model SS-F5-3A). Solar simulator illumination intensity was determined at 100 mW·cm⁻² using a monocrystal silicon reference cell with KG5 filter. Short circuit currents under AM1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The external quantum efficiency was measured by a Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.). The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak XT profilometer.

Atomic force microscopy (AFM) images were recorded using a Digital Instruments Nano scope IIIa multimode atomic force microscope in tapping mode under ambient conditions.

Synthesis

2,6-Dibromo-4,8-bis(4-chloro-5-(5-iodopentyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (M-I**):** To a solution of compound **M-Br** (200 mg, 0.19 mmol) in acetone (10 mL), NaI (85 mg, 0.57 mmol) was added. The reaction mixture was refluxed under nitrogen for 12 h. The reactant was extracted by CH₂Cl₂ (200 mL) and dried over anhydrous Na₂SO₄. After removing solvent, the crude product was purified by silica gel chromatography (dichloromethane:petroleum ether, *V*:*V*=1:5 as eluent) to obtain **M-I** (206 mg, yield 95%) as pale yellow solid. ¹H-NMR (CDCl₃, 400 MHz, δ, ppm): 7.55 (s, 2H), 7.15 (s, 2H), 3.18 (t, *J*=7.34 Hz, 4H), 2.88 (t, *J*=7.64 Hz, 4H), 1.82 (m, 4H), 1.74 (m, 4H), 1.29 (m, 32H). ¹³C-NMR (CDCl₃, 100 MHz, δ, ppm): 140.27, 139.93, 135.99, 134.39, 128.25, 125.67, 122.31, 121.65, 117.43, 33.58, 30.50, 30.47, 29.53, 29.50, 29.47, 29.40, 29.24, 29.14, 28.54, 27.92, 7.25. MS *m/z*: [M]⁺, Calcd. for C₄₂H₅₂Br₂Cl₂I₂S₄: 1169.8; Found: 1169.8.

(5,5'-(2,6-Dibromobenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-diyl)-bis(3-chlorothiophene-5,2-diyl)) bis(butane-4,1-diyl) dipropionate (M-OAc**):** Compound **M-I** (200 mg, 0.17 mmol) and CH₃COOK (101 mg, 1.03 mmol) were added in DMF (5 mL). The reaction mixture was heated at 80 °C under nitrogen for 6 h. The reactant was extracted by CH₂Cl₂ (200 mL) and dried over anhydrous Na₂SO₄. After removing solvent, the crude product was purified by silica gel chromatography (dichloromethane:petroleum ether, *V*:*V*=2:1 as eluent) to obtain **M-OAc** (0.55 g, yield 96%) as pale yellow solid. ¹H-NMR (CDCl₃, 400 MHz, δ, ppm): 7.55 (s, 2H), 7.16 (s, 2H), 4.07 (t, *J*=6.82 Hz, 4H), 2.88 (t, *J*=7.62 Hz, 4H), 2.04 (s, 6H), 1.75 (m, 4H), 1.62 (m, 4H), 1.45 (m, 4H), 1.30 (m, 24H). ¹³C-NMR (CDCl₃, 100 MHz, δ, ppm): 171.19, 140.27, 139.94, 135.99, 134.39, 128.25, 125.66, 122.31, 121.65, 117.42, 64.64, 30.48, 29.57, 29.53, 29.50, 29.25, 29.17, 28.62, 27.92, 25.91, 20.98. MS *m/z*: [M]⁺, Calcd. for C₄₆H₅₈Br₂Cl₂O₄S₄: 1032.1; Found: 1032.1.

PBDB-T-R: To a degassed solution of monomer **M-R** (54.5 μmol), monomer **BDD-Sn** (50.9 mg, 54.5 μmol) in toluene (2 mL) and Pd(PPh₃)₄ (1.69 mg, 1.5 μmol) were added. The mixture was stirred at 115 °C for 36 h, then it was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was extracted with acetone, hexane and chloroform. Then the chloroform solvent was collected, evaporated and precipitated in acetone. Finally, it was collected by filtering over a 0.45 μm PTFE membrane filter and dried in a vacuum oven to yield polymer **PBDB-T-R** as a dark solid.

PBDB-T-H: 62 mg, 82%, $M_n=49.3$ kDa, $M_w=78.4$ kDa and $D_M=1.59$ (GPC, *o*-DCB, 140 °C).

PBDB-T-I: 73 mg, 87%, $M_n=30.6$ kDa, $M_w=42.0$ kDa and $D_M=1.59$.

PBDB-T-OAc: 59 mg, 75%, $M_n=29.4$ kDa, $M_w=43.7$ kDa and $D_M=1.96$.

RESULTS AND DISCUSSION

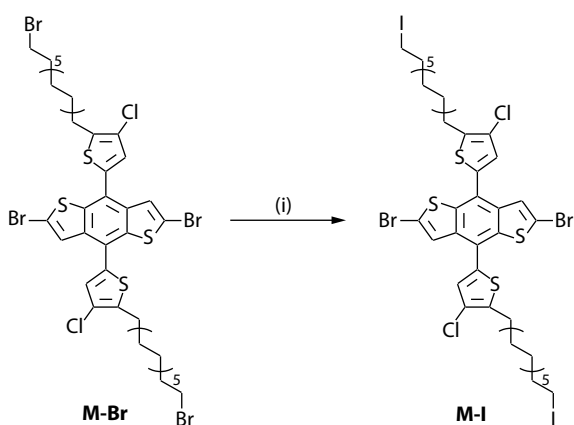
Synthesis and Characterization of Polymers PBDB-T-R

The detailed synthetic routes to the monomers were described in the experimental (Schemes 1 and 2). The iodinated monomer **M-I** was easily prepared from the brominated precursor **M-Br** with NaI as iodinated agent, which was then converted into acetate monomer **M-OAc** by using a simple reaction (Scheme 2) with a high yield. The two monomers were then used to perform Stille-coupling polymerization to yield the polymers PBDB-T-I and PBDB-T-OAc (Fig. 1a). The polymer PBDB-T-H without substitutions was prepared according to our previous work.^[37] The molecular weight of the polymers was determined by high temperature gel permeation chromatography (GPC) with *o*-DCB as eluent, as summarized in Table S1 (in the

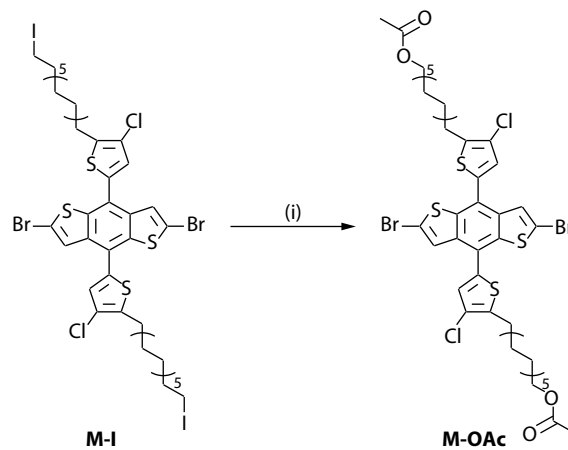
electronic supplementary information, ESI). All three polymers showed good solubility in CF and chlorobenzene, and high stability up to 300 °C, as shown in thermogravimetric analysis (Fig. S1a in ESI). Iodinated PBDB-T-I exhibited relatively low decomposition temperature at ~300 °C, which would be due to the weak C–I bonds. Differential scanning calorimetry (DSC) measurement shows that the conjugated polymers have no thermal transition in the range of measured temperature (Figs. S1b–S1d in ESI).

Optical and Electrochemical Property

The UV-Vis absorption spectra of donor polymers and **Y6** in CF and in thin films are shown in Fig. S2 (in ESI) and Fig. 2(a). The donor polymers show similar UV-Vis absorption around 300–750 nm, which is complementary to the absorption of **Y6**. All the donor polymers show two absorption peaks, a peak around 580 nm (due to the intramolecular interaction of conjugated backbones) and a peak around 620 nm (due to the aggregation of conjugated backbones). The relatively high absorption intensity around 620 nm for polymer PBDB-T-I and PBDB-T-OAc compared to that of PBDB-T-H indicates that PBDB-T-I and PBDB-T-OAc may have better aggregated or crystalline



Scheme 1 Synthetic route to the monomer **M-I**. (i) NaI, acetone, 12 h.



Scheme 2 Synthetic route to the monomer **M-OAc**. (ii) CH_3COOK , DMF, 80 °C, 6 h.

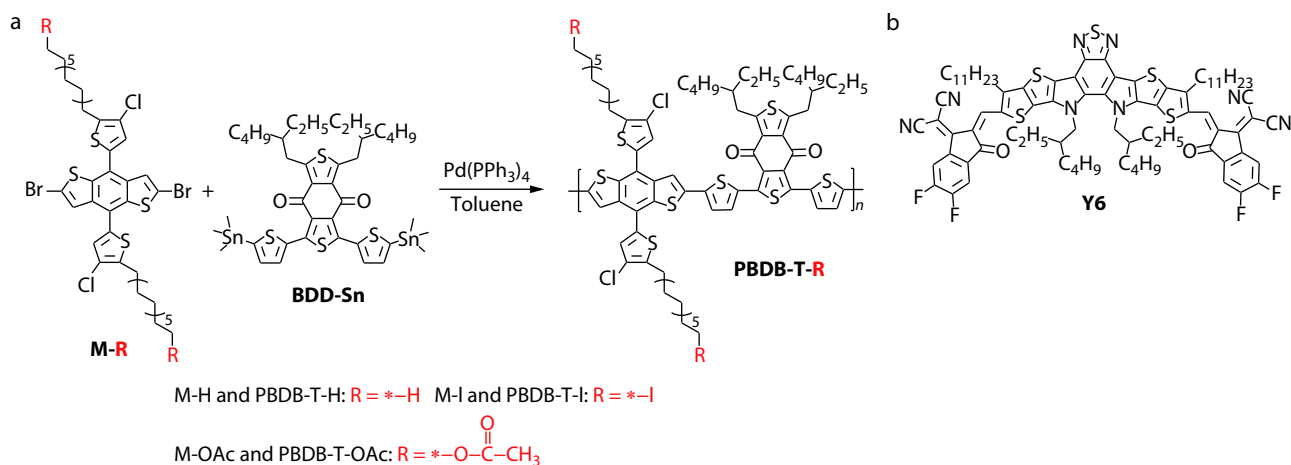


Fig. 1 (a) The chemical structures of the conjugated polymers in this work and their synthetic routes. (b) The chemical structure of the electron acceptor **Y6**.

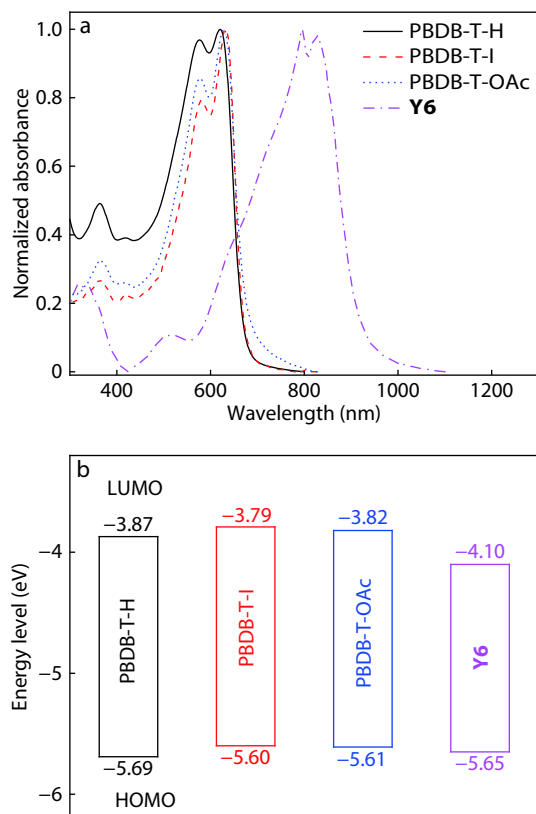


Fig. 2 (a) Optical absorption spectra of thin films based on the conjugated polymers and the acceptor **Y6**. (b) HOMO/LUMO energy levels determined from cyclic voltammetry measurements (versus Fc/Fc^+).

tendency than the polymer PBDB-T-H.

The highest occupied molecular orbital (HOMO) level and lowest unoccupied molecular orbital (LUMO) level of donor polymers were measured by cyclic voltammogram (CV) measurements (Fig. S3 in ESI), which are then summarized in Fig. 2(b) and Table S1 (in ESI). The PBDB-T-H has the HOMO level of -5.69 eV and the LUMO level of -3.87 eV, while the PBDB-T-I and PBDB-T-OAc show up-shift HOMO energy levels (-5.60 and -5.61 eV) and LUMO energy levels (-3.79 and -3.82 eV). The up-shift energy levels may be caused by the electron-rich end groups (I and OAc), or the different aggregated behavior of these polymers.

Photovoltaic Performance

We then fabricated NFOSCs based on PBDB-T-R:Y6 blends with an inverted configuration (ITO/ZnO/PBDB-T-R:Y6/MoO₃/Ag). Since both the donor polymers and Y6 can be dissolved in CF, we used CF as the solvent for active layer deposition. To obtain the best device performance, the fabrication conditions, including additive (DIO) and annealing temperature, were carefully optimized, as summarized in Tables S2–S4 (in ESI). The optimized J - V characteristics and the parameters are summarized in Fig. 3(a) and Table 1.

When adding DIO as additive, PBDB-T-H:Y6 based solar cells obtained a high PCE of 10.18% compared to the cell fabricated from CF without additive (9.05%). PBDB-T-I:Y6 and PBDB-T-OAc:Y6 based solar cells showed better PCEs (12.63%

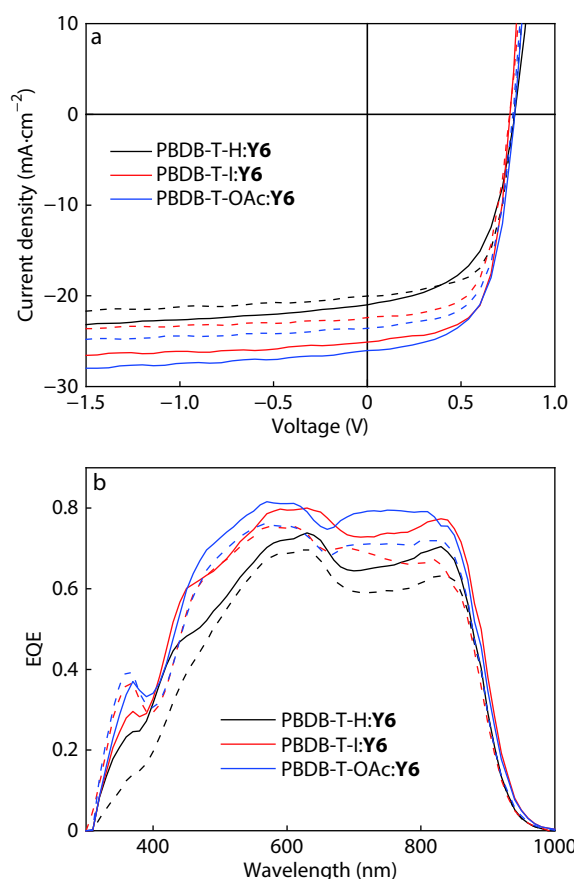


Fig. 3 Characteristics of the optimized solar cells based on PBDB-T-R:Y6 blends: (a) J - V characteristics under white light illumination; (b) EQE of the optimized OSCs. Solid lines for active layers fabricated from CF and dashed lines for active layers fabricated from CF/DIO (0.5%).

and 12.59%) without additive, while the PCEs were dropped to 10.86% and 11.60% when using DIO as additive. The higher PCEs are mainly attributed to the higher short-circuit current density (J_{sc}), which can be confirmed by the external quantum efficiency (EQE) measurement (Fig. 3b). PBDB-T-I and PBDB-T-OAc based cells exhibited higher EQE spectra when the photoactive layers were fabricated from CF without additive. We also used the monomer **M-OAc** (Fig. 1) to make a new polymer PBDB-T-OAc with OAc as end group, as shown in Fig. S4 (in ESI). OSCs based on PBDB-T-OAc:Y6 blends fabricated from CF exhibited a higher PCE of 6.18% than that from CF/DIO (5.01%) (Table S5 in ESI). This result is consistent with our observation that DIO has the negative effect on the photovoltaic performance in the OAc-contained polymers. We further fabricated ternary organic solar cells by using two donors PBDB-T-H and PBDB-T-I (or OAc) (Table S6 in ESI). Interestingly, ternary blends based on PBDB-T-I exhibited a high PCE when being fabricated from CF, while PBDB-T-OAc contained ternary blends had a high PCE from CF/DIO. Since in ternary solar cells the properties of donor polymers, such as energy levels and crystallinity, have complicated effect on the photovoltaic performance, currently we are unable to provide an explanation about the contrary results shown in Table S6

Table 1 Characteristics of optimized solar cells based on PBDB-T-R:Y6 blends.

Donor	Solvent	<i>d</i> (nm)	<i>J</i> _{sc} (mA·cm ⁻²)	<i>V</i> _{oc} (V)	FF	PCE (%)
PBDB-T-H ^a	CF	80	20.99 (20.71±0.70)	0.79 (0.80±0.008)	0.55 (0.53±0.028)	9.05 (8.75±0.22)
	CF/DIO (0.5%)	80	20.13 (19.93±0.40)	0.78 (0.77±0.008)	0.65 (0.63±0.018)	10.18 (9.62±0.24)
PBDB-T-I ^b	CF	65	25.11 (24.42±0.62)	0.76 (0.76±0.013)	0.66 (0.66±0.009)	12.63 (12.23±0.17)
	CF/DIO (0.5%)	75	22.39 (22.67±0.65)	0.76 (0.76±0.005)	0.64 (0.63±0.016)	10.86 (10.64±0.18)
PBDB-T-OAc ^b	CF	80	26.04 (25.57±0.68)	0.79 (0.79±0.003)	0.62 (0.61±0.015)	12.59 (12.35±0.12)
	CF/DIO (0.5%)	90	23.59 (23.78±0.23)	0.78 (0.78±0.007)	0.63 (0.61±0.010)	11.60 (11.29±0.15)

Optimized ratio of D:A is 1:1.2. ^a Thermal treatment at 110 °C. ^b Thermal treatment at 150 °C.

(in ESI).

SCLC Test and Morphology Characterization

We then use space-charge limited current (SCLC), atomic force microscopy (AFM) and grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements to study the morphology and charge transport properties in these blends. Firstly, from SCLC measurement (Fig. S5 in ESI and Table 2), PBDB-T-I:Y6 and PBDB-T-OAc:Y6 exhibited similar hole mobilities but slightly low electron mobilities as compared to PBDB-T-H:Y6 blends. In addition, the ratio of electron and hole mobilities (μ_e/μ_h) was slightly low in PBDB-T-H:Y6 blends from CF/DIO, PBDB-T-I (or OAc):Y6 blends from CF, indicating that in these devices they showed balanced charge transport properties. This is consistent with the better photovoltaic performance as shown in Table 1.

We then used atomic force microscopy to study the mor-

phology of the photoactive layers, as shown in Fig. 4. PBDB-T-H:Y6 blend films fabricated from CF/DIO exhibited relatively low roughness of 3.45 nm with small domain sizes. In addition, PBDB-T-R:Y6 (R = I and OAc) blend films fabricated from CF showed low roughness of 0.94 and 1.08 nm, while the roughness was significantly enhanced to 4.54 and 1.89 nm by using CF/DIO as solvent. These results are consistent with the high PCEs in these cells, and also indicate that I and OAc units can be used to tune the morphology.

GIWAXS was further used to study the morphology of blends, as shown in Fig. 5 and the crystalline parameters are summarized at Table 3. All the blends fabricated from CF with or without DIO exhibited (100) diffraction peaks at the out-of-plane direction and (010) diffraction peaks at the in-plane direction, indicating the face-on orientation of conjugated back-

Table 2 Hole and electron mobilities of OSCs based on PBDB-T-R:Y6 blends from SCLC measurements.

Blend	Solvent	μ_h (cm ² ·V ⁻¹ ·s ⁻¹)	μ_e (cm ² ·V ⁻¹ ·s ⁻¹)	μ_e/μ_h
PBDB-T-H:Y6	CF	1.04×10^{-4}	1.49×10^{-3}	14.3
	CF/DIO (0.5%)	9.64×10^{-5}	1.20×10^{-4}	12.5
PBDB-T-I:Y6	CF	1.12×10^{-4}	4.95×10^{-4}	4.4
	CF/DIO (0.5%)	8.20×10^{-5}	4.24×10^{-4}	5.2
PBDB-T-OAc:Y6	CF	1.22×10^{-4}	5.50×10^{-4}	4.5
	CF/DIO (0.5%)	7.50×10^{-5}	4.46×10^{-4}	6.0

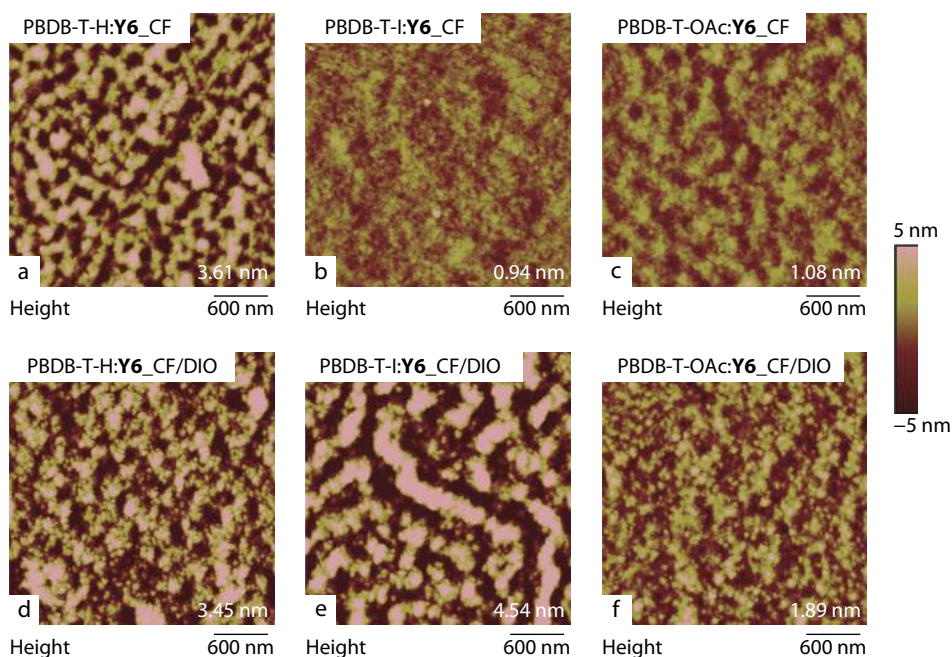


Fig. 4 AFM height images (3 μm × 3 μm) of the photoactive layers. The root mean square roughness (RMS) is also included.

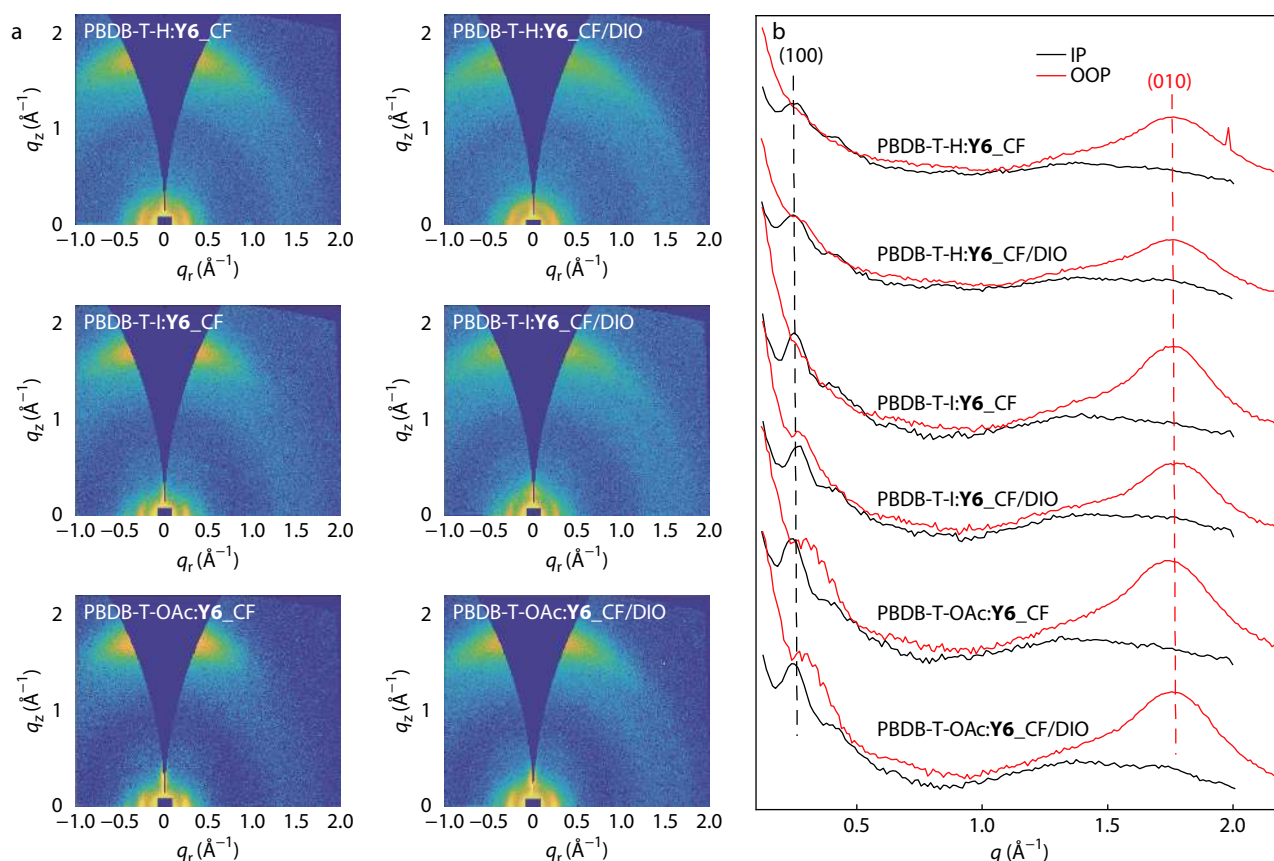


Fig. 5 Characteristics of the blended thin films spin-casted on Si substrates: (a) GIWAXS patterns; (b) the out-of-plane (OOP) and in-plane (IP) cuts of the corresponding GIWAXS patterns.

Table 3 Crystallographic parameters of thin films based on the polymer blended with Y6.

Donor	Solvent	IP (100)			OOP (010)		
		q ($\text{\AA}^{-1}$)	d ($\text{\AA}$)	CL ^a (nm)	q ($\text{\AA}^{-1}$)	d ($\text{\AA}$)	CL ^a (nm)
PBDB-T-H	CF	0.25	24.8	4.6	1.76	3.6	1.8
	CF/DIO	0.25	24.8	5.2	1.76	3.6	1.9
PBDB-T-I	CF	0.25	24.9	7.4	1.76	3.6	2.2
	CF/DIO	0.28	22.4	6.1	1.78	3.5	2.0
PBDB-T-OAc	CF	0.25	25.0	6.9	1.75	3.6	2.1
	CF/DIO	0.24	25.9	5.8	1.75	3.6	2.0

^a CL = $1.8\pi/\text{FWHM}$, where FWHM is the full-width at half-maximum for peaks in the intensity profile.

bones. Notably, PBDB-T-H:Y6 fabricated from CF/DIO, PBDB-T-I (or OAc):Y6 fabricated from CF exhibited high coherence lengths (CLs) (Table 3). Low roughness, small domain size and high CLs in PBDB-T-I (or OAc):Y6 films prepared from CF solution compared to the films from CF/DIO solution indicate that I and OAc units are able to reduce the aggregation and meanwhile enhance the crystallinity of the polymers, which explains the balanced charge transport and hence better PCEs in NFOSCs without adding DIO.

CONCLUSIONS

In conclusion, two conjugated polymers containing I and OAc as the end groups of side chains were developed for NFOSCs, in which the PCEs up to 12.63% were obtained. Importantly, we observed that the new polymers can act as self-additive for

fabricating photoactive layers, resulting in additive-free NFOSCs. Our work reveals that the end group engineering of side chains enables conjugated polymers to have special properties, which is helpful for high performance NFOSCs.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-020-2490-y>.

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