

Supplementary Information

Solution-processed bulk heterojunction solar cells based on porphyrin small molecules with very low energy losses comparable to perovskite solar cells

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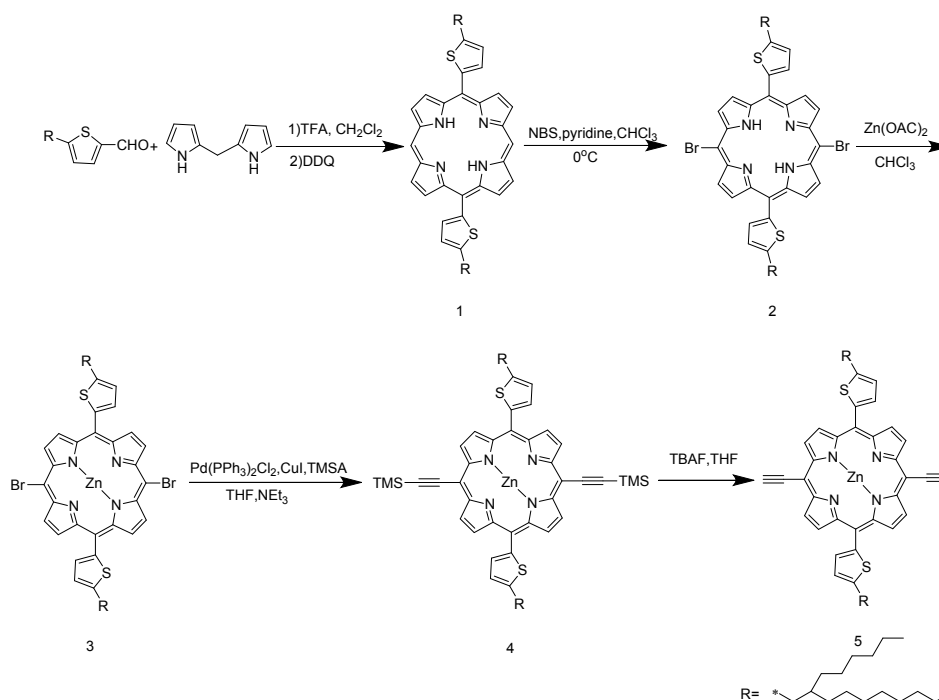
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1. Compounds synthesis



Synthesis of 5,15-Diethynyl-10,20-bis(5-(2-hexyldecyl)-thienyl)-porphyrin zinc

2-(2-hexyldecyl)-thiophene and 5-(2-hexyldecyl)thiophene-2-carbaldehyde were synthesized according to reported procedures.¹

5,15-Bis-(5-(2-hexyldecyl)-thienyl)-porphyrin (1)

A solution of 5-(2-hexyldecyl)thiophene-2-carbaldehyde (8.4g, 25mmol) and dipyrromethane (3.65g, 25mmol) in CH₂Cl₂ (1.5L) was purged with nitrogen for 30 min, and then trifluoroacetic acid (TFA) (0.15 mL) was added. The mixture was stirred for 12h at room temperature, and then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (9.25g) was added. After the mixture was stirred at room temperature for an additional 0.5h, 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_2 /methanol gave 1 as a purple solid. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 10.27(s, 2H), 9.35(q, 8H), 7.74(d, 2H), 7.20(d, 2H), 3.09(d, 4H), 1.93(m, 2H), 1.61-1.25(m, 48H), 0.95-0.82(m, 12H), -2.96(s, 2H)

5,15-Dibromo-10,20-bis-(5-(2-hexyldecyl)-thienyl)-porphyrin (2)

Porphyrin 1 (1.08g, 1.174mmol) and pyridine (50 mL) were dissolved in 600 mL chloroform and then cooled to 0°C . To the cold solution, N-bromosuccinimide (438mg, 2.466mmol) 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 (4:1) as the eluent. Recrystallization from CHCl_2 /methanol gave 2 as a purple solid. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 9.51 (d, 4H), 9.03 (s, 4H), 7.61 (d, 2H), 7.11 (d, 2H), 3.03 (d, 4H), 1.95 – 1.78 (m, 2H), 1.64 – 1.20 (m, 48H), 1.01 – 0.80 (m, 12H), -2.82 (s, 2H)

5,15-Dibromo-10,20-bis-(5-(2-hexyldecyl)-thienyl)-porphyrin zinc (3)

To a solution of 2 (539 mg, 0.5 mmol) in chloroform (50 mL), was added a solution of $\text{Zn}(\text{OAc})_2$ (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. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 9.00(d, 4H), 8.51(d, 4H), 7.79(d, 2H), 7.23(d, 2H), 3.03(d, 4H), 1.85(m, 2H), 1.63-1.19(m, 48H), 1.01-0.79(m, 12H)

5,15-Bis(trimethylsilyl ethynyl)-10,20-bis(5-(2-hexyldecyl)-thienyl)-porphyrin zinc

(4)

Porphyrin 3 (896mg, 0.786mmol) was dissolved in THF (40mL) and triethylamine (20mL) was added. The mixture was purged with nitrogen for 30 min. Then Pd(PPh₃)₂Cl₂ (55 mg, 0.078mmol), CuI (14.8 mg, 0.078 mmol), and trimethylsilylacetylene (308 mg, 3.14mmol) 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 Na₂SO₄ and concentrated. Finally, the residue was purified by column chromatography (silica gel, CH₂Cl₂/petroleum ether (1:2.5) to afford 4 as a purple solid. ¹H NMR (600 MHz, CDCl₃) δ 9.61(d, 4H), 9.12(d, 4H), 7.67(d, 2H), 7.15(d, 2H), 3.05(d, 4H), 1.87(m, 2H), 1.61-1.18(m, 48H), 0.93-0.87(m, 12H), 0.61(s, 18H)

5,15-Diethynyl-10,20-bis(5-(2-hexyldecyl)-thienyl)-porphyrin zinc (5)

Tetrabutylammonium fluoride (1.451 mL, 1M in THF) was added to a stirred solution of porphyrin 4 (835 mg, 0.71mmol) 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 Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, CHCl₃/petroleum ether (3/1)) to give 5 as a deep blue crystals. ¹H NMR (300 MHz, CDCl₃) δ 9.65(d, 4H), 9.18(d, 4H), 7.68(d, 2H), 7.16(d, 2H), 4.11(s, 2H), 3.08(d, 4H), 1.92(m, 2H), 1.57-1.22(m, 48H), 0.94-0.88(m, 12H)

2. Device fabrication and characterization

We fabricated the solution-processed bulk-heterojunction solar cells as follows: Indium tin oxide (ITO) coated glass substrates were cleaned prior to device fabrication by sonication in detergent, distilled water, acetone and isopropyl alcohol. After treated with an oxygen plasma for 10 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 140°C for 20 min in air and then transferred to a N₂-glovebox. The active layers, composed of Por-Rod (or Por-CNRod) and PC71BM (1:1 w/w), were deposited on top of the PEDOT:PSS layer (40 nm) from a chlorobenzene solution. The thicknesses of active layers were an average of 100 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 cm².

3. Single carrier hole-only device and electron-only device

The hole-only mobility and the electron-only mobility 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(120 nm)/MoO₃(10 nm)/Ag(~60 nm) and ITO/ZnO(40 nm)/active layers/Ca(5 nm)/Al(80 nm), respectively. The films were prepared by dissolving Por-Rod or Por-CNRod with PC₇₁BM in chlorobenzene using the different conditions the same as device fabrication on the top of surface of a PEDOT:PSS or ZnO substrate. Finally, MoO₃/Ag or Ca/Al

were thermally evaporated onto the active layer in a high-vacuum chamber. The electric-field dependent SCLC mobility was estimated using the following equation:^[2]

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \frac{E^2}{d} \mu_0 \exp\left[-\beta \sqrt{E}\right]$$

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.

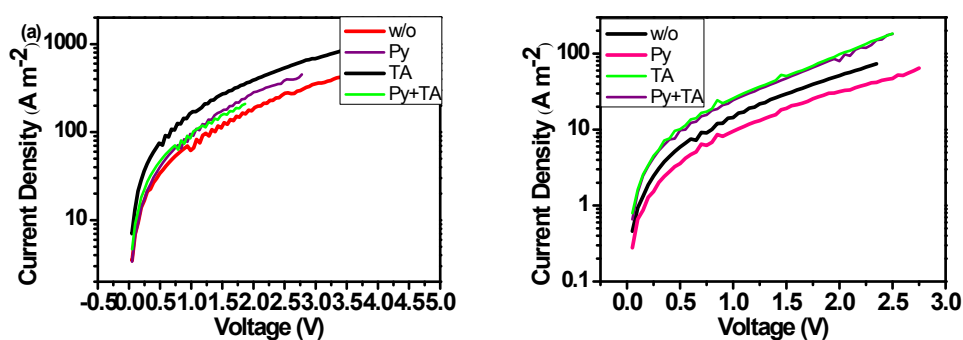


Figure S1. J - V characteristics of the hole-only devices (figure a) and the electron-only devices (figure b).

Table S1 Electron and hole mobilities for Por-Rod or Por-CNRod:PC₇₁BM, with different conditions.

Molecules	Conditions ^a	Hole (cm ² /(V.s))	Electron (cm ² /(V.s))
Por-Rod	w/o	1.56×10^{-5}	4.30×10^{-6}
	Py ^a	5.37×10^{-5}	2.05×10^{-6}
	TA ^a	1.76×10^{-4}	1.02×10^{-5}
	Py+TA	8.5×10^{-5}	8.91×10^{-6}
Por-CNRod	Py+TA	7.5×10^{-6}	/

^a The footnote is the same to Table 2.

4. Morphology Characterization

Grazing incidence x-ray diffraction (GIXD) was done at either beamline 7.3.3 Lawrence Berkeley National Lab (LBNL). The sample was put inside a helium chamber, and Pilatus 2M detector was used to collect the signal. GIXD results were analyzed using Nika software package and peak information was accessed by gaussian fitting (see Figure S6 for example). RSoXS was performed at beamline 11.0.1.2 Lawrence Berkeley National Lab. Thin films was flowed and transferred onto Si₃N₄ substrate and experiment was done in transition mode.

5.

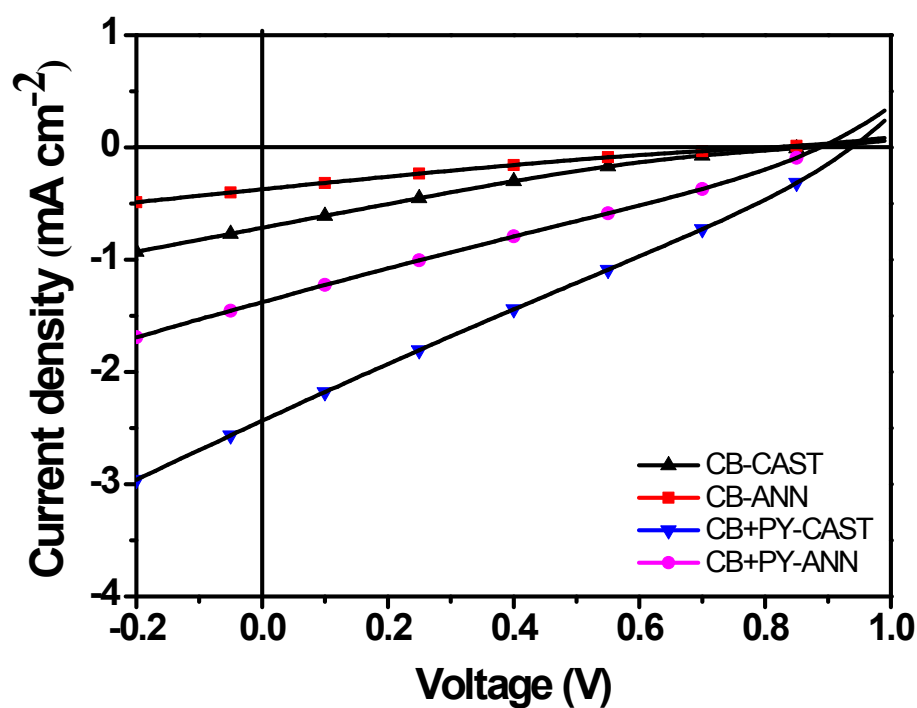


Figure S2. *J*-*V* curves of the OSCs with the device structure of ITO/PEDOT:PSS/ Por-CNRod:PC₇₁BM (1:11, w/w)/PFN/Al.

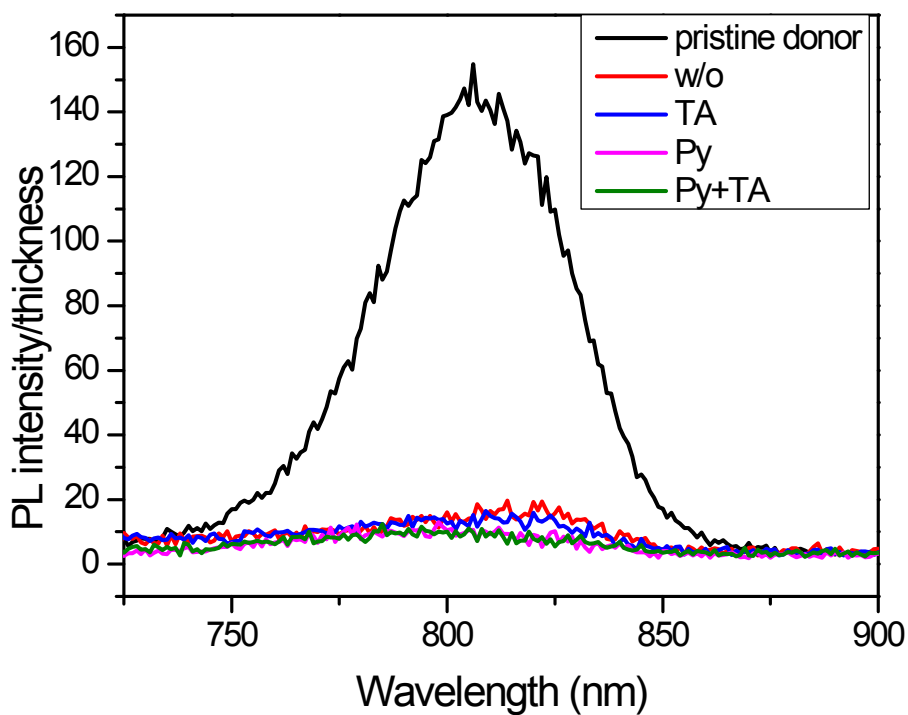


Figure S3. Photoluminescence (PL) spectra of pristine donor film and blend films without any post treatments (w/o), processed with pyridine (Py) and processed with pyridine and thermal annealing (Py+TA), based on Por-Rod.

6. References:

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2. P. W. M. Blom, M. J. M. deJong and M. G. vanMunster, *Phys. Rev. B*, 1997, 55, R656-R659.
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