

**Supporting information**

**Modifying the Chemical Structure of a Porphyrin Small Molecule with Benzothiophene Groups for the Reproducible Fabrication of High Performance Solar Cells**

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## 1. Materials

Tetrahydrofuran (THF) and toluene were distilled from sodium-benzophenone under nitrogen prior to being used. Triethylamine (NEt<sub>3</sub>), dimethoxyethane, CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> were distilled from CaH<sub>2</sub> prior to use. All reagents, unless otherwise noted, were obtained from Aldrich, Acros, and TCI Chemical Co. and used without further purification. All manipulations involving air-sensitive reagents were performed under an atmosphere of argon or N<sub>2</sub>. 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione were synthesized according to reported procedures.<sup>1</sup>

## 2. Instruments and methods

The chemical structures of the as-prepared compounds were identified by <sup>1</sup>H-NMR spectra measured on a Bruker AVANCE Digital 600MHz spectrometer in deuterated chloroform/benzene. Matrix assisted laser desorption/ionization mass spectrometry (MALDI-TOF MS) was acquired on a Bruker Daltonics BIFLEX III MALDI-TOF Analyzer using MALDI mode. Elemental analysis was measured on an Elementar vario EL cube. UV-Vis absorption spectra was obtained using a Shimadzu UV-3600 spectrophotometer. Photoluminescence measurements were carried out in neat and blend films with a FluorologMax-4 spectrofluorometer. Cyclic voltammetry (CV) data was collected on a CHI660C electrochemical workstation at scan rate of 50 mV s<sup>-1</sup> in the nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in acetonitrile (CH<sub>3</sub>CN). A glassy-carbon electrode coated with a thin **DPPEZnP-BzTBO** film, Pt wire and an Ag/AgCl (0.1 M) electrode were used as the working electrode, the counter electrode and the reference electrode, respectively. The atomic force microscopy (AFM) measurements were conducted on NanoScope NS3A system (Digital Instrument). The mobilities of the blend films of **DPPEZnP-BzTBO** with PC<sub>61</sub>BM were determined by fitting the dark current to the model of the space charge limited current (SCLC). Films were prepared by dissolving

**DPPEZnP-BzTBO** and PC<sub>61</sub>BM (1:1.2 w/w) in chlorobenzene (CB) with 7 vol% pyridine (PY) as additives (1% pyridine for **DPPEZnP-TEH**), followed by spin-coating on the top surface of a PEDOT: PSS substrate. The structure of hole-only and electron-only devices was ITO/PEDOT: PSS (40nm)/active layer/MoO<sub>3</sub> (10nm)/Al and ITO/ZnO (40nm)/active layer/PFN (10nm)/Al, and the mobilities were estimated by electric-field dependent SCLC method<sup>2</sup>.

### 3. Fabrication and characterization of photovoltaic devices

Solution-processed solar cell devices were fabricated as follows: Indium tin oxide (ITO) coated glass substrates were cleaned by sonication in acetone, detergent, distilled water, and isopropyl alcohol. After treated with an oxygen plasma for 5 min, 40 nm thick poly(styrene sulfonate)-doped poly(ethylene-dioxythiophene) (PEDOT:PSS) (Bayer Baytron 4083) layer was spin-coated on the ITO-coated glass substrates from aqueous solution (3000 rpm for 30 s). The substrates were subsequently dried at 130°C for 20 min in air and then transferred to a N<sub>2</sub>-glovebox. The active layers, composed of **DPPEZnP-BzTBO**/ **DPPEZnP-TEH** and PC<sub>61</sub>BM (1:1.2 w/w), were deposited on top of the PEDOT:PSS layer from CB with 7 vol% (1 vol% for **DPPEZnP-TEH**) pyridine as additives. The thicknesses of active layers were an average of 100 nm as measured by a profilometer. To obtain high photovoltaic performance, the films were thermal annealed (TA) at 110 °C for 10 minutes and solvent vapor annealed (SVA) by chloroform. The ultra-thin poly[(9,9-bis(3'-(N,N-dimethylamino)-propyl)-2,7-fluorene)]-alt-2,7-(9,9-dioctylfluorene) (PFN) layer was deposited by spin casting from a 0.02% (w/v) solution in methanol (from 2000 rpm for 30 s). Finally, Al (~100 nm) was evaporated with a shadow mask as the top electrode and the effective area was measured to be 0.16 cm<sup>2</sup>. The current-density-voltage (*J-V*) characteristics were measured with a Keithley 236 digital source meter under AM 1.5 solar simulator (Oriel model 91192) at 100 mW cm<sup>-2</sup>. The spectral response was measured

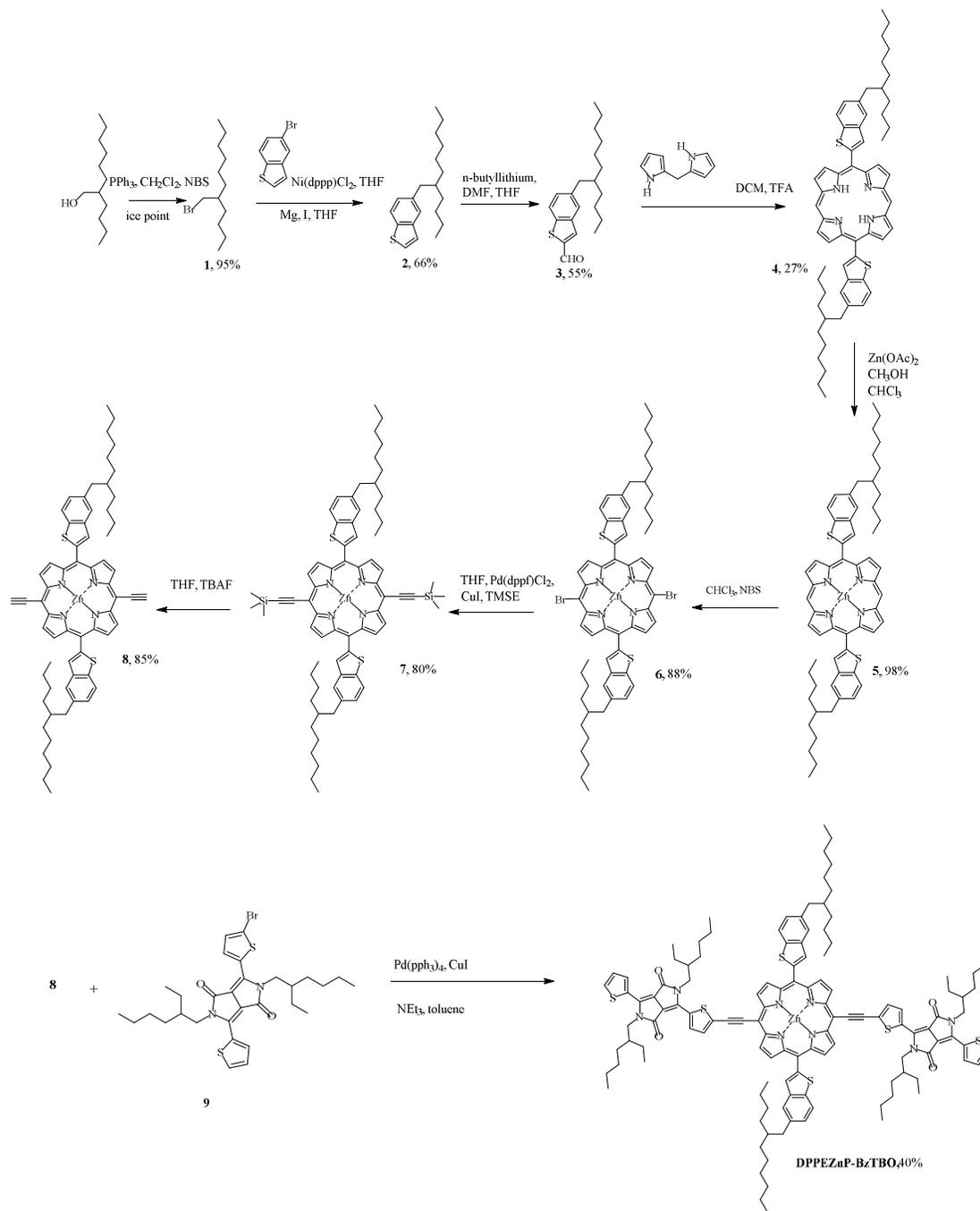
with a commercial photo modulation spectroscopic setup (Oriel). A calibrated Si photodiode was used to determine the photosensitivity.

SVA was conducted in a glove box filled with nitrogen. Chloroform (0.2 ml) were injected into a 30-mm glass Petri dish. The Petri dish was closed for 5 min to let the vapor saturate the treatment chamber. Then as-cast films were attached on the backside of the Petri dish lid, which was quickly swapped with the lid covering the solvent-containing Petri dish. The film was about 1 cm above the solvent level during the SVA. After certain duration, the film was removed from the treatment chamber. The optimal duration in this study was 80 s.

#### **4. Synthetic procedures and characterizations**

##### **5-(bromomethyl)undecane (1):**

2-butyloctan-1-ol (26.83 g, 143.81 mmol) and Triphenyl phosphine (56.61 g, 215.70 mmol) were dissolved into dichloromethane (200mL) and stirred in dark at 0 °C under argon atmosphere, N-bromosuccinimide (38.42g, 215.70mmol) was added in small portions. The mixture was allowed to warm to room temperature and stirred overnight. Then about half of the solvent was removed by rotary evaporator. The mixture was poured into petroleum ether (boiling point 60-90 °C, 200 mL) and the precipitate was removed by filtration and discarded. The filtrate was collected and the solvent removed. The resulting mixture was purified by column chromatography on silica gel using petroleum ether as eluent, yielding a colorless liquid (51.12g, 95%). <sup>1</sup>H NMR (600 MHz, Chloroform-d): δ 3.44 (d, 2 H), 1.60 (s, 1H), 1.16–1.45 (m, 16), 0.83–0.94 (m, 6 H).



**Scheme S1.** The synthetic route of **DPPEZnP-BzTBO**.

### **5-(2-butyloctyl)benzo[b]thiophene (2):**

A mixture of magnesium (2.73 g, 112.45 mmol), a small amount of iodine and anhydrous THF (50 mL) was heated to 60 °C under argon atmosphere. 5-(bromomethyl)undecane (14.01 g, 56.22 mmol) in anhydrous THF (10 mL) was added dropwise. The reaction mixture was refluxed for 2 h and then allowed to cool to room

temperature. The solution was added dropwise to a mixture of 5-bromobenzo[b]thiophene (8.00 g, 37.48 mmol), [1,3-bis(diphenylphosphino)propane]dichloronickel(II) (Ni-(dppp)<sub>2</sub>Cl<sub>2</sub>, 0.81 g, 1.49 mmol), and anhydrous THF (60 mL) at 0 °C. Then the mixture was allowed to warm to room temperature and stirred overnight. The mixture was quenched with saturated NH<sub>4</sub>Cl (100mL) and then washed with water. The crude product was dried with Na<sub>2</sub>SO<sub>4</sub> and further purified by column chromatography on silica gel using petroleum ether as the eluent to give a light yellow liquid (7.48 g, 66% yield). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*, δ): 7.78 (d, 1H), 7.59 (s, 1H), 7.41 (d, 1H), 7.28 (d, 1H), 7.16 (d, 1H), 2.65 (d, 2H), 1.67 (m, 1H), 1.36–1.25 (m, 16H), 0.90–0.87 (m, 6H).

#### **5-(2-butyloctyl)benzo[b]thiophene-2-carbaldehyde(3):**

To a solution of 5-(2-butyloctyl)benzo[b]thiophene (6.00 g, 19.83 mmol) in anhydrous THF (140 mL) cooled at -78 °C was added dropwise n-butyllithium (13.63 mL, 1.6 M in hexane, 21.81 mmol) under argon atmosphere. After 1 hour of stirring at -78 °C, N,N-Dimethylformamide (2.90 g, 39.66 mmol) was added dropwise. After 3h at -78 °C, the reaction mixture was allowed to warm to room temperature and stirred overnight. Then the mixture was quenched by saturated aqueous NH<sub>4</sub>Cl (50mL) and washed with water. The crude product was dried with Na<sub>2</sub>SO<sub>4</sub> and further purified by column chromatography on silica gel using a mixture of dichloromethane and petroleum ether (1:2) as the eluent to give a light yellow liquid (3.60 g, 55 %). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*, δ): 10.10 (s, 1H), 7.97 (s, 1H), 7.78 (d, 1H), 7.70 (s, 1H), 7.34 (d, 1H), 2.65 (d, 2H), 1.67 (m, 1H), 1.36–1.25 (m, 16H), 0.90–0.87 (m, 6H).

#### **5,15-bis(5-(2-butyloctyl)benzo[b]thiophen-2-yl)porphyrin (4)**

To a solution of 5-(2-butyloctyl)benzo[b]thiophene-2-carbaldehyde (6.00 g, 18.15 mmol) and di(1H-pyrrol-2-yl)methane (2.65 g, 18.15 mmol) in anhydrous dichloromethane (2 L) was added dropwise trifluoroacetic acid (1 mL) in anhydrous dichloromethane (50 mL) under argon atmosphere, and the reaction mixture was stirred overnight at room temperature.

2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (3.2 g) was added and the mixture was stirred at room temperature for an additional 2h. Then the solvent was removed, and the residue was purified by column chromatography on silica gel using dichloromethane as eluent to give a purple solid (2.23 g, 27 %). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*, δ): 10.27 (s, 2H), 9.41 (d, 4H), 9.33 (d, 4H), 8.11 (s, 2H), 8.02 (d, 2H), 7.90 (s, 2H), 7.43 (dd, 2H), 2.85 (m, 4H), 1.87 (m, 2H), 1.55-1.15 (m, 32H), 1.05-0.90 (m, 12H). -3.03 (s, 2H).

**5,15-bis(5-(2-butyloctyl)benzo[b]thiophen-2-yl)porphyrin zinc (5):**

To a solution of 4 (1.87 g, 2.05 mmol) in chloroform (150 mL) was added a solution of Zn(OAc)<sub>2</sub> (1.50 mg, 8.2 mmol) in methanol (36 mL). The reaction mixture was refluxed for 6 h, and then washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed, and the residue was recrystallization from CHCl<sub>3</sub>/methanol to give a red solid (1.96 g, 98%). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*, δ): 10.08 (s, 2H), 9.36 (d, 4H), 9.27 (d, 4H), 8.06 (s, 2H), 8.01 (d, 2H), 7.90 (s, 2H), 7.42 (dd, 2H), 2.85 (m, 4H), 1.87 (m, 2H), 1.55-1.15 (m, 32H), 1.02-0.90 (m, 12H).

**5,15-dibromo-10,20-bis(5-(2-butyloctyl)benzo[b]thiophen-2-yl)porphyrin zinc (6):**

To a solution of 5 (1.70 g, 1.74 mmol) and pyridine (35 mL) in chloroform (150 mL) was added N-Bromosuccinimide (681 mg, 3.83 mmol) at 0°C, and the mixture was stirred for 30 min. Then the mixture was allowed to warm up to room temperature and then stirred for 4 h. After the reaction was quenched by addition of acetone, the mixture was washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Then the solvent was removed, and the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (2:1) as the eluent to give 6 as a purple solid (1.70 g, 88%). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*, δ): 9.63 (d, 4H), 9.18 (d, 4H), 8.03(s, 2H), 7.94(d, 2H), 7.86 (s, 1H), 7.40 (dd, 2H), 2.83 (m, 4H), 1.85 (m, 2H), 1.60-1.15 (m, 32H), 1.15-0.75 (m, 12H)

**5,15-bis(trimethylsilyl)ethynyl)-10,20-bis(5-(2-butyloctyl)benzo[b]thiophen-2-yl)porphyrin zinc (7):**

6 (1.20 g, 1.06 mmol) was dissolved in anhydrous THF (50mL) and anhydrous triethylamine (25 mL) was added. The mixture was purged with nitrogen for 30 min. Then Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (37.1 mg, 0.053 mmol), CuI (10.60 mg, 0.053 mmol), and trimethylsilylacetylene (400 mg, 4 mmol) were added. After the mixture was stirred at room temperature for 3 days under nitrogen, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:1) to afford 7 as a green solid (989 mg, 80%). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*, δ): 9.56 (d, 4H), 9.17 (d, 4H), 8.06 (d, 2H), 7.98 (d, 2H), 7.90 (d, 2H), 7.42 (d, 2H), 2.85 (m, 4H), 1.88 (m, 2H), 1.65-1.30 (m, 32H), 1.15-0.85 (m, 12H), 0.75-0.55 (m, 18H).

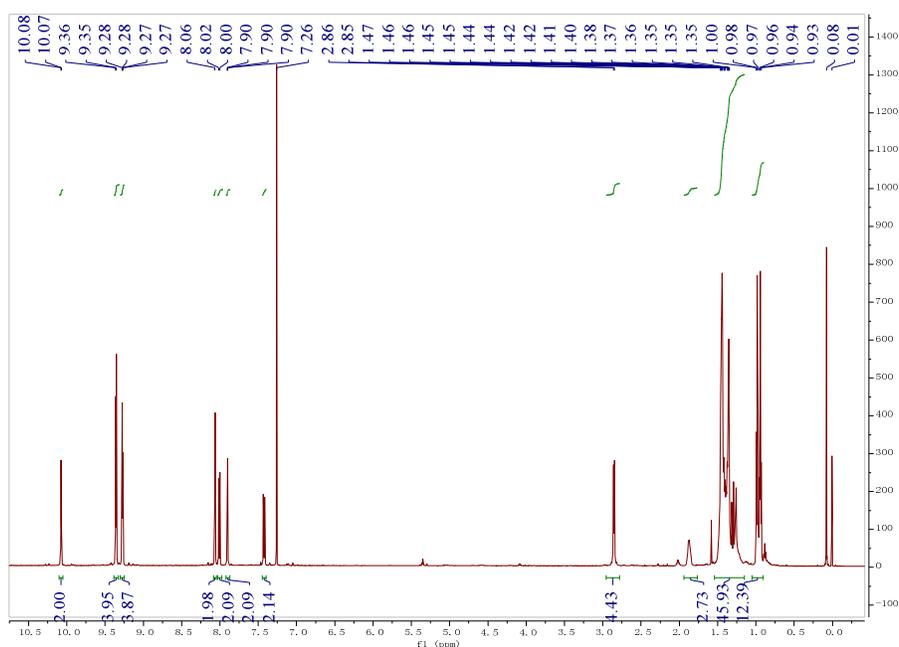
**5,15-diethynyl-10,20-bis(5-(2-butyloctyl)benzo[b]thiophen-2-yl)porphyrin zinc (8):**

Tetrabutylammonium fluoride (1.30 mL, 1M in THF) was added to a stirred solution of 7 (700 mg, 0.60 mmol) in THF (50 mL). After the mixture was stirred for 5 min, water was added to quench the reaction. The solution was extracted with chloroform and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent, the residue was purified by column chromatography on silica gel using ether/dichloromethane (1:1) and then by GPC to give 8 as a green solid (521 mg, 85%). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*, δ): 9.58 (d, 4H), 9.29 (d, 4H), 8.07 (d, 2H), 7.97 (d, 2H), 7.88 (d, 2H), 7.41 (d, 2H), 4.12 (s, 2H), 2.83 (m, 4H), 1.83 (m, 2H), 1.75-1.10 (m, 32H), 1.15-0.75 (m, 12H).

**5,15-bis(2,5-bis(2-ethylhexyl)-3,6-di-thienyl-2-yl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione-5'-yl-ethynyl)-10,20-bis(5-(2-butyloctyl)benzo[b]thiophen-2-yl)-porphyrin zinc (DPPEZnP-BzTBO):**

8 (54.20 mg, 0.053 mmol), 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (9, 95.99 mg, 0.159 mmol) were dissolved in anhydrous toluene (10 mL)

and anhydrous triethylamine (5 mL), and the mixture was deoxygenated with argon for 30 min before Pd(PPh<sub>3</sub>)<sub>4</sub> (11.54 mg, 0.01mmol) and CuI (1.91 mg, 0.01 mmol) were added. The mixture was stirred at 80 °C for 72 h under the protection of argon. After cooled to room temperature, the reaction was quenched with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Then the solvent was evaporated, and the residue was purified by column chromatography on silica gel and then by GPC to give the target product as a dark purple solid in 40% yield. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*, δ): 9.04 (br, 8H), 8.52 (br, 4H), 7.99 (br, 4H), 7.85 (br, 2H), 7.45 (br, 2H), 7.35 (br, 2H), 7.07 (br, 4H), 3.37 (m, 8H), 2.90 (m, 4H), 1.93 (br, 2H), 1.73 (m, 4H), 1.60-1.38 (m, 32H), 1.38-1.14 (m, 18H), 1.14-0.73 (m, 38H), 0.73-0.55 (m, 12H). MALDI-TOF m/z: Calcd for C<sub>124</sub>H<sub>144</sub>N<sub>8</sub>O<sub>4</sub>S<sub>6</sub>Zn, 2068.31; Found, 2068.02. Anal. calcd for C<sub>124</sub>H<sub>144</sub>N<sub>8</sub>O<sub>4</sub>S<sub>6</sub>Zn: C, 72.01; H, 7.02; N, 5.42%. Found: C, 72.43; H, 7.12; N, 4.85%.



**Figure S1.** <sup>1</sup>H NMR spectrum of 4 in CDCl<sub>3</sub> at room temperature.

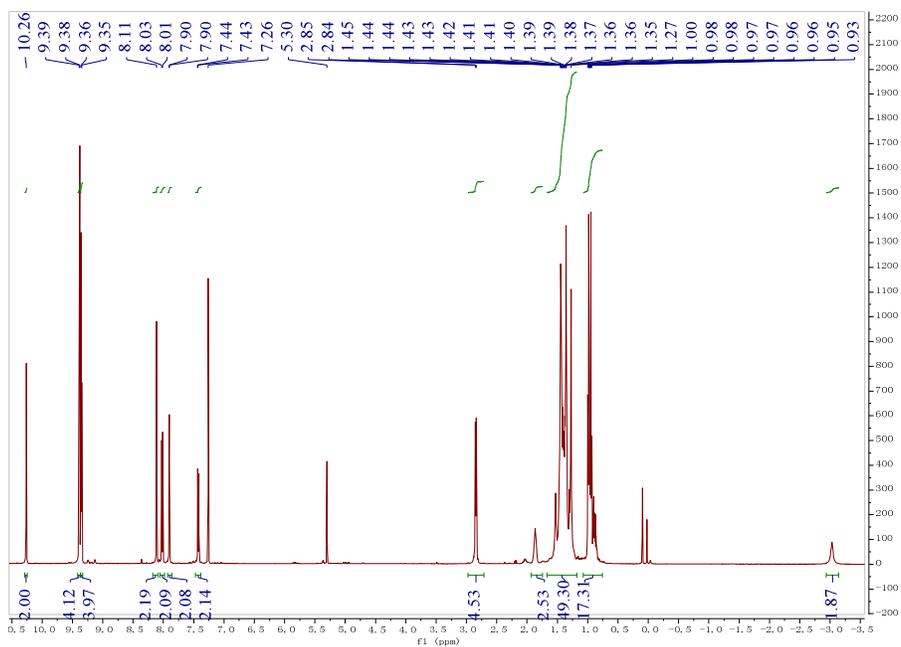


Figure S2.  $^1\text{H}$  NMR spectrum of 5 in  $\text{CDCl}_3$  at room temperature.

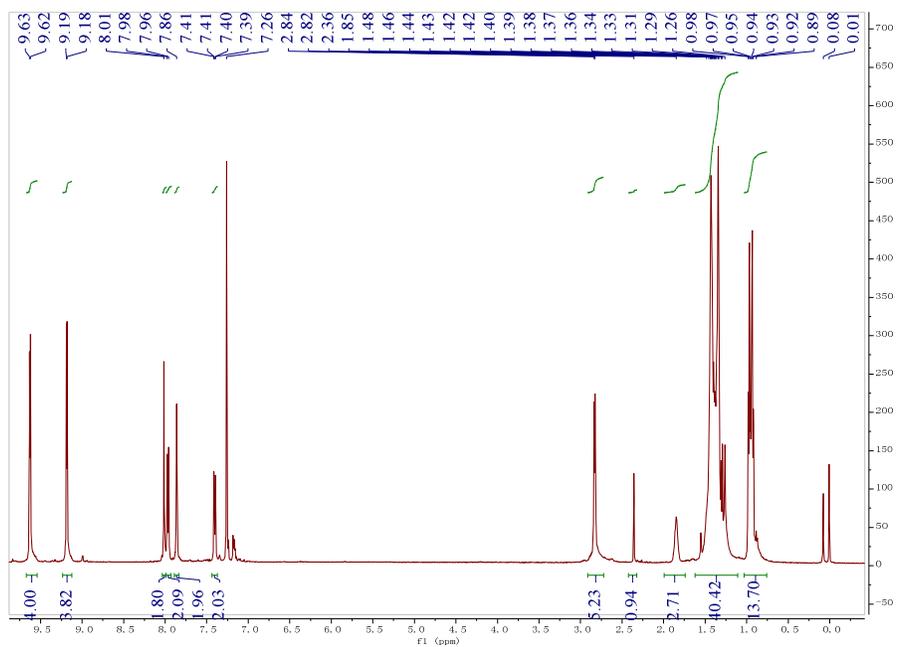
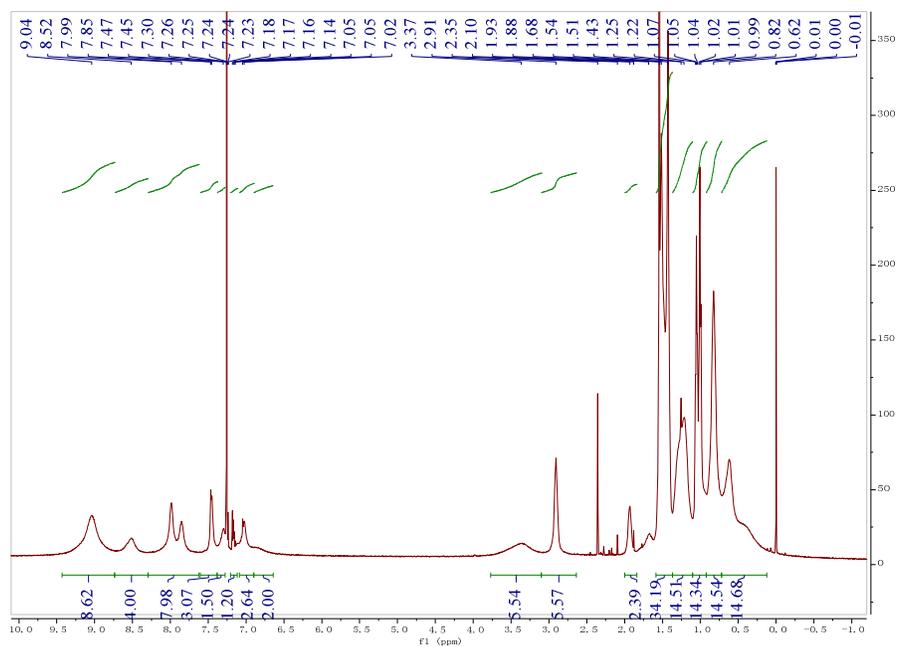
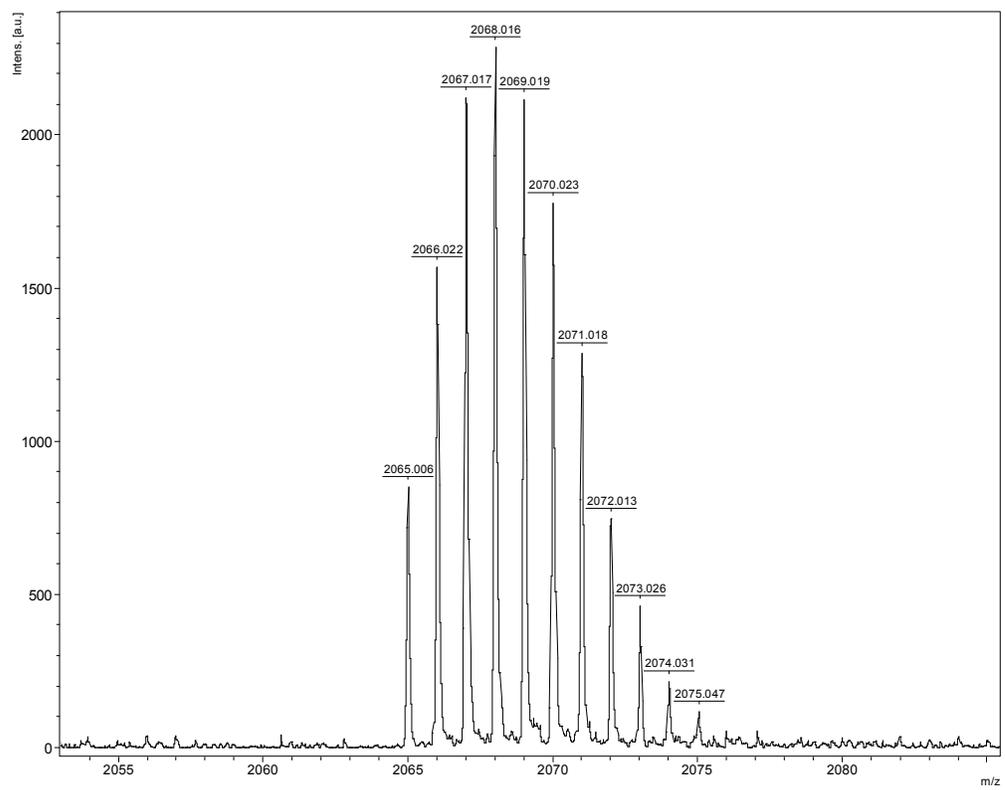
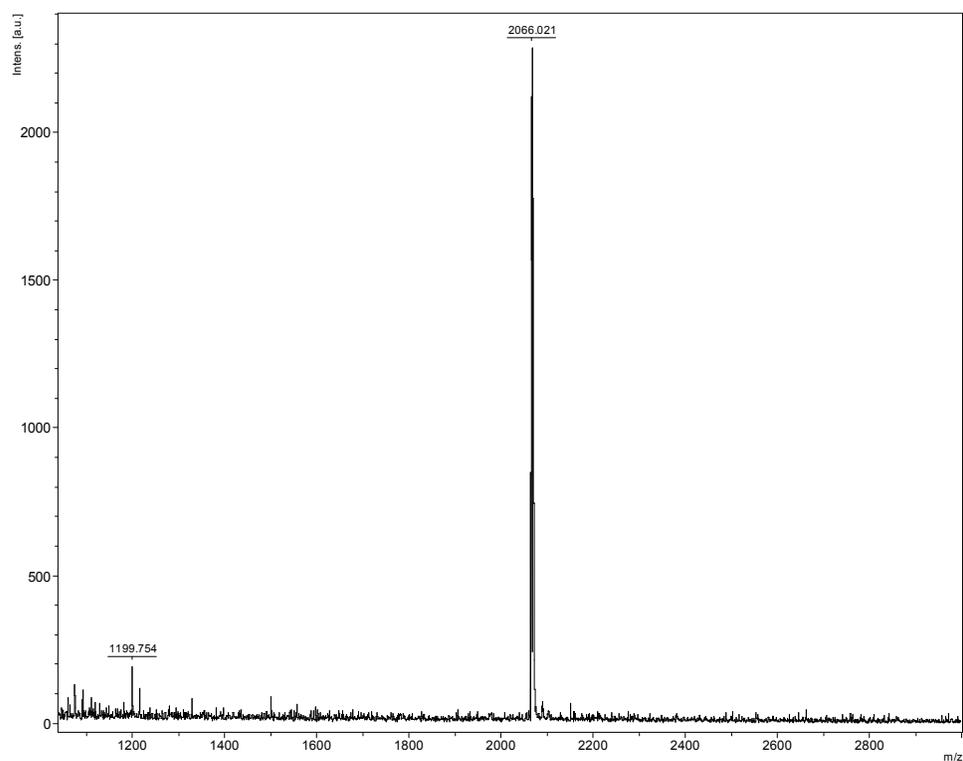


Figure S3.  $^1\text{H}$  NMR spectrum of 6 in  $\text{CDCl}_3$  at room temperature.

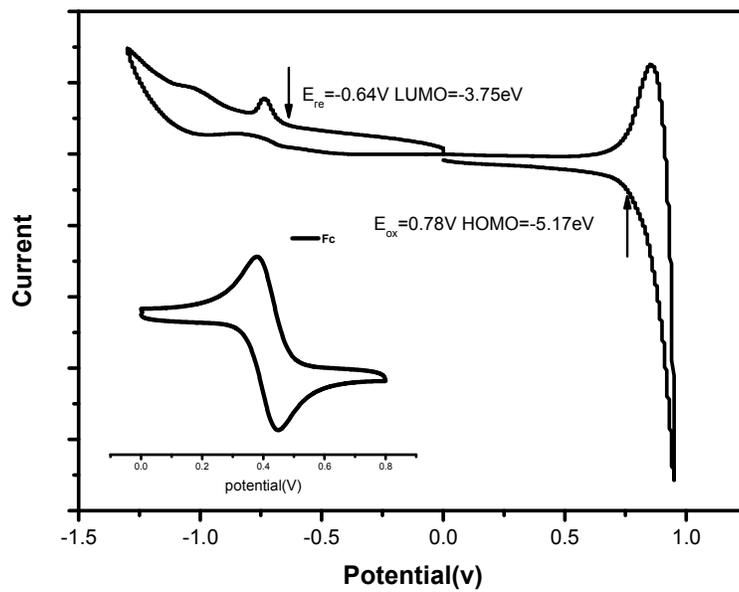


**Figure S4.**  $^1\text{H}$  NMR spectrum of **DPPEZnP-BzTBO** in  $\text{CDCl}_3$  at room temperature.

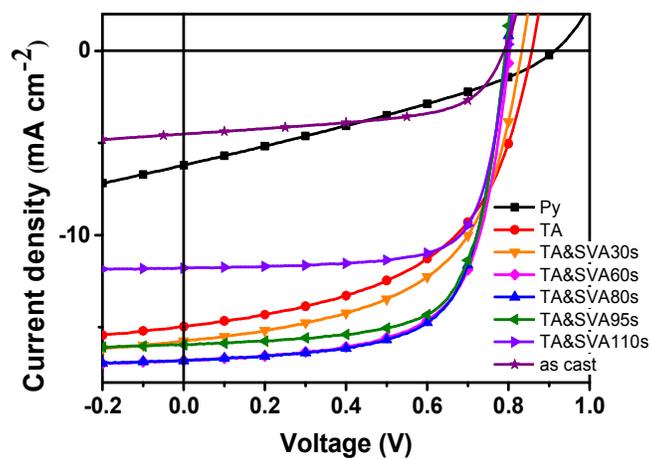




**Figure S5.** Maldi-TOF mass spectrum of **DPPEZnP-BzTBO**.



**Figure S6.** Cyclic voltage curves of **DPPEZnP-BzTBO**.



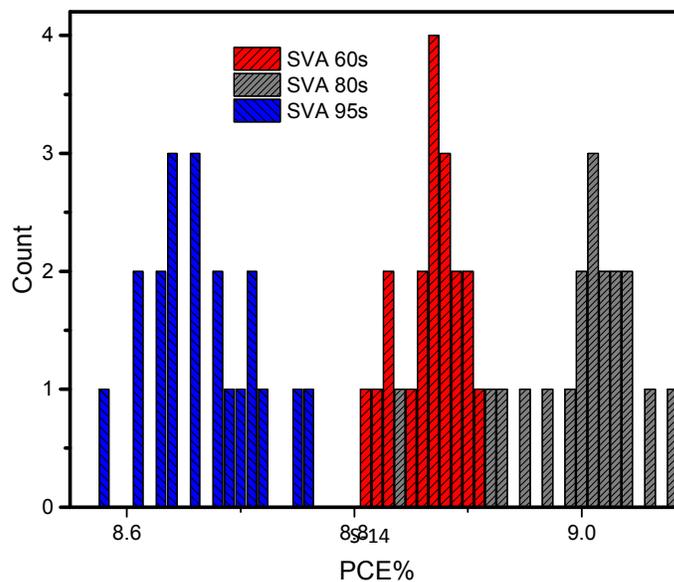
**Figure S7.** Characteristic J–V curves of solar cells based on **DPPEZnP-BzTBO** under AM 1.5G

**Table S1.** Device photovoltaic parameters of **DPPEZnP-BzTBO** under AM1.5 G, 100 mW cm<sup>-2</sup>.

Material	<i>PY</i>	<i>TA</i>	<i>SVA</i> (s)	<i>J<sub>SC</sub></i> (mA cm <sup>-2</sup> )	<i>V<sub>OC</sub></i> (V)	<i>FF</i> (%)	PCE (%)
<b>DPPEZnP-BzTBO</b>	0%	N	N	4.51	0.79	57.74	2.06 <sup>a</sup> (1.95±0.10) <sup>b</sup>
		Y	N	4.11	0.83	58.09	1.98(1.77±0.12)
		Y	Y	4.64	0.78	60.10	2.17(2.06±0.11)
	7%	N	N	6.21	0.91	31.06	1.75 (1.66±0.08)
		Y	N	15.04	0.85	55.35	7.07 (6.90±0.10)
		Y	30	15.75	0.83	56.71	7.41(7.33±0.08)
		Y	60	16.81	0.80	66.23	8.91 (8.87±0.03)
		Y	80	16.82	0.80	67.54	9.08 (9.00±0.06)
		Y	95	15.81	0.80	69.26	8.76(8.66±0.05)
		Y	110	11.79	0.80	72.80	6.78(6.53±0.13)

<sup>a</sup>The best PCE and <sup>b</sup>the average value of PCE standard deviation of more than ten devices.

illumination (100 mW cm<sup>-2</sup>)



**Figure S8.** Statistical histogram of PCEs of devices based

on **DPPEZnP-BzTBO** upon SVA for 60s, 80s, 95s (20 devices for each condition).



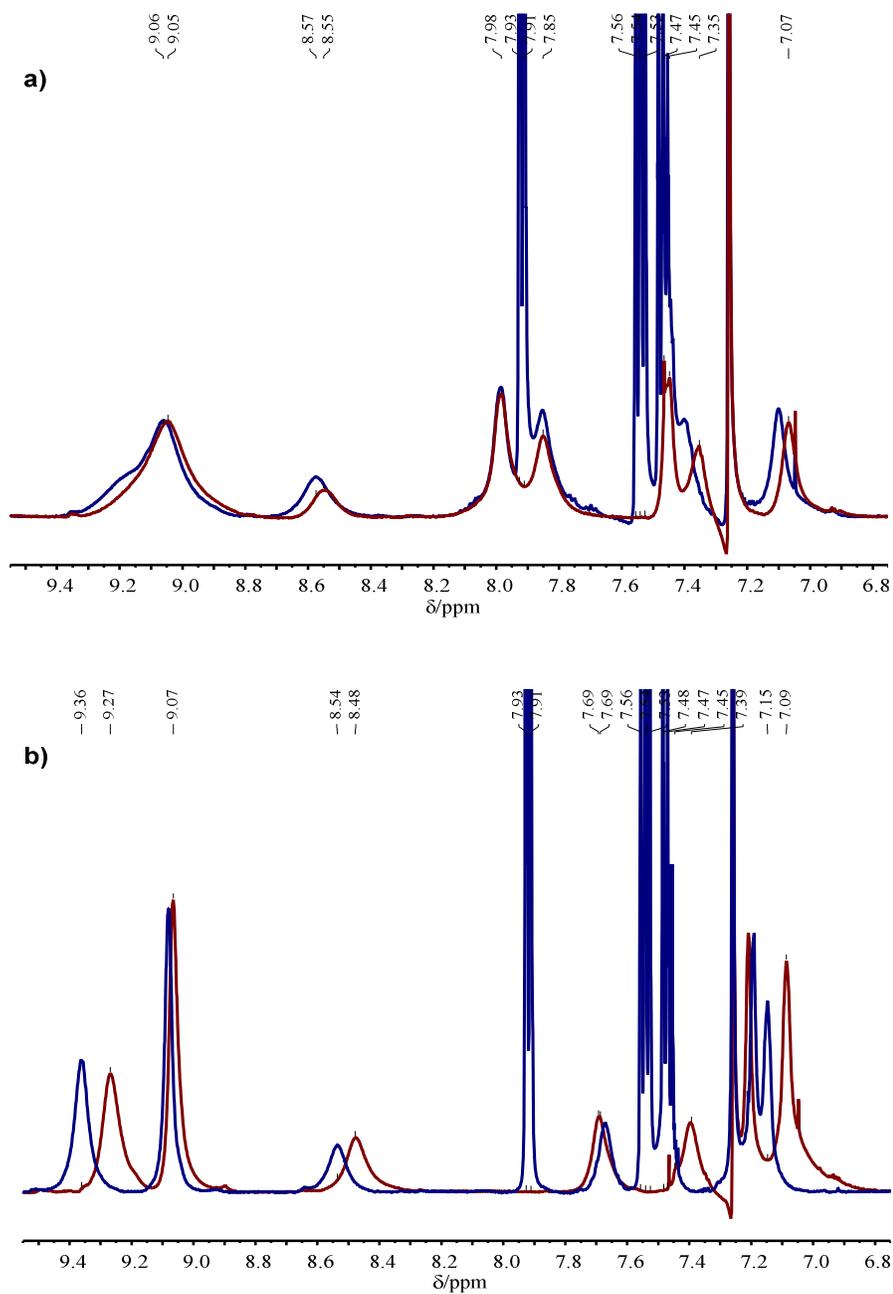
**Figure S9.** The optimum geometry and electron-state-density distribution of LUMO (left) and HOMO (right) of **DPPEZnP-BzTBO** (Alkyl chains are omitted for the simplification of calculations.).

**Table S2.** Optical Absorption Properties and Molecular Energy Levels of the SMs

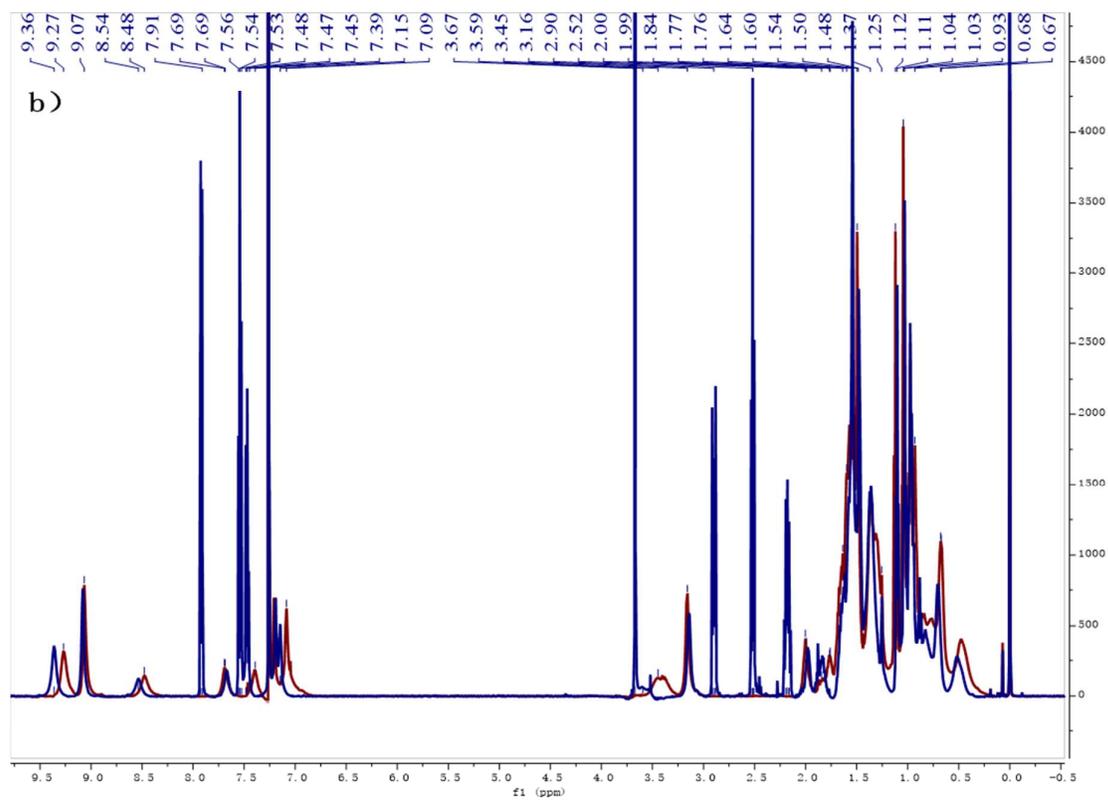
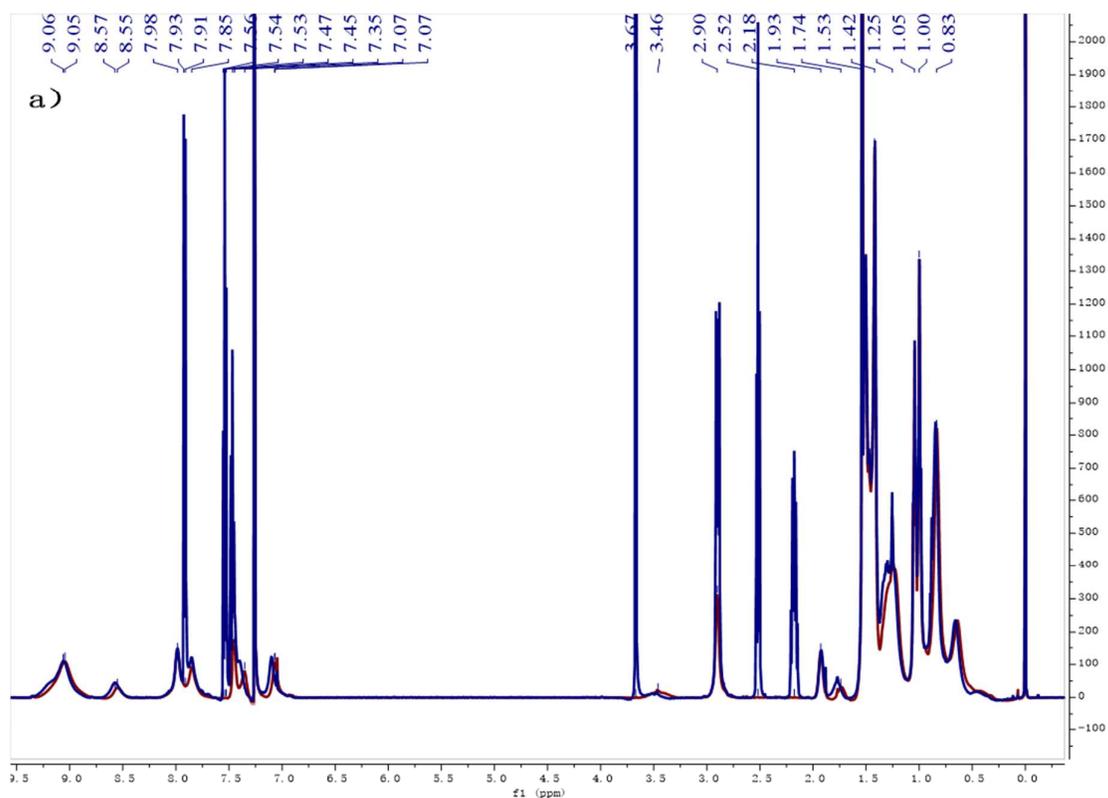
Material	HOMO <sup>a</sup> (eV)	LUMO <sup>a</sup> (eV)	E <sub>g</sub> <sup>b</sup> (eV)	E <sub>g</sub> <sup>opt c</sup> (eV)	HOMO <sup>d</sup> (eV)	LUMO <sup>d</sup> (eV)
<b>DPPEZnP-BzTBO</b>	-5.17	-3.75	1.42	1.40	-4.78	-3.00
<b>DPPEZnP-TEH<sup>e</sup></b>	-5.14	-3.76	1.38	1.37	-4.75	-2.99

<sup>a</sup>Measured by cyclic voltammetry according to the empirical formulas  $E_{\text{HOMO}} = -e (E_{\text{ox}} + 4.388 \text{ V})$  and  $E_{\text{LUMO}} = -e (E_{\text{re}} + 4.388 \text{ V})$ . <sup>b</sup>Calculated from the equation  $E_{\text{g}}^{\text{opt}} = E_{\text{LUMO}} - E_{\text{HOMO}}$ . <sup>c</sup>Calculated from the onset of the film absorption. <sup>d</sup>Calculated via DFT. <sup>e</sup>data from ref.

3.

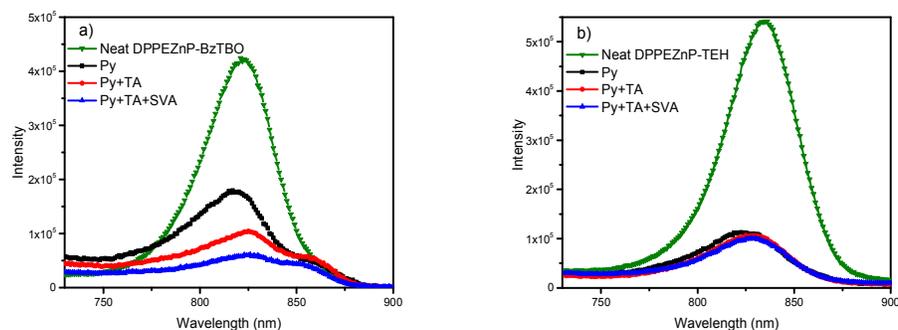


**Figure S10.**  $^1\text{H}$  NMR spectra of (a) **DPPEZnP-BzTBO** (red) and **DPPEZnP-BzTBO:PC<sub>61</sub>BM** (1:1.2 w/w, blue), and (b) **DPPEZnP-TEH** (red) and **DPPEZnP-TEH:PC<sub>61</sub>BM** (1:1.2 w/w, blue) in  $\text{CDCl}_3$  at room temperature. The concentrations of porphyrins are all 6.4 mg/mL.

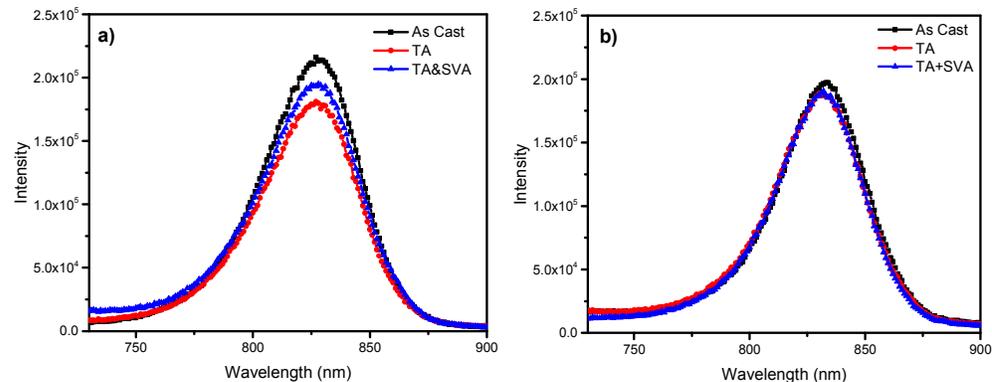


**Figure S11.**  $^1\text{H}$  NMR spectra of (a) **DPPEZnP-BzTBO** (red) and **DPPEZnP-BzTBO:PC<sub>61</sub>BM** (1:1.2 w/w, blue), and (b) **DPPEZnP-TEH** (red) and **DPPEZnP-BzTBO:PC<sub>61</sub>BM** (1:1.2 w/w, blue).

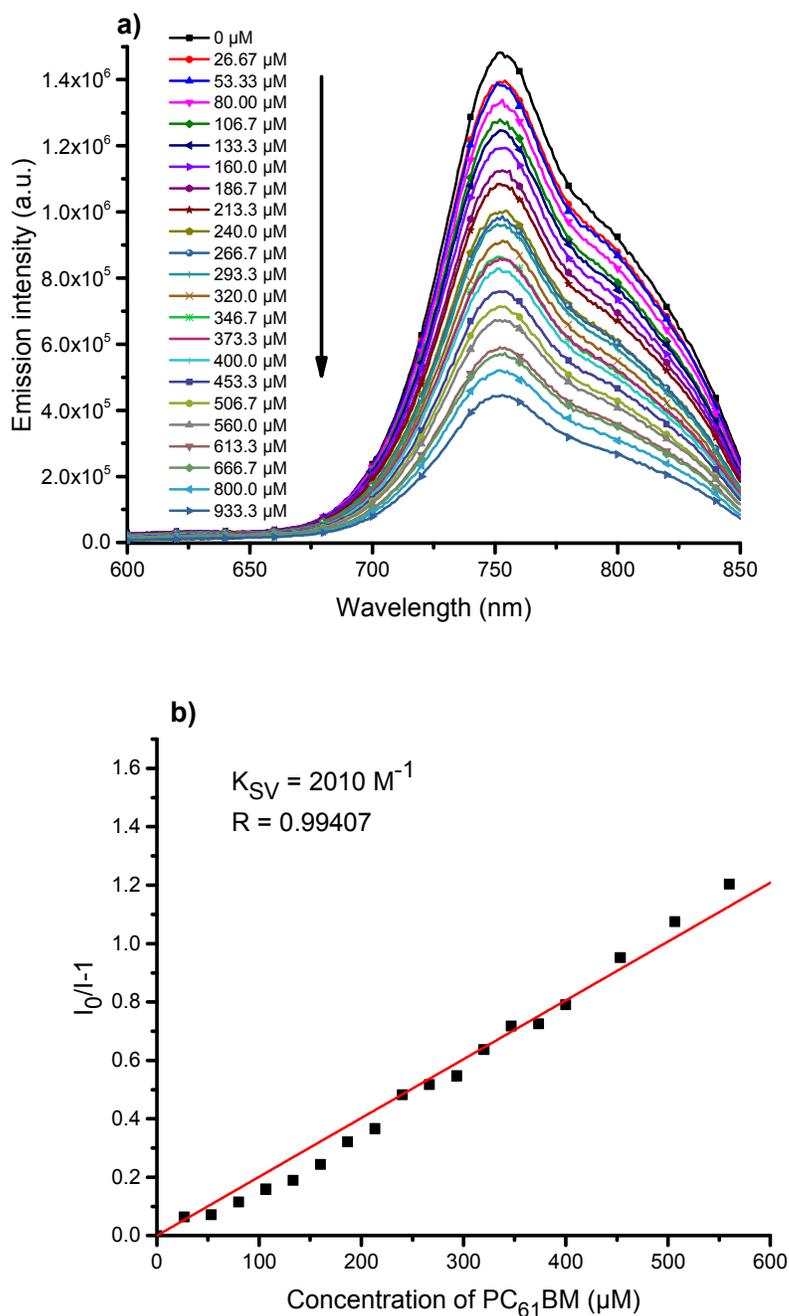
**DPPEZnP-TEH:PC61BM** (1:1.2 w/w, blue) in  $\text{CDCl}_3$  at room temperature. The concentrations of porphyrins are all 6.4 mg/mL.



**Figure S12.** Photoluminescence spectra of (a) neat **DPPEZnP-BzTBO** and (b) **DPPEZnP-TEH** films (thickness:  $50 \pm 5$  nm) and their blends with  $\text{PC}_{61}\text{BM}$  (1:1.2 w/w, thickness:  $100 \pm 5$  nm) processed under different treatments ( $\lambda_{\text{EX}} = 571$  nm, all samples were measured under the same test conditions.).



**Figure S13.** Photoluminescence (PL) spectra of (a) neat **DPPEZnP-BzTBO** film and (b) neat **DPPEZnP-TEH** film processed under different treatments ( $\lambda_{\text{EX}} = 571$  nm, and all samples were measured under the same test condition).



**Figure S14.** (a) Emission spectra and (b) Ksv curve of **DPPEZnP-BzTBO** in chlorobenzene ( $10^{-5} \text{ M}$ ) in the presence of various concentrations of **PC<sub>61</sub>BM** under excitation at 571 nm.

## ■ REFERENCES

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