Supporting Information

Chemically Driving Supramolecular Self-assembly of Porphyrin

Donors for High-Performance Organic Solar Cells

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Experimental Section

Materials preparation

All commercial chemicals (analytical grade) were used as received. Organic solvents were dried before use according to the standard procedures. 5,15-Dibromo-10,20-bis(2-octylundecyl)-zinc(II)porphyrin was synthesized according to published method.¹ The intermediate **S1**, **S2**, **C1**, **C2**, **C3** and **BrPor** were synthesized according to reported methods.²⁻⁶

Thin-film Preparation

Drop-down coated film was prepared by dropping the coating solution (10 μ M) onto a quartz substrate (2.5 mm × 12.5 mm × 45 mm) and spread the solution evenly by tilting the substrate at a slope about 15° and let the solvent evaporated to afford a thin film. Spin-coated film was prepared by spinning the chloroform or chlorobenzene (3 M) solution with 2 vol% pyridine additive on a quartz substrate (2.5 mm × 45 mm) or a silicon wafer substrate at 3000 rpm in counter-clockwise direction.

Theoretical calculations

The molecular geometries, the energy levels of frontal molecular orbits and frequencies of **Por-S** and **Por-C** were calculated using density functional theory (DFT) at B3LYP/6-31G(d) level using Gaussian 09 Rev D.01.⁷ For simplicity of calculation, methyl was used as the side-chain substituent.⁸

Space-charge-limited current (SCLC) mobility measurement. These hole-only/electron-only devices used the configurations of ITO/ZnO/Active layer/LiF/Al and ITO/PEDOT/Active layer/MoO₃/Al, respectively. The carrier mobility was measured using the SCLC model at low voltage, which is described by Equation (1):

$$J = \left(\frac{8}{9}\right) \varepsilon_r \varepsilon_0 \mu(\frac{V^2}{L^3}) \tag{1}$$

where ε_r is the dielectric constant (assumed to be 3), ε_0 is the permittivity of free space (8.85 × 10⁻¹² F·m⁻¹); μ is the electron mobility of the charge carrier; V is voltage drop across the device, which obtained by the applied voltage minus a built-in voltage of ~0.1 V; L (~100 nm) is the thickness of the active layer.

OSC Device Fabrication

Bulk-heterojunction solar cell devices 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(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 N₂-glovebox. The active layers were spun from solution of donor material: PC₇₁BM 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 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 mm².

Characterization

UV-vis spectra were performed on a Cary UV-300 spectrophotometer (agilent technologies, USA). Circular Dichroism (CD) were recorded on Fast Modular UV-Vis Spectrometer/Polarimeter (MOS-450AF/AF-CD, Kromatek) in the transmission mode. The high-resolution mass spectra were performed on a Bruker Autoflex MALDITOF mass spectrometer. Transmission electron microscopy (TEM) was conducted on a Tecnai G2 20 S-TWIN Transmission Electron Microscope (FEI, USA) using a 200 kV accelerating voltage. High-resolution scanning electron microscopy was conducted on a LEO 1530 Field Emission scanning

electron microscope operated at 20 kV. The photovoltaic characterization was carried out using a computer-programmed Keithley 2400 source/meter and a Newport's Oriel class A solar simulator, with simulated AM1.5 sunlight having an energy density of 100 mW cm⁻². External quantum efficiency (EQE) was measured using a 300 W Xenon Lamp (Oriel 6258) as the light source and a Cornerstone 260 Oriel 74125 monochromator with a resolution of 10 nm. The light intensity was calibrated with a NREL-recommended Si detector (Oriel 71030NS), and the short-circuit currents were determined with an Oriel 70310 optical power meter. Grazing incidence X-ray diffraction (GIWAXS) was performed at BL16B1 beamline of Shanghai Synchrotron Radiation Facility. The sample-to-detector distance was 200 mm and the wavelength of incident X-ray was 0.124 nm. The incidence angle of X ray was 0.10°.



Synthesis of S3

Bromide (10.0 mmol, 1 equivalent) in 30 mL THF and 15 mL triethylamine was degassed and backfilled with nitrogen for at least three times. Bis(triphenylphosphine) palladium(II) dichloride (0.20 mmol, 2 mol% equivalent) and copper iodide (0.20 mmol, 2 mol% equivalent) were added to the flask. The mixture was bubbling with nitrogen for half hour. Trimethylsilylacetylene (10.0 mmol mL, 10 equivalent) was injected into the flask via syringe. The mixture was stirred for 3 hours at 50 °C and then filtered. The filtrate was concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel to give a colourless oil (yield: 50%).

 $\label{eq:homoson} {}^{1}\text{HNMR} \mbox{ (400 MHz, ppm, CDCl}_3): 7.37 \mbox{ (s, 1H), 7.25 \mbox{ (s, 1H), 2.93-2.88 \mbox{ (m, 4H), 1.69-1.63 \mbox{ (m, 4H), 1.47-1.44 \mbox{ (m, 4H), 1.32-1.25 \mbox{ (m, 8H), 0.91-0.88 \mbox{ (s, 6H), 0.28 \mbox{ (s, 9H)}. } {}^{13}\text{C}\,\text{NMR} \mbox{ (100 MHz, ppm, CDCl}_3): 190.7, 139.2, 137.7, 134.3, 134.7, 126.7, 86.9, 34.4, 31.3, 28.6.28.4, 22.54, 14.05, 0. 1. }$

Synthesis of S4 and C4.

BuLi (2.8 mmol, 1 equivalent) was added dropwise into the flask containing **S3** or **C3** (2.8 mmol, 1 equivalent) in 30 mL dry THF at -78 °C under nitrogen atmosphere. The solution was stirred at -78 °C for 1 h and N-formylpiperidine (2.8 mmol, 1 equivalent) was added in one portion. The reaction was then stirred at room temperature for 1 hour, and subsequently quenched with water. The solution was washed with water and extracted with dichloromethane. The solvent was removed under reduced pressure to obtain the crude product. The crude product was used directly in the next reaction.

Synthesis of S5 and C5.

 K_2CO_3 (30.0 mmol, 3 equivalent) was added to **S4** or **C4** (10.0 mmol) in 60 mL THF and 30 mL methanol. The mixture was stirred at room temperature for 12 hours. The resulting mixture was dissolved in 120 mL dichloromethane and washed with water, brine and finally dried over anhydrous Mg_2SO_4 to afford **S5** or **C5**.

S5 was obtained as a white solid in 54% yield. ¹HNMR (400 MHz, ppm, CDCl₃): 10.46 (s, 1H), 7.71 (s, 1H), 7.55 (s, 1H), 3.68 (s, 1H), 3.03-3.01 (m, 4H), 1.46-1.34 (m, 4H), 1.46-1.36 (m, 4H), 1.34-1.32 (m, 8H), 0.92 (5, j=8, 6H). ¹³C NMR (100 MHz, ppm, CDCl₃): 190.7, 139.2, 137.7, 134.3, 134.7, 126.7, 86.9, 80.4, 34.4, 31.3, 28.6.28.4, 22.54, 14.05.

C5 was obtained as a white solid in 81% yield. ¹HNMR (400 MHz, ppm, CDCl₃): 10.26 (s, 2H), 7.61 (s, 1H), 7.25 (s, 1H), 3.68 (s, 1H), 3.03-3.01 (m, 4H), 1.46-1.34 (m, 4H), 1.46-1.36 (m, 4H), 1.34-1.32 (m, 8H), 0.93 (5, j=8, 6H). ¹³C NMR (100 MHz, ppm, CDCl₃): 191.7, 142.2, 134.3, 132.2, 130.7, 129.1, 92.8, 78.1, 33.7, 28.4, 22.54, 14.05.

Synthesis of 1 and 2.

4-Ethynyl-2,5-dihexylbenzaldehyde or 4-ethynyl-2,5-bis(hexylthio)benzaldehyde (0.70 mmol) and **BrPor** (0.30 mmol) in 30 THF and 15 mL Et₃N was degassed with nitrogen for 30 min. Pd(PPh₃)₄ (0.04 mmol) and Cul (0.04 mmol) were added and the solution was stirred at 60 °C for 12 h under nitrogen. The solvent was removed under reduced pressure, and the crude product was purified by preparative silica gel thin layer chromatography using CHCl₃/hexane (3:1) as eluent. Recrystallization from CHCl₃/methanol gave 1 or 2 as a green solid.

1 was obtained in 73% yield. ¹H NMR (400 MHz, ppm, CDCl₃): 10.53 (s, 2H), 9.90 (s, 2H), 9.67-9.60 (d, *J* = 28, 4H), 8.03 (s, 2H), 7.91 (s, 2H), 5.16 (s, 2H), 3.30-3.25 (m, 4H), 3.10 (m, 4H), 2.89 (m, 4H), 2.00-1.78 (m, 8H), 1.56-1.37 (m, 8H), 1.37-0.90 (m, 82H), 0.88-0.70 (m, 18H).

2 was obtained in 81% yield. ¹HNMR (400 MHz, ppm, CDCl₃): 10.57 (s, 2H), 9.96-9.94 (m, 4H), 9.68-9.59 (m, 4H), 8.05 (s, 2H), 7.94 (s, 2H), 5.18 (s, 2H), 3.26 (m, 4H), 3.10 (m, 4H), 2.91 (m, 4H), 2.69-2.62 (m, 8H), 1.58-0.92 (m, 96), 0.74-0.72 (m, 12H).

Synthesis of Por-S and Por-C.

A solution of 1 or 2 (0.13 mmol) and 3-ethylrhodanine (0.13 mmol) in dry CHCl₃ with two drops of piperidine was stirred at 60 °C for 12 h under nitrogen atmosphere. The reaction was quenched with 30 mL water and extracted with CHCl₃. The dried organic layer was concentrated under reduced pressure and the crude product was purified by silica gel thin layer chromatography using CHCl₃/hexane as eluent. The isolated product was recrystallized from a mixture of CHCl₃ and methanol to give **Por-S** or **Por-C** as a green solid.

Por-S was obtained in 71 % yield.

¹HNMR (400 MHz, ppm, CDCl₃): 9.85-9.84 (m, 4H), 9.66-9.58 (m, 4H), 8.37 (s, 2H), 8.02-7.98 (m, 2H), 7.46 (s, 2H), 5.17 (s, 2H), 4.23-4.21 (m, 4H), 3.29-3.25 (t, *J* =8, 4H), 3.10 (m, 4H), 2.93-2.91 (m, 4H), 2.73-2.70 (m, 4H), 2.11-1.97 (m, 4H), 1.68-1.52 (m, 8H), 1.52-0.72 (m, 106).

(MALDI-TOF, m/z) calculated for C₁₁₀H₁₅₄N₆O₂S₈Zn: 1912.9589.

Por-C was obtained in 75% yield.

¹H NMR (400 MHz, ppm, CHCl₃): 9.96 (m, 4H), 9.69-9.60 (m, 4H), 8.39(s, 2H), 8.08 (s, 2H), 7.55 (s, 2H), 5.20 (s, 2H), 4.27-4.23 (m, 4H), 3.30 (m, 4H), 3.09-3.08 (m, 4H), 2.93 (m, 4H), 1.98 (m, 2H), 1.76-1.02 (m, 108H), 0.79-0.73 (m, 12H). (MALDI-TOF, m/z) calculated for $C_{110}H_{154}N_6O_2S_4Zn$: 1785.3037.



Figure S1 ¹H NMR of molecule Por-S.





Figure S3. MALDI-TOF-MS spectrum of molecule Por-S.



Figure S4. MALDI-TOF-MS spectrum of molecule Por-C.

Table S1. Parameters (100) of GIWAXS results of neat, blend-films of Por-S, Por-C and PC71BM with various post-processing technologies.

Sample	<i>q</i> (100)/ nm ⁻¹	<i>d /</i> nm	FWHM/ nm ⁻¹	<i>CL/</i> nm
Por-S	3.15	1.99	0.21	27.83
TA Por-S/ PCBM	3.17	1.98	0.30	19.48
SVA Por-S/ PCBM	3.14	2.00	0.27	21.64
Por-C	3.44	1.83	0.34	17.18
TA Por-C/ PCBM	3.33	1.89	0.60	9.74
SVA Por-C/ PCBM	3.35	1.88	0.58	10.07

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

Table S2. Other Parameters of GIWAXS results of neat, blend-films of Por	-S/PC ₇₁ BM and Por-C/PC ₇₁ BM with various post-processing technologies.
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Sample	q (200)/ nm⁻¹	d/ nm	q (010)/ nm⁻¹	d/ nm	qª / nm ⁻¹
Por-S	6.18	1.02	17.8	0.35	
TA Por-S/ PCBM	5.73	1.10	17.8	0.35	13.76
SVA Por-S/ PCBM	6.09	1.03	17.8	0.35	13.76
Por-C	6.72	0.93	16.76	0.37	
TA Por-C/ PCBM	6.50	0.97	16.61	0.38	13.76, 19.52
SVA Por-C/ PCBM	6.45	0.97	14.50	0.43	13.76, 19.52

a: The scattering peaks from amorphous phase. The layer space (*d*) is calculated according to $d=2\pi/q$ (nm), and coherence length is calculated to $CL=CL=2\pi k/FWHM$ (nm), k=0.93.



Figure S5. Tapping mode AFM phase images ($1.5 \times 1.5 \mu m$) of active layers of Por-S/PC₇₁BM (1:1.2, w/w) (a, c) and Por-C/PC₇₁BM (1:1.2, w/w) (b, d) before and after SVA processing.



Figure S6. Hole-only mobility (a) and electron-only mobility (b) of SVA-TA Por-S/PC71BM and SVA-TA Por-C/PC71BM blended films.

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