

## Supporting information

### Side-chain engineering for efficient nonfullerene polymer solar cells based on wide-bandgap polymer donor

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### Materials

All chemicals and solvents were reagent grades and purchased from Alfa Aesar and TCI. ITIC was purchased from Solarmer Materials Inc, 4,7-bis(5-bromothiophen-2-yl)-5,6-difluoro-2-(2-butyloctyl)-2*H*-benzo[*d*][1,2,3]triazole (**BTz-2F**) were purchased from Suna Tech Inc, respectively. 4,8-Bis(5-(2-butyloctylthio)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (**BDTTS**) was synthesized according to the following procedures.

### *Synthesis of compound 3*

Compound **1** (8.8 g, 31 mmol) and 60 mL dry THF were added into a flask under argon protection. The solution was cooled to -78 °C and 14.2 mL of *n*-butyllithium (34 mmol, 2.4 M in hexane) was slowly added dropwise. The mixture was then warmed to room temperature and stirred for 2 hour. Subsequently, compound **2** (1.7 g, 7.8 mmol) was added to the reaction mixture, and then stirred for 2 h at 50 °C. After cooling to ambient temperature, a mixture of SnCl<sub>2</sub>·2H<sub>2</sub>O (13.6 g, 60.7 mmol) in 10% HCl (30 mL) was added and the mixture was stirred for an additional 1.5 h. After that, the reaction mixture was poured into water and extracted with ether. The organic layer was washed with water three times and then dried over MgSO<sub>4</sub>. After the removal of solvent, the crude product was purified by column chromatography on a silica gel using hexane as the eluent to afford compound **3** (3.5 g, yield 59%) as a yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS), δ (ppm): 7.61 (d, *J* = 5.5 Hz, 2H), 7.47 (d, *J* = 5.5 Hz, 2H), 7.32 (d, *J* = 3.4 Hz, 2H), 7.21 (d, *J* = 3.3 Hz, 2H), 2.93 (d, *J* = 6.0 Hz, 4H), 1.70-1.68 (m, 2H), 1.46-1.42 (m, 8H), 1.30-1.28 (m, 24H), 0.91-0.88 (m, 12H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, TMS), (ppm): 142.10, 138.96, 137.60, 136.48, 132.43, 128.26, 127.77, 123.60, 123.04, 43.97, 37.82, 32.94, 32.62, 31.85, 29.57, 28.76, 26.52, 22.94, 22.67, 14.12, 14.10. MALDI-TOF MS (*m/z*) for C<sub>42</sub>H<sub>58</sub>S<sub>6</sub>, Calcd: 754.29, Found: 754.37.

### *Synthesis of compound **BDTTS***

Compound **3** (2.9 g, 3.9 mmol) and 50 mL dry THF were mixed at -78 °C under argon protection, 4.1 mL of *n*-butyllithium (9.8 mmol, 2.4 M in hexane) was slowly added dropwise. The reaction mixture was then stirred at -78 °C for 1 h and at room temperature

for 1 h. Subsequently, chlorotrimethylstannane (1.0 M in hexane, 11.7 mL) was added at -78 °C and the mixture was stirred over night at room temperature. Then, the mixture was extracted with diethyl ether, the combined organic phase was washed with water three times, and dried over MgSO<sub>4</sub>. After the removal of solvent, the crude product was purified by recrystallization using ethanol to obtain the target compound **BDTTS** as a yellowish-brown solid (3.4 g, yield 81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS), δ (ppm): 7.69-7.60 (m, 2H), 7.34 (d, *J* = 3.2 Hz, 2H), 7.22 (d, *J* = 3.3 Hz, 2H), 2.94 (d, *J* = 6.1 Hz, 4H), 1.74-1.68 (m, 2H), 1.52-1.40 (m, 8H), 1.29-1.27 (m, 24H), 0.95-0.82 (m, 12H), 0.51-0.31 (m, 18H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, TMS), (ppm): 143.26, 142.98, 137.28, 137.04, 132.45, 130.68, 128.24, 128.14, 121.91, 44.06, 37.79, 32.92, 32.58, 31.82, 29.57, 28.73, 26.47, 22.93, 22.66, 14.11, 14.10, -8.33. MALDI-TOF MS (*m/z*) for C<sub>48</sub>H<sub>74</sub>S<sub>6</sub>Sn<sub>2</sub>, Calcd: 1080.22, Found: 1080.33.

#### *Synthesis of **PSBZ***

In a dry 50 mL flask, Pd(PPh<sub>3</sub>)<sub>4</sub> (15 mg) was added to a solution of **BDTTS** (324 mg, 0.30 mmol) and **BTz-2F** (194 mg, 0.30 mmol) in 12 mL degassed toluene under nitrogen and stirred vigorously at 110 °C for 8 h until the reaction system becomes a viscous state. Then the mixture was poured into methanol (100 mL) and the precipitation was occurred. The polymer was dissolved in chloroform and the solution was filtered through a silica gel column. The collected chloroform solution was concentrated and precipitated with methanol to get the dark-red solid (213 mg, 57%). Anal. Calcd for C<sub>68</sub>H<sub>87</sub>F<sub>2</sub>N<sub>3</sub>S<sub>8</sub> (%): C, 65.81; H, 7.07. Found (%): C, 64.72; H, 7.59. Mn = 30.5 kDa, PDI = 2.28.

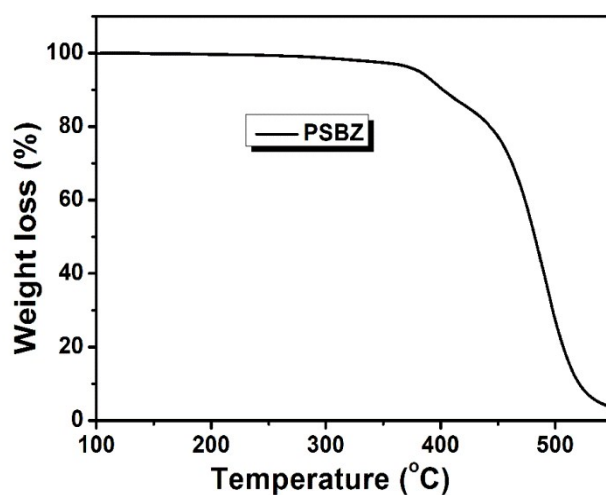
#### **Experimental Section**

*Measurements:*  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured in  $\text{CDCl}_3$  on Bruker AV 400 MHz FT-NMR spectrometer. Mass spectra were obtained with a Shimadzu QP2010 spectrometer. Elemental analysis was carried out on a flash EA1112 analyzer. Gel Permeation Chromatography (GPC) was carried out on Agilent Technologies PL-GPC-220 at 160 °C, where 1,2,4-trichlorobenzene as the eluent and polystyrene as the standard. Elemental analysis was performed on a flash EA1112 analyzer. Thermogravimetric analysis (TGA) was measured on a Perkin-Elmer TGA-7 at a heating rate of 10 °C/min under inert atmosphere. Differential scanning calorimetry (DSC) was taken on a TA DSC Q-200 at a scan rate of 2 °C/min under inert atmosphere. UV-vis absorption spectrum was recorded on a UV-Vis-NIR Spectrophotometer of Agilent Technologies Cary Series, in which the extinction coefficient was defined by the absorption intensity of the active layer with a thick of 1 cm (80 nm for PSBZ). The electrochemical cyclic voltammetry (CV) was taken on a Electrochemical Workstation of Zahner Ennium IM6 in a acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ), where glassy carbon disk,  $\text{Ag}/\text{Ag}^+$  electrode, and Pt wire as working electrode, reference electrode and counter electrode, respectively. 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 taken on an Edinburgh Instrument FLS 980. Atomic force microscopy (AFM) measurements were performed on a Dimension 3100 (Veeco) Atomic Force Microscope in the tapping mode. Transmission electron microscopy (TEM) was performed using a Tecnai G2 F20 S-TWIN instrument at 200

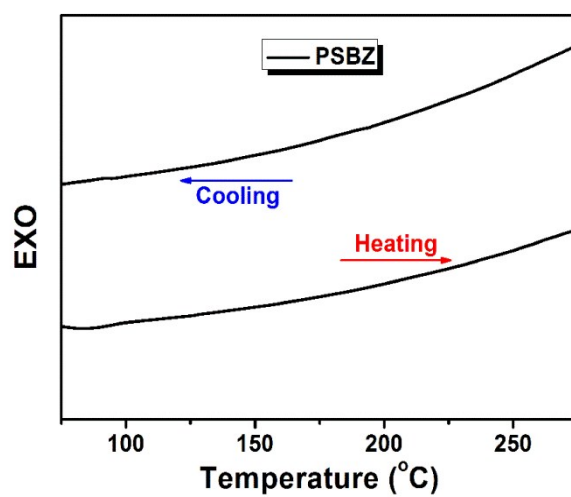
kV accelerating voltage, where the polymer:ITIC films were prepared by the following processing techniques for the TEM measurement: The polymer:ITIC films were spin-cast on the ITO/PEDOT:PSS substrates, and then the resulting substrates with the polymer:ITIC films were submerged in deionized water to make these polymer:ITIC films float onto the water/air interface, and finally the floated polymer:ITIC films were picked up on unsupported 200 mesh copper grids.

***Device Fabrication and characterization:*** The PSC devices structure was ITO/ZnO/PSBZ:ITIC/MoO<sub>3</sub>/Al. In an ultrasonic bath, the ITO-coated glass (10  $\Omega$ /sq) was cleaned with deionized water, acetone and isopropanol, respectively. After UV-ozone treating for 20 min, then the ZnO layer was deposited by spin-coating at 5000 rpm from a ZnO solution on the ITO substrate and then baked in the titanium plate under 200 °C for 2 h. In a nitrogen glove box containing less than 5 ppm moisture and oxygen, the active layers were then deposited atop the ZnO layer by spin-coating a CB solution of PSBZ:ITIC with a blend concentration of 20 mg/mL. The thickness of the active layers was controlled by adjusting the spin speed during the spin-coating process and measured by a KLA Tencor D-100 profilometer. Finally, 10 nm MoO<sub>3</sub> and 80 nm Al were evaporated on the active layer under vacuum at a pressure of ca.  $4 \times 10^{-4}$  Pa, and through a shadow mask to determine the active area of the devices ( $\sim 4 \times 5$  mm<sup>2</sup>). The PCE values of the PSCs were measured under a illumination of AM 1.5G (100 mW/cm<sup>2</sup>) using a SS-F5-3A solar simulator (AAA grade,  $50 \times 50$  mm<sup>2</sup> photobeam size) of Enli Technology CO., Ltd.. A  $2 \times 2$  cm<sup>2</sup> monocrystalline silicon reference cell (SRC-00019) was purchased from Enli Technology CO., Ltd.. Mask made by laser beam cutting

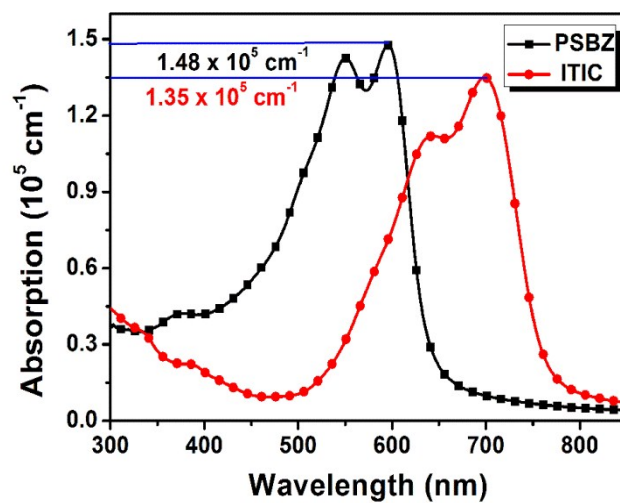
technology with a defined area of 9 mm<sup>2</sup> was used to determine the effective area for accurate measurement. All the measurements with mask or without mask gave consistent results with relative errors within 2%. PCE statistics were obtained using 20 individual devices fabricated under the same conditions. The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 of Enli Technology CO., Ltd.. The light intensity at each wavelength was calibrated with a standard single crystal Si photovoltaic cell.



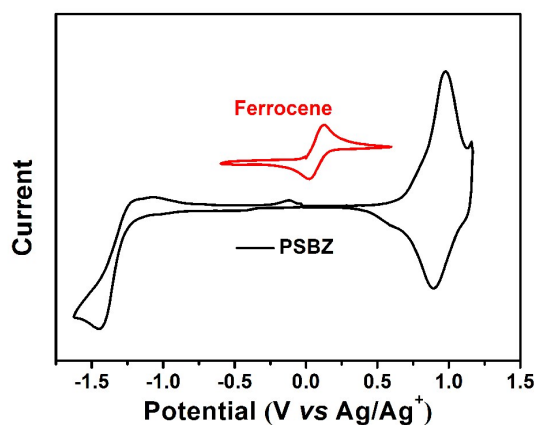
**Fig. S1** TGA curve of PSBZ at a scan rate of 10 °C/min under nitrogen atmosphere.



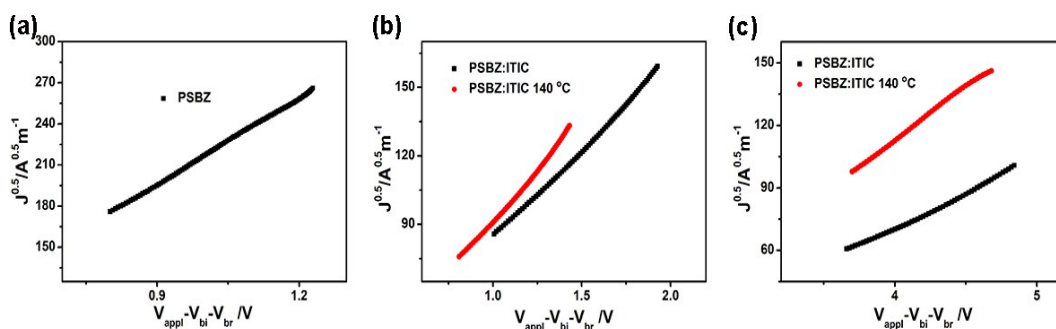
**Fig. S2** DSC curve of PSBZ at a scan rate of 2 °C/min under nitrogen atmosphere.



**Fig. S3** UV-vis absorption spectra of PSBZ and ITIC in films.



**Fig. S4** Cyclic voltammograms of PSBZ film on a glassy carbon electrode measured in a 0.1 mol L<sup>-1</sup> Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile solution at a scan rate of 50 mV s<sup>-1</sup>.

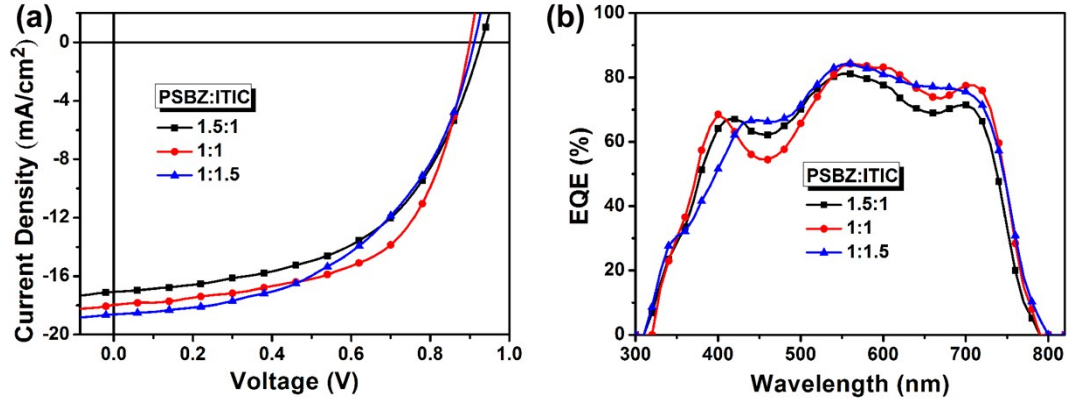


**Fig. S5** The  $J$ - $V$  curves of (a) and (b) the hole-only devices with the structure of ITO/PEDOT:PSS/polymer or actively layer/MoO<sub>3</sub>/Al, and (c) the electron-only devices with the structure of ITO/ZnO/actively layer/Ca/Al according to the SCLC model.

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

	hole mobilities (cm <sup>2</sup> /Vs)	electron mobilities (cm <sup>2</sup> /Vs)
PSBZ	$7.56 \times 10^{-3}$	
blends: as-cast	$1.07 \times 10^{-4}$	$5.16 \times 10^{-4}$



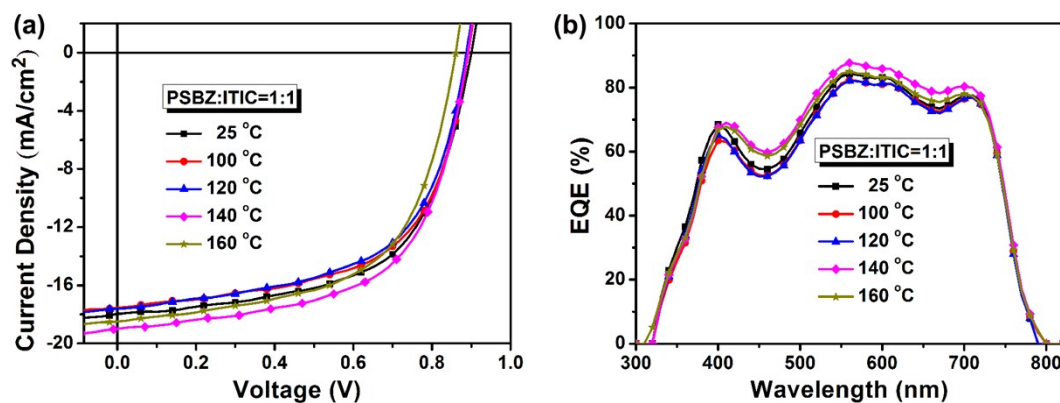


**Fig. S6** (a) The  $J$ - $V$  curves and (b) EQE curves of the PSCs based on PSBZ:ITIC with different D/A ratios (w/w) under the AM 1.5G illumination ( $100 \text{ mW cm}^{-2}$ ).

**Table S2** Photovoltaic performance parameters of the PSCs based on PSBZ:ITIC with different D/A ratios (w/w) under the AM 1.5G illumination ( $100 \text{ mW cm}^{-2}$ ).

D/A ratios	$V_{oc}$	$J_{sc}$	$FF$	$PCE_{max}$
[w/w]	[V]	[mA cm <sup>-2</sup> ]	[%]	[%]
1:1.5	0.93	17.1	54	8.5
	(0.93 ± 0.01)	(16.8 ± 0.2)	(52 ± 1)	(8.1 ± 0.2)
1:1	0.90	18.0	60	9.7
	(0.90 ± 0.01)	(17.6 ± 0.3)	(58 ± 1)	(9.4 ± 0.2)
1:1.5	0.91	18.4	51	8.5
	(0.91 ± 0.01)	(17.8 ± 0.4)	(49 ± 2)	(8.1 ± 0.3)

The average values and standard deviations of device parameters based on 20 devices are shown in brackets.



**Fig. S7** (a) The  $J$ - $V$  curves and (b) EQE curves of the PSCs based on PSBZ:ITIC (1:1, w/w) with different annealing temperatures under the AM 1.5G illumination ( $100 \text{ mW cm}^{-2}$ ).

**Table S3** Photovoltaic parameters of the PSCs based on PSBZ:ITIC (1:1, w/w) with different annealing temperatures under the AM 1.5G illumination ( $100 \text{ mW cm}^{-2}$ ).

Annealing temperature [°C]	$V_{oc}$ [V]	$J_{sc}$ [ $\text{mA cm}^{-2}$ ]	$FF$ [%]	$PCE_{max}$ [%]
as-cast	0.90 ( $0.90 \pm 0.01$ )	18.0 ( $17.6 \pm 0.3$ )	60 ( $58 \pm 1$ )	9.7 ( $9.4 \pm 0.2$ )
100	0.89 ( $0.89 \pm 0.01$ )	17.6 ( $17.1 \pm 0.3$ )	60 ( $57 \pm 1$ )	9.3 ( $9.0 \pm 0.2$ )
120	0.89 ( $0.89 \pm 0.01$ )	17.6 ( $17.2 \pm 0.2$ )	59 ( $57 \pm 2$ )	9.2 ( $8.8 \pm 0.3$ )
140	0.89 ( $0.89 \pm 0.01$ )	19.0 ( $18.6 \pm 0.3$ )	62 ( $60 \pm 1$ )	10.5 ( $10.2 \pm 0.2$ )
160	0.86 ( $0.86 \pm 0.01$ )	18.5 ( $17.8 \pm 0.4$ )	59 ( $56 \pm 2$ )	9.4 ( $8.8 \pm 0.4$ )

The average values and standard deviations of device parameters based on 20 devices are shown in brackets.

