

ARTICLE

## Panchromatic Terthiophenyl-benzodithiophene Conjugated Porphyrin Donor for Efficient Organic Solar Cells

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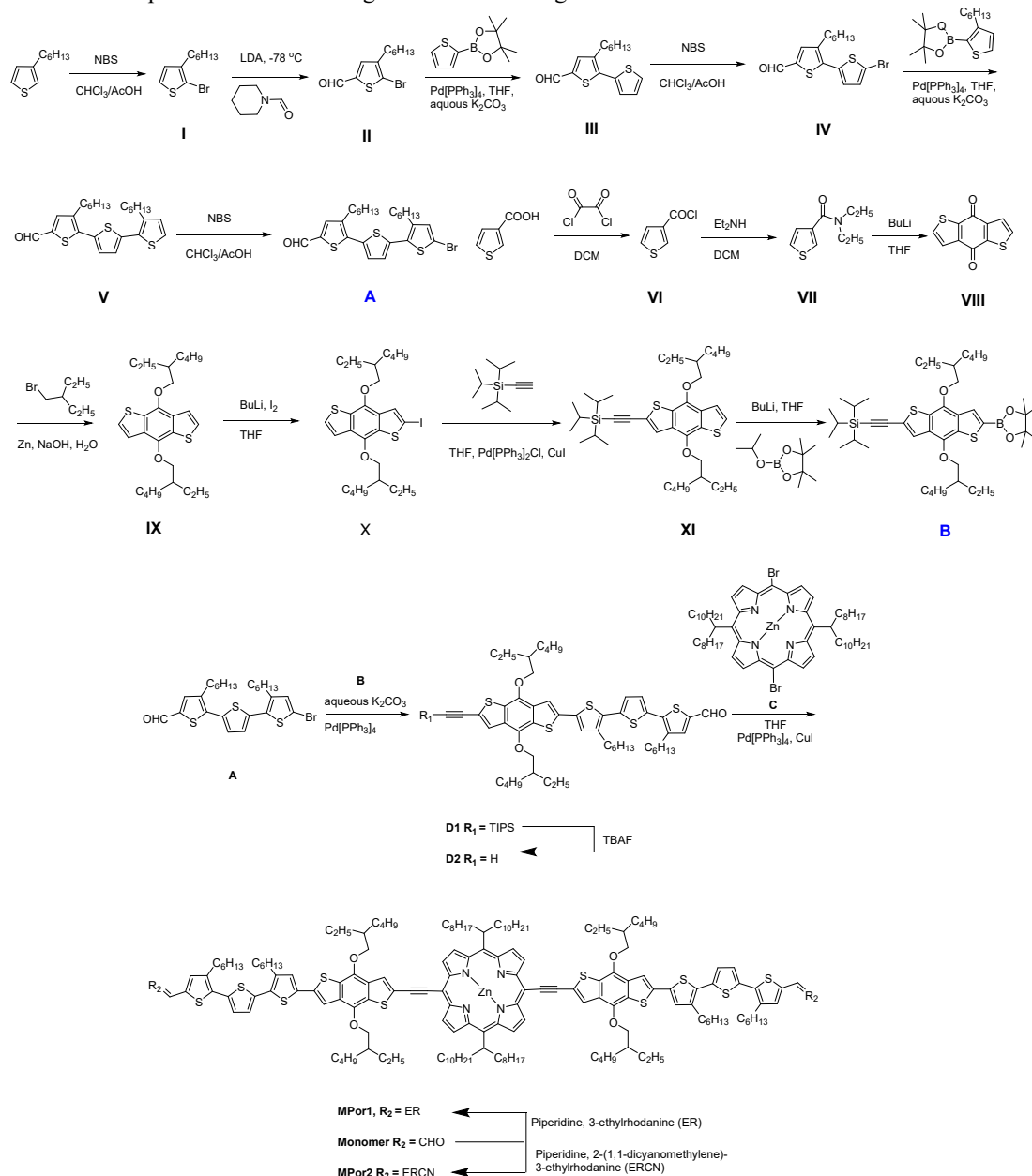
### Experimental Section

**Materials preparation.** All the chemicals commercially available as analytical reagent and were used as received. All the organic solvents were dried before use according to the standard procedures. Di-alkylthio-substituted BDT and Di-alkyloxy-substituted BDT in were synthesized as to previous papers.<sup>1,2</sup>

**Device Fabrication of OSCs.** Solution-processed bulk-heterojunction solar cells were fabricated as described below. Indium tin oxide (ITO) coated glass substrates were cleaned prior to device fabrication by sonication in acetone, detergent, distilled water, and isopropyl alcohol. After treated with an oxygen plasma for 5 min, 40 nm thick poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT: PSS) (Bayer Baytron 4083) layer was spin-coated on the ITO-coated glass substrates at 2500 rpm for 30s, the substrates were subsequently dried at 150°C for 10 min in air and then transferred to a N<sub>2</sub>-glovebox. The active layers were spun from solution of donor material: PC<sub>71</sub>BM at weight ratio of 1:1.2 with an overall concentration of 20 mg/mL in chlorobenzene. The preparing process was operated at 1000 rpm for 60 s. And then the active layer was placed on heating plate at 100 °C for 5 min for thermal annealing (TA) or placed in a glass petri dish containing 4.0 mL THF for 0 or 20 s for solvent vapor annealing (SVA). The thicknesses of active layers were measured by a profilometer and the films' thickness are approximately 90 nm. Finally, Al (~80 nm) was evaporated with a shadow mask as the top electrode. The effective area was measured to be 16 mm<sup>2</sup>.

**Characterization.** <sup>1</sup>H NMR was recorded on spectrometer operating at 400 MHz. UV-vis spectra were performed at room temperature in quartz cuvettes using a Cary UV-300 spectrophotometer (Agilent Technologies, USA) in dichloromethane (DCM), chloroform (CF) solutions and films. The excitation and fluorescence spectra were performed at room temperature in glass cuvettes using a LS55B spectrophotometer (PerkinElmer, USA) in dichloromethane (DCM), chloroform (CF) solutions. The cyclic voltammetry (CV) of sample films was examined using a CHI-600E electrochemical workstation (CH Instrument, USA) and operated at a scan rate of 50 mV·s<sup>-1</sup>; The solvent used was anhydrous acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte. The potentials were measured against an Ag/Ag<sup>+</sup> (0.01 M AgNO<sub>3</sub>) reference electrode; the ferrocene/ferrocenium ion (Fc/Fc<sup>+</sup>) pair was used as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising and background currents of the cyclic voltammograms. HOMO and LUMO energy levels were estimated relative to the energy level of the ferrocene reference (4.8 eV below vacuum level). Three-electrode cell consists of a platinum wire as auxiliary electrode, an Ag/AgCl reference electrode and a glassy carbon working electrode. The high-resolution mass spectra were characterized from a Bruker Autoflex MALDITOF mass spectrometer. mass spectrometer in positive ion mode. The photovoltaic performance of the devices was measured with a computer-programmed

Keithley 2400 source/meter and a Newport's Oriol class A solar simulator, which simulated the AM1.5 sunlight with an energy density of  $100 \text{ mW cm}^{-2}$  and was certified to the JIS C 8912 standard. External quantum efficiency (EQE) was measured with a 300 W Xenon Lamp (Oriol 6258) as the light source and a Cornerstone 260 Oriol 74125 monochromator with a resolution of 10 nm. The light intensity was calibrated with a NREL-recommended Si detector (Oriol 71030NS), and the short-circuit currents were determined with an Oriol 70310 optical power meter. Atomic force microscopic (AFM) images were acquired using a Veeco Nano Scope IV Multi-Mode AFM system with the tapping mode. Time resolved fluorescence decay dynamics were measured by confocal optical microscopy (Nanofinder FLEX2, Tokyo Instruments, Inc.) combined with TCSPC module (Becker & Hickl, SPC-150). Grazing incidence x-ray diffraction (GIWAXS) was performed at BL16B1 beamline of Shanghai Synchrotron Radiation Facility. The sample-to-detector distance is 200 mm and the wavelength of incident X-ray is 0.124 nm. The incidence angle of X ray is  $0.10^\circ$ . Then the data were collected by a mar165CCD. The samples used for GIWAXS measurements were prepared by spin-coating the blend solutions onto Si wafers. Thermogravimetric analysis (TGA) (TA Instruments Corporate, 159 Lukens Drive New Castle, DE, USA) measurements were performed under nitrogen flow at a heating rate of  $20^\circ \text{C min}^{-1}$ .

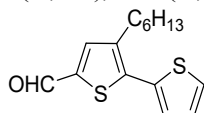


**Scheme S1** Synthetic routes of molecules **MPor1** and **MPor2**.

N-bromosuccinimide (4.72 g, 26.6 mmol) was added in portions at an interval of 15-30 min to 3-hexylthiophene (4.48 mg, 26.6 mmol) in 15 mL ice-cooled 2:1 chloroform/acetic acid mixture. The reaction mixture was stirred for 4 h at room temperature. The

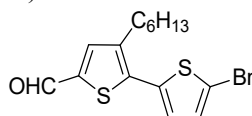
reaction solution was then washed with water and extracted with dichloromethane. The organic layer dried with anhydrous  $\text{MgSO}_4$  was evaporated to dryness to afford I as light-yellow liquid (6.18 g, 99%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz, ppm): 7.22 (d,  $J = 6$  Hz, 2H), 6.87(d,  $J = 6$  Hz, 2H), 2.65(t,  $J = 8$  Hz, 2H), 1.70–1.41 (m, 2H), 1.36–1.28(m, 6H), 1.01–0.94(t, 3H).

Lithium diisopropylamide (2.20 ml, 2.0 M in hexane, 4.4 mmol) was added dropwise to a stirred solution of 2-bromo-3-hexylthiophene (1.00 g, 4.00 mmol) in dry THF (100 ml), under argon at  $-78$  oC. The reaction mixture was kept under this condition for a further 2 h before N-formylpiperidine (0.50 ml, 4.40 mmol) was added dropwise. The mixture was stirred at room temperature for 12 h and quenched with hydrochloric acid (3%, 10 ml). The product was extracted into dichloromethane and the combined organic extracts were washed with brine and dried by anhydrous magnesium sulfate. The crude product was purified by column chromatography (hexane/dichloromethane, 10: 1) to afford compound II as yellow liquid. Yield 0.78 g (70%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz, ppm): 9.76 (s, 1H), 7.45 (s, 1H), 2.63 (t, 2H), 1.60 (m, 2H), 1.35 (m, 6H), 0.83 (t, 3H).



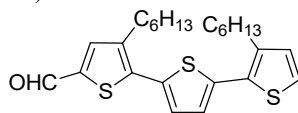
## III

4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (0.64 g, 3.02 mmol), Compound II (0.56 g, 2.02 mmol),  $[\text{Pd}(\text{PPh}_3)_4]$  (0.14 g, 0.12 mmol), and 2.0 mL saturated aqueous  $\text{K}_2\text{CO}_3$  in 20 mL THF was degassed with  $\text{N}_2$  for 5 min and then heated at reflux for 24 h under  $\text{N}_2$  atmosphere.  $\text{CH}_2\text{Cl}_2$  (100 ml) was then added and the organic layer was washed with water for several times. The dried solvents were removed under vacuum condition. The crude product was purified on silica-gel column chromatography using EA/hexane (1:20) as eluent to afford compound III as yellow oil (0.50g, 0.14 mmol, 68%).  $^1\text{H NMR}$  (400 MHz, ppm,  $\text{CDCl}_3$ ): 9.84 (s, 1H), 7.61 (s, 1H), 7.45 (d,  $J = 4$  Hz, 1H), 7.29 (d,  $J = 3.8$  Hz, 1H), 7.12 – 7.10 (m, 1H), 2.85 – 2.70 (t,  $J = 8$  Hz, 2H), 1.69 – 1.61 (m, 2H), 1.45 – 1.24 (m, 6H), 0.87 (t,  $J = 8$  Hz, 3H).



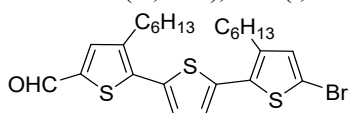
## IV

NBS (1.20 g, 6.7 mmol) was added in portions to compound III (1.8 g, 6.5 mmol) in 40 mL chloroform and 40 mL acetic acid at ice-water bath. The solution was stirred for 6h at room temperature and then the solution was washed with water and extracted with dichloromethane. The dried organic layer was concentrated by reduced pressure. The crude product was purified by silica-gel column chromatography using dichloromethane/hexane (1/3, v/v) as eluent to afford compound IV as yellow solid (1.75 g, 76 %).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , ppm): 9.81 (s, 1H), 7.63 (s, 1H), 7.04 (d,  $J = 4$  Hz, 1H), 7.04(d,  $J = 3.8$  Hz, 1H), 2.76 (t,  $J = 8$  Hz, 2H), 1.82–1.59 (m, 2H), 1.46–1.17 (m, 6H), 0.89 (t,  $J = 6$  Hz, 3H).



## V

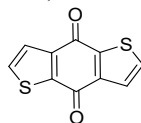
Compound IV (2 g, 5.62 mmol) and 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.48 g, 8.42 mmol)  $\text{Pd}(\text{PPh}_3)_4$  (0.18 g, 3 mol%) and 3 mL saturated aqueous  $\text{K}_2\text{CO}_3$  in 30 mL toluene was stirred for 17 h at  $110$  °C under  $\text{N}_2$  atmosphere. The cooled solution was washed with brine and then was extracted with chloromethane. The combined organic layer was dried on anhydrous magnesium sulfate and concentrated to afford the solid product. The crude product was purified by silica-gel column chromatography using dichloromethane/hexane (1/3, v/v) to afford V as red solid (2.0 g, 83.3%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , ppm): 9.84 (s, 1H), 7.59 (s, 1H), 7.18 (d,  $J = 4$  Hz, 1H), 7.14 (d,  $J = 4$  Hz, 1H), 7.10 (s, 1H), 6.87 (s, 1H), 2.83 (t,  $J = 7.8$  Hz, 2H), 2.63–2.59 (t,  $J = 8$  Hz, 2H), 1.80 – 1.60 (m, 4H), 1.48 – 1.21 (m, 12H), 0.90 (t,  $J = 8$  Hz, 6H).



## C

NBS (2.56 g, 14.4 mmol) was added in portions to compound V (6.4 g, 14.4 mmol) in 40 mL chloroform at  $0$  °C. The resulted solution was stirred for 24 h at room temperature. The resulted solution was washed by brine and was extracted with chloromethane.

the combined organic layer was dried on anhydrous magnesium sulfate and concentrated to afford the solid product. Purification by column chromatography of silica-gel with chloromethane/hexane (1/3, v/v) to afford compound C as yellow solid (7.0 g, 93 % yield).  $^1\text{H NMR}$  (400 MHz, ppm,  $\text{CDCl}_3$ ): 9.86 (s, 1H), 7.63 (s, 1H), 7.19 (d,  $J = 4$  Hz, 1H), 7.09 (d,  $J = 4$  Hz, 1H), 6.94 (s, 1H), 2.83 (t,  $J = 7.8$  Hz, 2H), 2.60–2.56 (t,  $J = 7.9$  Hz, 2H), 1.79–1.69 (m, 2H), 1.52–1.24 (m, 14H), 0.98–0.91 (t,  $J = 8$  Hz, 6H).



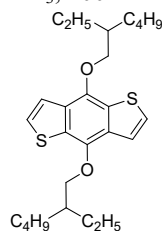
VIII

Oxalyl chloride (152.40 g, 1.20 mol) was added in one portion to thiophene-3-carboxylic acid (76.80 g, 0.60 mol) in 60 mL dichloromethane at 0 °C,

The mixture solution was stirred for 12–16 h at room temperature to form clear solution and then the solvent and unreacted oxalyl chloride were removed by rotary evaporation to afford B2 as colourless solid. The VI were used for next step without further purification.

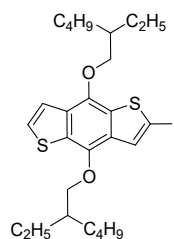
VI in 200 mL dichloromethane was slowly added to diethyl-amine (125.00 mL, 1.20 mol) in 200 mL dichloromethane at 0 °C. The resulted solution was stirred at room temperature for 0.5 h and then washed by water for 3 times. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent was removed by reduced pressure. The crude product was purified by flash silica-gel column chromatography using chloroform as eluent to afford VII as pale-yellow oil (0.56 mol, 92%)  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz, ppm): 7.49 (s, 1H), 7.33 (d, 1H), 7.19 (d, 1H), 3.40 (m, 4H), 1.20 (t, 6H).

*N*-butyllithium (40 mL, 2.5 M) was dropwise added into VII (0.1 mol, 18.3 g) in 100 mL of THF within 30 min under an inert atmosphere at 0 °C. The resulted solution was stirred at room temperature for 0.5 h. The resulted solution was poured into 250 mL ice water and stirred for 6 hours. The mixture was filtrated and washed by 100 mL water, 25 mL methanol and 25 mL hexane to afford VIII as yellow solid (17.0 g, 77%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz, ppm): 7.76 (d, 2 H), 7.96 (d, 2 H).



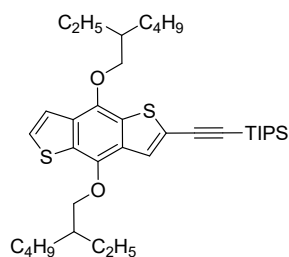
IX

VIII (2.20 g, 10.0 mmol), NaOH (6.00 g, 150.0 mmol) and zinc powder (1.43 g, 22.0 mmol) in 30 mL water was well stirred and heated to reflux for 1 h. 2-Ethylhexyl bromide (11.59 g, 60.0 mmol) and tetrabutylammonium bromide with catalytic amount were added into the reacting solution and continue to reflux for 4 h. The solution was washed by cold water and extracted by dichloromethane. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and solvent was removed by reduced pressure. The crude product was purified by silica-gel column chromatography using hexane as eluent to afford IX as colourless oil (2.01 g, 40 %).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz, ppm): 7.49–7.45 (d,  $J = 4.8$  Hz, 2H), 7.36–7.31 (d,  $J = 4.8$  Hz, 2H), 3.97–3.83 (m, 4H), 1.63–1.48 (m, 2H), 1.37–1.08 (m, 16H), 0.91–0.73 (m, 12H).



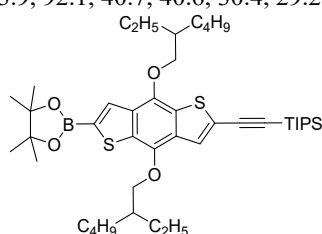
I-BDT1

BuLi (1 mL, 2.5 mmol, 2.5 M) was added dropwise to IX (1.04 g, 2.33 mmol) in 20 mL dry THF over 50 min at  $-78$  °C under  $\text{N}_2$  protection. The mixture was stirred for 30 min at  $-78$  °C. And iodine (0.7 g, 2.75 mmol) in 5 mL dry THF was injected to the solution by syringe. The reaction was stirred for 15 min and quenched with water. The solution was washed by water and extracted by dichloromethane. The dried organic phase was concentrated with rotary evaporator. And the crude product was purified by silica gel column chromatography with hexane as eluent to obtain pure product X (0.99 g, 74%).  $^1\text{H NMR}$  (400 MHz, ppm,  $\text{CDCl}_3$ ): 7.65 (s, 1H), 7.45–7.44 (d,  $J = 4$ , 1H), 7.41–7.39 (d,  $J = 7.9$  Hz, 1H), 4.15–4.12 (m, 4H), 1.80–1.78 (m, 2H), 1.65–1.25 (t, 16 H), 1.03–1.00 (m, 12H).  $^{13}\text{C NMR}$  (400 MHz, ppm,  $\text{CDCl}_3$ ): 143.3, 143.2, 131.5, 130.3, 130.2, 126.5, 120.2, 40.7, 40.6, 30.4, 29.2, 23.2, 14.2, 14.2, 11.4.



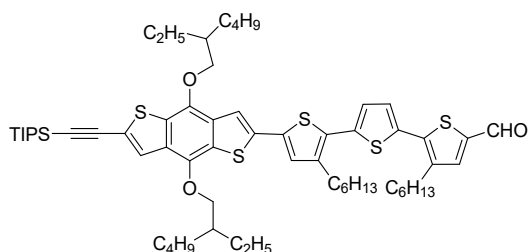
TIPS-BDT1

Iodine compound (1.27 g, 10.00 mmol) in 30 mL THF and 15 mL triethylamine was degassed and backfilled with nitrogen for at least three times. Bis(triphenylphosphine) palladium(II) dichloride (213.4 mg, 0.20 mmol) and copper(I) iodide (38.1 mg, 0.20 mmol) were added to the flask. The mixture was bubbling with nitrogen for half hour. And (triisopropylsilyl)acetylene (18.2 g, 100.00 mmol) was injected into the flask via syringe. The resulted solution was stirred for 3 h at 50 °C and then filtered. The resulted filtrate was concentrated under vacuum condition and the crude product was purified by silica gel column chromatography to obtain pristine product. Yield (87 %).  $^1\text{H NMR}$  (400 MHz, ppm,  $\text{CDCl}_3$ ): 7.65 (s, 1H), 7.44–7.42 (d,  $J = 4$ , 1H), 7.40–7.38 (d,  $J = 7.9$  Hz, 1H), 4.15–4.13 (m, 4H), 1.80–1.78 (m, 2H), 1.65–1.25 (m, 37H), 1.03–0.94 (m, 12H), 0.27 (s, 9H).  $^{13}\text{C NMR}$  (400 MHz, ppm,  $\text{CDCl}_3$ ): 143.3, 143.2, 131.5, 130.3, 130.2, 126.5, 120.2, 93.9, 92.1, 40.7, 40.6, 30.4, 29.2, 23.2, 21.4, 18.8, 14.2, 14.2, 11.4.



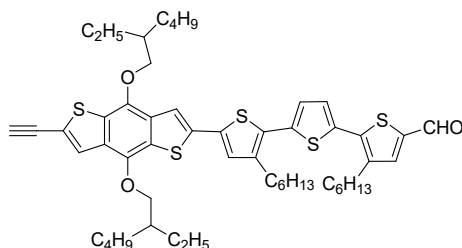
TIPS-BDT1-B

BuLi (1.1 mL, 2.8 mmol, 2.5 M in hexane) was added into the flask dropwise to TIPS-BDT1 (1.76 g, 2.8 mmol) in 30 mL dry THF at  $-78$  °C during 0.5 h under  $\text{N}_2$  protection. The resulted mixture was continuously stirred for 1 h at  $-78$  °C and isopropoxyboronic acid pinacol ester (0.52 g, 2.8 mmol) was added in to the solution in one portion. The reaction was stirred for 1 hour at room temperature, and then quenched by water. The solution was washed and extracted by dichloromethane. The solvent was removed by reduced pressure to obtain the crude product. The crude product was purified via flash silica-gel column chromatography using dichloromethane/hexane (3:1, v/v) as eluent to obtain pure TIPS-BDT1-B, (86%). The collected product was used for next step without further purification.



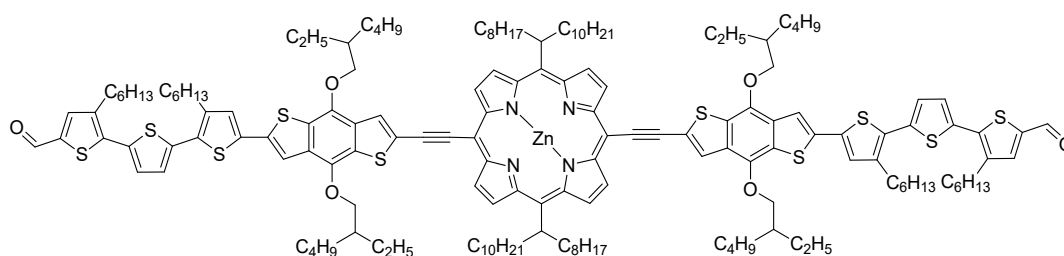
D1

TIPS-BDT1-B (2.63 g, 3.5 mmol), compound C (1.57 g, 3.0 mmol) and 3 mL aqueous saturated  $\text{K}_2\text{CO}_3$  were added to 30 THF and the solution was degassed with nitrogen for 30 min.  $\text{Pd}(\text{PPh}_3)_4$  (173.6 mg, 0.15 mmol) were added and the solution was stirred at 70 °C for 24 h under nitrogen. The solution was washed with brine, extracted with dichloromethane and concentrated under reduced pressure. The solid residue was purified via silica-gel column chromatography using a  $\text{CHCl}_3$ /hexane (1:1) mixture as eluents to afford D1 as yellow solid.  $^1\text{H NMR}$  (400 MHz, ppm,  $\text{CDCl}_3$ ): 9.84 (s, 1H), 7.61 (s, 1H), 7.54 (s, 1H), 7.47 (s, 1H), 7.26 (s, 1H), 7.16 (s, 2H), 4.17–4.14 (s, 4H), 2.82–2.79 (m, 4H), 1.84–0.91 (m, 48H).  $^{13}\text{C NMR}$  (400 MHz, ppm,  $\text{CDCl}_3$ ): 182.5, 144.3, 143.9, 140.3, 135.6, 133.2, 130.4, 128.9, 127.9, 125.8, 122.8, 116.1, 99.9, 98.4, 40.7, 31.7, 30.4, 29.7, 29.3, 29.2, 23.9, 23.2, 22.7, 22.6, 18.7, 14.2, 14.1, 11.4, 11.3.



D2

Tetrabutylammonium fluoride (1 ml, 1.0 mmol, 1 M in THF) was added to D1 (1.07 g, 1.0 mmol) in about 60 mL dry THF. The mixture was stirred for 15 min at 25 °C. The resulting mixture was washed with water and extracted by dichloromethane and finally dried over anhydrous Mg<sub>2</sub>SO<sub>4</sub>. The solvent was removed by reduced pressure and the crude product was purified via silica-gel column chromatography using CHCl<sub>3</sub>/hexane (1:1) as eluent to obtain pure D2 as orange solid (0.40 g, 60 %). <sup>1</sup>H NMR (400 MHz, ppm, CDCl<sub>3</sub>): 9.84 (s, 1H), 7.61 (s, 1H), 7.60 (s, 1H), 7.47 (s, 1H), 7.26 (s, 1H), 7.16 (s, 2H), 4.18-4.14 (m, 4H), 3.48 (s, 1H), 2.84-2.80 (m, 4H), 1.82-0.88 (m, 48H). <sup>13</sup>C NMR (400 MHz, ppm, CDCl<sub>3</sub>): 182.6, 140.5, 136.8, 135.5, 134.9, 133.4, 130.7, 130.5, 130.3, 128.6, 127.9, 126.7, 126.4, 121.2, 116.0, 83.3, 40.7, 31.7, 30.4, 29.7, 29.3, 29.3, 29.2, 23.9, 23.8, 23.2, 23.1, 22.7, 22.6, 14.2, 14.1, 11.4.

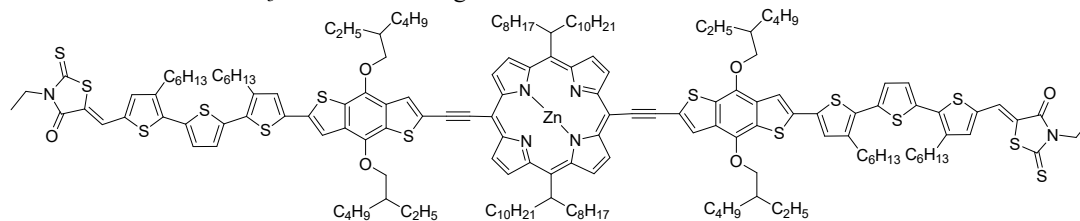


Monomer

D2 (0.64 g, 0.71 mmol) and brominated porphyrins (0.32 g, 0.30 mmol) were put in 30 THF and 15 mL Et<sub>3</sub>N and then degassed with nitrogen for 30 min. Pd(PPh<sub>3</sub>)<sub>4</sub> (42.7 mg, 0.04 mmol) and CuI (7.7 mg, 0.04 mmol) were added and the solution was continued to stir at 60 °C for 12 h under nitrogen. The solvent was removed under vacuum condition, and the solid product was purified by preparative thin layer chromatography using a CHCl<sub>3</sub>/hexane (1:1) mixture as eluents. Recrystallization from CHCl<sub>3</sub>/methanol gave Por-BA, SPor-SBA and Por-BTA as a green solid. <sup>1</sup>H NMR (400 MHz, ppm, CDCl<sub>3</sub>): 9.86 (s, 2H), 9.75-9.64 (m, 8H), 8.00 (s, 2H), 7.85 (s, 2H), 7.62 (s, 2H), 7.59 (s, 2H), 7.26 (s, 2ZH), 7.23-7.20 (m, 4H), 5.22 (s, 2H), 4.37-4.33 (m, 8H), 2.98-2.72 (m, 16H), 1.96-0.77 (m, 172H).

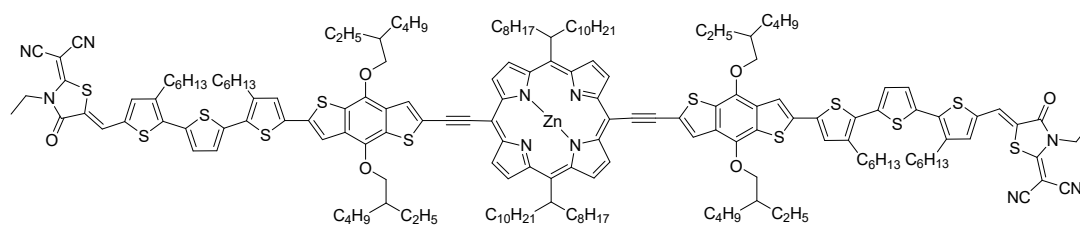
#### General Synthetic Route of **MPor1** and **MPor2**.

Monomer (0.13 mmol) and 3-ethylrhodanine or 2-(1,1-dicyanomethylene)-3-ethylrhodanine (CNR) (0.13 mmol) in dry CHCl<sub>3</sub> were added piperidine and the solution was stirred at 60 °C for 12 h under nitrogen atmosphere. The reaction was then stopped by adding 30 mL water and the resulted solution was extracted with CHCl<sub>3</sub>. The dried and combined organic layer was concentrated under vacuum condition and the crude product was purified by silica gel thin layer chromatography using CHCl<sub>3</sub>/hexane as eluent and recrystallized from a mixture of CHCl<sub>3</sub> and methanol to get **MPor1** and **MPor2** as dark brown solid.



MPor1

Yield (80 %). <sup>1</sup>H NMR (400 MHz, ppm, CDCl<sub>3</sub>): 9.70-9.62 (m, 8H), 7.95 (s, 2H), 7.74 (s, 2H), 7.66 (s, 2H), 7.54 (s, 2H), 7.19-7.17 (m, 6H), 5.21 (s, 2H), 4.37-4.32 (m, 8H), 4.20-4.18 (m, 4H), 3.00-2.72 (m, 16H), 1.96-0.76 (m, 178H). (MALDI-TOF, m/z) calculated: 3016.3333.



MPor2

Yield (85 %).  $^1\text{H NMR}$  (400 MHz, ppm,  $\text{CDCl}_3$ ): 9.70-9.64 (m, 8H), 7.93 (s, 2H), 7.70 (s, 2H), 7.47 (s, 2H), 7.20 (s, 2H), 7.10 (s, 4H), 7.03 (s, 2H), 5.21 (s, 2H), 4.34-4.33 (m, 8H), 4.24-4.23 (m, 4H), 3.00-2.96 (m, 16H), 2.00-0.76 (m, 178H). (MALDI-TOF,  $m/z$ ) calculated: 3079.1507.

Table S1. Selected parameters for the vertical excitation (UV-vis absorption) of the compounds. Electronic excitation energies (eV) and oscillator strengths (f), configurations of the low-lying excited states of MPor1. Calculated by TDDFT//B3LYP/GENECP, based on the optimized ground state geometries (No specific solvent was defined in all the calculation).

TDDFT/B3LYP/ GENECP					
Electronic transition a		Excitation energy	f b	Composition c	CI d
Absorption	$S_0 \rightarrow S_1$ (Soret-band)	1.61 eV (768 nm)	2.8705	$H \rightarrow L$	0.6378
				$H \rightarrow L+1$	0.1973
				$H \rightarrow L+2$	0.1709
	$S_0 \rightarrow S_3$ (1)	1.82 eV (679 nm)	0.8232	$H-3 \rightarrow L+3$	-0.1091
				$H \rightarrow L$	0.1515
				$H \rightarrow L+1$	0.1843
				$H \rightarrow L+2$	0.643
				$H-2 \rightarrow L$	0.1124
	$S_0 \rightarrow S_6$ (2)	2.0747 (598)	0.7956	$H-2 \rightarrow L+1$	0.1098
				$H-1 \rightarrow L$	-0.2297
				$H-1 \rightarrow L+1$	0.6177
				$H \rightarrow L+2$	-0.1116
				$H-5 \rightarrow L$	0.1507
	$S_0 \rightarrow S_{14}$ (Q-band)	2.42 eV (511 nm)	0.4112	$H-5 \rightarrow L+1$	0.1561
				$H-4 \rightarrow L$	-0.3125
				$H-4 \rightarrow L+1$	0.1449
				$H-3 \rightarrow L+1$	-0.12906
				$H-1 \rightarrow L+2$	0.1162
				$H \rightarrow L+4$	0.4817
				$H \rightarrow L+5$	0.4694

<sup>a</sup> Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength. <sup>b</sup> Oscillator strength. <sup>c</sup> H stands for HOMO and L stands for LUMO. Only the main configurations are presented. <sup>d</sup> Coefficient of the wavefunction for each excitation. The CI coefficients are in absolute values.

Table S2. Selected parameters for the vertical excitation (UV-vis absorption) of the compounds. Electronic excitation energies (eV) and oscillator strengths (f), configurations of the low-lying excited states of MPor2. Calculated by TDDFT//B3LYP/GENECP, based on the optimized ground state geometries (No specific solvent was defined in all the calculation).

TDDFT/B3LYP/ GENECP					
Electronic transition a		Excitation energy	f b	Composition c	CI d
Absorption	S0→S1 (Soret-band)	1.53 eV (811 nm)	1.7115	H→L	0.6683
				H→L+1	0.1571
				H→L+2	-0.1195
	S0→ S3 (1)	1.78 eV (697 nm)	2.1202	H-3 → L+3	-0.1193
				H-1 → L	-0.1041
				H → L+1	0.1139
				H → L	0.1209
				H → L+1	0.1394
	S0→ S5 (2)	1.99 (621)	0.4573	H → L+2	0.6377
				H-2 → L+1	0.1367
				H-1 → L	-0.2191
	S0→S14 (Q-band)	2.38 eV (521 nm)	0.3670	H-1 → L+1	0.6168
H → L+2				-0.1753	
H-5 → L				-0.1202	
H-5 → L+1				-0.2474	
H-4 → L				-0.2320	
H-4 → L+1				0.1547	
H-1 → L+2				0.1367	
H → L+4	0.5146				
			H → L+5	-0.1723	

a Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength. b Oscillator strength. c H stands for HOMO and L stands for LUMO. Only the main configurations are presented. d Coefficient of the wavefunction for each excitations. The CI coefficients are in absolute values.

Table 3 Parameters at (100) diffraction of GIWAXS results of neat, blend-films of MPor1/PC<sub>71</sub>BM with various post-processed technologies.

MPor1	q (nm <sup>-1</sup> )	d (nm)	FWHM (nm <sup>-1</sup> )	CL (nm)
Neat	3.53	1.78	0.345	16.94
TA Blend1	3.66	1.72	0.51	11.46
SVA+TA Blend1	3.69	1.70	0.49	11.93

Note. The layer space (d-spacing) is calculated according to  $d=2\pi/q$ , and coherence length is calculated to  $CL= 2\pi k/q$ ,  $k = 0.93$ .

Table 4 Parameters at (100) diffraction of GIWAXS results of neat, blend-films of MPor2/PC<sub>71</sub>BM with various post-processed technologies.

MPor2	q (nm <sup>-1</sup> )	d (nm)	FWHM (nm <sup>-1</sup> )	CL (nm)
Neat	3.81	1.65	0.53	11.03
TA Blend2	3.81	1.65	0.47	12.43
SVA+TA Blend2	3.80	1.66	0.49	12.33

Note. The layer space (d-spacing) is calculated according to  $d=2\pi/q$ , and coherence length is calculated to  $CL= 2\pi k/q$ ,  $k = 0.93$ .



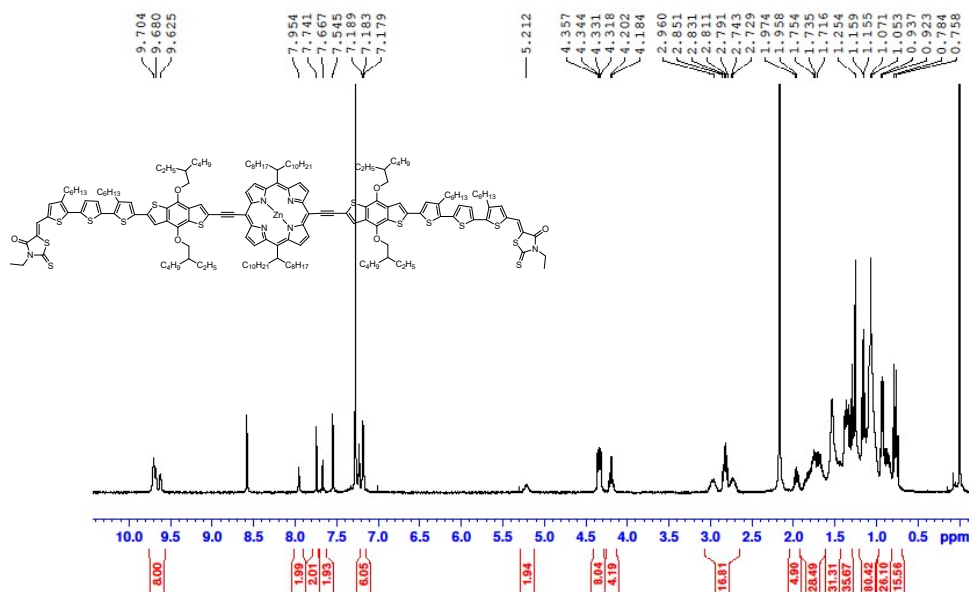
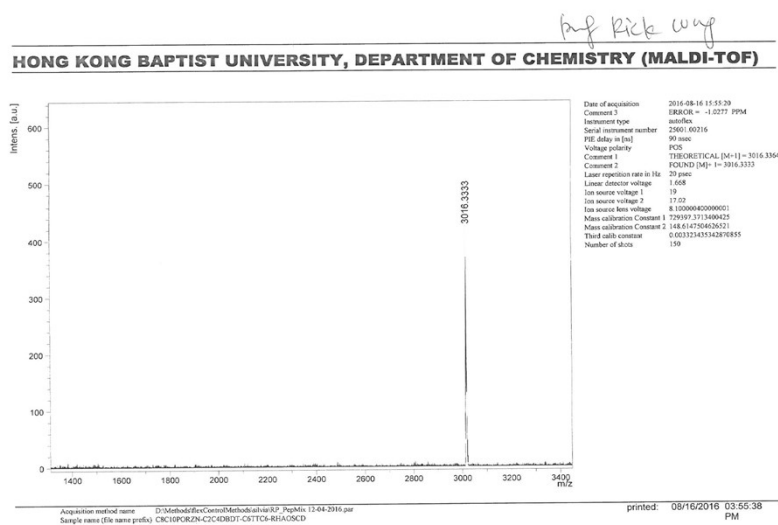
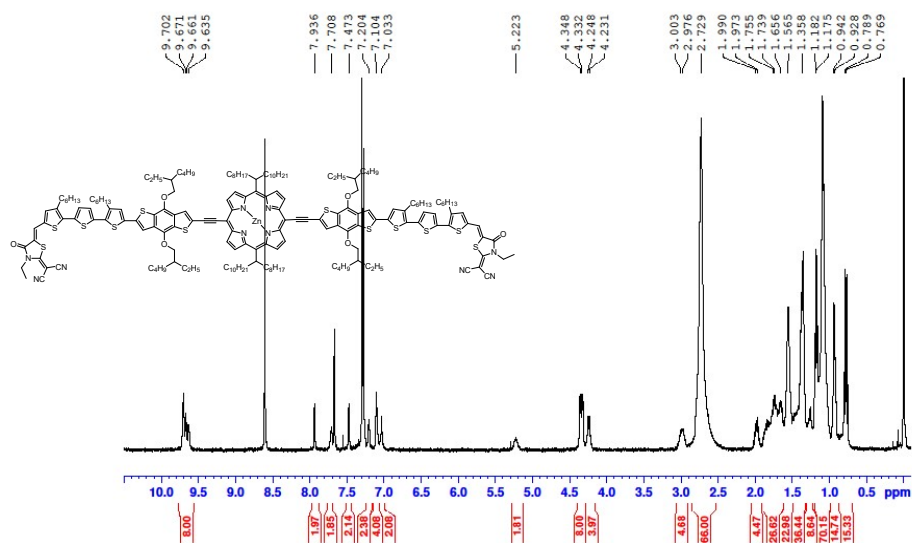
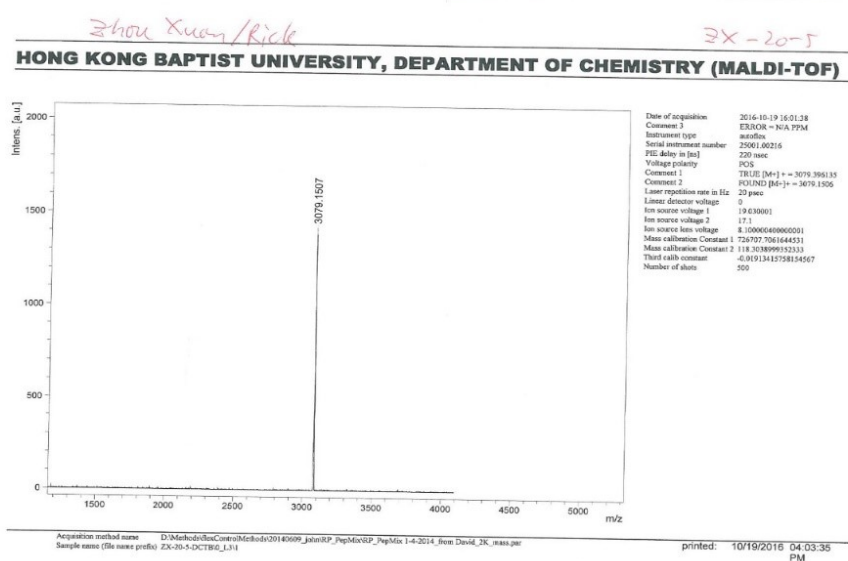
Figure S1  $^1\text{H}$  NMR of molecule MPor1.

Figure S2 MALDI-TOF-MS spectrum of molecule MPor1.

Figure S3  $^1\text{H}$  NMR of molecule **MPor2**.Figure S4 MALDI-TOF-MS spectrum of molecule **MPor2**.

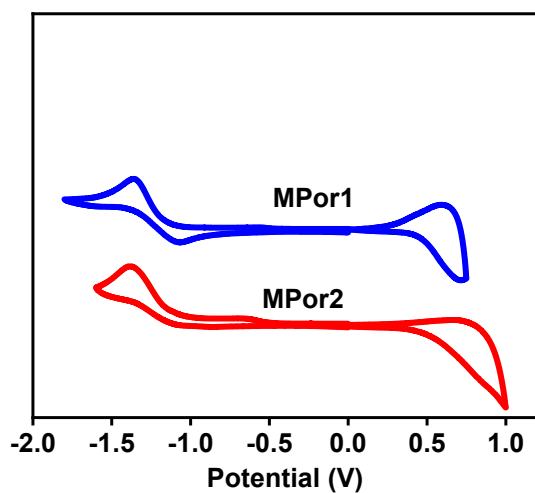


Figure S5. Cyclic voltammograms of MPor1 and MPor2.

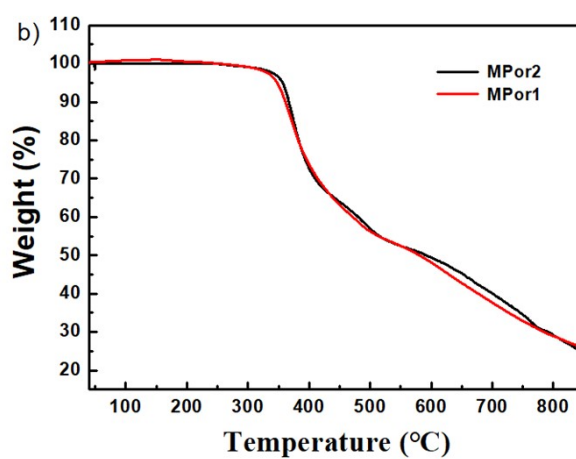


Figure 6s. DSC and TGA data of final compounds of MPor1 and MPor2.

**Reference.**

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2. J. Hou, M.-H. Park, S. Zhang, Y. Yao, L.-M. Chen, J.-H. Li and Y. Yang, *Macromolecules.*, 2008, **41**, 6012-6018.