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# Supporting Information

## Efficient Non-fullerene Polymer Solar Cells Based on a Wide Bandgap Polymer of Meta-alkoxy-phenyl-substituted Benzodithiophene and Difluorobenzotriazole

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### Experimental section

### Materials.

The chemicals and solvents were reagent grades and purchased from TCI Chemical, Aldrich, J&K and Alfa Aesar. The monomer (BDT-m-OP) was synthesized according to previously reported procedures.[1,2] 4,7-bis(5-bromothiophen-2-yl)-5,6-difluoro-2-(2-butyloctyl)-2*H*-benzo[*d*][1,2,3]triazole (FBTZ) was purchased from Suna Tech Inc. ITIC was purchased from Solarmer Materials Inc.

### Synthesis of the polymer PBFZ-OP.

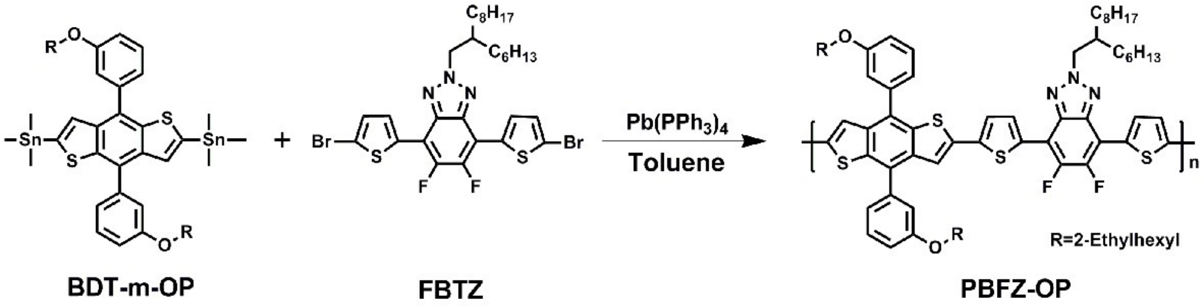
In a dry 50 mL round bottom flask, BDT-m-OP (0.30 mmol, 277 mg) and FBTZ (0.30 mmol, 210 mg) were dissolved in 10 mL toluene. After flushed with argon for 20 min, 17 mg of $Pd(PPh_3)_4$ was added into the flask, then the mixture was flushed with argon for another 30 min. The solution was stirred at 110 °C for 13 hours under argon atmosphere and the reactant was cooled down to room temperature, and the polymer was poured into 100 mL methanol. The polymer was collected by filtration and subjected to Soxhlet extraction with methanol, hexane, and chloroform in the end. The collected chloroform solution was evaporated under reduced pressure and precipitated with 100 mL of methanol. The polymer was collected by filtration and dried under vacuum. Anal. Calcd for $C_{68}H_{83}F_2N_3O_2S_4$ (%): C, 71.60; H, 7.33; N, 3.68; Found (%):C, 71.92; H, 7.25; N, 3.65. *Mn* = 24.1 kDa, PDI = 1.95. $^1$H NMR (400 MHz, $CDCl_3$, TMS), δ (ppm): 8.24 (br, aromatic protons), 7.53 (br, aromatic protons), 7.30 (br, aromatic protons), 7.11 (br, aromatic protons), 4.74 (br, aliphatic protons), 3.95 (br, aliphatic protons), 2.52-2.01 (br, aliphatic protons), 1.55 (br, aliphatic protons), 1.26 (br, aliphatic protons), 0.99-0.84 (br, aliphatic protons).

**Instruments and measurements.**

Elemental analysis was carried out on a flash EA1112 analyzer. UV-Vis absorption spectrum was 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. The three-electrode system included glassy carbon disk, platinum wire, and $Ag/Ag^+$ electrode as the working electrode, counter electrode and reference electrode, respectively. The molecular weight of the polymer was measured by the GPC method with polystyrene as the standard and 1, 2, 4-tricholorobenzene as the solvent at 160 $^oC$ using Agilent Technologies PL-GPC220. Photoluminescence (PL) spectra was 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 $^oC$/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).[3] Samples were prepared on a Si substrate under the same conditions as those used for device fabrication. The 10 KeV X-ray beam was incident at a grazing angle of 0.11°-0.15°, which maximized the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector. RSoXS transmission measurements were performed at beamline 11.0.1.2 at the Advanced Light Source (ALS).[4,5] Samples for R-SoXS measurements were prepared on a PSS modified Si substrate under the same conditions as those used for device fabrication, and then transferred by floating in water to a 1.5 mm × 1.5 mm, 100 nm thick $Si_3N_4$ membrane supported by a 5 mm × 5 mm, 200 μm thick Si frame (Norcada Inc.). 2-D scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MTE). The sample detector distance was calibrated from diffraction peaks of a triblock copolymer poly(isoprene-b-styrene-b-2-vinyl pyridine), which has a known spacing of 391 Å. The beam size at the sample is approximately 100 μm by 200 μm.

**Device fabrication and characterization.**

The PSCs devices were fabricated with the structure of ITO/ZnO/**PBFZ-OP**: ITIC/$MoO_3$/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. The active layer was deposited atop the ZnO layer by spin-coating a CF solution of **PBFZ-OP**: ITIC with a blend concentration of 16 mg/mL inside a nitrogen box containing less than 5 ppm oxygen and moisture. Finally, 10 nm $MoO_3$ and 80 nm Al were sequentially evaporated on the active layer in the vacuum chamber under a pressure of ca. $4 \times 10^{-4}$ 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 of the PSCs was measured under a 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 polymer **PBFZ-OP**.

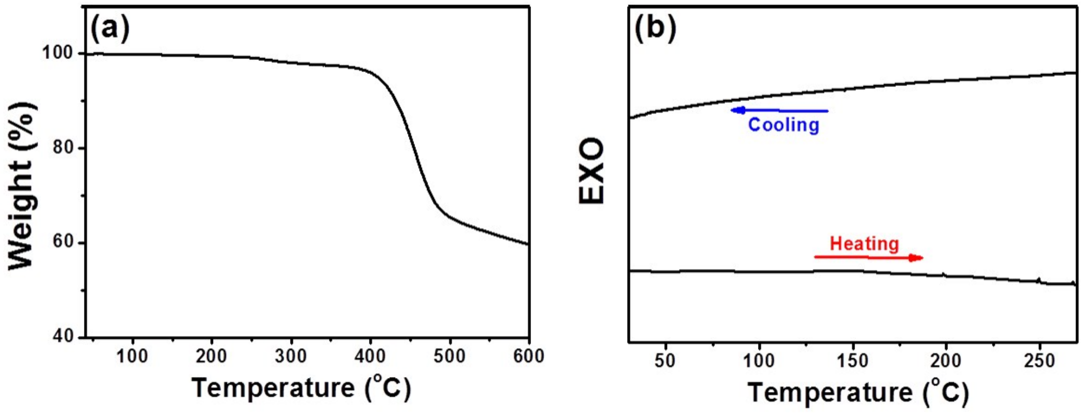


**Fig. S1** TGA and DSC curves of **PBFZ-OP** at a scan rate of 10 ˚C/min under nitrogen.

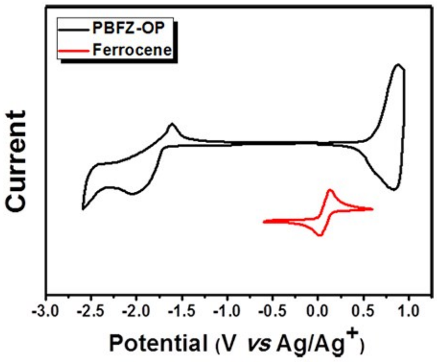


**Fig. S2** Cyclic voltammogram of **PBFZ-OP** film.

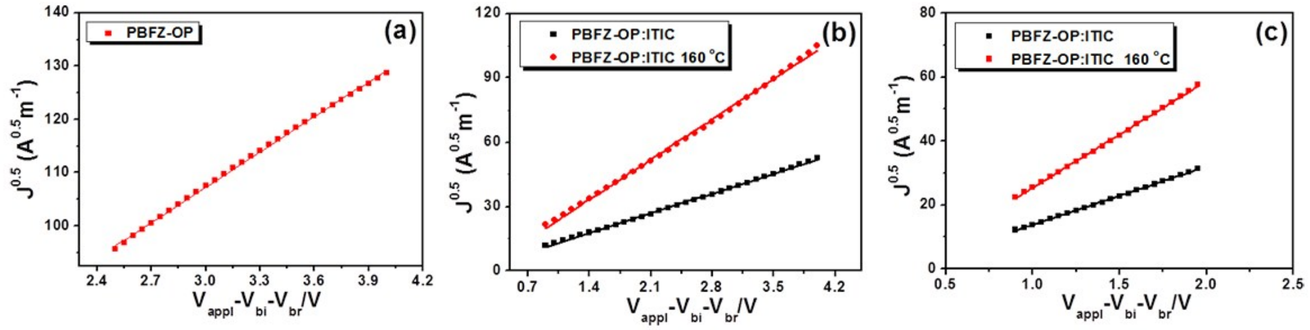


**Fig. S3** $J^{0.5}$ *vs* V plots of (a) and (b) the hole-only devices with the structure of ITO/PEDOT:PSS/polymer or actively layer/$MoO_3$/Al, and (c) the electron-only devices with the structure of ITO/ZnO/actively layer/Ca/Al according to the SCLC model.

**Table S1** Charge mobilities of the device active layers measured by SCLC method.

| condition | $\mu_h$ ($cm^2$/Vs) | $\mu_e$($cm^2$/Vs) | $\mu_h / \mu_e$ |
|---|---|---|---|
| Pure **PBFZ-OP** | $7.28\times10^{-4}$ | - | - |
| **PBFZ-OP**: ITIC as-cast | $9.98\times10^{-5}$ | $1.08\times10^{-4}$ | 1.11 |
| **PBFZ-OP**: ITIC TA | $3.25\times10^{-4}$ | $2.62\times10^{-4}$ | 1.07 |

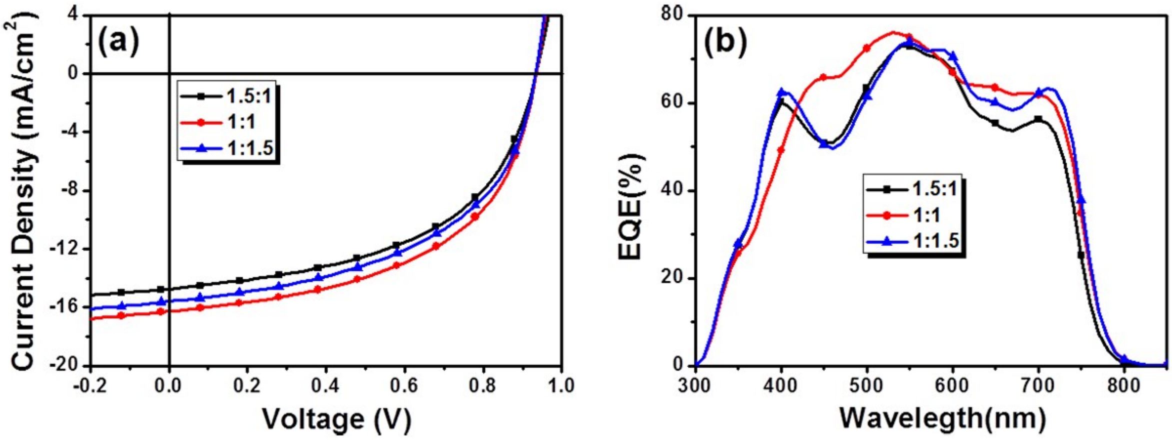


**Fig. S4** (a) *J-V* curves and (b) EQE curves of the PSCs based on **PBFZ-OP**: ITIC blends with different D/A ratios (w/w).

**Table S2** Photovoltaic performance parameters of the PSCs based on **PBFZ-OP**: ITIC with different D/A ratios (w/w) under the illumination of AM1.5G (100 mW/cm$^2$).

| D/A Ratio | $V_{oc}$ (V) | $J_{sc}[J_{sc}{}^{a)}]$ (mA/cm$^2$) | $FF$ (%) | $PCE[PCE_{\mathrm{ave}}{}^{b)}]$ (%) |
|---|---|---|---|---|
| 1:1.5 | 0.93 | 14.8(14.1) | 51.8 | 7.1(7.0) |
| 1:1 | 0.93 | 16.3(15.6) | 53.0 | 8.0(7.8) |
| 1.5:1 | 0.93 | 15.6(15.0) | 51.2 | 7.4(7.2) |

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

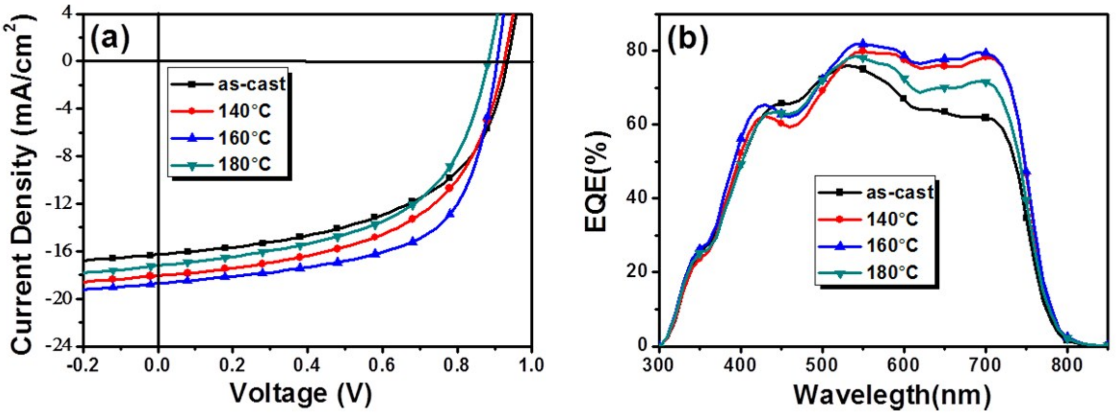


**Fig. S5** (a) The *J-V* curves and (b) EQE curves of the PSCs based on **PBFZ-OP**: ITIC (1:1, w/w) with different annealing temperatures.

**Table S3** Photovoltaic parameters of the PSCs based on **PBFZ-OP**: ITIC (1:1, w/w) with different annealing temperatures under the illumination of AM1.5G (100 mW cm$^{-2}$).

| Temperature (℃) | $V_{oc}$ (V) | $J_{sc}[J_{sc}{}^{a)}]$ (mA/cm$^2$) | $FF$ (%) | $PCE[PCE_{\mathrm{ave}}{}^{b)}]$ (%) |
|---|---|---|---|---|
| as-cast | 0.93 | 16.3(15.6) | 53.0 | 8.0(7.8) |
| 140 | 0.92 | 18.0(17.3) | 54.2 | 9.0(8.9) |
| 160 | 0.91 | 18.7(17.8) | 61.8 | 10.5(10.4) |
| 180 | 0.89 | 17.2(16.5) | 54.4 | 8.3(8.2) |

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

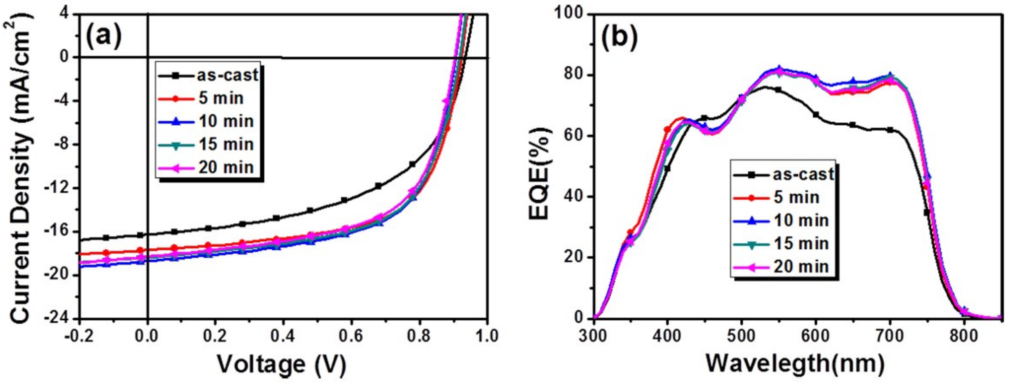


**Fig. S6** (a) *J-V* characteristics and (b) EQE curves of the PSCs based on **PBFZ-OP:** ITIC (160 $^{o}$C) with different annealing time.

**Table S4** Photovoltaic parameters of the PSCs based on **PBFZ-OP**: ITIC (160 $^{o}$C) with different annealing time under the illumination of AM1.5G (100 mW/cm$^2$).

| Time (min) | $V_{oc}$ (V) | $J_{sc}$[$J_{sc}$ $^{a)}$] (mA/cm2) | FF (%) | PCE[PCE$_{ave}$$^{b)}$] (%) |
|---|---|---|---|---|
| as-cast | 0.93 | 16.3(15.6) | 53.0 | 8.0(7.8) |
| 5 | 0.92 | 17.7(17.4) | 63.4 | 10.3(10.1) |
| 10 | 0.91 | 18.7(17.8) | 61.8 | 10.5(10.4) |
| 15 | 0.91 | 18.4(17.4) | 60.4 | 10.1(10.0) |
| 20 | 0.90 | 18.3(17.5) | 60.9 | 10.0(9.8) |

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

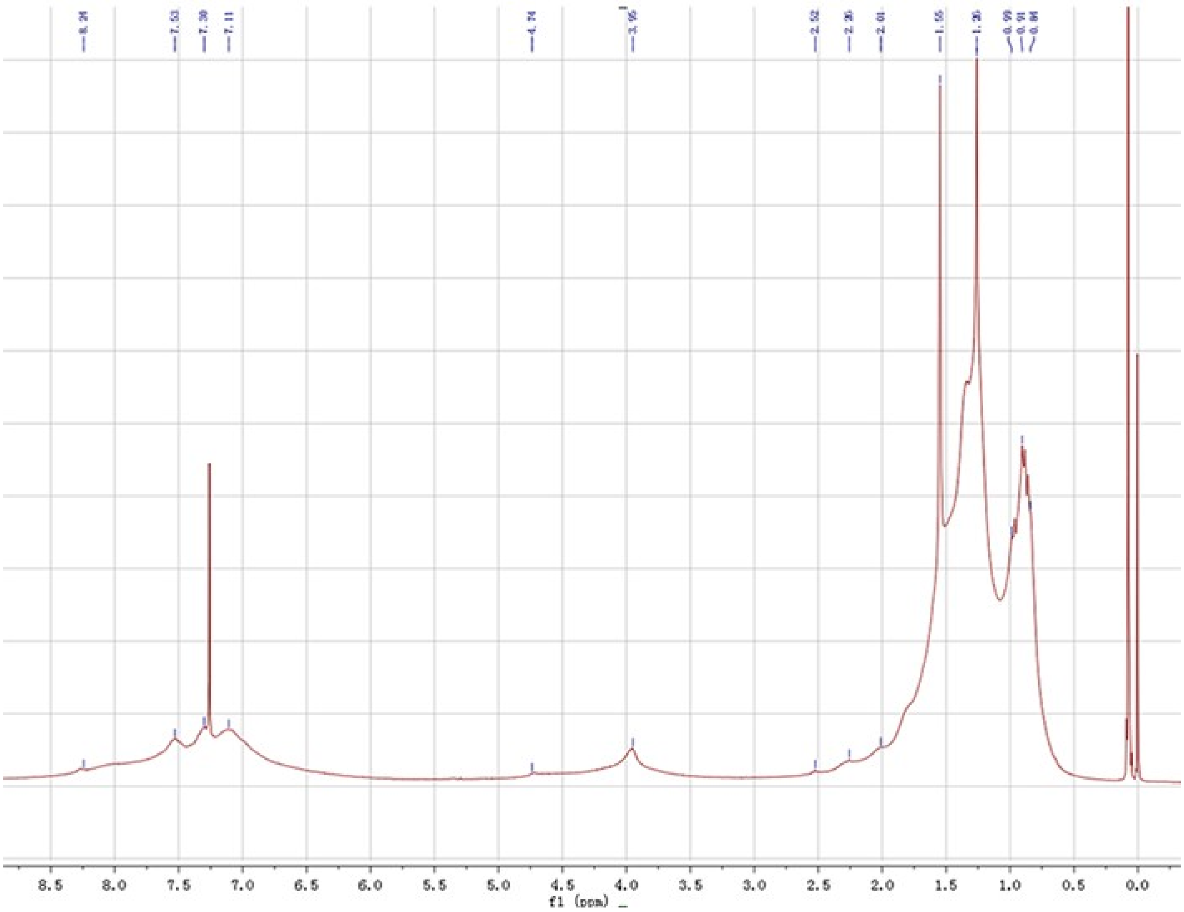


**Fig. S7** The $^1$H NMR spectrum of polymer **PBFZ-OP** in $CDCl_3$ solution.

## References

1. M. J. Zhang, X. Guo, W. Ma, S. Zhang, L. Huo, H. Ade, J. Hou, *Adv. Mater.*, 2014, **26**, 2089.
2. Z. Xu, Q. P. Fan, X. Y. Meng, X. Guo, W. Y. Su, W. Ma, M. J. Zhang, and Y. F. Li, *Chem. Mater.*, 2017, **29**, 4811.
3. A. Hexemer, W. Bras, J. Glossinger, E. Schaible, E. Gann, R. Kirian, A. MacDowell, M. Church, B. Rude, H. Padmore, *J. Phys. Conf. Ser.*, 2010, **247**, 012007.
4. E. Gann, A. T. Young, B. A. Collins, H. Yan, J. Nasiatka, H. A. Padmore, H. Ade, A. Hexemer, C. Wang, *Rev. Sci. Instrum.*, 2012, **83**, 045110.
5. Y. Wu, Z. Wang, X. Meng, W. Ma, *Prog. Chem.*, 2017, **29**, 93.