

Supporting Information

Non-fullerene Polymer Solar Cells Based on a trifluoromethyl Substituted Wide Bandgap Conjugated Polymer with 10.4% Efficiency

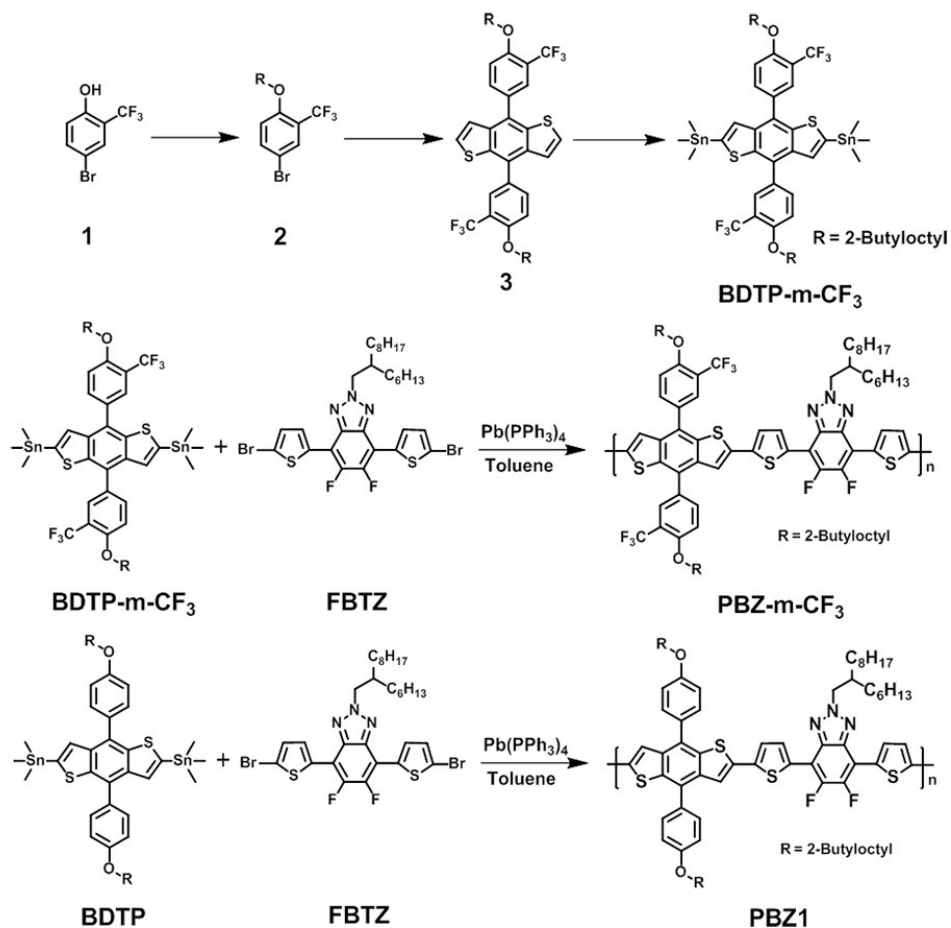
Wanbin Li^a, Guangda Li^a, Xia Guo^a,*YongWang^a, Huan Guo^a, Qingqing Xu^a, Maojie Zhang^a,*
Yongfang Li^{ab}

^a Laboratory of Advanced Optoelectronic Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China.

*E-mail: mjzhang@suda.edu.cn, guoxia@suda.edu.cn

^b Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

Experimental section



Scheme S1 The synthetic route of the monomer BDTP-*m*-CF₃ and the polymers of **PBZ-*m*-CF₃** and **PBZ1**.

Materials.

All chemicals and solvents were reagent grades and purchased from Alfa Aesar, J&K, Aldrich and TCI Chemical, respectively. benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione and difluorobenzotriazole (FBTZ) were purchased from Suna Tech Inc. ITIC was purchased from Solarmer Materials Inc. The monomer BDTP was synthesized according to the literature.¹ The synthetic routes for the monomer BDTP-*m*-CF₃ and the copolymers of **PBZ-*m*-CF₃** and **PBZ1** are shown in **Scheme S1**. The detailed synthetic routes for BDTP-*m*-CF₃, **PBZ-*m*-CF₃** and **PBZ1** are as follows.

Synthesis of compound 2.

Under protection of argon, 4-bromo-2-(trifluoromethyl)phenol (10.85 g, 45 mmol) and K₂CO₃ (12.42 g, 90 mmol) was added into 150 mL DMF in a two-neck flask. After stirring for 5 min, 5-(bromomethyl)undecane (13.46 g, 54 mmol) was added. The mixture was heated to 90 °C for 24 h in darkness. The cooled mixture was filtered through a Buchner funnel to remove solids and the organic liquid was collected. The organic liquid was extracted with diethyl ether three times. The combined organic phase was dried over anhydrous magnesium sulfate (MgSO₄). After removing the organic solvents, the crude product was purified on a silica gel column eluting with petroleum ether. Compound 2 was obtained as pale yellow oil (16.95 g, 92%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.66 (s, 1H), 7.57 (d, 1H), 6.87 (d, 1H), 3.90 (d, 2H), 1.81 (m, 1H), 1.46-1.28 (m, 15H), 0.90-0.88 (m, 6H).

Synthesis of compound 3.

Under protection of argon, 4-bromo-1-((2-butyloctyl)oxy)-2-(trifluoromethyl)benzene (16.37 g, 40 mmol) was slowly added to magnesium turnings (0.96 g, 40 mmol) in THF (40 mL) with a catalytic amount of I₂. The mixture was kept at 80 °C for 6 h and then the solution was cooled to room temperature. Then, benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (2.86 g, 13 mmol) was added, and the

mixture stirred for 2 hour at 50°C. After cooling down to the room temperature, SnCl₂·2H₂O (20.48 g, 91 mmol) in 10% HCl (80 mL) was added, and the mixture was stirred overnight at 50°C. The reaction mixture was poured into ice water and extracted by diethyl ether twice, and the combined organic phase was concentrated. Further purification was carried out by column chromatography using petroleum ether as eluent to obtain product as a white solid (7.05 g, 64%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.91 (s, 2H), 7.83 (d, 2H), 7.44 (d, 2H), 7.29 (d, 2H), 7.20 (d, 2H), 4.05 (d, 4H), 1.89 (m, 2H), 1.57-1.31 (br, 32H), 0.94-0.90 (t, 12H). ¹³C NMR (600 MHz, CDCl₃), δ (ppm): 157.10, 138.37, 136.26, 134.03, 130.54, 129.03, 128.16, 127.65, 122.62, 112.88, 71.21, 37.95, 31.83, 31.19, 30.87, 29.65, 29.04, 26.82, 23.02, 22.69, 14.11. MS (MALDI): calculated: 846.394, found: 846.389 (M⁺).

Synthesis of compound BDTP-m-CF₃.

To a solution of compound 3 (3.38 g, 4 mmol) in THF (40 mL) at -78 °C was slowly added LDA (5 mL, 2.0 M). After the addition, the mixture was kept at -78 °C for 1.5h; trimethyltin chloride solution in THF (12 mL, 1.0 M) was added. The solution was then stirred at room temperature 2h and quenched with 50ml of water. The mixture was extracted with diethyl ether twice. After drying over MgSO₄, the solvent was removed and the residue was recrystallized from ethanol to afford the compound BDTP-m-CF₃ (3.80 g, 81%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.92 (s, 2H), 7.84 (d, 2H), 7.30 (s, 2H), 7.20 (d, 2H), 4.06 (d, 4H), 1.89 (m, 2H), 1.55-1.26 (br, 32H), 0.94 (t, 12H), 0.37 (t, 18H). ¹³C NMR (600 MHz, CDCl₃), δ (ppm): 156.90, 142.69, 137.10, 134.08, 131.21, 130.26, 128.31, 127.41, 112.78, 71.17, 37.99, 31.84, 31.22, 30.90, 29.66, 29.07, 26.84, 23.03, 22.70, 14.11, -8.34. MS (MALDI): calculated: 1174.323, found: 1172.295 (M⁺).

Synthesis of the polymer PBZ-m-CF₃.

In a 50 mL double-neck round bottom flask, compound BDTP-m-CF₃ (0.3 mmol, 352mg) and compound FBTZ (0.3 mmol, 210 mg) were dissolved in 10 mL toluene. After being purged with argon for 20 min, 18 mg of Pd(PPh₃)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 15 h under argon atmosphere. When the reaction mixture was cooled down to room temperature, the polymer was 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 polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum. The yield was 84%. GPC: $M_w = 58.5$ K; $M_n = 33.6$ K; $\bar{D} = 1.74$. Anal. Calcd for $C_{78}H_{97}F_8N_3O_2S_4$ (%): C, 67.45; H, 7.04; N, 3.03; Found (%): C, 66.76; H, 6.87; N, 2.98.

Synthesis of the polymer **PBZ1**.

The polymer **PBZ1** was synthesized by the same synthetic procedure of **PBZ-m-CF₃** with the monomer BDTP (0.3 mmol, 311 mg) and FBTZ (0.3 mmol, 210 mg), Pd(PPh₃)₄ 18 mg in 10 mL toluene. The yield was 82%. GPC: $M_w = 51.3$ K; $M_n = 27.3$ K; $\bar{D} = 1.88$. Anal. Calcd for $C_{76}H_{99}F_2N_3O_2S_4$ (%): C, 72.86; H, 7.96; N, 3.35; Found (%): C, 71.83; H, 7.75; N, 3.25.

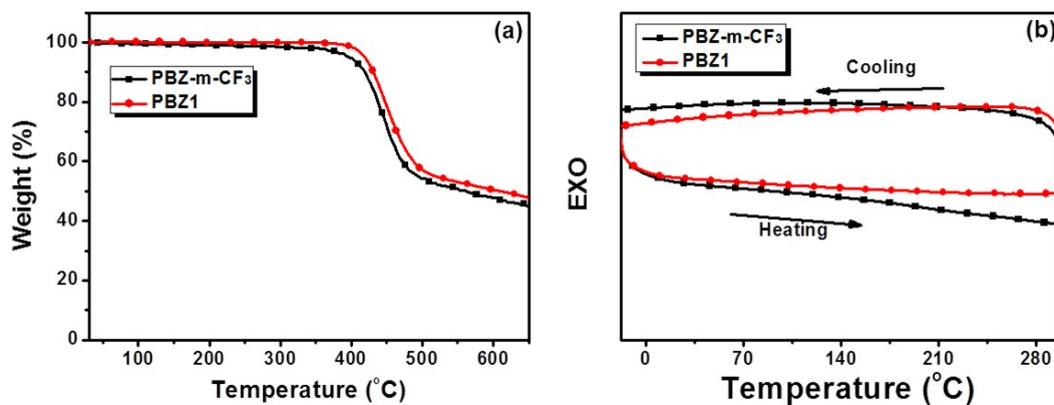


Fig. S1 (a) TGA and (b) DSC curves of **PBZ-m-CF₃** and **PBZ1** at a scan rate of 10 °C/min under nitrogen atmosphere.

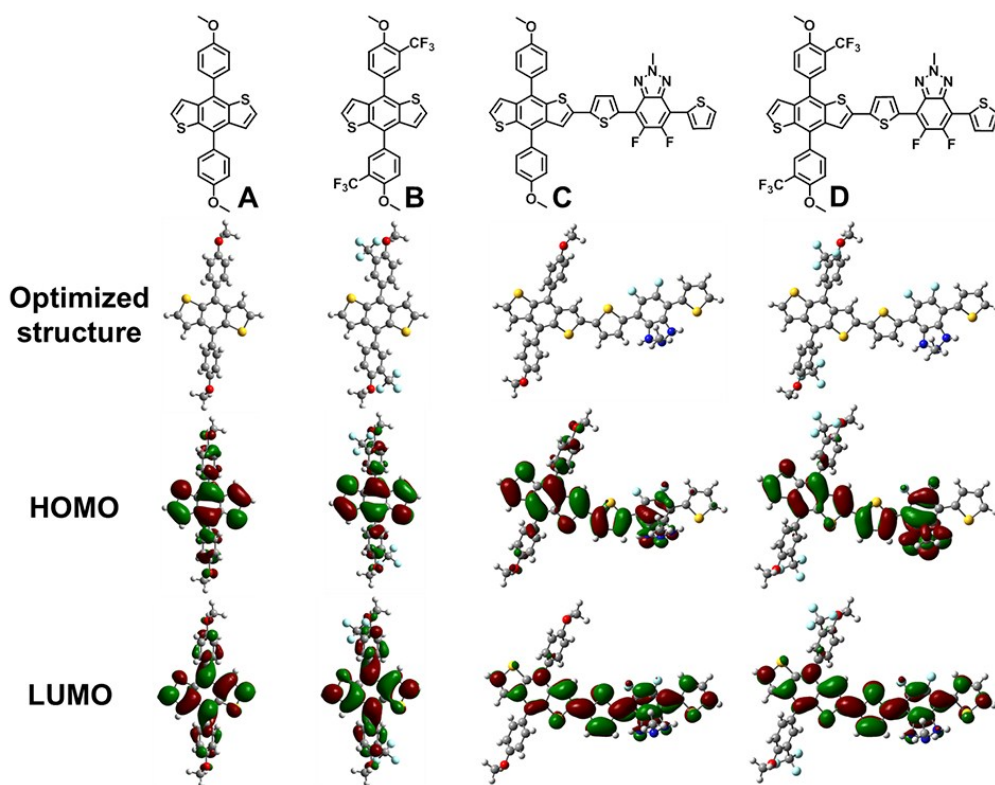


Fig. S2 The geometry-optimized structures, and the frontier molecular orbitals for monomer (A and B) and one repeat unit (C and D) by DFT at the B3LYP/6-31G (d,p) level.

Table S1 The corresponding HOMO and LUMO levels and the dipole moment by DFT theoretical calculation.

Structure	HOMO (eV)	LUMO (eV)	Dipole (Debye)
A	-5.06	-1.01	2.0217
B	-5.35	-1.30	0.0012
C	-4.97	-1.85	1.5282
D	-5.13	-1.99	3.6063

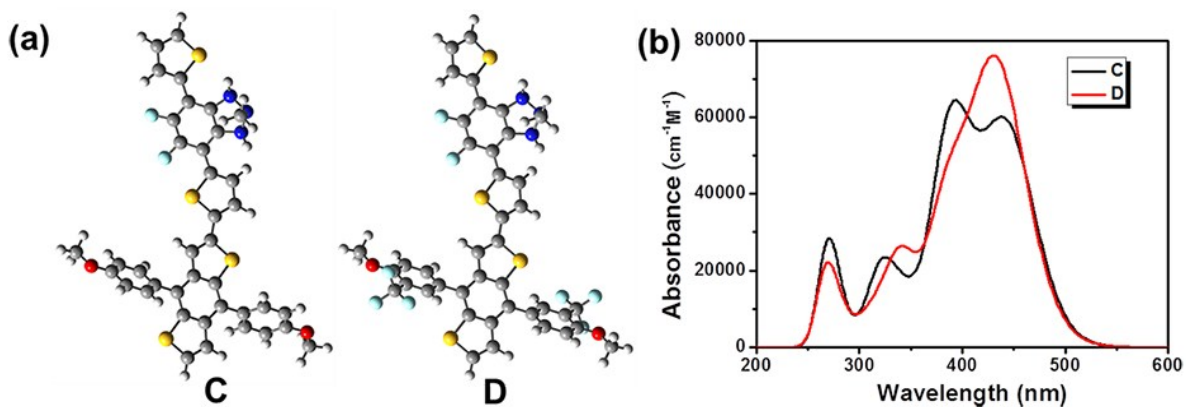


Fig. S3 (a) The geometry-optimized structures of one repeat unit (C and D), and (b) calculated UV-vis absorption spectra of C and D by TD-DFT at the B3LYP/6-31G (d,p) level.

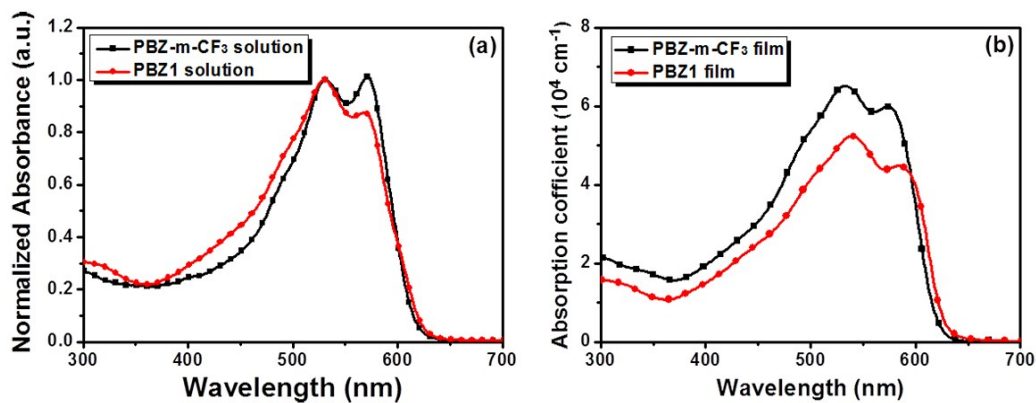


Fig. S4 UV-vis absorption spectra of PBZ-m-CF₃ and PBZ1.

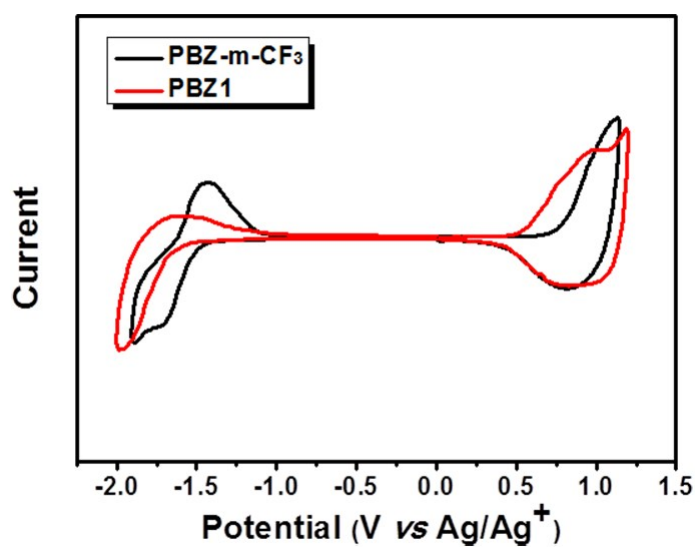


Fig. S5 Cyclic voltammogram of PBZ-m-CF₃ and PBZ1.

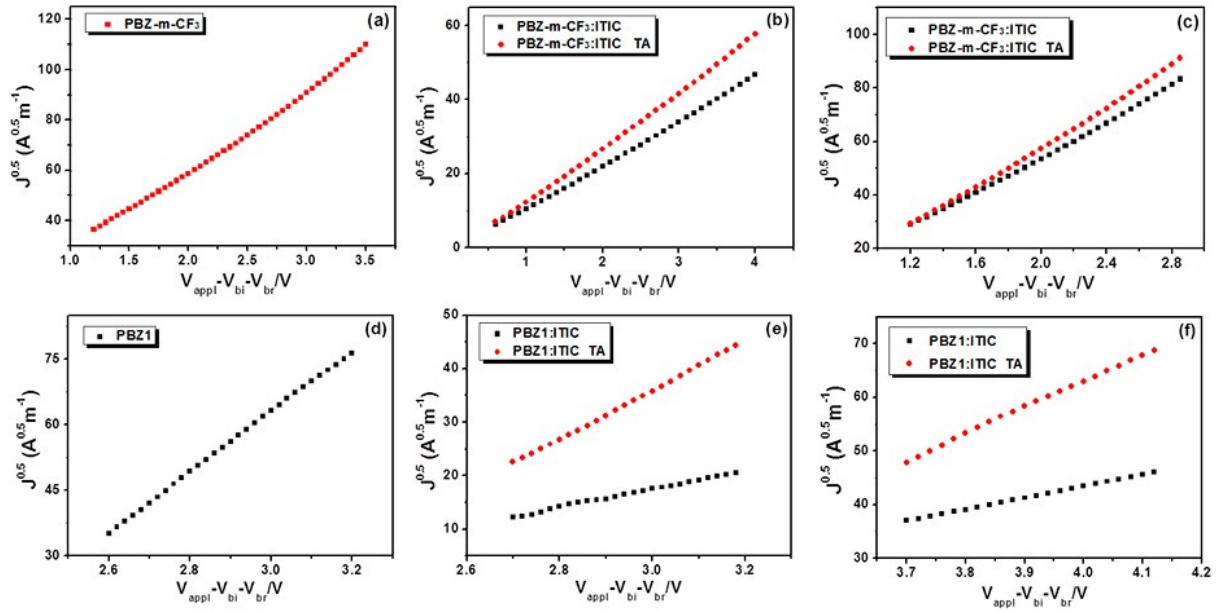


Fig. S6 $J^{0.5}$ vs V plots of (a), (b), (d), (e) the hole-only devices, and (c), (f) the electron-only devices according to the SCLC method.

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

condition	μ_h (cm ² /Vs)	μ_e (cm ² /Vs)	μ_h/μ_e
Pure PBZ-m-CF₃	7.86×10^{-4}	-	-
PBZ-m-CF₃ : ITIC as-cast	3.26×10^{-4}	2.29×10^{-4}	1.42
PBZ-m-CF₃ : ITIC TA	5.08×10^{-4}	3.96×10^{-4}	1.28
Pure PBZ1	7.23×10^{-4}	-	-
PBZ1 : ITIC as-cast	3.03×10^{-4}	1.88×10^{-4}	1.61
PBZ1 : ITIC TA	4.36×10^{-4}	2.98×10^{-4}	1.46

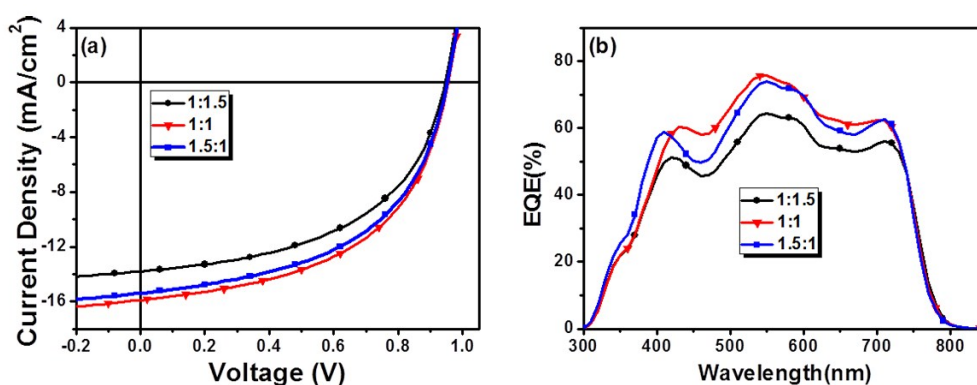


Fig. S7 (a) J - V curves and (b) EQE curves of the PSCs based on **PBZ-m-CF₃**: ITIC blends with different D/A ratios (w/w).

Table S3 Photovoltaic performance of the PSCs based on **PBZ-m-CF₃**: ITIC with different D/A ratios (w/w) under the illumination of AM1.5G (100 mW/cm²).

D/A Ratio	V_{oc} (V)	J_{sc} [$J_{sc}^{a)}$] (mA/cm ²)	FF (%)	PCE[PCE _{ave} ^{b)}] (%)
1:1.5	0.94	13.8 (13.2)	51.4	6.7 (6.4)
1:1	0.95	15.9 (15.3)	52.3	7.9 (7.8)
1.5:1	0.95	15.4 (14.7)	51.7	7.6 (7.4)

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

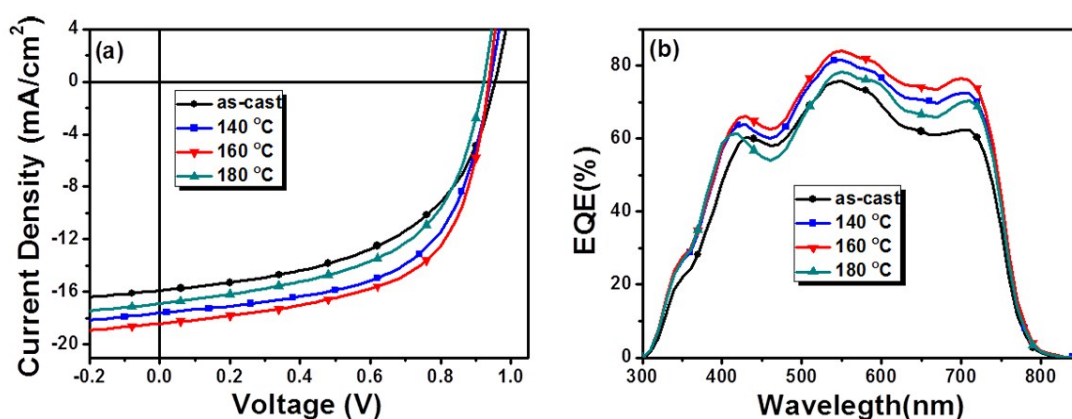


Fig. S8 (a) The J - V curves and (b) EQE curves of the PSCs based on **PBZ-m-CF₃**: ITIC (1:1, w/w) (10 min) with different annealing temperature.

Table S4 Photovoltaic performance of the PSCs based on **PBZ-m-CF₃**: ITIC (1:1, w/w) (10 min) with different annealing temperature under the illumination of AM1.5G (100 mW cm⁻²).

Temperature (°C)	V_{oc} (V)	$J_{sc}[J_{sc}^{a}]$ (mA/cm ²)	FF (%)	PCE[PCE _{ave} ^b] (%)
as-cast	0.95	15.9 (15.3)	52.3	7.9 (7.8)
140	0.94	17.6 (16.9)	58.8	9.7 (9.5)
160	0.94	18.4 (17.6)	60.2	10.4 (10.3)
180	0.92	16.9 (16.1)	55.2	8.6 (8.4)

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

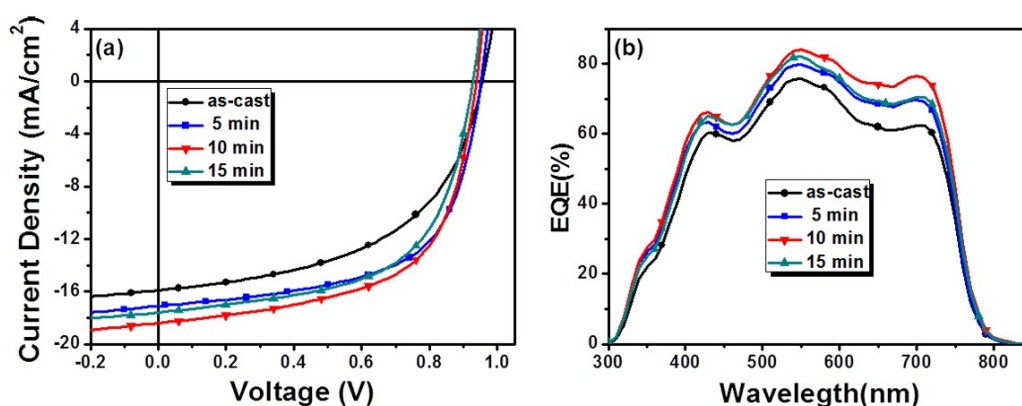


Fig. S9 (a) J - V curves and (b) EQE curves of the PSCs based on **PBZ-m-CF₃**: ITIC (160 °C) with different annealing time.

Table S5 Photovoltaic performance of the PSCs based on **PBZ-m-CF₃**: ITIC (160 °C) with different annealing time under the illumination of AM1.5G (100 mW/cm²).

Time (min)	V_{oc} (V)	$J_{sc}[J_{sc}^{a}]$ (mA/cm ²)	FF (%)	PCE[PCE _{ave} ^b] (%)
As-cast	0.95	15.9 (15.3)	52.3	7.9 (7.8)
5	0.95	17.1 (16.4)	61.1	9.9 (9.7)
10	0.94	18.4 (17.6)	60.2	10.4 (10.3)
15	0.93	17.6 (16.8)	59.3	9.7 (9.5)

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

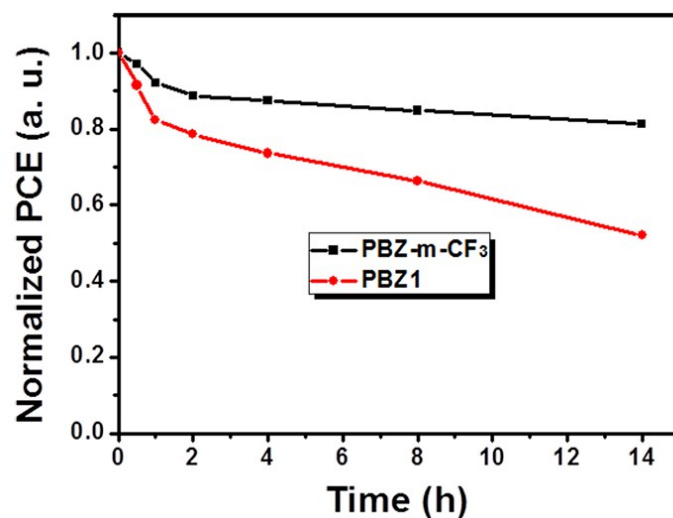


Fig. S10 The curves of normalized PCE versus time under thermal annealing at 80 °C for polymers: ITIC-based devices in glove box.

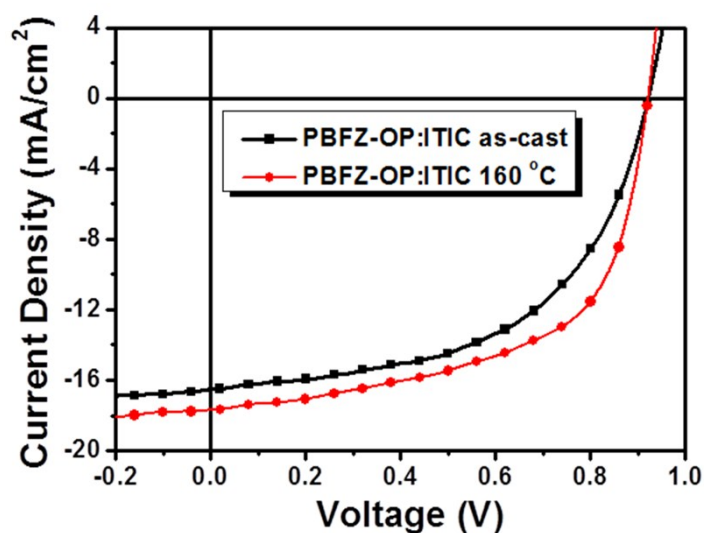


Fig. S11 J - V curves of the PSCs based on PBFZ-OP: ITIC (1:1, w/w) with toluene as solvent.

Table S6 Photovoltaic performance of the PSCs based on PBFZ-OP: ITIC (1:1, w/w) with toluene as solvent under the illumination of AM1.5G (100 mW/cm²).

Condition	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
As-cast	0.92	16.5	54.0	8.2
160 °C, 10 min	0.92	17.7	58.9	9.6

Instruments and measurements.

^1H NMR and ^{13}C NMR spectra were measured on Bruker AV FT-NMR spectrometer. Elemental analysis was carried out on a flash EA1112 analyzer. Mass spectra were obtained with a Shimadzu QP2010 spectrometer. UV-Vis absorption spectra were measured by an Agilent Carry-5000 UV-Vis spectrophotometer. Electrochemical cyclic voltammetry (CV) was performed on a Zahner Zennium 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 electrode, Pt wire and Ag/Ag^+ electrode as the working electrode, counter electrode and reference electrode, respectively. The potential of the Ag/Ag^+ reference electrode was internally calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc^+), and the Ag/Ag^+ reference electrode possesses an energy level of -4.71 eV. The molecular weight of the polymer was measured by the GPC method with polystyrene as the standard and 1,2,4-trichlorobenzene as the solvent at 160 °C using Agilent Technologies PL-GPC220. Thermo gravimetric analysis (TGA) was performed on Discovery TGA from TA Instruments Inc. under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on a TA DSC Q-200 at a scan rate of 10 °C/min under nitrogen atmosphere. X-ray diffraction (XRD) measurement was performed using a Bruker D8 Advance Instrument at 40 kV voltage and 200 mA current with $\text{Cu K}\alpha$ radiation. Photoluminescence (PL) spectra were performed on an Edinburgh Instrument FLS 980. The atomic force microscopy (AFM) measurement of the surface morphology of samples was conducted 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 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/cm²) 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 Technology Co. Ltd.). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

Fabrication and characterization of devices

Polymer solar cells were fabricated with the structure of ITO/ZnO/Active layer/MoO₃/Al. The ITO-coated glass was cleaned with deionized water, acetone and isopropanol, respectively. 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 °C for 1 h. The solution of polymers: ITIC blend in toluene was spin cast atop ZnO layer to form the active layer. Finally, MoO₃ (10 nm) and Al (80 nm) were sequentially evaporated through a shadow mask to define the active area of the devices (~4 mm²) in a vacuum chamber (<1×10⁻⁴ Pa).

References

1. J. Shin, M. Kim, B. Kang, J. Lee, H. G. Kim and K. Cho, *J. Mater. Chem. A*, 2017, **5**, 16702.