Supplementary Information for

Synthesis and Characterization of Diporphyrin Sensitizers for Dye-Sensitized Solar Cells

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Experiments

General

All reagents and solvents were obtained from commercial sources and used without further purification unless otherwise noted. THF was dried over sodium/benzophenone and freshly distilled before use. Tetra-n-butylammonium hexafluorophosphate (TBAPF₆) was recrystallized twice from absolute ethanol and further dried for two days under vacuum. Column chromatography was performed on silica gel (Merck, 70-230 Mesh ASTM).

Spectral and electrochemical measurements

¹H NMR spectra (Varian spectrometer) at 400 MHz, UV-visible spectra (Varian Cary 50), UV-visible-NIR spectra (Shimadzu UV-3600), emission spectra (a JASCO FP-6000 spectrofluorometer), FAB-MS mass spectra (JMS-SX/SX102A Tandem Mass spectrometer, operating in the positive ion detection mode) was recorded on the indicated instrument. Electrochemistry was performed with a three-electrode potentiostat (CH Instruments, Model 750A) in THF deoxygenated by purging with prepurified Ar gas. Cyclic voltammetry was conducted with the use of a home-made three-electrode cell equipped with a BAS glassy carbon (0.07 cm²) 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.

**Synthetic procedures**

3: A Schlenk tube was charged with 1 (330 mg, 0.31 mmol), 2 (200 mg, 0.21 mmol), Pd$_2$(dba)$_3$ (58 mg, 0.06 mmol) and AsPh$_3$ (160 mg, 0.52 mmol). These reagents were dissolved in a degassed mixture of THF (100 mL) and NEt$_3$ (20 mL) and stirred at 85 °C for 20 h. After solvent was removed under vacuum and the residue was purified on a column chromatograph (silica gel) using CH$_2$Cl$_2$/hexane/pyridine (3/7/0.001) as eluent and recrystallization from THF/CH$_3$OH gave 3 (318 mg, 80%). $^1$H NMR (CDCl$_3$/pyridine-d$_5$, 400 MHz) $\delta$H = 10.40 (d, $J$ = 4.4 Hz, 2H), 10.39 (d, $J$ = 4.4 Hz, 2H), 9.69 (d, $J$ = 4.4 Hz, 2H), 9.12 (d, $J$ = 4.4 Hz, 2H), 9.05 (d, $J$ = 4.4 Hz, 2H), 8.91 (d, $J$ = 4.4 Hz, 2H), 8.87 (d, $J$ = 4.4 Hz, 2H), 8.85 (d, $J$ = 4.8 Hz, 2H), 8.10 (d, $J$ = 1.6 Hz, 4H), 8.07 (d, $J$ = 1.6 Hz, 4H), 8.04 (d, $J$ = 1.6 Hz, 2H), 7.80 (s, 2H), 7.89 (s, 2H), 7.75 (s, 1H), 1.57 (s, 36H), 1.55 (s, 36H), 1.51 (s, 18H), 1.43-1.45 (m, 21H); $^{13}$C NMR (CDCl$_3$/pyridine-d$_5$, 100.56 MHz): $\delta$C = 152.54, 152.30, 152.11, 150.42, 150.05, 150.00, 149.91, 149.63, 148.19, 148.09, 148.01, 141.93, 141.59, 135.51, 132.84, 132.59, 131.78, 131.47, 130.33, 129.37, 129.24, 123.88, 120.53, 120.35, 110.21, 102.85, 101.30, 96.77, 34.68, 34.64, 31.44, 31.40, 29.33, 18.80, 11.64; UV-Vis (CH$_2$Cl$_2$: pyridine = 100:1): $\lambda_{\text{max}}$/nm (rel.int.) = 420 (0.49), 438 (0.45), 452 (0.42), 488 (1.00), 570 (0.05), 743 (0.28); FAB-MS: $m/z$ calcd for C$_{123}$H$_{142}$N$_8$O$_2$Zn$_2$Si: 1890; found 1892 ([M+2H]$^+$).
YDD0: To a solution of porphyrin 3 (150 mg, 0.08 mmol) in dry THF (15 mL) was added TBAF (1M in THF, 0.19 ml, 0.64 mmol). The solution was stirred at 25 °C 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 vacuum. A Schlenk tube with the deprotected product was charged with 4-iodobenzoic acid (80 mg, 0.323 mmol), Pd2(dba)3 (22 mg, 0.024 mmol), and AsPh3 (62 mg, 0.20 mmol). These reagents were dissolved in a degassed mixture of THF (37 mL) and NEt3 (7.4 mL), and stirred at 85 °C for 5 h. The solvent was removed under vacuum and the residue was purified on a column chromatograph (silica gel) using CH2Cl2/CH3OH (95/5) as eluent. Recrystallization from THF/CH3OH gave YDD0 (122 mg, 81%). 1H NMR (CDCl3/pyridine-d5, 400 MHz) δH = 10.40 (t, J = 4.8 Hz, 4H), 7.34 (d, J = 4 Hz, 2H), 9.13 (d, J = 4.4 Hz, 2H), 9.07 (d, J = 4.4 Hz, 2H), 8.95 (d, J = 4.8 Hz, 2H), 8.87-8.84 (m, 4H), 8.32 (br, 2H), 8.10 (s, 10H), 8.04 (s, 2H), 7.82 (s, 2H), 7.79 (s, 2H), 7.76 (s, 1H), 1.58 (s, 36H), 1.55 (s, 36H), 1.52 (s, 18H); 13C NMR (CDCl3/pyridine-d5, 100.56 MHz); δC = 207.09, 152.77, 152.12, 150.61, 150.07, 149.85, 142.25, 142.15, 141.69, 133.09, 132.83, 131.99, 131.67, 131.08, 130.31, 129.88, 129.70, 129.50, 124.38, 120.57, 34.99, 31.76, 31.73; UV-vis (CH2Cl2: pyridine = 100:1): λmax/nm(ε, 103M⁻¹cm⁻¹) = 429 (186), 445 (199), 490 (265), 547 (20) 753 (77); FAB-MS: m/z calec for C121H126N8O2 Zn2: 1854; found 1856 ([M+2H]+).

6: A Schlenk tube was charged with 4 (300 mg, 0.30 mmol), 5 (454 mg, 0.45 mmol), Cs2CO3 (781 mg, 2.40 mmol), and Pd(PPh3)4 (138 mg, 0.12 mmol). These reagents were dissolved in a degassed mixture of toluene (31 mL) and DMF (76 mL), and stirred at 85 °C for 5 h. After concentrated, the residue was poured down a short silica gel column using CH2Cl2: hexane (1:4 mL) as the eluent. Recrystallization from CH2Cl2/CH3OH gave solid (287 mg, 53%). Then, the product was dissolved in CH2Cl2 and a saturated solution of Zn(OAc)2 2H2O in methanol was added to the solution. The resulting mixture was refluxed for 2 h. Thereafter, the solvent was removed under reduced pressure and then the solid was recrystallized from CH2Cl2/MeOH to give 6 (285 mg, 95%). 1H NMR (CDCl3, 400 MHz) δH = 9.91 (d, J
= 4.8 Hz, 2H), 9.09-9.07 (m, 4H), 9.03 (d, \( J = 4.8 \) Hz, 2H), 8.70 (d, \( J = 4.4 \) Hz, 2H), 8.64 (d, \( J = 4.4 \) Hz, 2H), 8.16 (d, 2H), 8.14 (d, \( J = 5.2 \) Hz, 2H), 8.10-8.06 (m, 10H), 7.83 (t, 1H), 7.70 (t, 2H), 7.68 (t, 2H), 1.57 (s, 18H), 1.51-1.49 (m, 21H), 1.45 (s, 36H), 1.43 (s, 36H); \(^{13}\)C NMR (CDCl\(_3\), 100.56 MHz): \( \delta_C = 154.72, 154.65, 152.59, 150.94, 150.70, 150.42, 149.97, 148.59, 148.49, 141.91, 141.71, 141.35, 134.13, 133.64, 133.07, 132.25, 132.08, 131.98, 130.99, 129.57, 129.53, 129.35, 124.08, 123.26, 123.21, 121.30, 120.93, 120.87, 120.73, 118.89, 109.59, 100.76, 97.83, 77.16, 35.04, 34.95, 31.77, 31.66, 29.67, 19.16, 18.53, 11.99, 9.8; UV-Vis (CH\(_2\)Cl\(_2\): pyridine = 100:1): \( \lambda_{\text{max}}/\text{nm} \) (rel.int.) = 434 (0.66), 470 (1.00), 583 (0.12), 632 (0.11); FAB-MS: \( m/z \) calcd for C\(_{121}\)H\(_{142}\)N\(_8\)Si Zn\(_2\): 1866; found 1868 ([M+2H]\(^+\)).

**YDD1**: To a solution of porphyrin \( 6 \) (130 mg, 0.07 mmol) in dry THF (12 mL) was added TBAF (1M in THF, 0.17 mL, 0.56 mmol). The solution was stirred at 25 °C 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 vacuum. A Schlenk tube with the deprotected product was charged with 4-iodobenzoic acid (52 mg, 0.21 mmol), Pd\(_2\)(dba)\(_3\) (19 mg, 0.021 mmol), and AsPh\(_3\) (54 mg, 0.18 mmol). These reagents were dissolved in a degassed mixture of THF (32 mL) and NEt\(_3\) (6.4 mL) and stirred at 85 °C for 5 h. The solvent was removed under vacuum and the residue was purified on a column chromatograph (silica gel) using CH\(_2\)Cl\(_2\)/CH\(_3\)OH (95/5) as eluent. Recrystallization from CH\(_2\)Cl\(_2\)/CH\(_3\)OH gave **YDD1** (110 mg, 86\%). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta_H = 9.95 \) (d, \( J = 4.8 \) Hz, 2H), 9.14 (d, \( J = 4.8 \) Hz, 2H), 9.09 (d, \( J = 4.8 \) Hz, 2H), 9.04 (d, \( J = 4.8 \) Hz, 2H), 8.72 (d, \( J = 4.8 \) Hz, 2H), 8.66 (d, \( J = 4.8 \) Hz, 2H), 8.14 (d, \( J = 8.0 \) Hz, 2H), 8.20 (d, \( J = 8.0 \) Hz, 2H), 8.17-8.10 (m, 14H), 7.83 (s, 1H), 7.72 (s, 2H), 7.69 (s, 2H), 1.57 (s, 18H), 1.50 (s, 36H), 1.43 (s, 36H); \(^{13}\)C NMR (CDCl\(_3\), 100.56 MHz): \( \delta_C = 154.70, 152.20, 150.99, 150.72, 150.64, 150.35, 149.96, 148.71, 148.62, 148.51, 141.74, 141.30, 134.34, 133.60, 133.30, 132.31, 132.19, 132.03, 131.50, 130.62, 130.50, 129.66, 129.56, 124.51, 123.31, 123.23, 121.89, 120.98, 120.77, 118.77, 124.51, 99.39, 96.72, 95.57, 35.09, 35.01, 34.98, 31.80, 31.69, 29.70; UV-Vis (CH\(_2\)Cl\(_2\): pyridine = 100:1): \( \lambda_{\text{max}}/\text{nm} \) (rel.int.) = 434 (178), 474 (310), 577 (33.3), 642
(45.7); FAB-MS: m/z calcd for C_{119}H_{126}N_{8}O_{2}Zn_{2}: 1830; found 1832 ([M+2H]^+).

7: A Schlenk tube was charged with 6 (120 mg, 0.064 mmol), Sc(OTf)_3 (252 mg, 0.51 mmol), and DDQ (116 mg, 0.51 mmol) under a dinitrogen atmosphere. Degassed toluene (120 mL) was added and the resulting solution was stirred at 120 °C. After 2 h, the mixture was diluted with THF and filtered through a short neutral alumina column. The solvent was removed under vacuum and the residue was purified on a column chromatograph (silica gel) using CH_2Cl_2/hexane/pyridine (1/1/0.02) as eluent. Recrystallization from THF/CH_3OH gave 7 (77 mg, 65%).  

1H NMR (CDCl_3/pyridine-d_5, 400 MHz) δ_H = 8.56 (d, J = 3.6 Hz, 4H), 8.43 (d, J = 4.4 Hz, 2H), 7.59 (d, J = 4.8 Hz, 2H), 7.56-7.49 (m, 19H), 7.42 (d, J = 4.8 Hz, 2H), 6.96 (s, 2H), 6.94 (s, 2H), 1.41 (s, 36H), 1.39 (s, 36H), 1.36 (s, 36H), 1.36 (s, 18H), 1.25-1.24 (m, 21H); 13C NMR (CDCl_3/pyridine-d_5, 100.56 MHz): δ_C = 155.13, 154.97, 153.67, 153.46, 153.36, 152.83, 152.48, 148.39, 148.34, 140.59, 140.39, 140.33, 135.92, 135.78, 131.66, 130.80, 130.40, 129.16, 127.90, 127.87, 127.39, 127.20, 126.91, 126.30, 120.56, 120.48, 120.38, 119.82, 116.56, 109.14, 102.40, 96.14, 77.16, 66.76, 65.91, 54.37, 34.72, 31.55, 31.52, 31.47, 18.86, 11.66; UV-Vis (CH_2Cl_2: pyridine = 100:1): λ_max/nm (rel.int) = 433 (1.00), 487 (0.52), 575 (1.18), 1004 (0.19), 1157 (0.37); FAB-MS: m/z calcd for C_{121}H_{138}N_8SiZn_2: 1862; found 1864 ([M+2H]^+).

YDD2: To a solution of porphyrin 7 (110 mg, 0.06 mmol) in dry THF (10 mL) was added TBAF (1M in THF, 0.14 mL, 0.47 mmol). The solution was stirred at 25
°C 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 vacuum. A Schlenk tube with the deprotected product was charged with 4-iodobenzoic acid (73 mg, 0.3 mmol), Pd2(dba)3 (16 mg, 0.018 mmol), and AsPh3 (45mg, 0.15 mmol). These reagents were dissolved in a degassed mixture of THF (27 mL) and NEt3 (5.4 mL), and stirred at 85 °C for 5 h. The solvent was removed under vacuum and the residue was purified on a column chromatograph (silica gel) using CH2Cl2/CH3OH (95/5) as eluent. Recrystallization from THF/CH3OH gave YDD2 (87 mg, 81%). 1H NMR (CDCl3/pyridine-d5, 400 MHz) δH = 8.49 (d, J = 4.4 Hz, 2H), 8.17 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 4.4 Hz, 2H), 7.57-7.48 (m, 17H), 7.41 (d, J = 4.4 Hz, 2H), 6.94 (s, 2H), 6.91 (s, 2H), 1.42 (s, 36H), 1.39 (s, 36H), 1.36 (s, 18H).

13C NMR (CDCl3/pyridine-d5, 100.56 MHz): δC = 168.84, 155.20, 154.88, 153.77, 153.68, 153.50, 152.96, 152.49, 149.32, 148.92, 148.54, 148.45, 140.63, 140.41, 140.36, 136.09, 135.86, 131.95, 130.88, 130.64, 130.49, 129.93, 128.92, 128.48, 128.21, 127.94, 127.75, 127.25, 127.08, 126.66, 126.58, 126.43, 123.73, 120.59, 120.52, 120.42, 116.48, 101.41, 95.50, 94.86, 34.84, 34.81, 31.65, 31.63, 31.57; UV-vis (CH2Cl2 : pyridine = 100:1): λmax/nm(ε, 103M-1cm-1) = 437 (116), 492 (68.1), 580 (167), 1011 (26.3), 1169 (58.7); FAB-MS: m/z calcd for C119H122N8O2 Zn2: 1826; found 1828 ([M+2H]+).

10: A mixture of powdered AuCl3 (126 mg, 0.43 mmol) and AgOTf (66 mg, 0.26 mmol) was added at once to a solution of 8 (198 mg, 0.21 mmol) and 9 (175 mg, 0.21 mmol) in dichloroethane (140 mL) at room temperature under a nitrogen atmosphere. The reaction mixture was stirred for 3 min, while noting a drastic color change of the solution from orange to red-purple. The reaction was quenched immediately with saturated NaHCO3 aqueous solution (100 mL) and stirred for additional 5 min. The reaction mixture was diluted with CHCl3 (150 mL), washed with water (3 x 100 mL) and brine, and dried over MgSO4. After removal of the solvent under reduced pressure, the residue was purified on a column chromatograph (silica gel) using CHCl3/ hexane.
(1/9) as eluent. Recrystallization from CHCl₃/CH₃OH gave a deep purple solid (178 mg, 48%). The solid was redissolved in a mixture of CHCl₃ (28 mL) and concentrated H₂SO₄ (11 mL) and stirred at room temperature for 2 h in the dark. The reaction mixture was washed with aqueous NaOH (10%) and dried over MgSO₄. Evaporation of the solvent gave 10 (72 mg, 42%). ¹H NMR (CDCl₃, 400 MHz): δ_H = 9.53 (dd, J = 4.4, 4.8 Hz, 2H), 9.23 (dd, J = 4.8, 4.8 Hz, 2H), 9.14 (bs, 2H), 8.63-8.59 (m, 3H), 8.53-8.50 (m, 2H), 8.47 (d, J = 4.8 Hz, 1H), 8.43-8.41 (m, 2H), 8.14 (s, 4H), 8.01 (dd, J = 2.0, 2.0 Hz, 4H), 7.94 (d, J = 1.6 Hz, 2H), 7.86 (s, 1H), 7.83 (s, 1H), 7.81 (s, 1H), 7.79 (s, 1H), 7.73 (s, 1H), 1.63 (s, 18H), 1.60 (s, 18H), 1.58 (s, 18H), 1.56 (s, 18H), 1.50 (s, 18H), 0.65 (s, 2H), 0.53 (s, 2H); UV-Vis (CH₂Cl₂: pyridine = 100:1): λ_max/nm (rel.int) = 426 (1.00), 498 (0.51), 543 (0.40), 616 (0.32), 823 (0.43); FAB-MS: m/z calcd for C₁₁₀H₁₂₃N₈Br: 1636; found 1638 ([M+2H]⁺).

11: Porphyrin 10 (200 mg, 0.12 mmol) was dissolved in CHCl₃, and a saturated solution of Zn(OAc)₂ 2H₂O in methanol was added to the solution. The resulting mixture was refluxed for 2 h. Thereafter, the solvent was removed under reduced pressure and recrystallized from CHCl₃/MeOH to give a purple solid (204 mg, 95%). A Schlenk tube with the solid was charged with triisopropylsilylacetylene (0.15 mL, 0.65 mmol), Pd₂(PPh₃)₂Cl₂ (28.6 mg, 0.04 mmol), and CuI (7.8 mg, 0.04 mmol). These reagents were dissolved in a degassed mixture of THF (16 mL) and NEt₃ (1.6 mL) and stirred at 85 °C for 5 h under dinitrogen. The solvent was removed under vacuum. The residue was purified on a column chromatograph (silica gel) using CH₂Cl₂/Hexane (1/3) as eluent and recrystallization from CH₂Cl₂/CH₃OH gave 11 (181 mg, 81%). ¹H NMR (CDCl₃, 400 MHz): δ_H = 9.74 (dd, J = 5.2, 4.8 Hz, 2H), 9.40 (t, J = 4.4 Hz, 2H), 9.34 (s, 1H), 9.29 (s, 1H), 8.76 (d, J = 4.8 Hz, 1H), 8.72-8.70 (m, 2H), 8.67 (d, J = 4.8 Hz, 1H), 8.63 (d, J = 4.8 Hz, 1H), 8.59 (d, J = 4.8 Hz, 1H), 8.56-8.54 (m, 2H), 8.17 (t, J = 1.6 Hz, 4H), 8.03 (dd, J = 2.0, 2.0 Hz, 4H), 7.95 (d, J = 1.6 Hz, 2H), 7.85 (t, J = 1.6 Hz, 1H), 7.82 (t, J = 2.0 Hz, 1H), 7.81 (t, J = 2.0 Hz, 1H), 7.79 (t, J = 2.0 Hz, 1H), 7.73 (t, J = 2.0 Hz, 1H), 1.63 (s, 18H), 1.60 (s, 18H), 1.58 (s,
YDD3: To a solution of porphyrin 11 (58 mg, 0.03 mmol) in dry THF (58 mL) was added TBAF (1M in THF, 0.046 mL, 0.16 mmol). The solution was stirred at 25 °C for 30 min under dinitrogen. The mixture was quenched with H2O and then extracted with CHCl3. The organic layer was dried over anhydrous MgSO4 and the solvent was removed under vacuum. A Schlenk tube with the deprotected product was charged with 4-iodobenzoic acid (36 mg, 0.15 mmol), Pd2(dba)3 (8.0 mg, 9 μmol), and AsPh3 (22 mg, 0.07 mmol). These reagents were dissolved in a degassed mixture of THF (13 mL) and NEt3 (2.7 mL) and stirred at 85 °C for 5 h. The solvent was removed under vacuum. The residue was purified on a column chromatograph (silica gel) using CH2Cl2/CH3OH (95/5) as eluent and recrystallization from CHCl3/CH3OH gave YDD3 (45 mg, 82%). 

YDD3 : To a solution of porphyrin 11 (58 mg, 0.03 mmol) in dry THF (58 mL) was added TBAF (1M in THF, 0.046 mL, 0.16 mmol). The solution was stirred at 25 °C for 30 min under dinitrogen. The mixture was quenched with H2O and then extracted with CHCl3. The organic layer was dried over anhydrous MgSO4 and the solvent was removed under vacuum. A Schlenk tube with the deprotected product was charged with 4-iodobenzoic acid (36 mg, 0.15 mmol), Pd2(dba)3 (8.0 mg, 9 μmol), and AsPh3 (22 mg, 0.07 mmol). These reagents were dissolved in a degassed mixture of THF (13 mL) and NEt3 (2.7 mL) and stirred at 85 °C for 5 h. The solvent was removed under vacuum. The residue was purified on a column chromatograph (silica gel) using CH2Cl2/CH3OH (95/5) as eluent and recrystallization from CHCl3/CH3OH gave YDD3 (45 mg, 82%).
Electrode preparation and device fabrication

The photoanodes composed of nanocrystalline TiO$_2$ were prepared using the sol-gel method reported elsewhere.$^{[S1]}$ A paste composed of about 20 nm TiO$_2$ particles for the transparent nanocrystalline layer was coated on a TiCl$_4$-treated FTO glass substrate (FTO, 30 $\Omega$/□) to obtain the required thickness by repetitive screen printing. To improve the performance of DSSC, one additional scattering layer (particle size 200-600 nm) was screen-printed on the transparent nanocrystalline layer. The TiO$_2$ working electrodes were gradually heated according to a programmed procedure: (1) heating at 80 °C for 15 min; (2) heating at 135 °C for 10 min; (3) heating at 325 °C for 30 min; (4) heating at 375 °C for 5 min; (5) heating at 450 °C for 15 min; (6) heating at 500 °C for 15 min. The resulting layer was composed of 8 $\mu$m thickness of transparent active layer and 4 $\mu$m thickness of scattering layer, which were treated again by 0.04 M TiCl$_4$ aqueous solution at 70 °C for 30 min and sintered at 500 °C for 30 min. After cooling in air, the sintered TiO$_2$ films were immersed in dye solutions (concentration 0.2 mM in anhydrous ethanol at 25 °C for 12 h) containing 0.4 mM chenodeoxycholic acid (CDCA) for dye loading onto the working electrodes. The counter electrode was made by spin-coating the H$_2$PtCl$_6$/isopropanol solution onto an indium-doped tin oxide (ITO; 5.5 $\Omega$/□) glass substrate (typical size 1.0×1.5 cm$^2$) through thermal decomposition at 380 oC for 30 min. The two electrodes were assembled into a cell of sandwich type and sealed with a hot-melt film (SX1170, thickness 25 $\mu$m). The electrolyte solution for YD0 and YDDD0-YDDD3 devices contains LiI (0.1 M), I$_2$ (0.05 M), PMII (0.6 M) and 4-tert-butylpyridine (0.5 M) in a solvent mixture containing acetonitrile and valeronitrile (volume ratio 1:1).$^{[S2]}$

Dye-loading examination

To determine the dye-loading amount of YD0 and YDDD0-YDDD3 on TiO$_2$ films, the dye was desorbed in tetrabutylammonium hydroxide (0.1 M, TBAOH, Fluka) in ethanol (3 mL). The calibration curves for YD0 and YDDD0-YDDD3 in EtOH in the presence of 0.1 M TBAOH were derived to obtain the absorption coefficients shown in Fig. S3a. The absorption spectra of the desorbed dye solutions (Fig. S3b) were recorded with a UV-vis spectrometer (Jasco, V-570 for YD2 and Varian, Cary 50 for others). The amounts of dye coverage on TiO$_2$ films shown in Table 1 were obtained from the measured absorbances of the Q(0,0) bands in the spectra (cuvette thickness 2 mm) and the calibrated absorption coefficients at the same spectral position according to Beers’ law.

Photovoltaic characterization
The current-voltage characteristics were determined with a digital source meter (Keithley 2400) with the device under one-solar AM 1.5 irradiation from a solar simulator (SAN-EI, XES-502S) calibrated with a standard silicon reference cell (VLSI standards, Oriel PN 91150V). When the device is irradiated with the solar simulator, the source meter sends a voltage ($V$) to the device, and the photocurrent ($I$) is read at each step controlled with a computer via a GPIB interface. The efficiency ($\eta$) of conversion of light to electricity is obtained with these relations, $\eta = \frac{J_{sc} V_{oc} FF}{P_{in}}$, in which $J_{sc}$ /mA cm$^{-2}$ is the current density measured at short circuit, and $V_{oc}$ /V is the voltage measured at open circuit. $P_{in}$ is the input radiation power (for one-solar illumination $P_{in} = 100$ mW cm$^{-2}$) and FF is the fill factor. For all measurements, the DSSC devices were covered with a black mask of aperture area 0.16 cm$^2$ to ensure the measured photocurrent not being exaggerated. The spectra of the incident photons-to-current conversion efficiency (IPCE) of the corresponding devices were obtained with a system comprising a Xe lamp (PTi A-1010, 150 W), a monochromator (Dongwoo DM150i, 1200 gr/mm blazed at 500 nm), and a source meter (Keithley 2400). A standard Si photodiode (ThorLabs FDS1010) served as a reference to calibrate the power density of the light source at each wavelength. Both photocurrent densities of the target device and the reference Si cell were measured under the same experimental conditions (excitation beam size ~0.08 cm$^2$) so to obtain the efficiency of the device from a comparison of the current ratio and the value of the reference cell at each wavelength.\[53\]


Fig. S1  Cyclic voltammograms of YD0 and YDD0-YDD3 in THF containing 0.1 M TBAPF₆ at 25 °C.
Fig. S2 Energy-level diagram and the corresponding molecular orbitals of porphyrins YD0 and YDD0–YDD3 calculated at the B3LYP/6-31G(d) level of theory.
**Fig. S3**  (a) Spectral photocurrent densities of **YD0** and **YDD0-YDD3** obtained from multiplication of the AM 1.5G solar spectra (thin black dotted curve) by the corresponding IPCE values of the DSSC devices; (b) integrated photocurrent densities of **YD0** and **YDD0-YDD3** devices to estimate $J_{SC}$ according to the integral

$$J_{SC} = \int q \cdot IPCE(\lambda) \cdot F(\lambda) \ d\lambda.$$
Fig. S4  (a) Calibrated absorption spectra of YD0 and YDD0-YDD3 in ethanol in the presence of 0.1 M TBAOH; (b) dye-loading absorption spectra of the YD0 and YDD0-YDD3 solutions containing 0.1 M TBAOH in ethanol desorbed from the corresponding porphyrin-sensitized TiO₂ films.