Electronic Supplementary Information

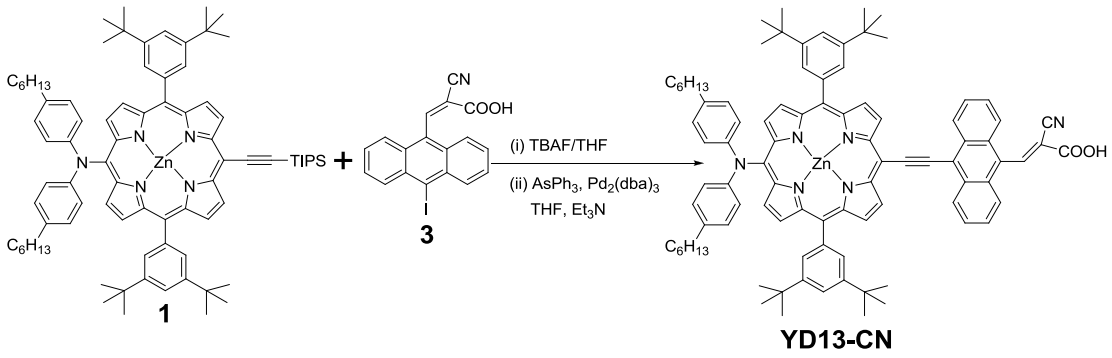
Experimental

All reagents and solvents were obtained from commercial sources and used without further purification, unless otherwise noted. CH_2Cl_2 was dried over CaH_2 and freshly distilled before use. THF was dried over sodium/benzophenone and freshly distilled before use. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) 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).

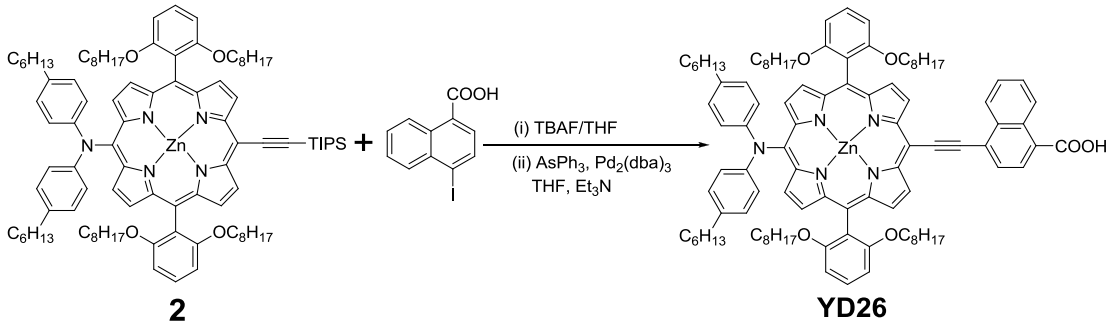
Spectral and Electrochemical Measurements

^1H NMR spectra (Varian spectrometer, 400 MHz), UV-visible spectra (Varian Cary 50), UV-visible-NIR spectra (Shimadzu UV-3600), emission spectra (JASCO FP-6000 spectrofluorimeter), high resolution mass spectra (LT Orbitrap XL, Thermo Fisher Scientific) and FAB mass spectra (JMS-SX/SX102A Tandem Mass spectrometer) were recorded on the indicated instruments. Electrochemical tests were performed with a three-electrode potentiostat (CH Instruments, Model 750A) in THF deoxygenated on purging with prepurified dinitrogen gas. Cyclic voltammetry was conducted with a three-electrode cell equipped with a BAS glassy carbon disk (0.07 cm^2) as the working electrode, a platinum wire as auxiliary electrode, and an Ag/AgCl (saturated) reference electrode, which is separated from the bulk solution with a double junction filled with an electrolyte solution. The working electrode was polished with aluminum (0.03 μm) on felt pads (Buehler) and treated ultrasonically for 1 min before each experiment. The reproducibility of individual potential values was within ±5 mV.

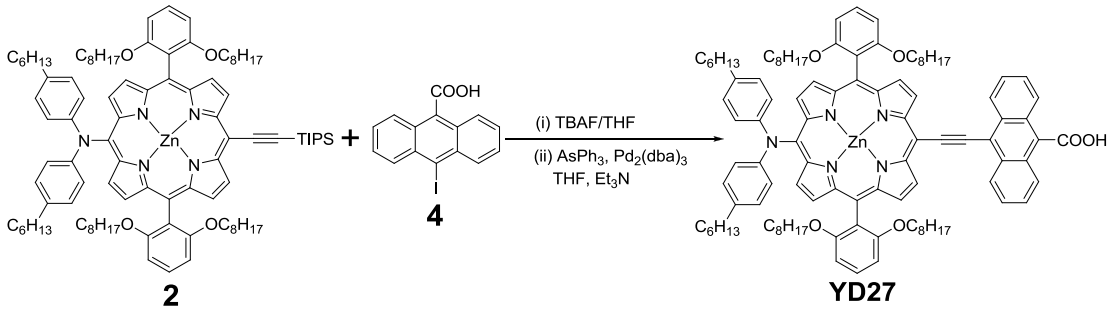
Synthesis of Porphyrin Dyes:



Synthesis of YD13-CN: To the solution of Porphyrin **1**[1] (150 mg, 0.12 mmol) in THF (15 mL) was added TBAF (0.5 mL, 1 M in THF, 0.57 mmol) and it was stirred at 23 ^{o}C for 5 min. The solvent was removed under decreased pressure then H_2O was added and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under vacuum. The above obtained residue porphyrin, 2-cyano-3-(10-iodoanthracen-9-yl)acrylic acid **3** (90 mg, 0.23 mmol), $Pd_2(dba)_3$ (10.0 mg, 0.012 mmol) and $AsPh_3$ (28.0 mg, 0.09 mmol) were placed in an oven dry schlenk tube and degassed for 10 min then degassed mixture of THF (30 mL) and Et_3N (10 mL) were added and the solution was refluxed under N_2 for 12 h and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel) using CH_2Cl_2 /methanol = 92/8 as eluent. Recrystallization from CH_2Cl_2/CH_3OH gave **YD13-CN** as dark green solid 119 mg, 72 % yield. ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD) δ 9.85 (d, *J* = 4.4 Hz, 2H), 9.30 (d, *J* = 8.8 Hz, 2H), 9.12 (s, 1H), 9.1 (s, 2H), 8.88 (d, *J* = 4.4 Hz, 2H), 8.64 (d, *J* = 4.4 Hz, 2H), 8.11 (d, *J* = 8.8 Hz, 2H), 7.93 (s, 4H), 7.73 (t, *J* = 7.2 Hz, 2H), 7.66 (s, 2H), 7.62(t, *J* = 7.2 Hz, 2H), 7.15 (d, *J* =8.8 Hz, 4H), 6.88 (d, *J* =8.8 Hz, 4H), 2.37 (t, *J* = 8.4 Hz, 4H), 1.42 (s, 36H), 1.26 (br, 16H), 0.73 (t, *J*=6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD) δ 152.2, 151.9, 150.4, 149.9, 149.7, 148.3, 141.4, 134.5, 132.9, 132.6, 132.3, 129.2, 128.6, 128.5, 126.7, 126.6, 125.8, 124.1, 123.0, 122.1, 121.0, 120.6, 106.4, 98.7, 34.6, 31.3, 28.6, 22.9, 22.1, 19.7, 19.2, 13.1; UV-vis (THF): λ_{max}/nm (rel. int.) = 481 (1.00), 582 (0.09), 662 (0.33); HRMS: *m/z* calcd. for $C_{92}H_{94}N_6O_2Zn$: 1378.6724, found: 1378.6756 ($[M]^+$).

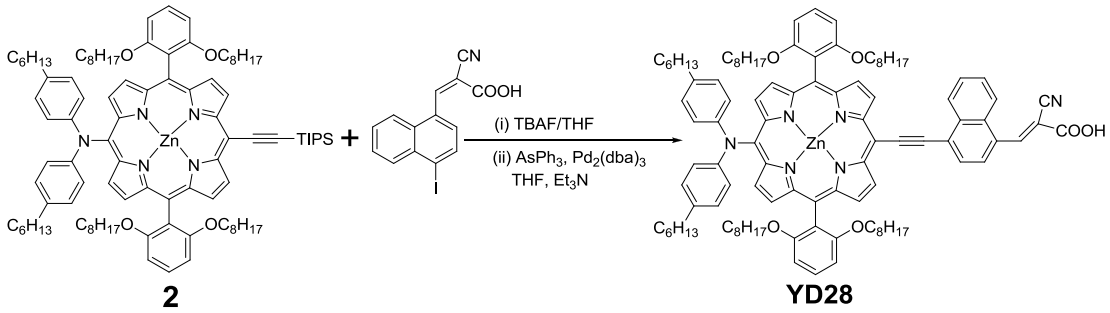


Synthesis of YD26: To the solution of Porphyrin **2**[2] (100 mg, 0.064 mmol) in THF (15 mL) was added TBAF (0.3 mL, 1 M in THF, 0.33 mmol). The solution was stirred at 23 ^{o}C for 5 min. and then solvent was removed under reduced pressure and then extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under vacuum. The residue porphyrin, 4-iodo-1-naphthoic acid (78 mg, 0.23 mmol), $Pd_2(dba)_3$ (7.0 mg, 0.007 mmol) and $AsPh_3$ (16.0 mg, 0.05 mmol) were placed in an oven dry schlenk tube and degassed for 10 min then degassed mixture of THF (30 mL) and Et_3N (10 mL) were added and the solution was refluxed under N_2 for 5 h and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel) using CH_2Cl_2/methanol= 97/3 as eluent. Recrystallization from CH_2Cl_2/CH_3OH gave **YD26** as a green solid 100 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD) δ 9.78 (d, *J* = 4.4 Hz, 2H), 9.18 (d, *J* = 4.4 Hz, 2H), 9.22-9.17 (m, 2H), 8.93 (d, *J* = 4.8 Hz, 2H), 8.69 (d, *J* = 4.8 Hz, 2H), 8.49 (d, *J* = 7.6 Hz, 1H), 8.26 (d, *J* = 7.6 Hz, 1H), 7.79-7.85 (m, 2H), 7.66 (t, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 4H), 6.96(d, *J* =8.8 Hz, 4H), 6.93(d, *J* =8.8 Hz, 4H), 3.85(t, *J* =6.4 Hz, 8H), 2.46 (t, *J* = 7.2 Hz, 4H), 1.47-1.43 (m, 4H), 1.26 (br, 12H), 0.99 (t, *J* =7.6 Hz, 16H), 0.86-0.65 (m, 14H), 0.62-0.43 (m, 36H); ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD) δ 159.8, 152.1, 151.9, 150.7, 150.3, 150.0, 134.4, 133.9, 132.7, 131.8, 131.6, 131.3, 130.3, 130.1, 129.6, 129.1, 128.6, 128.3, 126.9, 126.6, 121.8, 113.7, 105.5, 100.2, 98.2, 68.8, 43.9, 35.2, 31.7, 31.4, 29.6, 29.3, 28.6, 28.4, 25.1, 22.5, 22.2, 13.9, 13.7; UV-vis (THF) : λ_{max}/nm (rel. int.) = 456 (1.00), 583 (0.06), 648 (0.16); HRMS: *m/z* calcd. for $C_{101}H_{123}N_5O_6Zn$: 1565.8759, found: 1565.8764 ([M]$^+$).



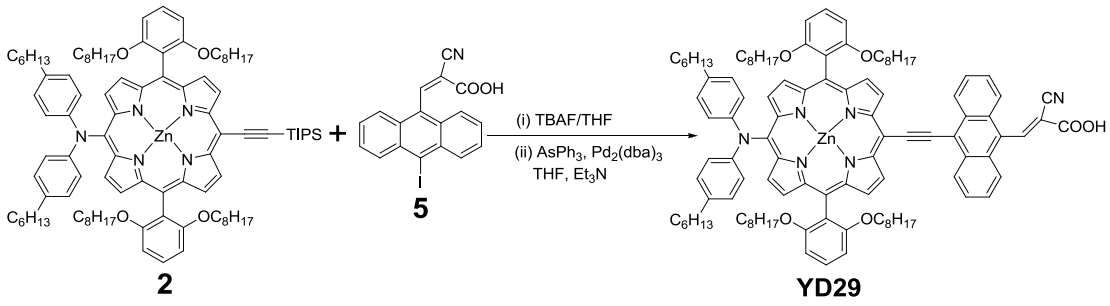
Synthesis of YD27: The preparation of **YD27** employed a synthetic route similar to that for **YD26** except that 10-iodoanthracene-9-carboxylic acid **4** (78 mg, 0.23 mmol) was used as linker and the solution was refluxed for 8h to give green solid 90 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD) δ 9.91 (d, *J* = 4.8 Hz, 2H), 9.38 (d, *J* = 8.4 Hz, 2H), 9.13 (d, *J* = 4.8 Hz, 2H), 8.89 (d, *J* = 4.8 Hz, 2H), 8.64 (d, *J* = 4.8 Hz, 2H), 8.43 (d, *J* = 8.4 Hz, 2H), 7.78 (t, *J* = 6.8 Hz, 2H), 7.75-7.63 (m, 4H), 7.23 (d, *J* = 8.8 Hz, 4H), 7.01 (d, *J* = 8.4 Hz, 4H), 6.93 (d, *J* = 8.8 Hz, 4H), 3.86 (t, *J* =7.2 Hz, 8H), 2.47 (t, *J* = 7.2 Hz, 4H), 1.53 (br, 4H), 1.27 (br, 16H), 0.86 (t, *J* =4.0 Hz, 8H), 0.72-0.60 (m, 16H), 0.66-0.49 (m, 38H); ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD) δ 159.8, 152.0, 151.9, 150.7, 150.3, 150.0, 134.4, 134.0, 132.7, 131.8, 131.6, 130.3, 131.0, 129.6, 129.2, 128.5, 126.9, 126.5, 121.4, 100.2, 98.2, 68.8, 45.6, 35.2, 31.7, 31.5, 31.0, 29.6, 29.0, 28.4, 25.1,

22.6, 22.5, 13.9, 13.7; UV-vis (THF) : λ_{max}/nm (rel. int.) = 481 (1.00), 584 (0.06), 657 (0.25); HRMS: *m/z* calcd. for $C_{105}H_{125}N_5O_6Zn$: 1615.8916, found: 1615.8914 ($[M]^+$).



2 **YD28**

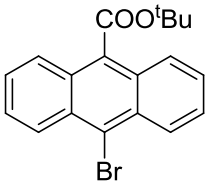
Synthesis of YD28: The preparation of **YD28** employed a synthetic route similar to that for **YD26** except that 2-cyano-3-(4-iodonaphthalen-1-yl) acrylic acid (78.0 mgs, 0.23 mmol) was used as linker and the solution was refluxed for 12h to afford dark green solid 77 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$) δ 9.57 (d, J = 4.4 Hz, 2H), 9.04 (d, J = 8.0 Hz, 1H), 8.97 (s, 1H), 8.94 (d, J = 4.4 Hz, 2H), 8.69 (d, J = 4.4 Hz, 2H), 8.43 (d, J = 8.4 Hz, 2H), 8.29 (d, J = 7.2 Hz, 1H), 8.15 (t, J = 8.4 Hz, 2H), 7.69 (t, J = 6.8 Hz, 1H), 7.63 (t, J = 6.8 Hz, 1H), 7.51 (t, J = 8.4 Hz, 2H), 7.06 (d, J = 8.0 Hz, 4H), 6.83 (d, J = 8.4 Hz, 4H), 6.75 (d, J =8.4 Hz, 4H), 3.69 (t, J = 6.8 Hz, 8H), 2.29 (t, J = 7.6 Hz, 4H), 1.37-1.34 (m, 4H), 1.08 (br, 12H), 0.84 (t, J =6.8 Hz, 8H), 0.79-0.66 (m, 16H), 0.59-0.43 (m, 42H); ^{13}C NMR (100 MHz, $CDCl_3/CD_3OD$) δ 160.1, 152.3, 151.8, 134.7, 150.0, 149.9, 149.7, 146.8, 142.5, 134.0, 132.9, 131.7, 131.2, 129.3, 128.6, 128.1, 127.7, 127.2, 126.6, 126.2, 125.2, 125.1, 124.8, 124.6, 120.9, 105.7, 100.2, 99.1, 68.9, 40.6, 37.6, 31.8, 31.5, 29.1, 28.7, 28.5, 25.2, 22.6, 22.4, 14.0, 13.8; UV-vis (THF) : λ_{max}/nm (rel. int.) = 464 (1.00), 584 (0.07), 655 (0.25); HRMS: *m/z* calcd. for $C_{104}H_{124}N_6O_6Zn$: 1616.8868, found: 1616.8870 ($[M]^+$).



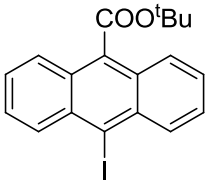
2 **5** **YD29**

Synthesis of YD29: The preparation of **YD29** employed a synthetic route similar to that for **YD28** except that 2-cyano-3-(10-iodoanthracen-9-yl) acrylic acid **5** (90.0 mg, 0.23 mmol) used as linker and refluxed for 12h to give dark green solid 72 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$) δ 9.88 (d, J = 4.4 Hz, 2H), 9.45 (d, J = 8.8 Hz, 2H), 9.27 (s, 1H), 9.12 (d, J = 3.6 Hz, 2H), 8.89 (d, J = 4.4 Hz, 2H), 8.63 (d, J = 4.8 Hz, 2H), 8.21 (d, J = 8.4 Hz, 2H), 7.81 (t, J =

6.8 Hz, 2H), 7.73-7.63 (m, 4H), 7.23 (d, J = 8.0 Hz, 4H), 6.98 (d, J = 8.0 Hz, 4H), 6.91 (d, J =8.4 Hz, 4H), 3.87 (s, 8H), 2.45 (t, J = 7.6 Hz, 4H), 1.52 (br, 6H), 1.25 (br, 16H), 1.02-0.95 (m, 14H), 0.87-0.66 (m, 12H), 0.59-0.48 (m, 34H); ^{13}C NMR (100 MHz, $CDCl_3/CD_3OD$) δ 159.1, 152.3, 151.7, 150.5, 150.3, 150.0, 149.9, 145.1, 142.5, 134.0, 132.1, 131.9, 131.7, 129.3, 128.9, 128.5, 128.1, 126.6, 126.2, 121.0, 113.4, 105.1, 101.7, 68.4, 35.8, 31.2, 31.0, 30.9, 28.5, 28.2, 27.9, 24.7, 22.1, 21.7, 13.4, 13.1; UV-vis (THF) : λ_{max}/nm (rel. int.) = 481 (1.00), 582 (0.09), 660 (0.34); HRMS: *m/z* calcd. for $C_{108}H_{126}N_6O_6Zn$: 1666.9025, found: 1666.9056 ($[M]^+$).

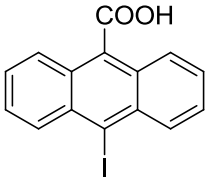


Preparation of *tert*-butyl 10-bromoanthracene-9-carboxylate: Synthesis of the compound followed a modified literature procedure.[3] A $CHCl_3$ solution (40 mL) containing 10-bromo-9-anthracenecarboxylic acid[4] (2.0 g, 6.6 mmol) and thionyl chloride (2 mL) was heated under reflux until the solution became homogeneous (ca.3h). The solution was condensed in vacuo to give 2.2 g, 100% of 10-bromoanthracene-9-carbonyl chloride as a yellow solid. The crude product was used in the following procedure without purification. To a solution of *t*-butyl alcohol (0.5 mL, 5.0 mmol) and pyridine (0.6 mL, 6.6 mmol) in dry $CHCl_3$ (10 ml) was slowly added 10-bromoanthracene-9-carbonyl chloride[5] (1.1 g, 3.3 mmol) at room temperature. After the reaction for 2 days at room temperature, the solvent was removed and the residue was extracted with ethyl ether, washed with brine and water. The ether layer was dried over $MgSO_4$, and then was removed to give a crude product. Purification was carried out by silica gel column chromatography eluting with hexane/ethyl acetate = 10/1 to give pure product yellow solid 1.5g, 64% yield. Spectral data identical with literature reports.[3]

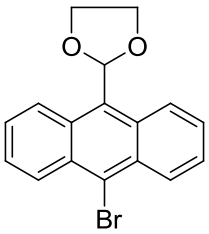


Preparation of *tert*-butyl 10-iodoanthracene-9-carboxylate: *tert*-butyl 10-bromoanthracene-9-carboxylate (0.7 g, 2.0 mmol) in THF (6.0 mL) was cooled to -90 ^{o}C, producing a yellow suspension. Dropwise addition of *n*-BuLi (1.4 mL, 2.2 mmol, 1.6 M in hexanes) to this suspension gave an orange yellow solution after 30 min additional stirring. After further stirring for 3h, the solution was treated with Iodine (0.4 g, 3.0 mmol) then slowly brought to room temperature and continued to stir overnight and the solvent was removed. Purification was carried out by silica gel column chromatography eluting with hexane/ethyl acetate = 10/1 to give light yellow solid 0.42 g, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54-8.51 (m, 2H), 7.98-7.96

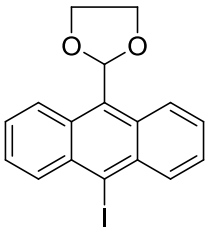
(m, 2H), 7.61-7.54 (m, 4H), 1.78 (s, 9H). FAB-MS: *m/z* calcd. for $C_{19}H_{17}IO_2$: 404; found: 404 ($[M]^+$).



Preparation of 10-iodoanthracene-9-carboxylic acid: To a solution *tert*-butyl 10-iodoanthracene-9-carboxylate (0.7 g, 1.7 mmol) in 10 ml dichloromethane was added zinc bromide (2.0 g, 8.7 mmol) and the solution stirred for 48 h. At this time, 40 ml of water was added and the mixture was stirred for 2h. The layers were separated and aqueous layer was extracted with 2x30 ml of dichloromethane. The combined organic portions were dried over $MgSO_4$, filtered and solvent removed by evaporation to give light yellow solid 0.54g, 94% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.47 (d, J = 8.4 Hz, 2H), 8.0 (d, J = 8.4 Hz, 2H), 7.75-7.67 (m, 4H). FAB-MS: *m/z* calcd. for $C_{15}H_9IO_2$: 348; found: 348 ($[M]^+$).

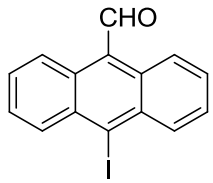


2-(10-Bromoanthracen-9-yl)-1,3-dioxolane: 10-bromoanthracene-9-carbaldehyde[5] (6.0 g, 21.1 mmol) in dry toluene (125 mL) was added *p*-toluenesulfonic acid monohydride (0.2 g, 2.1 mmmol) and ethylene glycol (2.0 g, 31.57 mmol) were refluxed with Dean-Stark adaptor for 21 h. After cooling down to room temperature, the reaction mixture was washed with aq.$NaHCO_3$ (three times), water, and saturated NaCl solution, and dried over anhydrous Na_2SO_4. Concentration in vacuo, afforded crude product which was recrystallized from hexane-dichloromethane mixture to yield 5.89g, 86% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.63 (d, J =7.6 Hz, 2H), 8.65 (d, J =9.6 Hz, 2H), 7.52-7.61 (m, 4H), 7.01 (s, 1H), 4.50-4.54 (m, 2H), 4.30-4.26 (m, 2H); FAB-MS: *m/z* calcd. for $C_{17}H_{13}BrO_2$: 328; found: 327 ($[M-H]^+$).

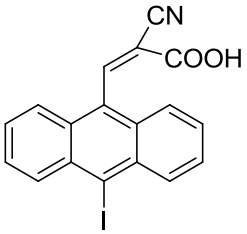


2-(10-Iodoanthracen-9-yl)-1,3-dioxolane: Following a standard procedure,[6] *n*-Butyllithium (9.7 mL, 15.5 mmol, 1.6 M in hexanes) was added dropwise over the period of 30 min to a

vigorously stirred suspension of 2-(10-bromoanthracen-9-yl)-1,3-dioxolane (4.2 g, 12.9 mmol) in anhydrous diethyl ether (200 mL). The mixture was stirred for an additional 2 h after which iodine (4.0 g, 15.5 mmol) was added in several portions over 20 min. The reaction mixture was stirred for an additional 2 h until the color changes to dark brown. The ethereal solution was washed several times with aqueous sodium thiosulfate (25% w/w), dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum to obtain the crude product. The crude product was purified by column chromatography to give light yellow solid 3.0 g, 62% yield identified as the title compound. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.58-8.60 (m, 2H), 8.52-8.50 (m, 2H), 7.50-7.58 (m, 4H), 7.08 (s, 1H), 4.50-4.54 (m, 2H), 4.30-4.26 (m, 2H); FAB-MS: *m/z* calcd. for $C_{17}H_{13}IO_2$: 376; found: 376([M]$^+$).



10-Iodoanthracene-9-carbaldehyde: A mixture of 2-(10-iodoanthracen-9-yl)-1,3-dioxolane (1.7 g, 4.6 mmol) and p-toluenesulfonic acid monohydrate (110 mg, 0.57 mmol) in 50 mL of acetone was stirred for 4 h at room temperature. The reaction mixture was poured into water, extracted with CH_2Cl_2 (3 x 30 mL), and dried over Na_2SO_4. After concentration in vacuo, the crude product was purified by column chromatography on silica gel (eluent dichloromethane-hexane 1:1) to afford yellow needles 1.4 g, 89% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.51 (s, 1H), 8.89-8.91 (m, 2H), 8.70-8.67 (m, 2H), 7.73-7.66 (m, 4H); FAB-MS: *m/z* calcd. for $C_{15}H_9IO$: 332; found: 332 ([M]$^+$)



2-Cyano-3-(10-iodoanthracen-9-yl)acrylic acid: Piperidine (0.5 mL, 4.9 mmol) was added to a solution of 10-iodoanthracene-9-carbaldehyde (0.8 g, 2.45 mmol) and cyanoacetic acid (0.4 g, 4.9 mmol) in acetonitrile (245 mL) and THF (61 mL) at room temperature under nitrogen. The mixture was heated to reflux for 12 h and then poured into an aqueous NH_4Cl solution. The aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure the residue was purified by flash chromatography to afford light yellow solid 0.96g, 98% yield. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.59 (d, J =12.8 Hz, 2H), 7.92 (d, J = 9.6 Hz, 2H), 7.75-7.62 (m, 4H); FAB-MS: *m/z* calcd. for $C_{18}H_{10}INO_2$: 399; found: 399 ([M]$^+$).

Device Fabrication and Photovoltaic Characterization

The devices were fabricated with a working electrode based on TiO_2 nanoparticles (NP) and a Pt-coated counter electrode reported elsewhere.[7,8] For the working electrode, a paste composed of TiO_2 NP (particle size ~20 nm) prepared with a sol-gel method for the transparent nanocrystalline layer was coated on a $TiCl_4$-treated FTO glass substrate (TEC 7, Hartford, USA) to obtain the required thickness of the film with repetitive screen printing. To improve the performance of the device, we screen-printed an additional scattering layer (particle size ~300 nm) on the transparent active layer. The thicknesses of the TiO2 active layer and scattering layer are 10 and 4 μm, respectively. The TiO_2 electrode was immersed in a solution containing porphyrin (0.15 mM) and CDCA (10 mM) in ethanol/toluene (volume ratio 4:1) at 25 ℃ for 3 h. The porphyrin-sensitized working electrode was assembled with the counter electrode into a cell of sandwich type and sealed with a hot-melt film (SX1170, thickness 60 m) at 90 °C. The electrolyte solution containing LiI (0.1 M), I_2 (0.05 M), PMII (1.0 M), 4-tert-butylpyridine (0.5 M) in a mixture of acetonitrile and valeronitrile (volume ratio 85:15) was introduced into the space between the two electrodes, so completing the fabrication of these DSSC devices. The photovoltaic performance of a device was assessed through measurement of an I–V curve with a solar simulator (AM-1.5 G, XES-502S, SAN-EI), calibrated with a standard silicon reference cell (Oriel PN 91150V, VLSI standards). The incident monochromatic efficiencies for conversion from photons to current (IPCE) spectra of the corresponding devices were measured with a system comprising a Xe lamp (PTi A-1010, 150 W), a monochromator (PTi, 1200 gr mm^{-1} blazed at 500 nm), and a source meter (Keithley 2400, computer-controlled). A standard Si photodiode (Hamamatsu S1337-1012BQ) served as a reference to calibrate the power density of the lamp at each wavelength.

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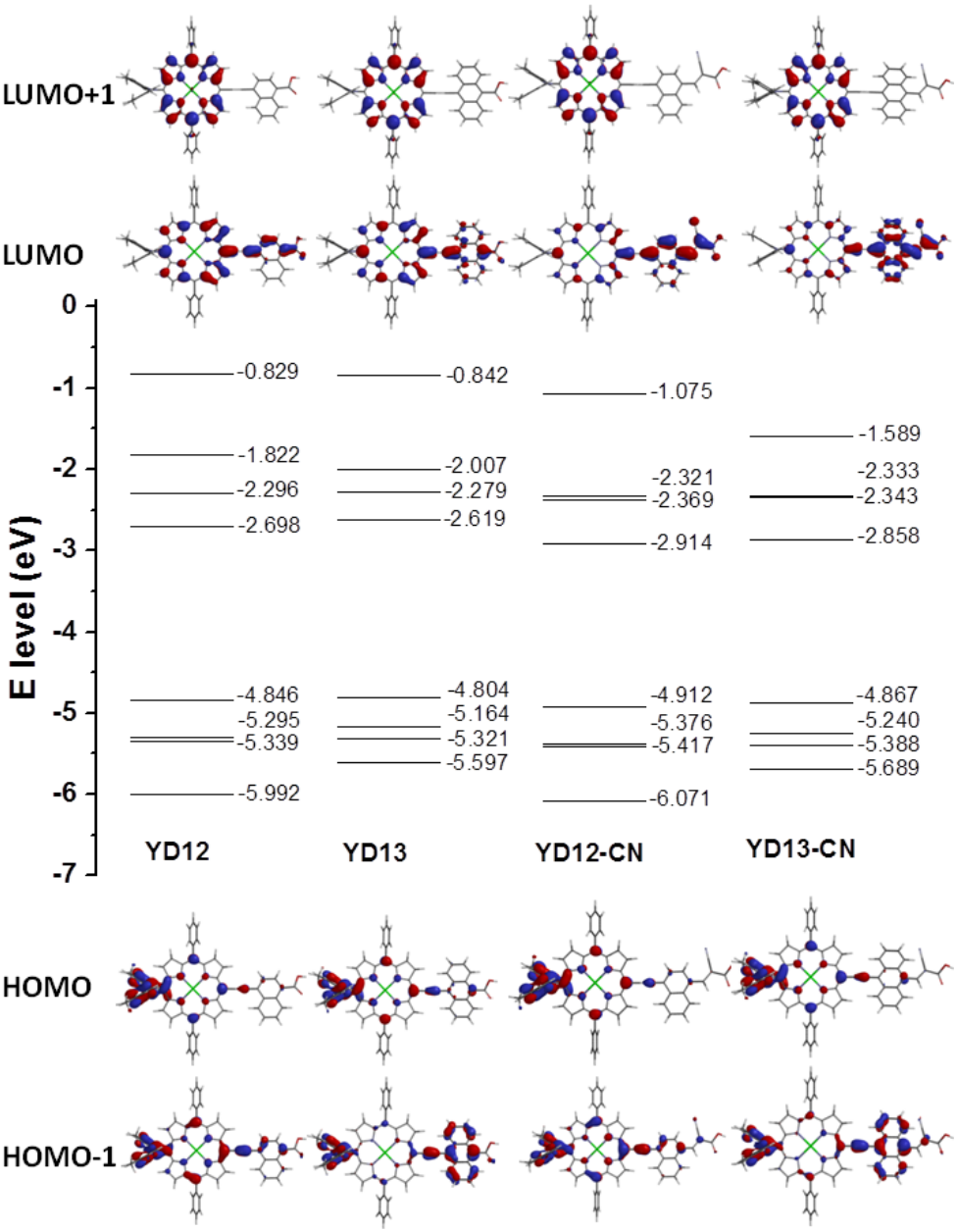

Figure S1 Energy-level diagram and the corresponding molecular orbitals of porphyrins **YD12**, **YD13**, **YD12-CN**, and **YD13-CN** calculated by DFT at the B3LYP/6-31G* level.

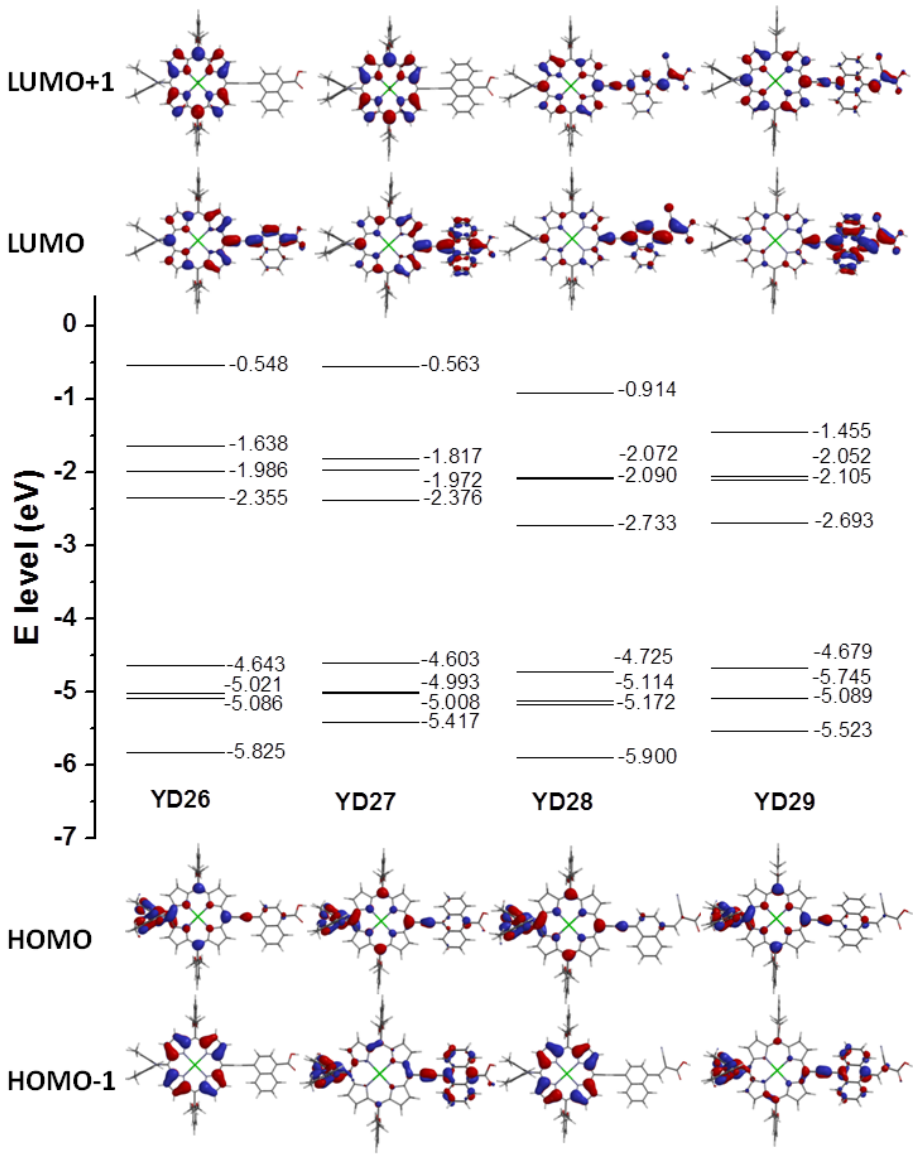

Figure S2 Energy-level diagram and the corresponding molecular orbitals of porphyrins **YD26**–**YD29** calculated by DFT at the B3LYP/6-31G* level.