Supporting information

Porphyrin dimers as donors for solution-processed bulk heterojunction organic solar cells

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1) General:

All reagents and solvents were obtained from commercial sources and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium-benzophenone under nitrogen prior to use it. Triethylamine (NEt₃) and CH_2Cl_2 were distilled from CaH_2 Prior to use. Air-sensitive reagents were weighed under an atmosphere of N₂. KC0, KC1 and KC2 were synthesized according to literature methods. ^[1-4]

2) Spectral and electrochemical measurements:

¹H NMR conducted on Varian at 400 MHz and ¹³C are conducted on Varian and Agilent Technologies at 100 MHz or 150 MHz. UV-visible spectra were conducted on Varian Cary 50 CONC spectrometer. ESI and APCI (Atmospheric Pressure Chemical Ionization) Mass spectra were acquired on Finnigan LCQ ion-trap mass spectrometer (Thermo Finnigan Corporation, San Jose, CA). Electrochemistry was performed with a three-electrode potentiostat (CH Instruments, Model 750A) in THF deoxygenated by purging with prepurified Argon gas. Cyclic voltammetry was conducted with the use of a home -made three-electrode cell equipped with a glassy carbon (0.07 cm^2) disk as the working electrode, a platinum wire as the auxiliary electrode, and a Home-made Ag/AgCl (saturated) reference electrode. The reference electrode is separated from the bulk solution by a double junction filled with electrolyte solution. Potentials are reported vs Ag/AgCl (saturated) and referenced to the ferrocene/ferrocenium (Fc/Fc⁺) couple which occurs at $E_{1/2} = +0.63$ V vs Ag/AgCl (saturated). The working electrode was polished with 0.03 µm alumina on Buehler felt pads and washed with deionized water prior to each experiment. The reproducibility of individual potential values was within ± 5 mV.

3) Experimental procedure:

[5-Bromo-10,20-bis (3,5-dioctyloxyphenyl)porphyrin] zinc(II) (1):

To a stirred solution of KC0 (1 g, 0.96 mmol) in DCM (750 mL) and pyridine (8 mL) was added NBS (130 mg, 1.15 mmol) at 0 °C slowly dropwise, after stirring 5 to 6 hours, the reaction was quenched with acetone (5 mL). The solvent was removed

under reduced pressure. The residue was purified with column chromatography (silica gel) using DCM / Hexane (1:4) to as eluent to give the product (700 mg, 66%); ¹H-NMR (CDCl₃ 400 MHz) δ 10.19 (s, 1H, *meso*), 9.79 (d, *J*=4.8 Hz, 2H, β), 9.34 (d, *J*=4.8 Hz, 2H, β), 9.15 (m, 4H, β), 7.36 (d, *J*=2.4 Hz, 4H, Ar), 6.89 (t, *J*=2 Hz,2H, Ar), 4.12 (t, *J*=6.8 Hz, 8H, alkyl), 1.87 (p, *J*=8 Hz, 8H, alkyl), 1.51 (p, *J*=8 Hz, 8H, alkyl), 1.39-1.26 (m, 32H, alkyl), 0.86 (t, *J*= 6.4 Hz, 12H, alkyl). ¹³C-NMR (CDCl₃ 100 MHz) δ 158.2, 150.3, 150.3, 150.2, 149.3, 143.9, 133.1, 133.0, 132.8, 132.0, 121.0, 114.3, 106.4, 104.8, 100.9, 68.3, 31.7, 29.3, 29.3, 26.1, 22.6, 14.0; ESI-MS: m/z calcd for C₆₄H₈₃BrN₄0₄Zn: 1117.6; found 1117.6 (100%).

[5,15-Bis(3,5-dioctyloxyphenyl)-10-(triisoprophylsilyl)ethynylporphyrin]Zinc (II)(2):

A mixture of zinc complex of **1** (0.7 g, 0.6 mmol), triisoprophylacetylene (0.4 mL, 1.8 mmol), Pd(pph₃)Cl₂ (44 mg, 0.06 mmol), CuI(17.8 mg, 0.09 mmol), THF (50 mL) and NEt₃ (5 mL) was gently refluxed for 4 h under nitrogen. The solvent was removed under vacuum. The reside was purified by column chromatography (silica gel) using DCM/ Hexane (1:3) as eluent to give the product (580 mg, 79%) as purple solid; ¹H-NMR (CDCl₃ 400 MHz) δ 10.19 (s, 1H, *meso*), 9.80 (d, *J*=4.4 Hz, 1H, β), 9.33 (d, *J*= 4.4 Hz, 2H, β), 9.14 (m, 4H β), 7.36 (d, *J*=2 Hz, 4H, Ar), 6.89 (d, *J*=2 Hz,2H, Ar), 4.12 (t, *J*=6.8 Hz, 8H, alkyl), 1.87 (p, *J*=6.8 Hz, 8H, alkyl), 1.51 (m, 26H, alkyl), 1.39-1.26 (m, 35H, alkyl), 0.86 (t, *J*= 6.8 Hz, 12H, alkyl). ¹³C-NMR (CDCl₃ 100 MHz) δ 158.0, 152.4, 150.1, 149.6, 149.4, 143.9, 132.9, 132.4, 131.6, 130.9, 121.1, 114.5, 109.7, 107.1, 101.1, 100.4, 97.7, 68.3, 31.8, 29.7, 29.3, 29.2, 26.0, 22.6, 19.1, 14.0, 11.9; ESI-MS: m/z calcd for C₇₅H₁₀₄N₄O₄SiZn: 1216.1; found 1217.9 (78%).

5-Iodo-10,20-bis (3,5-dioctyloxyphenyl)porphyrin (3):

To a stirred solution of porphyrin (700 mg, 0.71 mmol) and iodine (81 mg, 0.64 mmol) in dry chloroform (250 mL) was added $PhI(CF_3CO_2)_2$ (330 mg, 0.78 mmol) through powder funnel. The solution was stirred at room temperature for 30 min at dark condition. The reaction was quenched with sodium bicarbonate and sodium thiosulfate .The solvent was removed under reduced pressure. The residue was

purified with column chromatography (silica gel) using DCM/Hexane (2:8) as eluent to give the product (500 mg, 63%). ¹H-NMR (CDCl₃ 400 MHz) δ 10.16 (s, 1H, *meso*), 9.72 (d, *J*=4.8 Hz, 2H, β), 9.27 (d, *J*=4.4 Hz, 2H, β), 9.07 (m, 4H, β), 7.36 (t, *J*=2 Hz, 4H, Ar), 6.89 (t, *J*=1.2 Hz, 2H, Ar), 4.14 (t, *J*=6.4 Hz, 8H, alkyl), 1.88(m, *J*=7.2 Hz, 8H, alkyl), 1.51 (m, 8H, alkyl), 1.37-0.87 (m, 32H, alkyl), 0.86 (t, *J*= 6.4 Hz, 12H, alkyl), -3.04 (s, 2H, N-H).

[5-Iodo-10,20-bis (3,5-dioctyloxyphenyl)porphyrin] zinc(II) (4):

A suspension of 5-Iodo,10, 20-bis(3,5-dioctloxyphenyl) porphyrin (500 mg, 0.45 mmol) and Zn(OAc)₂.2H₂O (1 g, 4.54 mmol) in a mixture of DCM (100 mL)and MeOH (70 mL) was stirred at room temperature for 3 h. The reaction was quenched with water (100 mL), and the mixture was extracted with DCM (2 x 100 mL). The combined extracts were washed with water and dried over anhydrous MgSO₄.The solvent was removed under reduced pressure to give pink product (480 mg, 90%) ¹H-NMR (CDCl₃ 400 MHz) δ 10.18 (s, 1H, *meso*), 9.80 (d, *J*=4.8 Hz, 2H, β), 9.33 (d, *J*=4.4 Hz, 2H, β), 9.15 (m, *J*= 4.4 Hz, 4H, β), 7.34 (d, *J*=1.2 Hz, 4H, Ar), 6.89 (d, *J*=1.2 Hz, 2H, Ar), 4.12 (t, *J*=6.8 Hz, 8H, alkyl), 1.87 (m, 8H, alkyl), 1.50 (m, 8H, alkyl), 1.39-1.25 (m, 32H, alkyl), 0.86 (t, *J*= 6.4 Hz, 12H, alkyl). ¹³C-NMR (CDCl₃ 100 MHz) δ 158.7, 152.2, 151.4, 150.7, 144.4, 138.1, 133.4, 132.5, 129.8, 121.6, 114.8, 107.2, 101.4, 68.8, 32.2, 30.1, 29.8, 29.8, 29.7, 26.5, 23.1, 14.5; ESI-MS: m/z calcd for C₆₄H₈₃IN₄O₄Zn: 1164.6; found 1163.6.

Synthesis of porphyrin dimer KC1:

To a solution of porphyrin **2** (395 mg, 0.37 mmol) in dry THF (10 mL) was added TBAF (0.5 mL, 1M in THF). The solution was stirred at 25 °C for 30 min under dinitrogen condition. The mixture was quenched with water and extracted with CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The residue and [5-Iodo-10,20-bis(3,5-dioctyloxypenyl)porphyrin]zinc(II) (compound **4**) (520 mg, 0.44 mmol) were dissolved in a mixture of dry THF (35 mL) and NEt₃ (5 mL) and The solution was degassed with nitrogen for 30 min, Pd₂(dba)₃ (102 mg, 0.11 mmol), and AsPh₃(285 mg, 0.93 mmol) were added to the mixture. The solution was refluxed for 12 h under dinitrogen. The solvent was removed under reduced pressure. The residue pressure. The residue for 12 h under dinitrogen. The solvent was removed under reduced pressure.

Recrystallization from DCM/MeOH to give **KC1** (260 mg, 31 %) as a green solid. ¹H-NMR (CDCl₃ 400 MHz) δ 10.49 (d, *J*=4.4 Hz, 4H, β), 10.24 (s, 2H, *meso*), 9.35 (m, *J*=4.8 Hz, 8H, β), 9.15 (d, *J*= 4.4 Hz, 4H, β), 7.47 (d, *J*=2 Hz, 8H, Ar), 6.93 (t, *J*=2.4 Hz, 4H, Ar), 4.17 (t, *J*=6.8 Hz, 16H, alkyl), 1.87 (p, *J*=8 Hz, 16H, alkyl), 1.51 (m, 16H, alkyl), 1.39-1.31 (m, 64H, alkyl), 0.84 (t, *J*= 6.4 Hz, 24H, alkyl). ¹³C-NMR (CDCl₃ 150 MHz) δ 158.1, 152.4, 150.0, 144.7, 132.6, 132.1, 131.4, 130.4, 121.1, 114.5, 106.9, 101.1, 100.5, 100.3, 68.2, 31.7, 29.6, 29.3, 29.3, 29.1, 26.0, 22.5, 13.9; APCI-HRMS: m/z calcd for C₁₃₀H₁₆₆N₈O₈Zn₂: 2096.1484; found 2096.1435.

Synthesis of porphyrin dimer KC2:

To a solution of porphyrin 2 (100 mg, 0.09 mmol) was dissolved in dry THF (10 ml) and TBAF (0.6 mL, 1M in THF) was added. The reaction mixture was stirred at room temperature for 30 min under dinitrogen condition. The mixture was quenched with water and extracted with CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄ and the solvent was removed under reducing pressure. The crude product was dried 30 min under vacuum, then dissolved in dry CH₂Cl₂ (100 mL) and the resulting mixture was stirred vigorously for 15 min under air atmosphere. Copper (I) chloride (280 mg, 2.82 mmol) was added to the solution and the mixture was stirred for additional 2 min. TMEDA (0.42 mL, 2.82 mmol) was added to the solution and the reaction mixture was vigorously stirred for 90 min. Water was added to quench the reaction. The organic layer was washed with water until the washings were no longer colored blue. The crude product was purified by column chromatography (silica gel) using only DCM as eluent. Recrystallization from DCM/ MeOH to give KC2 (135 mg, 70 %) as green glass. ¹H-NMR (CDCl₃ 400 MHz) δ 10.18 (s, 2H, meso), 10.03 (d, J=4.8 Hz, 3H, meso), 9.33 (d, J=4.8 Hz, 4H, β), 9.24 (d, J= 4.4 Hz, 4H, β), 9.14 (d, J=4 Hz, 4H β), 7.43 (d, J=2.4 Hz, 8H, Ar), 6.92 (t, J=2.4 Hz, 4H, Ar), 4.16 (t, J=6.4 Hz, 16H, alkyl), 1.87 (t-t, J=6.8 Hz, 16H, alkyl), 1.51 (t-t, J=7.6 Hz, 74H, alkyl), 1.36-1.24 (m, 84H, alkyl), 0.86 (t, J=7.2 Hz, 34H, alkyl). ¹³C-NMR (CDCl₃) 150 MHz) & 157.8, 152.7, 150.1, 144.2, 132.6, 131.8, 131.3, 130.1, 121.1, 114.1, 107.7, 100.1, 97.3, 87.9, 81.4, 67.9, 31.4, 29.3, 29.0, 28.8, 25.7, 22.2, 13.7; APCI-HRMS: m/z calcd for C₁₃₂H₁₆₆N₈O₈Zn₂: 2120.1484; found 2120.1564.

Dye	E _{onset} (ox) ^a /V	E _{onset} (red) ^a /V	HOMO ^b /eV	LUMO ^c /eV
KC0	+0.34	-1.90	-5.14	-2.90
KC1	+0.17	-1.62	-4.97	-3.18
KC2	+0.28	-1.65	-5.08	-3.15

Table S1: Electrochemical data of KC0, KC1, and KC2.

^aRedox potentials are measured in THF containing 0.1 M (*n*-Bu)₄N]PF₆ as supporting electrolyte. Potential are referenced to ferrocene/ferrocenium (Fc/Fc⁺) couple. ^bHOMO energy levels were calculated using the following equation: HOMO level = $-(E_{onset}(ox)+4.8)$ eV. ^cLUMO energy levels were calculated using the following equation: LUMO level = $-(E_{onset}(red) + 4.8)$ eV.^[5.6]

5)



Figure S1. J - V characteristics for KC0:PC₇₀BM blend device.



Figure S2. The surface morphology of KC2:PC₇₀BM:CN film deposited on ZnO on ITO-coated glass substrate.

7)



Figure S3. $J^{1/2} - V$ measured from the hole only devices based on the structure of ITO/PEDOT:PSS/KC1 (or KC2)/MoO₃/Ag. The thicknesses for KC1 and KC2 films are 90 and 100 nm, respectively. The solid lines are the fits

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