Supplementary Information

Solution-processed bulk heterojunction solar cells based on a porphyrin small molecule with 7% power conversion efficiency

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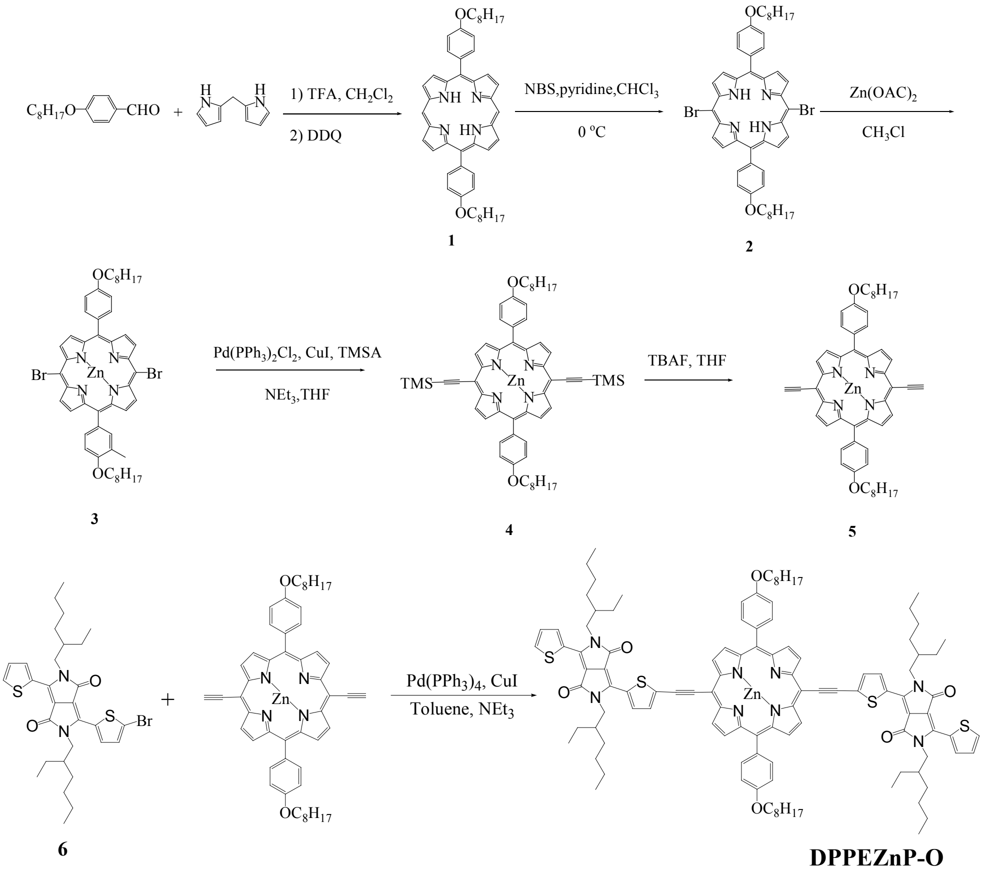
1. Synthesis of DPPEZnP-O



Scheme S1. Synthetic routines of DPPEZnP-O.

5,15-Bis-(4-octyloxy-phenyl)-porphyrin (**1**)

A solution of 4-octyloxy-benzaldehyde (6.2g, 26.5mmol) and dipyrromethane (3.88g, 26.6 mmol) in CH_2Cl_2 (1.25L) was purged with nitrogen for 30 min, and then trifluoroacetic acid (TFA) (0.1 mL) was added. The mixture was stirred for 12h at room temperature, and then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (9g) was added. After the mixture was stirred at room temperature for an additional 1h, the reaction was quenched by triethylamine (5 mL). Then the solvent was removed, and the residue was purified by flash column chromatography on silica gel using dichloromethane as the eluent. Recrystallization from $CHCl_3$/methanol gave **1** as a purple solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.30 (s, 2H), 9.39 (d, 4H), 9.12 (d, 4H), 8.17 (d, 4H),7.33 (d, 4H), 4.28 (t, 4H), 2.02(m, 4H), 1.62(m, 4H), 1.48 (m, 20H), 0.97 (t, 6H)， -3.2 (s, 2H)。

5,15-Dibromo-10,20-bis-(4-octyloxy-phenyl)-porphyrin (**2**)

Porphyrin **1** (144 mg, 0.2 mmol) and pyridine (1 mL) were dissolved in 100 mL chloroform and then cooled to 0℃. To the cold solution, N-bromosuccinimide was added and the mixture was stirred at 0 °C for 30 min. Then the reaction was quenched by acetone, and the mixture was washed with water and dried over anhydrous Na_2SO_4. After the solvent was removed, the residue was purified by flash column chromatography on silica gel using petroleum ether/dichloromethane (1:3) as the eluent. Recrystallization from $CHCl_3$/methanol gave **2** as a purple solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.39 (d, 4H), 9.12 (d, 4H), 8.17 (d, 4H),7.33 (d, 4H), 4.28 (t, 4H), 2.02(m, 4H), 1.62(m, 4H), 1.48 (m, 20H), 0.97 (t, 6H)， -3.2 (s, 2H).

5,15-Dibromo-10,20-bis(4- octyloxy-phenyl)-porphyrin zinc (**3**)

To a solution of **2** (437 mg, 0.5 mmol) in chloroform (50 mL), was added a solution of $Zn(OAc)_2$ (243 mg, 1.2 mmol) in methanol (12 mL). The reaction mixture was refluxed for 2h and then washed with water and dried over anhydrous Na_2SO_4. After the solvent was removed, the residue was recrystallized from $CHCl_3$/methanol gave a purple solid **3**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.64 (d, 4H), 8.90 (d, 4H), 8.03 (d, 4H),7.29 (d, 4H), 4.27 (t, 4H), 2.01(m, 4H), 1.63(m, 4H), 1.45 (m, 20H), 0.94 (t, 6H).

5,15-Bis(trimethylsilyethynyl)-10,20-bis(4- octyloxy-phenyl)-porphyrin zinc (**4**)

Porphyrin **3** (468mg, 0.5 mmol) was dissolved in THF (50mL) and triethylamine (25mL) was added. The mixture was purged with nitrogen for 30 min. Then $Pd(PPh_3)_2Cl_2$ (17.5 mg, 0.025 mmol), CuI (5 mg, 0.025 mmol), and trimethylsilyacetylene (200 mg, 2 mmol) were added. The mixture was stirred at room temperature for 24h under nitrogen, the reaction was quenched with saturated brine. After the mixture was extracted with dichloromethane a few times, the combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Finally, the residue was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether (1:1) to afford **4** as a purple solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.68 (d, 4H), 8.95 (d, 4H), 8.06 (d, 4H),7.31 (d, 4H), 4.26 (t, 4H), 2.01(m, 4H), 1.62(m, 4H), 1.44 (m, 20H), 0.93 (t, 6H) , 0.61 (t, 18H).

5,15-Diethynyl-10,20-bis(4- octyloxy-phenyl)porphyrin zinc (**5**)

Tetrabutylammonium fluoride (0.72 mL, 1M in THF) was added to a stirred solution of porphyrin **4** (308 mg, 0.35 mmol) in THF (40 mL). After the mixture was stirred for 5 min, water was added to quench the reaction. Then the solution was extracted with chloroform, washed with water and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether (1/1)) to give **5** as a deep blue needle crystals. ^{1}H NMR (300MHz, $CDCl_3$): δ 9.75 (d, 4H), 8.96 (d, 4H), 8.07 (d, 4H), 7.29(d, 4H), 4.28 (t, 4H), 2.02(m, 4H), 1.65(m, 4H), 1.40 (m, 20H), 0.96 (t, 6H).

3-(5-Bromo-thiophen-2-yl)-2,5-bis-(2-ethyl-hexyl)-6-thiophen-2-yl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (**6**)

Compound **6** was synthesized according to the procedures in Supporting Information reported previously.[1] ^{1}H NMR (300MHz, $CDCl_3$), δ 8.91 (d, 1H), 8.64 (d, 1H), 7.64

(d, 1H), 7.28 (t, 1H), 7.22 (d, H), 4.02 (m, 2), 3.96 (m, 2), 1.83 (m, 2H), 1.36-1.26 (m,16H), 0.86 (m, 12H)。 ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.65, 140.89, 138.94, 135.53, 135.09, 131.37, 131.25, 130.82, 129.75, 128.48, 118.62, 108.15, 45.93, 39.11, 39.06, 30.19, 28.33, 23.56, 23.02, 14.00, 10.46.

5,15-Bis(2,5-bis-(2-ethyl-hexyl)-3,6-di-thienyl-2-yl-2,5-dihydro-pyrrolo[3,4-c] pyrrole-1,4-dione-5'-yl-ethynyl)-10,20-bis(4-octyloxy-phenyl)-porphyrin zinc (DPPEZnP-O)

To a 50 mL two necked round-bottom flask were added 5,15-diethynyl-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin zinc **5** (826 mg, 1.0 mmol), **6** (1.50g, 2.5 mmol), anhydrous toluene (100 mL) and triethylamine (50 mL), and the mixture was deoxygenated with N_2 for 30 min before Pd $(PPh_3)_4$ (200 mg, 0.2 mmol) and CuI (40 mg, 0.2 mmol) were added. Then the mixture was stirred at 80℃ for 72 h under the protection of Ar. After cooled to room temperature, the mixture was washed with water and dried over anhydrous Na_2SO_4. Then the solvent was removed, and the residue was purified first by column chromatography on silica gel and then by GPC HPLC to give a black solid DPPEZnP-O. DPPEZnP-O does not show satisfied NMR spectra due to its expanded π structure. Mass (MALDI-TOF): Obs. 2356.28; Calcd. for $C_{144}H_{192}N_8O_8S_2Zn$, 2356.76.

2. Instruments

^{1}H NMR and ^{13}C NMR spectra were conducted on a Bruker AVANCE Digital 300 MHZ spectrometer in deuterated chloroform using tetramethylsilane as an internal standard. Mass Spectrometry (MS) data was obtained on a Bruker Daltonics BIFLEX Ⅲ 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) was carried out 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 platinum electrode coated with a thin DPPEZnP-O film, a Pt wire and a saturated calomel electrode were used as the working electrode, the counter electrode and the reference electrode, respectively. The atomic force microscopy (AFM) measurements of the surface morphology of active films were conducted on a NanoScope NS3A system (Digital Instrument).

Transmission electron microscopy (TEM) was performed on a JEM-2010HR transmission electron microscope at an acceleration voltage of 200 kV, and the samples were prepared by spin-casting the blend solution on ITO/PEDOT:PSS substrate, floating the films on a water surface, transferring to copper grids, and drying in a vacuum oven overnight. 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.

3. OSC devices fabrication

Solution-processed bulk-heterojunction solar cells were fabricated as follows: 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(styrene sulfonate)-doped poly(ethylene-dioxythiophene) (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 130℃ for 20 min in air and then transferred to a N_2-glovebox. The active layers, composed of DPPEZnP-O and $PC_{61}BM$ (1:1.2 w/w), were deposited on top of the PEDOT:PSS layer (40 nm) from a chlorobenzene solution with or without DIO as additive, followed by drying under inert atmosphere over night. The thicknesses of active layers were an average of 140 nm as measured by a profilometer. 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 (~80 nm) was evaporated with a shadow mask as the top electrode. The effective area was measured to be 0.16 cm^2.

4. Hole-only devices fabrication

The mobilities of the active layers were determined by fitting the dark current to the model of the space charge limited current (SCLC) in the configuration of ITO/PEDOT:PSS(40 nm)/active layer/MoO_3(10 nm)/Ag(~60 nm). The solutions were prepared by dissolving DPPEZnP-O with $PC_{61}BM$ in chlorobenzene with and without DIO, followed by spin-coating on top of the PEDOT:PSS layer, and then drying under inert atmosphere over night. Finally, MoO_3 and Ag were thermally evaporated onto the active layer in a high-vacuum chamber. The electric-field dependent SCLC mobility was estimated using Equation (1).[2]

$$J = \frac{9}{8}\varepsilon\varepsilon_0\frac{E^2}{d}\mu_0\exp(\beta\sqrt{E}) \qquad (1)$$

Where J is the current, μ_0 is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layer, β is the field activation factor and E is the effective electric field.

5. TEM images of the blend films processed without and with 0.4% DIO

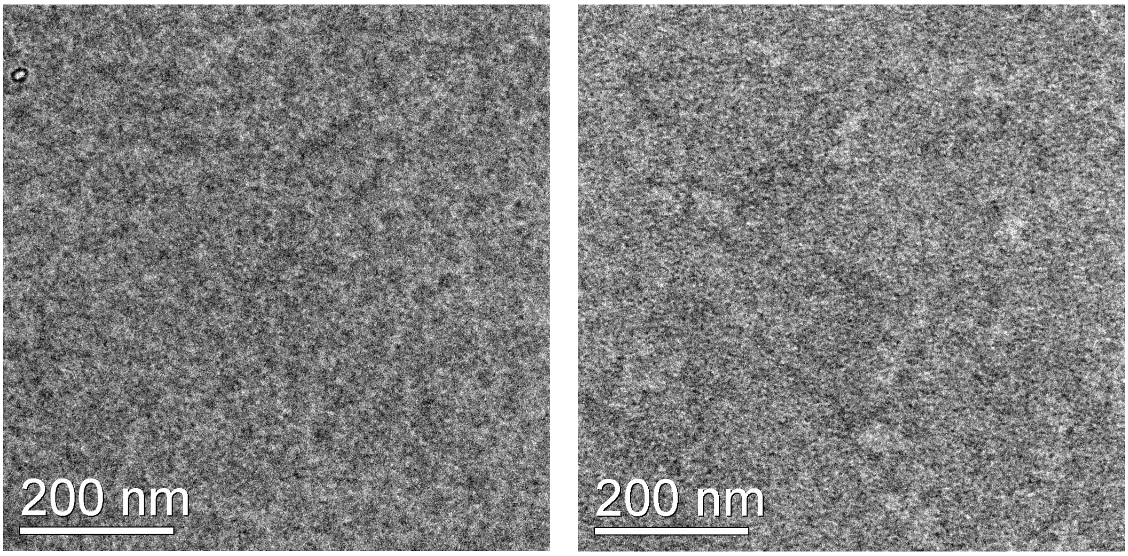


Figure S1. TEM images of the blend films processed without (left) and with 0.4% DIO (right).

6. Reference

1. L. Li, Y. Huang, J. Peng, Y. Cao and X. Peng, *J. Mater. Chem. A*, 2013, **1**, 2144-2150.
2. P. W. M. Blom, M. J. M. deJong and M. G. vanMunster, *Phys. Rev. B*, 1997, **55**, R656-R659.