Supporting Information

Wide Bandgap Conjugated Polymer Donor Based on Alkoxyl-fluorophenyl Substituted Benzodithiophene for High Performance Non-fullerene Polymer Solar cells

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Experimental section

Materials.

All chemicals and solvents were reagent grades and purchased from Alfa Aesar, J&K, Aldrich and TCI Chemical, respectively. IT-4F was purchased from Solarmer Materials Inc. Monomer M1, M2 and M3 were synthesized according to previously reported literature.[1,2] The synthetic route of polymers **POPB** and **PFOPB** is shown in **Scheme S1.** The detailed synthetic processes for **POPB** and **PFOPB** are as follows.

Synthesis of of two polymers.

In a 50 mL double-neck round bottom flask, compound M1 (or M2) (0.3 mmol) and compound M3 (0.3 mmol) were dissolved in 10 mL toluene and 1mL DMF. After being purged with argon for 20 min, 18 mg of $Pd(PPh_3)_4$ was added into the flask as the catalyst, and then the reaction mixture was purged with argon for another 30 min. The reaction mixture was stirred and heated to reflux for

2 h under argon atmosphere. When the reaction mixture was cooled down to room temperature, the polymers were precipitated by addition of 100 mL methanol, collected by filtration and then subjected to Soxhlet extraction with methanol, hexane, and chloroform in the end. The polymers were recovered as solid from the chloroform fraction by precipitation from methanol. The solids were dried under vacuum. The yield and test results of two polymers are as follows.

POPB. The yield was 74%. Anal. Calcd for $C_{80}H_{100}O_4S_6$ (%): C, 72.90; H, 7.65; Found (%): C, 72.69; H, 7.35.

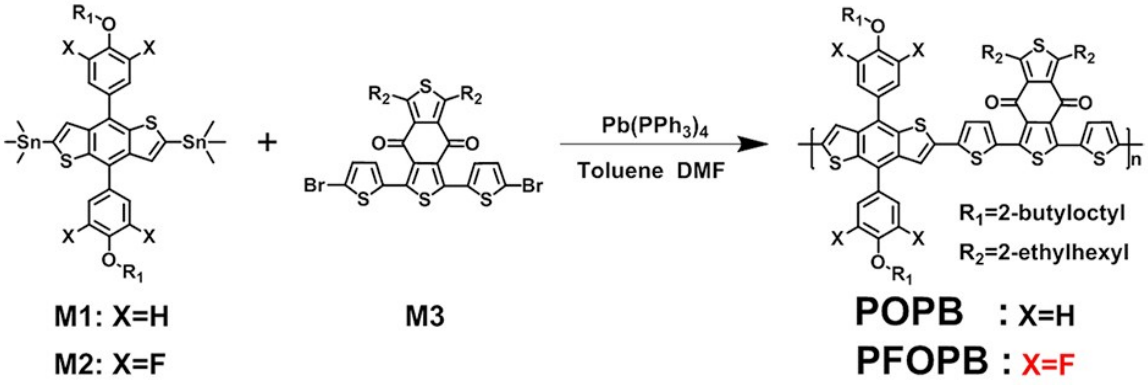
PFOPB. The yield was 81%. Anal. Calcd for $C_{80}H_{96}F_4O_4S_6$ (%): C, 69.13; H, 6.96; Found (%): C, 68.89; H, 6.71.

Instruments and measurements.

UV-Vis absorption spectra were measured by an Agilent Carry-5000 UV-Vis spectrophotometer. Electrochemical cyclic voltammetry (CV) was performed on a Zahner Zennium IM6 electrochemical workstation with a three-electrode system in 0.1 mol/L Bu_4NPF_6 acetonitrile solutions at a scan rate of 50 mV/s. Elemental analysis was carried out on a flash EA1112 analyzer. The molecular weights of two polymers were measured by the Agilent Technologies PL-GPC220. Photoluminescence (PL) spectra were performed on an Edinburgh Instrument FLS 980. Thermogravimetric analysis (TGA) was measured on Discovery TGA from TA Instruments Inc. at a heating rate of 10 °C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on a TA DSC Q-200 at a scan rate of 10 ^{o}C/min under nitrogen atmosphere. The atomic force microscopy (AFM) measurement was carried out on a Dimension 3100 (Veeco) Atomic Force Microscope in the tapping mode. Transmission electron microscopy (TEM) was performed on a Tecnai G2 F20 S-TWIN instrument at 200 kV accelerating voltage. The GIXD measurements were performed at beamline 7.3.3 at the Advanced Light Source (ALS). RSoXS transmission measurements were performed at beamline 11.0.1.2 at the Advanced Light Source (ALS).

Device fabrication and characterization.

The PSCs devices were fabricated with the structure of ITO/ZnO/PFN/active layer/MoO$_3$/Al. The ITO-coated glass substrate was cleaned with deionized water, acetone, and isopropanol, respectively. Subsequently, the pre-cleaned ITO-coated glass substrate was treated by UV-ozone for 20 min. Then, the ZnO precursor was spin-coated onto the pre-cleaned ITO glass at 5000 rpm and annealed in the titanium plate under 200 ^{o}C for 1 h. Then the solution of PFN which was dissolved in methanol and a small volume (0.25 % by volume) of acetic acid with concentration of 0.2 mg/mL was spin-coated on the surface of ZnO-coated ITO with 3000 *rpm* for 30 s. The active layer was deposited atop the ZnO layer by spin-coating a chlorobenzene solution of polymer:IT-4F (1:1.5,w/w) with a blend concentration of 20 mg/mL inside a nitrogen box containing less than 5 ppm oxygen and moisture. Finally, 10 nm MoO$_3$ and 100 nm Al were sequentially evaporated on the active layer in the vacuum chamber under a pressure of ca. 2.5×10^{-4} Pa. The effective area of one cell is 4 mm^2. The current-voltage (*J-V*) characteristics of the devices were measured on a Keithley 2450 Source Measure Unit. The power conversion efficiency (PCE) was measured under an illumination of AM 1.5G (100 mW/cm^2) using a SS-F5-3A (Enli Technology Co. Ltd.) solar simulator (AAA grade, 50 mm x 50 mm photobeam size). The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technololy Co. Ltd.). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.



Scheme S1 The synthetic route of **POPB** and **PFOPB**.

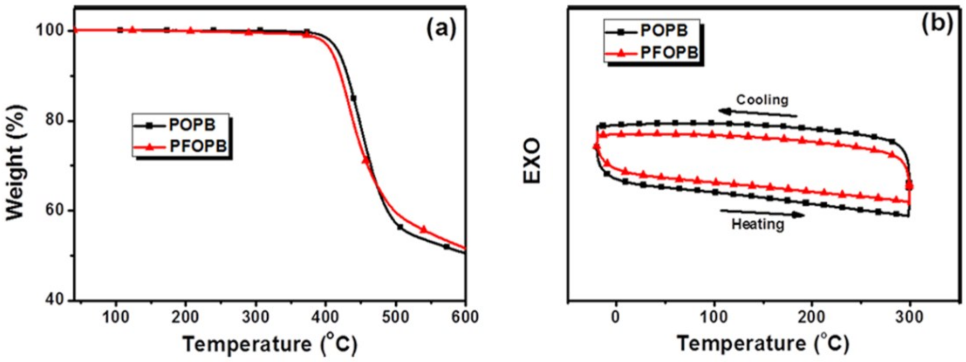


Fig. S1 (a) TGA and (b) DSC curves of two polymers under nitrogen atmosphere.

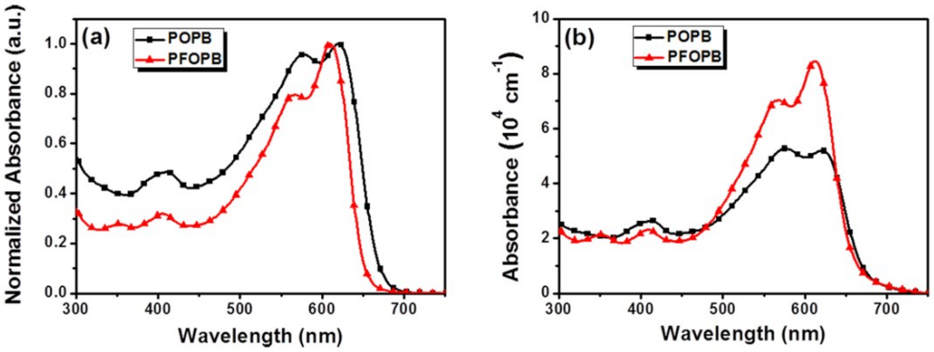


Fig. S2 UV–vis absorption spectra of two polymers (a) in dilute chloroform solution and (b) in thin films.

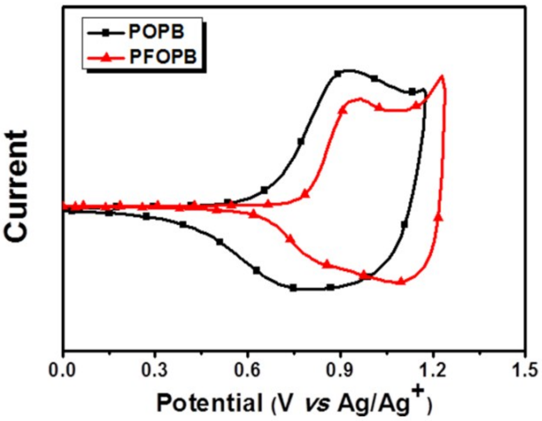


Fig. S3 Cyclic voltammogram of two polymer films.

Table S1 Molecular weights of two polymers.

Polymer	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI (M_w/M_n)

POPB	22.9	51.7	2.25
PFOPB	28.5	54.2	1.96

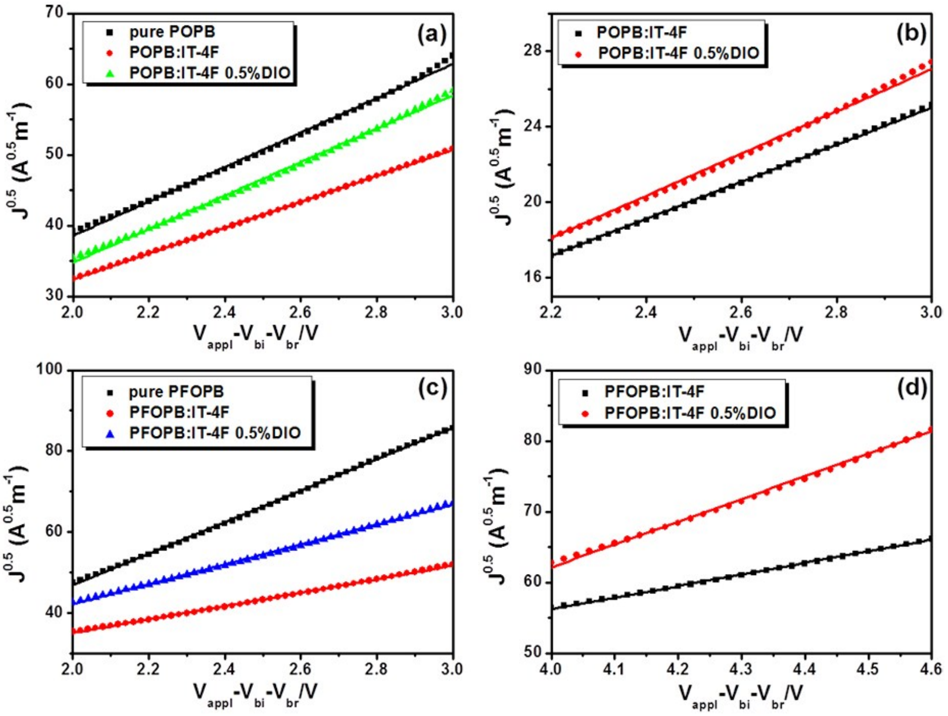


Fig. S4 $J^{0.5}$ *vs* V plots of (a), (c) the hole-only devices with the structure of ITO/PEDOT:PSS/polymer or active layer/MoO_3/Al, and (b), (d) the electron-only devices with the structure of ITO/ZnO/PFN/active layer/PFN/Al according to the SCLC model.

Table S2 Charge mobilities of the active layers measured by SCLC method.

condition	μ_h (cm^2/Vs)	μ_e(cm^2/Vs)	μ_h / μ_e
Pure **POPB**	3.96×10^{-4}		
POPB:IT-4F	1.75×10^{-4}	1.02×10^{-4}	1.72
POPB:IT-4F 0.5% DIO	3.15×10^{-4}	1.86×10^{-4}	1.69
Pure **PFOPB**	1.51×10^{-3}		
PFOPB:IT-4F	4.17×10^{-4}	3.16×10^{-4}	1.32
PFOPB:IT-4F 0.5% DIO	4.43×10^{-4}	3.46×10^{-4}	1.28

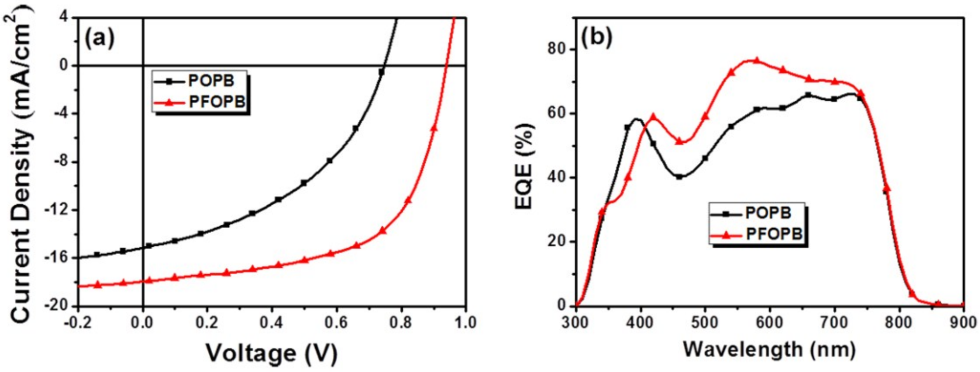


Fig. S5 (a) *J-V* curves of the PSCs based on polymers:IT-4F (1:1.5, w/w) without additive under the illumination of AM 1.5G, 100 mW/cm^2. (b) EQE curves of the corresponding devices.

Table S3 Photovoltaic parameters of the PSCs based on polymers:IT-4F (1:1.5, w/w) without additive under the illumination of AM1.5G (100 mW cm^{-2}).

Polymer	V_{oc} (V)	J_{sc}[a] (mA/cm^2)	*FF* (%)	PCE[b] (%)
POPB	0.75	15.2 (15.0)	43.3	4.9 (4.8)
PFOPB	0.94	17.8 (17.2)	60.4	10.1 (10.0)

(a)Values calculated from EQE in brackets. (b)Average PCEs in brackets for 20 devices.

Table S4 GIWAXS test performance parameters of the polymers:IT-4F (1:1.5, w/w) blend films with 0.5% DIO additive.

	out of plane (010)			
	location (Å^{-1})	FWHM	CL (Å)	d-space (Å)
POPB	1.70	0.22	25.64	3.70
POPB:IT-4F	1.71	0.20	27.70	3.66
PFOPB	1.67	0.18	31.84	3.77
PFOPB:IT-4F	1.69	0.16	35.85	3.73

References

1. J. Shin, M. Kim, B. Kang, J. Lee, H. G. Kim and K. Cho, *J. Mater. Chem. A*, 2017, **5**, 16702.
2. T. Liu, X. Pan, X. Meng, Y. Liu, D. Wei, W. Ma, L. Huo, X. Sun, T. H. Lee, M. Huang, H. Choi, J. Y. Kim, W. C. H. Choy, and Y. Sun, *Adv. Mater.*, 2017, **29**, 1604251.