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%).¹HNMR (DMSO-d₆, 500Hz) δH 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 MgSO₄, 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%).¹HNMR (CDCl₃, 500Hz) δH 7.48 (d, J = 8Hz, 4H), 7.38 (d, J = 8Hz, 2H), 7.08-7.09 (m, 6H), 7.02 (d, J = 8Hz, 2H), 6.76 (s, 2H), 2.84 (t, J = 7.5Hz, 4H), 1.68 (m, 4H), 1.34-1.45 (m, 12H), 0.89 (t, J = 6Hz, 6H). MS (EI): Calcd for C₃₈H₄₂BrNS₂, 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 Pd(PPh₃)₂Cl₂ (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 MgSO₄, 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 H₂O and then extracted with CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄ 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%).¹HNMR (CDCl₃, 500Hz) δH 7.52 (d, J = 8.5Hz, 4H), 7.41 (d, J = 8.5Hz, 2H), 7.07-7.14 (m, 8H), 6.77 (s, 2H), 3.09 (s, 1H), 2.87 (t, J = 7.0Hz, 4H), 1.74-1.77 (m, 4H), 1.38-1.45 (m, 12H), 0.97 (t, J = 6Hz, 6H). MS (EI): Calcd for C₄₀H₄₃NS₂, 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 Pd(dppf)Cl₂ (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%).

1H NMR (CDCl₃, 500Hz) δH 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%).

1H NMR (CDCl₃, 500Hz) δH 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) δC 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 C₁₀₇H₄₁N₅O₄S₂SiZn, 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%). ¹H NMR (CDCl₃, 500Hz) δH 9.83 (d, J = 4.5Hz, 2H), 9.03-9.04 (m, 4H), 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). ¹³C NMR (CDCl₃, 500Hz) δC 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%). ¹H NMR (CDCl₃, 500Hz) δH 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). ¹³C NMR (CDCl₃, 500Hz) δC 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 C$_{115}$H$_{145}$N$_5$O$_4$S$_2$SiZn, 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 H$_2$O and then extracted with CH$_2$Cl$_2$. The organic layer was dried over anhydrous MgSO$_4$ 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) underdinitrogen, then Pd$_2$(dba)$_3$ (46 mg, 0.050 mmol) and AsPh$_3$ (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 (CH$_2$Cl$_2$/MeOH = 20/1), recrystallization from MeOH/Ether to give dye JP1 (180 mg, 61%) as a green solid. $^1$HNMR (CDCl$_3$, 500Hz) $\delta$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). $^{13}$CNMR (CDCl$_3$, 500Hz) $\delta$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 C$_{109}$H$_{127}$N$_5$O$_6$Si$_2$Zn, 1764.78; found, 1762.42.

**Synthesis of dye JP2**

The preparation method was the same as that of dye JP1. $^1$HNMR (CDCl$_3$, 500Hz) $\delta$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 = 3.5Hz, 1H), 7.71 (t, J = 8.5Hz, 2H), 7.64 (d, J = 3.5Hz, 1H), 7.35 (d, J = 8Hz, 4H), 7.27-7.29 (m, 4H), 7.02 (d, J = 8.5Hz, 4H), 6.96 (d, J = 3.5Hz, 2H), 6.68 (d, J = 3.5Hz, 2H), 3.89 (t, J = 6.5Hz, 8H), 2.78 (t, J = 7.5Hz, 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). $^{13}$CNMR (CDCl$_3$, 500Hz) $\delta$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 C$_{103}$H$_{123}$N$_5$O$_6$S$_3$Zn, 1688.68; found, 1686.42.

Synthesis of dye JP3

The preparation method was the same as that of dye JP1. $^1$HNMR (CDCl$_3$, 500Hz) $\delta$H 9.62 (d, J = 4.5Hz, 2H), 9.49 (d, J = 4.5Hz, 2H), 8.68 (d, J = 4.5Hz, 2H), 8.84 (d, J = 4.5Hz, 2H), 7.82 (d, J = 8.4Hz, 2H), 7.71 (t, J = 8.4Hz, 2H), 7.49 (d, J = 8.8Hz, 4H), 7.45 (s, 1H), 7.26 (s, 1H), 7.20 (d, J = 8.8Hz, 4H), 7.06 (d, J = 3.2Hz, 2H), 7.02 (d, J = 8.4Hz, 4H), 6.70 (d, J = 3.2Hz, 2H), 3.87 (t, J = 6.4Hz, 8H), 2.79 (t, J = 7.2Hz, 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). $^{13}$CNMR (CDCl$_3$, 500Hz) $\delta$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, 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 C$_{111}$H$_{127}$N$_5$O$_6$S$_3$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