

Supporting information

Improvement of Photovoltaic Performance of DSSCs by Modifying Panchromatic Zinc Porphyrin Dyes with Heterocyclic Units

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General information

All solvents were treated by standard methods before use and all chemicals were purchased from commercial suppliers and used without further purification unless indicated otherwise. *N, N*-Dimethylformamide, toluene and tetrahydrofuran were dried and distilled from CaH₂.

The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DRX (500 MHz) NMR spectrometer with tetramethylsilane (TMS) as the internal standard. The mass spectra were measured in ESI Mass Spectrometer (LCQ Fleet).

Experimental Details:

Synthesis of compound 2

Under an nitrogen, compound **1** (5.4 g, 18.4 mmol), bis(4-bromophenyl)amine (2 g, 6.1 mmol), K₂CO₃ (2.5 g, 18.4 mmol) and Pd(PPh₃)₄ (353 mg, 0.306 mmol) were dissolved in 1, 4-dioxane (60 mL) and H₂O (20 mL). The mixture was heated under 90°C for overnight. The reaction mixture was cooled to room temperature and the solvent was evaporated, the mixture was extracted by EtOAc (3×50 mL). The combined organic layers were washed with brine, dried over MgSO₄, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/EA = 10/1) to give the compound **2** as a white solid (2.9 g, 94%). ¹H NMR (DMSO-*d*₆, 500Hz) δ_H 8.46 (s, 1H), 7.47-7.48 (m, 4H), 7.10-7.15 (m, 6H), 6.79 (s, 2H), 2.78 (t, *J* = 7.5Hz, 4H), 1.64 (m, 4H), 1.30-1.37 (m, 12H), 0.88 (t, *J* = 6Hz, 6H). MS (EI): Calcd for C₃₂H₃₉NS₂, 501.79; found, 501.4.

Synthesis of compound 3

Under an nitrogen, compound **1** (6.1 g, 20.8 mmol), tris(4-bromophenyl)amine (5 g, 10.4 mmol), K₂CO₃ (4.3 g, 31.1 mmol) and Pd(PPh₃)₄ (600 mg, 0.519 mmol) were dissolved in 1, 4-dioxane (100 mL) and H₂O (30 mL). The mixture was heated under 90°C for overnight. The reaction mixture was cooled to room temperature and the solvent was evaporated, the mixture was extracted by EtOAc (3×50 mL). The

combined organic layers were washed with brine, dried over MgSO_4 , and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE) to give the compound **3** as a white solid (2.1 g, 31%). $^1\text{H NMR}$ (CDCl_3 , 500Hz) δ_{H} 7.48 (d, $J = 8\text{Hz}$, 4H), 7.38 (d, $J = 8\text{Hz}$, 2H), 7.08-7.09 (m, 6H), 7.02 (d, $J = 8\text{Hz}$, 2H), 6.76 (s, 2H), 2.84 (t, $J = 7.5\text{Hz}$, 4H), 1.68 (m, 4H), 1.34-1.45 (m, 12H), 0.89 (t, $J = 6\text{Hz}$, 6H). MS (EI): Calcd for $\text{C}_{38}\text{H}_{42}\text{BrNS}_2$, 656.78; found, 657.4.

Synthesis of compound 4

A mixture of compound **3** (1 g, 1.52 mmol), trimethylsilylacetylene (0.3 g, 3.05 mmol) and CuI (0.104 g, 0.548 mmol) in TEA (30 mL) was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.427 g, 0.609 mmol) under dinitrogen. The mixture was heated under 80°C for overnight. The reaction mixture was cooled to room temperature and the solvent was evaporated, the mixture was extracted by EtOAc (3×50 mL). The combined organic layers were washed with brine, dried over MgSO_4 , and evaporated in vacuo. The residue was dissolved in anhydrous THF (20 mL) without further purification and TBAF (0.4 mL, 1 M THF) was added. The reaction mixture was stirred at room temperature for 30 min under dinitrogen. The mixture was quenched with H_2O and then extracted with CH_2Cl_2 . The organic layer was dried over anhydrous MgSO_4 and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (PE) to give the compound **4** as a yellow solid (0.8 g, 87%). $^1\text{H NMR}$ (CDCl_3 , 500Hz) δ_{H} 7.52 (d, $J = 8.5\text{Hz}$, 4H), 7.41 (d, $J = 8.5\text{Hz}$, 2H), 7.07-7.14 (m, 8H), 6.77 (s, 2H), 3.09 (s, 1H), 2.87 (t, $J = 7.0\text{Hz}$, 4H), 1.74-1.77 (m, 4H), 1.38-1.45 (m, 12H), 0.97 (t, $J = 6\text{Hz}$, 6H). MS (EI): Calcd for $\text{C}_{40}\text{H}_{43}\text{NS}_2$, 601.91; found, 601.4.

Synthesis of compound 5

A mixture of compound **3** (1 g, 1.52 mmol), bis(pinacolato)diboron (0.773 g, 3.05 mmol) and KOAc (0.448 g, 4.57 mmol) in DMF (30 mL) was added $\text{Pd}(\text{dppf})\text{Cl}_2$ (0.111 g, 0.152 mmol) under dinitrogen. The mixture was heated under 80°C for

overnight. The reaction mixture was cooled to room temperature and H₂O (100 mL) was added, the mixture was extracted by EtOAc (3×50 mL). The combined organic layers were washed with brine, dried over MgSO₄, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/EA=10/1) to give the compound **5** as a yellow solid (0.82 g, 77%).¹HNMR (CDCl₃, 500Hz) δ_H 7.73-7.76 (m, 2H), 7.47-7.51 (m, 4H), 7.10-7.15 (m, 8H), 6.77 (s, 2H), 2.88 (t, *J* = 7.5Hz, 4H), 1.70 (m, 4H), 1.38-1.44 (m, 24H), 0.95 (t, *J* = 6Hz, 6H). MS (EI): Calcd for C₄₄H₅₄NO₂S₂, 703.85; found, 703.4.

Synthesis of compound 7

A mixture of compound **2** (773 mg, 1.54 mmol), compound **6** (500 mg, 0.385 mmol) [1] and 60 % NaH (62 mg, 1.54 mmol), DPEphos (75 mg, 0.138 mmol) and Pd(OAc)₂ (21 mg, 0.092 mmol) in dry toluene (30 mL) was refluxed for overnight under dinitrogen. The solvent was removed under vacuum. The residue was purified by column chromatography (silica gel) using DCM/hexanes = 1/4 as eluent to give the product as a green solid (350 mg, 53%).¹HNMR (CDCl₃, 500Hz) δ_H 9.71 (d, *J* = 4.5Hz, 2H), 9.22 (d, *J* = 4.5Hz, 2H), 8.91 (d, *J* = 4.5Hz, 2H), 8.78 (d, *J* = 4.5Hz, 2H), 7.64 (t, *J* = 8.5Hz, 2H), 7.33-7.39 (m, 7H), 6.95-6.99 (m, 7H), 6.67 (s, 2H), 3.86 (t, *J* = 6.5Hz, 8H), 2.77 (t, *J* = 7.5Hz, 4H), 1.63-1.69 (m, 4H), 1.41-1.51 (m, 21H), 1.36-1.38 (m, 4H), 1.31 (t, 12H), 1.00-1.03 (m, 8H), 0.80-0.89 (m, 22H), 0.51-0.65 (m, 44H). ¹³CNMR (CDCl₃, 500Hz) δ_C 159.8, 152.5, 151.3, 151.2, 150.7, 150.3, 144.5, 141.7, 132.3, 132.1, 130.7, 130.0, 129.8, 127.3, 126.1, 124.7, 122.9, 121.7, 121.4, 120.6, 114.5, 109.9, 105.1, 99.6, 96.6, 68.5, 31.5, 30.2, 28.7, 28.5, 28.4, 25.1, 22.5, 22.2, 19.1, 14.1, 13.7, 11.9. MS (ESI): Calcd for C₁₀₇H₁₄₁N₅O₄S₂SiZn, 1718.89; found, 1718.00.

Synthesis of compound 8

Under an nitrogen, compound **5** (406 mg, 0.577 mmol), compound **6** (500 mg, 0.385 mmol), K₂CO₃ (106 mg, 0.770 mmol) and Pd(PPh₃)₄ (22 mg, 0.019 mmol) were dissolved in 1, 4-dioxane (20 mL) and H₂O (10 mL). The mixture was heated

under 90°C for overnight. The reaction mixture was cooled to room temperature and extracted by CH₂Cl₂ (3×20 mL). The combined organic layers were washed with brine, dried over MgSO₄, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/CH₂Cl₂ = 4/1) to give the compound **8** as a green solid (520 mg, 75%). ¹HNMR (CDCl₃, 500Hz) δ_H 9.83 (d, *J* = 4.5Hz, 2H), 9.03-9.04 (m, 4H), 8.96 (d, *J* = 4.5Hz, 2H), 7.77 (t, *J* = 8.0Hz, 2H), 7.66 (d, *J* = 9Hz, 4H), 7.56 (d, *J* = 8.0Hz, 2H), 7.48 (d, *J* = 8.5Hz, 4H), 7.16 (d, *J* = 3.5Hz, 2H), 7.09 (d, *J* = 9Hz, 4H), 6.79 (d, *J* = 3.5Hz, 2H), 3.88 (t, *J* = 6.0Hz, 8H), 2.88 (t, *J* = 8.0Hz, 4H), 1.76-1.80 (m, 4H), 1.53-1.56 (m, 21H), 1.47-1.50 (m, 4H), 1.39-1.42 (m, 12H), 1.02-1.06 (m, 8H), 0.80-0.99 (m, 22H), 0.48-0.65 (m, 44H). ¹³CNMR (CDCl₃, 500Hz) δ_C 160.1, 152.6, 151.1, 150.4, 149.6, 146.6, 145.1, 141.4, 137.7, 135.4, 132.1, 131.7, 131.0, 130.7, 129.8, 126.5, 125.1, 124.7, 122.1, 121.7, 121.4, 121.1, 114.5, 110.2, 105.4, 98.8, 96.1, 68.7, 31.7, 31.3, 30.3, 28.8, 28.6, 25.2, 22.6, 22.2, 19.2, 14.1, 13.8, 12.1. MS (ESI): Calcd for C₁₁₃H₁₄₅N₅O₄S₂SiZn, 1794.99; found, 1794.00.

Synthesis of compound **9**

A mixture of compound **4** (347 mg, 0.577 mmol), compound **6** (500 mg, 0.385 mmol) and AsPh₃ (236 mg, 0.770 mmol) in THF (50 mL) and TEA (10 mL) was added Pd₂(dba)₃ (105 mg, 0.115 mmol) under dinitrogen. The mixture was heated under 80°C for 5 h. The reaction mixture was cooled to room temperature and the solvent was evaporated, The residue was purified by silica gel column chromatography (PE/CH₂Cl₂ = 4/1) to give the compound **9** as a green solid (0.38 g, 55%). ¹HNMR (CDCl₃, 500Hz) δ_H 9.70 (d, *J* = 4.5Hz, 2H), 9.67 (d, *J* = 4.5Hz, 2H), 8.88-8.89 (m, 4H), 7.89 (d, *J* = 8.5Hz, 2H), 7.70 (t, *J* = 8.5Hz, 2H), 7.56 (d, *J* = 8.5Hz, 4H), 7.24 (d, *J* = 8.5Hz, 4H), 7.12 (d, *J* = 3.5Hz, 2H), 7.02 (d, *J* = 8.5Hz, 6H), 6.77 (d, *J* = 3.5Hz, 2H), 3.86 (t, *J* = 6.0Hz, 8H), 2.83 (t, *J* = 7.0Hz, 4H), 1.70-1.75 (m, 4H), 1.43-1.45 (m, 21H), 1.28-1.36 (m, 16H), 0.97-1.01 (m, 8H), 0.77-0.93 (m, 22H), 0.47-0.60 (m, 44H). ¹³CNMR (CDCl₃, 500Hz) δ_C 159.9, 152.2, 151.4, 150.6, 147.2, 145.9, 145.3, 141.2, 132.6, 131.9, 131.7, 130.7, 130.5, 130.1, 129.7, 126.4, 125.0, 124.9,

123.2, 122.1, 120.9, 115.6, 110.0, 105.3, 101.0, 100.1, 95.9, 95.4, 68.7, 53.4, 31.6, 31.2, 30.9, 30.2, 28.7, 28.5, 25.2, 22.5, 22.1, 19.1, 14.1, 13.7, 11.9. MS (ESI): Calcd for C₁₁₅H₁₄₅N₅O₄S₂SiZn, 1819.01; found, 1820.08.

Synthesis of dye JP1

To a solution of compound **8** (300 mg, 0.167 mmol) in anhydrous THF (20 mL) was added TBAF (0.6 mL, 1 M in THF). The solution was stirred at room temperature for 30 min under dinitrogen. The mixture was quenched with H₂O and then extracted with CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The residue and 5-bromo-2-thiophenecarboxylic acid (138 mg, 0.668 mmol) were dissolved in a mixture of anhydrous THF (40 mL) and TEA (10 mL) under dinitrogen, then Pd₂(dba)₃ (46 mg, 0.050 mmol) and AsPh₃ (102 mg, 0.334 mmol) were added to the mixture. The solution was refluxed for 6 h. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (CH₂Cl₂/MeOH = 20/1), recrystallization from MeOH/Ether to give dye **JP1** (180 mg, 61%) as a green solid. ¹HNMR (CDCl₃, 500Hz) δ_H 9.62 (d, *J* = 4.5Hz, 2H), 8.96 (d, *J* = 4.5Hz, 2H), 8.93 (d, *J* = 4.5Hz, 2H), 8.85 (d, *J* = 4.5Hz, 2H), 8.06 (t, *J* = 8.0Hz, 2H), 7.73 (d, *J* = 8.5Hz, 2H), 7.61 (d, *J* = 8.0Hz, 4H), 7.48 (d, *J* = 8.0Hz, 2H), 7.39 (d, *J* = 8.0Hz, 4H), 7.13 (d, *J* = 3.0Hz, 2H), 7.04 (d, *J* = 8.5Hz, 6H), 6.77 (d, *J* = 3.0Hz, 2H), 3.88 (t, *J* = 6.5Hz, 8H), 2.85 (t, *J* = 7.5Hz, 4H), 1.70-1.77 (m, 4H), 1.28 (s, 12H), 0.89-1.01 (m, 18H), 0.79-0.85 (m, 12H), 0.42-0.64 (m, 36H). ¹³CNMR (CDCl₃, 500Hz) δ_C 159.9, 151.8, 151.2, 150.2, 149.5, 146.6, 145.1, 141.4, 135.6, 134.9, 132.4, 131.9, 131.3, 130.9, 129.9, 129.7, 126.5, 125.0, 124.7, 122.0, 121.6, 121.2, 114.8, 105.2, 68.6, 31.7, 31.6, 31.3, 30.3, 29.7, 29.5, 29.3, 28.8, 28.7, 28.6, 28.5, 25.2, 22.6, 22.2, 14.1, 13.8. MS (ESI): Calcd for C₁₀₉H₁₂₇N₅O₆S₃Zn, 1764.78; found, 1762.42.

Synthesis of dye JP2

The preparation method was the same as that of dye **JP1**. ¹HNMR (CDCl₃, 500Hz) δ_H 9.61 (d, *J* = 4.5Hz, 2H), 9.15 (d, *J* = 4.5Hz, 2H), 8.92 (d, *J* = 4.5Hz, 2H), 8.74 (d, *J* =

4.5Hz, 2H), 7.93 (d, $J = 3.5\text{Hz}$, 1H), 7.71 (t, $J = 8.5\text{Hz}$, 2H), 7.64 (d, $J = 3.5\text{Hz}$, 1H), 7.35 (d, $J = 8\text{Hz}$, 4H), 7.27-7.29 (m, 4H), 7.02 (d, $J = 8.5\text{Hz}$, 4H), 6.96 (d, $J = 3.5\text{Hz}$, 2H), 6.68 (d, $J = 3.5\text{Hz}$, 2H), 3.89 (t, $J = 6.5\text{Hz}$, 8H), 2.78 (t, $J = 7.5\text{Hz}$, 4H), 1.64-1.70 (m, 4H), 1.29 (s, 12H), 0.95-1.04 (m, 8H), 0.89-0.94 (m, 22H), 0.53-0.80 (m, 36H). ^{13}C NMR (CDCl_3 , 500Hz) δ_{C} 159.8, 151.8, 151.2, 150.6, 150.4, 144.5, 143.9, 141.7, 139.3, 132.4, 130.1, 129.9, 127.2, 126.0, 124.7, 122.2, 121.8, 121.4, 120.7, 114.8, 105.1, 68.5, 31.9, 31.5, 31.4, 30.2, 29.7, 29.3, 29.1, 28.9, 28.7, 28.6, 28.5, 28.4, 27.2, 25.1, 22.7, 22.3, 14.1, 14.0, 13.8. MS (ESI): Calcd for $\text{C}_{103}\text{H}_{123}\text{N}_5\text{O}_6\text{S}_3\text{Zn}$, 1688.68; found, 1686.42.

Synthesis of dye JP3

The preparation method was the same as that of dye **JP1**. ^1H NMR (CDCl_3 , 500Hz) δ_{H} 9.62 (d, $J = 4.5\text{Hz}$, 2H), 9.49 (d, $J = 4.5\text{Hz}$, 2H), 8.87 (d, $J = 4.5\text{Hz}$, 2H), 8.84 (d, $J = 4.5\text{Hz}$, 2H), 7.82 (d, $J = 8.4\text{Hz}$, 2H), 7.71 (t, $J = 8.4\text{Hz}$, 2H), 7.49 (d, $J = 8.8\text{Hz}$, 4H), 7.45 (s, 1H), 7.26 (s, 1H), 7.20 (d, $J = 8.8\text{Hz}$, 4H), 7.06 (d, $J = 3.2\text{Hz}$, 2H), 7.02 (d, $J = 8.4\text{Hz}$, 4H), 6.70 (d, $J = 3.2\text{Hz}$, 2H), 3.87 (t, $J = 6.4\text{Hz}$, 8H), 2.79 (t, $J = 7.2\text{Hz}$, 4H), 1.65-1.72 (m, 4H), 1.25 (s, 12H), 0.95-1.02 (m, 8H), 0.81-0.89 (m, 14H), 0.61-0.66 (m, 8H), 0.42-0.57 (m, 36H). ^{13}C NMR (CDCl_3 , 500Hz) δ_{C} 159.9, 151.6, 151.5, 150.8, 150.5, 147.3, 145.9, 145.3, 141.2, 134.8, 132.6, 132.3, 131.7, 131.4, 130.7, 130.2, 129.9, 126.5, 125.0, 124.9, 123.1, 122.1, 120.8, 117.4, 115.6, 105.2, 68.7, 31.7, 31.6, 31.4, 30.3, 29.7, 28.8, 28.7, 28.6, 28.5, 25.3, 22.7, 22.6, 22.3, 14.1, 13.9. MS (ESI): Calcd for $\text{C}_{111}\text{H}_{127}\text{N}_5\text{O}_6\text{S}_3\text{Zn}$, 1788.80; found, 1788.00.

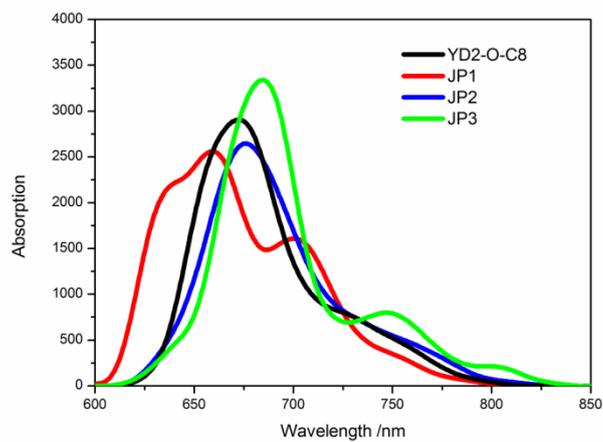


Fig. S1 Emission spectra of YD2-O-C8, JP1, JP2 and JP3 in THF

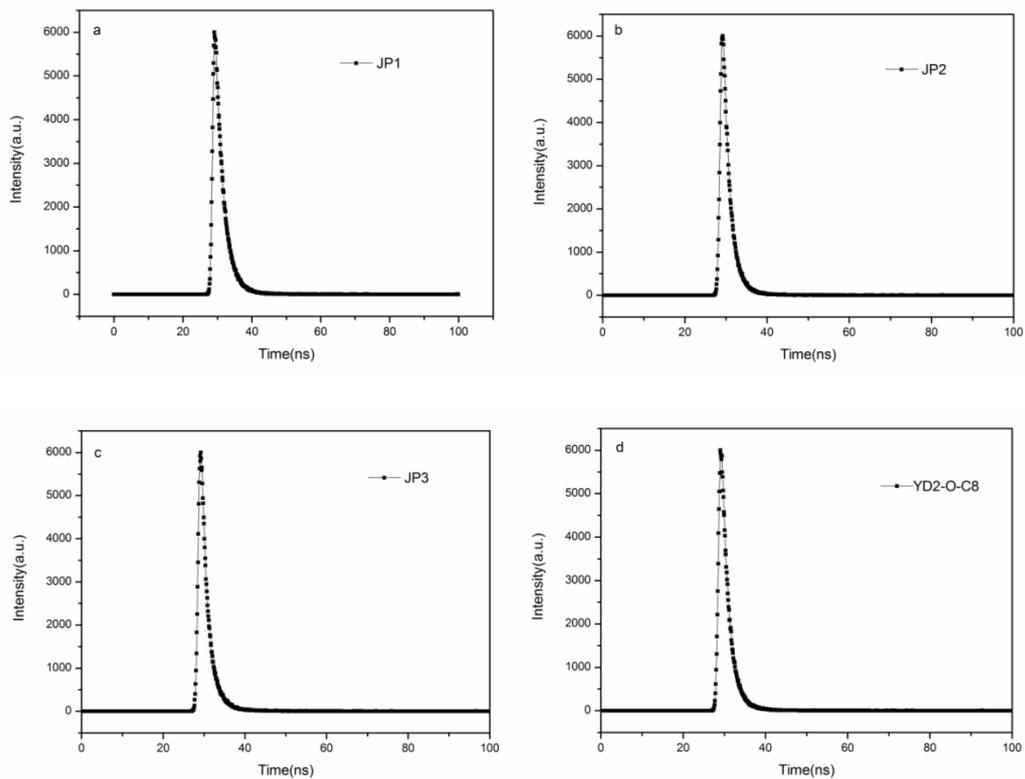


Fig. S2 Fluorescence decay curves of (a) JP1, (b) JP2, (c) JP3 and (d) YD2-O-C8.

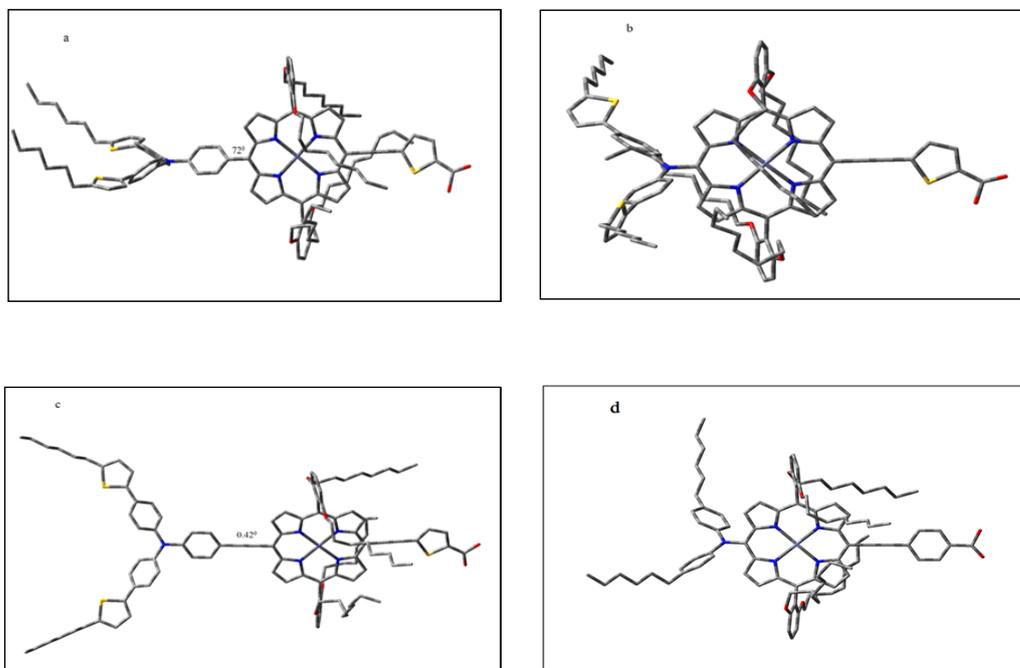


Fig. S3 The geometry optimized ground state molecular structures of (a) JP1, (b) JP2, (c) JP3 and (d) YD2-O-C8

References

- [1] A.Yella, H. W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W. G. Diau, C. Y. Yeh, S. M. Zakeeruddin and M. Grätzel, *Science*, 2011, **334**, 629-633.