Synthesis of Porphyrins Bearing *trans*-Thiols

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Supplementary Data

4-(Trimethylsilylethynyl)benzaldehyde.[7] To a solution of 4-iodobenzaldehyde (0.5 g, 2.15 mmol), in THF (2.7 mL) were added (trimethylsilyl)acetylene (0.44 mL, 0.31g, 3.18 mmol) and *N*,*N*-diisopropylethylamine (0.6 mL, 0.45 g, 3.46 mmol). The solution was allowed to stir under nitrogen for 30 min in a glove bag flushed with nitrogen. The catalysts bis(triphenylphosphine)palladium(II) chloride (0.076 g, 0.11 mmol) and copper iodide (0.0020 g, 2.1 mmol), dried *in vacuo*, were added and the reaction was allowed to stir for 24 h. The reaction was quenched with water and the organic phase was extracted with methylene chloride (2 × 15 mL). The combined organic extracts were dried over sodium sulfate and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography using hexane/methylene chloride (1:1, v/v) to provide 0.063 g (73%) of the title compound as a brown solid. MP: 60-66°C. IR (KBr) 2955.6, 2833.4, 2722.2, 2144.5, 1700.0, 1594.5, 1555.6, 1383.3, 1294.5, 1244.5, 1200.0, 1155.6, 861.1, 838.9, 755.6, 661.1 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.98 (s, 1 H), 7.81 (d, *J* = 8.37 Hz, 2 H), 7.59 (d, *J* = 8.28 Hz, 2 H), 0.13 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.38, 135.59, 132.47, 129.34, 103.83, 99.02, -0.21. Anal. Calcd for $C_{12}H_{14}OSi$: C, 71.00; H, 6.95. Found: C, 71.29; H, 6.96.

4-Ethynyl-1-benzaldehyde.[4] To a solution of 4-(trimethylsilylethynyl)benzaldehyde (0.093 g, 0.45 mmol) in methylene chloride (5 mL) and methanol (5 mL) was added potassium carbonate (0.47 g, 3.42 mmol). The solution was allowed to stir for 6 h before being poured into water. The aqueous layer was extracted with methylene chloride and the organic extracts were washed with brine. The combined organic layers were dried over sodium sulfate and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography using methylene choride to provide 0.056 g (95%) of the title compound as a pale yellow solid. MP: 84-86°C. IR (KBr) 3210.3, 1696.9, 1682.0, 1600.0, 1550.0, 1384.6, 1205.1, 1164.1, 825.6, 738.5 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.01 (s, 1 H), 7.81 (d, *J* = 8.4 Hz, 2 H), 7.63 (d, *J* = 8.25 Hz, 2 H), 3.27 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.38, 137.06, 133.83, 130.62, 129.43, 83.84, 82.28. FABMS Calcd for C_9H_6O: 130. Found: 130.

4-Thioacetyldiphenylethynylcarboxaldehyde (10). See the preparation of 4-(trimethylsilylethynyl)benzaldehyde for the synthetic protocol. The compounds used were 4-ethynylbenzaldehyde (0.049 g, 0.37 mmol), 1-iodo-4-thioacetylbenzene (0.123 g, 0.44 mmol), bis(triphenylphosphine)palladium(II) chloride (0.013 g, 0.06 mmol), copper iodide (0.35 mg, 0.18 mmol) and THF (0.2 mL). The residue was purified by silica gel column chromatography using methylene chloride/hexane (1:1, v/v) as the eluent. The solvent was removed *in vacuo* to afford 0.078 g (75%) of the title product as a yellow solid. MP: 122-123°C. IR (KBr) 3138.5, 2841.0 1697.4, 1594.9, 1379.5, 1287.2, 1123.1, 959.0, 820.5, 723.1 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.10 (s, 1 H), 7.84 (d, *J* = 8.4 Hz, 2 H), 7.65 (d, *J* = 8.25 Hz, 2 H), 7.55 (d, *J* = 8.4 Hz, 2 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 2.43 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.14, 192.31, 136.67, 135.34, 134.17, 133.27, 130.67, 130.26, 130.04, 124.76, 93.68,

91.18, 31.66. FABMS Calcd for $C_{17}H_{12}O_2S$: 280. Found: 280. Anal. Calcd for $C_{17}H_{12}O_2S$: C, 72.83; H, 4.34. Found: C, 72.21; H, 4.35.

5,15-Bis(4-thioacetyldiphenylethynyl)-10,20-bis(phenyl)porphyrin (11). A solution of **10** (0.10 g, 0.35 mmol) and *meso*-(4-phenyl)dipyrrromethane (0.079 g, 0.36 mmol), in $CHCl_3$ (36 mL) at room temperature was degassed under nitrogen for 15 min. This was followed by the addition of two drops of $BF_3{\cdot}OEt_2$. The solution was left stirring under nitrogen for 1 h after which time DDQ (0.081 g, 0.36 mmol) was added and stirring continued for another 1 h. The solvent was removed *in vacuo* and the crude sample was purified by silica gel column chromatography using methylene chloride as the eluent followed by a second column purification with methylene chloride/hexane (1:1, v/v) to provide 0.047 g (27%) of the title compound in the first major fraction as a purple powder. MP: 200-204°C. IR (KBr) 3435.9, 3128.2, 1625.6, 1384.6, 1123.1, 800 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (m , 8 H), 8.19 (d, *J* = 7.92 Hz, 8 H), 7.91 (d, *J* = 7.83 Hz, 4 H), 7.70-7.76 (m, 10 H), 7.45 (d, *J* = 8.19 Hz, 4 H), 2.46 (s, 6 H), -2.79 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.49, 142.47, 141.99, 134.59, 134.52, 134.32, 132.31, 130.06, 128.24, 127.79, 126.71, 124.52, 122.48, 122.43, 120.53, 120.44, 119.47, 119.37, 119.31, 119.21, 91.0, 89.81, 30.32. UV/Vis (CH_2Cl_2) λ_{max} (log ε): 450.92 (5.52), 570.12 (3.23), 619.50 (3.91), 670.58 (4.73). FABMS Calcd for $C_{64}H_{42}N_4O_2S_2$: 962. Found: 962. Anal. Calcd for $C_{64}H_{42}N_4O_2S_2.CHCl_3$: C, 72.11; H, 4.00; N, 5.17. Found: C, 73.15; H, 4.33; N, 5.17.

5,15-Bis(4-thioacetyldiphenylethynyl)-10,20-bis(4-methylphenyl)porphyrin) (12). See the preparation of **11** for the synthetic protocol. The compounds used were 4-iodothioacetyldiphenylethynylaldehyde **10** (0.125 g, 0.45 mmol), *meso*-(4- phenyl)dipyrrromethane (0.1 g, 0.45 mmol), $CHCl_3$ (36.66 mL), two drops of $BF_3{\cdot}OEt_2$, and DDQ (0.10 g, 0.45 mmol). The solvent was removed *in vacuo* and the sample was purified by silica gel column chromatography using methylene chloride as the eluent followed by a second column purification with methylene chloride/hexane (1:1, v/v) to provide 0.059 g (27%) of the title compound in the first major fraction as a purple solid. MP: 214-216°C. IR (KBr) 3433.3, 3128.2, 1704.3, 1464.5, 1384.6, 1108.5, 963.2, 796.2, 730.8 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89-8.84 (m, 8 H), 8.19 (d, *J* = 8.19 Hz, 4 H), 8.07 (d, *J* = 7.89 Hz, 4 H), 7.9 (d, *J* = 7.95 Hz, 4 H), 7.68 (d, *J* = 8.22 Hz, 4 H), 7.53 (d, *J* = 7.89 Hz, 4 H), 7.45 (d, *J* = 8.34 Hz, 4 H), 2.69 (s, 6 H), 2.46 (s, 6 H), -2.75 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.50, 142.58, 139.07, 137.45, 134.58, 134.48, 134.32, 132.31, 130.04, 131.00, 128.22, 127.44, 124.54, 122.37, 120.70, 120.53, 119.16, 119.00, 91.03, 89.77, 30.32, 21.52. UV/Vis (CH_2Cl_2) λ_{max} (log ε): 456.03 (5.20), 617.80 (3.59), 679.10 (4.42). HRFABMS Calcd for $C_{66}H_{46}N_4O_2S_2$: 990.3062. Found: 990.3080. Anal. Calcd for $C_{66}H_{46}N_4O_2S_2$: C, 79.97; H, 4.67; N, 5.65. Found: C, 80.42; H, 4.98; N, 5.97.

5,15-Bis(4-thioacetyldiphenylethynyl)-10,20-bis(4-bromophenyl)porphyrin (13). See the preparation of **11** for the synthetic protocol. The compounds used **10** (0.061 g, 0.22 mmol), *meso*-(4-bromophenyl)dipyrromethane (0.065 g, 0.22 mmol), $CHCl_3$ (21.87 mL), two drops of $BF_3{\cdot}OEt_2$and DDQ (0.049 g, 0.22 mmol). The solvent was removed *in vacuo* and the crude sample was purified by silica gel column chromatography using methylene chloride followed by a second column purification with methylene chloride/hexane (1:1, v/v) to provide 0.034 g (28%) of the title compound in the first major fraction as a purple solid. MP: 204-206 °C. IR (KBr) 3435.9, 3138.5, 2923.1, 1625.6, 1461.5, 1384.6, 1117.9, 800 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (m, 8 H), 8.21 (d, *J* = 8.07 Hz, 4 H), 8.05 (d, *J* = 8.04 Hz, 4 H), 7.91 (m, 8 H), 7.68 (d, *J* = 8.22 Hz, 4 H), 7.48 (d, *J* = 8.19 Hz, 4 H), 2.46 (s, 6 H), -2.82 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.50, 142.25, 142.21, 140.86, 135.82, 134.57, 134.33, 132.43, 132.31, 130.10, 129.96, 128.27, 124.47, 122.59, 122.58, 119.69, 118.90, 90.90, 89.91, 30.34. UV/Vis (CH_2Cl_2) λ_{max} (log ε): 458.68 (5.69), 571.82 (3.32), 675.69 (4.92), 621.20 (4.10). HRFABMS calcd for $C_{64}H_{40}Br_2N_4O_2S_2$: 1119.1038. Found: 1119.1039. Anal. Calcd for $C_{64}H_{40}Br_2N_4O_2S_2$: C, 68.57; H, 3.59; N, 4.99. Found: C, 67.81; H, 3.92; N; 4.86.

5,15-Bis(4-thioacetyldiphenylethynyl)-10,20-bis(4-iodophenyl)porphyrin (14). See the preparation of **11** for the synthetic protocol. The compounds used were **10** (0.060 g, 0.21 mmol), *meso*-(4-iodophenyl)dipyrrromethane (0.075 g, 0.21 mmol), $CHCl_3$ (43 mL), two drops of $BF_3{\cdot}OEt_2$ and DDQ (0.049 g, 0.21 mmol). The solvent was removed *in vacuo* and the crude sample was purified by silica gel column chromatography using methylene chloride as the eluent followed by a second column purification with methylene chloride/hexanes (1:1, v/v) to provide 0.034 g (28%) of the title compound in the first major fraction as a purple powder. MP = 216-218 °C. IR (KBr) 3435.9, 3128.2, 1466.7, 1384.6, 1117.9, 800 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86-8.83 (m, 8 H), 8.17 (d, *J* = 8.13 Hz, 4 H), 8.05 (d, *J* = 8.19

Hz, 4 H), 7.89 (d, *J* = 7.95 Hz, 8 H), 7.67 (d, *J* = 8.22 Hz, 4 H), 7.45 (d, *J* = 8.19 Hz, 4 H), 2.46 (s, 6 H), -2.84 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.26, 143.26, 142.51, 137.13, 136.94, 135.59, 135.34, 133.34, 132.10, 131.14, 129.40 125.54, 123.67, 120.76, 120.07, 95.40, 92.07, 91.07, 31.61. HRFABMS Calcd for $C_{64}H_{40}I_2N_4O_2S_2$: 1214.0682. Found: 1214.0759. UV/Vis (CH_2Cl_2) λ_{max} (log ε): 457.88 (5.44), 578.63 (3.35), 614.39 (3.85), 673.99 (4.66). Anal. Calcd for $C_{64}H_{40}I_2N_4O_2S_2.CHCl_3$: C, 58.51; H, 3.09; N; 4.19. Found: C, 57.85; H, 3.15; N, 4.54.

***Meso*-(4-thioacetyldiphenylethynyl)dipyrromethane (15).** A solution of pyrrole (6 mL, 86.91 mmol) and **10** (0.055 g, 0.19 mmol) in methanol (0.27 mL) was treated with acetic acid (0.82 mL) at room temperature under nitrogen for 20 h. The reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic phase was dried over $MgSO_4$ and the solvents were removed *in vacuo*. The crude sample was purified by silica gel column chromatography using methylene chloride/triethylamine (100:1, v/v) and was isolated as the second light yellow band. The solvent was removed *in vacuo* to provide 0.067 g (86%) of the title product as a tan viscous oil. IR (KBr) 3394.9, 3169.2, 1384.6, 1117.9, 1025.6, 769.2, 717.9 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (br s, 2 H), 7.53 (d, *J* = 8.13 Hz, 2 H), 7.45 (d, *J* = 8.25 Hz, 2 H), 7.37 (d, *J* = 8.04 Hz, 2 H), 7.19 (d, *J* = 8.31 Hz, 2 H), 6.7 (br s, 2 H), 6.17 (dd, *J* = 5.4, 2.6 Hz, 2 H), 5.89 (br s, 2 H), 2.41 (s, 3 H), 5.41 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.43, 142.75, 134.17, 132.12, 131.92, 128.44, 127.96, 124.485, 121.405, 117.45, 108.43, 107.39, 90.96, 88.72, 43.94, 30.43. HRFABMS Calcd for $C_{25}H_{20}N_2OS$: 396.1296. Found: 396.1303.

5,10,15,20-*tetrakis*(4-thioacetyldiphenylethynyl)porphyrin (16). To a stirred solution of **10** (0.062 g, 0.22 mmol) and pyrrole (0.015 g, 0.22 mmol) in $CHCl_3$(22 mL) that contained 0.75% EtOH was added two drops of $BF_3{\cdot}OEt_2$. The reaction mixture was allowed to stir under nitrogen for 5 h. After 5 h, *p*-chloranil (0.05 g, 0.22 mmol) was added and the reaction mixture stirred for another 1 h. The solvent was removed *in vacuo* and the crude residue was purified by silica gel column chromatography using methylene chloride as the eluent followed by a second column purification using methylene chloride/hexane (5:1, v/v). The solvent was removed *in vacuo* to provide 0.02 g (29%) of purple solid. MP: 168-170°C. IR (KBr): 3403.2, 3128.2, 1703.3, 1464.5, 1336.4, 1304.7, 11108.5, 956.0, 883.3, 796.2, 738 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (s, 8 H), 8.19 (d, *J* = 8.13 Hz, 8 H), 7.91 (d, *J* = 8.13 Hz, 8 H), 7.62 (d, *J* = 8.67 Hz, 8 H), 7.45 (d, *J* = 8.13 Hz, 8 H), 2.46 (s, 12 H), -2.78 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.14, 142.13, 134.43, 134.17, 132.16, 129.96, 128.15, 124.37, 122.43, 119.51, 90.91, 89.85, 30.43. UV/Vis (CH_2Cl_2) λ_{max} (log ε): 464.55 (5.69), 628.01 (3.90), 685.91 (4.91). FABMS Calcd for $C_{84}H_{54}N_4O_4S_4$: 1310. Found: 1310.