## **Supporting Information**

## High-Efficiency Organic Solar Cells Enabled by Halogen

## Modification of Polymers Based on 2D Conjugated Benzobis(thiazole)

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#### Materials

All reactions were carried out in argon atmosphere. Common solvents were dried and purified by standard procedures. Column chromatography characterizations were performed with the use of silica gel (200-300 mesh). Compounds **1** was synthesized according to the literature methods.<sup>[1]</sup> Other reagents were purchased from commercial sources and used directly unless otherwise noted.

#### **General characterization**

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using a Bruker AVANCE-III 600 spectrometer with tetramethylsilane (TMS) as an internal standard. Mass spectra were measured in the MALDITOF mode. Elemental analysis was performed on a standard elemental analyzer. The molecular weights of the polymers were measured by GPC using 1,2,4-trichlorobenzene (TCB) as the solvent and polystyrene as the standard at 150 °C. TGA was performed on a SDT Q600 setup with a heating rate of 10 °C/min under nitrogen atmosphere. UV-vis absorption spectra were obtained on a Perkin Elmer Lambda 25 spectrophotometer. All film samples were spin-casted on quartz glass substrates. Cyclic voltammetry was measured on a CHI660D electrochemical workstation in a solution of tetrabutylammonium hexafluorophosphate ( $Bu_4NPF_6$ , 0.1

M) in acetonitrile at a scan rate of 100 mV/s. The three-electrode system was composed of a glass carbon electrode coated with the sample film as the working electrode, a Pt wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple was used as an internal reference. The HOMO levels of the polymers were determined using the oxidation onset value. Onset potentials are values obtained from the intersection of the two tangents drawn at the rising current and the baseline changing current of the CV curves. Atomic force microscopy (AFM) measurements were performed using an Agilent 5400 AFM in tapping mode under ambient conditions. The ground-state geometries of BDT-DTBT molecules were fully optimized with DFT method under B3LYP/6-31G(d, p) level.<sup>[2]</sup> For the 2D-GIWAXS characterizations, thin films of the polymers spin-coated on silicon substrates were used. Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline with detector Pilatus3R 1M, Dectris (X-ray Source: MetalJet-D2, Excillum).

### **Fabrication of Photovoltaic Devices**

PSC Conventional devices were fabricated with the configuration of ITO/PEDOT:PSS/Polymer:IT-4F/PDINO/Al. The ITO-coated glass substrates with a nominal sheet resistance of 15  $\Omega$ /sq were cleaned in an ultrasonic bath with detergent, ultrapure water, acetone, and isopropyl alcohol. After a 6 min oxygen plasma treatment, a thin layer of PEDOT:PSS (30 nm) was spin-coated onto the ITO anode and then dried at 160 °C for 20 min. The polymer and IT-4F were dissolved in chlorobenzene with a concentration of 10 mg/mL for polymer. The solution was stirred several hours at room temperature and spin-coated on the PEDOT:PSS layer. The thickness of the active layer was ~110 nm. Then a thin layer of PDINO was spin-coated onto the active layer at 4000 rpm for 30 s from the methanol solution (1.0 mg/mL). Finally, 100 nm Al layers were successively thermally evaporated onto the active layer at a pressure of  $4.0 \times 10^{-10}$ <sup>4</sup> Pa. The active area of the device in this work was 0.1 cm<sup>2</sup>. The current density-voltage (J-V) characteristics were recorded with a Keithley 2420 source measure unit under AM 1.5G illumination (100 mW/cm<sup>2</sup>) from a Newport solar simulator. A standard silicon

solar cell was used to calibrate the light intensity. The external quantum efficiencies (EQE) of the PSCs were measured using a certified Newport incident photon conversion efficiency (IPCE) measurement system.

#### **Mobility Measurements**

Hole-only devices were fabricated using the architectures ITO/PEDOT:PSS/Polymer:IT-4F/MoO<sub>3</sub>/Al. The mobility was extracted by fitting the current density-voltage curves using space charge limited current (SCLC),<sup>[3]</sup> which is described by the equation,

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_h \frac{V^2}{d^3}$$

where *J* is the current,  $\mu_h$  is the zero-filed mobility, and  $\varepsilon_0$  and  $\varepsilon_r$  are the permittivity of free space and relative permittivity of the material, respectively. *V* is the effective voltage, and *d* is the thickness of the organic layer. The effective voltage can be obtained by subtracting the built-in voltage ( $V_{bi}$ ) and the voltage drop ( $V_s$ ) from the substrate's series resistance from the applied voltage ( $V_{appl}$ ),  $V = V_{appl} - V_{bi} - V_s$ . The hole and electron mobility can be calculated from the slope of the  $J^{1/2} - V$  curves.

## Synthesis and characterization of polymers



Synthesis of 4,8-bis(5-(2-hexyldecyl)thiophen-2-yl)-2,6-di(thiophen-2-yl)benzo [1,2-d:4,5-d']bis(thiazole) (2)

Compound 1 (1.41g, 1.33 mmol), trimethyl(thiophen-2-yl)stannane (988 mg, 4.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> were dissolved in 30 mL of anhydrous toluene, and deoxygenated by argon for 30 min. The mixture was stirred at 115 °C for 24 hours. The mixture was

poured into water, extracted with dichloromethane, and dried over anhydrous  $Na_2SO_4$ . After concentration, the residue was purified by column chromatography to afford the product as a yellow solid (1.05 g, 81%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.86 (d, *J* = 3.6 Hz, 2H), 7.73 (d, *J* = 3.6 Hz, 2H), 7.52 (d, *J* = 4.9 Hz, 2H), 7.18-7.14 (m, 2H), 6.92 (d, *J* = 3.6 Hz, 2H), 2.90 (d, *J* = 6.6 Hz, 4H), 1.78 (br, 2H), 1.46-1.21 (m, 48H), 0.92-0.84 (m, 12H).

# Synthesis of 2,6-bis(5-bromothiophen-2-yl)-4,8-bis(5-(2-hexyldecyl)thiophen-2-yl) benzo[1,2-d:4,5-d']bis(thiazole) (3)

In a dry flask, compound **2** (480 mg, 0.49 mmol) was dissolved in 10 ml anhydrous THF under argon and cooled to -78 °C and n-BuLi (1.2 mL, 1.6 M in hexane) was added dropwise. The solution was stirred for two hours in the cold bath. After this period, a solution of tetrabromomethane (492 mg, 1.48 mmol) in 5 ml anhydrous THF was added. The reaction mixture was gradually warmed to room temperature and stirred overnight. The mixture was poured into water, extracted with dichloromethane, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After concentration, the residue was purified by column chromatography to afford the product as a yellow solid (375 mg, 63%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 (d, *J* = 3.6 Hz, 2H), 7.39 (d, *J* = 3.9 Hz, 2H), 7.09 (d, *J* = 3.9 Hz, 2H), 6.88 (d, *J* = 3.6 Hz, 2H), 2.89 (d, *J* = 6.5 Hz, 4H), 1.77 (br, 2H), 1.46-1.23 (m, 48H), 0.93- 0.84 (m, 12H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  159.4, 147.9, 147.36, 139.2, 136.3, 132.6, 131.0, 128.5, 128.4, 125.1, 121.5, 117.7, 39.9, 34.5, 33.4, 32.0, 31.9, 30.1, 29.7, 29.4, 26.8, 26.7, 22.8, 22.7, 14.2, 14.1. HRMS (APCI) *m/z* calcd for C<sub>56</sub>H<sub>74</sub>Br<sub>2</sub>N<sub>2</sub>S<sub>6</sub> [M+H]<sup>+</sup>: 1125.2616, found: 1125.2615.

#### General procedure for the synthesis of polymers



Monomer **BDT-X** (0.05 mmol), monomer **3** (0.05 mmol),  $Pd_2(dba)_3$  (0.9 mg) and  $P(o-tol)_3$  (1.8 mg) were mixed in 10 mL of toluene. The flask was purged three times with successive vacuum and argon filling cycles. The reaction mixture was stirred for 24 h at 120 °C under argon atmosphere. After cooling to room temperature, the mixture was precipitated in 100 mL methanol. The precipitate was filtered and washed with methanol, acetone and  $CH_2Cl_2$  successively in a Soxhlet apparatus to remove catalyst residues and oligomers. Finally, the polymer was extracted with chloroform. The chloroform fraction was concentrated and precipitated in methanol. The precipitate was filtered and dried in vacuum at 40 °C overnight to give the product.

PBB-H: 65 mg (yield: 84%). HT-GPC:  $M_n = 147$  kDa;  $M_w = 316$  kDa; PDI = 2.15. PBB-F: 64 mg (yield: 81%). HT-GPC:  $M_n = 35$  kDa;  $M_w = 78$  kDa; PDI = 2.23. PBB-Cl: 72 mg (yield: 89%). HT-GPC:  $M_n = 77$  kDa;  $M_w = 182$  kDa; PDI = 2.37.



**Figure S1**. TGA curves of the polymers measured at a heating rate of 10 °C min<sup>-1</sup> under nitrogen.



**Figure S2**. Theory calculated optimized molecular orbitals (a) and geometries (b) of polymers by DFT calculation at the B3LYP/6-31G(d) level (alkyl chains were ignored in order to simplify calculations).



**Figure S3**. Cyclic voltammograms of PBB-H, PBB-F and PBB-Cl on glassy carbon electrodes in 0.1 M  $Bu_4NPF_6$  in CH<sub>3</sub>CN at a scan rate of 100 mV s<sup>-1</sup>.



**Figure S4**. Recorded photovoltaic parameters in the devices with IT-4F as the acceptor materials.



Figure S5. J-V curves and photovoltaic parameters (inset) of the OSCs based on

another batch of PBB-H and PBB-Cl with Mn/PDI of 48KDa/2.35 and 49KDa/2.23, respectively.



**Figure S6**. Hole-only diodes made with pristine polymer (a) and optimized blends (b). The experimental data (hollow symbols) are fitted using the space-charge-limited current (SCLC) model (solid lines).



Figure S7. Line-cut profiles of GIWAXS patterns for (a) pristine and (b) blend films.

D:A Ratio	Additive	$V_{\rm OC}$ [V]	$J_{\rm SC}$ [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]
1:0.8		0.87	20.7	62.4	11.2
1:1		0.86	21.1	62.5	11.4
1:1.2		0.87	20.2	62.7	11.0
1:1 <sup>a</sup>		0.87	20.7	65.1	11.7
1:1	DPE	0.82	21.1	59.1	10.2
1:1	DIO	0.71	5.28	26.8	1.0
1:1	CN	0.85	19.8	49.5	8.29
1:1 <sup>a</sup>	DPE	0.82	21.5	67.8	12.0

**Table S1**. Photovoltaic performance of the devices based on PBB-H:IT-4F with different processing conditions under the illumination of AM1.5G, 100 mW/cm<sup>2</sup>.

<sup>*a*</sup> Thermal annealing at 100 °C for 10 min.

**Table S2**. Photovoltaic performance of the devices based on PBB-F:IT-4F with different processing conditions under the illumination of AM1.5G, 100 mW/cm<sup>2</sup>.

D:A Ratio	Additive	$V_{\rm OC}$ [V]	$J_{\rm SC}$ [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]
1:0.8		0.95	20.0	57.0	10.8
1:1		0.94	19.0	64.6	11.6
1:1.2		0.93	18.0	63.6	10.7
1:1 <sup>a</sup>		0.94	18.9	67.8	12.0
1:1	DPE	0.93	21.3	62.2	12.4
1:1	DIO	0.86	13.1	42.0	4.7
1:1	CN	0.94	19.8	62.0	11.5
1:1 <sup>a</sup>	DPE	0.92	22.4	71.1	14.7

<sup>*a*</sup> Thermal annealing at 100 °C for 10 min.

**Table S3**. Photovoltaic performance of the devices based on PBB-Cl:IT-4F with different processing conditions under the illumination of AM1.5G, 100 mW/cm<sup>2</sup>.

D:A Ratio	Additive	$V_{\rm OC}$ [V]	$J_{\rm SC}$ [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]
1:0.8		0.93	18.3	57.6	9.8
1:1		0.95	19.1	57.9	10.5
1:1.2		0.95	18.7	55.2	9.8
1:1 <sup>a</sup>		0.95	20.2	56.0	10.7
1:1	DPE	0.95	20.4	63.8	12.4
1:1	DIO	0.70	5.48	32.0	1.23
1:1	CN	0.95	15.8	49.0	7.37
1:1 <sup>a</sup>	DPE, TA	0.94	21.8	72.5	14.8

<sup>*a*</sup> Thermal annealing at 100 °C for 10 min.

polymer	$V_{\rm OC}$ (V)	$J_{\rm SC}$ (mA cm <sup>-2</sup> )	FF	PCE (%)	Ref.
PTO2	0.91	21.5	0.75	14.7	[4]
PBDB-T-SF	0.88	20.5	0.72	13.1	[5]
PDTB-EF-T	0.90	20.7	0.76	14.2	[6]
PBTA-TF	0.73	20.2	0.72	10.6	[7]
PTQ10	0.93	20.5	0.67	12.8	[8]
PQSi05	0.91	21.4	0.69	13.6	[9]
PBDE-DFDT	0.86	21.8	0.75	14.2	[9]
PBTz-2	0.92	19.7	0.69	12.2	[10]
PB2F-2Cl	0.92	20.5	0.66	12.5	[11]
PB3TCN-BO	0.91	21.2	0.69	13.4	[12]
TPD-3F	0.91	20.5	0.74	13.8	[13]
PBDBTz-2	0.86	17.9	0.67	10.4	[14]
PPN4T-2F	0.82	16.3	0.64	8.5	[15]
PDTPO-BDTT	0.81	19.2	0.70	10.9	[16]
PBDT-PhI	0.86	16.0	0.60	8.2	[17]
PDBT(E)BTz-d	0.95	14.7	0.55	7.8	[18]
PDBT-Cl	0.82	22.3	0.69	12.6	[19]
PBT1-2Cl	0.85	19.7	0.76	12.7	[20]
PBDT-SF-2TC	0.93	20.7	0.57	11.1	[21]
PBDS-TZ	0.80	20.0	0.73	12.0	[22]
PBT-Cl	0.77	22.6	0.66	11.6	[23]
PBZ-ClSi	0.93	19.2	0.71	12.8	[24]
PBN-S	0.89	21.0	0.70	13.1	[25]
PhI-ffBT	0.91	19.4	0.76	13.3	[26]
PCl(4)BDB - T	0.84	20.6	0.71	12.3	[27]
PBB-Cl	0.94	21.8	0.72	14.8	This work

**Table S4**. Reported photovoltaic performance of the devices with IT-4F as the acceptor materials.

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