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Supporting Information

Conjugated D-A porphyrin dimers for solution-processed bulk-heterojunction organic solar cells

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Experimental part

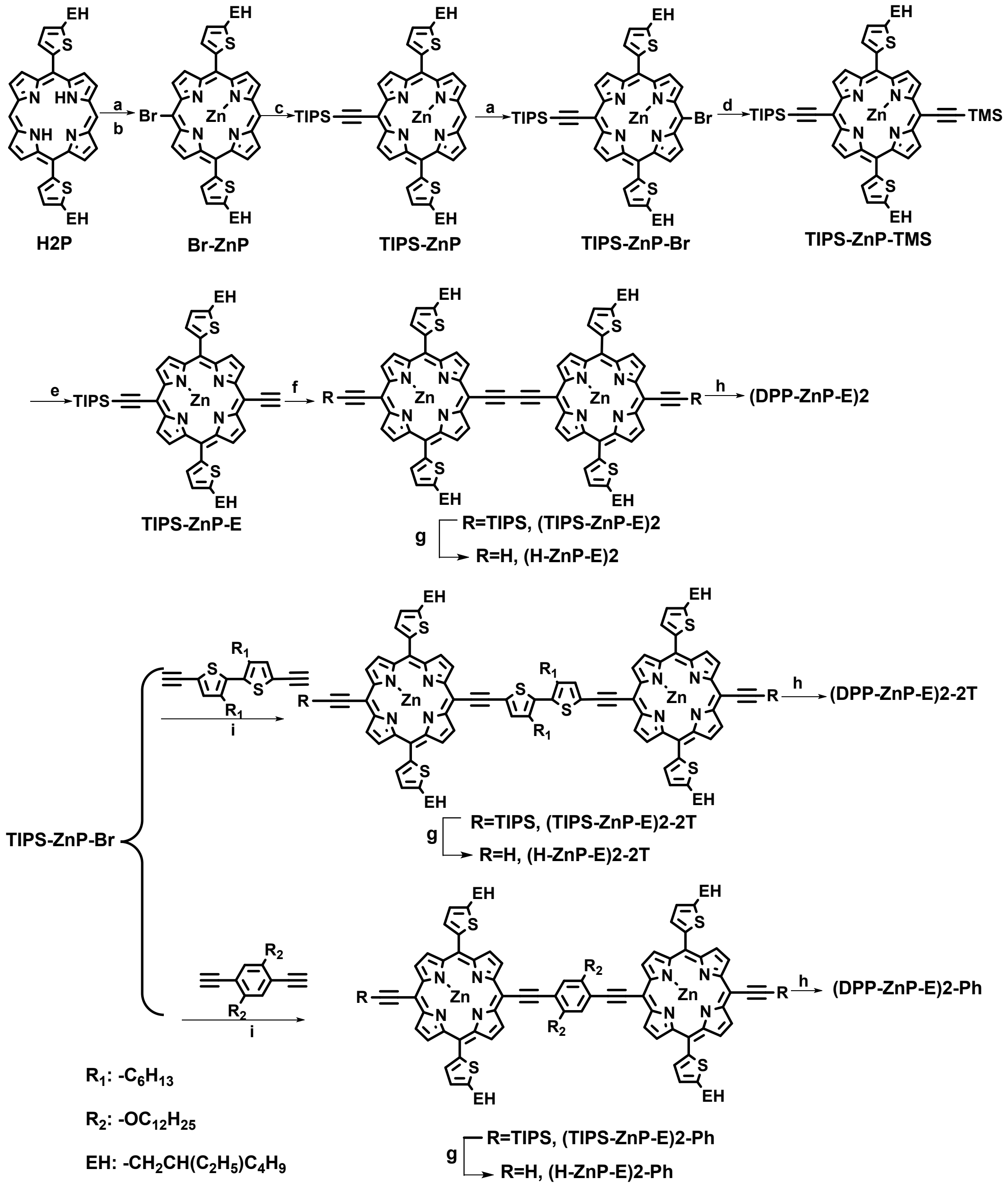
Material: [6, 6]-phenyl C_{61}-butyric acid methyl ester ($PC_{61}BM$) was purchased from 1-Material Chemscitech Incorporated. Other intermediate materials were purchased from TCI, Aldrich, and Energy Chemical Co. and used without further purification.

Solar cell fabrication: The devices were fabricated with a structure of glass/ITO/PEDOT:PSS/donor:acceptor/FNEZnP-OE/Al. The ITO-coated glass substrates were cleaned by ultrasonic treatment in acetone, detergent, distilled water, and isopropyl alcohol and treated with oxygen plasma for 5 minutes each and subsequently dried by nitrogen. A thin layer of PEDOT:PSS (Bayer Baytron 4083) was spin-coated on the ITO-coated glass substrates at 2500 rpm for 30 s, the substrates were subsequently dried at 150 ^{o}C for 10 min in air and then transferred to a N2-glovebox. The active layer was spin-coated from blend chlorobenzene solutions (containing1% pyridine) with an overall concentration of 16 mg/mL (from 1400 rpm for 40s), and then annealed at different temperature for 5 min, and the thicknesses of the active layers of (DPP-ZnP-E)2:$PC_{61}BM$, (DPP-ZnP-E)2-2T:$PC_{61}BM$ and (DPP-ZnP-E)2-Ph:$PC_{61}BM$ were measured to be 97(±8), 92(±10) nm and 105(±8) nm, respectively, by a profilometer. Then, FNEZnP-OE methanol solution (0.02% (w/v) was spin-coated at 2000 rpm for 30 s as the interlayer. Finally, Al (~80 nm) was evaporated with a shadow mask as the top electrode. The effective area was measured to be 0.16 cm^2.

The ^{1}H NMR spectra were measured on a Bruker AVANCE Digital 500MHz spectrometer in deuterated chloroform or deuterated chloroform with 5% deuterated pyridine containing tetramethylsilane as an internal standard. Mass spectra (MS) were obtained on a Bruker Daltonics BIFLEX MALDI-TOF Analyzer using MALDI mode. UV-Vis-NIR absorption spectra of the films on quartz substrates were measured using a Shimadzu UV-3600 spectrophotometer. Cyclic voltammetry (CV) data was collected on a CHI660C electrochemical workstation at scan rate of 50 mV s^{-1} in the nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN). A glassy-carbon electrode coated with a thin film of a porphyrin dimer, a 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 a NanoScope NS3A system (Digital Instrument).

The *J-V* characteristics were measured under AM 1.5 solar simulator (Japan, SAN-EI, XES-40S1) at 100 mW cm^{-2}, and data were collected using a Keithley 2400 digital source meter. The spectral response was measured with a DSR100UV-B spectrometer with a SR830 lock-in amplifier. A calibrated Si photodiode was used as a reference before each measurement.

1,4-bis(dodecyloxy)-2,5-diethynylbenzene, 5,5'-diethynyl-3,3'-dihexyl- 2,2'-bithiophene, **Br-ZnP**, **TIPS-ZnP**, **TIPS-ZnP-Br**, **TIPS-ZnP-TMS**, **TIPS-ZnP-E**, **(TIPS-ZnP-E)2**, **(TIPS-ZnP-E)2-2T**, **(TIPS-ZnP-E)2-Ph**, **(TIPS-ZnP-E)2-2T**, **(TIPS-ZnP-E)2-Ph** and 3-(5-bromo-thiophen-2-yl)-2,5-bis-(2-ethyl-hexyl)-6-thiophen-2-yl-2,5-dihydro-pyrrolopyrrole-1,4-dione (DPP-Br) were synthesized according to reported procedures,[1-5] and the details are shown below.



Scheme S1. Synthesis routes for (DPP-ZnP-E)2, (DPP-ZnP-E)2-2T and (DPP-ZnP-E)2-Ph: (a) NBS; (b) Zn(OAc)2; (c) TIPSA, $Pd(PPh_3)_2Cl_2$, CuI; (d) TMSA, $Pd(PPh_3)_2Cl_2$, CuI; (e)NaOH (aq., 1M); (f) CuCl, TMEDA, dry air; (g) TBAF; (h) DPP-Br, $Pd(PPh_3)_4$, CuI; (i) Pd_2dba_3, P(o-tolyl)$_3$.

(5-bromo-10,20-bis-(5-(2-ethylhexyl)-thienyl)-porphinato)zinc (II) (Br-ZnP). Compound **H2P** (1.03 g, 1.47 mmol) was dissolved in 300 ml chloroform with 3 ml pyridine. After the solution was cooled to 0 ˚C, *N*-bromosuccinimide (0.27 g, 1.47 mmol) was added and stirred for 30 min. Then the mixture was poured into water, washed with water, dried over anhydrous Na_2SO_4, and concentrated.

After the residue was chromatographed on silica gel, the mono-bromide porphyrin was obtained and then dissolved in a mixture of 200 ml chloroform. A solution of zinc acetate dihydrate (0.89 g, 4.05 mmol) in methanol (20 ml) was added, and the reaction mixture was stirred at 60 °C for 6 h. After routine procedures, the solvent was evaporated, and the residue was chromatographed on silicagel using $CHCl_3$ as the eluent to give the mono-bromoporphyrinatozinc compound (**Br-ZnP**) (618mg, 50%). ^{1}H NMR (500 MHz, Chloroform-d) δ/ppm 9.73 (s, 1H), 9.64 (d, $J = 4.7$ Hz, 2H), 9.18 (d, $J = 4.7$ Hz, 2H), 9.11 (d, $J = 4.4$ Hz, 2H), 9.04 (d, $J = 4.5$ Hz, 2H), 7.62 (d, $J = 3.2$ Hz, 2H), 7.16 (d, $J = 3.1$ Hz, 2H), 3.09 (dd, $J = 6.8$, 1.9 Hz, 4H), 1.88 (m, 2H), 1.72–1.39 (m, 14H), 1.01-1.11 (m, 12H). ^{13}C NMR (125 MHz, Chloroform-d) δ/ppm 152.5, 151.0, 150.8, 149.9, 149.1, 137.2, 132.8, 132.7, 132.6, 131.8, 124.8, 123.9, 113.2, 106.5, 105.4, 41.1, 32.7, 29.7, 29.1, 26.1, 23.2, 14.3, 11.1. MALDI−TOF Mass (m/z): calculated for $C_{44}H_{47}BrN_4S_2Zn$: 838.17; found: 838.13. UV-vis (THF), λ_{max}= 426 nm.

(5-((Triisopropylsilyl)ethynyl)-10,20-bis(5-(2-ethylhexyl)-thienyl)-porphinato)zinc (II) (TIPS-ZnP). The mono-bromo compound **Br-ZnP** (618 mg, 0.73 mmol) was dissolved in THF (20 mL), and then triethylamine (4 mL) was added. The mixture was purged with argon for 30 min. Then $Pd(PPh_3)_2Cl_2$ (51 mg, 0.07 mmol), CuI (14 mg, 0.07 mmol), and (triisopropylsilyl)acetylene (267 mg, 1.47 mmol) were added. After the mixture was stirred at room temperature for 24 h under Ar, the reaction was quenched with brine. Then the mixture was extracted with dichloromethane, dried with anhydrous Na_2SO_4 and concentrated. Finally, the residue was purified on column chromatography to afford **TIPS-ZnP** as a purple solid (677 mg, 98% yield). ^{1}H NMR (500 MHz, Chloroform-d) δ/ppm: 9.43 (s, 1H), 9.36 (d, $J = 4.6$ Hz, 2H), 9.09 (d, $J = 4.6$ Hz, 2H), 9.02 (d, $J = 4.6$ Hz, 2H), 8.94 (q, $J = 4.4$ Hz, 2H), 7.46 (d, $J = 3.2$ Hz, 2H), 7.02 (d, $J = 3.2$ Hz, 2H), 3.09 (d, $J = 6.9$ Hz, 4H), 1.88 (m, 2H), 1.72–1.39 (m, 35H), 1.01-1.11 (m, 12H). ^{13}C NMR (125 MHz, Chloroform-d) δ/ppm 147.8, 147.7, 146.3, 145.8, 144.8, 132.6, 128.1, 127.6, 127.2, 126.4, 119.9, 119.1, 109.0, 104.5, 103.0, 96.5, 93.4, 36.4, 28.0, 24.9, 24.3, 21.3, 18.4, 14.4, 9.5, 7.2, 6.3. MALDI−TOF Mass (m/z): calculated for $C_{55}H_{68}N_4S_2SiZn$: 940.39; found: 940.35. UV-vis (THF), λ_{max}= 434 nm.

(5-bromo-15-((triisopropylsilyl)ethynyl)-10,20-bis(5-(2-ethylhexyl)-thienyl)-porphinato)zinc (II) (**TIPS-ZnP-Br**). Compound **TIPS-ZnP** (600 mg, 0.64 mmol) was dissolved in 200 ml of chloroform and 2 ml of pyridine. After the reaction mixture was cooled to -5 ˚C, N-bromosuccinimide (400 mg, 2.25 mmol) was added to the reaction mixture and stirred for 30 min. Then the reaction mixture was washed with water, dried over Na_2SO_4, and concentrated. And the residue was purified first by column chromatography on silica gel to give a dark green solid (393mg, 61% yield). 1H NMR (500 MHz, Chloroform-d) δ/ppm 9.71 (d, *J* = 4.6 Hz, 2H), 9.61 (d, *J* = 4.7 Hz, 2H), 9.17 (d, *J* = 4.6 Hz, 2H), 9.12 (d, *J* = 4.6 Hz, 2H), 7.64 (d, *J* = 3.2 Hz, 2H), 7.14 (d, *J* = 3.3 Hz, 2H), 3.07 (d, *J* = 4.8 Hz, 4H), 1.85 (m, 2H), 1.69-1.38 (m, 16H), 1.11-0.94 (m, 12H), 0.92-0.80 (m, 21H). ^{13}C NMR (125 MHz, Chloroform-d) δ/ppm 153.3, 152.4, 151.5, 150.9, 149.5, 143.0, 137.2, 133.1, 133.0, 132.92, 131.4, 124.8, 123.9, 114.7, 109.2, 106.7, 101.4, 98.0, 41.1, 32.7, 29.6, 29.0, 26.0, 23.2, 19.1, 14.2, 11.9, 11.0. MALDI−TOF Mass (m/z): calculated for $C_{55}H_{67}BrN_4S_2SiZn$: 1018.30; found: 1018.25. UV-vis (THF), λ_{max}= 440 nm.

TIPS-ZnP-TMS. **TIPS-ZnP-Br** (266 mg, 0.26 mmol) was dissolved in THF (25 mL) with triethylamine (5 mL), and then $Pd(PPh_3)_2Cl_2$ (18 mg, 0.03 mmol), CuI (5 mg, 0.03 mmol), and trimethylsilyacetylene (126 mg, 1.3 mmol) were added. After the mixture was stirred at 60 ^oC for 12 h under argon, the reaction was quenched with brine. After the mixture was extracted with chloroform, dried with anhydrous Na_2SO_4 and concentrated. Finally, the residue was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether (1:4) to afford **TIPS-ZnP-TMS** as a dark green solid (216 mg, 83% yield).^1H NMR (500 MHz, Chloroform-d) δ/ppm 9.72 (d, *J* = 4.6 Hz, 2H), 9.66 (d, *J* = 4.6 Hz, 2H), 9.18 (dd, *J* = 7.5, 4.6 Hz, 4H), 7.66 (d, *J* = 3.2 Hz, 2H), 7.15 (d, *J* = 3.4 Hz, 2H), 3.08 (d, *J* = 6.8 Hz, 4H), 1.85 (m, 2H), 1.70-1.15 (m, 58H), 1.04 (m, 12H), 0.60 (s, 9H). ^{13}C NMR (125 MHz, Chloroform-d) δ/ppm 153.4, 152.2, 151.0, 149.8, 144.1, 137.6, 133.1, 133.0, 132.9, 131.4, 124.8, 123.9, 114.7, 109.2, 106.7, 101.4, 98.0, 41.1, 32.8, 32.7, 29.6, 29.0, 26.0, 23.2, 19.2, 14.3, 11.9. MALDI−TOF Mass (m/z): calculated for $C_{58}H_{76}N_4S_2Si_2Zn$: 1036.43; found: 1036.38. UV-vis (THF), λ_{max}= 444 nm.

(TIPS-ZnP-E)2. **TIPS-ZnP-TMS** (216 mg, 0.21 mmol) was dissolved in THF (15 ml) and MeOH (10 ml). An aqueous solution of NaOH (1 M, 1.02 ml) was added dropwise to the reaction flask and stirred at room temperature for 20 min. Then the reaction mixture was poured into water, extracted with CH_2Cl_2, dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography to give a dark green solid of **TIPS-ZnP-E**. Copper(I) chloride (1.236 g, 12.48 mmol) was added to a mixture of the green **TIPS-ZnP-E** (200 mg, 0.21 mmol) and TMEDA (1.82 mL, 12.07 mmol) in CH_2Cl_2/pyridine (1%) (250 mL). The mixture was stirred vigorously under dry air for 15 min and quenched with water. The organic layer was washed with water until all the copper salt had been removed and then the volatiles were removed under reduced pressure. The residue was chromatographed on silica gel using CH_2Cl_2 as eluent to isolate the desired product, which was then further purified via GPC to give a black solid **(TIPS-ZnP-E)2** (170 mg, 85%). ^{1}HNMR (500 MHz, $CDCl_3$) δ/ppm (ppm): 9.87 (d, *J* = 4.5 Hz, 4H), 9.70 (d, *J* = 4.5 Hz, 4H), 9.24(d, *J* = 4.5 Hz, 4H), 9.17(d, *J* = 4.5 Hz, 4H), 7.71 (d, *J* = 3.3 Hz, 4H), 7.18 (d, *J* = 3.3 Hz, 4H), 3.10 (d, *J* = 6.7 Hz, 8H), 1.88 (m, 4H), 1.80 (m, 4H), 1.40-1.69 (m, 74H), 0.98-1.11 (m, 24H). MALDI−TOF Mass (m/z): calculated for $C_{114}H_{134}N_8S_4Si_2Zn_2$: 1929.77; found: 1930.86. UV-vis (THF), λ_{max}=462 nm.

(TIPS-ZnP-E)2-2T and **(TIPS-ZnP-E)2-Ph**. **TIPS-ZnP-Br** (215 mg, 0.211 mmol) and 5,5'-diethynyl-3,3'-dihexyl-2,2'-bithiophene (35 mg, 0.09 mmol) or 1,4-bis(dodecyloxy)-2,5-diethynylbenzene (40 mg, 0.09 mmol) were dissolved in THF (20 mL) with triethylamine (4 mL). Then Pd_2dba_3 (24 mg, 0.03 mmol) and P(o-tolyl)$_3$ (64 mg, 0.21 mmol) were added. The mixture was stirred at 60 ^{o}C for 48 h under argon protection, then the reaction mixture was poured into water and extracted with $CHCl_3$ and washed with brine, dried over Na_2SO_4, and evaporated. The residue was chromatographed on silica gel using CH_2Cl_2 as eluent to isolate the desired product, which was then further purified via GPC to afford **(TIPS-ZnP-E)2-2T** (61% yield) or **(TIPS-ZnP-E)2-Ph** (64% yield).

(TIPS-ZnP-E)2-2T: ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm (ppm): 9.71 (dd, *J* = 9.5, 4.6 Hz, 8H), 9.19(dd, *J* = 6.0, 4.6 Hz, 8H), 7.71-7.65 (m, 6H), 7.17 (d, *J* = 3.3 Hz, 4H), 3.09 (d, *J* = 6.8 Hz, 8H), 2.83 (t, *J* = 7.8 Hz, 4H), 1.78-1.92 (m, 8H), 1.35-1.69 (m, 86H), 0.91-1.11 (m, 30H). MALDI−TOF Mass (m/z): calculated for $C1_{34}H_{162}N_8S_6Si_2Zn_2$: 2261.93; found: 2262.76. UV-vis (THF), λ_{max}=460 nm.

(TIPS-ZnP-E)2-Ph: ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm (ppm): 9.72 (d, 4 *J* = 4.5 Hz,H), 9.57 (d, *J* = 4.5 Hz, 4H), 9.10(dd, *J* = 18.3, 4.4 Hz, 8H), 7.66 (d, *J* = 3.2 Hz, 4H), 7.38 (s, 2H), 7.17 (d, *J* = 3.5 Hz, 4H), 4.36 (t, *J* = .5 Hz, 4H), 3.11 (d, *J* = 6.8 Hz, 8H), 1.90 (m, 4H), 1.80 (m, 4H), 1.30-1.71 (m, 110H), 0.91-1.11 (m, 30H). MALDI−TOF Mass (m/z): calculated for $C_{144}H_{186}N_8O_2S_4Si_2Zn_2$:

2374.17; found: 2375.56. UV-vis (THF), λ_{max}=460 nm.

(H-ZnP-E)2, **(H-ZnP-E)2-2T** and **(H-ZnP-E)2-Ph**. TBAF (1 M in THF, 0.94 mmol) was added to **(TIPS-ZnP-E)2**, **(TIPS-ZnP-E)2-2T** or **(TIPS-ZnP-E)2-Ph** (0.04 mmol) in 10 mL of THF at room temperature. After the mixture was stirred for 15 min, the mixture was poured into water, extracted with $CHCl_3$ and dried over Na_2SO_4, it was allowed to pass through a short silica gel column and to afford crude **(H-ZnP-E)2**, **(H-ZnP-E)2-2T** and **(H-ZnP-E)2-Ph**, respectively, which were used directly for the next reaction without further purification.

(DPP-ZnP-E)2, **(DPP-ZnP-E)2-2T** and **(DPP-ZnP-E)2-Ph**. (H-ZnP-E)2, (H-ZnP-E)2-2T or (H-ZnP-E)2-Ph (0.04 mmol) was dissolved in THF (8 mL) and triethylamine (4 mL) with DPP-Br (72 mg, 0.12 mmol). Then $Pd(PPh_3)_4$ (4.8 mg, 4 μmol) and CuI (0.8 mg, 4 μmol) were added. After the mixture was stirred at 60 ^oC for 48 h under argon, the reaction was quenched with saturated brine. After the mixture was extracted with chloroform, dried with anhydrous Na_2SO_4 and concentrated. The residue was column chromatographed on silica gel using CH_2Cl_2 as eluent to give a black solid of **(DPP-ZnP-E)2** (93 mg, 88% yield), **(DPP-ZnP-E)2-2T** (90 mg, 75% yield) or **(DPP-ZnP-E)2-Ph** (97 mg, 80 % yield).

(DPP-ZnP-E)2: ^{1}HNMR (500 MHz, $CDCl_3$+5%Py) δ/ppm (ppm): 9.37 (m, 8H), 9.16 (t, *J* = 4.6 Hz, 8H), 8.84 (d, *J* = 3.4 Hz, 2H), 8.48 (s, 2H), 7.81 (d, *J* = 3.1 Hz, 4H), 7.30 (d, *J* = 4.0 Hz, 2H),7.25 (d, *J* = 3.1 Hz, 4H), 7.21 (s,2H), 7.09 (t, *J* = 4.3 Hz, 2H), 3.70 (m, 8H), 3.16 (d, *J* = 6.5 Hz, 8H), 1.96 (m, 4H), 1.8 (m, 4H) 1.16-1.07 (m, 64H), 0.76-1.05 (m, 48H). MALDI−TOF Mass (m/z): calculated for $C_{156}H_{170}N_{12}O_4S_8Zn_2$: 2664.98; found: 2664.64. Anal. calcd. For $C_{156}H_{170}N_{12}O_4S_8Zn_2$ (%): C 70.32, H 6.43, N 6.31, Found: C 70.59, H 6.54, N 6.46.

(DPP-ZnP-E)2-2T: ^{1}HNMR (500 MHz, $CDCl_3$+5%Py) δ/ppm (ppm): 9.66 (d, *J* = 4.4 Hz, 4H), 9.44 (d, *J* = 4.4 Hz, 4H), 9.14 (dd, *J* = 7.4, 4.5 Hz, 8H), 8.81 (d, *J* = 3.5 Hz, 4H), 8.49 (t, *J* = 4.7 Hz, 2H), 7.72 (d, *J* = 3.3 Hz, 4H), 7.50 (d, *J* = 4.9 Hz, 4H),7.44 (s, 2H), 7.22 (t, *J* = 3.9 Hz, 2H), 7.16 (s, 4H), 3.86 (m, 4H), 3.08 (d, *J* = 6.7 Hz, 8H), 2.66 (t, *J* = 7.6 Hz, 4H),1.87 (m, 4H), 1.73 (m, 4H), 1.09-1.67 (m, 82H), 0.76-1.09 (m, 54H). MALDI−TOF Mass (m/z): calculated for $C_{176}H_{198}N_{12}O_4S_{10}Zn_2$: 2996.14; found: 2996.06. Anal. calcd. For $C_{176}H_{198}N_{12}O_4S_{10}Zn_2$ (%): C 70.53, H 6.66, N 5.61, Found: C 70.29, H 6.87, N 5.69.

(DPP-ZnP-E)2-Ph does not show satisfied NMR spectrum even we tried many times. MALDI−TOF Mass (m/z): calculated for $C_{186}H_{222}N_{12}O_6S_8Zn_2$: 3107.38; found: 3107.46. Anal. calcd. For $C_{186}H_{222}N_{12}O_6S_8Zn_2$ (%): C 71.85, H 7.20, N 5.41, Found: C 71.13H 7.27 N 5.43.

All the porphyrin dimers did not show satisfied ^{13}C NMR spectra even when 5% pyridine-d5 was used possibly due to the extend π-conjugation and strong self-aggregation at high concentration.

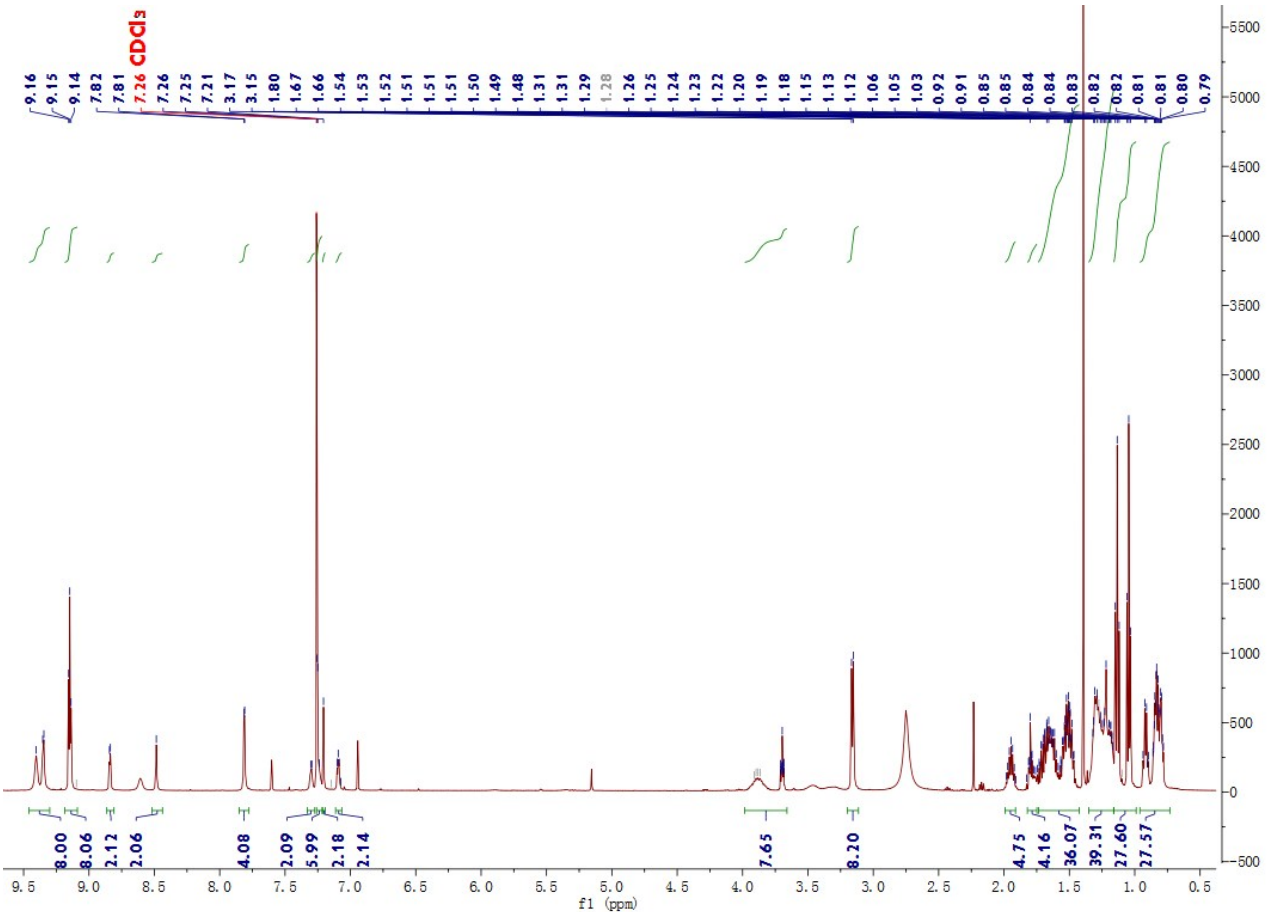


Figure S1. The ^1H NMR(500 MHz) spectrum of **(DPP-ZnP-E)2** in $CDCl_3$ with 5% Pyridine-d_5.

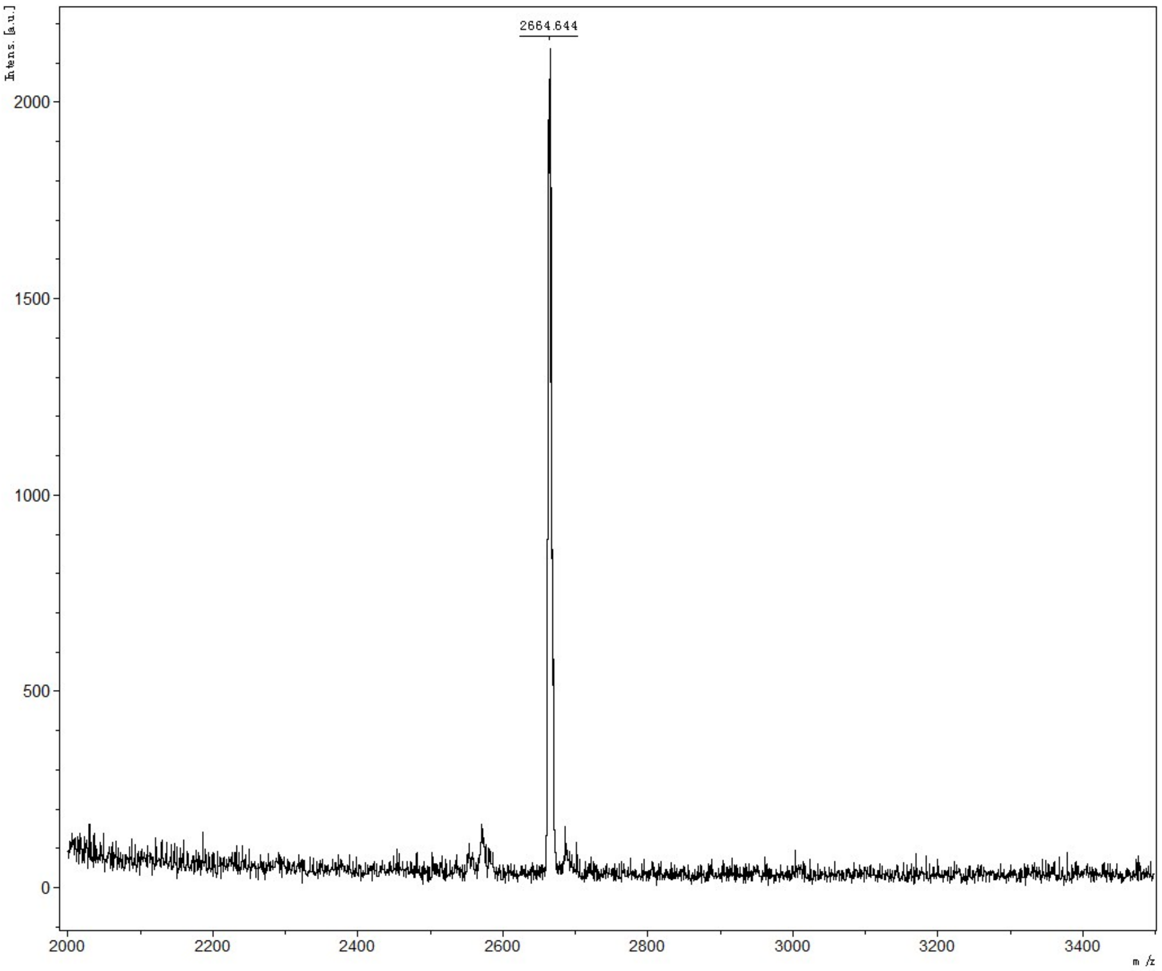


Figure S2. The MALDI-TOF mass spectrum of **(DPP-ZnP-E)2**.

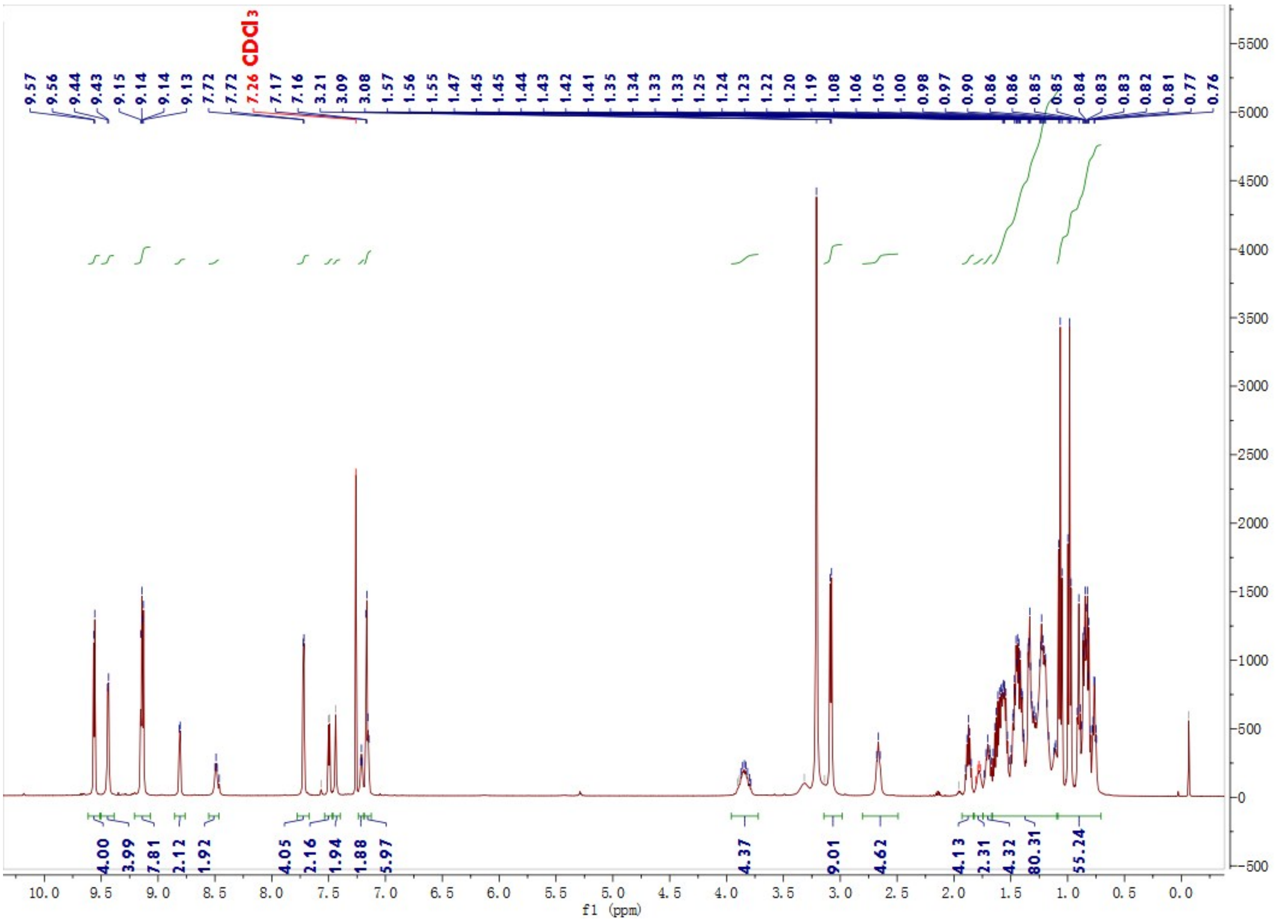


Figure S3. The ^{1}H NMR(500 MHz) spectrum of **(DPP-ZnP-E)2-2T** in $CDCl_3$ with 5% Pyridine-d_5.

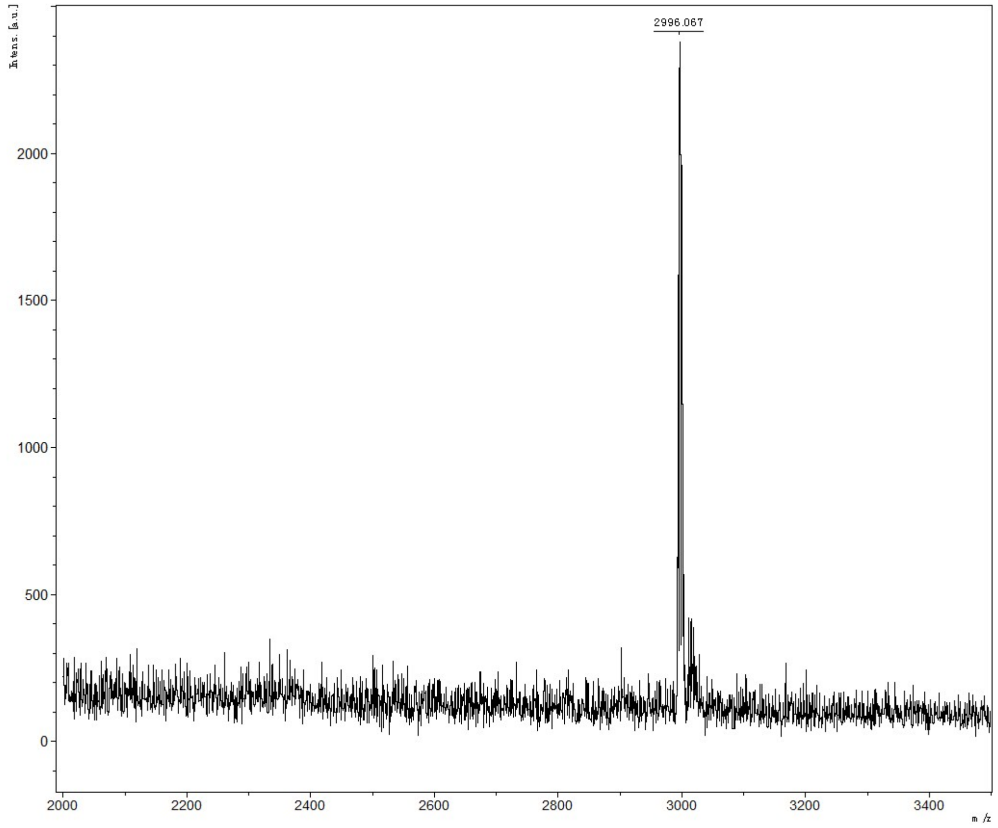


Figure S4. The MALDI-TOF mass spectrum of **(DPP-ZnP-E)2-2T**.

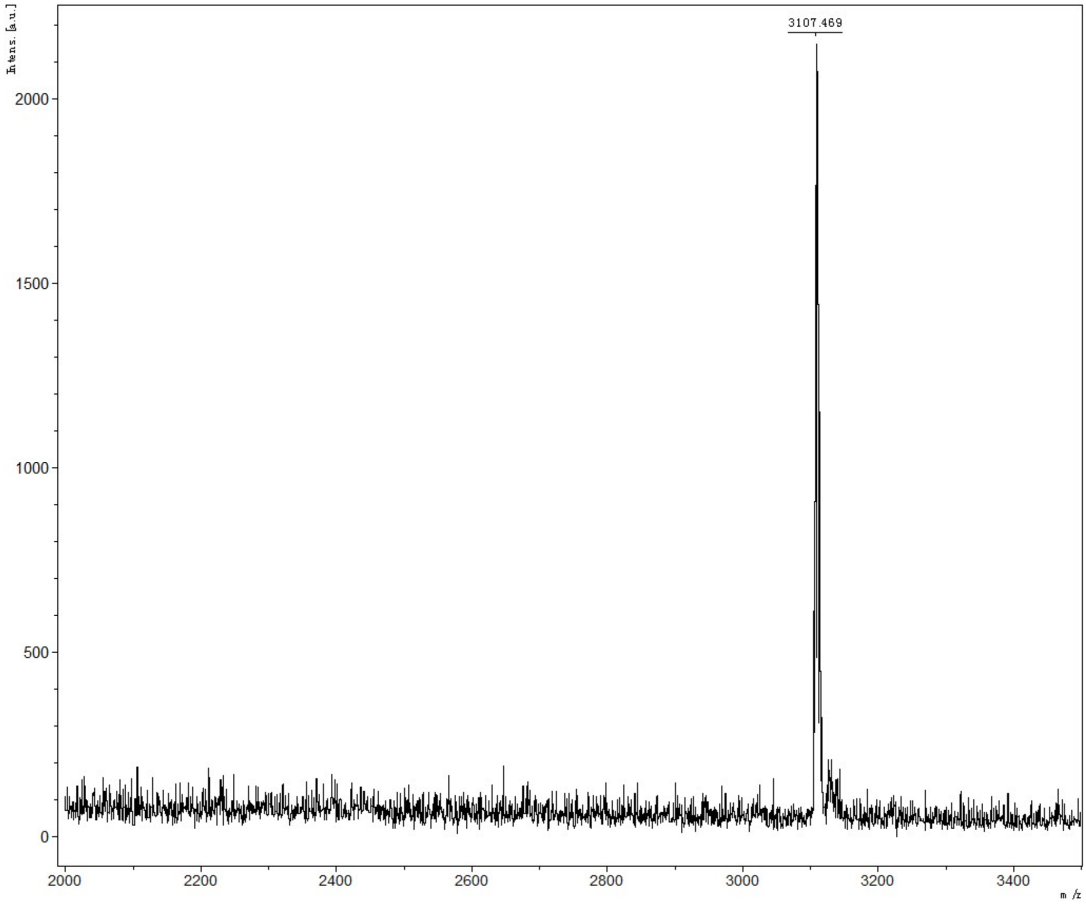


Figure S5. The MALDI-TOF mass spectrum of **(DPP-ZnP-E)2-Ph**.

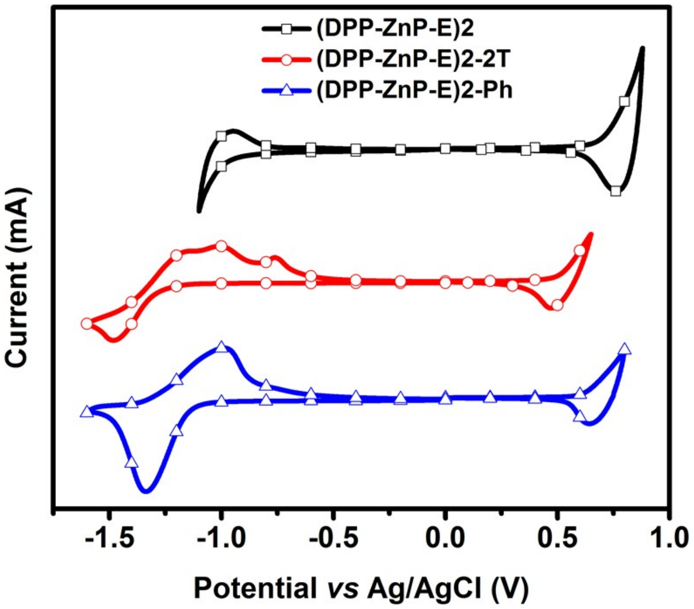


Figure S6. Cyclic voltammogram of **(DPP-ZnP-E)2**, **(DPP-ZnP-E)2-2T** and **(DPP-ZnP-E)2-Ph** films on a glassy carbon disk measured in 0.1 mol L^{-1} $Bu_4NPF_6CH_3CN$ solutions with scan rate of 50 mV s^{-1}.

Table S1. UV-vis-NIR absorption and redox data for **(DPP-ZnP-E)2**, **(DPP-ZnP-E)2-2T** and **(DPP-ZnP-E)2-Ph**.

Molecules	λ_{max} [nm] $^{a)}$	λ_{max} [nm] $^{b)}$	λ_{onset} [nm] $^{b)}$	E_g^{opt} [eV]	HOMO [eV]$^{c)}$	LUMO [eV] $^{c)}$	E_g^{cv} [eV]
(DPP-ZnP-E)2	470,733	493,830	914	1.36	-5.09	-3.49	1.60
(DPP-ZnP-E)2-2T	467,710	488, 758	856	1.45	-4.87	-3.21	1.66
(DPP-ZnP-E)2-Ph	470,733	502, 799	878	1.41	-5.03	-3.34	1.69

$^{a)}$ Measured in dilute THF solution, $^{b)}$ measured in film and $^{c)}$ estimated from the onsets of oxidation/reduction potential of cyclic voltammetry curves.

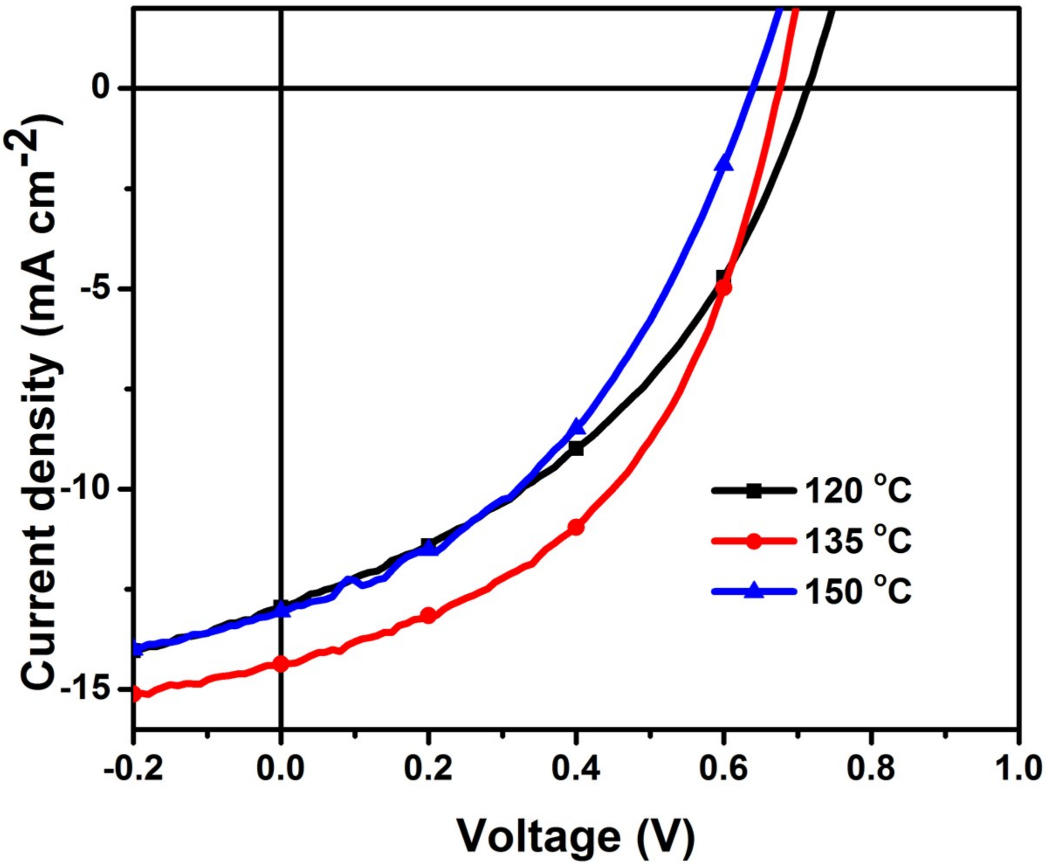


Figure S7. *J-V* curves of BHJ solar cells based on (DPP-ZnP-E)2:PC$_{61}$BM with different TA temperature under stimulated illumination of AM 1.5 G, 100 mW cm^{-2}.

Table S2. Photovoltaic performance of BHJ solar cells based on (DPP-ZnP-E)2:$PC_{61}BM$ cast from chlorobenzene (1% Py) with different TA temperature under stimulated illumination of AM 1.5 G, 100 $mWcm^{-2}$.

Temperature (^oC)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
No	4.04	0.80	26.84	0.86
120	12.97	0.72	40.09	3.74
135	13.82	0.67	45.86	4.24
150	13.05	0.64	40.6	3.39

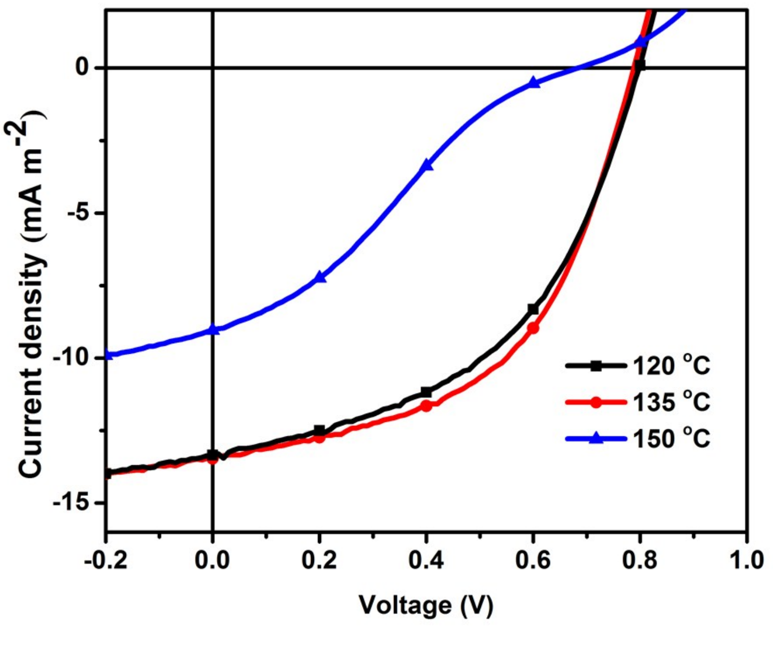


Figure S8. *J-V* curves of BHJ solar cells based on (DPP-ZnP-E)2-2T:$PC_{61}BM$ cast from chlorobenzene (1% Py) with different TA temperature under illumination of AM 1.5 G, 100 mW cm^{-2}.

Table S3. Photovoltaic performance of BHJ solar cells based on (DPP-ZnP-E)2-2T:$PC_{61}BM$ cast from chlorobenzene (1% Py) with different TA under illumination of AM 1.5 G, 100 $mWcm^{-2}$.

Temperature (^{o}C)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
No	6.76	0.89	33.8	2.03
120	13.34	0.80	47.98	5.12
135	13.46	0.79	51.77	5.50
150	9.05	0.68	26.89	1.65

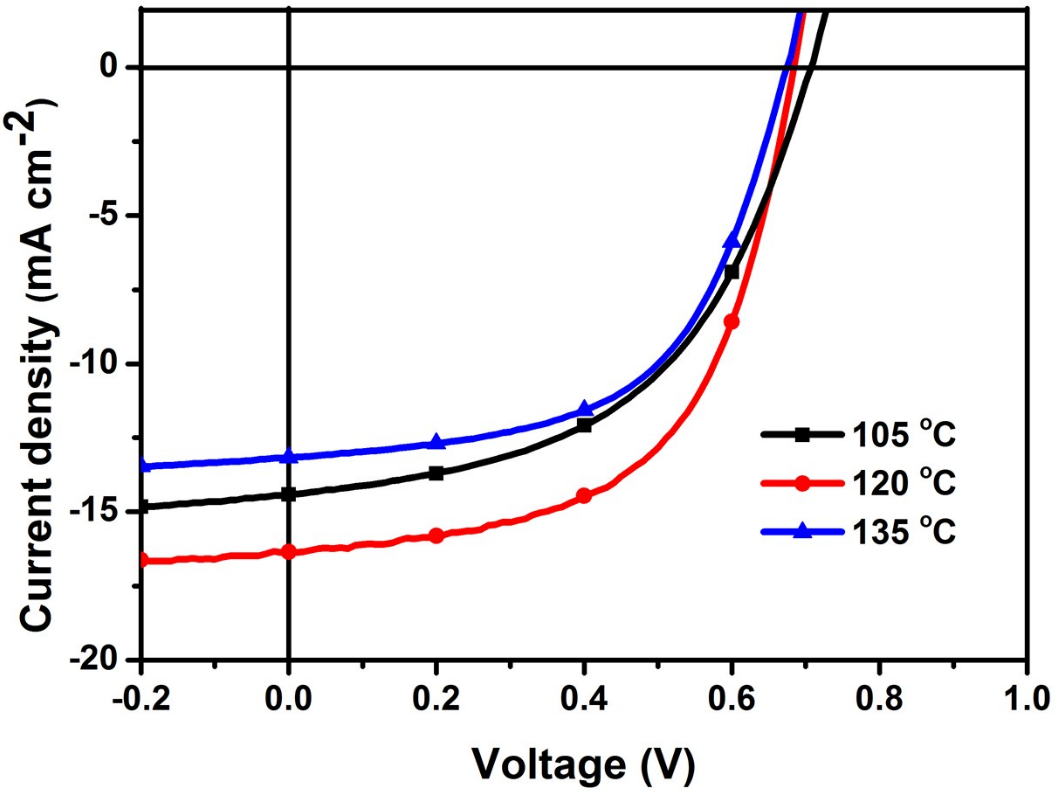


Figure S9. *J-V* curves of BHJ solar cells based on (DPP-ZnP-E)2-Ph:$PC_{61}BM$ cast from chlorobenzene (1% Py) with different TA temperature under illumination of AM 1.5 G, 100 mW cm^{-2}.

Table S4. Photovoltaic performance of BHJ solar cells based on (DPP-ZnP-E)2-Ph:$PC_{61}BM$ cast from chlorobenzene (1% Py) with different TA temperature under illumination of AM 1.5 G, 100 $mWcm^{-2}$.

Temperature (^{o}C)	J_{sc} ($mA\ cm^{-2}$)	V_{oc} (V)	FF (%)	PCE (%)
No	11.17	0.8	35.93	3.21
105	14.41	0.71	50.55	5.17
120	16.34	0.68	57.77	6.42
135	13.16	0.66	58.86	5.01

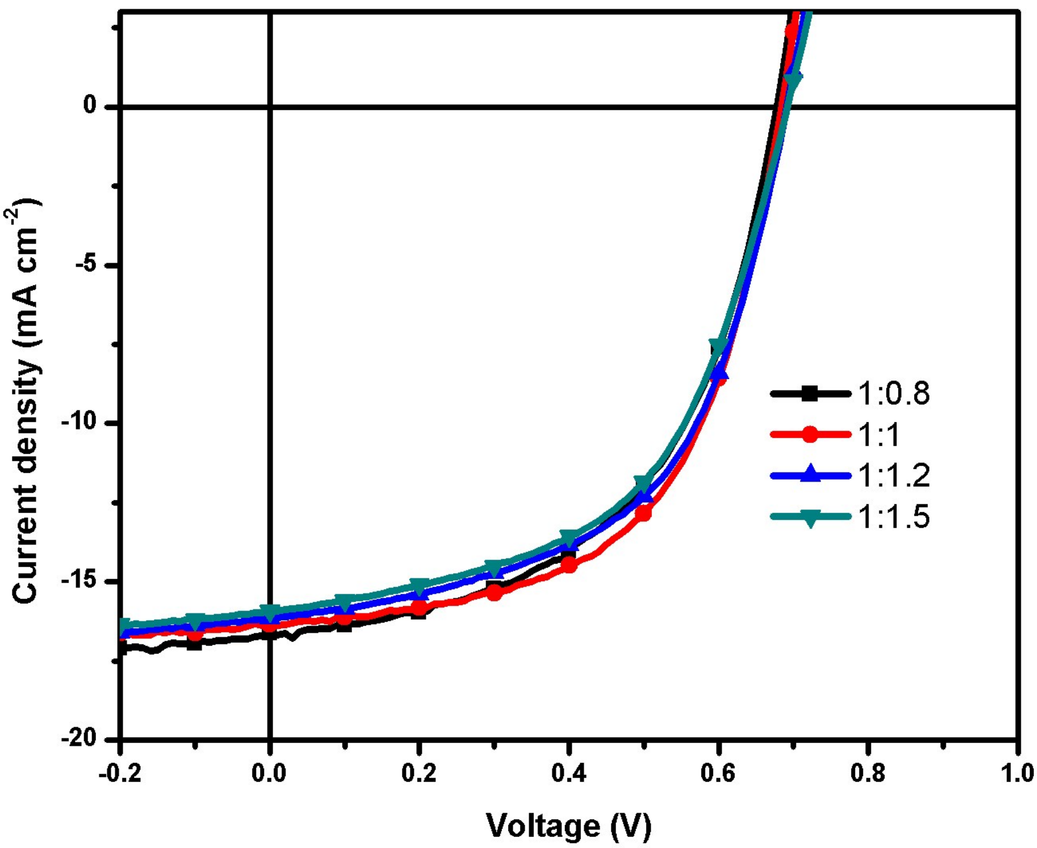


Figure S10. *J-V* curves of BHJ solar cells based on (DPP-ZnP-E)2-Ph:PC$_{61}$BM with different radio under illumination of AM 1.5 G, 100 mW cm^{-2}.

Table S5. Photovoltaic performance of BHJ solar cells based on (DPP-ZnP-E)2-Ph:PC$_{61}$BM cast from chlorobenzene (1% Py) with different radio under illumination of AM 1.5 G, 100 mWcm^{-2}.

(DPP-ZnP-E)2-Ph:PC$_{61}$BM	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
1:0.8	16.62	0.68	52.87	5.97
1:1	16.34	0.68	57.77	6.42
1:1.2	16.14	0.69	55.31	6.16
1:1.5	15.92	0.69	53.91	5.92

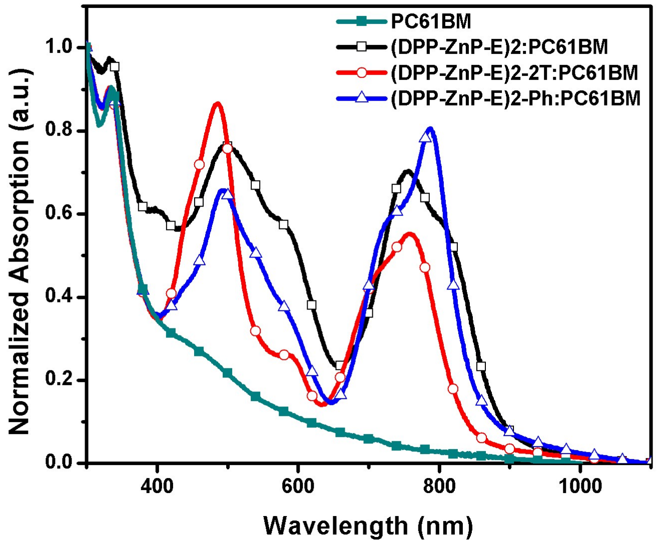


Figure S11. UV-Vis-NIR absorption spectra of the blend films of **(DPP-ZnP-E)2**, **(DPP-ZnP-E)2-2T** and **(DPP-ZnP-E)2-Ph** with $PC_{61}BM$ and the pure film of $PC_{61}BM$.

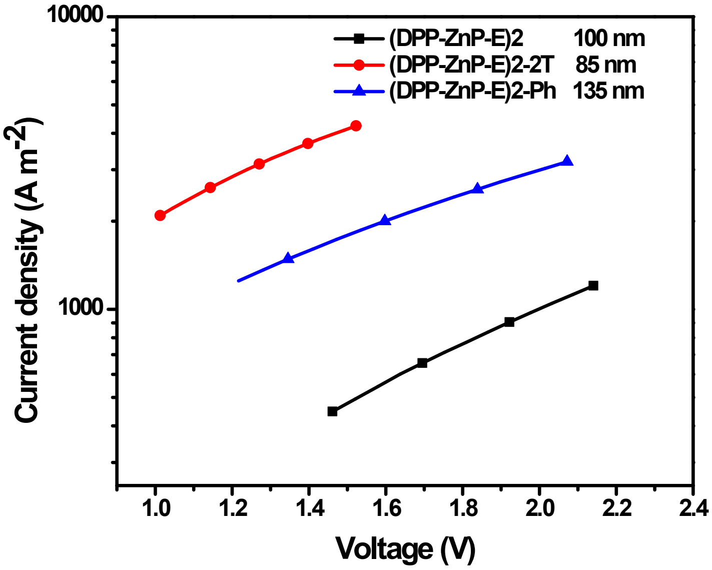


Figure S12. *J-V* characteristics under dark for hole-only devices based on **(DPP-ZnP-E)2**, **(DPP-ZnP-E)2-2T** and **(DPP-ZnP-E)2-Ph** blend with $PC_{61}BM$.

The mobility was described by the following equation:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8L^3}$$

Where J is the current density, L is the active-layer thickness, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), ε_r is the relative dielectric constant of the active layer, μ is the zero-field mobility, V is the voltage drop across the device.

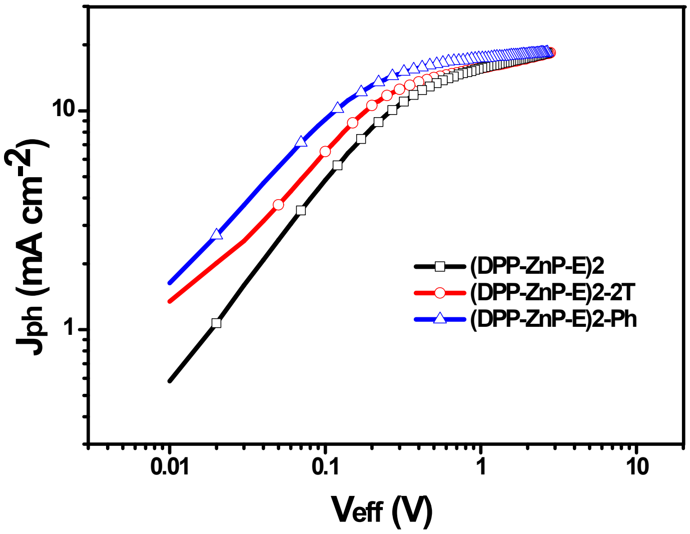


Figure S13. Photocurrent density versus effective voltage (J_{ph} -V_{eff}) characteristics for the three optimized devices under incident light intensity of stimulated AM 1.5G 100 mWm^{-2}.

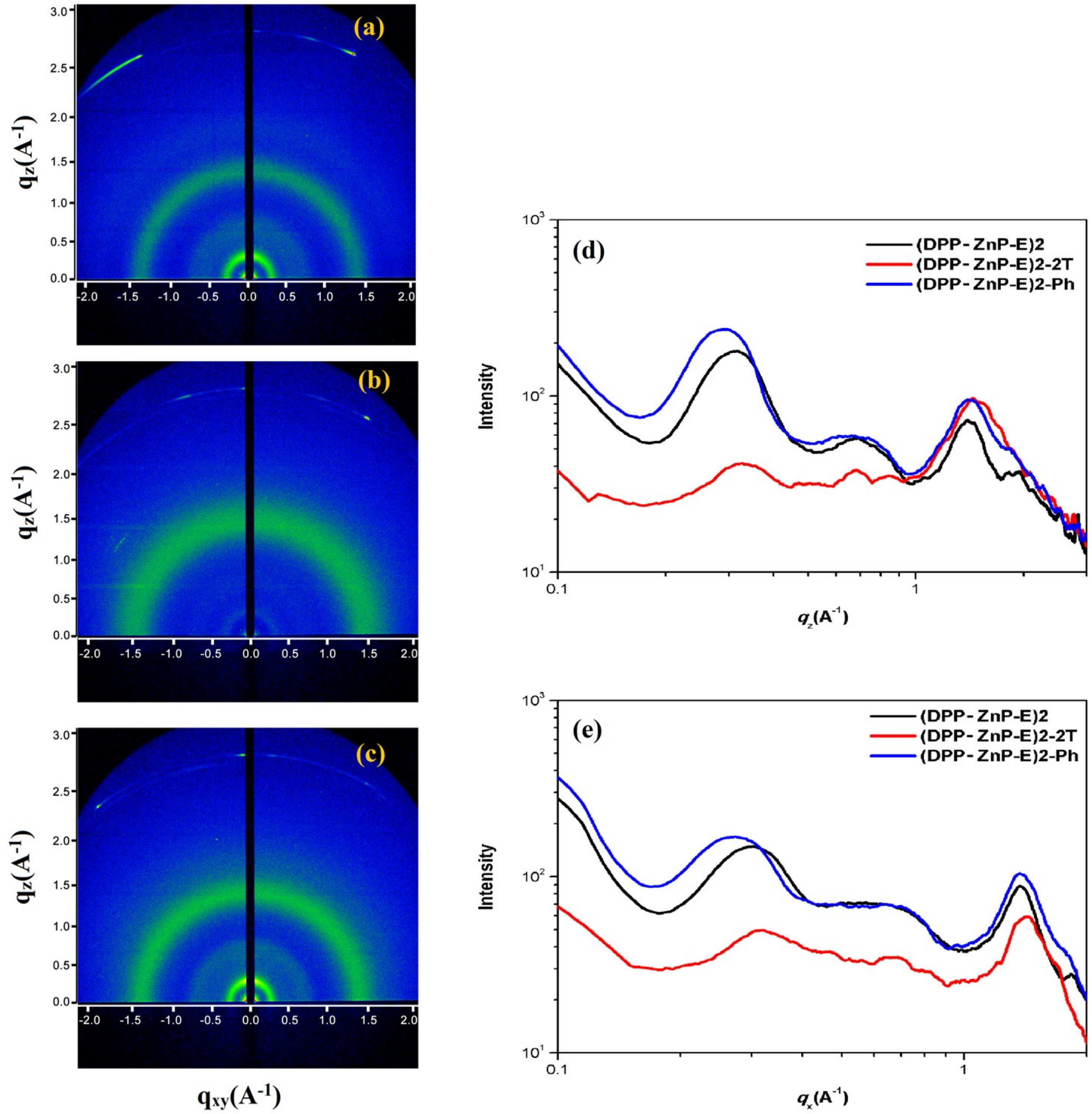


Figure S14. GIXD data of blend films of **(DPP-ZnP-E)2**:PC$_{61}$BM (a), **(DPP-ZnP-E)2-2T**:PC$_{61}$BM (b) and **(DPP-ZnP-E)2-Ph**:PC$_{61}$BM (c); out-of-plane (d) and in-plane (e) line-cult profiles of GIXD of the blend films.

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