

## Supporting Information for

### Naphthalene Diimide-difluorobenzene-based Polymer Acceptors for All-polymer Solar Cells

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## 1. Experimental section

**Materials and instruments** All chemicals and reagents were purchased from Aldrich and used without further purification. ((2,5-difluoro-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethyl-stannane)<sup>[1]</sup> and 4,9-dibromo-2,7-bis(2-octyldodecyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8-(2H,7H)-tetraone<sup>[2]</sup> were prepared according reported procedures. All the reactions were conducted under nitrogen atmosphere.

Nuclear magnetic resonance (NMR) spectra were measured on a Bruker Ultrashield 400 Plus NMR spectrometer. Thermogravimetric analyses (TGA) were recorded on a TA instrument Q5000IR at a heating rate of 20 °C min<sup>-1</sup> under nitrogen atmosphere. Gel permeation chromatography (GPC) were conducted on a ShimadzuSIL-20A liquid chromatography instrument using 1,2,4-trichlorobenzene as eluent at 160 °C with polystyrene as standards. UV-vis spectra were recorded on a Perkin Elmer Lambda 20 UV-vis spectrophotometer. Elemental analyses were conducted on a Vario EL III elementary analysis apparatus. Cyclic voltammetry (CV) measurements were carried out on a CHI 600 electrochemical analyzer with a three-electrode cell in a deoxygenated anhydrous acetonitrile solution of tetra-*n*-butylammonium-hexafluorophosphate (0.1 M) under nitrogen atmosphere. A platinum disk electrode, platinum-wire, and Ag/AgCl electrode were used as a working electrode, a counter electrode, and a reference electrode, respectively, with the polymer thin film for evaluation coated on the surface of platinum disk electrode. The CV curves were calibrated using ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple as an external standard, which was measured under the same condition before and after the measurement of samples.

### Polymer Acceptor Synthesis

*Structurally Random Polymer Acceptor, PI.* A mixture of 2,5-bis(trimethylstannyl)thiophene (0.123 g, 0.3000 mmol), 1,4-dibromo-2,5-difluorobenzene (0.041 g, 0.1500 mmol), 4,9-dibromo-2,7-bis(2-octyldodecyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (0.148 g,

0.1500 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (5.5 mg, 0.0060 mmol), and P(*o*-tolyl)<sub>3</sub> (7.3 mg, 0.0120 mmol) in anhydrous toluene (10 mL) in a Schlenk tube was subjected to three cycles of evacuation and admission of nitrogen and subsequently stirred at 90 °C for 20 h (the reaction was stopped when the mixed solution in tubes started to turn into a gel). After polymerization, the reaction mixture was allowed to cool to room temperature and poured into stirring methanol to precipitate the polymer product. The precipitate was collected by filtration and was further purified by sequential Soxhlet extractions with methanol, acetone, hexane and chloroform each for 24 h. The residue after Soxhlet extractions was then extracted with chlorobenzene. The combined chlorobenzene extracts were concentrated and added dropwise to methanol with vigorous stirring to precipitate the polymer product as a purple solid (134 mg, 81% yield). GPC analysis (160 °C, TCB):  $M_n = 22.3$  kg/mol, PDI = 4.57;  $T_d$  (5% loss) = 440 °C. The polymer could not be successfully characterized by NMR spectroscopy in common deuterated solvent even at high temperatures due to its limited solubility in common deuterated solvents. Anal. Calcd for C<sub>68</sub>H<sub>90</sub>F<sub>2</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>: C, 74.14; H, 8.24; N, 2.54. Found: C, 73.52; H, 7.98; N, 2.83.

*Structurally Regioregular Polymer Acceptor, P2.* **P2** was prepared from a mixture of ((2,5-difluoro-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethylstannane) (0.091 g, 0.1500 mmol), 4,9-dibromo-2,7-bis(2-octyldodecyl)benzo[*lmn*][3,8] phenanthroline-1,3,6,8(2H,7H)-tetraone (0.148 g, 0.1500 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (5.5 mg, 0.0060 mmol), and P(*o*-tolyl)<sub>3</sub> (7.3 mg, 0.0120 mmol) in anhydrous toluene (10 mL) in a Schlenk tube and isolated in accordance with the procedure for **P1** as before, and the reaction was stopped when the mixed solution in tubes started to turn into a gel. The final purified polymer product was a purple solid (149 mg; 90% yield). GPC analysis (160 °C, TCB):  $M_n = 44.8$  kg/mol, PDI = 6.38.  $T_d$  (5% loss) = 480 °C. The polymer could not be successfully characterized by NMR spectroscopy in common deuterated solvent even at high temperatures due to its limited solubility in common deuterated solvents. Anal. Calcd for C<sub>68</sub>H<sub>90</sub>F<sub>2</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>: C, 74.14; H, 8.24; N, 2.54. Found: C, 74.57; H, 7.33; N, 2.65.

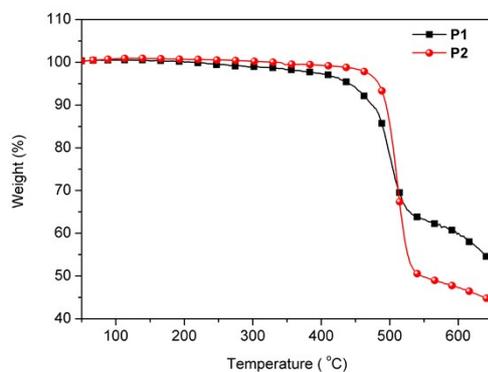
## ***2. All-PSC Device Fabrication and Characterization***

We used an all-PSC device structure of ITO/PEDOT:PSS/Polymer acceptor:polymer donor/LiF/Al. Patterned ITO glass substrate was firstly cleaned by deconex for 10 min at 120°C, and then cleaned with deionized water and acetone in an ultrasonic bath, followed by UV-ozone treatment. PEDOT:PSS was spin coated on the UV-ozone-treated substrate as anode buffer layer followed by annealing at 140°C for 10 min in air, thus forming a 30 nm film. An active layer solution of **P1** or **P2** with PTB7-Th at appropriate stoichiometry with 1 vol% DIO in *o*-DCB was prepared at a solid concentration of 12 mg mL<sup>-1</sup>. The solution was stirred at 80°C overnight before spin coated onto PEDOT:PSS-coated substrate in a glove box to form a ~100 nm active layer. The resulting active layer was annealed at 90°C for 30 minutes before LiF (1 nm) and Al (130 nm) were deposited on its surface under high vacuum thermal evaporation. The experimental all-PSC devices were characterized under 100 mW cm<sup>-2</sup> AM 1.5 G illumination conditions.

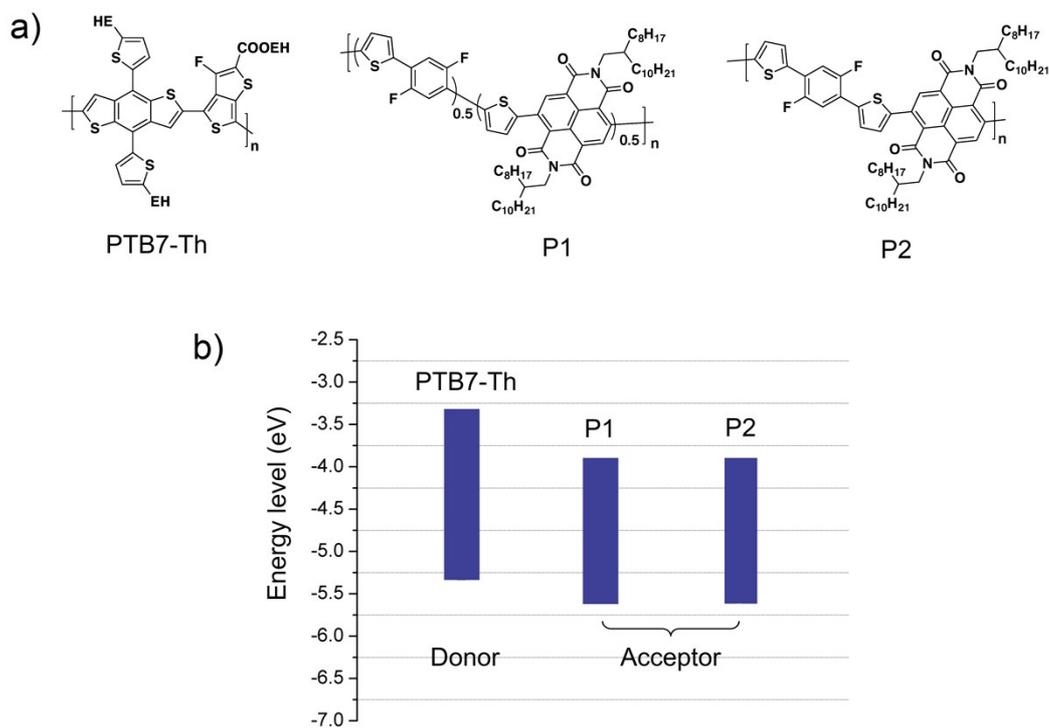
## ***3. Electron and Hole Mobility Measurement by J-V measurements***

The structure of the devices for mobility measurements was similar to the all-PSC devices. For the electron-only devices, the PEDOT:PSS layer is replaced with a 50 nm aluminum film which served as a hole blocking layer. For the hole-only devices, spiro-TPD:CuPc/Au was used as the top electrode. 10-nm Spiro-TPD:CuPc, prepared by thermal co-evaporation under high vacuum, was used as an electron blocking and trapping layer. A 130-nm thick gold layer was subsequently evaporated onto the Spiro-TPD:CuPc surface. After fabrication, the devices were put in an Oxford cryostat with a pressure of less than 20 mTorr for measurement.

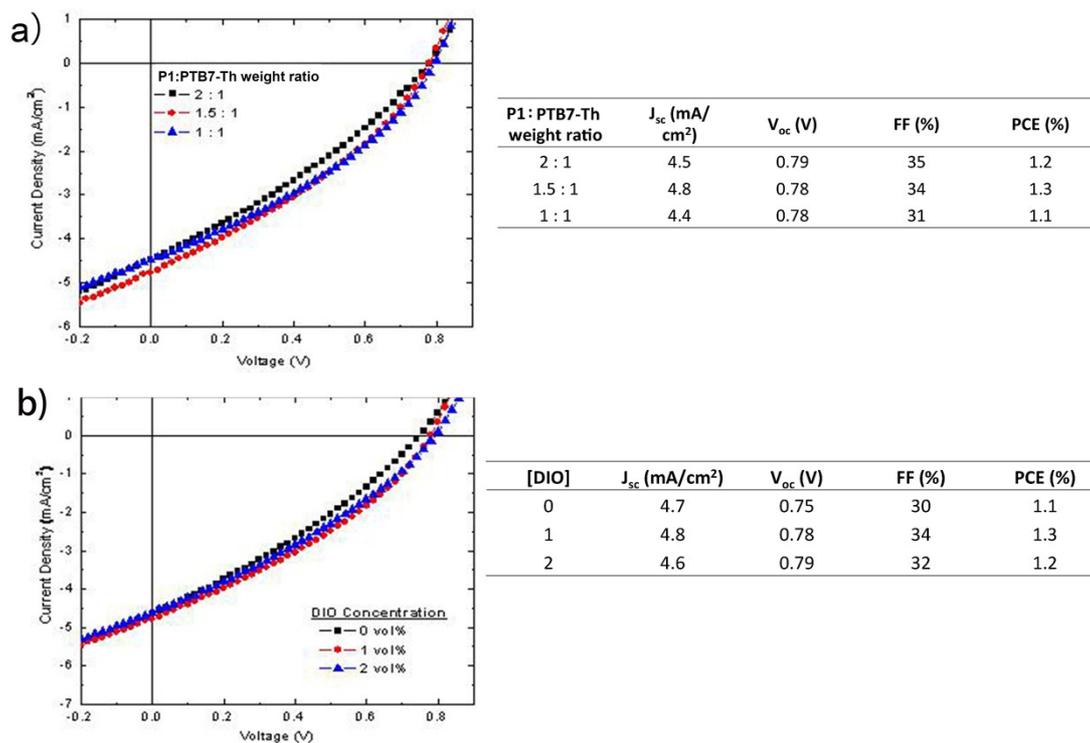
#### 4. Figures in ESI†



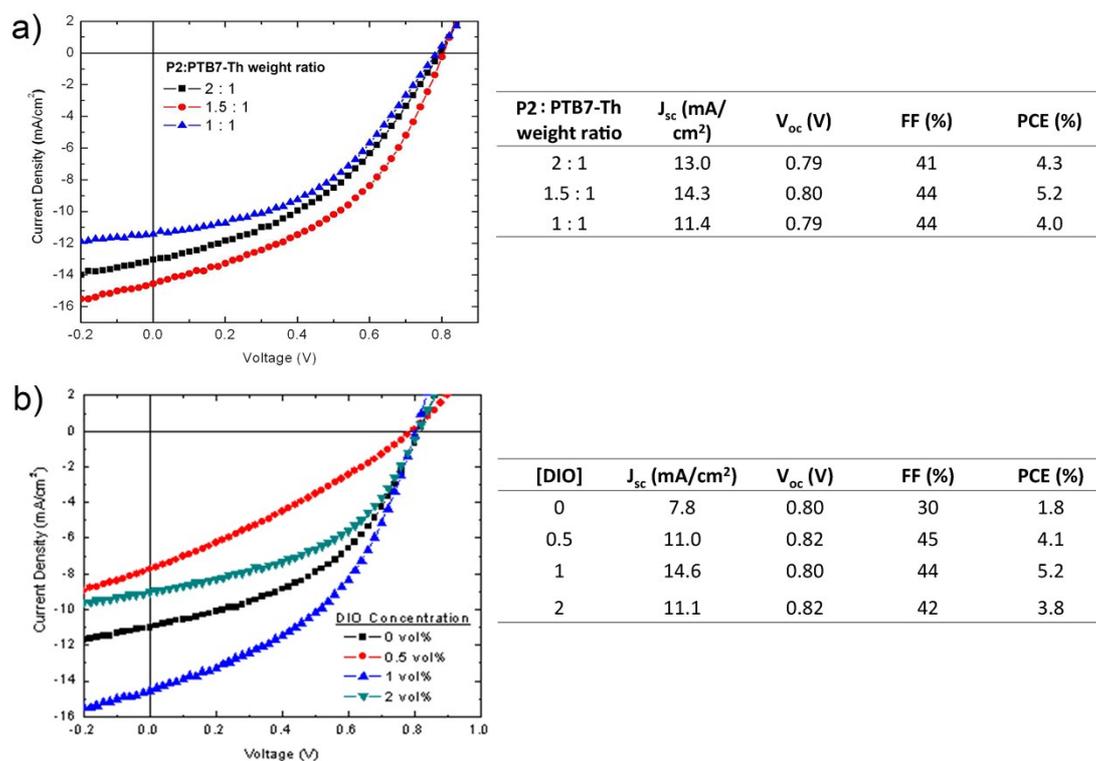
**Figure S1.** TGA plots of polymers at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere.



**Figure S2.** Chemical structures (a) and energy levels (b) of polymers PTB7-Th, **P1** and **P2**



**Figure S3.** Current density-voltage curves and data of all-PSC devices with different P1:PTB7-Th weight ratios in the active layers (a) and devices of P1:PTB7-Th with different DIO loadings (b).



**Figure S4.** Current density-voltage curves and data of all-PSC devices with different **P2:PTB7-Th** weight ratios in the active layers (a) and devices of **P2:PTB7-Th** with different DIO loadings (b).

## 5. Tables in ESI†

**Table S1.** Molecular weight and thermal properties of polymer acceptors, **P1** and **P2**

Polymer	$M_n^a$ [kDa]	$M_w^a$ [kDa]	PDI	$T_d^b$ [°C]
<b>P1</b>	22.3	285.9	4.57	440
<b>P2</b>	44.8	101.9	6.38	480

<sup>a</sup> Determined by GPC at 160 °C using 1,2,4-trichlorobenzene as an eluent against polystyrene standards. <sup>b</sup>5% weight loss temperature measured by TGA under nitrogen atmosphere.

**Table S2.** Optical and electrochemical properties of polymers **P1** and **P2**

Polymer	$\lambda_{\max}^a$ (nm)	$\lambda_{\max}^b(\epsilon^b)$ (nm)/(cm)	$E_g^{\text{opt}c}$ (eV)	$E_{\text{ox}}^{\text{onset}}/\text{LUM}$ O (V/eV)	HOMO <sup>d</sup> (eV)
<b>P1</b>	388, 570	388 (5.30×10 <sup>4</sup> ), 600 (4.19×10 <sup>4</sup> )	1.74	-0.44/-3.90	-5.64
<b>P2</b>	370, 585	388 (1.06×10 <sup>5</sup> ), 620 (5.67×10 <sup>4</sup> )	1.71	-0.44/-3.90	-5.61

<sup>a</sup> Measured in chlorobenzene solution. <sup>b</sup> Measured as thin film. <sup>c</sup> Optical band gap,

<sup>d</sup> Calculated from the LUMO energy level and optical band gap.

**Table S3.** Performance characteristics of all-PSCs with active layers of **P1**:PTBT-Th and **P2**: PTBT-Th (1:1.5, w/w) with 1 vol % DIO Additive (under Standard Solar Illumination Conditions)

Polymer acceptor	$V_{\text{oc}}$ (V)	$J_{\text{sc}}$ (mA/cm <sup>2</sup> )	FF (%)	PCE <sup>a</sup> (%)
<b>P1</b>	0.78	4.80	34	1.30 (1.11)
<b>P2</b>	0.80	14.3	44	5.20 (5.13)

<sup>a</sup> Average PCEs given in parentheses.

**Table S4.** The hole and electron mobilities of active blend layer (**P1**:PTB7-Th or **P2**:PTB7-Th blend (1:1.5,  $w_{(\text{Acceptor})}/w_{(\text{Donor})}$ ) with 1 vol % DIO Additive) investigated by the space charge limited current (SCLC) method

Active blend layer	$\mu_e$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_h$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_e/\mu_h$
<b>P1</b> :PTB7-Th	$1.3 \times 10^{-6}$	$7.3 \times 10^{-5}$	0.018
<b>P2</b> :PTB7-Th	$2.1 \times 10^{-4}$	$1.6 \times 10^{-4}$	1.313

### *Reference*

- [1] M. Christian, G. Eliot, M. Chris, T. Mukundan, *J. Mater. Chem. C* **2015**, 3, 8916.  
[2] Z. Fei, Y. Han, J. Martin, F. Scholes, M. Al-Hashimi, S. AlQaradawi, N. Stingelin, T. Anthopoulos, M. Heeney, *Macromolecules*, **2016**, 49, 6384.