Supporting Information

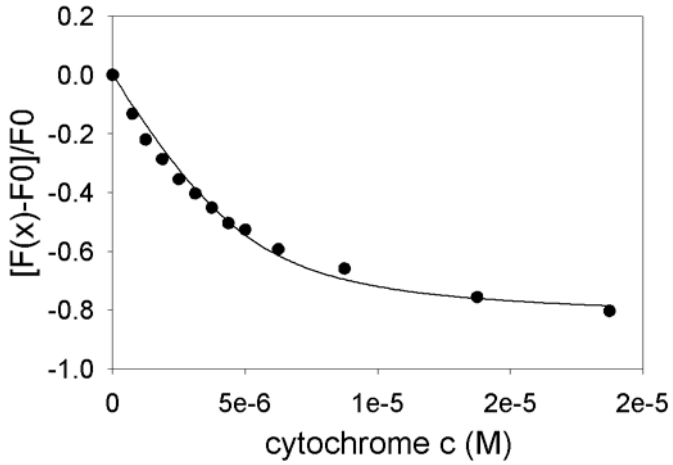
Compound 2. To a solution of m-tetrakis-(4-carboxyphenyl) porphyrin **1** (100 mg, 0.126mmol) in 25mL of dry CH_2Cl_2 was added oxalyl chloride (790 mg, 6.22 mmol) and a catalytic amount of DMF (1μL), and the mixture was stirred at room temperature overnight. The reaction mixture was evaporated in vacuo to give the acid chloride. The residue was dissolved in dry THF (2 mL) and a solution of L-aspartic acid β-*t*-butyl α-methyl ester hydrochloride (240 mg, 1.01 mmol) and DIEA (1.04 g, 8.06 mmol) in dry CH_2Cl_2 (2 mL) was added and stirred at room temperature for 3h. The solvent and excess reagent were evaporated and the crude product was taken up in 150mL of CH_2Cl_2 and washed with 1N NaOH (100 mL), 10% citric acid (100 mL), and brine (100 mL) and dried over Na_2SO_4. The organic layer was evaporated and was purified by preparative TLC (SiO_2, 10% MeOH/CH_2Cl_2) to give the fully protected product. Further treatment with 95%TFA/H_2O (15 mL) at room temperature for 4h followed by evaporation afforded the final product as a dark green solid (143 mg, 87%): mp > 300°C;^{1}H NMR (400MHz, DMSO-d_6); δ 9.31 (d, J = 7.33 Hz, 4H), 8.88 (s, 8H), 8.6 (s, b, 4H), 8.37 (d, J = 7.83, 8H), 8.32 (d, J = 7.83, 8H), 4.99 (m, 4H) 3.75 (s, 12H), 3.01 (dd, J = 16.42, 5.31 Hz, 4H), 2.90 (dd, J = 16.42, 8.08, 4H), -2.94 (s, b, 2H); MALDI-TOF MS *m/e* calcd for $C_{68}H_{58}N_8O_{20}$ $[M + H]^+$ 1307.4, found 1307. 7.

Compound 3. To a solution of m-tetrakis-(4-carboxyphenyl) porphyrin **1** (43 mg, 0.054 mmol) in 11mL of dry CH_2Cl_2 was added oxalyl chloride (340 mg, 2.67 mmol) and a catalytic amount of DMF (0.3uL), and the mixture was stirred at room temperature overnight. The reaction mixture was evaporated in vacuo to give the acid chloride. The residue was dissolved in dry THF (0.9 mL) and a solution of L-aspartic acid β-*t*-butyl α-*t*-butyl ester hydrochloride (122 mg, 0.43 mmol) and DIEA (450 mg, 3.46 mmol) in dry CH_2Cl_2 (0.9 mL) was added and stirred at room temperature for 3h. The solvent and excess reagent were evaporated and the crude product was taken up in 50mL of CH_2Cl_2 and washed with 1N NaOH (50 mL), 10% citric acid (50 mL), and brine (50 mL) and dried over Na_2SO_4. The organic layer was evaporated and was purified by preparative TLC (SiO_2, 10% MeOH/CH_2Cl_2) to give the fully protected product. Further treatment with 95%TFA/H_2O (5 mL) at room temperature for 4h followed by evaporation afforded the final product as a dark green solid (51mg, 76%): mp > 300°C; ^{1}H NMR (400MHz, DMSO-d_6); δ 9.17 (d, J = 7.8 Hz, 4H), 8.88 (s, 8H), 8.36 (d, J = 8.34 Hz, 8H), 8.32 (d, J = 8.34 Hz, 8H), 5.90 (s, b, 8H), 4.93 (m, 4H), 2.98 (dd, J = 16.42, 5.56 Hz, 4H), 2.86 (dd, J = 16.42, 8.34 Hz, 4H), -2.94 (s, b, 2H); ESI-MS *m/e* calcd for $C_{64}H_{50}N_8O_{20}$ $[M + H]^+$ 1251.3, found 1251.3.

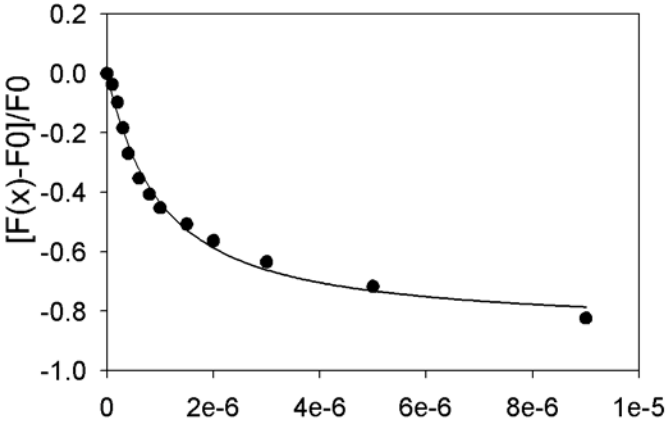
Compound 4: To a solution of m-tetrakis-(4-carboxyphenyl) porphyrin **1** (51 mg, 0.064 mmol) in 12mL of dry CH_2Cl_2 was added oxalyl chloride (400 mg, 3.16 mmol) and a catalytic amount of DMF (0.4 uL), and the mixture was stirred at room temperature overnight. The reaction mixture was evaporated in vacuo to give the acid chloride. The

residue was dissolved in dry THF (1.1 mL) and a solution of dipeptide H-Tyr(tBu)-Asp(OtBu)-OtBu (157 mg, 0.32 mmol) and DIEA (524 mg, 4.06 mmol) in dry CH_2Cl_2 (1.1 mL) was added and stirred at room temperature for 3h. The solvent and excess reagent were evaporated and the crude product was taken up in 60 mL of CH_2Cl_2 and washed with 1N NaOH (60 mL), 10% citric acid (60 mL), and brine (60 mL) and dried over Na_2SO_4. The organic layer was evaporated and was taken up in CH_2Cl_2 (3 mL) and hexane was added to form a precipitate. The crude precipitate was collected and purified by preparative TLC (SiO_2, 10% MeOH/CH_2Cl_2) to give the fully protected product. Further treatment with 95%TFA/H_2O (5 mL) at room temperature for 4h followed by evaporation afforded the final product as a dark green solid (97mg, 80%): mp > 300°C; ^{1}H NMR (400MHz, DMSO-d_6), δ 8.91 (d, J = 6.82 Hz, 4H), 8.84 (s, 8H), 8.59 (d, J = 7.07, 4H), 8.31 (d, J = 6.82, 8H), 8.24 (d, J = 6.82, 8H), 7.28 (d, J = 8.08, 8H), 6.72 (d, J = 8.08, 8H), 5.65 (s, b, 8H), 4.85 (m, 4H), 4.67 (m, 4H), 3.13 (m, 4H), 2.98 (m, 4H), 2.82 (dd, J = 16.17, 5.05, 4H) 2.70 (dd, J = 16.17, 6.32, 4H), -2.94 (s, b, 2H); MALDI-TOF MS *m/e* calcd for $C_{100}H_{86}N_{12}O_{28}$ $[M + H]^+$ 1903.6, found 1904.5

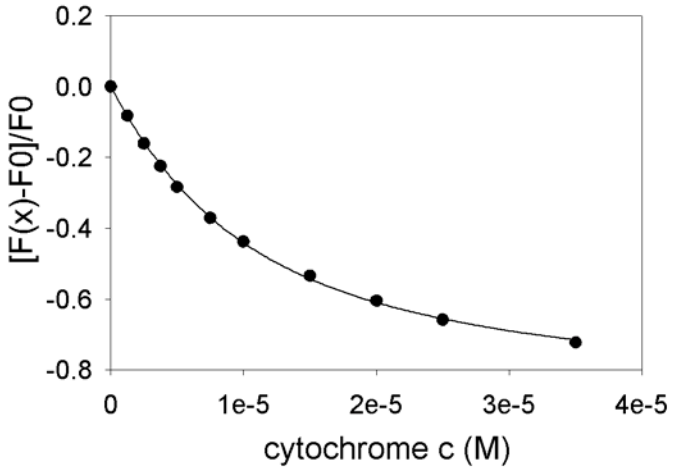
Fluorescence Titrations



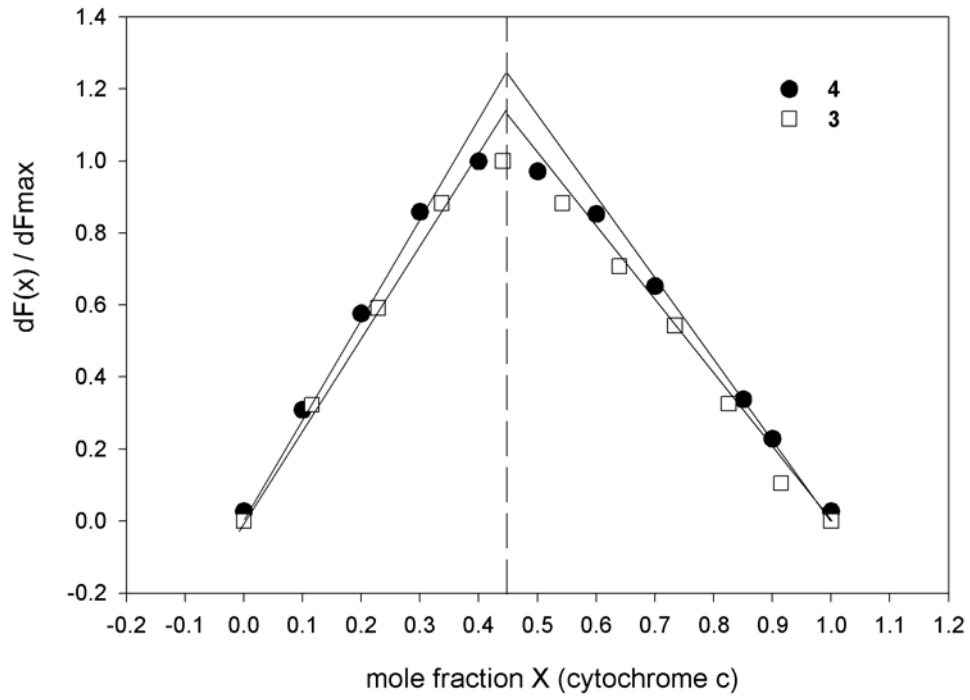
Compound 1. Titrations were carried out with 5μM initial receptor concentration in 5mM sodium phosphate buffer, pH = 7.4, at 298K.



Compound 2. Titrations were carried out with 250nM initial receptor concentration in 5mM sodium phosphate buffer, pH = 7.4, at 298K.



Coproporphyrin. Titrations were carried out with 5μM initial receptor concentration in 5mM sodium phosphate buffer, pH = 7.4, at 298K.



Job plot of the change in fluorescence emission at 650nm as a function of the mole fraction of cytochrome c. The total concentration of the two species was held constant at 5µM (298K, pH 7.4 and 5mM phosphate buffer).