Supporting Information:
Synthesis and characterization of porphyrin sensitizers with various electron-donating substituents for highly efficient dye-sensitized solar cells

Chou-Pou Hsieh,[a] Hsueh-Pei Lu,[b] Chien-Lan Chiu,[a] Cheng-Wei Lee,[a] Shu-Han Chuang,[a] Chi-Lun Mai,[a] Wei-Nan Yen,[a] Shun-Ju Hsu,[b] Eric Wei-Guang Diau,*[b] and Chen-Yu Yeh*[a]

[a] Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan. E-mail: cyyeh@dragon.nchu.edu.tw.

[b] Department of Applied Chemistry, National Chiao Tung University, Hsinchu 300, Taiwan. E-mail: diau@mail.nctu.edu.tw

Experiment Section

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 ($TBAPF_6$) 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

^{1}H 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), 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 (0.07 cm^2) disk as the working electrode, a platinum wire as the auxiliary electrode, and a 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) 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 0.03 μm aluminium on felt pads (Buehler) and treated ultrasonically for 1 min before each experiment. The reproducibility of individual potential values was within ±5 mV. The spectroelectrochemical experiments were accomplished with the use of a 1 mm cuvette, a 100-mesh platinum gauze as working electrode, a platinum wire as auxiliary electrode, and a Ag/AgCl (saturated) reference electrode.

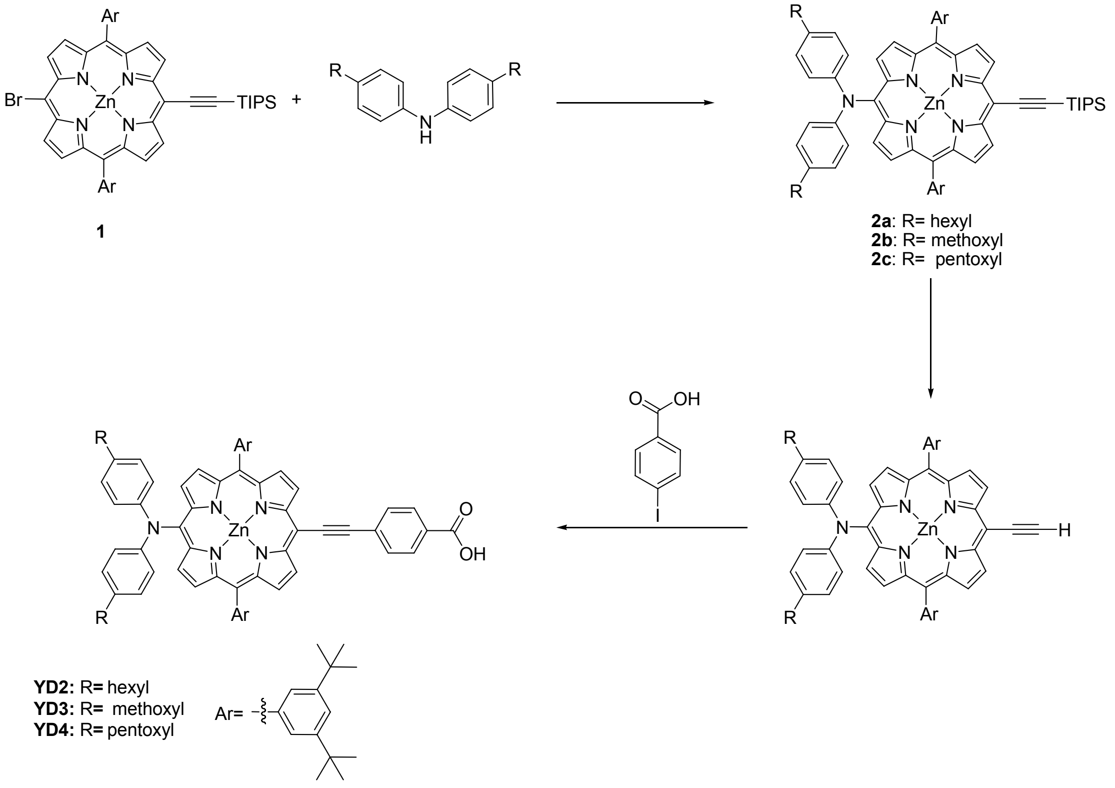
Device Fabrication

The porphyrins were sensitized onto TiO_2 nanoparticulate films to serve as working electrodes in DSSC devices. The TiO_2 nanoparticles (size ~20 nm) were screen-printed onto the F-doped SnO_2 (FTO, 30 Ω/□, Sinonar, Taiwan) glass substrate. The TiO_2 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. The electrode was then immersed in the porphyrin/ethanol solution (0.2 mM, 25 °C) containing chenodeoxycholic acid (CDCA, 0.4 mM) for dye loading onto the TiO_2 film at 25 °C for 12 h. The Pt counter electrodes were prepared on spin-coating drops of H_2PtCl_6 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 μm). The electrolyte solution containing LiI (0.1 M), I_2 (0.05 M), PMII (0.6 M), 4-*tert*-butylpyridine (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 carried out by an AM 1.5 solar simulator (SAN-EI, XES-502S) of a class A type calibrated by 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 these relations, $\eta = J_{sc}\ V_{oc}\ \mathrm{FF} / P_{in}$, 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 mW cm^{-2}) and FF is the fill factor. The incident monochromatic photon-to-current conversion efficiency (IPCE) spectra of the corresponding devices were obtained by a system containing 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, computer-controlled). A standard Si photodiode (ThorLabs FDS1010) was used 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 IPCE value of the device from comparing the current ratio and the value of the reference cell at each wavelength.

Synthetic Procedures.



Zinc(II) 5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(bis(4-hexylphenyl)amino)-20-(triisoproylsilylethynyl)porphyrin (2a)

A mixture of bis(4-hexylphenyl)amine (58.5 g. 0.173 mmol), and 60% NaH (28 mg, 0.42 mmol) in dry THF (5 mL) was stirred under dinitrogen for 5 min, and then porphyrin **1** (50 mg, 0.05 mmol), DPEphos (8 mg, 0.015 mmol) and Pd(OAc)$_2$ (2.2 mg, 0.01 mmol) were added to the mixture. The solution was refluxed for 5 h under dinitrogen. The solvent was removed in vacuum. The residue was purified on a column chromatograph (silica gel) using CH$_2$Cl$_2$/hexane = 1/4 as the eluent. Recrystallization from CH$_2$Cl$_2$/CH$_3$OH gave **2a** (39 mg, 62%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 9.75 (d, J = 4.8 Hz, 2H), 9.28 (d, J = 4.8 Hz, 2H), 8.95 (d, J = 4.8 Hz, 2H), 8.81 (d, J = 4.8 Hz, 2H), 8.00 (d, J = 1.6 Hz, 2H), 7.77 (d, J = 1.6 Hz, 2H), 7.21 (d, J = 8.4 Hz, 4H), 6.96 (d, J = 8.4 Hz, 2H), 2.46 (t, J = 7.6 Hz, 4H), 1.52 (s, 36H), 1.45 (m, 21H), 1.24 (m, 12H), 0.82 (t, J = 7.2 Hz, 6H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 152.7, 152.5, 150.5, 150.5, 149.9, 148.6, 141.2, 134.9, 133.2, 133.1, 130.8, 130.7, 129.3, 128.9, 124.0, 123.1, 122.0, 121.0, 109.5, 100.5, 97.6, 35.2, 35.0, 31.7, 31.6, 31.4, 29.0, 22.5, 19.1, 14.0, 11.9; UV-vis (CH$_2$Cl$_2$): λ_{max}/nm (ε, 10^3M^{-1}cm^{-1}) = 428 (233), 574 (12.3), 634 (27.2); FAB-MS: *m/z* calcd for C$_{83}$H$_{105}$N$_5$SiZn: 1264; found

1265 ([M+H]$^+$).

Zinc(II) 5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(bis(4-hexylphenyl)amino)-20-(4-carboxyphenylethynyl)porphyrin (YD2)

To a solution of porphyrin **2a** (25 mg, 0.02 mmol) in dry THF (5 mL) was added TBAF (0.08 mL, 1M in THF). The solution was stirred at 25 °C 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 Na_2SO_4 and the solvent was removed under vacuum. The residue and 4-iodobenzoic acid (10 mg, 0.04 mmol) were dissolved in dry THF (5 mL) and NEt_3 (1 mL) and degassed with dinitrogen for 10 min, and then $Pd_2(dba)_3$ (4.4 mg, 0.005 mmol) and $AsPh_3$ (12 mg, 0.04 mmol) were added to the mixture. The solution was refluxed for 4.5 h under dinitrogen. The solvent was removed under vacuum. The residue was purified on a column chromatograph (silica gel) using CH_2Cl_2/CH_3OH = 20/1 as the eluent. Recrystallization from CH_2Cl_2/CH_3OH gave **YD2** (20.6 mg, 85%). ^1H NMR ($CDCl_3$/pyridine-d_5, 400 MHz) δ 9.79 (d, *J* = 4.8 Hz, 2H), 9.29 (d, *J* = 4.8 Hz, 2H), 9.00 (d, *J* = 4.8 Hz, 2H), 8.83 (d, *J* = 4.8 Hz, 2H), 8.27 (d, *J* = 8.4 Hz, 2H), 8.11 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 1.6 Hz, 4H), 7.79 (d, *J* = 1.6 Hz, 2H), 7.22 (d, *J* = 9.2 Hz, 4H), 6.98 (d, *J* = 9.2 Hz, 4H), 2.47 (t, *J* = 7.6 Hz, 4H), 1.50 (s, 36H), 1.26 (m, 16H), 0.84 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.9, 152.2, 150.6, 150.3, 149.9, 148.4, 141.7, 134.6, 132.9, 131.1, 130.1, 129.7, 128.8, 123.8, 123.3, 123.1, 122.8, 121.9, 120.6, 98.5, 96.7, 95.3, 35.2, 35.0, 31.7, 31.4, 29.0, 22.5, 14.0; UV-vis (ethanol): λ_{max}/nm (ε, $10^3 M^{-1} cm^{-1}$) = 444 (217), 589 (10.8), 648 (33.7); FAB-MS: *m/z* calcd for $C_{81}H_{89}N_5O_2Zn$: 1228; found 1228 ([M]$^+$).

Zinc(II) 5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(bis(4-methoxyphenyl)amino)-20-(triisopropylsilylethynyl)porphyrin (2b)

A mixture of bis(4-methoxyphenyl)amine (40 mg, 0.175 mmol), and 60% NaH (28 mg, 0.42 mmol) in dry THF (10 mL) was stirred under dinitrogen for 5 min, and then porphyrin **1** (50 mg, 0.05 mmol), DPEphos (8 mg, 0.015 mmol) and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) were added to the mixture. The solution was refluxed for 5 h under dinitrogen. The solvent was removed in vacuum. The residue was purified on a column chromatograph (silica gel) using CH_2Cl_2/hexane = 1/3 as the eluent. Recrystallization from CH_2Cl_2/CH_3OH gave **2b** (24 mg, 42 %). ^1H NMR ($CDCl_3$/pyridine-d_5, 400 MHz) δ 9.66 (d, *J* = 4.8 Hz, 2H), 9.15 (d, *J* = 4.8 Hz, 2H), 8.84 (d, *J* = 4.8 Hz, 2H), 8.70 (d, *J* = 4.8 Hz, 2H), 7.94 (d, *J* = 1.6 Hz, 4H), 7.73 (d, *J* = 1.6 Hz, 2H), 7.16 (d, *J* = 9.2 Hz, 4H), 6.66 (d, *J* = 9.2 Hz, 4H), 3.68 (s, 6H), 1.50 (s, 36H), 1.45-1.43 (m, 21H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.2, 152.7, 152.1, 150.3, 149.6, 148.3, 147.1, 141.8, 132.8, 130.4, 130.2, 129.4, 123.1, 122.8, 120.7, 114.3, 110.5, 99.4, 96.4, 55.4, 34.9, 31.7, 19.1, 11.9; UV-vis (CH_2Cl_2): λ_{max}/nm (ε, $10^3 M^{-1} cm^{-1}$) = 435 (189), 590 (6.9), 652 (17.2); FAB-MS: *m/z* calcd for $C_{73}H_{85}N_5O_2SiZn$: 1156; found 1157 ($[M+H]^+$).

Zinc(II) 5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(bis(4-methoxyphenyl)amino)-20-(4-carboxylphenylethynyl)porphyrin (YD3)

To a solution of porphyrin **2b** (24.0 mg, 0.02 mmol) in dry THF (5 mL) was added TBAF (0.08 mL, 1M in THF). The solution was stirred at 25 °C 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 Na_2SO_4 and the solvent was removed under vacuum. The residue and 4-iodobenzoic acid (10 mg, 0.04 mmol) were dissolved in dry THF (5 mL) and NEt_3 (1 mL) and degassed with dinitrogen for 10 min, and then $Pd_2(dba)_3$ (4.4 mg, 0.005 mmol) and $AsPh_3$ (12 mg, 0.04 mmol) were added to the mixture. The solution was refluxed for 4.5 h under dinitrogen. The solvent was removedunder vacuum. The residue was purified on a column chromatograph (silica gel) using CH_2Cl_2/CH_3OH = 30/1 as the eluent. Recrystallization from CH_2Cl_2/CH_3OH gave **YD3** (13.9 mg, 60 %). ^{1}H NMR ($CDCl_3$/pyridine-d_5, 400 MHz) δ 9.71 (d, *J* = 4.8 Hz, 2H), 9.17 (d, *J* = 4.8 Hz, 2H), 8.89 (d, *J* = 4.8 Hz, 2H), 8.72 (d, *J* = 4.8 Hz, 2H), 8.30 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 1.6 Hz, 4H), 7.75 (d, *J* = 1.6 Hz, 2H), 7.17 (d, *J* = 9.2 Hz, 4H), 6.68 (d, *J* = 9.2 Hz, 4H), 3.68 (s, 6H), 1.51 (s, 36H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.9, 153.2, 152.3, 152.2, 150.3, 149.8, 148.5, 147.2, 141.7, 135.8, 131.1, 130.8, 130.4, 130.1, 129.7, 128.8, 124.3, 123.2, 120.7, 98.4, 96.6, 95.3, 55.4, 34.9, 31.7; UV-vis (ethanol): λ_{max}/nm (ε, $10^3 M^{-1} cm^{-1}$) = 440 (141), 592 (5.9), 664 (16.9); FAB-MS: *m/z* calcd for $C_{71}H_{69}N_5O_4Zn$: 1120; found 1121 ($[M+H]^+$).

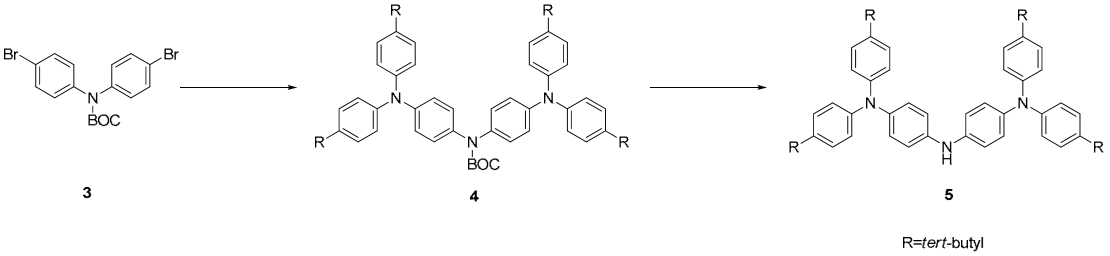
Zinc(II) 5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(bis(4-pentoxyphenyl)amino)-20-(triisopropylsilylethynyl)porphyrin (2c)

A mixture of bis(4-pentoxylphenyl)amine (178 mg, 0.52 mmol), and 60% NaH (84 mg, 2.1 mmol) in dry THF (20 mL) was stirred under dinitrogen for 5 min, and then porphyrin **1** (150 mg, 0.15 mmol), DPEphos (24.0 mg, 0.04 mmol) and $Pd(OAc)_2$ (6.6 mg, 0.03 mmol) were added to the mixture. The solution was refluxed for 5 h under dinitrogen. The solvent was removed in vacuum. The residue was purified on a column chromatograph (silica gel) using CH_2Cl_2/hexane = 1/3 as the eluent. Recrystallization from CH_2Cl_2/CH_3OH gave **2c** (75.4 mg, 40%). ^1H NMR ($CDCl_3$/pyridine-d_5, 400 MHz) δ 9.66 (d, *J* = 4.8 Hz, 2H), 9.15 (d, *J* = 4.8 Hz, 2H), 8.84 (d, *J* = 4.8 Hz, 2H), 8.69 (d, *J* = 4.8 Hz, 2H), 7.93 (d, *J* = 1.6 Hz, 4H), 7.72 (d, *J* = 1.6 Hz, 2H), 7.13 (d, *J* = 9.2 Hz, 4H), 6.65 (d, *J* = 9.2 Hz, 4H), 3.81 (t, *J* = 6.4 Hz, 4H), 1.68 (m, 4H), 1.49 (s, 36H), 1.45-1.43 (m, 21H), 1.32-1.27 (m, 8H), 0.85 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.9, 152.8, 152.6, 150.4, 149.8, 148.7, 147.0, 141.3, 133.1, 130.7, 129.4, 124.6, 123.2, 123.1, 121.0, 115.2, 109.6, 100.3, 97.5, 68.3, 50.1, 35.0, 31.7, 29.0, 28.2, 22.4, 19.1, 18.8, 18.5, 13.9, 12.0; UV-vis (CH_2Cl_2): λ_{max}/nm (ε, $10^3 M^{-1} cm^{-1}$) = 434 (191), 589 (7.1), 650 (17.9); FAB-MS: *m/z* calcd for $C_{81}H_{101}N_5O_2SiZn$: 1268; found 1269 ($[M+H]^+$).

Zinc(II) 5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(bis(4-pentoxyphenyl)amino)-20-(4-carboxylphenylethynyl)porphyrin (YD4)

To a solution of porphyrin **2c** (50 mg, 0.04 mmol) in dry THF (5 mL) was added TBAF (0.16 mL, 1M in THF). The solution was stirred at 25 °C 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 Na_2SO_4 and the solvent was removed under vacuum. The residue and 4-iodobenzoic acid (20 mg, 0.08 mmol) were dissolved in dry THF (5 mL) and NEt_3 (1 mL) and degassed with dinitrogen for 10 min, and then $Pd_2(dba)_3$ (9 mg, 0.01 mmol) and $AsPh_3$ (30 mg, 0.09 mmol) were added to the mixture. The solution was refluxed for 4.5 h under dinitrogen. The solvent was removed under vacuum. The residue was purified on a column chromatograph (silica gel) using CH_2Cl_2/CH_3OH = 60/1 as the eluent. Recrystallization from CH_2Cl_2/methanol gave **YD4** (31.5 mg, 65 %). ^1H NMR ($CDCl_3$/pyridine-d_5, 400 MHz) δ 9.70 (d, *J* = 4.8 Hz, 2H), 9.16 (d, *J* = 4.8 Hz, 2H), 8.88 (d, *J* = 4.8 Hz, 2H), 8.70 (d, *J* = 4.4 Hz, 2H), 8.30 (d, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 1.6 Hz, 4H), 7.74 (d, *J* = 1.6 Hz, 2H), 7.15 (d, *J* = 9.2 Hz, 4H), 6.67 (d, *J* = 9.2 Hz, 4H), 3.82 (t, *J* = 6.4 Hz, 4H), 1.68 (m, 4H), 1.50 (s, 36H), 1.37-1.29 (m, 8H), 0.86 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.0, 152.7, 152.4, 150.4, 150.0, 148.8, 147.0, 141.1, 133.4, 133.2, 131.4, 130.9, 130.4, 129.9, 129.6, 128.2, 125.2, 123.6, 123.3, 121.1, 115.2, 114.8, 99.0, 96.6, 95.4, 68.3, 35.1, 31.8, 29.0, 28.2, 22.4, 13.9; UV-vis (ethanol): λ_{max}/nm (ε, 10^3M^{-1}cm^{-1}) = 438 (143), 591 (5.4), 653 (17.6); FAB-MS: *m/z* calcd for $C_{79}H_{85}N_5O_4Zn$: 1232; found 1232 ([M]$^+$).

Preparation of arylamine 5[1]

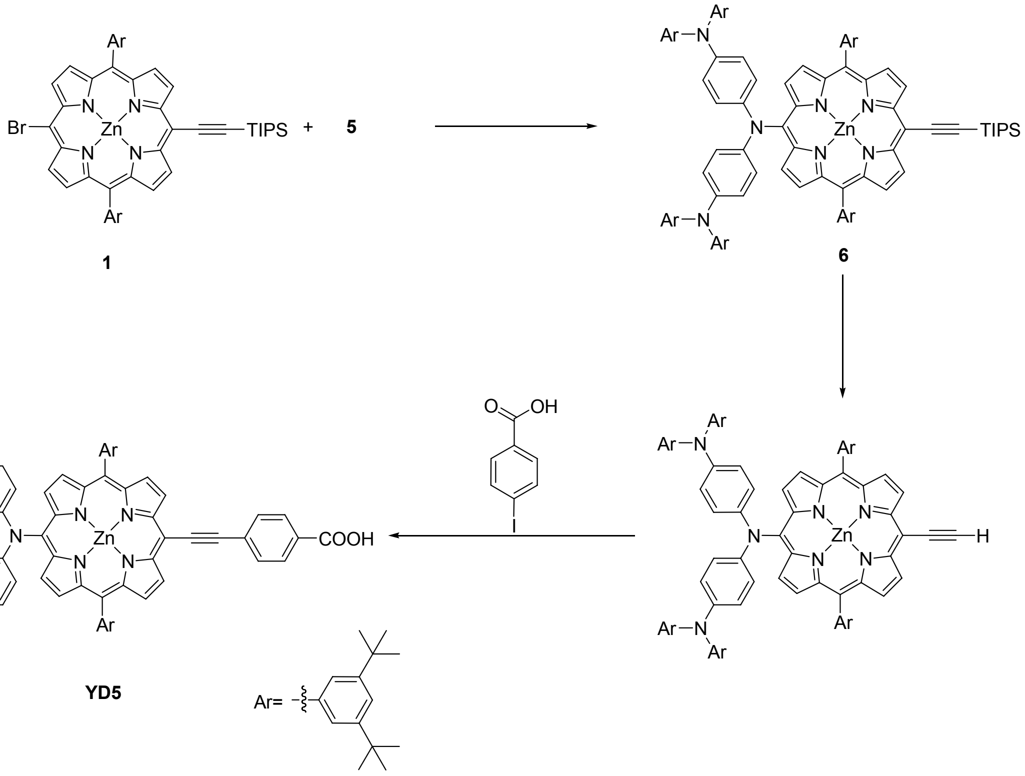


N-tert-Butoxycarbonyl-*N,N*-bis[4-(di-*tert*-butylphenylamino)phenyl]amine (4)

Dibrominated arylamine **3** (0.45 g, 1.05 mmol), bis(4-tert-butylphenyl)amine (0.89 g, 3.16 mmol), sodium *tert*-butoxide (0.39 g, 4.05 mmol), Pd(OAc)$_2$ (15.95 mg, 0.0725 mmol) and 1,1′-bis-(diphenylphosphanyl)ferrocene (DPPF) (76.5 mg, 0.139 mmol), were dissolved in toluene (15 mL) in a Schlenk flask under argon. The reaction mixture was heated to reflux for 96 h. The mixture was wased with water and then dried over $MgSO_4$. The solvent was removed under vacuum. The residue was purified on a column chromatograph (silica gel) using CH_2Cl_2/hexane = 2/1 as the eluent afforded pure **4** (0.52 g, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25 (m, 8H), 7.09 (d, *J* = 8.8 Hz, 4H), 7.04-7.00 (m, 12H), 1.48 (s, 9H), 1.31 (s, 36H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.3, 145.6, 145.5, 145.1, 137.0, 127.4, 126.0, 123.8, 123.3, 80.8, 34.2, 29.4, 28.3; FAB-MS: *m/z* calcd for $C_{57}H_{69}N_3O_2$: 827 ; found 827 ([M]$^+$).

N,N-Bis[4-(di-*tert*-butylphenylamino)phenyl]amine (5)

Compound **4** (0.5 g, 0.6 mmol) was dissolved in trifluoracetic acid (15.3 mL) and the reaction mixture was stirred at room temperature for 10 min. After evaporation of TFA, toluene was added to the residue, then the mixture washed with saturated aqueous solution of NaOH and dried over $MgSO_4$. Evaporation of solvent and recrystallization from hexane/toluene affored pure **5** (365 mg, 83%). ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 7.78 (br, 1H), 7.14 (br, 8H), 6.97-6.94 (m, 4H), 6.89-6.84 (m, 12H), 1.22 (s, 36H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.4, 144.3, 141.9, 138.6, 126.2, 125.6, 122.3, 118.5, 34.0, 31.2; FAB-MS: *m/z* calcd for $C_{52}H_{61}N_3$: 727; found 728 ($[M+H]^+$).



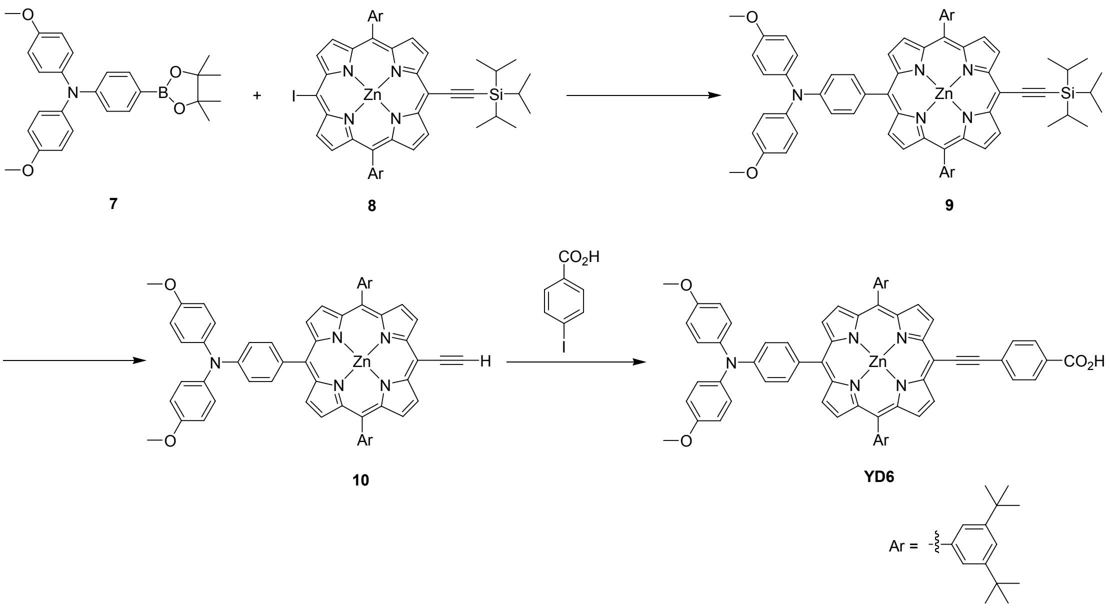
Zinc(II) 5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(*N,N*-bis(4-(di-*tert*-butylphenylamino)phenyl)amino)-20-(triisopropylsilylethynyl)porphyrin (6)

A mixture of *N,N*-bis[4-(di-*tert*-butylphenylamino)phenyl]amine (126 mg, 0.17 mmol), and 60% NaH (28 mg, 0.42 mmol) in dry THF (10 mL) was stirred under dinitrogen for 5 min, and then porphyrin **1** (50 mg, 0.05 mmol), DPEphos (8 mg, 0.015 mmol) and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) were added to the mixture. The solution was refluxed for 5 h under dinitrogen. The solvent was removed in vacuum. The residue was purified on a column chromatograph (silica gel) using CH_2Cl_2/hexane = 1/3 as the eluent. Recrystallization from CH_2Cl_2/CH_3OH gave **6** (36.1 mg, 45%). ^1H NMR ($CDCl_3$, 400 MHz) δ 9.75 (d, *J* = 4.8 Hz, 2H), 9.35 (d, *J* = 4.8 Hz, 2H), 8.97 (d, *J* = 4.8 Hz, 2H), 8.87 (d, *J* = 4.8 Hz, 2H), 8.04 (d, *J* = 1.6 Hz, 4H), 7.81 (d, *J* = 1.6 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 4H), 7.15 (d, *J* = 6.8 Hz, 2H), 6.95 (d, *J* = 6.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 4H), 1.53 (s, 36H), 1.50-1.43 (m, 21H), 1.26 (s, 36H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.7, 152.4, 150.4, 149.9, 148.7, 148.0, 145.3, 144.7, 141.2, 140.8, 133.2, 133.1, 130.9, 130.7, 129.4, 125.7, 125.2, 123.2, 122.9, 121.0, 109.4, 100.6, 97.7, 35.0, 34.1, 31.7, 31.3, 29.7, 19.1, 11.9; UV-vis

(CH_2Cl_2): λ_{max}/nm (ε, $10^3 M^{-1} cm^{-1}$) = 432 (339), 646 (31.5); FAB-MS: *m/z* calcd for $C_{111}H_{131}N_7SiZn$: 1655; found 1655 ($[M]^+$).

Zinc(II) 5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(*N,N*-bis(4-(di-*tert*-butylphenylamino)phenyl)amino)-20-(4-carboxylphenylethynyl)porphyrin (YD5)

To a solution of porphyrin **6** (33 mg, 0.02 mmol) in dry THF (5 mL) was added TBAF (0.08 mL, 1M in THF). The solution was stirred at 25 °C 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 Na_2SO_4 and the solvent was removed under vacuum. The residue and 4-iodobenzoic acid (10 mg, 0.04 mmol) were dissolved in dry THF (10 mL) and NEt_3 (2 mL) and degassed with dinitrogen for 10 min, and then $Pd_2(dba)_3$ (4.4 mg, 0.005 mmol) and $AsPh_3$ (15 mg, 0.045 mmol) were added to the mixture. The solution was refluxed for 4.5 h under dinitrogen. The solvent was removed under vacuum. The residue was purified on a column chromatograph (silica gel) using CH_2Cl_2/CH_3OH = 50/1 as the eluent. Recrystallization from CH_2Cl_2/CH_3OH gave **YD5** (21.5 mg, 67 %). ^1H NMR ($CDCl_3$, 400 MHz) δ 9.77 (d, *J* = 4.8 Hz, 2H), 9.36 (d, *J* = 4.8 Hz,2H), 9.02 (d, *J* = 4.4 Hz, 2H), 8.89 (d, *J* = 4.4 Hz, 2H), 8.24 (d, *J* = 7.6 Hz, 2H), 8.10 (d, *J* = 7.6 Hz, 2H), 8.08 (d, *J* = 1.6 Hz, 4H), 7.83 (d, *J* = 2.0 Hz, 2H), 7.23-7.15 (m, 12H), 6.98-6.91 (m, 12H), 1.58 (s, 36H), 1.26 (s, 36H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.5, 152.4, 150.4, 151.0, 148.8, 148.1, 145.3, 144.7, 141.1, 140.9, 133.4, 133.3, 131.4, 130.4, 129.7, 125.7, 125.2, 123.6, 123.0, 122.9, 121.0, 99.2, 96.5, 95.5, 35.1, 34.1, 31.8, 31.4; UV-vis (ethanol): λ_{max}/nm (ε, $10^3 M^{-1} cm^{-1}$) = 441 (307), 659 (27.2); FAB-MS: *m/z* calcd for $C_{109}H_{115}N_7O_2Zn$: 1619; found 1621 ($[M+2H]^+$).

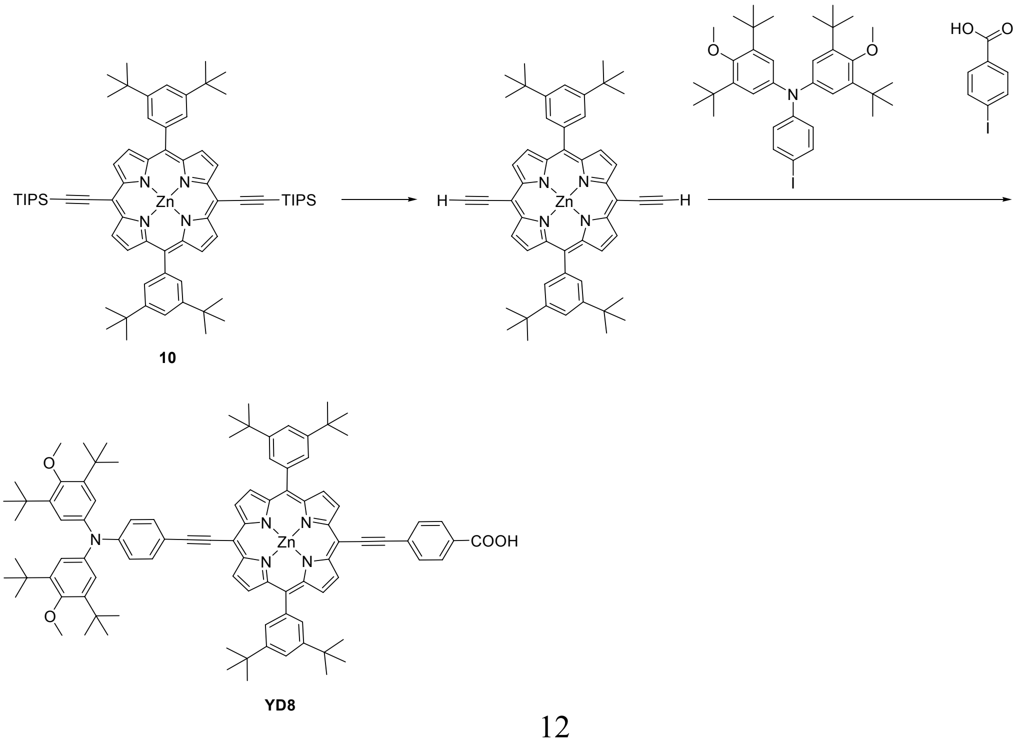


Zinc(II) 5-(triisopropylsilylethynyl)-10,20-bis(3,5-di-*tert*-butylphenyl)-15-(N,N-bis(4-methoxyphenyl)aminophenyl)porphyrin (9)

A mixture of compound **7** (8 mg, 0.02 mmol) and porphyrin **8** (13 mg, 0.01 mmol) in dry DMF (6 mL) degassed with nitrogen for 10 mins, and then K_3PO_4 (10 mg, 0.05 mmol) and $Pd(PPh_3)_4$ (4 mg, 3 μmol) were added. The reaction mixture was stirred for 3 h at temperature 90 ℃ and then extrated with CH_2Cl_2. Before the solvent was evaporated to dryness in vacuum, the organic layer was washed with Na_2SO_4. The product was purified by column chromatography on silica gel using CH_2Cl_2:Hexane (1:2) as the eluent. Solvent was removed under reduced pressure and the residue was then recrystallized from CH_2Cl_2/CH_3OH to give a pure dark blue solid (10 mg, 66 %).^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 9.80 (d, *J* = 4.8 Hz, 2H), 9.03 (d, *J* = 4.8 Hz, 4H), 8.92 (d, *J* = 4.8 Hz, 2H), 8.06 (d, *J* = 4.8 Hz, 4H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.81 (s, 2H), 7.34 (d, *J* = 9.2 Hz, 4H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 9.2 Hz, 4H), 3.84 (s, 6H), 1.54 (s, 36H), 1.44-1.42 (m, 21H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 152.7, 150.7, 150.1, 148.6, 141.0, 135.0, 133.2, 132.2, 131.9, 130.8, 129.5, 127.0, 123.2, 120.9, 118.1, 114.9, 55.53, 35.0, 31.8, 30.9, 29.7, 19.1, 11.9; UV/Vis : (CH_2Cl_2): λ_{max}/nm (ε, $10^3 M^{-1} cm^{-1}$) = 431 (33.8), 563 (19.5), 609 (21,4); FAB-MS: *m/z* calcd for $C_{79}H_{89}N_5O_2SiZn$: 1232; found 1233 ($[M+H]^+$).

Zinc(II) 5-(4-Carboxyphenylethynyl)-10,20-bis(3,5-di-*tert*-butylphenyl)-15-(N,N-bis(4-methoxyphenyl)aminophenyl)porphyrin (YD6)

To a solution of porphyrin **9** (17 mg, 0.02 mmol) in dry THF (5 mL) was added TBAF (0.08 mL, 1M in THF). The solution was stirred at 25 °C 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 Na_2SO_4 and the solvent was removed under vacuum. The residue and 4-iodobenzoic acid (6.0 mg, 0.02 mmol) were dissolved in dry THF (10 mL) and NEt_3 (5 mL) and degassed with dinitrogen for 10 min, and then $Pd_2(dba)_3$ (2.0 mg, 2 μmol) and $AsPh_3$ (1.0 mg, 3 μmol) were added to the mixture. The solution was refluxed for 4.5 h under dinitrogen. The solvent was removed under vacuum. The residue was purified on a column chromatograph (silica gel) using CH_2Cl_2/CH_3OH = 9/1 as the eluent. Recrystallization from CH_2Cl_2/methanol gave **YD6** (12 mg, 63 %). ^{1}H NMR (400 MHz, $CDCl_3$/pyridine-d_5) δ_H = 9.27 (d, J = 4.8 Hz, 2H), 8.97 (d, J = 4.8 Hz, 2H), 8.94 (d, J = 4.8 Hz, 2H), 8.84 (d, J = 4.8 Hz, 2H), 8.30 (d, J = 8.4 Hz, 2H), 8.09 (d, J = 8.4 Hz, 2H), 8.04 (s, 4H), 7.96 (d, J = 8.4 Hz, 2H), 7.79 (s, 2H), 7.33 (d, J = 9.2 Hz, 4H), 7.26 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 9.2 Hz, 4H), 3.84 (s, 6H), 1.54 (s, 36H); ^{13}C NMR (75 MHz, $CDCl_3$/pyridine-d_5) δ 155.94, 150.75, 149.96, 148.35, 147.97, 142.01, 141.17, 135.16, 133.06, 131.63, 131.09, 129.95, 126.85, 123.43, 123.28, 123.10, 122.77, 120.58, 118.20, 114.83, 55.52, 35.01, 31.75, 29.68; UV/Vis (ethanol): λ_{max}/nm (ε, $10^3 M^{-1} cm^{-1}$) = 443 (216), 579 (8.0), 628 (20.8); FAB-MS: *m/z* calcd for $C_{77}H_{73}N_5O_4Zn$: 1196; found 1197 ($[M+H]^+$).



Zinc(II) 5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(N,N-bis(3,5-di-*tert*-butyl-4-methoxyphenyl)aminophenylethynyl)-20-(4-carboxylphenylethynyl)porphyrin (YD8)

To a solution of porphyrin **10** (100 mg, 0.125 mmol) in dry THF (5 mL) was added TBAF (0.24 mL, 1M in THF). The solution was stirred at 25 ^{o}C 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 Na_2SO_4 and the solvent was removed under vacuum. The residue , 4-iodobenzoic acid (37 mg, 0.15 mmol) and N,N-bis(3,5-di-*tert*-butyl-4-methoxyphenyl)-N-(4-iodophenyl)amine (98 mg, 0.15 mmol) were dissolved in dry THF (60 mL) and NEt_3 (12.5 mL) and degassed with dinitrogen for 10 min, and then $Pd_2(dba)_3$ (34 mg, 0.038 mmol) and $AsPh_3$ (95 mg, 0.03 mmol) were added to the mixture. The solution was refluxed for 4.5 h under dinitrogen. The solvent was removed under vacuum. The residue was purified by column chromatography on silica gel using CH_2Cl_2/CH_3OH = 9.5/1 as the eluent. Recrystallization from CH_2Cl_2/CH_3OH gave **YD8** (21.5 mg, 70 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.71 (d, *J* = 4.8 Hz, 2H), 9.69 (d, *J* = 4.8 Hz, 2H), 8.89 (d, *J* = 4.8 Hz, 4H), 8.87 (d, *J* = 4.8 Hz, 2H), 8.30 (d, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 1.6 Hz, 4H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 1.6 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 7.06 (s, 4H), 1.53 (s, 36H), 1.38 (s, 36H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.7, 152.0, 151.6, 150.3, 150.2, 148.5, 144.3, 141.7, 141.5, 132.9, 132.5, 132.2, 131.1, 130.2, 130.1, 129.9, 123.5, 120.7, 120.5, 115.2, 102.4, 101.8, 99.3, 97.5, 96.4, 95.63, 92.5, 64.2, 35.9, 35.0, 32.1, 31.7; UV-vis (ethanol): λ_{max}/nm (ε, $10^3 M^{-1} cm^{-1}$) = 457 (136), 671 (49.9); FAB-MS: *m/z* calcd for $C_{95}H_{105}N_5O_4Zn$: 1446; found 1448 ($[M+2H]^+$).

References

1. Y. Hirao, H. Ino, A. Ito and K. Tanaka, *J. Phys. Chem. A*, 2006, **110**, 4866-4872.

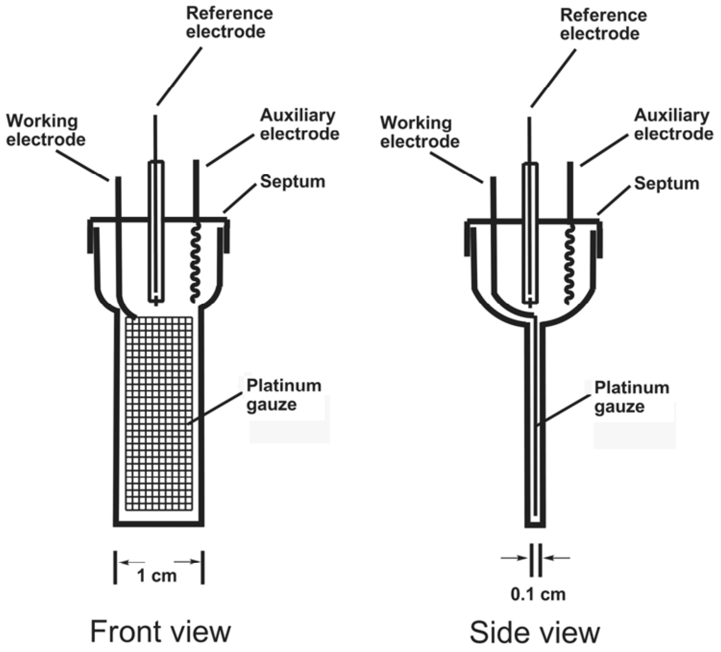


Fig. S1 Schematic diagram for the spectroelectrochemical cell.