Supporting Information

A Panchromatic Anthracene-Fused Porphyrin Sensitizer for Dye-Sensitized Solar Cells

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Synthesis

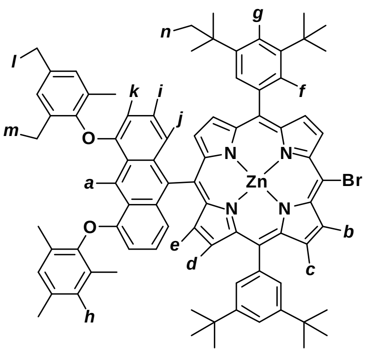
a. General Procedures

Known compounds [5-[10-(1,8-bis(2,4,6-trimethylphenyoxy)anthracene)]-10,20-bis-(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II)[1] and methyl 4-iodobenzoate[2] were synthesized according to literature procedures.

The handling of all air/ water sensitive materials was carried out using standard high vacuum techniques. Freeze-thaw degassing was affected by freezing under nitrogen, pumping under vacuum, thawing in the absence of gases then re-freezing and pumping under vacuum. This process was repeated at least three times and, on the final cycle, the flask was saturated with nitrogen. Dried DCM, toluene and THF were obtained by passing through alumina under nitrogen in the solvent purification systems and then further dried over activated molecular sieves (3 Ǻ, 8–12 mesh); diisopropylamine, was distilled from CaH_2. Unless specified otherwise all other solvents were used as commercially supplied. Where mentioned, ‘PET’ refers to 40:60 petroleum ether. Where mixtures of solvents were used, ratios are reported by volume. Flash chromatography was carried out on silica gel 60 under positive pressure. Size exclusion chromatography was carried out under gravity using cross-linked polystyrene Bio-Beads® SX-1 (200 – 400 mesh) in THF. Analytical thin layer chromatography was carried out on aluminum backed silica gel 60 F254 plates. Visualization was achieved using UV light when necessary. All UV-Vis spectra were recorded in solution using a Perkin-Elmer Lambda 20 spectrometer (1 cm path length quartz cell). UV-vis-NIR spectra were recorded using a Perkin-Elmer Lambda 9 photospectrometer. NMR spectra were recorded at room temperature using Bruker AV400 (400/100 MHz), Bruker AVC500 (500/125 MHz) and Bruker AV(700/175 MHz) instruments. ^1H and ^{13}C NMR spectra are reported in parts per million (ppm) relative to tetramethylsilane (δ_H 0.00); coupling constants (J) are given in Hertz and are quoted to the nearest 0.1 Hz and are accurate to ±0.4 Hz. MALDI-TOF mass spectrometry was carried out using a Micromass MALDI micro MX spectrometer with dithranol matrix. Only molecular ions and major peaks are reported.

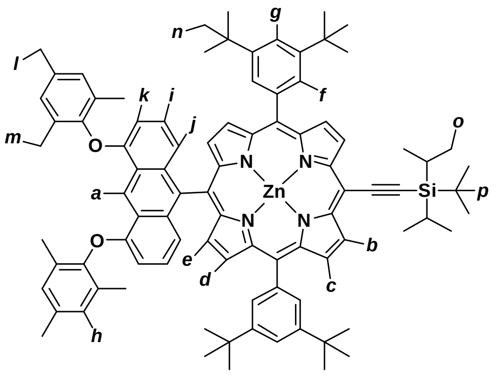
b. Synthesis

[5-Bromo-15-[10-(1,8-bis(2,4,6-trimethylphenyoxy)anthracene)]-10,20-bis-(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) (2)



To a solution of [5-[10-(1,8-bis(2,4,6-trimethylphenyoxy)anthracene)]-10,20-bis-(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) **1** (0.200 g, 0.167 mmol) in $CHCl_3$/1% pyridine (150 mL) was added drop-wise whilst stirring, a solution of *N*-bromosuccinimide (0.033 g, 0.185 mmol) in $CHCl_3$/1% pyridine (50 mL). The extent of the reaction was monitored by TLC. At completion (30 min), acetone (100 mL) was added and the reaction mixture was stirred for a further 10 min. The solvents were then removed and the product was precipitated from DCM/methanol to yield bromoporphyrin **2** (0.203 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$/ pyridine-d_5) δH 10.23 (s, 1H, H_a), 9.72 (d, 2H, J = 4.7 Hz, H_b), 8.95 (d, 2H, J = 4.7 Hz, H_c), 8.71 (d, 2H, J = 4.7 Hz, H_d), 8.33 (d, 2H, J = 4.7 Hz, H_e), 8.00 (d, 4H, J = 1.9 Hz, H_f), 7.74 (t, 2H, J = 1.9 Hz, H_g), 6.99 (s, 4H, H_h), 6.62 (dd, 2H, J_1 = 7.3 Hz, J_2 = 9.1 Hz, H_i), 6.45 (d, 2H, J = 9.1 Hz, H_j), 6.24 (d, 2H, J = 7.3 Hz, H_k), 2.34 (s, 6H, H_l), 2.30 (s, 12H, H_m), 1.49 (s, 36H, H_n) ^{13}C NMR (125 MHz, $CDCl_3$/ pyridine-d_5) δC 153.9, 151.6, 151.0, 150.4, 149.3 (x 2), 148.3, 142.0, 136.7, 136.6, 134.5, 133.1, 132.9, 132.2, 131.9, 131.1, 129.8, 129.6, 125.3, 123.3, 122.5, 121.8, 120.6, 116.6, 116.5, 104.2, 103.5, 35.0, 31.7, 20.9, 16.4. λ_{max} / nm ($CHCl_3$/ 1% pyridine) (log ε) 416 (4.73) shoulder, 436 (5.69), 570 (4.28), 610 (4.07). (MALDI TOF MS+) 1273.26 ($C_{80}H_{79}O_2N_4ZnBr$; [M]+, requires 1273.48). Anal. calc. for $C_{80}H_{79}O_2N_4ZnBr$: C 75.43, H 6.25, N 4.40. Found: C 75.39, H 6.15, N 4.37.

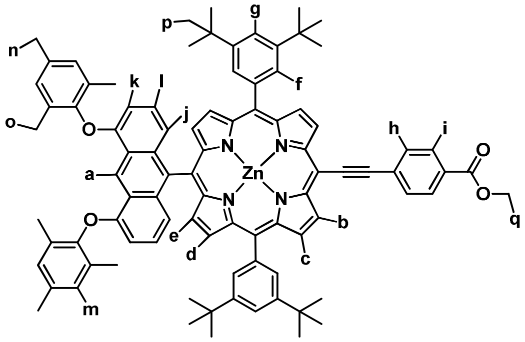
[5-(Triisopropylsilylacetylene)-15-[10-(1,8-bis(2,4,6-trimethylphenyoxy)anthracene)]-10,20-bis-(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) (3)



A 2-necked flask was dried under vacuum and charged with [5-bromo-15-[10-(1,8-bis(2,4,6-trimethylphenyoxy)anthracene)]-10,20-bis-(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) **2** (0.200 g, 0.157 mmol), CuI (0.006 g, 0.032 mmol), PPh_3 (0.033 g, 0.126 mmol) and $Pd_2(dba)_3$ (0.029 g, 0.032 mmol). These compounds were dried for a further 3 h under vacuum then purged with nitrogen. To this was added dry toluene (9.0 mL) and freshly distilled diisopropylamine (3.0 mL). The reaction mixture was freeze-thaw degassed and the TIPS-acetylene (0.88 mL, 3.92

mmol) was added by syringe. The reaction mixture was heated to 80 °C and the extent of the reaction was monitored by TLC. At completion (3 h), the reaction mixture was allowed to cool and the solvents were removed. The residue was purified by silica gel chromatography (1:1 DCM:PET) and precipitated (DCM/methanol) to yield porphyrin **3** as a purple powder (0.177 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δH 10.28 (s, 1H, H_a), 9.85 (d, 2H, J = 4.5 Hz, H_b), 9.05 (d, 2H, J = 4.5 Hz, H_c), 8.78 (d, 2H, J = 4.5 Hz, H_d), 8.45 (d, 2H, J = 4.5 Hz, H_e), 8.05 (d, 4H, J = 1.9 Hz, H_f). 7.76 (t, 2H, J = 1.9 Hz, H_g), 7.01 (s, 4H, H_h), 6.75 (dd, 2H, J_1 = 7.3 Hz, J_2 = 8.9 Hz, H_i), 6.63 (d, 2H, J = 8.9 Hz, H_j), 6.29 (d, 2H, J = 7.3 Hz, H_k), 2.36 (s, 6H, H_l), 2.34 (s, 12H, H_m), 1.51 (s, 36H, H_n), 1.49-1.46 (m, 21H, H_{o+p}) ^{13}C NMR (125 MHz, $CDCl_3$) δC 154.0, 152.5, 151.2, 150.6, 150.4, 149.3, 148.6, 141.3, 136.6, 135.8, 134.5, 133.2, 132.8, 132.1, 131.1, 130.9, 129.6, 129.4, 125.7, 123.5, 123.2, 121.8, 120.9, 118.4, 116.9, 109.5, 103.7, 100.5, 97.6, 35.0, 31.7, 20.9, 19.2, 16.4, 11.9. λ_{max} / nm ($CHCl_3$) (log ε) 416 (4.71) shoulder, 435 (5.66), 564 (4.26), 604 (4.16). (MALDI TOF MS+) 1375.73 ($C_{91}H_{100}O_2N_4ZnSi$; [M]+, requires 1375.70). Anal. calc. for $C_{91}H_{100}O_2N_4ZnSi$: C 79.47, H 7.33, N 4.07. Found: C 79.57, H 7.45, N 3.98.

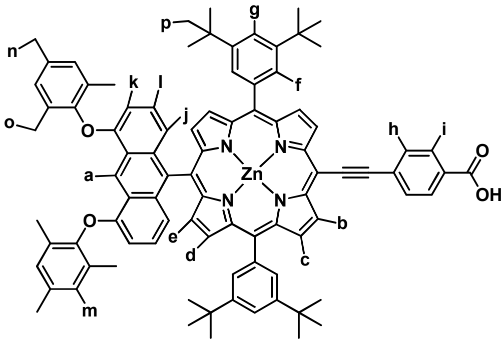
[5-(Methyl-4-ethynylbenzoate)-15-[10-(1,8-bis(2,4,6-trimethylphenyoxy)anthracene)]-10,20-bis-(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) (4)



A 2-necked flask was dried under vacuum and charged with [5-(triisopropylsilylacetylene)-15-[10-(1,8-bis(2,4,6-trimethylphenyoxy)anthracene)]-10,20-bis-(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) **3** (0.050 g, 0.036 mmol), methyl 4-iodobenzoate (0.048 g, 0.183 mmol), CuI (0.001 g, 0.007 mmol), PPh_3 (0.008 g, 0.029 mmol) and $Pd_2(dba)_3$ (0.007 g, 0.007 mmol). These compounds were dried for a further 3 h under vacuum then purged with nitrogen. To this was added dry THF (3.0 mL) and freshly distilled diisopropylamine (2.0 mL). The reaction mixture was freeze-thaw degassed three times and purged with nitrogen. To this was added TBAF (1.0 M in THF, 0.037 mL, 0.037 mmol) by syringe and the reaction mixture was warmed to 50 °C and stirred. The extent of the reaction was monitored by TLC. At completion (3 h) the mixture was allowed to cool and the solvents were removed. The solid residue was dissolved in DCM and passed over a short silica plug (DCM). The solvents were again removed and the solid residue was dissolved in toluene/ 1% pyridine and passed through a short size exclusion column to remove excess iodo-benzoic ester. The solvents were removed and the residue was precipitated from DCM/methanol to yield porphyrin **4** as a green powder (0.036 g, 74%). ^{1}H NMR (500 MHz, $CDCl_3$/ pyridine-d_5) δH 10.22 (s, 1H, H_a), 9.78

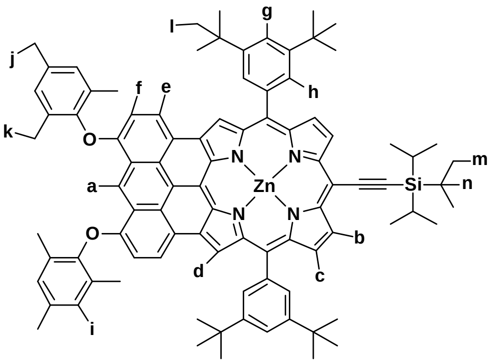
(d, 2H, J = 4.6 Hz, H_b), 8.98 (d, 2H, J = 4.6 Hz, H_c), 8.68 (d, 2H, J = 4.6 Hz, H_d), 8.31 (d, 2H, J = 4.6 Hz, H_e), 8.22 (d, 2H, J = 8.5 Hz, H_i), 8.08 (d, 2H, J = 8.5 Hz, H_h), 8.01 (d, 4H, J = 1.8 Hz, H_f), 7.74 (t, 2H, J = 1.8 Hz, H_g), 6.98 (s, 4H, H_m), 6.63 (dd, 2H, J_1 = 7.3 Hz J_2 = 9.0 Hz, H_l), 6.47 (d, 2H, J = 9.0 Hz, H_j), 6.24 (d, 2H, J = 7.3 Hz, H_k), 3.99 (s, 3H, H_q), 2.33 (s, 6H, H_n), 2.30 (s, 12H, H_o), 1.49 (s, 36H, H_p). ^{13}C NMR (125 MHz, $CDCl_3$/ pyridine-d_5) δC 166.7, 154.0, 152.1, 151.3, 150.8, 150.4, 149.3, 148.7, 141.2, 136.5, 135.7, 134.5, 133.3, 132.9, 132.3, 131.3, 131.1, 130.5, 129.8, 129.7 (x2), 129.2, 129.1, 125.7, 123.6, 123.5, 121.7, 121.0, 118.9, 117.0, 103.7, 99.4, 96.1, 95.5, 52.2, 35.0, 31.7, 20.9, 16.4. λ_{max} / nm ($CHCl_3$) (log ε) 445 (5.89), 568 (4.53), 615 (4.74). (MALDI TOF MS+) 1353.46 ($C_{90}H_{86}N_4O_4Zn$; [M]+, requires 1353.60). Anal. calc. for $C_{90}H_{86}N_4O_4Zn$: C 79.89, H 6.41, N 4.14. Found: C 79.95, H 6.48, N 4.21.

[5-(4-Ethynylbenzoic acid)-15-[10-(1,8-bis(2,4,6-trimethylphenyoxy)anthracene)]-10,20-bis-(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) (P2)



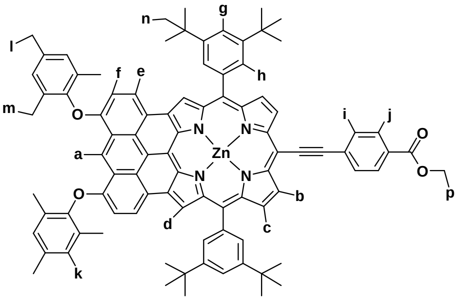
To a solution of [5-(methyl-4-ethynylbenzoate)-15-[10-(1,8-bis(2,4,6-trimethylphenyoxy)anthracene)]-10,20-bis-(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) **4** (0.020 g, 0.015 mmol) in THF (5.0 mL) was added methanol (3.0 mL) and sodium hydroxide solution (aq) (8.0 M, 1.0 mL, 8.00 mmol). The reaction mixture was stirred at room temperature and the extent of the reaction was monitored by TLC. At completion (5 h) water (10.0 mL) was added to the mixture together with acetic acid (1.0 mL). The organic layer was extracted with DCM and washed with water (3 × 10 mL). The solvent was then removed and solid residue was dissolved in DCM and precipitated from DCM/pentane to yield porphyrin **P2** as a green solid (0.016 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$/ methanol-d_4) δH 10.25 (s, 1H, H_a), 9.81 (d, 2H, J = 4.6 Hz, H_b), 9.02 (d, 2H, J = 4.6 Hz, H_c), 8.71 (d, 2H, J = 4.6 Hz, H_d), 8.37 (d, 2H, J = 4.6 Hz, H_e), 8.25 (d, 2H, J = 8.2 Hz, H_i), 8.11 (d, 2H, J = 8.2 Hz, H_h), 8.05 (d, 4H, J = 1.8 Hz, H_f), 7.75 (t, 2H, J = 1.8 Hz, H_g), 6.99 (s, 4H, H_m), 6.73 (dd, 2H, J_1 = 7.3 Hz, J_2 = 8.9 Hz, H_l), 6.63 (d, 2H, J = 8.9 Hz, H_j), 6.27 (d, 2H, J = 7.3 Hz, H_k), 2.34 (s, 6H, H_n), 2.32 (s, 12H, H_o), 1.50 (s, 36H, H_p). ^{13}C NMR (125 MHz, $CDCl_3$/methanol-d_4) 168.5, 157.2, 153.7, 150.0, 149.9, 148.9 (x 2), 145.2, 141.7, 135.1, 134.7, 133.3, 131.0, 130.9, 130.1, 129.9, 129.6 (x 2), 129.5, 129.4, 128.8, 127.7, 125.6, 124.9, 123.7, 122.8, 120.8, 120.3, 118.9, 111.6, 107.6, 97.4, 96.7, 94.8, 35.1, 31.8, 20.9, 16.4. λ_{max} / nm ($CHCl_3$/1% pyridine) (log ε) 453 (5.69), 584 (4.18), 639 (4.67). m.p. > 300 °C. (MALDI TOF MS+) 1339.58 ($C_{89}H_{84}O_4N_4Zn$; [M]+, requires 1339.59).

[5-(Triisopropylsilylacetylene)-13,15,17-[4,5,10-(1,8-bis(2,4,6-trimethylphenyoxy)anthracene)]-10,20-bis-(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) (5)



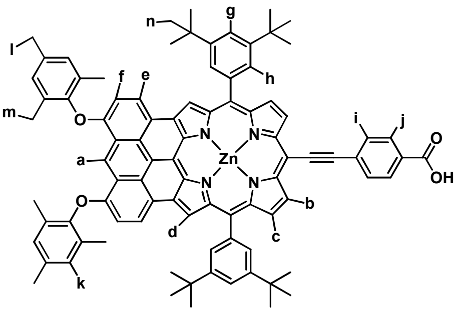
This novel compound was prepared by modification of literature fusion conditions.[1] To a solution of [5-(triisopropylsilylacetylene)-15-[10-(1,8-bis(2,4,6-trimethylphenyoxy)anthracene)]-10,20-bis-(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) **3** (0.010 g, 0.007 mmol) and zinc(II) chloride (0.050 g, 0.370 mmol) in dry DCM (3.0 mL) was added $FeCl_3$ (0.012 g, 0.074 mmol) in dry nitromethane (1.0 mL) and the reaction mixture was stirred under nitrogen. After 30 min 1,8-bis(dimethylamino)naphthalene (proton sponge) was added (0.016 g, 0.074 mmol) and the mixture was stirred for another 30 min. After this time $FeCl_3$ (0.012 g, 0.074 mmol) in nitromethane (1.0 mL) was added and the mixture was stirred for a further 30 min after which time 1,8-bis(dimethylamino)naphthalene (0.016 g, 0.074 mmol) was again added. This $FeCl_3$/1,8-bis(dimethylamino)naphthalene cycle was repeated for a third time, with a 30 min interval between addition of the two different reagents. Saturated $NaHCO_3$ (aq, 10 mL) was then added to quench the reaction. The organic layer was separated and washed with water (3 × 10 mL). The organic layer was collected and the solvents removed. The solid residue was purified by silica gel chromatography (2:1 PET:DCM) and precipitated from DCM/methanol to yield porphyrin **5** as a dark solid (0.006 g, 63%). ^1H NMR (400 MHz, $CDCl_3$/ pyridine-d_5) δH 10.27 (s, 1H, H_a), 9.43 (d, 2H, J = 4.5 Hz, H_b), 9.13 (s, 2H, H_d), 8.77 (d, 2H, J = 8.0 Hz, H_e), 8.71 (d, 2H, J = 4.8 Hz, H_c), 8.08 (d, 4H, J = 1.9 Hz, H_h), 7.80 (t, 2H, J = 1.9 Hz, H_g), 7.06 (s, 4H, H_i), 6.80 (d, 2H, J = 8.0 Hz, H_f), 2.41 (s, 6H, H_j), 2.32 (s, 12H, H_k), 1.57 (s, 36H, H_l), 1.41-1.45 (m, 21H, H_{m+n}). ^{13}C NMR (125 MHz, $CDCl_3$/ pyridine-d_5) 156.9, 154.0, 150.1, 149.9, 149.0, 148.6, 145.3, 142.1, 135.0, 134.6, 133.0, 131.0, 129.8, 129.7, 129.4, 128.9, 128.3, 125.2, 124.9, 123.8, 123.1, 120.7, 119.4, 119.0, 111.0, 110.9, 107.5, 98.1, 95.6, 35.0, 31.8, 20.9, 19.2, 16.4, 12.0. λ_{max} / nm ($CHCl_3$) (log ε) 886 (4.99), 798 (4.76), 598 (4.87), 548 (4.90), 508 (4.73), 473 (5.06), 448 (4.92), 414 (4.77), 395 (4.79), 343 (4.98), 330 (4.88). (MALDI TOF MS+) 1371.69 ($C_{91}H_{96}O_2N_4ZnSi$; [M]+, requires 1371.67).

[5-(Methyl-4-ethynylbenzoate)-13,15,17-[4,5,10-(1,8-bis(2,4,6-trimethylphenyoxy)anthracene)]-10,20-bis-(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) (6)

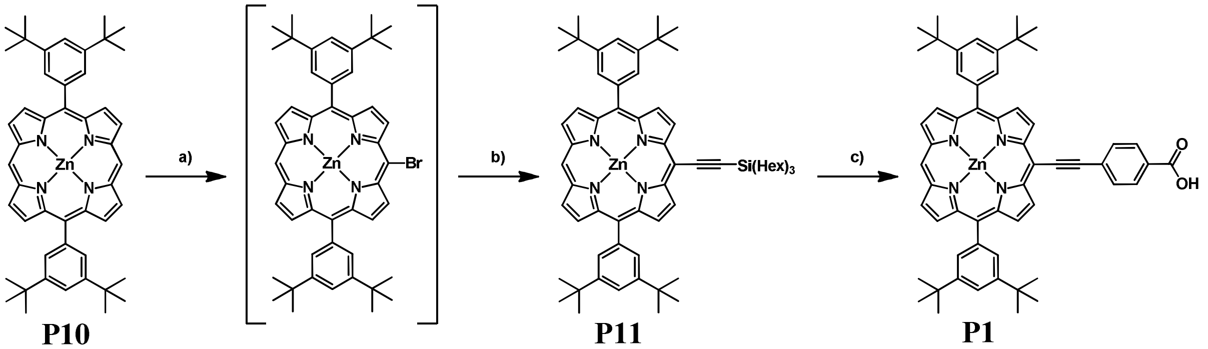


A 2-necked flask was dried under vacuum and charged with [5-(triisopropylsilylacetylene)-13,15,17-[4,5,10-(1,8-bis(2,4,6-trimethylphenyoxy)anthracene)]-10,20-bis-(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) **5** (0.032 g, 0.023 mmol), methyl 4-iodobenzoate (0.033 g, 0.125 mmol), CuI (0.001 g, 0.005 mmol), PPh$_3$ (0.005 g, 0.019 mmol) and Pd$_2$(dba)$_3$ (0.005 g, 0.005 mmol). These compounds were dried for a further 3 h under vacuum then purged with nitrogen. To this was added dry THF (3.0 mL) and freshly distilled diisopropylamine (1.5 mL). The reaction mixture was freeze-thaw degassed three times and purged with nitrogen. To this was added TBAF (1.0 M in THF, 0.026 mL, 0.026 mmol) by syringe and the reaction mixture was warmed to 50 °C and stirred. The extent of the reaction was monitored by TLC. At completion (3 h) the mixture was allowed to cool and the solvents were removed. The solid residue was dissolved in DCM and passed over a short silica plug (DCM). The solvents were again removed and the solid residue was dissolved in toluene/ 1% pyridine and passed through a short size exclusion column (toluene/1% pyridine) to remove excess benzoic ester. The solvents were removed and the residue was precipitated from DCM/methanol to yield porphyrin **6** as a black powder (0.026 g, 83%).^{1}H NMR (400 MHz, CDCl$_3$/pyridine-d_5) δH 10.33 (s, 1H, H$_a$), 9.48 (d, 2H, J = 4.5 Hz, H$_b$), 9.19 (s, 2H, H$_d$), 8.82 (d, 2H, J = 8.1 Hz, H$_e$), 8.79 (d, 2H, J = 4.5 Hz, H$_c$), 8.20 (d, 2H, J = 8.6 Hz, H$_j$), 8.13 (d, 4H, J = 1.7 Hz, H$_h$), 8.03 (d, 2H, J = 8.6 Hz, H$_i$), 7.83 (t, 2H, J = 1.7 Hz, H$_g$), 7.07 (s, 4H, H$_k$), 6.83 (d, 2H, J = 8.1 Hz, H$_f$), 4.00 (s, 3H, H$_p$), 2.42 (s, 6H, H$_l$), 2.33 (s, 12H, H$_m$), 1.60 (s, 36H, H$_n$). ^{13}C NMR (125 MHz, CDCl$_3$/pyridine-d_5) δC 166.8, 157.1, 153.7, 150.1, 150.0, 149.0, 148.8, 145.3, 142.0, 135.1, 134.7, 133.2, 131.0, 129.9, 129.8, 129.7 (x 2), 129.3, 129.2, 128.6, 128.1, 125.7, 124.9, 123.8, 123.2, 123.0, 120.7, 119.9, 119.0, 111.5, 107.6, 98.0, 96.5, 94.7, 52.2, 35.1, 31.8, 20.9, 16.4. λ_{max} / nm (CHCl$_3$) (log ε) 418 (4.55), 490 (5.00), 565 (4.60), 609 (4.63), 755 (4.16), 829 (4.56), 925 (4.80). *m/z* (MALDI TOF MS+) 1349.55 ($C_{90}H_{82}N_4O_4Zn$; [M]+, requires 1349.57). Anal. calc. for $C_{90}H_{82}N_4O_4Zn$: C 80.13, H 6.13, N 4.15. Found: C 80.22, H 6.06, N 4.06.

[5-(4-Ethynylbenzoic acid)-13,15,17-[4,5,10-(1,8-bis(2,4,6-trimethylphenyoxy)anthracene)]-10,20-bis-(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) (P3)

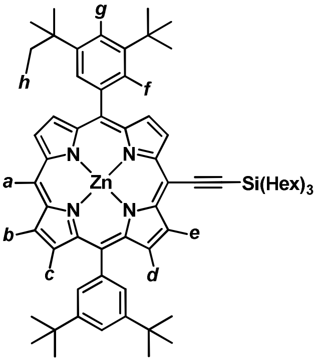


To a solution of [5-(methyl-4-ethynylbenzoate)-13,15,17-[4,5,10-(1,8-bis(2,4,6-trimethylphenyoxy)anthracene)]-10,20-bis-(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) **6** (0.018 g, 0.013 mmol) in THF (5.0 mL) was added methanol (3.0 mL) and sodium hydroxide solution (aq, 8 M, 1.0 mL, 8.00 mmol). The reaction mixture was stirred at room temperature and the extent of the reaction was monitored by TLC. At completion (5 h) water (10 mL) was added to the mixture together with acetic acid (1.0 mL). The organic layer was extracted with DCM and washed with water (3 × 10 mL). The solvent was then removed and solid residue was dissolved in DCM and precipitated from pentane to yield porphyrin **P3** as a black solid (0.015 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$/ methanol-d_4) δH 10.36 (s, 1H, H_a), 9.49 (d, 2H, J = 4.6 Hz, H_b), 9.21 (s, 2H, H_d), 8.85 (d, 2H, J = 8.0 Hz, H_e), 8.80 (d, 2H, J = 4.6 Hz, H_c), 8.21 (d, 2H, J = 8.3 Hz, H_j), 8.15 (d, 4H, J = 1.8 Hz, H_h), 8.03 (d, 2H, J = 8.3 Hz, H_i), 7.84 (t, 2H, J = 1.8 Hz, H_g), 7.06 (s, 4H, H_k), 6.85 (d, 2H, J = 8.0 Hz, H_f), 2.41 (s, 6H, H_l), 2.33 (s, 12H, H_m), 1.59 (s, 36 H, H_n).^{13}C NMR (125 MHz, $CDCl_3$/ methanol-d_4) δC 168.5, 157.2, 153.7, 150.0, 149.8, 148.9 (× 2), 145.1, 141.7, 135.1, 134.6, 133.3, 131.0, 130.9, 130.1, 129.8, 129.6, 129.5, 129.4, 129.0, 127.7, 125.6, 124.8, 123.7, 122.7, 120.8, 120.3, 118.9, 111.5, 107.6, 97.3, 96.6, 94.8, 35.0, 31.7, 20.9, 16.3 (1 aromatic signal missing; probably overlapping with other signals, unidentifiable by HSQC/DEPT). λ_{max} / nm ($CHCl_3$/1% pyridine) (log ε) 418 (4.55), 488 (5.00), 565 (4.60), 609 (4.63), 757 (4.16), 829 (4.56), 924 (4.80). (MALDI TOF MS+) 1335.57 ($C_{89}H_{80}O_4N_4Zn$; [M]+, requires 1335.56).



Scheme S1: Synthesis of **P1** from known compound **7**. a) *N*-Bromosuccinimide (1.05 eq.), $CHCl_3$, pyridine, r.t, 15 min. b) Trihexylsilylacetylene, $Pd_2(dba)_3$, CuI, PPh_3, THF, toluene, NEt_3, 40 °C, 17 h, 40% (over 2 steps). c) 4-Iodobenzoic acid, TBAF, $Pd_2(dba)_3$, CuI, PPh_3, THF, NEt_3, 50 °C, 2 h, 60%.

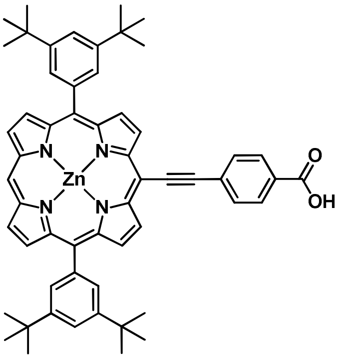
[5-(Trihexylsilylethynyl)-10,20-bis(3,5-di-*tert*-butylphenyl)-porphyrinato] zinc(II) (8)



10,20-Bis(3,5-di-tert-butylphenyl)-porphyrinato] zinc(II) **7** (500 mg, 0.67 mmol) was dissolved in chloroform (36 mL) and pyridine (0.25 mL). *N*-Bromosuccinimide (130 mg, 0.73 mmol) was dissolved in chloroform (36 mL) and pyridine (0.25 mL). The *N*-bromosuccinimide solution was added drop-wise to the porphyrin solution and the mixture stirred for 15 min. Acetone was added to quench the excess *N*-bromosuccinimide. The solution was concentrated and passed through a short silica plug, eluting with dichloromethane. The solvents were removed and the crude mix of mono- and bis-brominated products used without further purification. The mix of products (560 mg), Pd$_2$(dba)$_3$ (79 mg, 0.087 mmol), PPh$_3$ (170 mg, 0.63 mmol) and CuI (63 mg, 0.33 mmol) were dried under vacuum in pre-dried glassware. The vessel was pump degassed and purged 3 times with N$_2$. Tetrahydrofuran (18 mL), dry triethylamine (18 mL) and dry toluene (18 mL) were added via syringe and the mixture degassed successively. Trihexylsilylacetylene (340 mg, 1.1 mmol) was added via syringe and the mixture stirred at 40 °C for 17 h. The solution was concentrated then the residue passed through a short silica plug eluting with tetrahydrofuran. The solvent was removed, the residue redissolved in a small volume of tetrahydrofuran (< 4.0 mL), and passed through a SEC column eluting with tetrahydrofuran. The collected fractions containing a mixture of products were columned a second time. The desired fractions were concentrated then precipitation from dichloromethane/methanol yielded porphyrin **8** as a green solid (279 mg, 40% over two steps).

^{1}H NMR (400 MHz, CDCl$_3$/d$_5$ pyridine) 10.09 (s, 1 H, H_a), 9.75 (d, 2 H, J = 4.4 Hz, H_e), 9.27 (d, 2 H, J = 4.4 Hz, H_b), 8.99 (d, 4 H, J = 4.6 Hz, $H_{c,d}$), 8.06 (d, 4 H, J = 1.7 Hz, H_f), 7.80 (t, 2 H, J = 1.9 Hz, H_g), 0.57 - 1.83 (m, 147 H, H_h, hexyl). ^{13}C NMR (126 MHz, CDCl$_3$/d$_5$ pyridine) 152.2, 150.7, 150.0, 149.2, 142.0, 132.7, 132.3, 131.4, 130.5, 129.9, 122.4, 120.6, 110.0, 107.1, 98.9, 98.2, 35.0, 33.4, 31.8, 31.7, 24.4, 22.7, 14.2, 14.0. (MALDI TOF MS+) 1056.12 ($C_{68}H_{90}N_4SiZn$; [M]+, requires 1055.63).

[15-(4-Carboxyphenylethynyl)-10,20-bis(3,5-di-*tert*-butylphenyl)-porphyrinato] zinc(II) (P1)



[5-(Trihexylsilylethynyl)-10,20-bis(3,5-di-*tert*-butylphenyl)-porphyrinato] zinc(II) **8** (60 mg, 0.057 mmol), 4-iodobenzoic acid (17 mg, 0.068 mmol), Pd$_2$(dba)$_3$ (2.6 mg, 0.0028 mmol), PPh$_3$ (2.9 mg, 0.011 mmol) and CuI (1.1 mg, 0.0057 mmol) were dried under vacuum in a pre-dried flask. The vessel was pump degassed and purged 3 times with N_2. Tetrahydrofuran (2.0 mL) and dry triethylamine (2.2 mL) were added via syringe and the mixture frozen. TBAF (1.0 M in THF, 0.28 mL, 0.28 mmol) was added via syringe and frozen. After successive freeze-thaw degas cycles, the mixture was heated to 50 °C and stirred under N_2. The reaction was removed from heat after 2 h and the solution concentrated. The residue was purified on silica eluting with chloroform containing 0–5% acetic acid. Fractions containing acetic acid were washed with 1.0 M aqueous K_2CO_3 until TLC (dichloromethane: 5% methanol) showed removal of unreacted 4-iodobenzoic acid. Precipitation from dichloromethane/heptane gave the title compound as a green solid (31 mg, 60%).

^{1}H NMR (400 MHz, d_6 dimethylsulfoxide) δH 10.28 (s, 1 H, H_a), 9.84 (d, 2 H, J = 4.6 Hz, H_e), 9.44 (d, 2 H, J = 4.4 Hz, H_b), 8.95 (d, 2 H, J = 4.6 Hz, H_d), 8.89 (d, 2 H, J = 4.4 Hz, H_c), 8.07 (d, 4 H, J = 1.5 Hz, H_f), 8.05 (d, 2 H, J = 8.3 Hz, H_j), 8.01 (d, 2 H, J = 8.2 Hz, H_i), 7.88 (t, 2 H, J = 1.6 Hz, H_g), 1.56 (s, 40 H, H_h). ^{13}C NMR (126 MHz, d_6 dimethylsulfoxide) 168.0, 150.9, 150.0, 149.2, 149.1, 148.4, 141.5, 141.4, 132.5, 132.4, 131.9, 130.5, 130.2, 129.7, 129.5, 123.2, 121.9, 120.6, 107.8, 98.7, 96.1, 93.6, 34.8, 31.6 (suspect missing carbon environment overlapping with d_5 pyridine, 148.4). λ_{max} / nm ($CHCl_3$/1% pyridine) (log ε) 445 (5.33), 577 (3.87), 629 (4.19). (MALDI TOF MS+) 893.21 ($C_{57}H_{56}O_2N_4Zn$; [M]+, requires 893.38).

Characterization

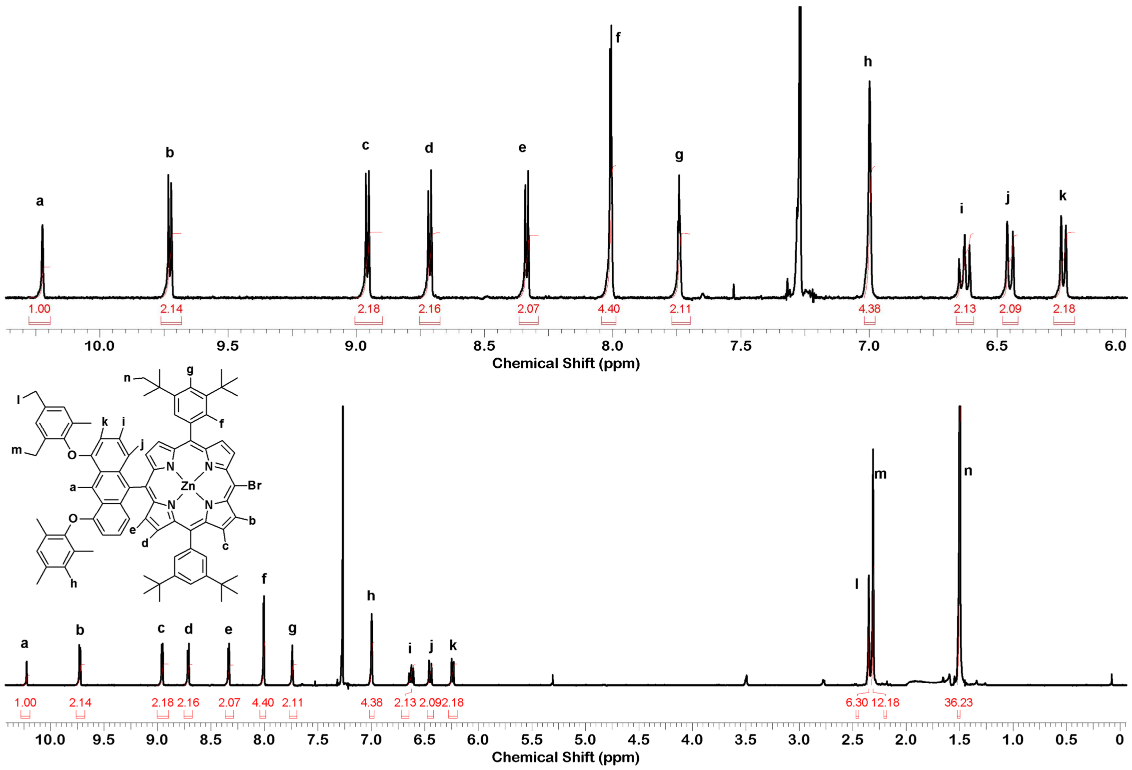


Figure S1. ^{1}H NMR spectrum of porphyrin **2** (400 MHz, CDCl3/ pyridine-d5, 298 K).

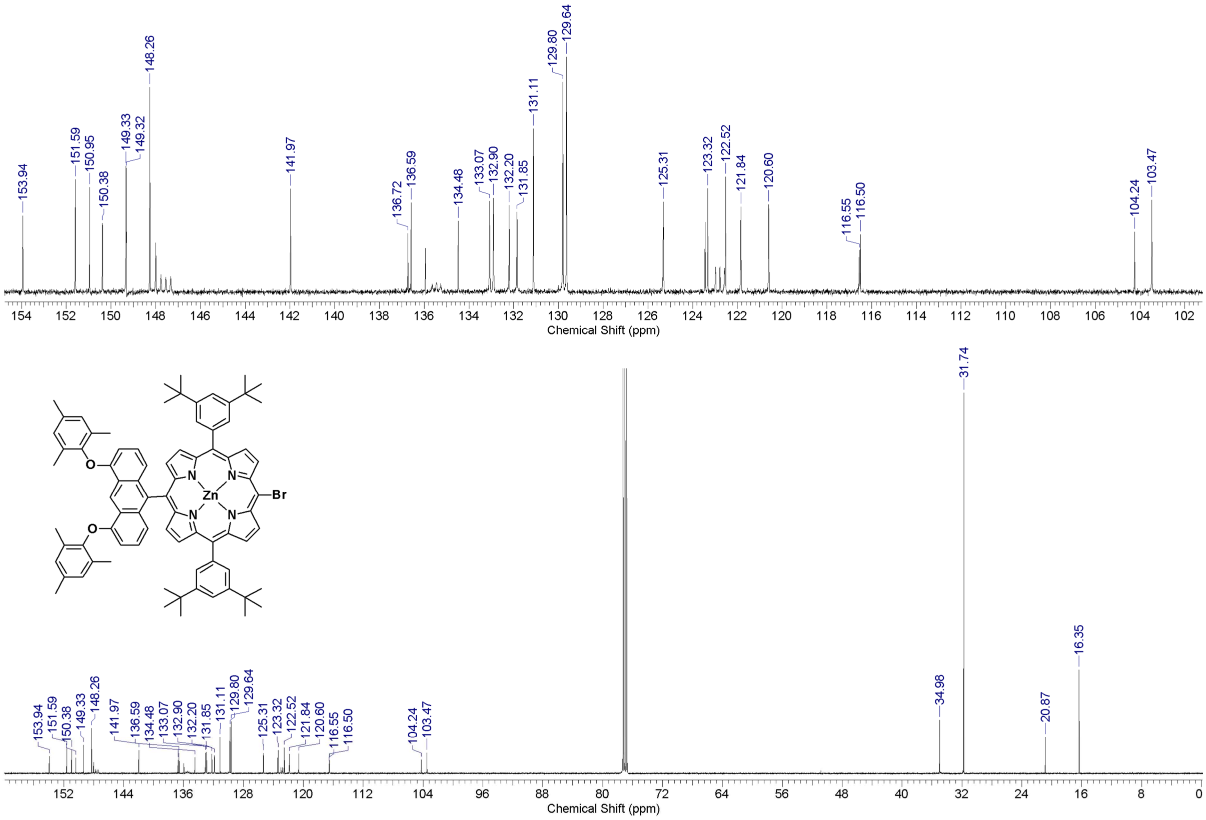


Figure S2. ^{13}C NMR spectrum of porphyrin **2** (125 MHz, CDCl3/pyridine-d5, 298 K).

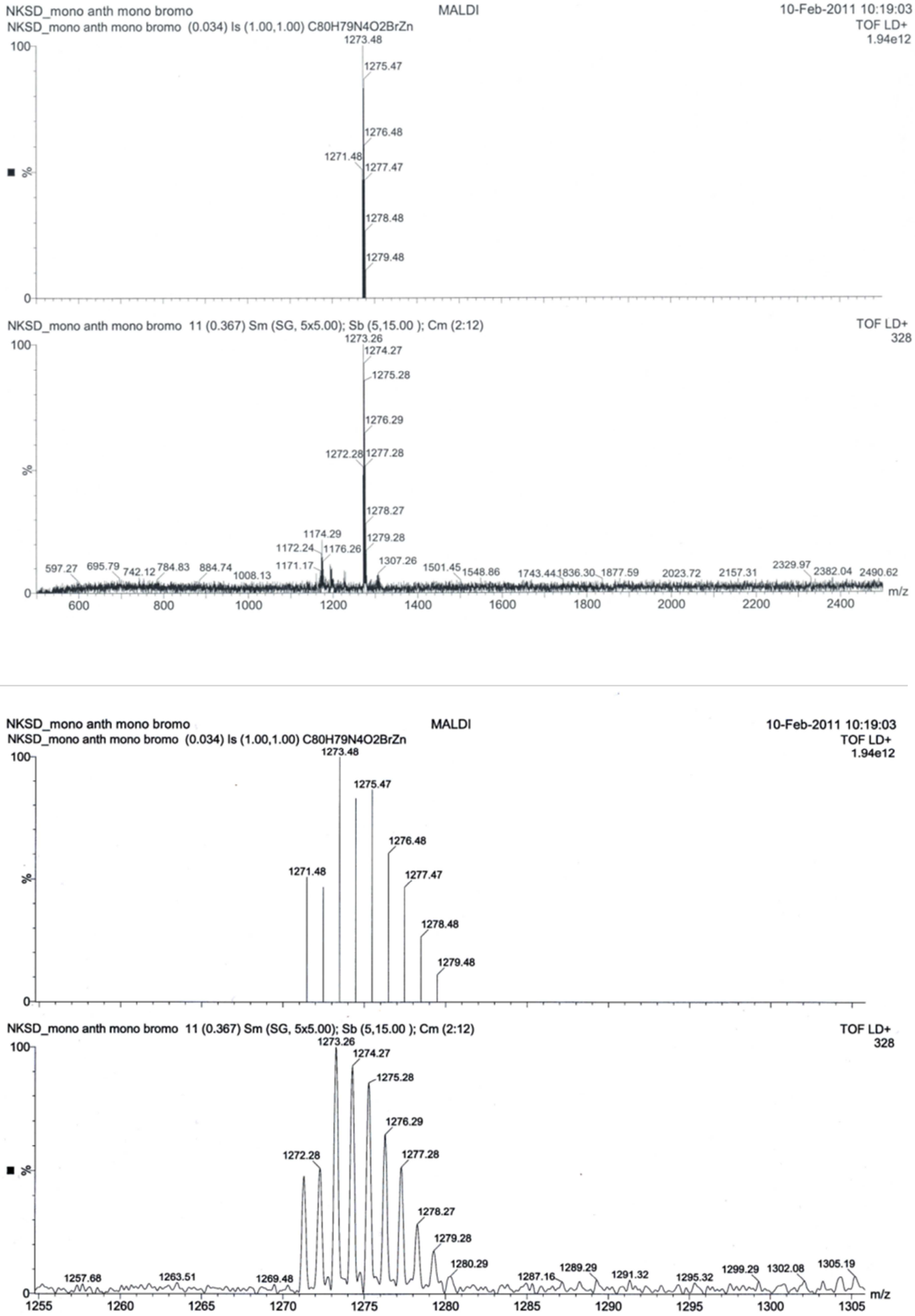


Figure S3. MALDI spectra for porphyrin **2** (upper traces: theoretical spectra; lower traces: observed spectra).

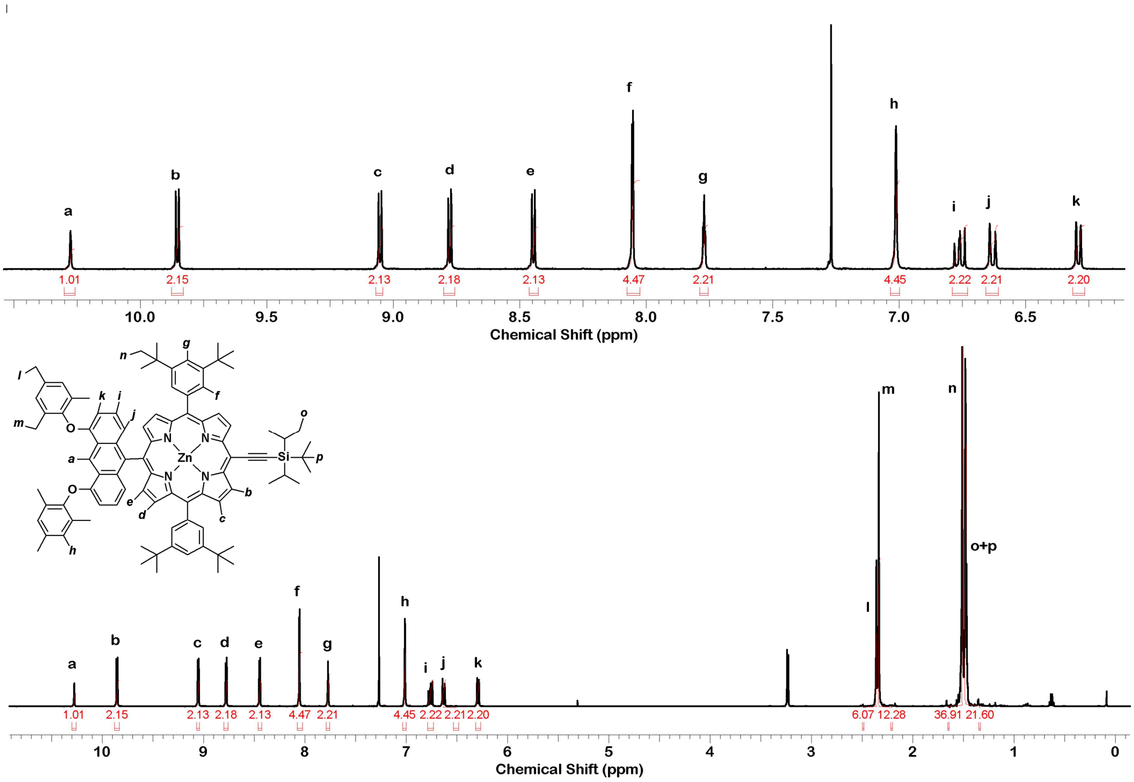


Figure S4. ^{1}H NMR spectrum of porphyrin **3** (400 MHz, $CDCl_3$, 298 K).

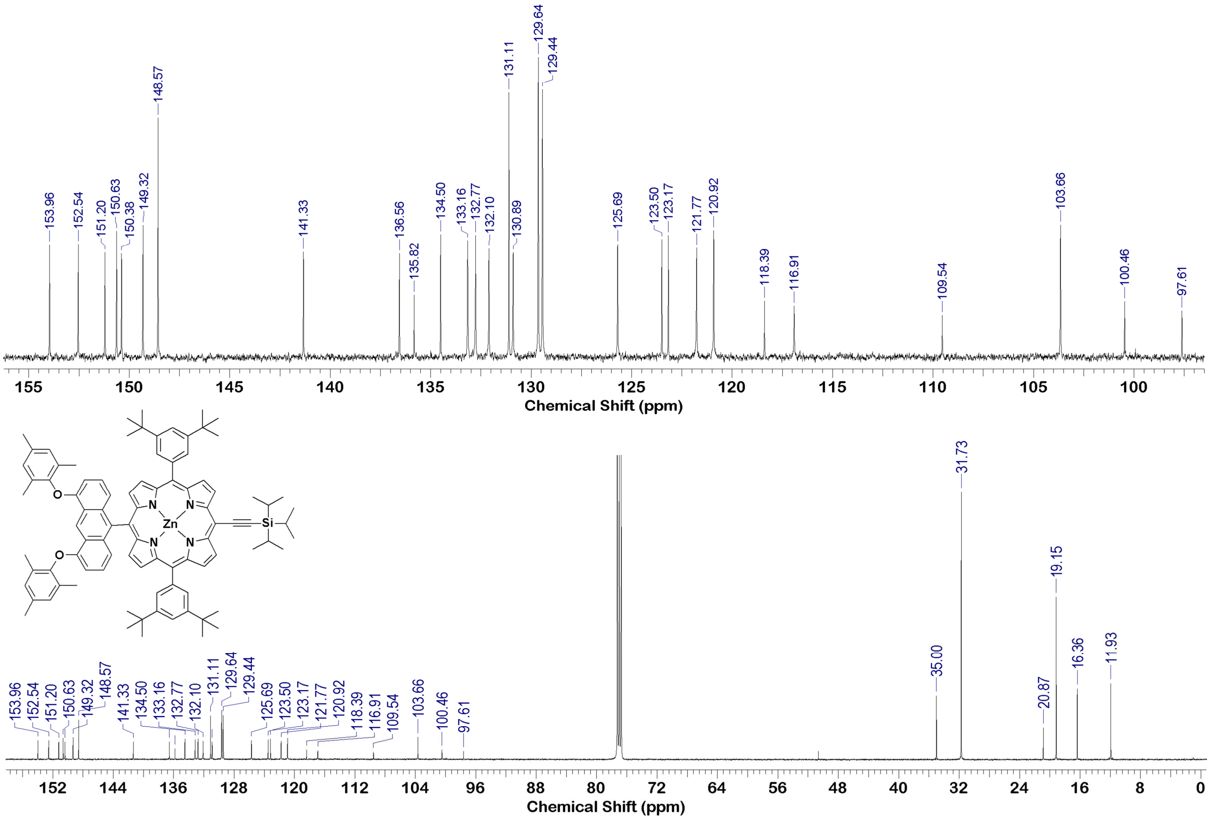


Figure S5. ^{13}C NMR spectrum of porphyrin **3** (125 MHz, $CDCl_3$, 298 K).

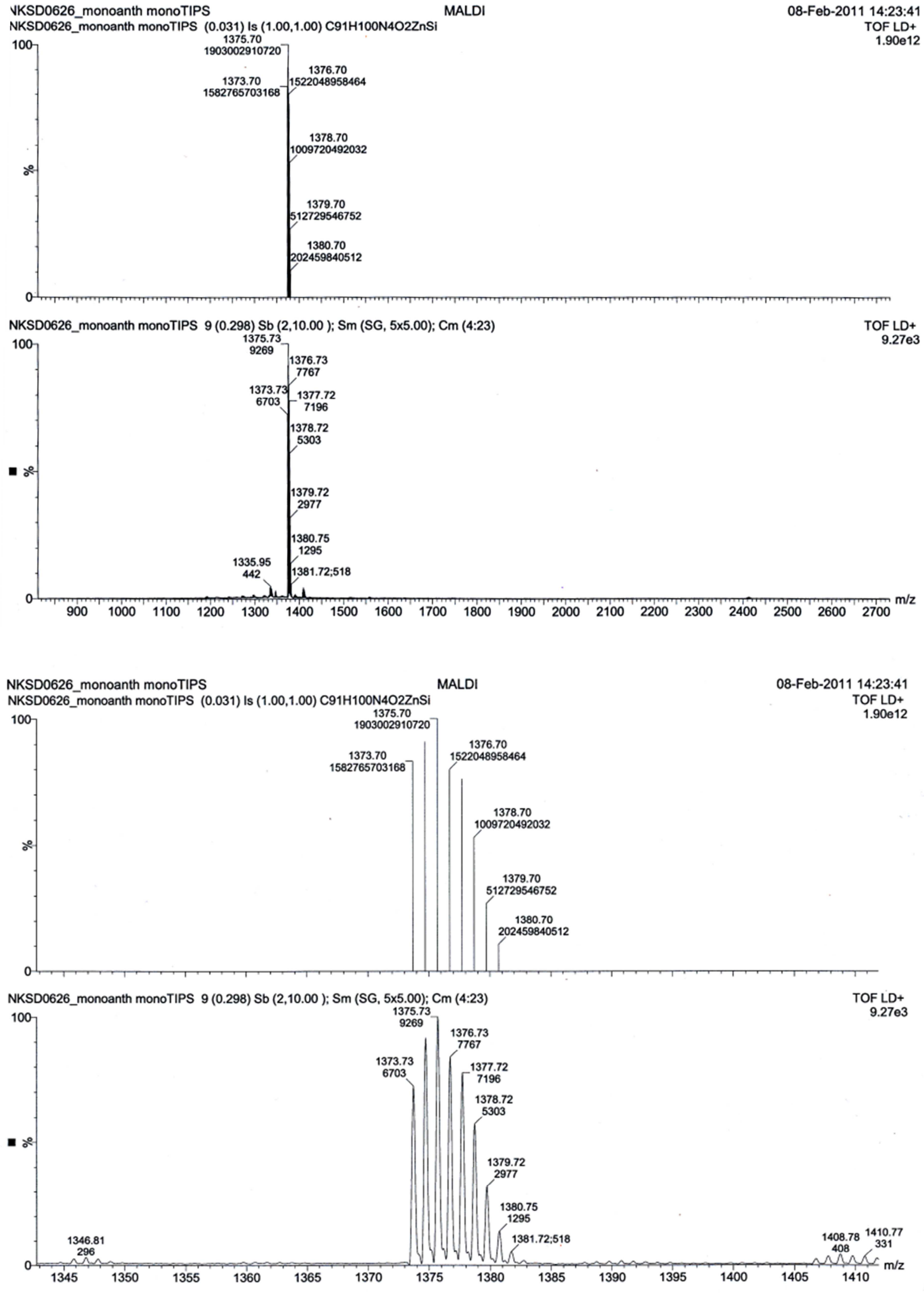


Figure S6. MALDI spectra for porphyrin **3** (upper traces: theoretical spectra; lower traces: observed spectra).

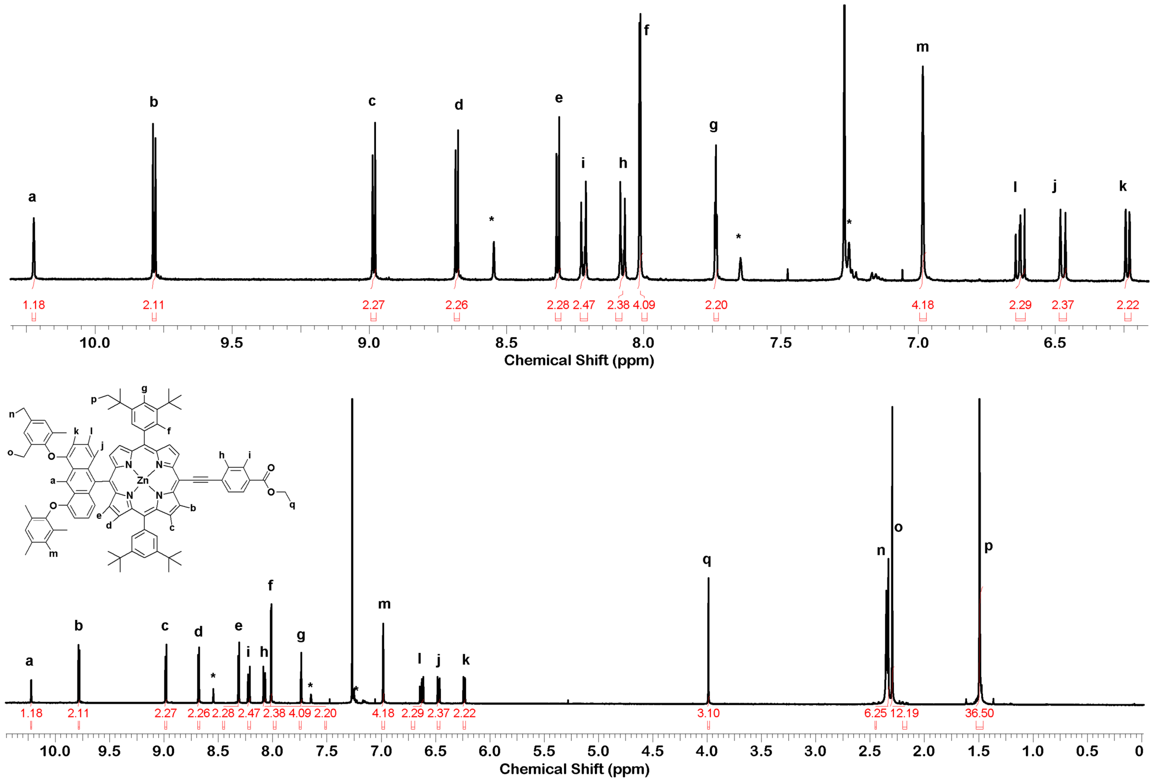


Figure S7. ^{1}H NMR spectrum of porphyrin **4** (400 MHz, $CDCl_3$/ pyridine-*d*$_5$, 298 K). * denotes pyridine signals.

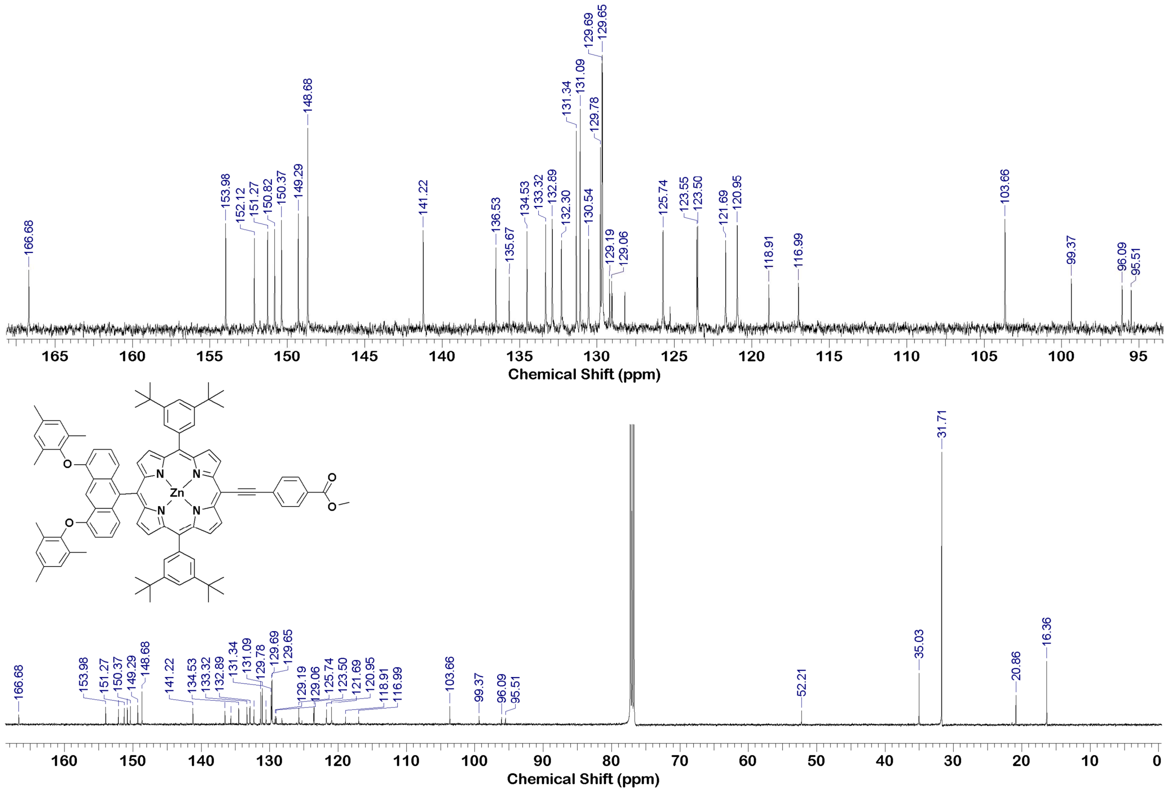


Figure S8. ^{13}C NMR spectrum of porphyrin **4** (125 MHz, $CDCl_3$/ pyridine-*d*$_5$, 298 K).

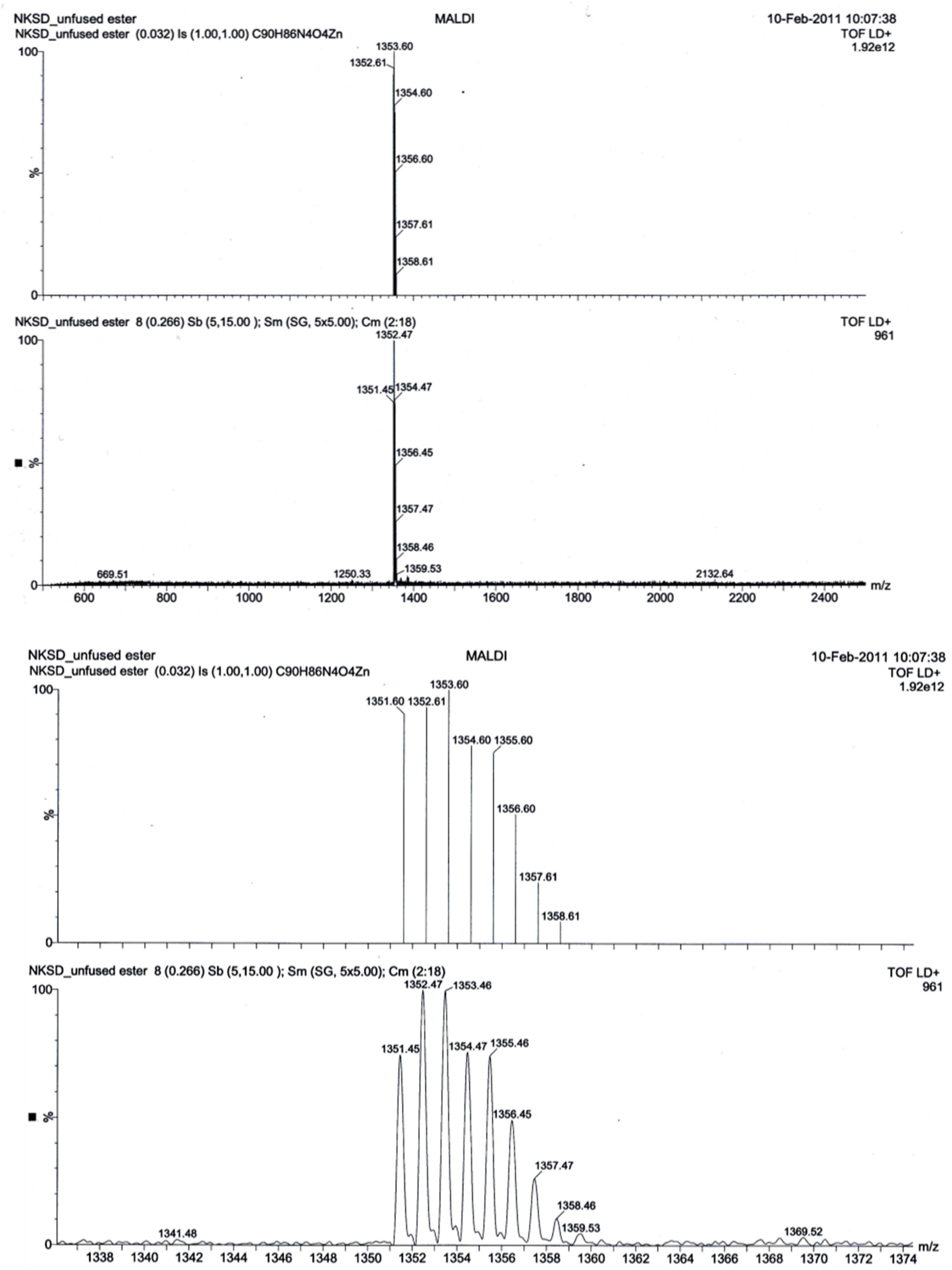


Figure S9. MALDI spectra for porphyrin **4** (upper traces: theoretical spectra; lower traces: observed spectra).

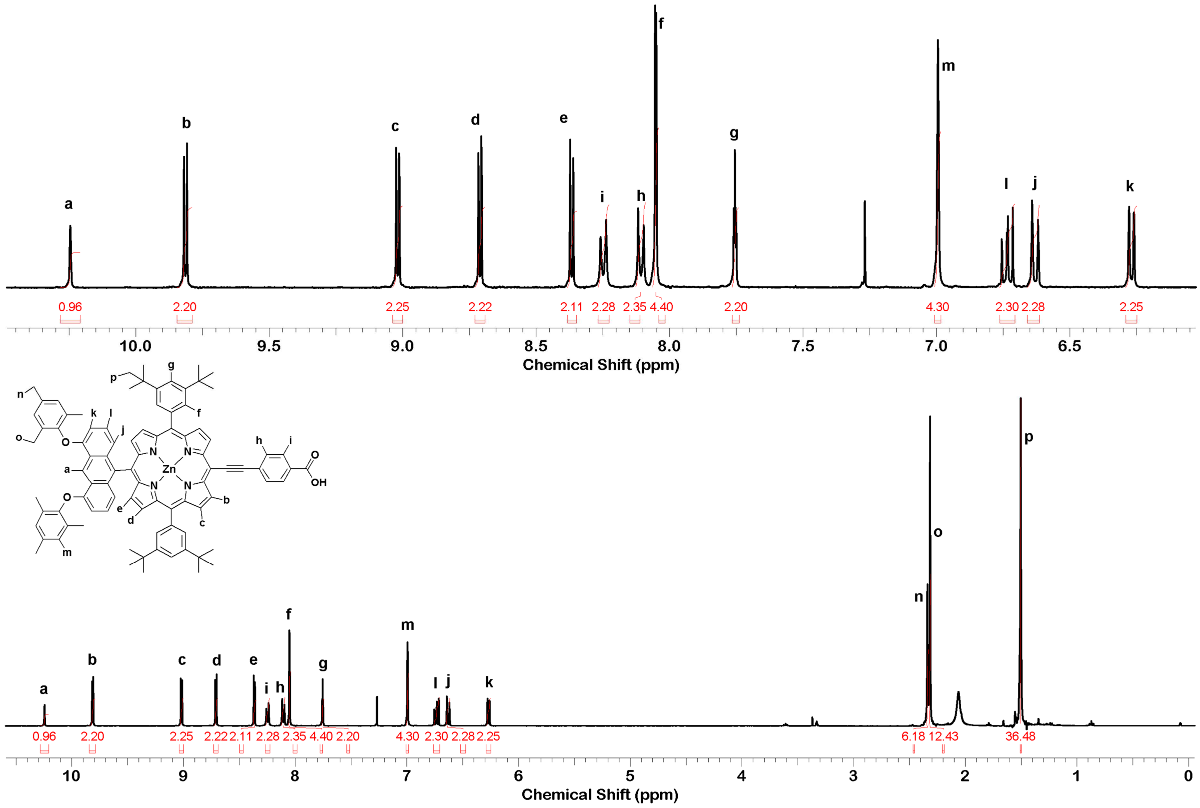


Figure S10. ^{1}H NMR spectrum of **P2** (400 MHz, CDCl$_3$/ methanol-d_4, 298 K).

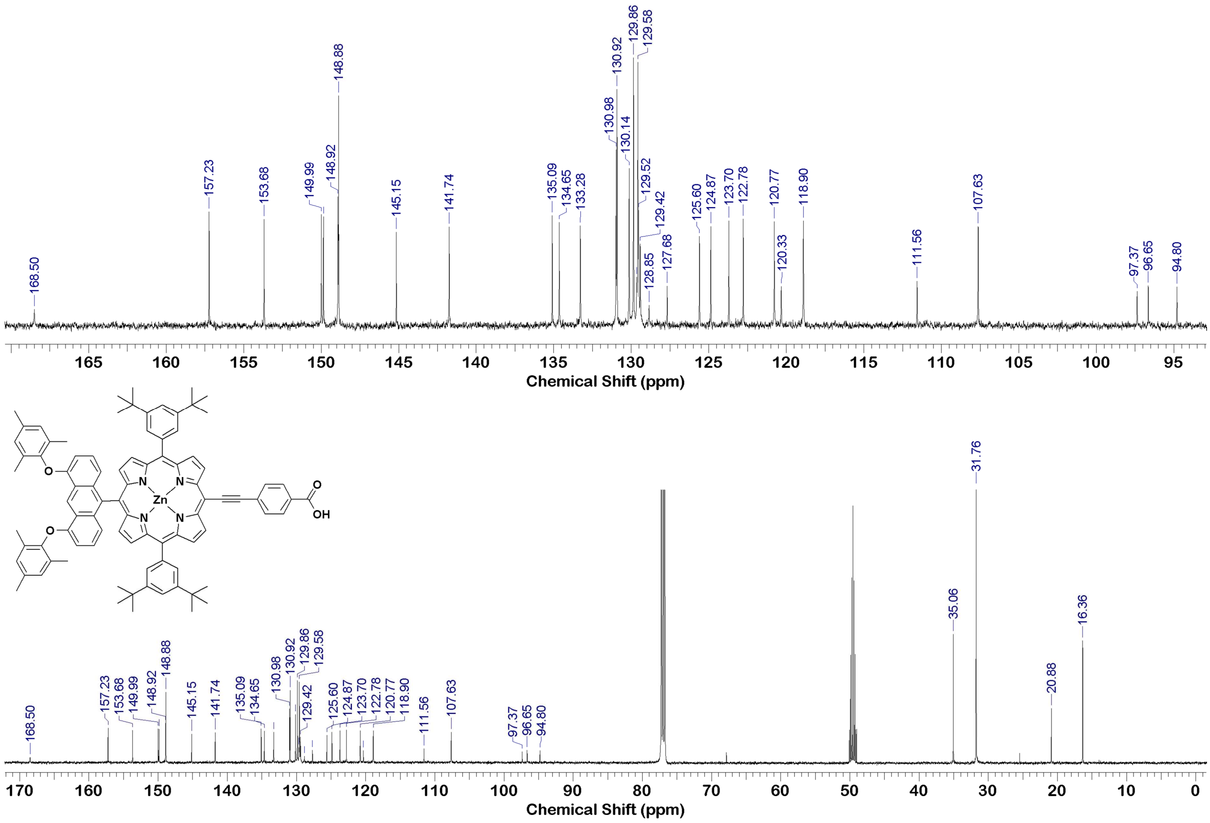


Figure S11. ^{13}C NMR spectrum of **P2** (125 MHz, CDCl$_3$/ methanol-d_4, 298 K).

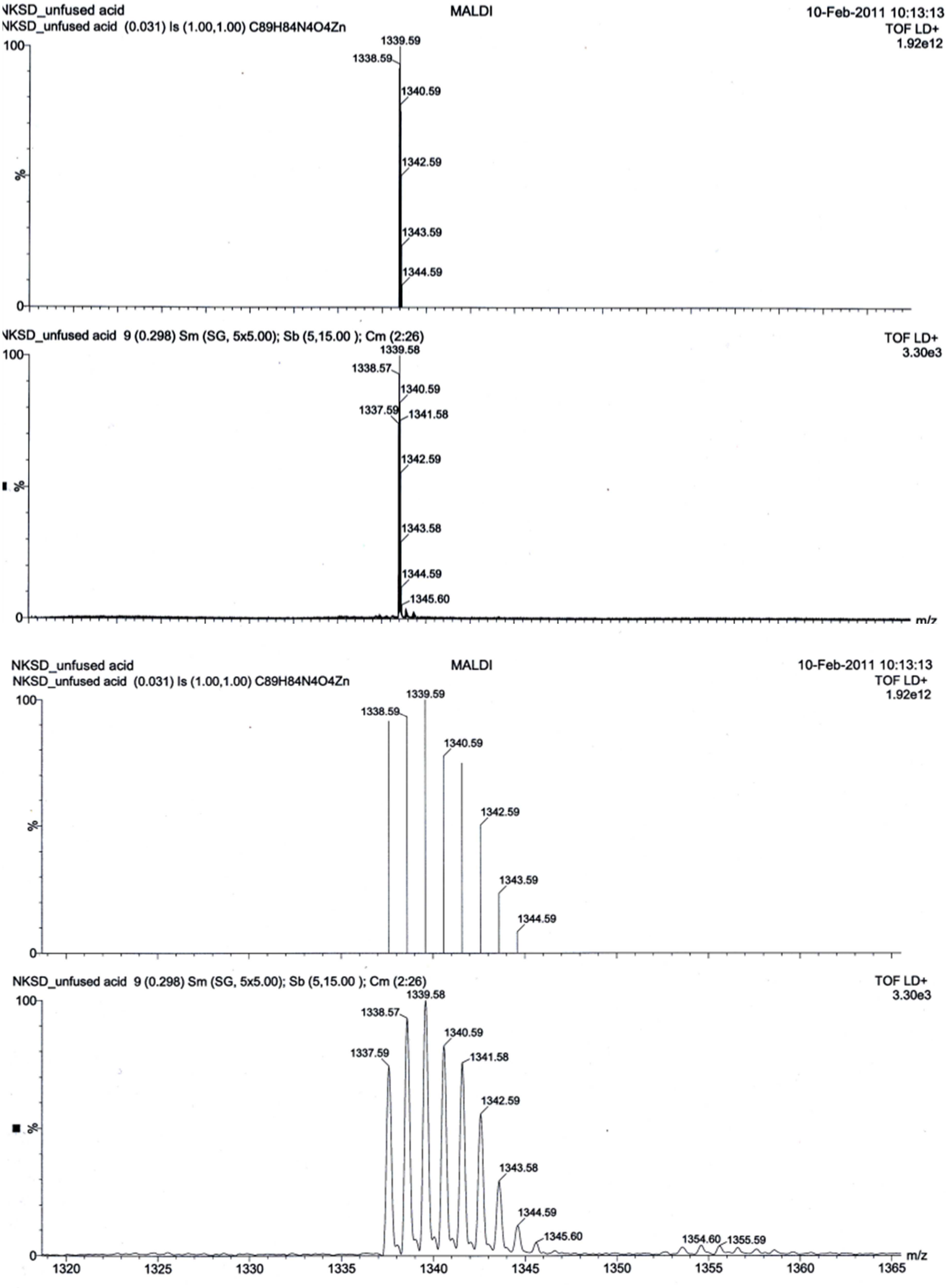


Figure S12. MALDI spectra for **P2** (upper traces: theoretical spectra; lower traces: observed spectra).

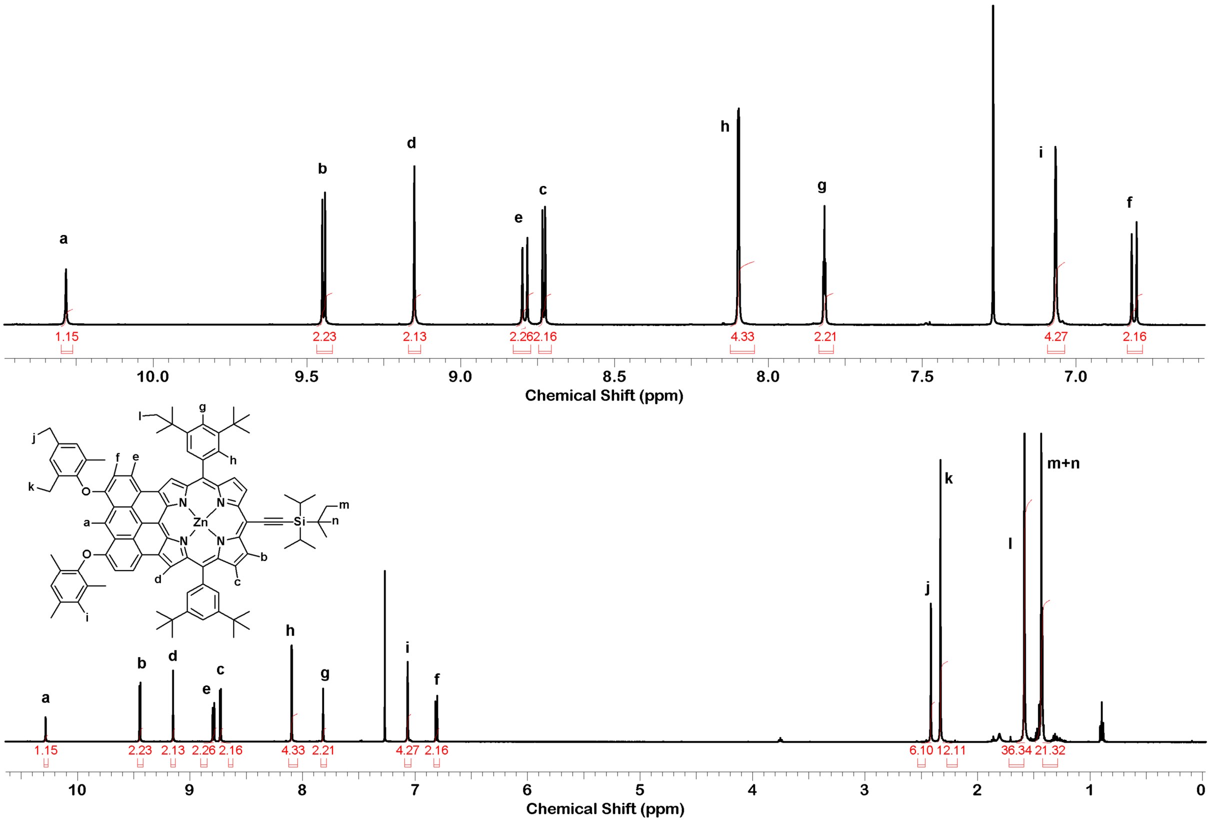


Figure S13. ^{1}H NMR spectrum of porphyrin **5** (400 MHz, $CDCl_3$/ pyridine-*d*$_5$, 298 K).

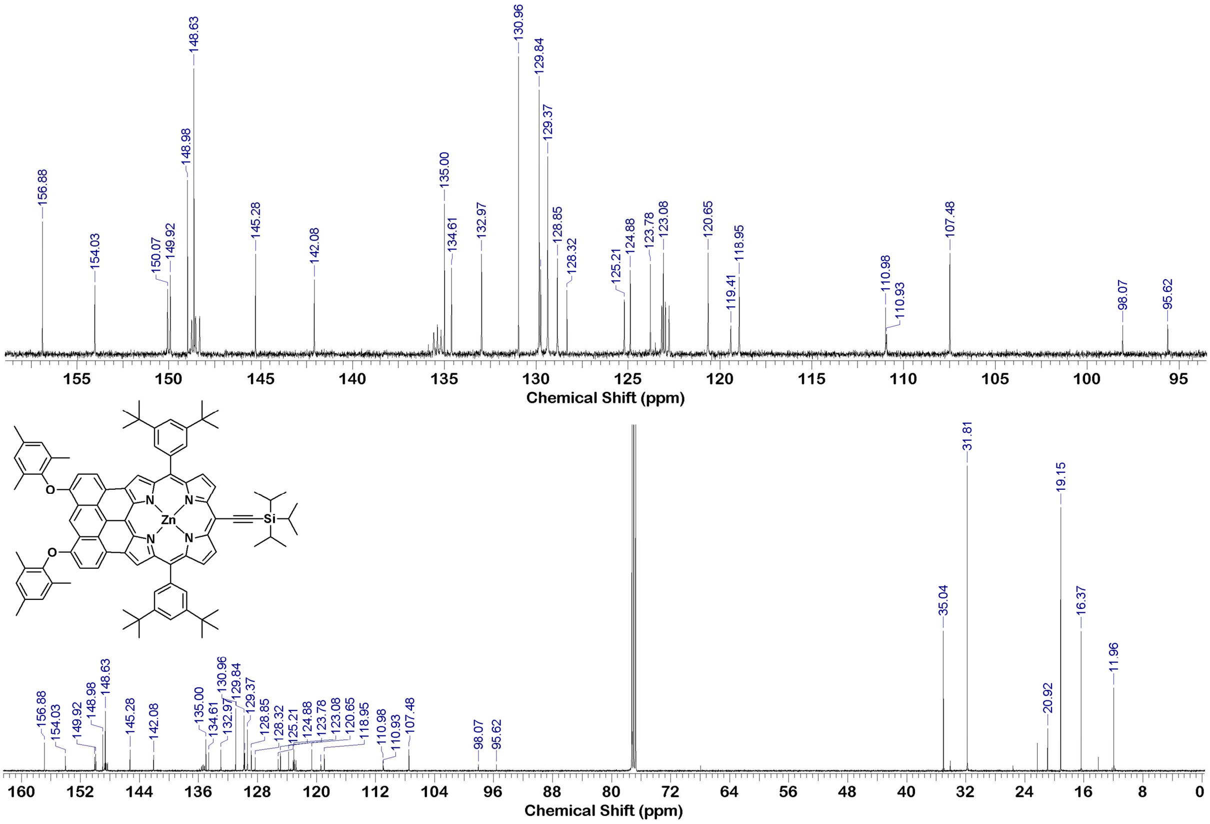


Figure S14. ^{13}C NMR spectrum of porphyrin **5** (125 MHz, $CDCl_3$/ pyridine-*d*$_5$, 298 K).

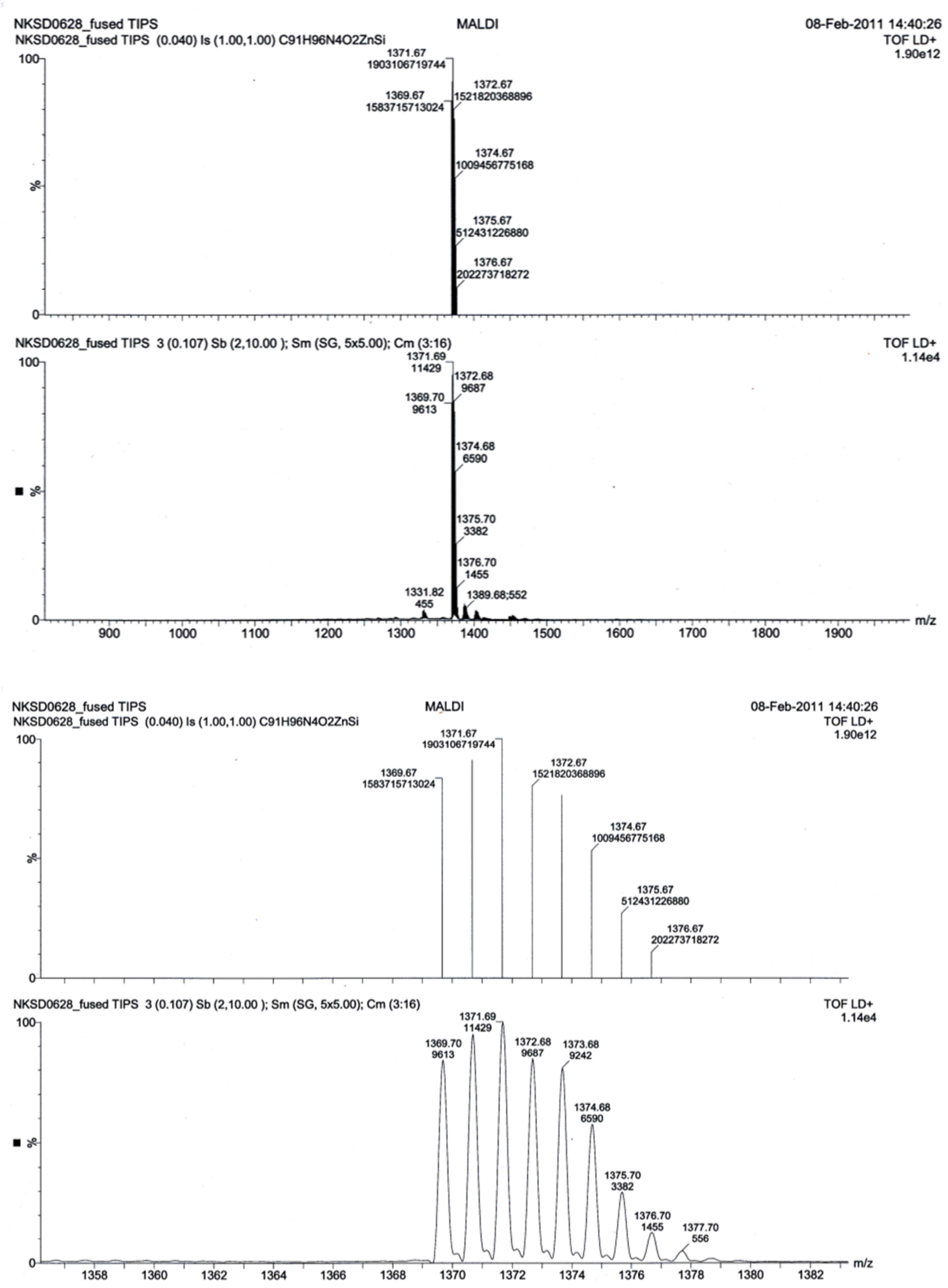


Figure S15. MALDI spectra for porphyrin **5** (upper traces: theoretical spectra; lower traces: observed spectra).

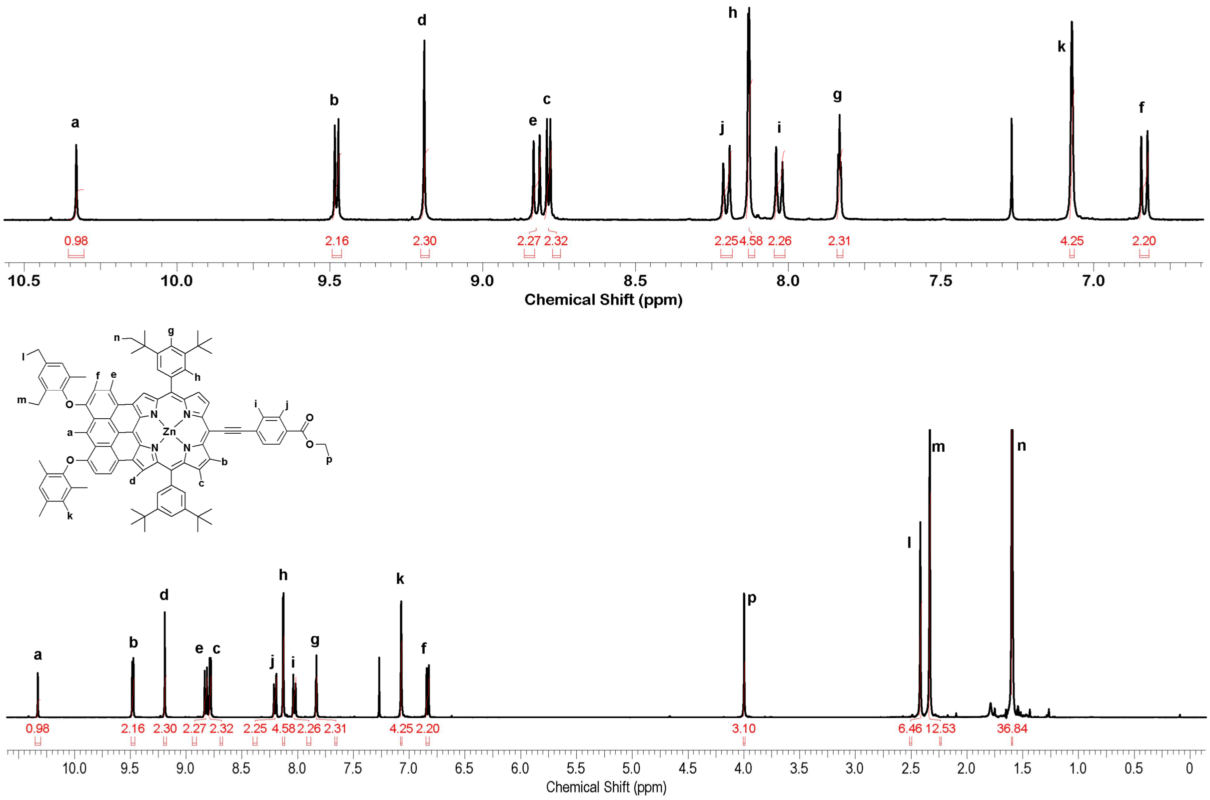


Figure S16. ^{1}H NMR spectrum of porphyrin **6** (400 MHz, $CDCl_3$/ pyridine-*d*$_5$, 298 K).

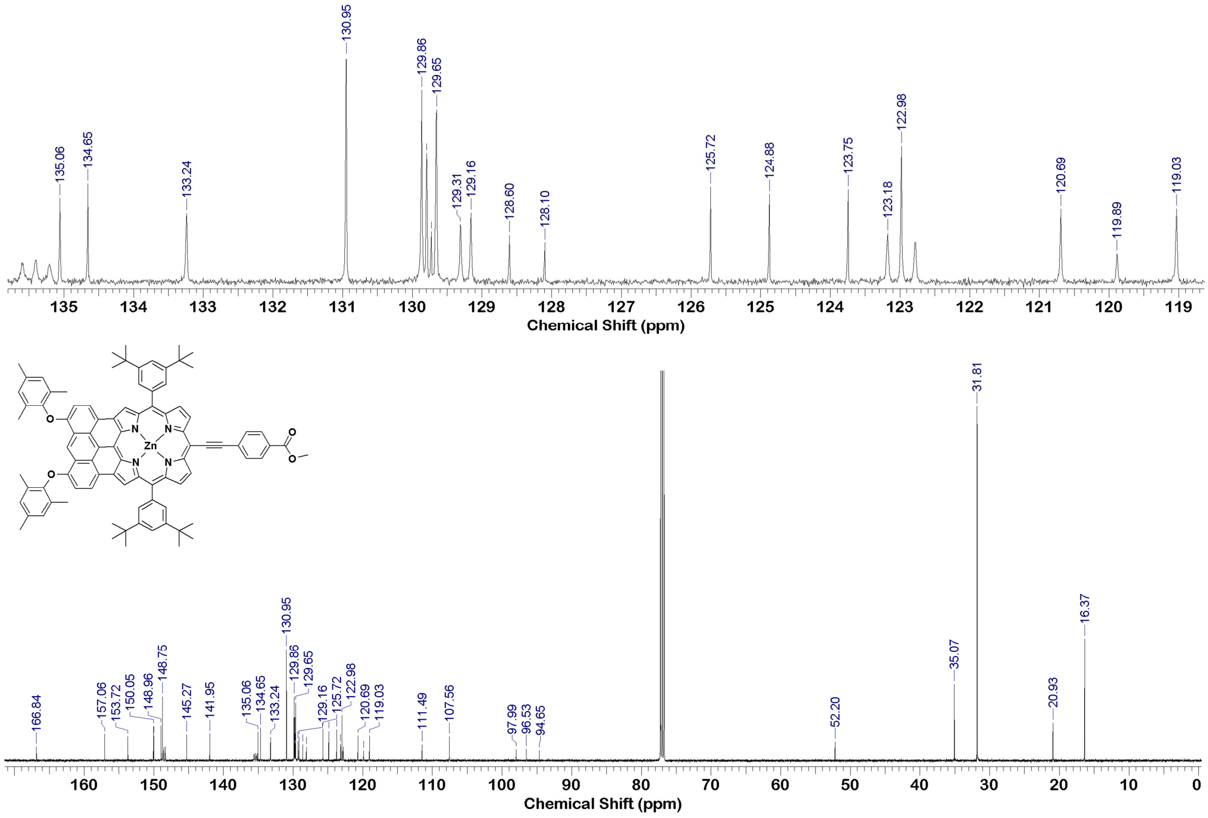


Figure S17. ^{13}C NMR spectrum of porphyrin **6** (125 MHz, $CDCl_3$/ pyridine-*d*$_5$, 298 K).

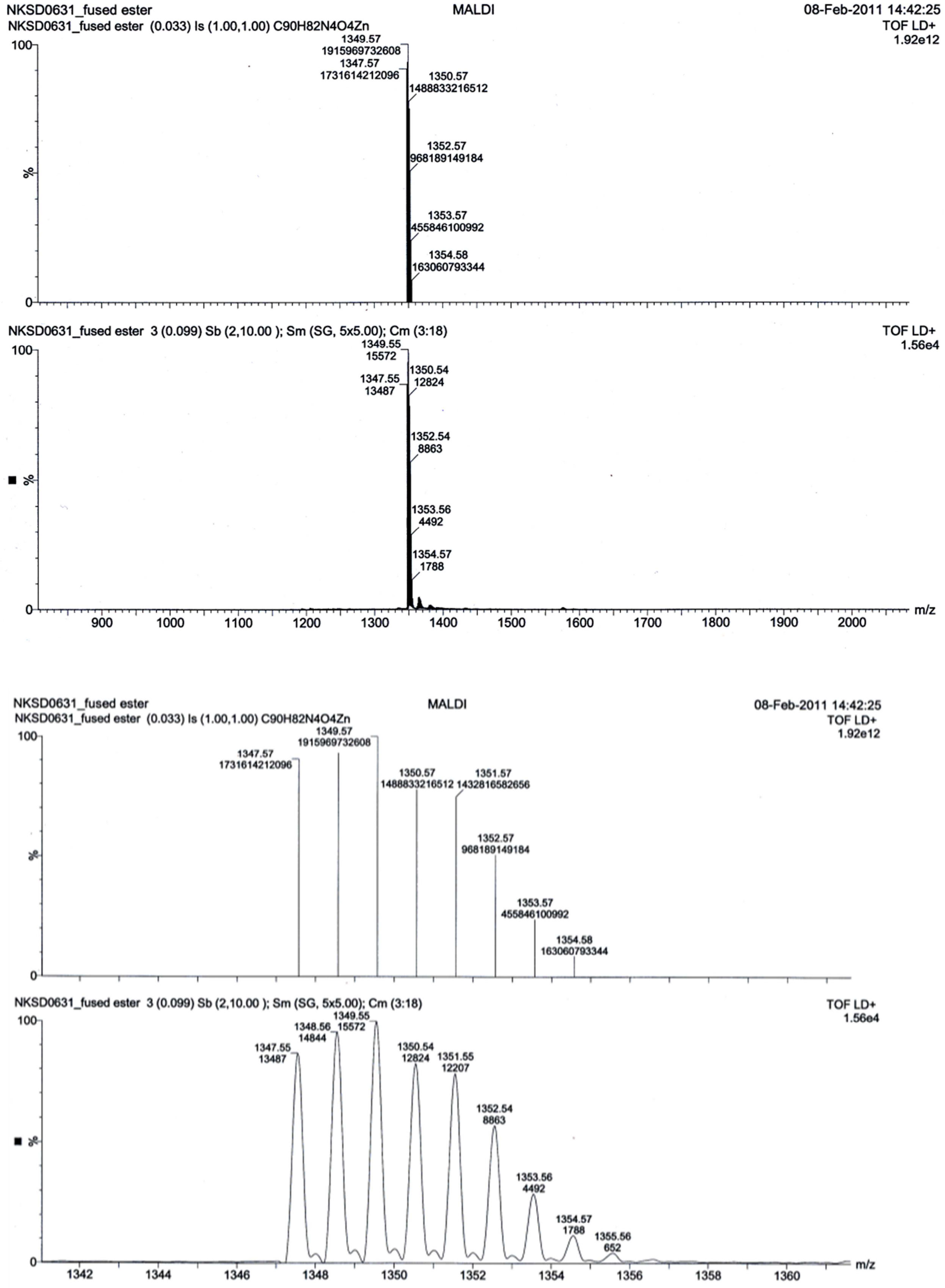


Figure S18. MALDI spectra for porphyrin **6** (upper traces: theoretical spectra; lower traces: observed spectra).

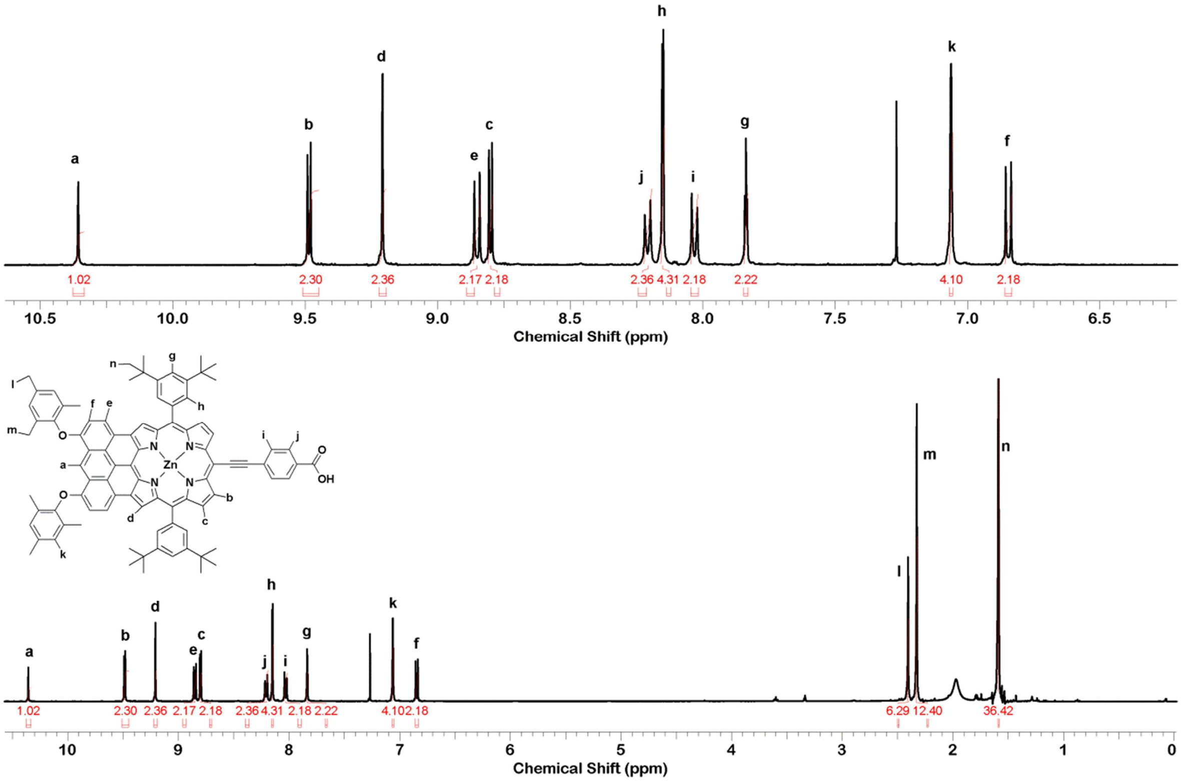


Figure S19. ^{1}H NMR spectrum of **P3** (400 MHz, CDCl$_3$/methanol-d_4, 298 K).

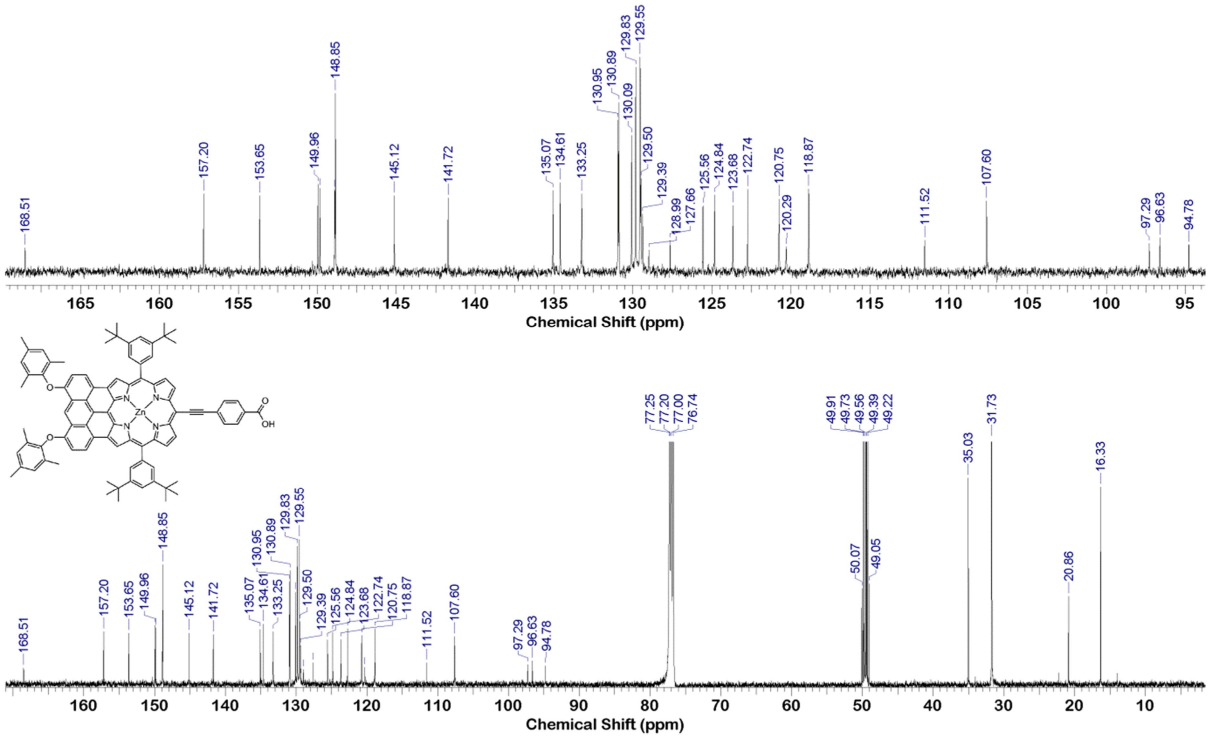


Figure S20. ^{13}C NMR spectrum of **P3** (125 MHz, CDCl$_3$/ methanol-d_4, 298 K).

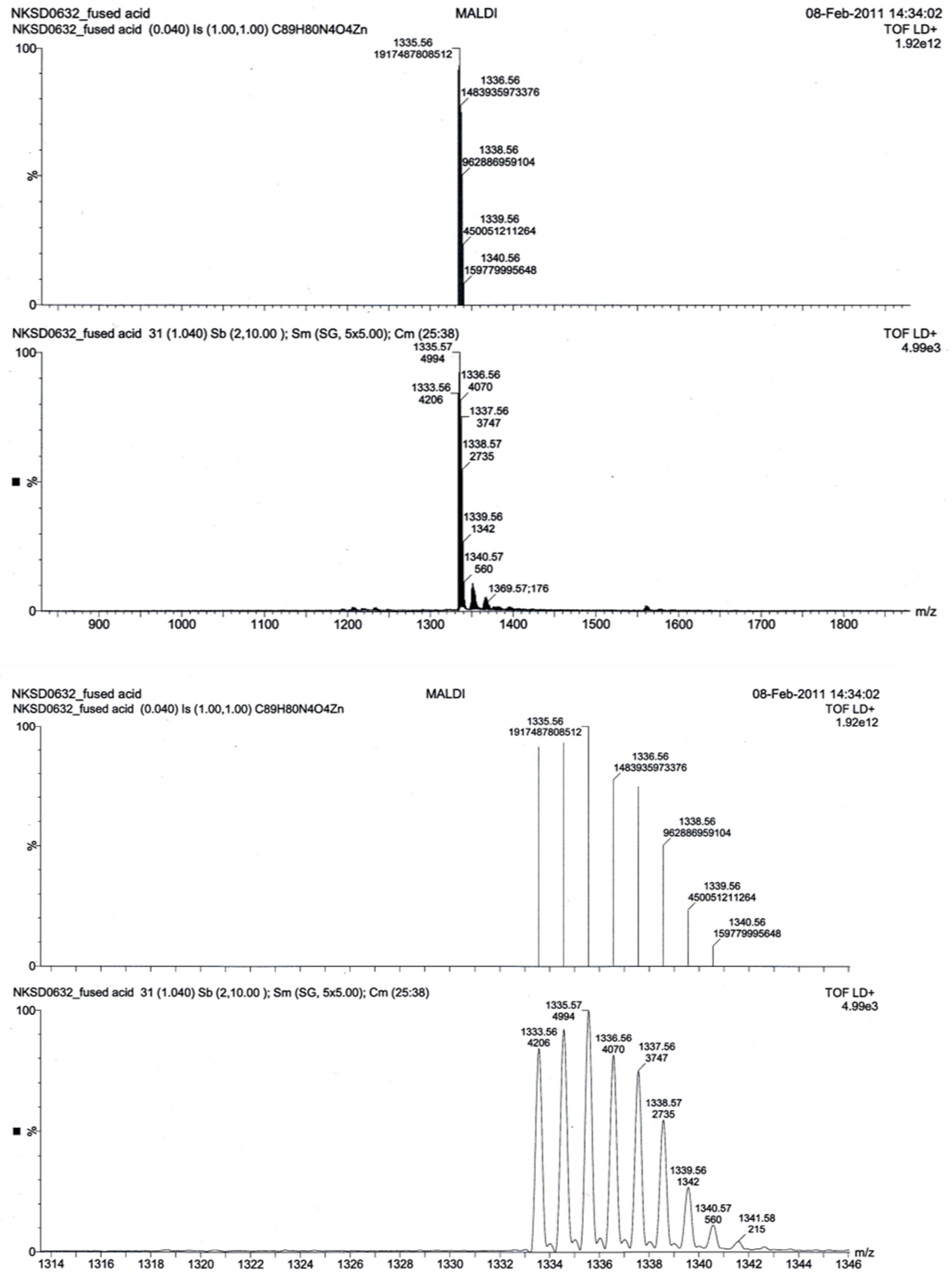


Figure S21. MALDI spectra for **P3** (upper traces: theoretical spectra; lower traces: observed spectra).

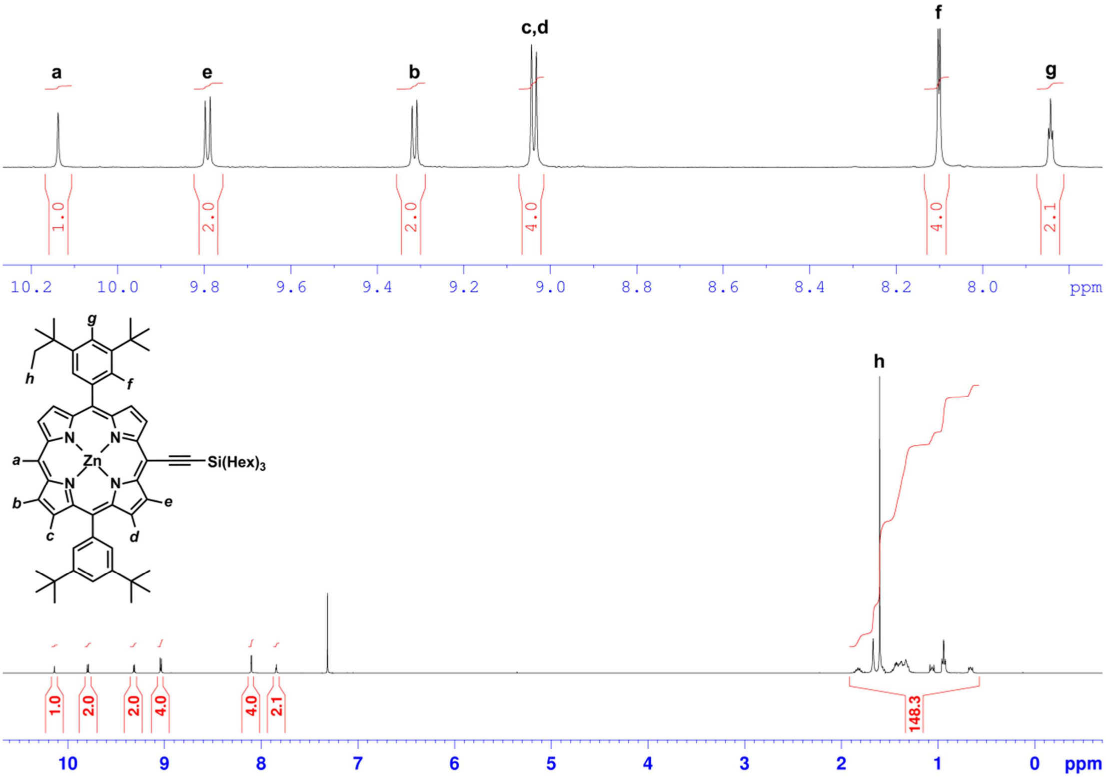


Figure S22. ^{1}H NMR spectrum of porphyrin **8** (400 MHz, CDCl$_3$/ d$_5$ pyridine, 298 K).

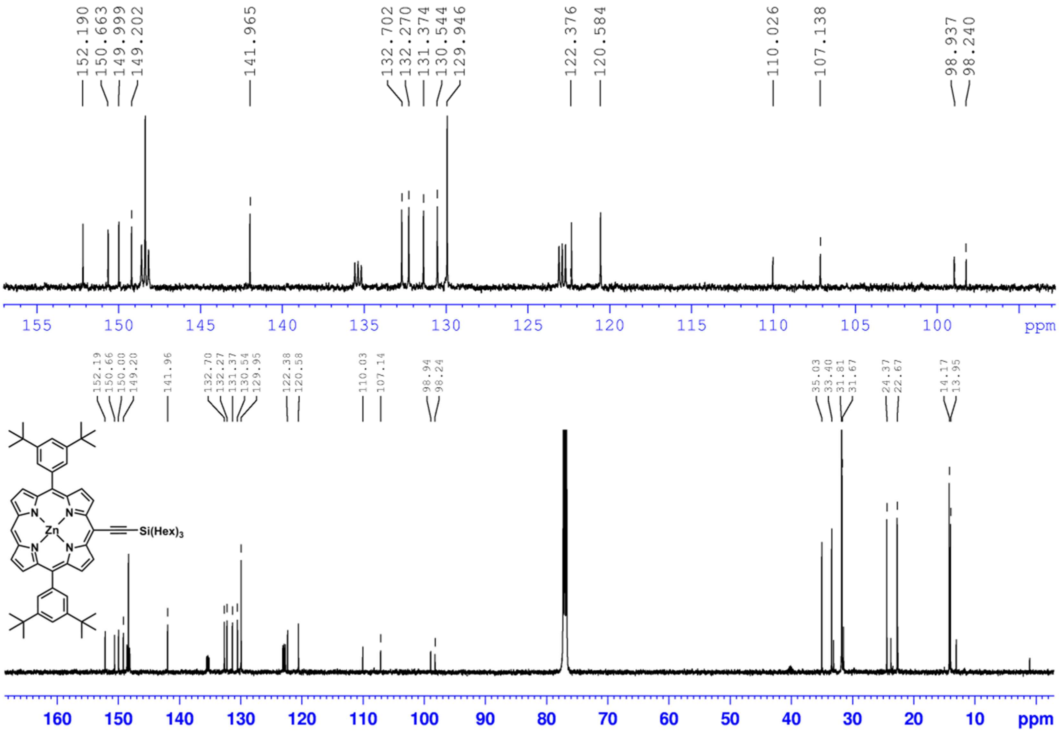


Figure S23. ^{13}C NMR spectrum of porphyrin **8** (126 MHz, CDCl$_3$/d$_5$ pyridine, 298 K).

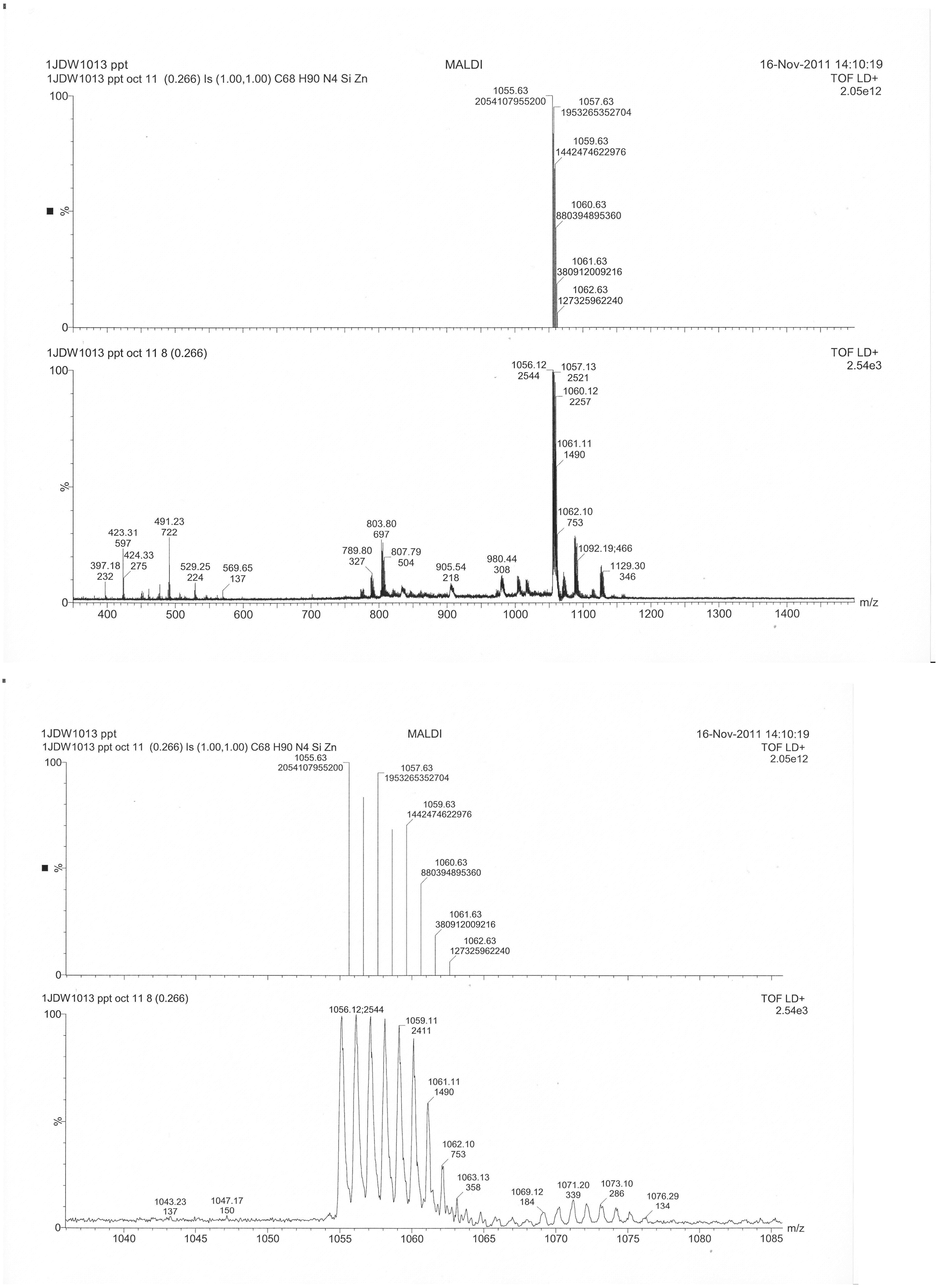


Figure S24. MALDI spectra for porphyrin **8** (upper traces: theoretical spectra; lower traces: observed spectra).

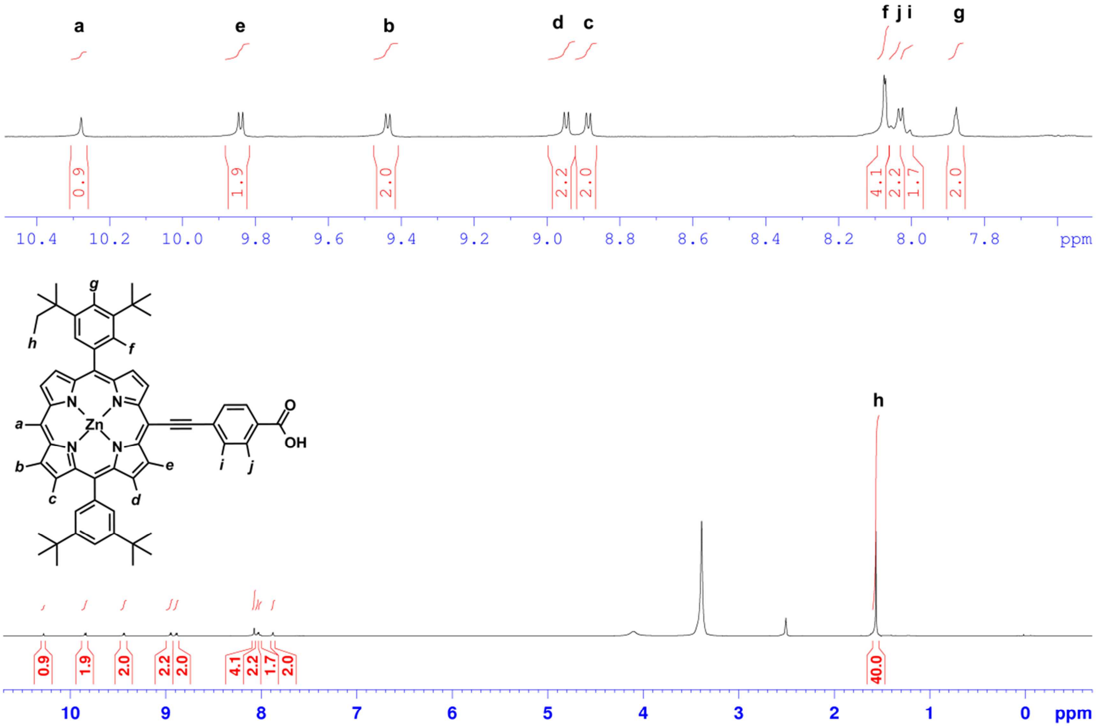


Figure S25. ^{1}H NMR spectrum of **P1** (400 MHz, d_6 dimethylsulfoxide, 298 K).

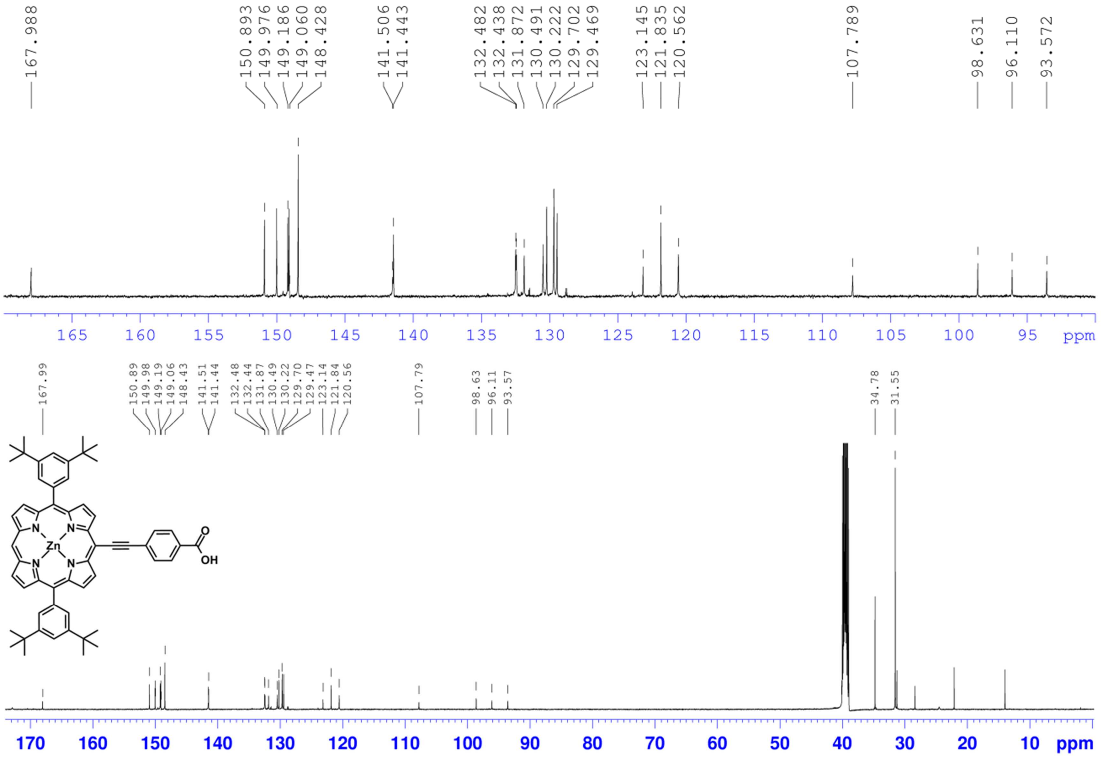
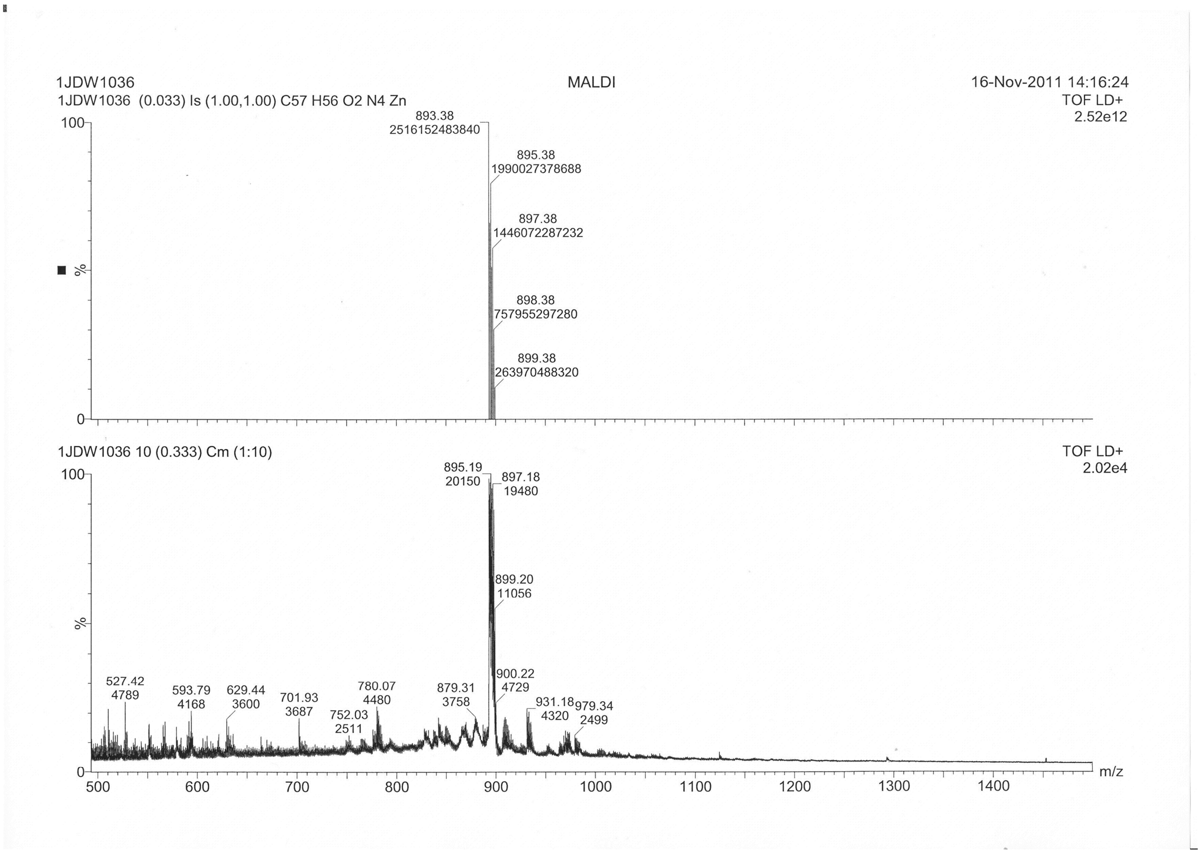


Figure S26. ^{13}C NMR spectrum of **P1** (126 MHz, d_6 dimethylsulfoxide, 298 K).



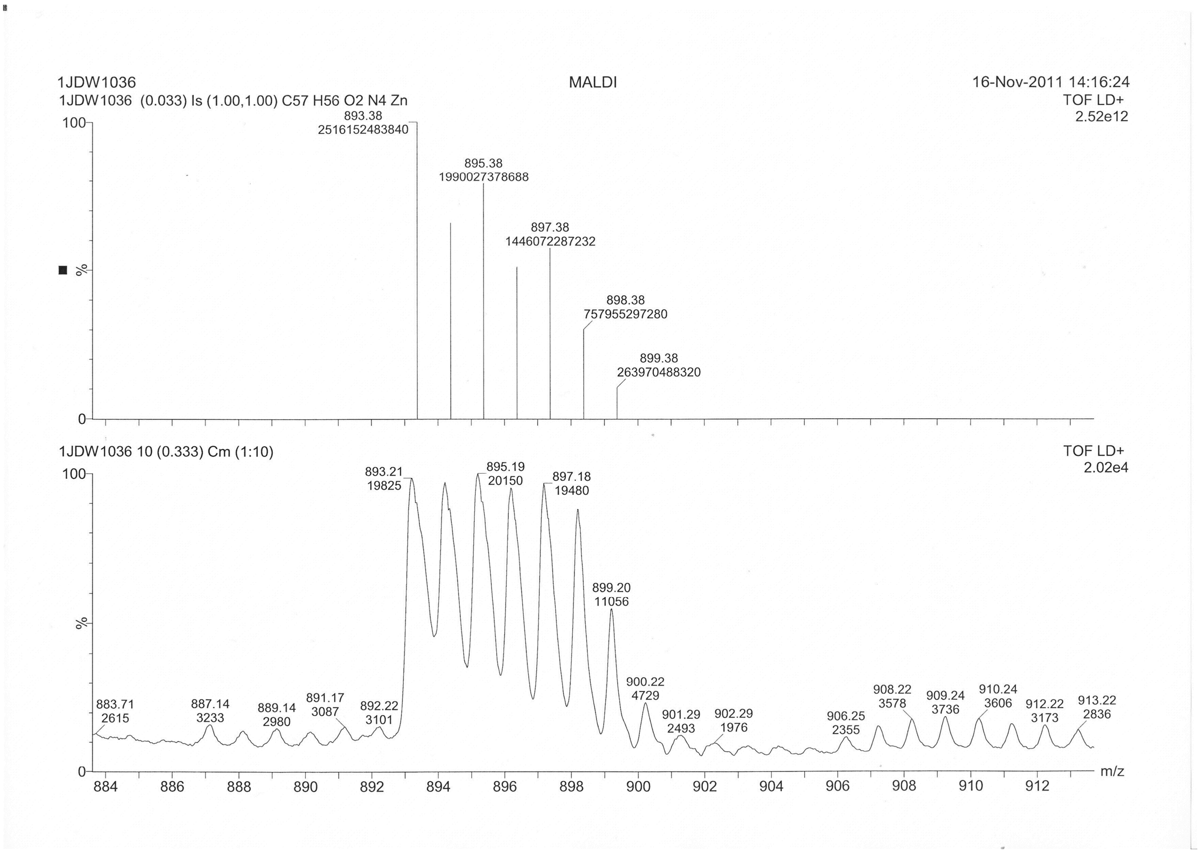


Figure S27. MALDI spectra for **P1** (upper traces: theoretical spectra; lower traces: observed spectra).

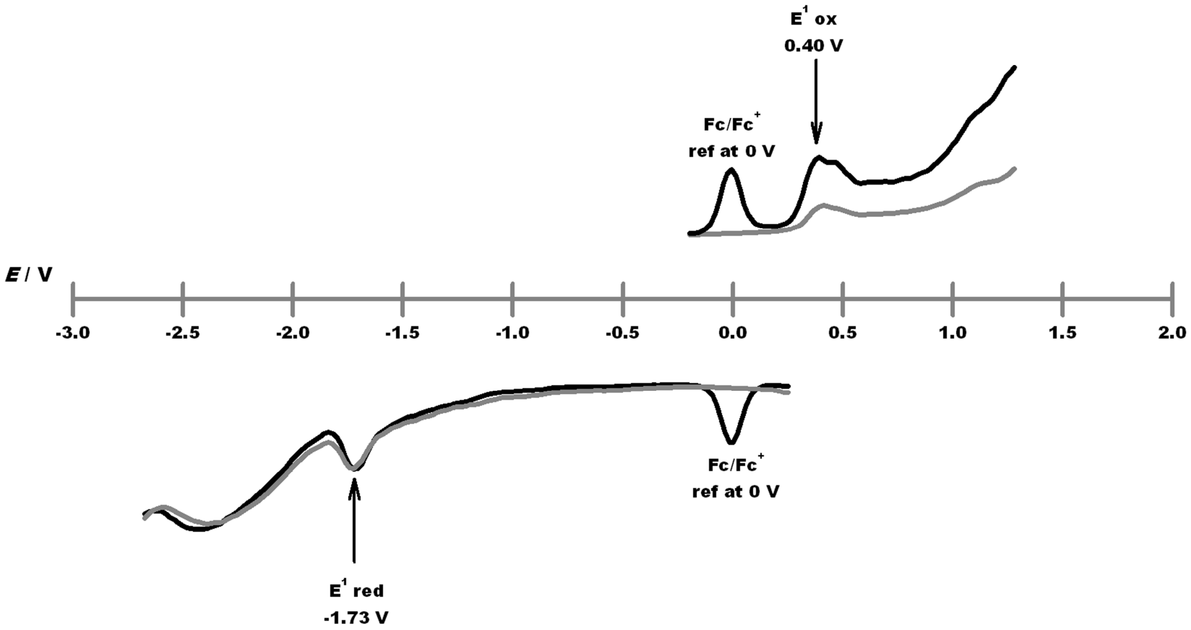


Figure S28. Square wave electrochemical experiment for **P1** (THF, 0.1 M Bu_4NPF_6; square wave frequency 8 Hz; glassy carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode). The gray lines represent the trace in the absence of internal ferrocene while the black lines show the measurements in the presence of ferrocene.

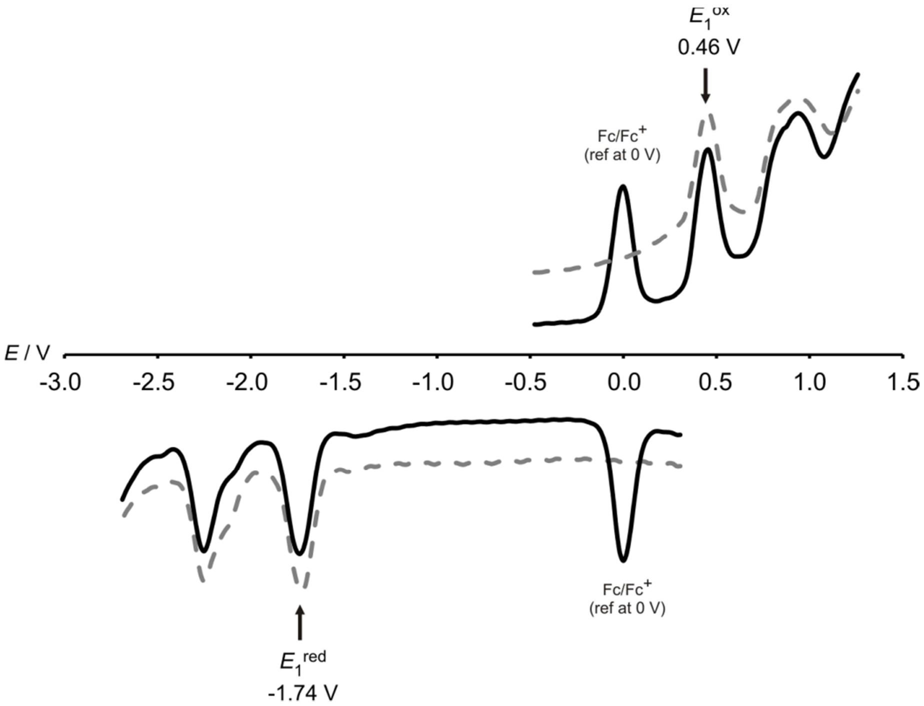


Figure S29. Square wave electrochemical experiment for **P2** (THF, 0.1 M Bu_4NPF_6; square wave frequency 8 Hz; glassy carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode). The gray dashed lines represent the trace in the absence of internal ferrocene while the black lines show the measurements in the presence of ferrocene.

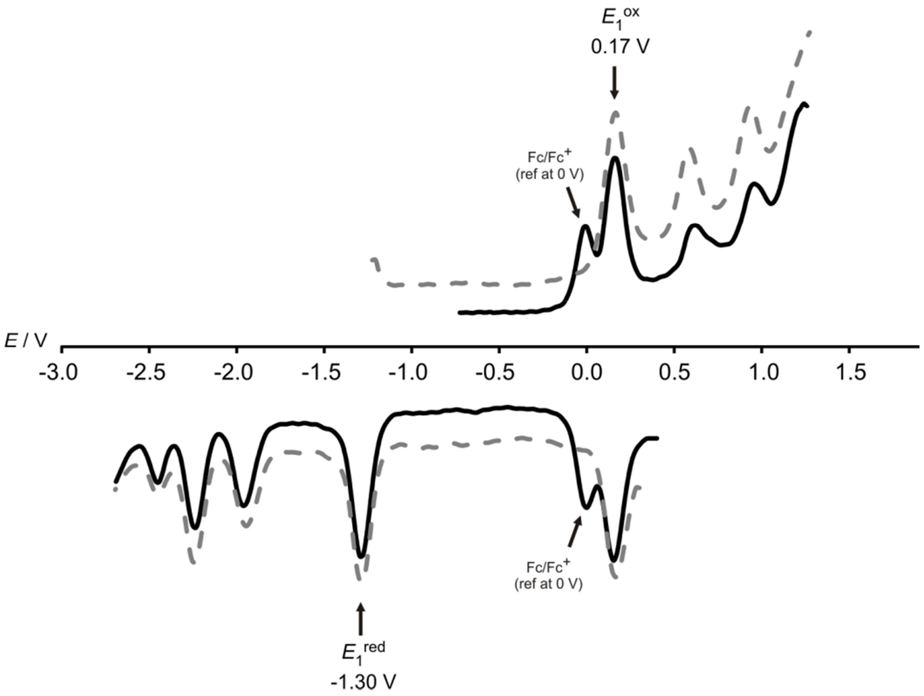


Figure S30. Square wave electrochemical experiment for **P3** (THF, 0.1 M Bu_4NPF_6; square wave frequency 8 Hz; glassy carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode). The grey dashed lines represent the trace in the absence of internal ferrocene while the black lines show the measurements in the presence of ferrocene.

Photoinduced Absorption Spectroscopy and Transient Absorbance Spectroscopy

Photoinduced absorption (PIA) spectra were obtained from porphyrin-loaded TiO_2 to identify the absorption peak of the dye cations. The films were excited with a monochromatic light beam (496.5 nm) with a power density of 50 $mWcm^{-2}$ at a frequency of 23 Hz. The PIA spectra shown in Fig. S31 indicate cation absorption peaks for each of the dyes in the region between 650 – 800 nm.

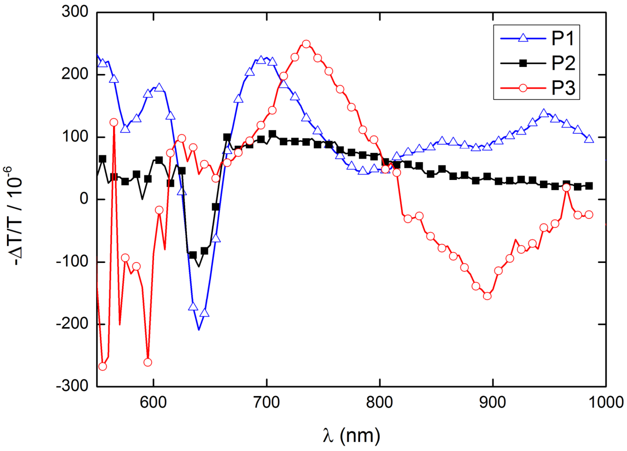


Figure S31. Photoinduced absorption spectra **P1**, **P2** and **P3** on TiO_2 probed following excitation at 496.5 nm.

Transient absorbance spectra were obtained from porphyrin-loaded TiO_2 films in an environment of 1-methoxypropionitrile (MPN) or of electrolyte E1. Figure S31 shows the transient absorbance decays for **P1** and **P2** probed at 700 nm following excitation at 510 nm. The lifetime for both decays are significantly longer than typical S_1–S_0 relaxation of a porphyrin hence we conclude that the observed processes originate from the decay of the cation absorbance following charge transfer from the dye to the oxide. When the dyed film is contained in an environment of MPN, i.e. when the only pathway to recover the ground state after cation formation is recombination with the conduction band electrons in the oxide, the time constant for the decays of **P1** and **P2** (derived from fitting a monoexponential decay) are 555 μs and 426.6 μs respectively. In contrast, when electrolyte is present the oxidized dye is intercepted by the iodide and therefore the lifetime of the cations are approximately two orders of magnitude shorter with a time constants of 1.65 μs and 3.6 μs for **P1** and **P2** respectively. The dye regeneration yields are calculated to be 99.7% and 99.2% for **P1** and **P2** respectively. These regeneration yields suggest that interception of the cation by electrons in the oxide conduction band rarely occurs because the dye is regenerated by the electrolyte on a much shorter timescale.

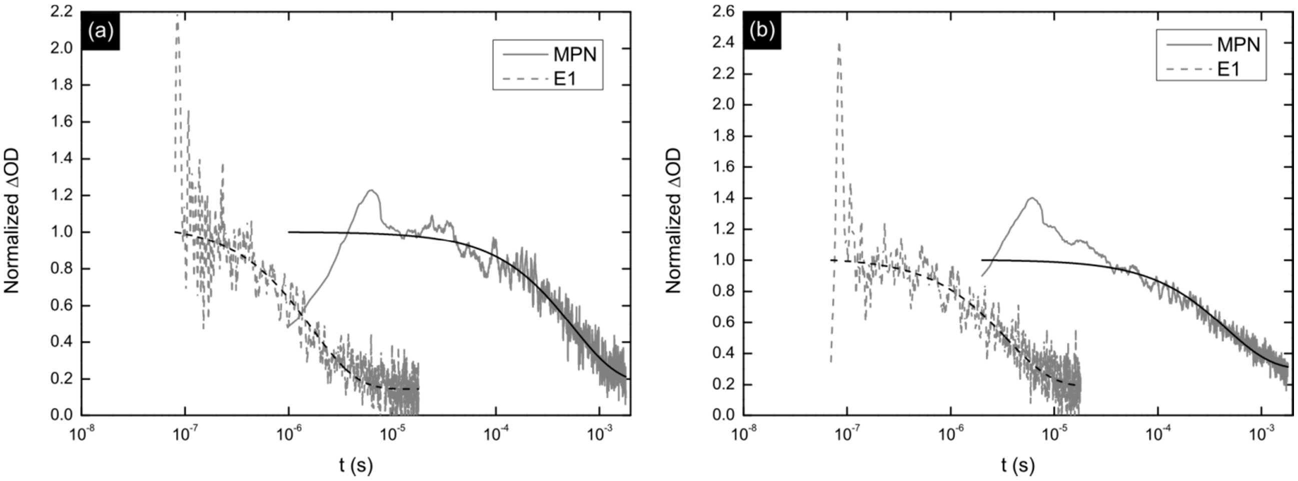


Figure S32. Normalized transient absorbance decay of the (a) P1 and (b) P2 cations on TiO_2 probed at 700 nm in MPN or in electrolyte E1, following excitation at 510 nm. Data are shown in grey and exponential fits are in black.

Incident Photon-to-Current Conversion Efficiency (IPCE)

The IPCE spectra were measured for devices based on porphyrin **P3** and various oxide and electrolyte configurations at 1 mW/cm^2 incident power density. The absolute IPCE spectra are shown in Fig. S31.

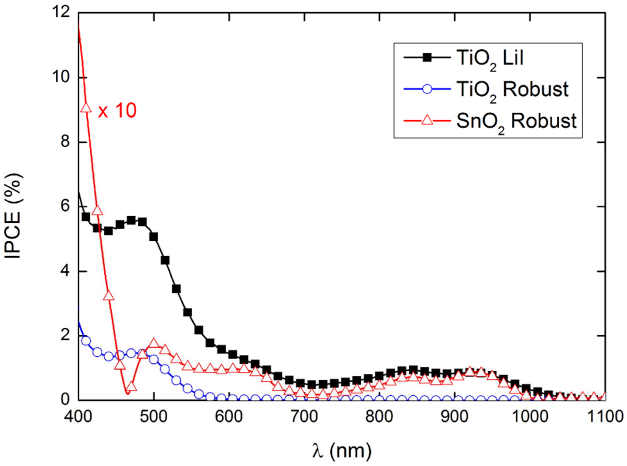


Figure S33. Incident photon-to-current conversion efficiency (IPCE) for **P3** with various oxide-electrolyte configurations. The spectrum for SnO_2 has been multiplied by 10.

References

1 N. K. S. Davis, A. L. Thompson, and H. L. Anderson, *Org. Lett.*, 2010, **12**, 2124–2127.

2 M. Shao and Y. Zhao, *Tetrahedron Lett.*, 2010, **51**, 2892–2895.