Electronic Supplementary Information for:

"Push-no-Pull" Porphyrins for Second Harmonic Generation Imaging

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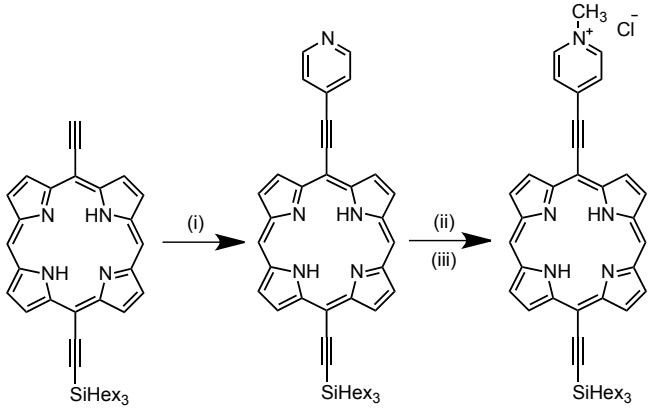
1. Synthesis and compound characterization

1.1 General Materials and Methods

5-Iodopent-1-yne,[1] 1-iodonaphthalene-3,6-disulfonic acid disodium salt,[2] dibromoporphyrin **9-Zn,**[3] 4-iodopyridine,[4] porphyrins[5] **1**, **2**, **3**, **5** and **13** were prepared as previously described. The manipulation of all air and/or water sensitive compounds was carried out using standard high vacuum techniques. Dichloromethane and THF were obtained either by distillation or by passing through a column of activated alumina. Diisopropylamine was distilled from CaH_2 under nitrogen before use. All other reagents were used as supplied by commercial agents. Analytical thin layer chromatography (TLC) was carried out on Merck® aluminum backed silica gel 60 GF254 plates and visualization when required was achieved using UV light or I_2. Column chromatography was carried out on silica gel 60 GF254 using a positive pressure of nitrogen. Size exclusion chromatography (SEC) was carried out using Bio-BeadsS-X1, 200-400 mesh (Bio-Rad). Where mixtures of solvents were used, ratios reported are by volume. NMR spectra were recorded at ambient probe temperature using either a Brucker DPX400 (400 MHz) or Brucker AVANCE AV500 (500 MHz). Chemical shifts are quoted as parts per million (ppm) relative to the internal signal of the solvent (chloroform/DMSO). UV/Vis spectra were recorded on a Perkin Elmer Lambda 20 UV-Vis. Mass spectra were carried out using Matrix Assisted Laser Desorption Ionization-Time of Flight (MALDI-TOF) and ElectroSpray Ionization (ESI), and only molecular ions and major peaks are reported.



Scheme S1. Synthetic route for porphyrin **4**: (i) 4-iodopyridine, $Pd_2(dba)_3$, PPh_3, CuI, toluene, *i*-Pr_2NH, 30 °C; (ii) MeI, THF; (iii) Dowex 1x8 200 mesh ion-exchange column (DMF).

1.3 Synthetic Procedures

Porphyrin 4. Monodeprotected porphyrin **13** (150 mg, 0.23 mmol), $Pd_2(dba)_3$ (20 mg, 0.02 mmol), PPh_3 (23 mg, 0.09 mmol) and CuI (10 mg, 0.05 mmol) were dried *in vacuo* for 1 h before toluene (5 mL) and diisopropylamine (5 mL) were added and the mixture freeze-pump-thaw degassed. 4-Iodopyridine (440 mg, 2.15 mmol) was added and the mixture stirred at 30 °C for 3 h under N_2. Upon completion, the mixture was passed through a silica plug (1:1 $CHCl_3$:THF) then purified by flash chromatography (5:1 $CHCl_3$:THF) to isolate the desired product. Fractions were evaporated to dryness to give porphyrin **12** as purple wax, (140 mg, 85%). Then, porphyrin **12** (25 mg, 0.035 mmol) was dissolved in THF (2 mL) and MeI (1.0 mL, 16 mmol) was added. After 5 h, all starting material was consumed according to TLC and the product was passed through a Dowex 1x8 200 mesh ion-exchange column (DMF). The resulting solution was precipitated from DMF with toluene and collected by filtration to give porphyrin **4** as an amorphous dark solid, (20 mg, 75%). UV/Vis (DMF): λ_{max} (nm) (ε x 10^3 $M^{-1}cm^{-1}$) = 437 (180), 590 (58), 671 nm (42). ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) = 10.52 (s, 2H), 9.97 (d, *J* = 4.5 Hz, 2H), 9.68 (d, *J* = 4.5 Hz, 2H), 9.5 (m, 4H), 9.24 (d, *J* = 6.8 Hz, 2H), 8.96 (d, *J* = 6.8 Hz, 2H), 4.45 (s, 3H), 1.7 (m, 6H), 1.5 (m, 6H), 1.1 (m, 12H), 0.9 (m, 6H), 0.8 (m, 9H). MS (ESI) *m/z* 732.4450 ($C_{48}H_{58}N_5SiCl$, $[M\text{-}Cl]^+$, requires 732.4456, 100%).

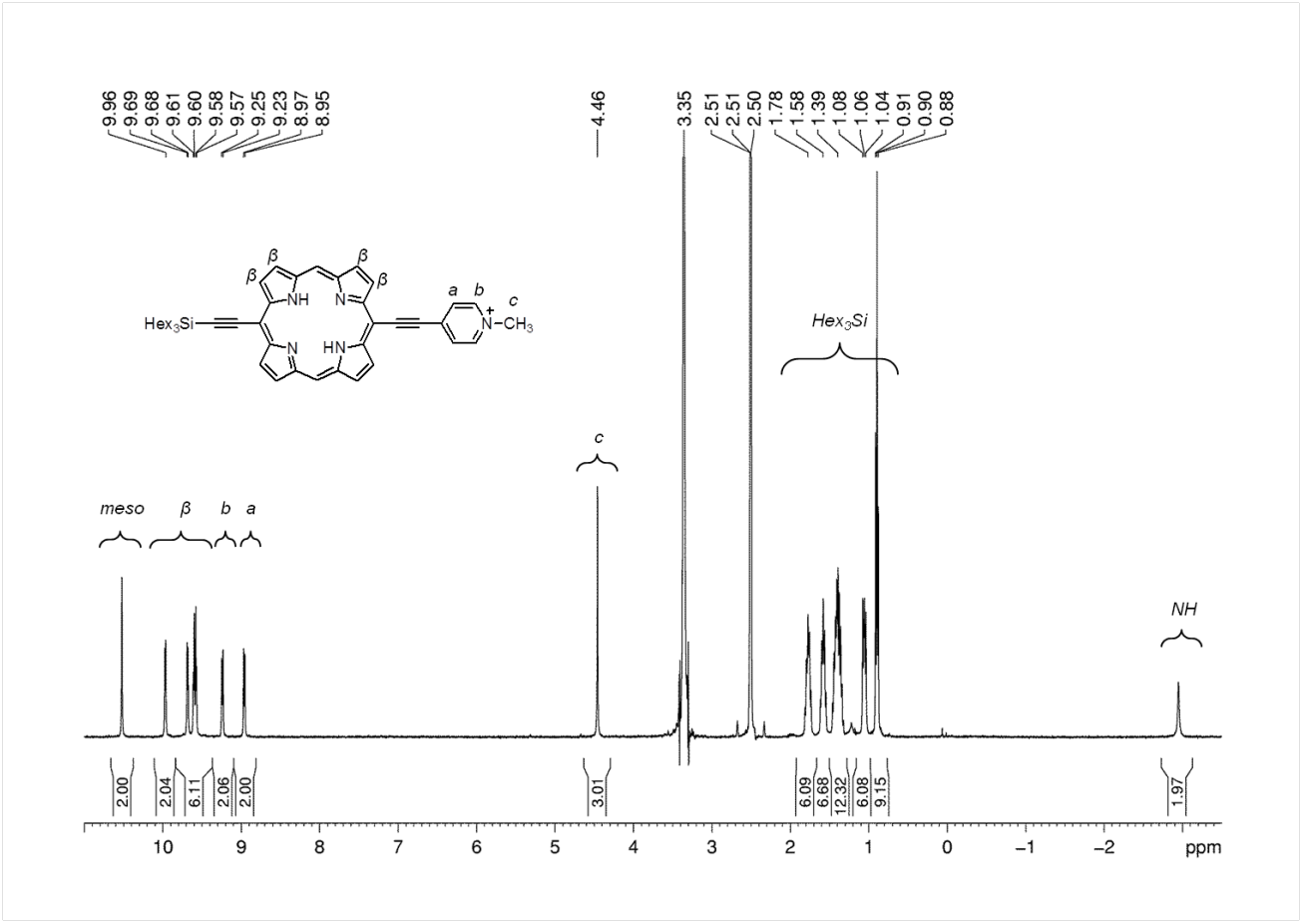


Figure S1. ^{1}H NMR spectrum of porphyrin **4** (400 MHz, DMSO-d_6).

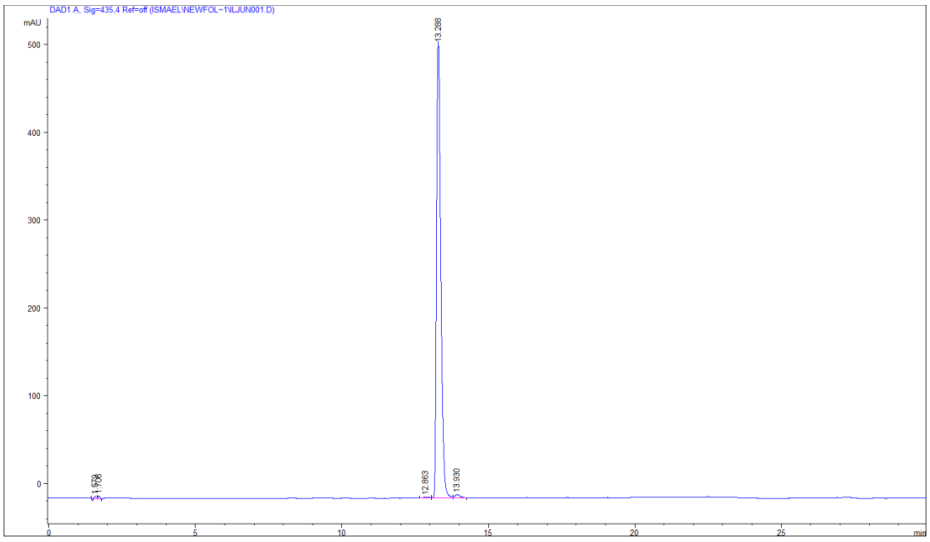


Figure S2. HPLC trace of porphyrin **4**. Retention time = 13.28 min.

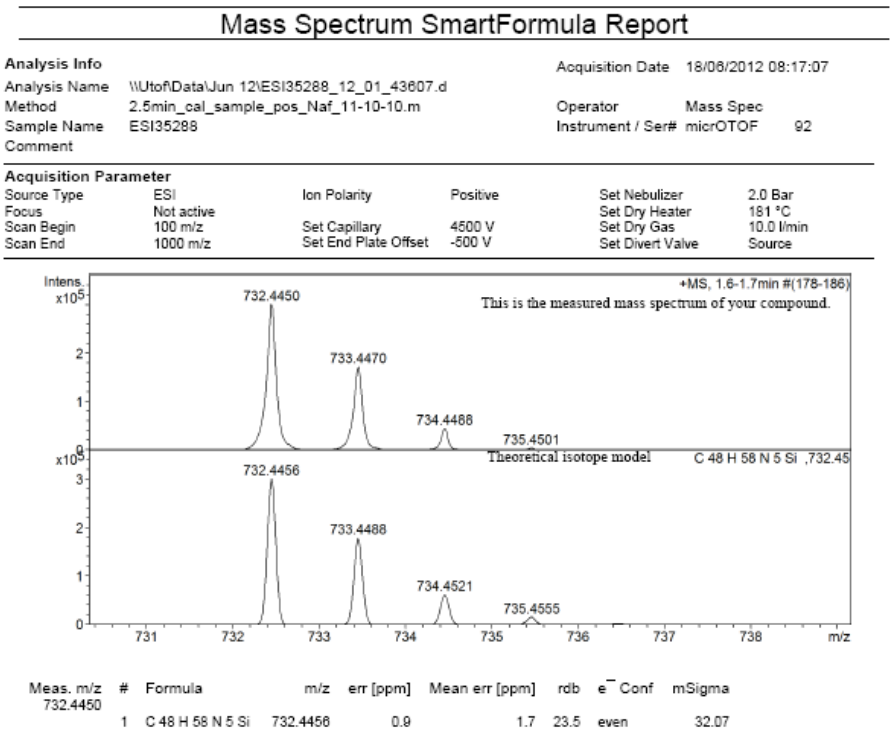


Figure S3. ESI+ mass spectrum of porphyrin **4**.

Porphyrin 3-Zn. To a stirred solution of porphyrin **3** (200 mg, 0.21 mmol) in CH_2Cl_2 (100 mL) a solution of zinc acetate dihydrate (600 mg, 2.73 mmol) in MeOH (8 mL) was added. The reaction mixture was stirred for 45 min, when TLC (CH_2Cl_2) confirmed completion. The solvent was removed by evaporation and the product was purified by flash chromatography on silica gel using CH_2Cl_2 as eluent. Fractions were evaporated to dryness to give porphyrin **3-Zn** as an amorphous dark solid, (210 mg, 98%). UV/Vis (DMF): λ_{max} (nm) (ε x 10^3 $M^{-1}cm^{-1}$) = 431 (157), 650 nm (79). ^{1}H NMR (400 MHz, $CDCl_3$ / 1% pyridine–d_5) δ (ppm) = 10.02 (s, 2H), 9.84 (d, *J* = 4.4 Hz, 2H), 9.74 (d, *J* = 4.4 Hz, 2H), 9.30 (d, *J* = 1.5 Hz, 2H), 9.27 (d, *J* = 1.5 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.39 (d, *J* = 7.3 Hz, 4H), 1.9-1.2 (m, 50H), 1.1-0.8 (m,19H). MS (ESI) *m/z* 1018.40 ($C_{64}H_{87}N_5SiZn$, $[M]^+$ requires 1018.61, 100%).

***N*,*N*,*N*-Triethyl-4-pentyn-1-aminium iodide (10)**. Triethylamine (3.0 mL, 21 mmol) was added dropwise to a stirred solution of 5-Iodopent-1-yne[1] (1.0 g, 5.1 mmol) in diethyl ether (5.0 mL). After stirring for 24 h the precipitate was filtered, washed with diethyl ether and dried *in vacuo* to give compound **10** as a white powder. (1.2 g, 80%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) = 3.25 (q, *J* = 7.2 Hz, 6H), 3.1 (m, 2H), 2.95 (s, 1H), 2.3 (d, 2H), 1.7 (m, 2H), 1.18 (s, *J* = 6.8 Hz, 9H). ^{13}C-NMR (100 MHz, DMSO-d_6): δ (ppm) = 83.70, 73.34, 55.75, 52.94, 21.18, 15.70, 8.04. MS (ESI) *m/z* 168.1745 ($C_{11}H_{22}NI$, $[M-I]^+$ requires 168.1747, 100%).

1-(Trimethylsilyl)ethynylnaphthalene-3,6-disulfonic acid disodium salt (11). 1-Iodonaphthalene-3,6-disulfonic acid disodium salt[2] (200 mg, 0.43 mmol), $Pd_2(dba)_3$ (20 mg, 22 µmol), triphenylphosphine (33 mg, 126 µmol) and copper(I) iodide (13 mg, 68 µmol) were dried *in vacuo* for 1 h. Trimethylsilyl acetylene (0.20 mL, 1.4 mmol), DMSO (2.0 mL) and diisopropylamine (1.0 mL) were added by syringe and the solution was degassed by three freeze-thaw cycles and stirred at room temperature for 5 hours under N_2. The mixture of solvents was evaporated under vacuum and the product was passed through a celite plug with DMSO as the eluent. After evaporation of the solvent, the residue was suspended in acetone and filtrated, giving the corresponding 1-(trimethylsilyl)ethynylnaphthalene-3,6-disulfonic acid disodium salt in 90% yield (170 mg). ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) = 8.19 (d, *J* = 1.6 Hz, 1H), 8.15 (s, 1H), 8.13 (d, *J* = 8.7 Hz, 1H), 7.87 (d, *J* = 1.6 Hz, 1H), 7.85 (dd, *J* = 8.7, *J* = 1.6 Hz, 1H), 0.33 (s, 9H, $SiCH_3$). ^{13}C-NMR (100 MHz, DMSO-d_6): δ (ppm) = 146.56, 145.24, 131.93, 131.31, 129.30, 125.87, 125.82, 125.33, 124.90, 119.29, 102.45, 99.75, 18.53, −0.06. MS (ESI) *m/z* 404.9902 ($C_{15}H_{14}Na_2O_6S_2Si$, $[M-Na]^-$ requires 404.9904, 100%).

Porphyrin 8-Zn. Dibromoporphyrin **9-Zn** (820 mg, 0.81 mmol), *N,N*-dioctylamino-4-trimethylsilylethynylbenzene (500 mg, 1.20 mmol), $Pd_2(dba)_3$ (23 mg, 25 µmol), triphenylphosphine (70 mg, 240 µmol) and copper(I) iodide (25 mg, 120 µmol) were dried *in vacuo* for 1 h. Toluene (7 mL), diisopropylamine (7 mL) and TBAF (1.0 M in THF, 2.00 mL, 2.0 mmol) were added by syringe and solution was degassed by three freeze-thaw cycles. The reaction mixture was stirred at 50 °C for 2 h under N_2. The reaction mixture was cooled to room temperature and diluted with CH_2Cl_2 (100 mL). The organic solution was washed with saturated ammonium chloride solution (100 mL), water (100 mL) and then dried over Na_2SO_4 and evaporated under vacuum. The green residue was subjected to chromatography on silica gel (50:1 to 25:1 CH_2Cl_2:THF) to give **8-Zn** (300 mg, 28%) as a green wax. ^{1}H NMR (500 MHz, $CDCl_3$ / 1% pyridine–d_5) δ (ppm) = 9.72 (d, *J* = 4.5 Hz, 2H), 9.59 (d, *J* = 4.6 Hz, 2H), 8.88 (d, *J* = 4.5 Hz, 2H), 8.85 (d, *J* = 4.6 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.7 (m, 4H), 7.5 (m, 2H), 7.3 (m, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 4.3 (m, 4H, 3.9 (m, 4H), 3.7 (m, 4H), 3.6 (m, 4H), 3.5 (m, 4H), 3.4 (m, 4H), 3.3 (m, 4H, NCH_2), 3.32 (s, 6H, OCH_3), 1.6 (m, 4H), 1.3 (m, 20H), 0.9 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$/ 1% pyridine–d_5) δ (ppm) =156.97, 152.50, 150.37, 149.81, 149.64, 149.54, 148.03, 144.16, 135.89, 132.90, 132.70, 132.47, 132.35, 130.96, 127.86, 127.14, 121.56, 121.32, 113.69, 111.50, 109.74, 104.99, 102.24, 98.00, 91.06, 71.86, 70.85, 70.63, 70.52, 69.88, 67.66, 58.96, 51.07, 31.84, 29.51, 29.34, 27.30, 27.18, 22.66, 14.12. MS (MALDI–TOF, DITRANOL) *m/z* 1267.92 ($C_{70}H_{84}BrN_5O_8Zn$, $[M]^+$, requires 1267.48, 100%).

Porphyrin 6-Zn. Porphyrin **8-Zn** (60 mg, 0.05 mmol), *N,N,N*-triethyl-4-pentyn-1-aminium iodide (**10**) (60 mg, 0.2 mmol), $Pd_2(dba)_3$ (5 mg, 6 µmol), triphenylphosphine (4 mg, 15 µmol) and copper(I) iodide (2 mg, 11 µmol) were dried *in vacuo* for 1 h. Toluene (3 mL), methanol (0.5 mL) and diisopropylamine (3 mL) were added by syringe and the solution was degassed by three freeze-thaw cycles. The mixture was stirred at 50 °C for 3 h under N_2. The solvent was evaporated and the residue was redissolved in $CHCl_3$ and passed through a celite plug. After evaporation, the residue was purified by size exclusion chromatography (Bio Beads S-X1, $CHCl_3$:pyridine 100:1). Compound **6-Zn** was isolated in 79% yield (49 mg). ^{1}H NMR (400 MHz, $CDCl_3$ / 1% pyridine–d_5) δ (ppm) = 9.61 (d, *J* = 4.5 Hz, 2H), 9.33 (d, *J* = 4.6 Hz, 2H), 9.33 (d, *J* = 4.6 Hz, 2H), 8.9 (m, 4H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.7 (m, 4H), 7.5 (m, 2H), 7.3 (m, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 4.3 (m, 4H, OCH_2), 3.9 (m, 4H, OCH_2), 3.7 (m, 4H, OCH_2), 3.6 (m, 4H, OCH_2), 3.5 (m, 4H, OCH_2), 3.4 (m, 4H, OCH_2), 3.3 (m, 4H, NCH_2), 3.25 (s, 6H, OCH_3), 3.0 (m, 2H), 2.7 (m, 2H), 1.5 (m, 6H), 2.4 (m, 6H), 1.2 (m, 22H), 0.9 (m, 6H, CH_3), 0.6 (m, 9H, CH_3). MS (MALDI-TOF, DITRANOL) *m/z* 1355.90 ($C_{81}H_{105}N_6O_8Zn$, $[M]^+$, requires 1356.12, 100%)

Porphyrin 6. Zinc porphyrin **6-Zn** (49 mg) was dissolved in a mixture of $CHCl_3$ (10 mL) and TFA (1.0 mL). After 20 min. stirring at room temperature, the reaction was quenched with $NaHCO_3$ saturated solution, and the organic layer was washed with water, dried over Na_2SO_4 and evaporated under vacuum. The residue was passed through a Dowex 1x8 200 mesh ion-exchange column (MeOH) and after evaporation, the product was purified by size exclusion chromatography (Bio Beads S-X1, $CHCl_3$). Compound **6** was isolated in 85% yield (37 mg). UV/Vis (DMF): λ_{max} (nm) (ε, x 10^3 $M^{-1}cm^{-1}$) = 428 (122), 621 (34), 705 nm (25). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 9.63 (d, *J* = 4.5 Hz, 2H), 9.37 (d, *J* = 4.6 Hz, 2H), 8.8 (m, 4H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.7 (m, 4H), 7.63 (t, *J* = 8.0 Hz, 2H), 7.34 (m, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 4.3 (m, 4H, OCH_2), 3.9 (m, 4H, OCH_2), 3.7 (m, 4H, OCH_2), 3.6 (m, 4H, OCH_2), 3.5 (m, 4H, OCH_2), 3.4 (m, 4H, OCH_2), 3.3 (m, 4H, NCH_2), 3.25 (s, 6H, OCH_3), 2.8 (m, 6H; CH_2), 2.0 (m, 2H), 1.6 (m, 4H), 1.3 (m, 24H), 1.1 (m, 9H, CH_3), 0.9 (m, 6H, CH_3), -1.98 (s, 2H, NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) = 162.33, 153.66, 146.92, 138.39, 137.21, 133.32, 132.41, 126.45, 125.96, 119.72, 116.69, 112.55, 108.12, 106.14,105.21, 102.30, 94.90, 87.68, 76.40, 75.18, 74.98, 74.75, 74.24, 72.70, 63.14, 60.66, 57.41, 55.21, 45.29, 36.41, 34.03, 33.89, 31.95, 31.55, 27.25, 26.12, 22.15, 19.12, 12.42, 12.33. MS (ESI) *m/z* 1291.8148 ($C_{81}H_{107}N_6O_8Cl$, $[M\text{-}Cl^-]^+$ requires 1291.8145, 100%).

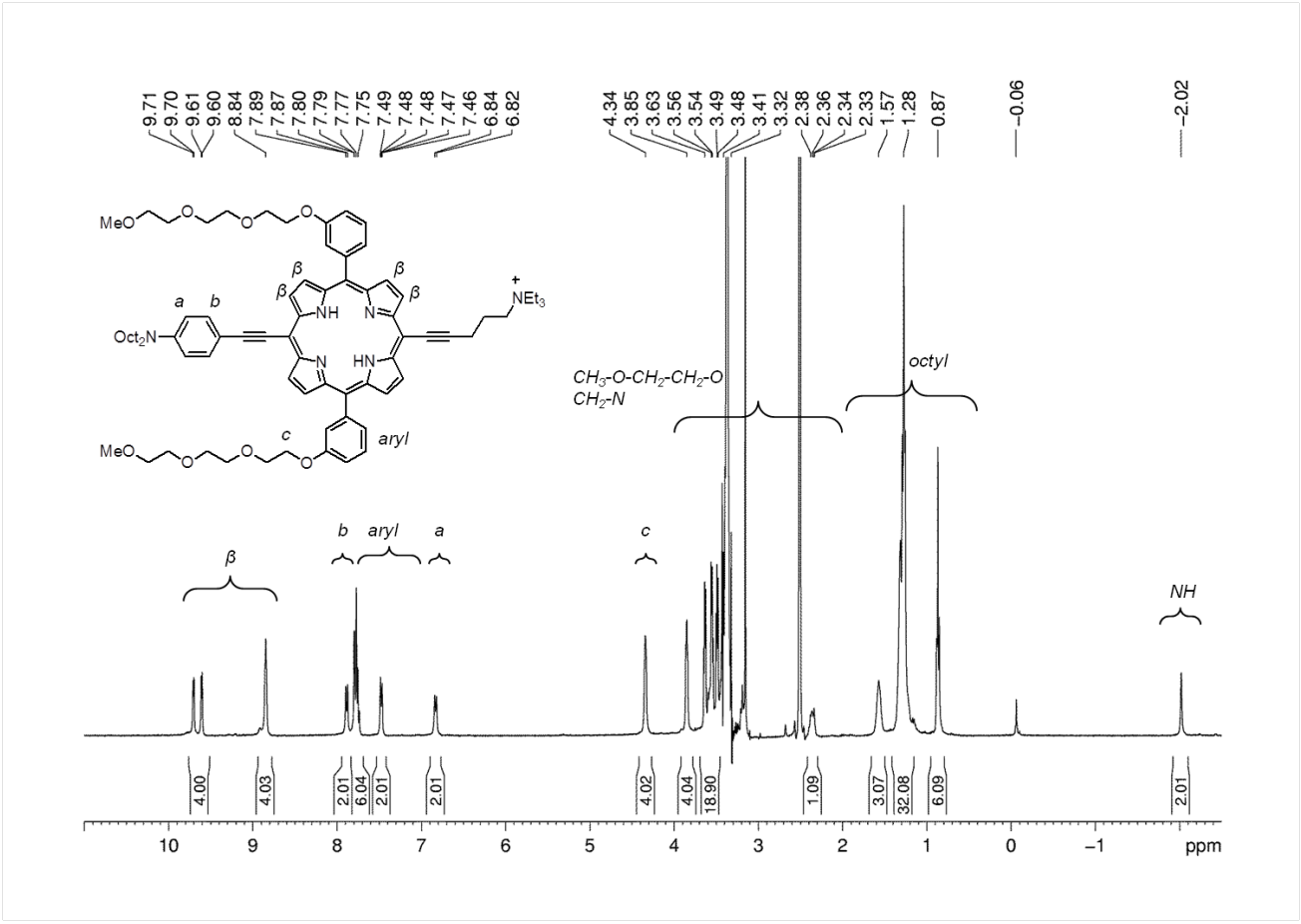


Figure S4. ^{1}H NMR spectrum of porphyrin **6** (400 MHz, DMSO-d_6).

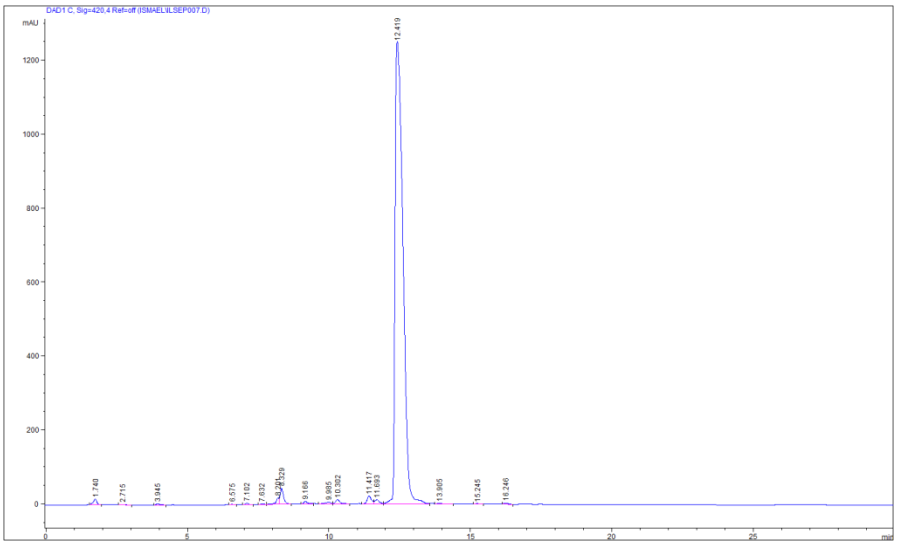


Figure S5. HPLC trace of porphyrin **6**. Retention time = 12.41 min.

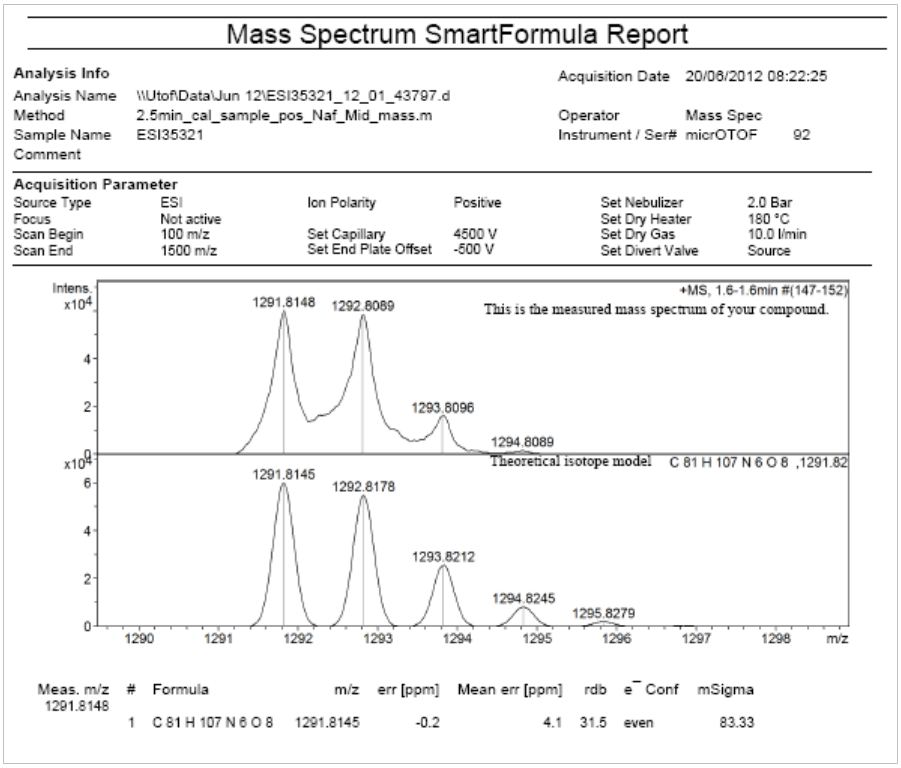


Figure S6. ESI+ mass spectrum of porphyrin **6**.

Porphyrin 7-Zn. Porphyrin **8-Zn** (60 mg, 0.05 mmol), 1-(trimethylsilyl)ethynylnaphthalene-3,6-disulfonic acid (60 mg, 0.14 mmol) (**11**), $Pd_2(dba)_3$ (5 mg, 6 µmol), triphenylphosphine (4 mg, 15 µmol) and copper(I) iodide (2 mg, 11 µmol) were dried *in vacuo* for 1 h. DMSO (2 mL), diisopropylamine (2 mL) and TBAF (1.0 M in THF, 0.2 mL, 0.2 mmol) were added by syringe and the solution was degassed by three freeze-thaw cycles. The mixture was stirred at 40 °C for 3 hours under N_2. The mixture of solvents was evaporated under vacuum and the solid residue was dissolved in $CHCl_3$ and passed through a celite plug. After evaporation, the residue was further purified by size exclusion chromatography (Bio Beads S-X1, $CHCl_3$:pyridine 100:1). Compound **7-Zn** was obtained as a green solid in 62% yield (48 mg). ^{1}H NMR (400 MHz, $CDCl_3$ / 1% pyridine–d_5) δ (ppm) = 9.98 (d, *J* = 4.5 Hz, 2H), 9.69 (d, *J* = 4.6 Hz, 2H), 8.96 (d, *J* = 4.5 Hz, 2H), 8.8 (m, 2H), 8.53 (m, 1H), 8.36 (s, 2H), 8.16 (d, *J* = 8.6 Hz, 1H), 7.8 (m, 8H), 7.48 (d, *J* = 8.6 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.3 (m, 4H, OCH_2), 3.9 (m, 4H, OCH_2), 3.7 (m, 4H, OCH_2), 3.6 (m, 4H, OCH_2), 3.5 (m, 4H, OCH_2), 3.4 (m, 4H, OCH_2), 3.10 (s, 6H, OCH_3), 3.10, 1.5 (m, 4H), 1.3 (m, 20H). MS (MALDI-TOF, DITRANOL) m/z 1541.95 ($C_{82}H_{89}N_5Na_2O_{14}S_2Zn$, $[M]^+$, requires 1541.49, 100%).

Porphyrin 7. Porphyrin **7-Zn** (45 mg, 0.03 mmol) was dissolved in a mixture of $CHCl_3$ (10 mL) and TFA (1.0 mL). After 20 min. stirring at room temperature, the reaction was quenched with $NaHCO_3$ saturated solution, and the organic layer was washed with water, dried over Na_2SO_4 and evaporated under vacuum. The residue was purified by size exclusion chromatography (Bio Beads S-X1, $CHCl_3$). Compound **7** was isolated in 65% yield (29 mg). UV/Vis (DMF): λ_{max} (nm) (ε, x 10^3 $M^{-1}cm^{-1}$) = 445 (97), 630 (35), 714 nm (33).^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) = 9.98 (d, *J* = 4.5 Hz, 2H), 9.69 (d, *J* = 4.6 Hz, 2H), 8.96 (d, *J* = 4.5 Hz, 2H), 8.8 (m, 2H), 8.53 (s, 1H), 8.36 (s, 2H), 8.16 (d, *J* = 8.6 Hz, 1H), 7.8 (m, 8H), 7.48 (d, *J* = 8.6 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.3 (m, 4H, OCH_2), 3.9 (m, 4H, OCH_2), 3.7 (m, 4H, OCH_2), 3.6 (m, 4H, OCH_2), 3.5 (m, 4H, OCH_2), 3.4 (m, 4H, OCH_2), 3.15 (s, 6H, OCH_3), 1.5 (m, 4H, CH_2), 1.3 (m, 20H, CH_2), 0.8 (m, 6H, CH_3), −1.79 (m, 2H, NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) = 157.17, 148.44, 147.27, 146.14, 141.69, 133.21, 132.25, 131.80, 129.26, 128.14, 127.25, 126.48, 126.07, 125.43, 121.82, 120.69, 119.86, 114.74, 111.46, 107.3, 107.32, 103.53, 101.22, 99.09, 95.96, 95.15, 89.84, 71.21, 69.99, 69.80, 69.57, 69.07, 67.52, 57.95, 57.46, 50.02, 31.22, 28.84, 28.70, 26.75, 26.35, 23.01, 22.07, 19.16, 13.94, 13.45; MS (ESI) *m/z* 716.7989 ($C_{82}H_{91}N_5Na_2O_{14}S_2$, $[M-2Na]^{-2}$ requires 716.8007, 100%).

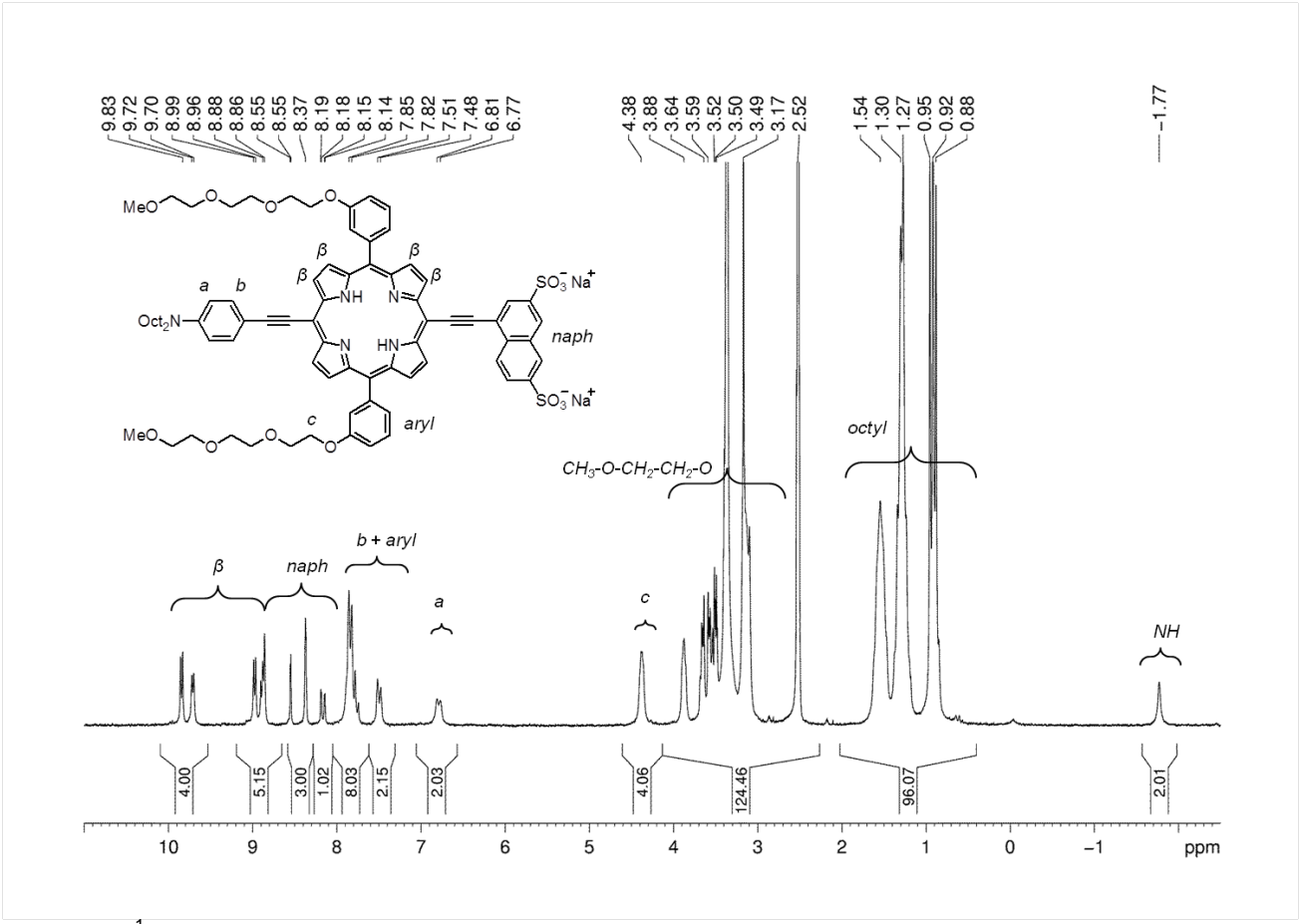


Figure S7. ^{1}H NMR spectrum of porphyrin **7** (400 MHz, DMSO-d_6).

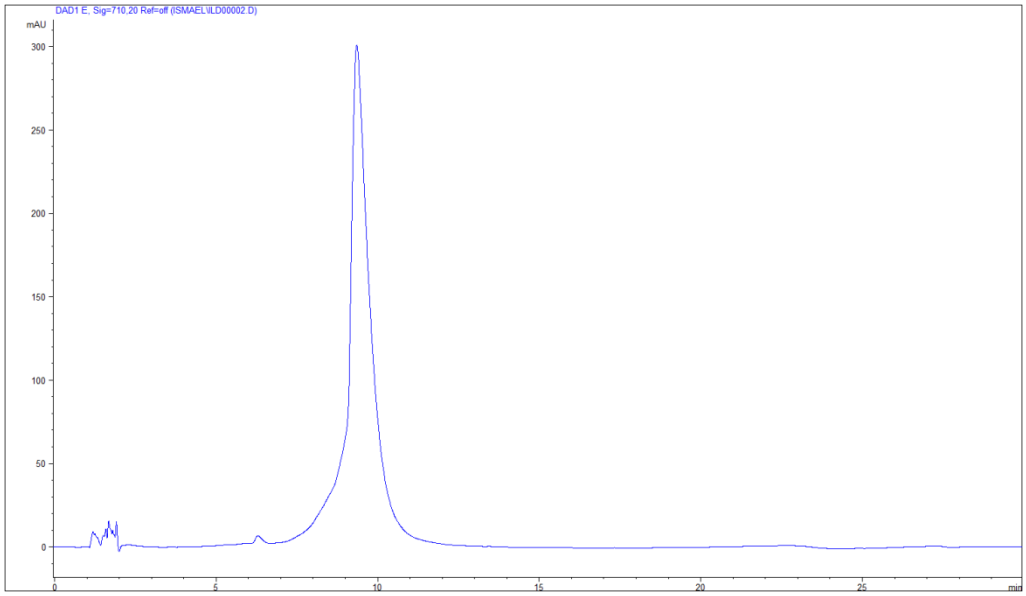


Figure S8. HPLC trace of porphyrin **7**. Retention time = 9.62 min.

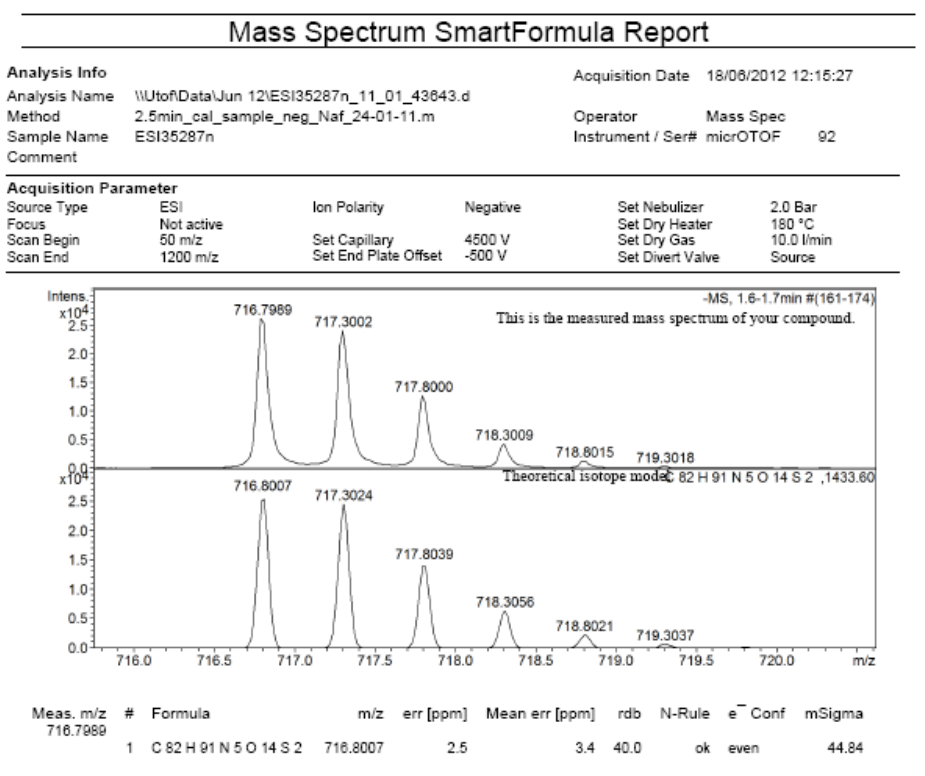


Figure S9. ESI+ mass spectrum of porphyrin **7**.

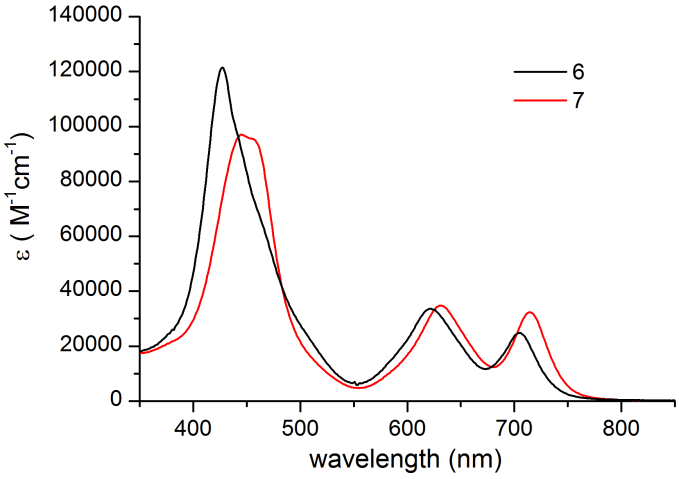


Figure S10. UV-vis spectra of **6** and **7** in DMF.

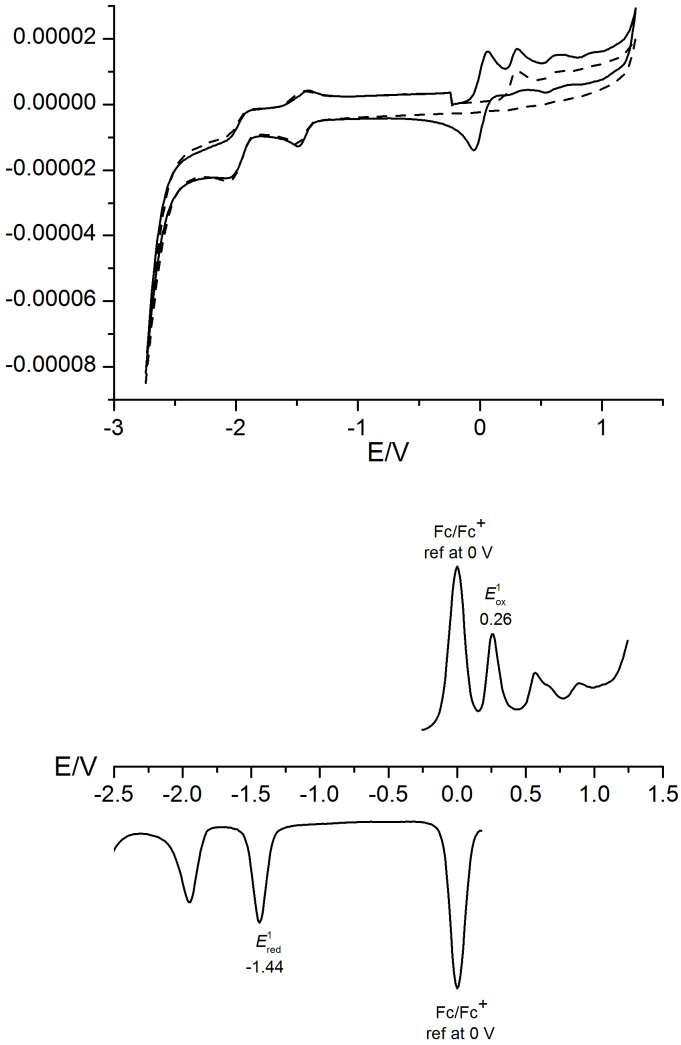


Figure S11. Top: Cyclic voltammogram (CH_2Cl_2, 0.1 M Bu_4NPF_6; scan rate 100 mV s^{-1}; glassy carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode) for porphyrin **3**. Square-wave experiments recorded for the same samples (CH_2Cl_2, 0.1 M Bu_4NPF_6; square-wave frequency 8 Hz; glassy carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode). The gray dashed lines represent the trace in the absence of internal ferrocene while the black lines show the measurements in the presence of ferrocene.

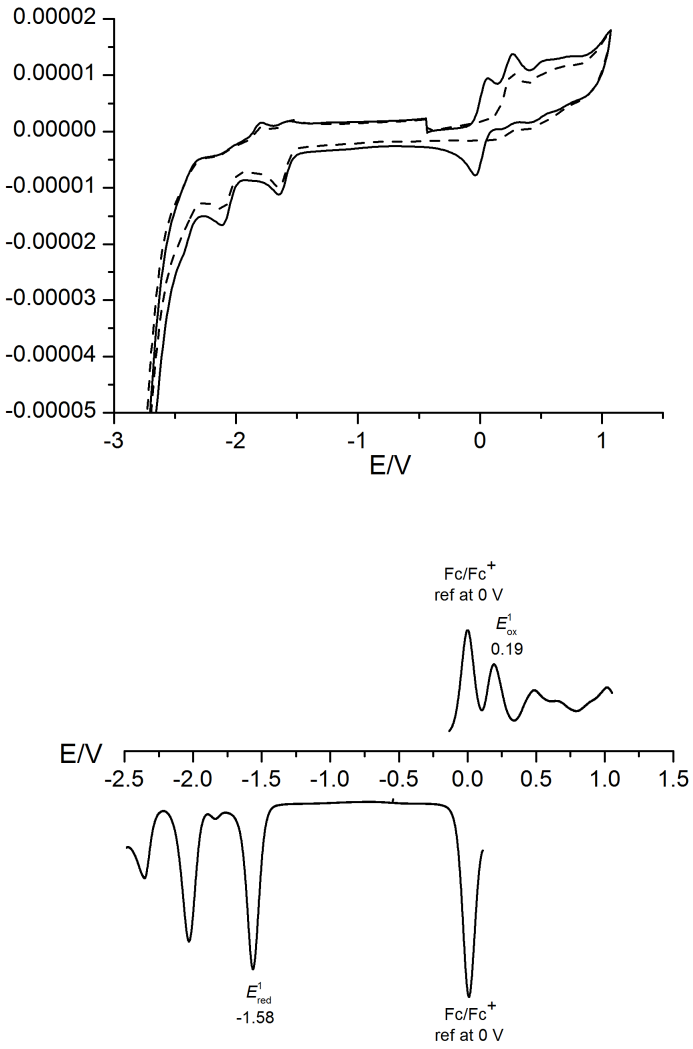


Figure S12. Top: Cyclic voltammogram (CH_2Cl_2, 0.1 M Bu_4NPF_6; scan rate 100 mV s^{-1}; glassy carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode) for porphyrin **3-Zn**. Square-wave experiments recorded for the same samples (CH_2Cl_2, 0.1 M Bu_4NPF_6; square-wave frequency 8 Hz; glassy carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode). The gray dashed lines represent the trace in the absence of internal ferrocene while the black lines show the measurements in the presence of ferrocene.

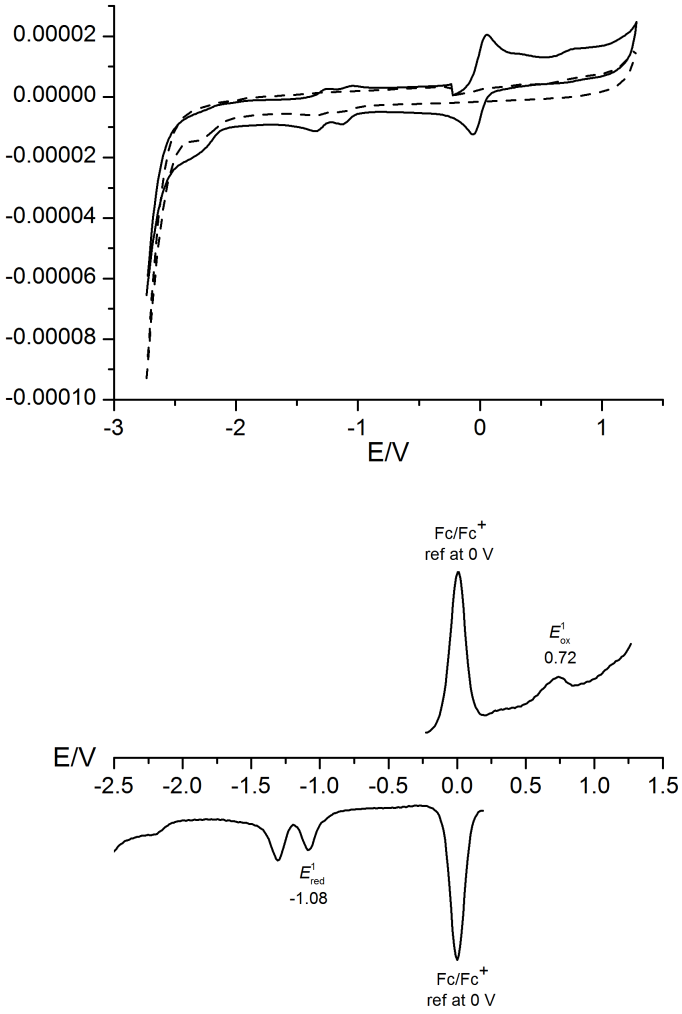


Figure S13. Top: Cyclic voltammogram (CH_2Cl_2, 0.1 M Bu_4NPF_6; scan rate 100 mV s^{-1}; glassy carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode) for porphyrin **4**. Square-wave experiments recorded for the same samples (CH_2Cl_2, 0.1 M Bu_4NPF_6; square-wave frequency 8 Hz; glassy carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode). The gray dashed lines represent the trace in the absence of internal ferrocene while the black lines show the measurements in the presence of ferrocene.

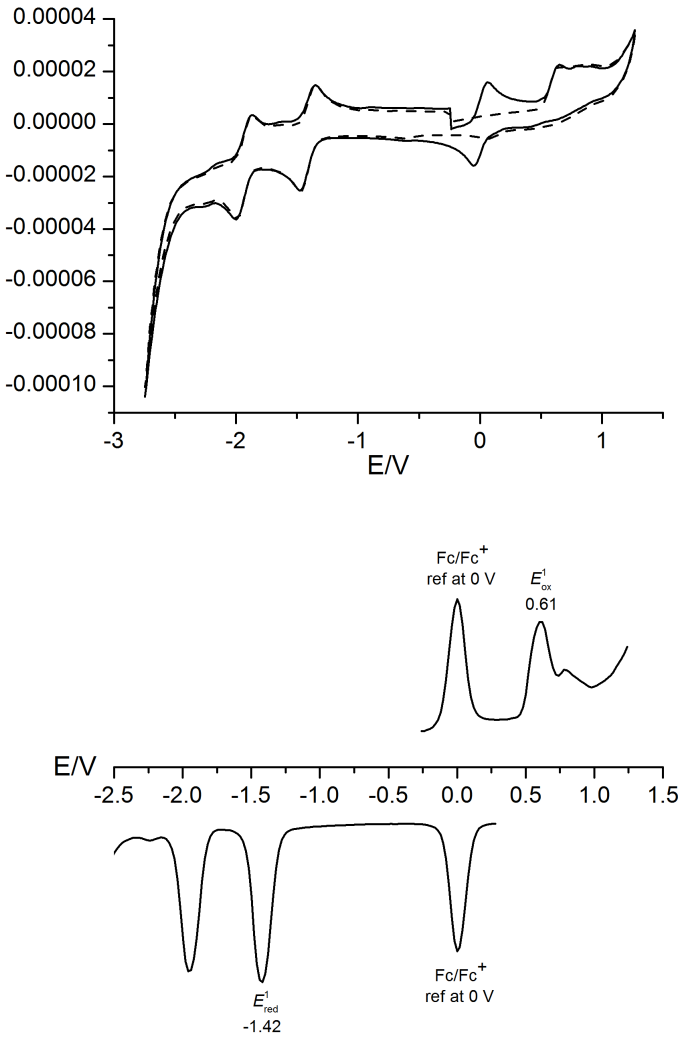


Figure S14. Top: Cyclic voltammogram (CH_2Cl_2, 0.1 M Bu_4NPF_6; scan rate 100 mV s^{-1}; glassy carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode) for porphyrin **5**. Square-wave experiments recorded for the same samples (CH_2Cl_2, 0.1 M Bu_4NPF_6; square-wave frequency 8 Hz; glassy carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode). The gray dashed lines represent the trace in the absence of internal ferrocene while the black lines show the measurements in the presence of ferrocene.

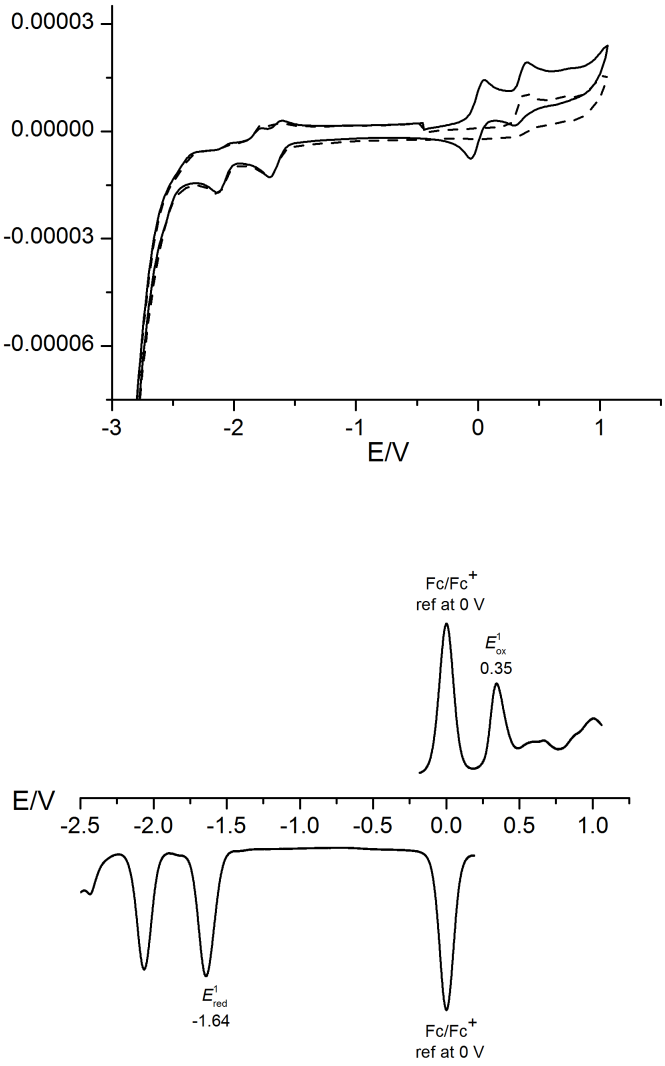


Figure S15. Top: Cyclic voltammogram (CH_2Cl_2, 0.1 M Bu_4NPF_6; scan rate 100 mV s^{-1}; glassy carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode) for porphyrin **5-Zn**. Square-wave experiments recorded for the same samples (CH_2Cl_2, 0.1 M Bu_4NPF_6; square-wave frequency 8 Hz; glassy carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode). The gray dashed lines represent the trace in the absence of internal ferrocene while the black lines show the measurements in the presence of ferrocene.

2. Hyper-Rayleigh Scattering

Femtosecond hyper-Rayleigh scattering experiments[6,7] were performed at 800 and 840 nm in dimethylformamide as the solvent. Crystal Violet in methanol was used as the reference, with a value of 338 × 10^{-30} esu at 800 nm and 405 × 10^{-30} esu at 840 nm for the octopolar β_{xxx} hyperpolarizability tensor component. Differences in local field factor (from the different solvents) and in geometrical factor (due to octopolar reference and dipolar unknowns) were taken into account. The high-frequency demodulation technique confirmed that there was no multiphoton fluorescence present at the second-harmonic wavelengths of 400 or 420 nm, in agreement with the one-photon spectra. The fluorescence-free hyperpolarizability values could thus be deduced as the average value of the modulation frequencies (80, 160 and 240 MHz).[8]

3. SHG Imaging

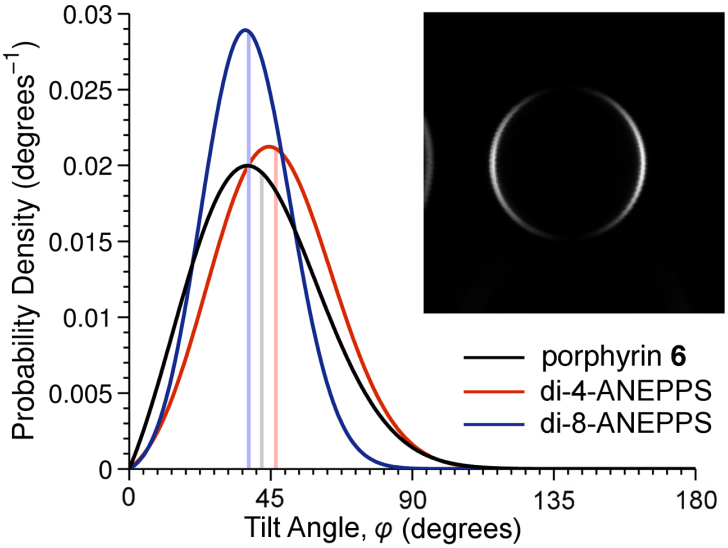


Figure S16. Tilt angle distribution for **6** (black) in droplet monolayer model membranes with tilt angle distributions of di-4-ANEPPS (red) and di-8-ANEPPS (blue) for comparison. Light vertical lines represent the tilt angle expectation value, <*φ*>. A typical SHG image of **6** is shown, inset.

The resolution of the dye tilt angle distribution was performed using a previously established method.[9] Porphyrin **6** localizes in membranes with a orientational distribution similar to that of conventional naphthylstyryl ANEPPS dyes, a configuration that is close to optimal for NLO imaging. While the mean tilt of **6** is similar to that of **di-8-ANEPPS** (<*φ*> = 38°), its ability to occupy a wider range of angles in the membrane cause an expected tilt of <*φ*> = 42°. Analogous dye **7** was not fluorescent enough to find an orientational distribution, however a brief analysis of its SHG images predict a lower tilt with <*φ*> = 37°.

4. References

1. T. Tashima, Y. Toriumi, Y. Mochizuki, T. Nonomura, S. Nagaoka, K. Furukawa, H. Tsuru, S. Adachi-Akahane and T. Ohwada, *Bioorg. Med. Chem.,* 2006, **14**, 8014.
2. H. W. Daniell, E. J. F. Klotz, B. Odell, T. D. W. Claridge and H. L. Anderson, *Angew. Chem., Int. Ed.*, 2007, **46**, 6845.
3. M. Balaz, H. A. Collins, E. Dahlstedt and H. L. Anderson, *Org. Biomol. Chem.*, 2009, **7**, 874.
4. A. C. Spivey, L. Shukla and J. F. Hayler, *Org. Lett.*, 2007, **9**, 891.
5. J. E. Reeve, H. A. Collins, K. De Mey, M. M. Kohl, K. J. Thorley, O. Paulsen, K. Clays and H. L. Anderson, *J. Am. Chem. Soc.,* 2009, **131**, 2758.
6. G. Olbrechts, R. Strobbe, K. Clays and A. Persoons, *Rev. Sci. Instrum.,* 1998, **69**, 2233.
7. K. Wostyn, K. Binnemans, K. Clays and A. Persoons, *Rev. Sci. Instrum.,* 2001, **72**, 3215.
8. J. E. Reeve, H. A. Collins, K. De Mey, M. M. Kohl, K. J. Thorley, O. Paulsen, K. Clays, H. L. Anderson, *J. Am. Chem. Soc.,* 2009, **131**, 2758.
9. J. E. Reeve, A. D. Corbett, I. Boczarow, T. Wilson, H. Bayley and H. L. Anderson, *Biophys. J.*, 2012, **103**, 907.