Electronic Supplementary Information

Design and Characterization of Porphyrin Sensitizers with a Push-pull Framework for Highly Efficient Dye-sensitized Solar Cells

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Figure S1. Absorption spectra of **YD0**, **YD2** and **YD14–YD17** sensitized on TiO₂ films (10 µm thickness without adding a scattering layer).

Experiments

General

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. 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 (JASCO FP-6000 spectrofluorometer), MALDI-TOF-MS and FAB-MS mass spectra (Bruker APEX II spectrometer and a JMS-SX/SX102A Tandem Mass spectrometer, respectively, operating in the positive-ion detection mode) 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 a Ag/AgCl (saturated) reference electrode; the reference electrode is separated from the bulk solution with a double junction filled with electrolyte solution. Potentials are reported vs. Ag/AgCl (saturated) with reference to a ferrocene/ferrocenium (Fc/Fc⁺) couple at $E_{1/2} = +0.63$ vs. Ag/AgCl (saturated) at 25 °C in THF. The working electrode was polished with aluminium (0.03 µm) on felt pads (Buehler) and treated ultrasonically for 1 min before each experiment. The reproducibility of individual potential values was within $\pm 5 \text{ mV}.$

Device Fabrication

The porphyrins were sensitized onto TiO_2 nanoparticulate films to serve as working electrodes in DSSC devices. The TiO₂ nanoparticles (size ~20 nm) were screen-printed onto the F-doped SnO₂ (FTO, TEC 7, Hartford, USA) glass substrate. The TiO₂ film was annealed 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. For all porphyrins except **YD15**, the electrode was immersed in the porphyrin/ethanol (in Cl₂H₂ for **YD15**) solution (0.2 mM, 25 °C) containing

chenodeoxycholic acid (CDCA, 0.4 mM) for dye loading onto the TiO₂ film at 25 °C for 6 h. The Pt counter electrodes were prepared on spin-coating drops of H₂PtCl₆ solution onto ITO glass and heating at 380 °C for 15 min. To prevent a short circuit, the two electrodes were assembled into a cell of sandwich type and sealed with a hot-melt film (SX1170, Solaronix, thickness 25 μ m). The electrolyte solution containing LiI (0.1 M), I₂(0.05 M), 1-methyl-3-propylimidazolium iodide (PMII, 0.6 M), 4-*tert*-butylpyridine (TBP, 0.5 M) in a mixture of acetonitrile and valeronitrile (volume ratio 1:1) was introduced into the space between the two electrodes, so completing the fabrication of these DSSC devices.

Photovoltaic Characterization

The current-voltage characteristics of the devices were performed with an AM-1.5 solar simulator (SAN-EI, XES-502S, type class A) calibrated with a Si-based reference cell (VLSI standards, Oriel PN 91150V). When the device is irradiated with the solar simulator, the source meter (Keithley 2400, computer-controlled) sends a voltage (V) to the device, and the photocurrent (I) is read at each step controlled by a computer via a GPIB interface. The efficiency (η) of conversion of light to electricity is obtained with this relation, $\eta = J_{sc} V_{oc} FF / P_{in}$, 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-sun illumination $P_{in} = 100 \text{ mW}$ cm⁻²) and FF is the filling factor. The incident monochromatic efficiency 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), monochromator (Dongwoo DM150i, 1200 gr/mm blazed at 500 nm), and source meter (Keithley 2400, computer-controlled). A standard Si photodiode (ThorLabs FDS1010) served as a reference to calibrate the power density of the light source at each wavelength. Photocurrent densities of both the target device and the reference Si cell were measured under the same experimental conditions (excitation beam size ~ 0.08 cm²) so to obtain the IPCE value of the device from comparing the current ratio and the value of the reference cell at each wavelength.

Synthetic Procedures



5-(3,5-Di-*tert*-butylphenyl)-15-(triisopropylsilylethynyl)porphyrin (1)

To a degassed solution of dipyrromethane (1.97 g, 13.5 mmol), 3,5-di-*tert*butylbenzaldehyde (1.47 g, 6.8 mmol), and 3-triisopropyl-2-propynal (1.42 g, 6.8 mmol) in dry CH_2Cl_2 (800 mL) was added $BF_3 \cdot OEt_2$ (0.61 g, 4.32 mmol). The

mixture was stirred at 0 °C in dark for 3 h and then DDQ (4.69 g, 20.2 mmol) was

added. After the solution was stirred at room temperature for a further 1 h, NEt₃ (0.7 ml) was added and the solvent was removed under reduced pressure. The product was isolated by column chromatography (silica gel) using CH₂Cl₂/hexane = 1/5 as eluent. Recrystallization from CH₂Cl₂/CH₃OH gave a purple solid (320 mg, 7%). ¹H NMR (CDCl₃, 400 MHz) δ 10.22 (s, 2H), 9.79 (d, *J* = 4.4 Hz, 2H), 9.40 (d, *J* = 4.8 Hz, 2H), 9.31 (d, *J* = 4.4 Hz, 2H), 9.06 (d, *J* = 4.4 Hz, 2H), 8.09 (d, *J* = 2.0 Hz, 2H), 7.84 (t, *J* = 1.2 Hz, 1H), 1.56 (s, 18H), 1.50-1.49 (m, 21H) , -2.73 (s, 1H) , -2.82 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 149.7, 149.2, 147.3, 145.5, 145.1, 140.2, 132.2, 131.6, 131.3, 130.0, 130.0, 122.4, 121.3, 108.2, 106.0, 98.5, 98.2, 35.1, 31.7, 30.9, 19.1, 11.9;

UV-vis (CH₂Cl₂): λ_{max}/nm ($\epsilon/10^{3}M^{-1}cm^{-1}$) = 418 (446), 518 (15.8), 554 (30.6), 588 (7.2), 645 (8.9); FAB-MS: *m/z* calcd for C₄₅H₅₄N₄Si: 678; found 679 ([M+H]⁺).

[5-(3,5-Di-tert-butylphenyl)-15-(triisopropylsilylethynyl)porphyrinato]zinc(II) (2)

To a solution of porphyrin **1** (87.5 mg, 0.129 mmol) in CH₂Cl₂ (100 mL) was added a CH₃OH (5 mL) solution of Zn(OAc)₂·2H₂O (283 mg, 1.29 mmol). After the mixture was stirred at room temperature for 0.5 h, the solvent was removed under reduced pressure. The residue was extracted with CH₂Cl₂, and the organic layer was collected and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The product was recrystallized from CH₂Cl₂/CH₃OH to give a purple solid (94 mg, 98%). ¹H NMR (CDCl₃, 400 MHz) δ 9.97 (s, 2H), 9.60 (d, *J* = 4.8 Hz, 2H), 9.27 (d, *J* = 4.8 Hz, 2H), 9.18 (d, *J* = 4.8 Hz, 2H), 9.10 (d, *J* = 4.4 Hz, 2H), 8.19 (d, *J* = 1.6 Hz, 2H), 7.87 (t, *J* = 1.6 Hz, 1H), 1.62 (s, 18H), 1.54-1.53 (m, 21H); ¹³C NMR (CDCl₃, 100 MHz) δ 151.3, 149.6, 148.8, 148.8, 148.0, 141.6, 132.6, 131.4, 131.3, 130.3, 129.9, 122.9, 121.0, 109.2, 106.2, 97.7, 97.0, 35.2, 31.9, 19.3, 12.1; UV-vis (CH₂Cl₂): λ_{max}/nm (ϵ , 10³M⁻¹cm⁻¹) = 420 (525), 516 (3.0), 551 (17.1), 587 (14.0); FAB-MS: *m*/z calcd for C4₅H₅₂N₄SiZn: 740; found 741 ([M+H]⁺).

[5,15-Dibromo-10-(3,5-di-*tert*-butylphenyl)-20-(triisopropylsilylethynyl)porphyrinato]zinc(II) (3)

To a solution of porphyrin **2** (133 mg, 0.179 mmol) in dry CH₂Cl₂ (100 mL) and pyridine (10 mL) was added NBS (95 mg, 0.537 mmol). The solution was stirred at room temperature for 0.5 h, and then quenched with acetone. The solvent was removed under reduced pressure. The product was isolated by column chromatography (silica gel) using CH₂Cl₂/hexane = 1/2 as eluent. Recrystallization from CH₂Cl₂/EtOH gave a purple solid (97 mg, 80%). ¹H NMR (CDCl₃, 400 MHz) δ 9.65 (d, *J* = 4.8 Hz, 2H), 9.63 (d, *J* = 4.8 Hz, 2H), 9.60 (d, *J* = 4.8 Hz, 2H), 8.89 (d, *J* = 4.8 Hz, 2H), 8.01 (d, *J* = 1.6 Hz, 2H), 7.83 (d, *J* = 2.0 Hz, 1H), 1.55 (s, 18H), 1.46-1.45 (m, 21H); ¹³C NMR (CDCl₃, 100 MHz) δ 152.6, 150.9, 150.0, 149.2, 148.9, 140.9, 134.0, 133.5, 132.9, 131.9, 129.8, 125.3, 131.3, 108.3, 105.8, 100.7, 99.2, 35.1, 31.8, 29.7, 19.2, 12.0; UV-vis (CH₂Cl₂): λ_{max}/nm (ϵ , 10³M⁻¹cm⁻¹) = 436 (384), 569 (11.6), 614 (9.5); FAB-MS: *m*/*z* calcd for C₄₅H₅₀Br₂N₄SiZn: 900; found 900 ([M]⁺).

[5,15-Bis(bis(4-hexylphenyl)amino)-10-(3,5-di-*tert*-butylphenyl)-20-(triisopropyl-silylethynyl)porphyrinato]zinc(II) (4)

A mixture of bis(4-hexylphenyl)amine (561 mg, 1.66 mmol) and 60% NaH (66 mg, 1.66 mmol) in dry THF (6 mL) was bubbled by N₂ for 5 min, and then added to a solution of porphyrin 3 (150 mg, 166 µmol), Pd(OAc)₂ (15 mg, 67 µmol), and DPEphos (72 mg, 133 µmol). After the solution was refluxed for 4 h under N₂, the solvent was removed under reduced pressure. The residue was purified on a column chromatography (silica gel) using CH_2Cl_2 /hexane = 1/4 as eluent. Recrystallization from CH₂Cl₂/CH₃OH gave a dark solid (106 mg, 45 %). ¹H NMR (CDCl₃, 400 MHz) δ 9.62 (d, J = 4.4 Hz, 2H), 9.31 (d, J = 4.4 Hz, 2H), 9.20 (d, J = 4.4 Hz, 2H), 8.73 (d, J = 4.8 Hz, 2H), 7.92 (d, J = 2.0 Hz, 2H), 7.73 (s, 1H), 7.20 (d, J = 8.4 Hz, 8H), 6.98 (d, J = 8.8 Hz, 8H), 2.49 (t, J = 7.6 Hz, 8H), 1.57-1.51 (m, 8H), 1.47 (s, 18H), 1.40-1.39 (m, 21H), 1.31-1.26 (m, 24H), 0.85 (t, J = 6.4 Hz, 12H); ¹³C NMR (CDCl₃, 100 MHz) & 153.2, 152.6, 152.0, 150.4, 149.8, 148.7, 140.9, 135.0, 133.7, 132.1, 131.5, 130.5, 129.2, 128.9, 124.0, 122.0, 121.1, 114.8, 108.8, 100.1, 97.7, 35.2, 35.0, 31.7, 31.4, 29.0, 22.6, 19.1, 14.0, 11.9; UV-vis (CH₂Cl₂): λ_{max}/nm (ϵ , 10³M⁻¹cm⁻¹) = 421 (134), 484 (44.8), 594 (7.0), 650 (13.2); FAB-MS: *m/z* calcd for C₉₃H₁₁₈N₆SiZn: 1411; found 1412 ([M+H]⁺).

[5,15-Bis(bis(4-hexylphenyl)amino)-10-(3,5-di-*tert*-butylphenyl)-20-(4-carboxy-phenylethynyl)porphyrinato]zinc(II) (YD14)

To a solution of porphyrin 4 (60 mg, 0.042 mmol) in dry THF (20 mL) was added TBAF (1M in THF, 0.424 mL, 0.424 mmol). The solution was stirred at room temperature for 0.5 h. The mixture was concentrated and then extracted with CH₂Cl₂/H₂O. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed under vacuum. The residue and 4-iodobenzoic acid (52 mg, 0.211 mmol) were dissolved in a mixture of THF (15 mL) and Et₃N (3 mL), and degassed with N₂ for 10 min, and then $Pd_2(dba)_3$ (10 mg, 0.011 mmol) and $AsPh_3$ (26 mg, 0.084 mmol) were added to the mixture. The solution was refluxed for 4 h under N_2 . The solvent was removed under reduced pressure. The residue was purified on a column chromatography (silica gel) using $CH_2Cl_2/CH_3OH = 20/1$ as the eluent. Recrystallization from CH₂Cl₂/CH₃OH gave a green solid (51 mg, 88%). ¹H NMR $(CDCl_3, 400 \text{ MHz}) \delta 9.62 \text{ (d, } J = 4.8 \text{ Hz}, 2\text{H}), 9.34 \text{ (d, } J = 4.8 \text{ Hz}, 2\text{H}), 9.19 \text{ (d, } J = 4.8 \text{ Hz}, 2\text{H})$ 5.2 Hz, 2H), 8.72 (d, J = 4.8 Hz, 2H), 8.18 (d, J = 7.6 Hz, 2H), 8.00 (d, J = 7.6 Hz, 2H), 7.92 (d, J = 1.6 Hz, 2H), 7.73 (s, 1H), 7.22 (d, J = 8.8 Hz, 8H), 7.00 (d, J = 8.8 Hz, 8H), 2.50 (t, J = 7.6 Hz, 8H), 1.57-1.52 (m, 8H), 1.48 (s, 18H), 1.28-1.26 (m, 24H), 0.85 (t, J = 6.4 Hz, 12H); ¹³C NMR (CDCl₃, 100 MHz) δ 153.4, 152.6, 151.5, 150.5, 149.8, 148.7, 140.9, 135.1, 133.8, 131.7, 131.6, 131.3, 130.5, 130.4, 129.7, 129.2, 124.5, 124.4, 122.1, 121.1, 98.7, 95.9, 95.4, 35.2, 35.0, 31.7, 31.4, 29.7, 29.1,

22.6, 14.0; UV-vis (CH₂Cl₂/1% pyridine): λ_{max}/nm (ϵ , 10³M⁻¹cm⁻¹) = 436 (131), 476 (94.0), 615 (10.4), 660 (26.7); FAB-MS: *m/z* calcd for C₉₁H₁₀₂N₆O₂Zn: 1376; found 1378 ([M+2H]⁺).



[5,15-Bis(bis(4-hexylphenyl)amino)-10,20-bis(triisopropylsilylethynyl)porphyrinato]zinc(II) (6)

A solution of bis(4-hexylphenyl)amine (450 mg, 1.33 mmol) and 60% NaH (54 mg, 1.33 mmol) in dry THF (5 mL) was bubbled by N₂ for 5 min, and then added to a mixture of porphyrin **5** (150 mg, 168 µmol), Pd(OAc)₂ (15 mg, 67 µmol), and DPEphos (53 mg, 98 µmol). The solution was refluxed for 4 h under N₂. The solvent was removed under reduced pressure and the residue was purified on a column chromatography (silica gel) using CH₂Cl₂/hexane = 1/4 as the eluent. Recrystallization from CH₂Cl₂/EtOH gave a dark green solid (132 mg, 56%). ¹H NMR (CDCl₃, 400 MHz) δ 9.53 (d, *J* = 4.4 Hz, 4H), 9.22 (d, *J* = 4.8 Hz, 4H), 7.18 (d, *J* = 8.4 Hz, 8H), 6.99 (d, *J* = 8.4 Hz, 8H), 2.50 (t, *J* = 7.6 Hz, 8H), 1.57-1.54 (m, 8H), 1.45-1.38 (m, 42H), 1.35-1.27 (m, 24H), 0.86 (t, *J* = 6.4 Hz, 12H); ¹³C NMR (CDCl₃, 100 MHz) δ 152.9, 151.7, 150.3, 135.2, 132.3, 131.3, 129.0, 124.7, 122.0, 114.8, 108.7, 108.6, 101.7, 98.5, 35.2, 31.7, 31.4, 29.0, 22.6, 19.0, 14.1, 11.8; UV-vis (CH₂Cl₂): λ_{max} /nm (ϵ , 10³M⁻¹cm⁻¹) = 430 (225), 503 (55.9), 606 (8.6), 670 (19.9); FAB-MS: *m/z* calcd for C₉₀H₁₁₈N₆Si₂Zn: 1403; found 1404 ([M+H]⁺).

[5,15-Bis(bis(4-hexylphenyl)amino)-10-(4-(N,N-bis(4-methoxyphenyl)amino)phenylethynyl)-20-(4-carboxyphenylethynyl)porphyrinato]zinc(II) (YD15)

To a solution of porphyrin 6 (100 mg, 0.07 mmol) in dry THF (20 mL) was added TBAF (1M in THF, 0.57 mL, 0.57 mmol). The solution was stirred at room temperature for 0.5 h. The mixture was concentrated and then extracted with CH₂Cl₂/H₂O. The organic layer was dried over anhydrous Na₂SO₄ and the solvent removed under vacuum. The residue, N,N-bis(4-methoxylphenyl)-Nwas (4-iodophenyl) amine (37 mg, 0.086 mmol), and 4-iodobenzoic acid (21 mg, 0.086 mmol) were dissolved in a mixture of THF (20 mL) and Et₃N (4 mL) and degassed with N₂ for 10 min, and then Pd₂(dba)₃ (33 mg, 36 μ mol) and AsPh₃ (88 mg, 0.29 mmol) were added to the mixture. The solution was refluxed for 5 h under N₂ and the solvent was removed under reduced pressure. The residue was purified on a column chromatography (silica gel) using $CH_2Cl_2/CH_3OH = 20/1$ as eluent. Recrystallization from CH₂Cl₂/EtOH gave a green solid (54 mg, 50%). ¹H NMR (CDCl₃/pyridine-d₅, 400 MHz) δ 9.46 (d, J = 2.4 Hz, 2H), 9.45 (d, J = 2.8 Hz, 2H), 9.15 (d, J = 4.8 Hz, 2H), 9.11 (d, J = 4.4 Hz, 2H), 8.24 (d, J = 8.8 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 2.8 Hz, 4H), 7.15 (d, J = 3.2 Hz, 8H), 6.99 (d, J = 8.8Hz, 2H), 6.95 (d, J = 8.4 Hz, 8H), 6.89 (d, J = 8.8 Hz, 4H), 3.83 (s, 6H), 2.48 (t, J = 7.2 Hz, 8H), 1.57-1.51 (m, 8H), 1.27-1.25 (m, 24H), 0.86 (t, J = 6.8 Hz, 12H); ¹³C NMR (CDCl₃/pyridine-d₅, 100 MHz) δ 156.4, 152.6, 151.4, 151.0, 150.5, 147.6, 140.2, 134.9, 132.3, 131.7, 131.3, 131.1, 130.8, 130.2, 128.8, 127.2, 124.9, 123.2, 122.0, 119.4, 114.9, 55.5, 35.2, 31.7, 31.5, 29.1, 22.6, 14.1; UV-vis (CH₂Cl₂/1% pyridine): λ_{max}/nm (ϵ , 10³M⁻¹cm⁻¹) = 440 (82.7), 488 (101), 707 (32.5); FAB-MS: m/zcalcd for C₉₉H₉₉N₇O₄Zn: 1514; found 1515 ([M+H]⁺).



5,15-Bis(4-(bis(4-*tert*-butylphenyl)amino)phenyl)porphyrin (7)

To a degassed solution of dipyromethane (0.73 g, 5 mmol) and 4-(bis(4-*tert*-butylphenyl)amino)benzaldehyde (1.93 g, 5 mmol) in dry CH₂Cl₂ (675

mL) was added TFA(0.17 ml, 2.25 mmol). After the solution was stirred at 0 °C in

dark for 3 h, DDQ (1.70 g, 7.5 mmol) was added. The solution was stirred at room temperature for further 1 h and then Et₃N (0.20 mL) was added. The solvent was removed under reduced pressure. The product was isolated by column chromatography (silica gel) using CH₂Cl₂/hexane (1:5) as eluent. Recrystallization from CH₂Cl₂/CH₃OH gave 7 (865 mg, 34%). ¹H NMR (CDCl₃, 400 MHz) δ 10.31(s, 2H), 9.42 (d, *J* = 4.4 Hz, 4H), 9.23 (d, *J* = 4.4 Hz, 4H), 8.11 (dd, *J* = 2 Hz, *J* = 1.6 Hz, 4H), 7.49 (d, *J* = 8.4 Hz, 4H), 7.45 (d, *J* = 6.8 Hz, 8H), 7.37 (d, *J* = 7.2 Hz, 8H), 1.40(s, 36H), -3.00(s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 147.9, 147.5, 146.2, 145.2, 145.0, 135.8, 134.3, 131.4, 131.1, 126.3, 124.6, 120.9, 119.2, 114.8, 105.1, 34.4, 31.6, 31.5, 22.6, 14.1; UV-vis (CH₂Cl₂): λ_{max}/nm (ϵ , 10³M⁻¹cm⁻¹) = 401 (111), 505 (15.4), 555 (15.2), 639 (6.9); FAB-MS: *m*/z calcd for C₇₂H₇₂N₆: 1021; found 1022 ([M+H]⁺)

[5,15-Bis(4-(bis(4-*tert*-butylphenyl)amino)phenyl)-10-bromoporphyrinato] zinc(II) (8)

To a solution of 7 (1 g, 0.979 mmol), in CH₂Cl₂ (800 mL) was added NBS (139 mg,

0.783 mmol) at 0 °C. After 1 h, the reaction was quenched with acetone (10 mL). The

solvent was removed under reduced pressure. The product was isolated by column chromatograph (silica gel) using CH₂Cl₂/hexane (1:3) as eluent. Recrystallization from CH₂Cl₂/CH₃OH gave solid (485 mg, 45%). The monobrominated product was dissolved in CH₂Cl₂ (300 mL) and treated with a CH₃OH (50 mL) solution of Zn(OAc)₂·2H₂O (968 mg, 4.408 mmol). The mixture was stirred at room temperature for 0.5 h. The solvent was removed under reduced pressure. The residue was extracted with CH₂Cl₂/H₂O, and the organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The product was recrystallized from CH₂Cl₂/CH₃OH to give **8** (507 mg, 99%). ¹H NMR (CDCl₃, 400 MHz) δ 10.16 (s, 1H), 9.76 (d, *J* = 4.8 Hz, 2H), 9.31 (d, *J* = 4.8 Hz, 2H), 9.11 (d, *J* = 4.8 Hz, 4H), 8.03 (d, *J* = 8 Hz, 4H), 7.47-7.42 (m, 12H), 7.36 (d, *J* = 8.8 Hz, 8H), 1.36 (s, 36H). ¹³C NMR (CDCl₃, 100 MHz) δ 155.7, 150.9, 150.8, 150.1, 149.2, 147.8, 146.1, 145.2,

135.4, 135.2, 133.2, 133.1, 132.7, 131.9, 126.3, 124.5, 121.3, 120.6, 106.5, 34.4, 31.5; UV-vis (CH₂Cl₂): λ_{max}/nm (ϵ , 10³M⁻¹cm⁻¹) = 412 (205), 553 (24.1), 598 (12.4) FAB-MS: *m/z* calcd for C₇₂H₆₉BrN₆Zn: 1162; found 1163 ([M+H]⁺)

[5,15-Bis(4-(bis(4-*tert*-butylphenyl)amino)phenyl)-10-(triisopropylsilylethynyl)porphyrinato]zinc(II) (9)

To a degassed solution of porphyrin **8** (300 mg, 0.257 mmol) and 3-triisopropyl-2-propynal (0.173 mL, 0.773mmol) in a mixture of THF (10 mL) and TEA (2 mL) was added CuI (5 mg, 26 µmol), and Pd(PPh₃)₂Cl₂ (18 mg, 26 µmol). After the solution was refluxed for 0.5 h under N₂, the solvent was removed under reduced pressure. The residue was purified on a column chromatography (silica gel) using CH₂Cl₂/hexane (1:2) as eluent. Recrystallization from CH₂Cl₂/CH₃OH gave **9** (270 mg, 83%). ¹H NMR (CDCl₃, 400 MHz) δ 10.18 (s, 1H), 9.88 (d, *J* = 4.8 Hz, 2H), 9.35 (d, *J* = 4.4 Hz, 2H), 9.18 (dd, *J* = 4.8 Hz, *J* = 4.4 Hz, 4H), 8.04 (d, *J* = 8 Hz, 4H), 7.47-7.43 (m, 12H), 7.36 (d, *J* = 8.8 Hz, 8H), 1.46-1.45 (m, 21H), 1.36 (s, 36H). ¹³C NMR (CDCl₃, 100 MHz) δ 152.2, 150.7, 150.2, 149.3, 147.7, 145.9, 145.2, 135.4, 135.3, 132.9, 132.5, 131.7, 130.9, 126.3, 124.4, 121.5, 120.8, 109.6, 107.3, 100.4, 97.8, 34.4, 31.9, 31.5, 29.7, 29.3, 22.7, 19.1, 17.8, 14.1, 11.9; UV-vis (CH₂Cl₂): λ_{max}/nm (ϵ , 10³M⁻¹cm⁻¹) = 424 (207), 563 (21.4), 606 (15.3); FAB-MS: *m/z* calcd for C₈₃H₉₀N₆SiZn: 1264; found 1266 ([M+2H]⁺)

[5,15-Bis(4-(bis(4-*tert*-butylphenyl)amino)phenyl)-10-bromo-20-(triisopropyl-silylethynyl)porphyrinato]zinc(II) (10)

To a solution of porphyrin **9** (300 mg, 0.237 mmol) in a mixture of CHCl₃ (100 mL) and pyridine (10 mL) was added NBS (50 mg, 0.285 mmol). The solution was stirred at room temperature for 0.5 h, then quenched with acetone. The solvent was removed under reduced pressure. The product was isolated by column chromatography (silica gel) using CH₂Cl₂/hexane (1:2) as eluent. Recrystallization from CH₂Cl₂/CH₃OH gave **10** (270 mg, 85%).¹H NMR (CDCl₃, 400 MHz) δ 9.78 (d, *J* = 5.2 Hz, 2H), 9.72 (d, *J* = 4.8 Hz, 2H), 9.08 (dd, *J* = 4.4 Hz, *J* = 4.4 Hz, 4H), 7.99 (d, *J* = 8.8 Hz, 4H), 7.45-7.42 (m, 12H), 7.35 (d, *J* = 8.4 Hz, 8H), 1.45-1.44 (m, 21H), 1.40 (s, 36H); ¹³C NMR (CDCl₃, 100 MHz) δ 153.1, 151.3, 150.6, 147.9, 146.2, 145.2, 135.3, 134.9, 133.4, 133.2, 132.9, 131.3, 126.3, 124.5, 122.7, 120.6, 34.4, 31.5, 30.0, 19.1, 11.9, 1.0; UV-vis (CH₂Cl₂): λ_{max} /nm (ϵ , 10³M⁻¹cm⁻¹) = 426 (225), 569 (17.9), 617 (20.3); FAB-MS: *m*/z calcd for C₈₃H₈₉BrN₆SiZn: 1342; found 1344 ([M+2H]⁺)

[5,15-Bis(4-(bis(4-*tert*-butylphenyl)amino)phenyl)-10-(bis(4-octylphenyl)amino)-20-(triisoproylsilylethynyl)porphyrinato]zinc(II) (11)

A solution of bis(4-octylphenyl)amine (88 mg, 0.223 mmol) and 60 % NaH (30 mg, 0.074 mmol) in dry THF (5 mL) was bubbled by N₂ for 5 min, and then added to a mixture of porphyrin 10 (100 mg, 74 µmol), Pd(OAc)₂ (3.3 mg, 15 µmol), and DPEphos (12 mg, 22 μ mol). The solution was refluxed for 5 h under N₂. The solvent was removed under reduced pressure. The residue was purified on a column chromatography (silica gel) using CH₂Cl₂/hexane (1:2) as the eluent. Recrystallization from CH₂Cl₂/CH₃OH gave **11** (55 mg, 45%).¹H NMR (CDCl₃, 400 MHz) δ 9.77 (dd, J = 1.2 Hz, J = 1.6 Hz, 2H), 9.29 (dd, J = 1.2 Hz, J = 1.6 Hz, 2H), 9.08 (dd, J = 1.2Hz, J = 1.2 Hz, 2H), 8.90 (dd, J = 1.2 Hz, J = 1.6 Hz, 2H), 7.41-7.38 (m, 12H), 7.30 (d, J = 8.8 Hz, 8H), 7.21 (d, J = 8 Hz, 4H), 6.96 (d, J = 8 Hz, 4H), 2.47 (t, J = 15.6 Hz, 4H)4H), 1.48-1.46 (m, 21H), 1.38 (s, 36H), 1.25-1.22 (m, 24H), 0.84 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) & 152.7, 150.6, 150.5, 150.4, 148.6, 148.2, 146.2, 145.2, 135.1, 135.0, 132.9, 130.8, 128.9, 126.7, 124.3, 122.1, 121.9, 121.5, 35.2, 34.4, 31.8, 31.5, 29.4, 19.2, 22.6, 19.1, 14.0, 11.9; UV-vis (CH₂Cl₂): λ_{max}/nm (ϵ , 10³M⁻¹cm⁻¹) = 424 (42.0), 565 (26.6), 577 (3.9), 645 (5.9); FAB-MS: *m/z* calcd for C₁₁₁H₁₃₁N₇SiZn: 1655; found 1657 ([M+2H]⁺)

[5,15-Bis(4-(bis(4-*tert*-butylphenyl)amino)phenyl)-10-(bis(4-octylphenyl)amino)-20-(4-carboxyphenylethynyl)porphyrinato]zinc(II) (YD-16)

To a solution of porphyrin **11** (40 mg, 0.024 mmol) in dry THF (4 mL) was added TBAF (1M in THF, 0.24 mL, 0.240 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 (13 mg, 0.053 mmol), Pd₂(dba)₃ (7 mg, 0.008 mmol), and AsPh₃ (16 mg, 0.053 mmol). These reagents were dissolved in a degassed mixture of THF (10 mL) and NEt₃ (2 mL) and stirred at 85 °C for 5 h. The solvent was removed under vacuum and the residue was purified on a column chromatography (silica gel) using CH₂Cl₂/CH₃OH (95:5) as eluent. Recrystallization from CH₂Cl₂/CH₃OH gave **YD-16** (19 mg, 50%).¹H NMR (CDCl₃, 400 MHz) δ 9.77 (d, *J* = 4.4 Hz, 2H), 9.28 (d, *J* = 4.4 Hz, 2H), 9.10 (d, *J* = 4.8 Hz, 2H), 8.89 (d, *J* = 4.8 Hz, 2H), 8.25 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.1 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 12H), 7.31 (d, *J* = 8.8 Hz, 8H), 7.21 (d, *J* = 8.4 Hz, 4H), 6.97 (d, *J* = 8.8 Hz, 4H), 2.48 (t, *J* = 7.2

Hz, 4H), 1.38 (s, 36H), 1.25-1.23 (m, 24H), 0.84 (s, 6H) ; ¹³C NMR (CDCl₃, 100 MHz) δ 152.2, 150.8, 150.1, 150.0, 147.4, 145.8, 145.3, 136.2, 125.2, 134.6, 132.5, 132.0, 130.9, 130.5, 130.3, 130.0, 129.1, 128.7, 126.2, 124.7, 124.2, 122.0, 121.6, 120.9, 35.2, 34.3, 31.9, 31.8, 31.5, 29.7, 29.6, 29.4, 29.3, 29.2, 29.1, 24.9, 22.7, 22.6, 14.1; UV-vis (CH₂Cl₂/1% pyridine): λ_{max}/nm (ϵ , 10³M⁻¹cm⁻¹) = 451 (112), 600 (8.8), 666 (23.6); FAB-MS: *m/z* calcd for C₁₀₉H₁₁₅N₇O₂Zn: 1619; found 1620 ([M+H]⁺)



5,15-Bis(3,5-di-tert-butyl-4-methoxyphenyl)porphyrin (12)

To a degassed solution of dipyrromethane (1.28 g, 8.78 mmol) and 3,5-di-*tert*-butyl-4-methoxybenzaldehyde (2.18 g, 8.78 mmol) in dry CH₂Cl₂ (1.30 L) was added TFA

(0.293 ml, 3.95 mmol). The solution was stirred at 0 °C in dark for 3 h and then DDQ

(2.99 g, 13.2 mmol) was added. After the solution was stirred at room temperature for 1 h, Et₃N (0.20 mL) was added. The solvent was removed under reduced pressure. The product was isolated by column chromatography (silica gel) using CH₂Cl₂ as eluent. Recrystallization from CH₂Cl₂/CH₃OH gave **12** (836 mg, 25.5 %). ¹H NMR (CDCl₃, 400 MHz) δ 10.32 (s, 2H), 9.42 (d, *J* = 4.8 Hz, 4H), 9.16 (d, *J* = 4.8 Hz, 4H), 8.20 (s, 4H), 4.05 (s, 6H), 1.68 (s, 36H), -3.00 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 159.2, 147.5, 145.0, 142.0, 135.5, 134.1, 131.5, 131.2, 120.0, 105.1, 77.3, 77.0, 76.7, 64.7, 36.1, 32.4, 32.3, 31.6, 22.6, 14.1; UV-vis (CH₂Cl₂): λ_{max}/nm (ϵ , 10³M⁻¹cm⁻¹) = 411 (295), 450 (4.0), 506 (12.8), 541 (6.5), 578 (4.7), 634 (2.0); FAB-MS: *m/z* calcd

for $C_{50}H_{58}N_4O_2$: 746; found 747 ([M+H]⁺).

[5-Bromo-10,20-bis(3,5-di-tert-butyl-4-methoxyphenyl)porphyrinato]zinc(II) (13)

A solution of 12 (0.9 g, 1.2 mmol), in CH₂Cl₂ (700 mL) was treated with NBS (193

mg, 1.08 mmol) at 0 °C. After 1 h, the reaction was quenched with acetone (20 mL).

The solvent was removed under reduced pressure. The product was isolated by column chromatograph (silica gel) using CH₂Cl₂/hexane (1:4) as the eluent. Recrystallization from CH₂Cl₂/CH₃OH gave solid (289 mg, 29.05 %). Then, the product was dissolved in CH₂Cl₂ (150 mL) which was treated with Zn(OAc)₂ 2H₂O (768 mg, 3.50 mmol) in CH₃OH (20 ml) was stirred at room temperature for 1 h. The solvent was removed under reduced pressure. The residue was extracted with CH₂Cl₂/H₂O, and the organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The product was recrystallized from CH₂Cl₂/CH₃OH to give **13** (289 mg, 27.2 %). ¹H NMR (CDCl₃, 400 MHz) δ 10.13 (s, 1H), 9.79 (d, *J* = 4.8 Hz, 2H), 9.33 (d, *J* = 4.4 Hz, 2H), 9.08 (t, *J* = 4.8 Hz, 4H), 8.12 (s, 4H), 4.05 (s, 6H), 1.67 (s, 36H); ¹³C NMR (CDCl₃, 100 MHz) δ 158.9, 150.8, 150.7, 150.0, 149.1, 141.3, 137.0, 134.0, 133.0, 132.8, 132.3, 131.7, 121.7, 106.0, 104.2, 77.3, 77.2, 77.0, 76.7, 64.7, 36.0, 32.5; UV-vis (CH₂Cl₂): λ_{max}/nm (ϵ , 10³M⁻¹ cm⁻¹) = 420 (387), 549 (19.0), 587 (3.9); FAB-MS: *m/z* calcd for C₅₀H₅₅BrN₄O₂Zn: 888; found 888 ([M]⁺).

[5-(Triisopropylsilyl)ethynyl-10,20-bis(3,5-di-*tert*-butyl-4-methoxyphenyl)porphyrinato]zinc(II) (14)

To a degassed solution of porphyrin **13** (350 mg, 0.39 mmol) and (triisopropylsilyl)acetylene (0.44 mL,1.97 mmol) in dry THF (70 mL) and Et₃N (25 mL) was added to a mixture of CuI (7.5 mg, 39 µmol), and Pd(PPh₃)₂Cl₂ (27.6 mg, 39 µmol). The solution was refluxed for 1.5 h under N₂. The solvent was removed under reduced pressure. The residue was purified on a column chromatography (silica gel) using CH₂Cl₂/hexane (1:3) as eluent. Recrystallization from CH₂Cl₂/CH₃OH gave **14** (330 mg, 85 %). ¹H NMR (CDCl₃, 400 MHz) δ 10.22 (s, 1H), 9.87 (d, *J* = 4.8 Hz, 2H), 9.37 (d, *J* = 4.8 Hz, 2H), 9.11 (t, *J* = 4.8 Hz, 4H) 8.13 (s, 4H), 4.04 (s, 6H), 1.65 (s, 36H), 1.46-1.45 (m, 21H); ¹³C NMR (CDCl₃, 100 MHz) δ 159.1, 152.3, 150.9, 150.2, 149.5, 141.5, 136.5, 133.6, 133.1, 132.7, 131.8, 130.9, 122.3, 109.6, 107.4, 77.3, 77.2, 77.0, 76.7, 64.7, 58.2, 36.0, 32.5, 19.1, 18.1, 11.9, 1.0; UV-vis (CH₂Cl₂): λ_{max} /nm (ϵ , 10³M⁻¹cm⁻¹) = 4.27 (390), 559 (18.0), 597 (9.7); FAB-MS: *m/z* calcd for

 $C_{61}H_{76}N_4O_2SiZn:$ 988; found 989 ([M+H]⁺).

[5-Bromo-15-(triisopropylsilyl)ethynyl-10,20-bis(3,5-di-*tert*-butyl-4-methoxy-phenyl)porphyrinato]zinc(II) (15)

To a solution of porphyrin **14** (430 mg, 0.443 mmol) in dry CHCl₃ (140mL) and pyridine (14ml) was added NBS (94.5 mg, 0.531 mmol). The solution was stirred at room temperature for 0.5 h, and then quenched with acetone. The solvent was removed under reduced pressure. The product was isolated by column chromatography (silica gel) using CH₂Cl₂/hexane (1:3) as eluent. Recrystallization from CH₂Cl₂/CH₃OH gave **15** (266 mg, 58%).¹H NMR (CDCl₃, 400 MHz) δ 9.78 (d, J = 4.4 Hz, 2H), 9.73 (d, J = 4.4 Hz, 2H), 9.01 (d, J = 4.4 Hz, 2H), 8.98 (d, J = 4.4 Hz, 2H), 8.07 (s, 4H), 4.03 (s, 6H), 1.64 (s, 36H), 1.44-1.42 (m, 21H); ¹³C NMR (CDCl₃, 100 MHz) δ 159.0, 153.0, 151.1, 150.4, 149.1, 141.2, 136.8, 133.6, 133.1, 132.9, 132.4, 130.9, 123.0, 77.3, 77.2, 77.0, 76.7, 64.6, 35.9, 32.4, 19.1, 11.9; UV-vis (CH₂Cl₂): λ_{max}/nm (ϵ , 10³M⁻¹cm⁻¹) = 432 (427), 570 (17.8), 613 (19.9); FAB-MS: *m/z* calcd for C₆₁H₇₅BrN₄O₂SiZn: 1068; found 1069 ([M+H]⁺).

[5-Bis(4-hexylphenyl)amino-15-(triisopropylsilyl)ethynyl-10,20-bis(3,5-di-*tert*-butyl-4-methoxyphenyl)porphyrinato]zinc(II) (16)

To a degassed solution of bis(4-hexylphenyl)amine (220 mg, 0.654 mmol) and 60 % NaH (224 mg, 3.36 mmol) in dry THF (10 mL) was added a mixture of porphyrin **15** (200 mg, 187 µmol), Pd(OAc)₂ (16.8 mg, 75 µmol), and DPEphos (60.4 mg, 112 µmol). The solution was refluxed for 5 h under N₂. The solvent was removed under reduced pressure. The residue was purified on a column chromatography (silica gel) using CH₂Cl₂/hexane (1:2) as the eluent. Recrystallization from CH₂Cl₂/CH₃OH gave **16** (80.6 mg, 26 %). ¹H NMR (CDCl₃, 400 MHz) δ 9.75 (d, *J* = 4.8 Hz, 2H), 9.29 (d, *J* = 4.8 Hz, 2H), 8.97 (d, *J* = 4.8 Hz, 2H), 8.82 (d, *J* = 4.8 Hz, 2H), 8.03 (s, 4H), 7.11 (d, *J* = 8.8 Hz, 4H), 6.61 (d, *J* = 8.8 Hz, 4H), 3.98 (s, 6H), 2.47 (t, *J* = 8.0 Hz, 4H) 1.60 (s, 36H), 1.45-1.43 (m, 21H), 1.26-1.24 (m, 16H), 0.83 (t, *J* = 6.8 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 167.4, 159.8, 159.1, 152.4, 150.5, 148.9, 141.5, 136.3, 134.9, 133.3, 133.1, 132.1, 130.8, 128.9, 122.7, 122.0, 85.3, 80.1, 77.3, 77.2, 77.0, 76.6, 64.6, 35.9, 35.2, 32.4, 31.7, 31.4, 29.0, 22.5, 19.1, 14.0, 11.9; UV-vis (CH₂Cl₂): λ_{max}/nm (ϵ , 10³M⁻¹cm⁻¹) = 429 (268), 577 (11.1), 634 (19.5); FAB-MS: *m/z* calcd for C₈₅H₁₀₉N₅O₂SiZn: 1325; found 1325 ([M]⁺).

[5,15-Bis(3,5-di-tert-butyl-4-methoxyphenyl)-10-(bis(4-hexylphenyl)amino)-20-(4-

carboxyphenylethynyl)porphyrinato]zinc(II) (YD17)

To a solution of porphyrin 16 (30 mg, 0.0226 mmol) in dry THF (10 mL) was added TBAF (1 M in THF, 80 µL, 0.08 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 (12.7 mg, 0.0513 mmol), $Pd_2(dba)_3$ (7 mg, 0.769 mmol), and AsPh₃ (15.7 mg, 0.0512 mmol). These reagents were dissolved in a degassed mixture of THF (5 mL) and NEt₃ (1 mL) and stirred at 85 °C for 4.5 h. The solvent was removed under vacuum and the residue was purified on a column chromatography (silica gel) using CH₂Cl₂/CH₃OH (20:1) as eluent. Recrystallization from CH₂Cl₂/CH₃OH gave **YD-17** (14.3 mg, 49.3 %). ¹H NMR (CDCl₃, 400 MHz) δ 9.79 (d, J = 4.4 Hz, 2H), 9.29 (d, J = 4.4 Hz, 2H), 9.02 (d, J = 4.4 Hz, 2H), 8.84 (d, J = 4.4 Hz, 2H)4.4Hz, 2H), 8.27 (d, J = 8.0 Hz, 2H), 8.11 (d, J = 8.0 Hz, 2H), 8.06 (s, 4H), 7.21 (d, J = 8.0 Hz, 4H), 6.97 (d, J = 8.0 Hz, 4H), 3.99 (s, 6H), 2.47 (t, J = 7.2 Hz, 4H) 1.62 (s, 36H), 1.28-1.25 (m, 16H), 0.84 (t, J = 6.8 Hz, 6H) ; ¹³C NMR (CDCl₃, 100 MHz) δ 159.2, 152.5, 152.3, 150.5, 150.1, 141.6, 136.2, 135.1, 133.6, 133.4, 133.3, 131.4, 131.0, 130.5, 128.9, 122.1, 108.7, 77.3, 77.0, 76.7, 64.7, 36.0, 35.2, 32.4, 31.7, 31.4, 29.0, 22.6, 14.1; UV-vis (CH₂Cl₂/1% pyridine): λ_{max}/nm (ϵ , 10³M⁻¹cm⁻¹) = 448 (218), 606 (9.7), 662 (36.1); FAB-MS: *m/z* calcd for C₈₃H₉₃N₅O₄Zn: 1289; found 1289 $([M]^+).$