

Electronic Supplementary Information for

Challenging PM6-alike donor polymers for pairing a Y-type state-of-art acceptor in binary blends for bulk heterojunction solar cells

Wei Xu,^a Wei He,^b Guojuan Li,^c Jingnan Wu,^a Cheng Yang,^d Zhong Cao,^e Pei Cheng,^b

Hongxiang Li,^{b,*} Zhengkun Du,^{f,*} and Donghong Yu^{a,g,*}

^a Department of Chemistry and Bioscience, Aalborg University, Fredrik Bajers Vej 7H, Aalborg East, DK-9220, Demark

^b College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, 610065 China

^c National Anti-Drug Laboratory Sichuan Regional Center, Chengdu, 610206 China

^d Key Laboratory of Green Chemistry & Technology of Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, Sichuan, China

^e Hunan Provincial Key Laboratory of Materials Protection for Electric Power and Transportation, and Hunan Provincial Key Laboratory of Cytochemistry, School of Chemistry and Biological Engineering, Changsha University of Science and Technology, Changsha 410114, China

^f College of Electrical Engineering and Automation, Shandong University of Science and Technology, Qingdao 266590, China

^g Sino-Danish Center for Education and Research, DK-8000, Aarhus, Denmark

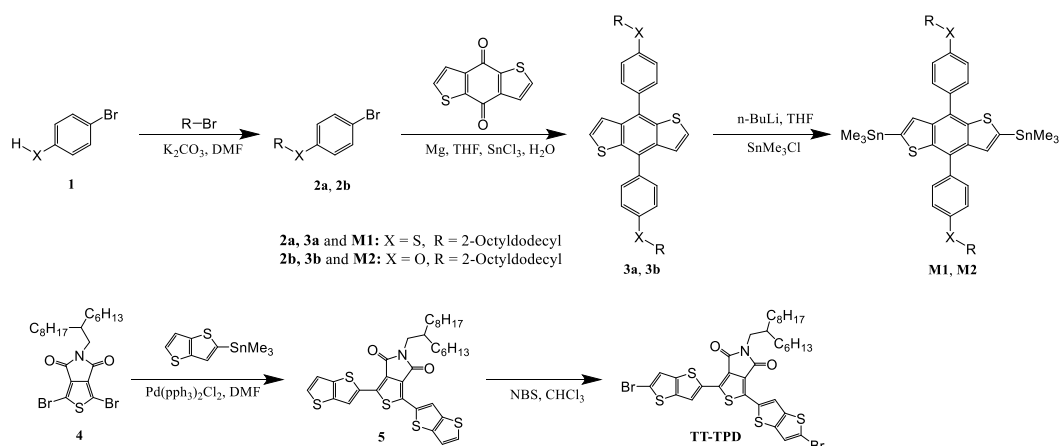
* Corresponding authors, email: lihongxiang@scu.edu.cn, zhengkundu@163.com, yu@bio.aau.dk

1. General information

All solvents and reagents were of reagent quality, purchased commercially, and used without further purification. NMR spectra were recorded at room temperature on Bruker Avance IIITM HD-600 (operating at 600 MHz for ¹H NMR and ¹³C NMR). Elemental analysis was measured by Euro Vector EA3000. The UV-visible spectra were obtained on a JASCO V-650 UV-vis spectrometer. And thermogravimetric analysis (TGA) are measured by STA 449 F3 Jupiter[®]. Atomic Force Microscope (AFM) were acquired by Smart SPM. Photovoltaic performance was characterized under illumination with an AM 1.5G (100 mW cm⁻²), and the *J-V* curves were recorded using a Keithley 2400 source meter. The EQE of solar cells were analyzed using a certified Newport incident photon conversion efficiency measurement system. 2D GIWAXS patterns of films prepared at different temperatures were obtained at 1W1A Diffuse X-ray Scattering Station, Beijing Synchrotron Radiation Facility (BSRF-1W1A). The monochromatic wavelength of the light source was 1.54 Å. The data was recorded by Pilatus 100 K from DECTRIS, Switzerland. The grazing incidence angles were 0.2°.

The CV (cyclic voltammetry) of the two polymers were recorded on a CH-Instruments Model 650A Electrochemical Workstation. Three-electrode configuration were using in measurement, Pt wires as both working electrode and counter electrode, and a freshly activated Ag wire as Ag/Ag⁺ pseudoreference electrode. To obtain the oxidation potentials, the reference electrode was calibrated by using the ferrocene/ferrocenium (Fc/Fc⁺), which has an absolutely potential of 4.8 eV versus the vacuum level. And the redox potential of Fc/Fc⁺ was obtained for calibration of 0.35 eV vs Ag/Ag⁺ electrode under the same conditions. A tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) solution (0.1 M solution in anhydrous acetonitrile) was used as a supporting electrolyte, and N₂ gas was bubbled prior to each measurement. Two polymers were deposit onto the working electrode by drop-casting from solutions of 10 mg/mL in CHCl₃. And ferrocene was used as an external standard vs Ag/Ag⁺ under these conditions. The HOMO and LUMO levels were calculated according to the formula $E_{HOMO} = - (E_{OX} + 4.8 - |Fc/Fc^+|)$ eV and $E_{LUMO} = E_{HOMO} - E_g^{opt}$, where the E_{OX} , E_g^{opt} and $|Fc/Fc^+|$ was determined from the oxidation onsets in the CV curves, the 1240/(onset absorption band edge of the polymer films) and the half-wave potential of ferrocene in CV curves, respectively.

2. Synthesis of Materials



Scheme S1. The synthetic pathway of **M1**, **M2** and **tt-TPD**.

1-Bromo-4-(2-octyldodecyl)X-benzene (X: thiol for 2a, and X: oxy for 2b)

Under nitrogen atmosphere, 4-bromophenol or 4-bromo-1-thiol-benzene (reagent **1**) (25 mmol), K₂CO₃ (4.1 g, 30 mmol) and were dissolved into 120 mL DMF. Then 1-bromo-2-ethyl-hexane (4.8 g, 25 mmol) was added dropwise into the mixture. And the reaction solution was kept stirring overnight at 150 °C in darkness. After cooling to room temperature, the mixture was quenched with water and extracted three times with ethyl acetate. Then the crude product was purified on a silica gel column eluting with petroleum ether. And purified compound **2** (yellow oil) was obtained for **2a** with a yield of 71% and **2b** with 68% yielded. ¹H NMR (600 MHz, CDCl₃, ppm) δ (**2a**) 7.46 (d, 2H), 6.96 (d, 2H), 3.28 (d, 2H), 1.72 (m, 1H), 1.38 (m, 32H), 0.91 (m, 6H); δ (**2b**) 7.36 (d, 2H), 7.16 (d, 2H), 3.05 (d, 2H), 1.60 (m, 1H), 1.35 (m, 32H), 0.89 (m, 6H).

4,8-Bis((2-octyldodecyl)X-1-phenyl)-benzo[1,2-b:4,5-b']-dithiophene (X: thiol for 3a, and X: oxy for 3b)

Magnesium spalls (0.73 g, 30.5 mmol) and few I₂ were put into a dried three necked round-bottom flask under nitrogen. The compounds **2a** or **2b** (24.2 mmol) in THF (40 mL) was added dropwise by using syringe. Then the mixture was refluxed until all magnesium consumed. Benzo[1,2-b:4,5-b']dithiophene- 4,8-dione (1.34 g, 6.1 mmol) in THF (40 mL) was added slowly into the flask and kept reflux for 12 h. Then, SnCl₂·2H₂O (10.95 g, 48.5 mmol) and 10% aqueous HCl was added dropwise into the mixture and stirred for another 2 h at 80°C. After cooling to room temperature, the mixture was quenched with water, and extracted with dichloromethane three times, then dried, concentrated, and purified by column chromatography, the final products were obtained for **3a**(39%) and **3b** (45%). ¹H NMR (600 MHz, CDCl₃, ppm) δ (**3a**) 7.67 (d,

4H), 7.42 (d, 2H), 7.35 (d, 2H), 7.09 (d, 4H), 3.08 (d, 4H), 1.73 (m, 2H), 1.54 (m, 64H), 0.91 (m, 12H); δ (**3b**) 7.65 (d, 4H), 7.50 (d, 2H), 7.40 (d, 2H), 7.33 (d, 4H), 3.04 (d, 4H), 1.74 (m, 2H), 1.33 (m, 64H), 0.89 (m, 12H).

2,6-Bis(trimethyltin)-4,8-bis((2-octyldodecyl)X-1-phenyl)-benzo[1,2-b:4,5-b']-dithiophene (M1: X is thiol and M2: X is oxy)

Dry THF (50 mL) solution of compound **3a** or **3b** (0.50 mmol) was cooled to -78°C in a round-bottom flask under argon, and *n*-butyllithium in *n*-hexane (8.65 mL, 13.84 mmol) was added dropwise. After warming up to room temperature, the mixture was stirred for 3 h. Then trimethyltin chloride solution in THF (16.4 mL) was added at 0°C and the reaction mixture was stirred at ambient temperature overnight. After quenching with water, extracting with dichloromethane (three times), drying over anhydrous sodium sulfate, and concentrating with a rotary evaporator, the residue was recrystallized from isopropanol to yield the target monomer as a light white (**M1**, 54%) and a pale-yellow (**M2**, 50%) solid.

M1: $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.66 (d, 4H), 7.52 (d, 4H), 7.38 (s, 2H), 3.07 (d, 4H), 1.82-1.74 (m, 2H), 1.55-1.42 (m, 8H), 1.40-1.22 (m, 56H), 0.90 (dt, 12H), 0.39 (t, 18H). $^{13}\text{C NMR}$ (600 MHz, CDCl_3 , ppm) δ 138.22, 138.14, 136.22, 136.13, 129.90, 129.75, 128.44, 127.30, 122.88, 38.11, 37.62, 33.31, 31.94, 31.93, 29.97, 29.96, 29.71, 29.67, 29.63, 29.38, 29.37, 26.60, 22.70, 14.13.

M2: $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.67 (d, 4H), 7.41 (t, 2H), 7.13 (d, 4H), 3.98 (d, 4H), 1.91-1.84 (m, 2H), 1.57-1.50 (m, 4H), 1.47-1.26 (m, 60H), 0.92 (dt, 12H), 0.38 (t, 18H). $^{13}\text{C NMR}$ (600 MHz, CDCl_3 , ppm) δ 158.52, 138.22, 136.22, 136.13, 132.14, 128.12, 127.30, 122.88, 116.38, 71.20, 37.90, 31.93, 31.91, 31.32, 30.01, 30.00, 29.67, 29.65, 29.62, 29.59, 29.36, 29.33, 26.83, 22.70, 14.13.

1,3-di(thieno[3,2-b]thiophen-2-yl)-5-(2-hexyldecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (5)

Compound **4** (1.2 g, 2.84 mmol) and 2-trimethyltin-thieno[3,2-b]thiophen (2.4g, 6.3 mmol) were dissolved in 12 mL of dry toluene under nitrogen atmosphere. Then after adding $\text{Pd}_2(\text{dba})_3$ (0.094 g, 0.01 mmol) and $\text{P}(\text{o-tol})_3$ (0.061 g, 0.02 mmol), the mixture was refluxed for 24h at 100°C. When cooling to room temperature, the product was extracted with 100 mL DCM for 3 times. After removing the solvent, the target product was obtained by purifying with silica gel column chromatography (1.56 g, 83% yield). $^1\text{H NMR}$ (600 MHz, CDCl_3 , ppm) δ 7.58 (d, 2H), 7.44 (d, 2H), 7.29 (s, 2H), 3.35 (d, 2H), 1.81 (m, 1H), 1.31 (m, 24H), 0.92 (m, 6H).

1,3-bis(5-bromo-thenio[3,2-b]thiophen-2-yl)-5-(2-hexyldecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (tt-TPD)

N-bromosuccinimide was added into the 25 mL DMF solution of compound **5** (1.56 g, 2.38mmol) under N₂ atmosphere and darkness. Then the mixture was stirred at room temperature for 4 h and filtered to obtain the precipitates. After thoroughly washing with methanol for 2 times and cold diethyl ether for once, the target product was purified by column chromatography to give 1.58 g (82% yield). ¹H NMR (600 MHz, CDCl₃, ppm) δ 7.17 (s, 2H), 6.92 (s, 2H), 3.34 (d, 2H), 1.80 (m, 1H), 1.30 (m, 24H), 0.91 (m, 6H).

Synthesis of PBDT-PS-ttTPD (P10) and PBDT-PO-ttTPD (P11)

Under Ar₂ atmosphere, **M1** or **M2** (0.15 mmol), Pd₂(dba)₃ (2 mg, 0.002 mmol), P(o-tol)₃ (4 mg, 0.013 mmol) and **tt-TPD** (0.15 mmol) were introduced into a 20 mL round-bottom flask. Then, 6 mL dry toluene was added, and the solution was heated to 110°C for 24 h. After cooling to room temperature, the mixture was poured into methanol, then filtered. The precipitate was extracted by using hexane, acetone, and chloroform, respectively with Soxhlet extraction. Then, the chloroform fraction was collected and dried overnight under vacuum. Finally, the target copolymers were obtained.

P10 (115 mg, yield 59.8 %). Elemental analysis calculated (%) for [C₇₂H₈₁NO₂S₉]: C, 71.44%; H, 8.26%; N, 0.85%; O, 1.94%; S, 17.51%; found: C 71.25%; H 8.13 %; N 0.83%; S 17.30 %.

P11 (106 mg, yield 56.4 %). Elemental analysis calculated (%) for [C₇₂H₈₁NO₄S₇]: C, 72.86%; H, 8.42%; N, 0.87%; O, 3.96%; S, 13.89%; found: C 72.66%; H 8.32%; N 0.85%; S 13.69 %.

3. Dihedral angle of the two polymers

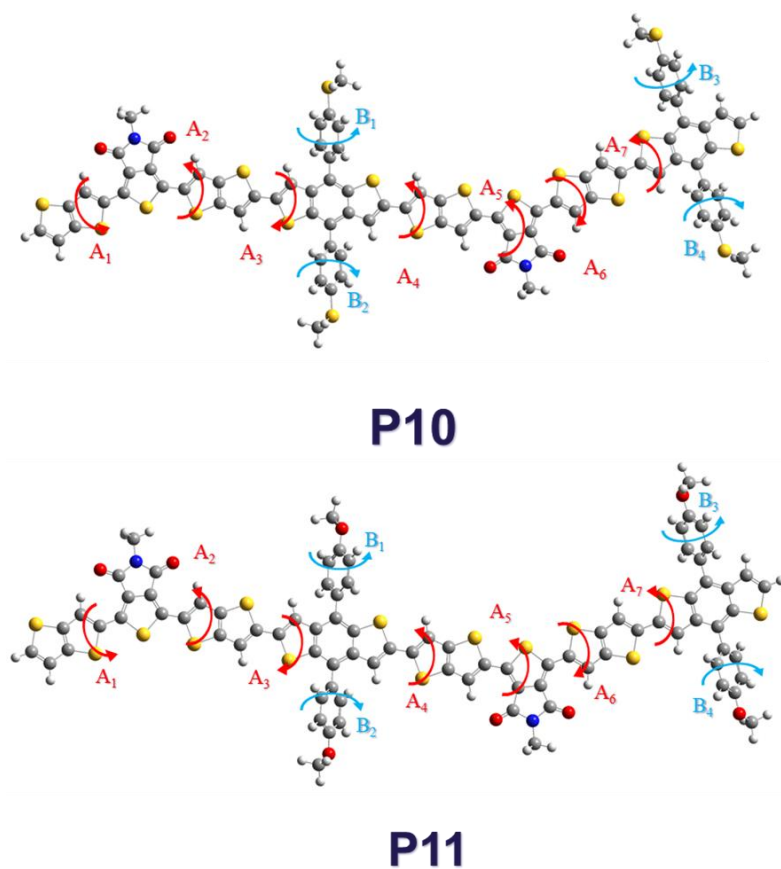


Figure S1. The optimized molecular structure of dimers, representing segments of two polymers.

Table S1. The dihedral angles of the optimal-structured molecules calculated by the density functional theory (DFT).

Polymers	Dihedral angles (°)										
	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇	B ₁	B ₂	B ₃	B ₄
P10	0.01	0.01	0.28	6.23	0.25	0.21	6.59	58.9	58.9	58.9	58.3
P11	0.01	0.25	0.29	5.34	0.21	0.11	5.84	59.0	59.0	59.3	58.6

4. Fabrication and Optimization of OPV devices

The SM-NFA OPV devices were fabricated on top of a pre-patterned ITO substrate with the conventional structure of ITO/PEDOT:PSS/Active layers/PFN-Br/Ag. After cleaning the ITO with aqueous detergent, deionized water, acetone, and 2-propanol,

UV-ozone treatment was applied for 15 min. Filtered PEDOT:PSS (CLEVIOS™ P VP AI 4083) was spin-coated on the ITO substrate to form a 30 nm-thick layer. Then the coated substrates were annealed on the thermal plate at 150 °C for 20 min. After annealing, the chlorobenzene (CB) solution of the blending active substances was spin-cast on top of the PEDOT:PSS layer to produce the active layer with a thickness of 100 nm under 2000 rpm in glovebox under N₂ atmosphere, and the coated substrates with active layer were annealed for 10 min at 100 °C. Then PNF-Br was spin-coated under 3000 rpm to form a 10 nm-thickness layer. Finally, the device fabrication was completed by thermal evaporation of 100 nm Ag as the anode in high vacuum (< 10⁻⁶ mbar). All the experimental details were summarized in the below tables. And for exhibiting better reproducibility of these devices, all data in the tables was average value calculated from 6 parallel devices.

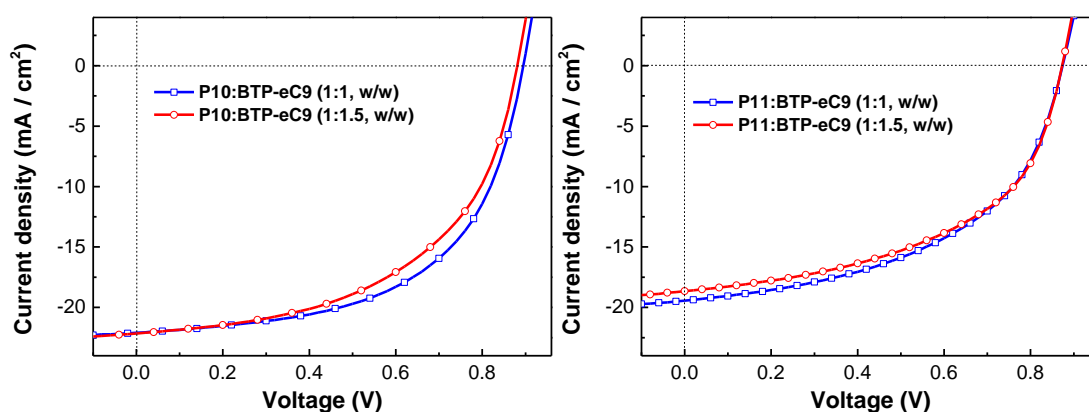


Figure S2. The J - V curves of polymers/BTP-eC9-based PSCs with different D-A weight ratios (1:1 and 1:1.5) under an illumination of AM 1.5 G, 100 mW cm⁻²

Table S2. Photovoltaic properties of the OPVs based on Polymers/BTP-eC9 with different weight ratio of donor and acceptor under an illumination of AM 1.5 G, 100 mW cm⁻²

Polymer/ BTP-eC9	D:A (w/w)	FF (%) ^a	V_{oc} (V) ^a	J_{sc} (mA cm ⁻²) ^a	PCE (%) ^a
P10	1:1	55.94	0.89	22.47	11.19
	1:1.5	52.40	0.88	22.46	10.34
P11	1:1	49.51	0.87	19.51	8.40
	1:1.5	50.66	0.87	18.33	8.05

^a The experimental data was average obtained from 6 parallel devices.

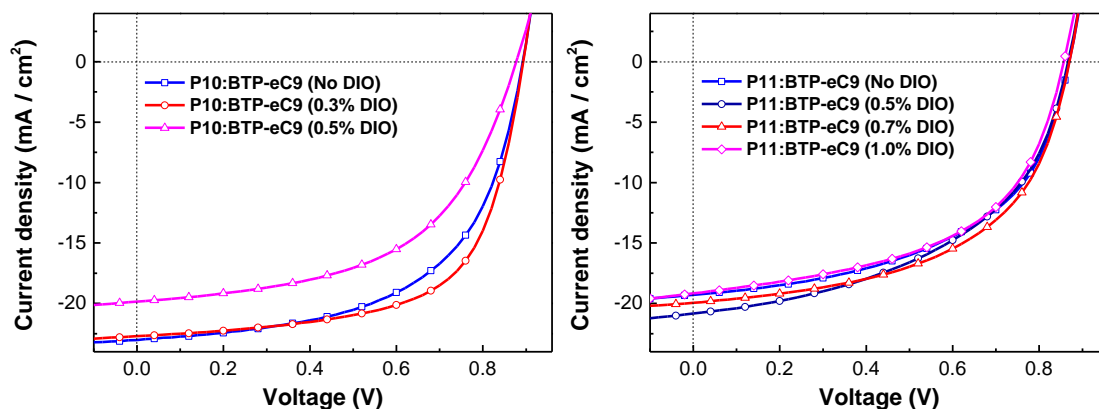


Figure S3. The J - V curves of polymers/BTP-eC9-based PSCs with and without additive volume ratios under an illumination of AM 1.5 G, 100 mW cm^{-2}

Table S3. Photovoltaic properties of the OPVs based on Polymers/BTP-eC9 (1:1, w/w) with different content of DIO under an illumination of AM 1.5 G, 100 mW cm^{-2}

Polymer/ BTP-eC9	DIO (vol%)	FF (%) ^a	V_{OC} (V) ^a	J_{SC} (mA cm^{-2}) ^a	PCE (%) ^a
P10	0	55.62	0.89	22.54	11.16
	0.3	61.58	0.89	22.94	12.53
	0.5	52.31	0.88	20.04	9.20
P11	0	50.37	0.87	19.33	8.49
	0.5	49.19	0.86	20.84	8.88
	0.7	52.83	0.87	20.01	9.20
	1	54.72	0.86	18.53	8.74

^a The experimental data was average obtained from 6 parallel devices.

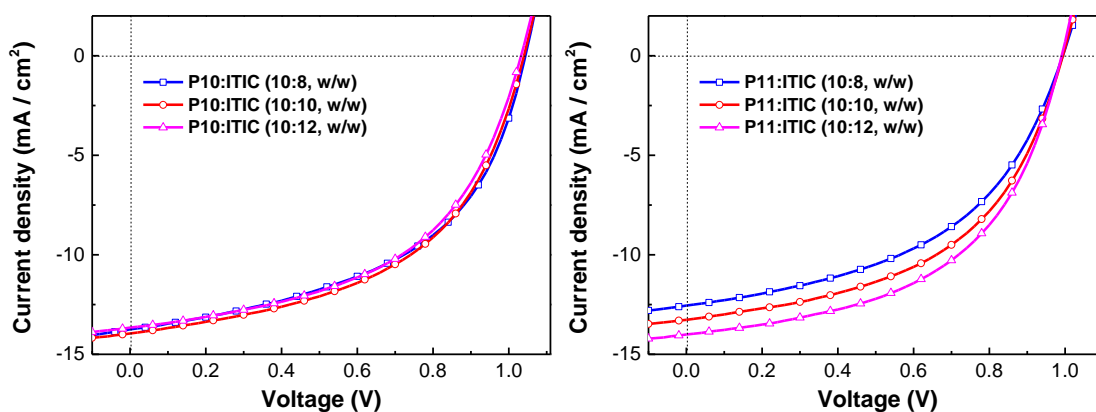


Figure S4. The J - V curves of polymers/ITIC-based PSCs with different D-A weight ratio under an illumination of AM 1.5 G, 100 mW cm^{-2}

Table S4. Photovoltaic properties of the OPVs based on Polymers (10 mg/mL)/ITIC under an illumination of AM 1.5 G, 100 mW cm⁻²

Polymer/ ITIC	D:A (w/w)	FF (%) ^a	V _{OC} (V) ^a	J _{SC} (mA cm ⁻²) ^a	PCE (%) ^a
P10	1:0.8	50.50	1.04	13.56	7.15
	1:1	50.81	1.04	13.60	7.17
	1:1.2	50.29	1.03	13.33	6.93
P11	1: 0.8	47.53	1.00	12.37	5.85
	1:1	50.16	0.99	13.25	6.59
	1:1.2	51.16	0.99	13.69	6.95

^a The experimental data was average obtained from 6 parallel devices.

5. Properties of charge transfer and recombination

The mobility properties of the active layer were determined by applying the space charge limited current (SCLC) method to the J - V measurements of the devices. The hole-only and electron-only polymers devices were designed as the vertical diodes with the structure of ITO/PEDOT:PSS/Active layers/Au and Ag/ZnO/Active layers/Ag, respectively, where the active layer were made of P10:BTP-eC9 with 1:1 w/w (CB 0.3% DIO, 2000 rpm) and P11:BTP-eC9 with 1:1 w/w (CB 0.7% DIO, 2000 rpm), respectively. And the mobilities were calculated from the SCLC using the following equation¹:

$$J_{SCLC} = (9/8)\epsilon_r\epsilon_0\mu(V^2/L^3)$$

where J is the current density, ϵ_r is the dielectric constant of the polymers, ϵ_0 is the permittivity of the vacuum, μ is the hole mobility, L is the thickness of the blend films, $V = V_{appl} - V_{bi}$, where V_{appl} is the applied potential, and V_{bi} is the built-in voltage which results from the difference in the work function of the anode and cathode.

Charge dissociation probability was characterized by the function of photogenerated current density (J_{ph}) versus effective applied voltage (V_{eff}). The J_{ph} is defined as the difference between J_L and J_D , where J_L and J_D are the current density of devices under light (100 mW cm⁻²) and dark, respectively. $V_{eff} = V_0 - V$, where V_0 is the voltage when $J_{ph} = 0$ and V is the applied voltage during the measurement. When the reverse voltage is greater than 2 V, the recombination is suppressed by a high internal electric field. Thus, J_{ph} will reach the saturated current density (J_{sat}). Consequently, $P_{diss} = J_{ph}/J_{sat}$ could be used to describe the charge dissociation probability.^{2,3} A higher P_{diss} is indicated the more effective charge dissociation. Besides, the relationship of J_{SC} and the light intensity (I) is $J_{SC} \propto I^\alpha$, where α is the degree of biomolecular recombination.

When $\alpha = 1$, dissociated free charges do not recombine during the movement process, and are all collected by the electrode, implying the recombination can be ignored. If α is less than 1, the bimolecular recombination will be present in the devices, and the smaller the value of α indicates the stronger bimolecular recombination. Meanwhile, $V_{OC} \propto n(kT/q) \cdot \ln(I)$, where K represents the Boltzmann constant, T is the Kelvin temperature, and q is the elementary charge. If the slope is close to $2 kT/q$, the trap-assisted recombination will occur inside the devices.^{4,5}

6. Other Supplemental Figures

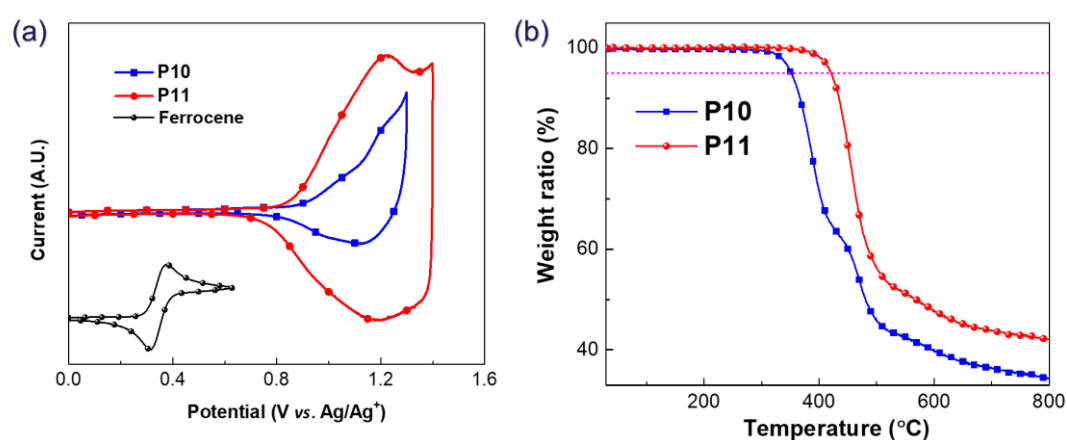


Figure S5. (a) Cyclic voltams of P10, P11, and Fc/Fc⁺, respectively; (b) TGA curves of two copolymers.

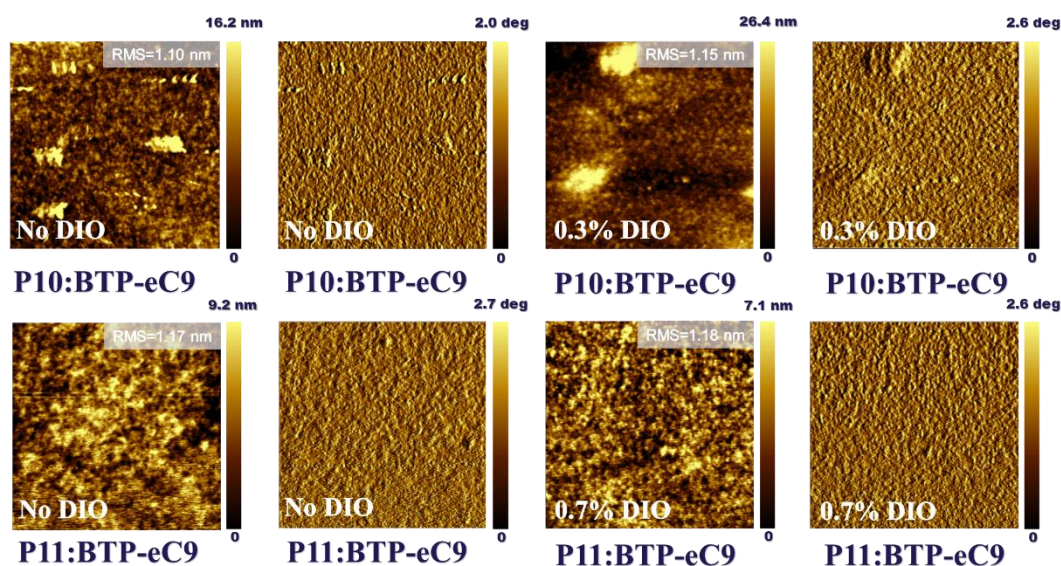


Figure S6. Atomic force microscopy height (a, c, e, and g) and phase (b, d, f, and h) diagrams of P10:BTP-eC9 (with/without DIO) and P11:BTP-eC9 (with/without DIO) thin films, $4 \mu\text{m} \times 4 \mu\text{m}$.

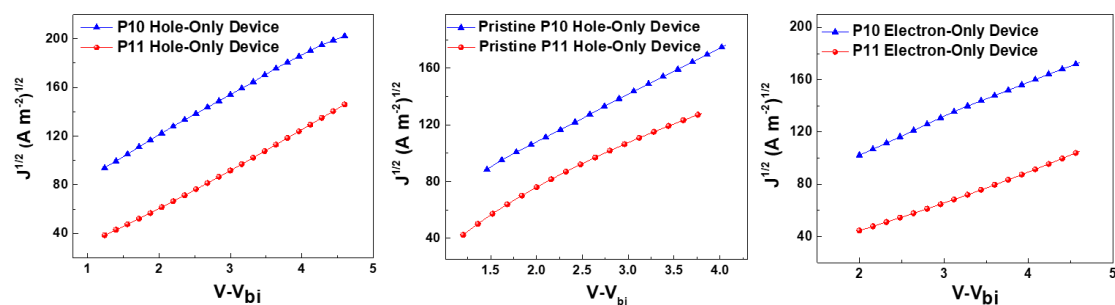


Figure S7. $J^{1/2}$ - V plots for the measurement of carrier mobilities in corresponding specific devices by the SCLC method.

Reference

- [1] C. Melzer, E. J. Koop, V. D. Mihailetschi, P. W. M. Blom, Hole Transport in Poly(phenylene vinylene)/Methanofullerene Bulk-Heterojunction Solar Cells, *Advanced Functional Materials*, 14 (2004), 865-870
- [2] P. W. M. Blom, V. D. Mihailetschi, L. J. A. Koster, D. E. Markov, Device Physics of Polymer:Fullerene Bulk Heterojunction Solar Cells, *Advanced Materials*, 19 (2007), 1551-1566
- [3] L. Huo, T. Liu, X. Sun, Y. Cai, A. J. Heeger, Y. Sun, Single-Junction Organic Solar Cells Based on a Novel Wide-Bandgap Polymer with Efficiency of 9.7%, *Advanced Materials*, 27 (2015), 2938-2944
- [4] L. J. A. Koster, V. D. Mihailetschi, R. Ramaker, P. W. M. Blom, Light intensity dependence of open-circuit voltage of polymer:fullerene solar cells, *Applied Physics Letters*, 86 (2005), 123509
- [5] A. K. K. Kyaw, D. H. Wang, D. Wynands, J. Zhang, T.-Q. Nguyen, G. C. Bazan, A. J. Heeger, Improved Light Harvesting and Improved Efficiency by Insertion of an Optical Spacer (ZnO) in Solution-Processed Small-Molecule Solar Cells, *Nano Letters*, 13 (2013), 3796-3801