APPENDIX 1

EXPERIMENTAL METHODS

A1.1 GENERAL EXPERIMENTAL METHODS

All solvents were dried and distilled before use, using standard procedures: tetrahydrofuran was distilled over benzophenone and sodium; *N,N*-dimethylformamide was dried over type 3 Å molecular sieves; acetone (AR grade) was distilled over type 4 Å molecular sieves; acetonitrile (AR grade), dichloromethane (AR grade), chloroform (AR grade) and triethylamine were distilled over calcium hydride. Ethanol free chloroform was obtained by passing chloroform (AR grade) through an alumina column to remove ethanol before being distilled over K_2CO_3.

Column chromatography on alumina was carried out using Aldrich aluminium oxide, activated, neutral (Brockmann I standard grade), and on silica using Aldrich silica gel (grade 9385, 230-400 mesh). Chromatotron chromatography was carried out on a model 7924T Chromatotron using plates coated with 2.0 mm thick Merck Silica gel 60 PF_{254} containing gypsum. Preparative TLC was performed on 20 x 20 cm glass plates coated with 1.0 mm thick Art. 7731 Kieselgel 60 G Merck silica. Analytical TLC was carried out on Merck silica gel 60 G_{254} pre-coated aluminium sheets.

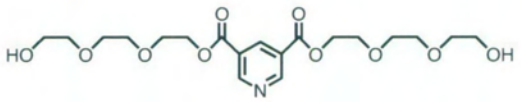
Solution NMR spectra were acquired on a 300 MHz Bruker AC-300P FT spectrometer at 303 K. HR MAS NMR spectra were acquired on a Bruker DRX400 spectrometer at room temperature using a Bruker HR MAS probe. Rotors containing a suspension of the beads in $CDCl_3$ were spun at 4 kHz. One-dimensional HR MAS spectra were obtained with 64 scans. CPMG pulse sequence contained 32 or 2000 π-pulses with a repetition time of 30 ms. Chemical shifts (δ) are reported in parts per million relative to residual solvent. Deuterated solvents were stored over type 3Å molecular sieves and used without any

further purification. UV-vis spectra were performed on a Varian Cary IE UV-VIS spectrophotometer or a Hewlett Packard 8452A diode array spectrometer. Melting points were determined using a Reichert microscopic hot-stage apparatus. Electrospray and electron-impact mass spectrometry were performed by the mass spectrometry service at the University of Wollongong or at the Australian National University Mass Spectrometry unit in which case the samples were run on a Bruker Apex 3 (4.7 T) fourier transform mass spectrometer with a 4.7 telsa superconducting magnet (resolution 10,000 - 20000 RP). Samples were scanned with NaI internal calibrant, and accurate mass data was formulated on a VG Opus 3.6 Data station using elemental analysis program.

A1.2 SYNTHETIC PROCEDURES

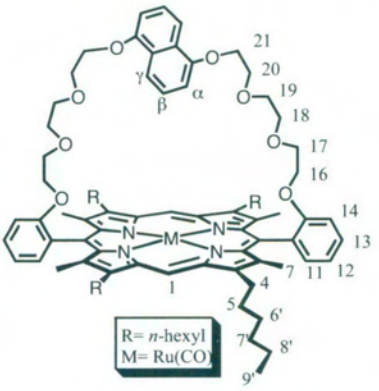
The synthesis of the free base naphthoquinol and hydroquinol strapped porphyrins has been previously reported.[1] Ruthenium (II) carbonyl **2.4**[2] and rhodium (III) iodo **2.11**[3] and **2.8**[4] unsubstituted porphyrins were synthesised according to literature procedures.

Pyridine-3,5-dicarboxylic acid bis-{2-[2-(2-hydroxy-ethoxy)-ethoxy]-ethyl} ester (2.2)



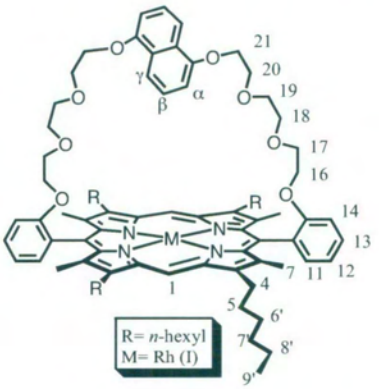
3,5-Pyridinedicarboxylic acid (328 mg, 1.96 mmol), Cs_2CO_3 (703 mg, 2.16 mmol) and 2-[2-(2-Chloro-ethoxy)-ethoxy]-ethanol (726 mg, 4.31 mmol) were dissolved in dry, degassed DMF (50 mL) and heated to 80 °C for 5 days. Upon cooling the mixture was diluted with CH_2Cl_2 (100 mL) and washed with Na_2CO_3 (50 mL) and water (2 x 50 mL). The organic layer was dried over Na_2SO_4 and the solvent was evaporated. The product was purified by chromatotron (2 mm silica plate) using 5% MeOH/CH_2Cl_2 as the eluent to give the pure product as a yellow oil (600 mg, 71%); m/z (EI-MS) $[M + H]^+$ 432.1866 $C_{19}H_{29}NO_{10}$ (calc. 432.1869); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.41 (2H, s, py Ar-H), 8.91 (1H, s, py Ar-H), 4.54-4.57 (4H, m, OCH_2), 3.85-3.88 (4H, m, OCH_2), 3.69-3.78 (12H, m, OCH_2), 3.62-3.65 (4H, m, OCH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 154.3, 138.2, 126.0, 72.6, 70.7, 70.2, 68.9, 64.7, 61.5.

[2,8,12,18-tetrahexyl-3,7,13,17-tetramethyl-5,15{2,2'-[2-{2-[2-(1,5-napthoxy)ethoxy]ethoxy}ethoxy]diphenyl}porphyrinatoruthenium(II) carbonyl (2.5)



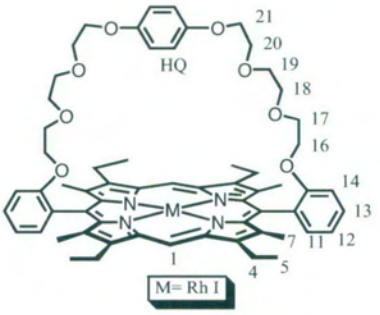
This compound was prepared using published procedures.[2] To dry toluene (15 mL) was added free base porphyrin (160 mg, 0.13 mmol) and triruthenium dodecacarbonyl (200 mg, 0.31 mmol). The mixture was freeze-pump-thawed before being refluxed under N_2 for 3 days. The crude mixture was cooled to room temperature before being filtered through celite and the solvent being removed. The product was purified via radial chromatography using CH_2Cl_2 as the eluent to give starting material (50%) and the product which crystallised from CH_2Cl_2/MeOH as a reddish/orange solid (74 mg, 42%), m.p. 94-96 °C; m/z (ESI-MS) $[M]^+$ 1396.6879 $C_{83}H_{104}N_4O_9{}^{96}Ru$ (calc. 1396.7804); ^1H NMR (300 MHz, $CDCl_3$) δ 9.93 (2H, s, 1), 7.74 (2H, t, *J* 7, 13), 7.61(2H, d, *J* 7, 11), 7.28-7.35 (4H, m, 12, 14), 7.12 (2H, d, *J* 9, γ), 6.66 (2H, t, *J* 8, β), 5.73 (2H, d, *J* 7, α), 4.15 (4H, m, 16), 3.87-3.92 (8H, m, 4), 3.16 (4H, m, 17), 3.05 (8H, m, 20, 21), 2.72 (4H, m, 19), 2.59 (4H, m, 18), 2.52 (12H, s,7), 2.22-2.27 (8H, m, 5), 1.80-1.86 (8H, m, 6'), 1.41-1.58 (16H, m, 7', 8'), 0.94-0.99 (12H, m, 9'); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.8, 158.4, 153.3, 142.7, 141.9, 141.1, 137.1, 135.4, 132.8, 129.7, 126.2, 124.4, 121.1, 115.4, 114.0, 112.0, 106.0, 98.7, 69.5, 69.2, 68.8, 68.7, 68.0, 67.0, 33.4, 32.0, 30.2, 26.9, 22.8, 14.4, 14.2; UV (λnm (ε $M^{-1}cm^{-1}$), CH_2Cl_2) 402 (1.95 x 10^5), 524 (1.53 x 10^4), 555 (1.01 x 10^4).

[2,8,12,18-tetrahexyl-3,7,13,17-tetramethyl-5,15{2,2'-[2-{2-[2-(1,5-napthoxy)ethoxy]ethoxy}ethoxy]diphenyl}porphyrinatorhodium(III) iodide (2.6)



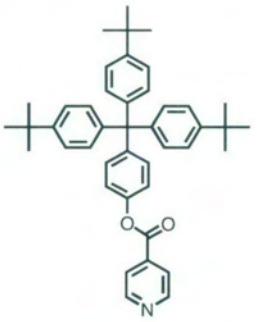
This compound was prepared using a variant of published procedures.[3] A mixture of free base porphyrin (100 mg, 0.078 mmol), anhydrous sodium acetate (63 mg, 0.85 mmol) and $[Rh(CO)_2Cl]_2$ (40 mg, 0.10 mmol) was evacuated under high vacuum and then purged with N_2. Freshly distilled, dry $CHCl_3$ (20 mL) was then cannulated in and the mixture was stirred under N_2 for 4 hours. Solid I_2 (60 mg, 0.24 mmol) was then added and the mixture was stirred overnight. The insoluble material was removed by filtration and the remaining solution was washed with sat. KI (25 mL) and H_2O (3 x 25 mL). The organic layer was dried over Na_2SO_4 and the solvent removed *in vacuo*. The product was purified via column chromatography using CH_2Cl_2 as the eluent followed by crystallisation from CH_2Cl_2/MeOH to give a deep red solid (70 mg, 60%), m.p. 165-167 °C; m/z (ESI-MS) $[M]^+$ 1502.5941 $C_{82}H_{104}N_4O_8RhI$ (calc. 1502.5954); ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.26 (2H, s, 1), 7.73 (2H, t, *J* 7, 13), 7.36-7.44 (4H, m, 11, 14), 7.24-7.29 (2H, t obscured by solvent peak, 12), 7.04 (2H, d, *J* 8, γ), 6.50 (2H, t, *J* 8, β), 5.52 (2H, d, *J* 8, α), 4.30 (4H, m, 16), 3.93-4.05 (8H, m, 4), 3.40-3.43 (4H, m, 17), 3.03 (8H, m, 20, 21), 2.83 (8H, m, 18, 19), 2.63 (12H, s, 7), 2.24-2.29 (8H, m, 5), 1.81-1.86 (8H, m, 6'), 1.41-1.58 (16H, m, 7', 8'), 0.94-0.99 (12H, m, 9'); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 152.7, 143.7, 141.5, 140.2, 138.3, 135.9, 132.1, 130.1, 125.4, 124.3, 121.2, 115.4, 113.9, 111.4, 105.7, 98.9, 69.7, 69.2, 68.9, 67.9, 67.0, 66.3, 33.5, 31.4, 30.2, 27.1, 22.8, 14.6, 14.2; UV (λnm (ε $M^{-1}cm^{-1}$), CH_2Cl_2) 416 (1.57 x 10^5), 528 (2.07 x 10^4), 559 (1.60 x 10^4).

[2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5,15{2,2'-[2-{2-[2-(1,4-phenoxy)ethoxy]ethoxy}ethoxy]diphenyl}porphyrinatorhodium(III) iodide (2.7)



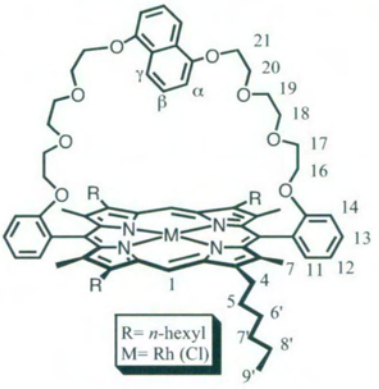
This compound was prepared using a variant of published procedures.[3] A mixture of free base porphyrin (20 mg, 0.02 mmol), anhydrous sodium acetate (16 mg, 0.2 mmol) and $[Rh(CO)_2Cl]_2$ (10 mg, 0.026 mmol) was evacuated under high vacuum and then purged with N_2. Freshly distilled, dry $CHCl_3$ (10 mL) was then cannulated in and the mixture was stirred under N_2 for 4 hours. Solid I_2 (15 mg, 0.06 mmol) was then added and the mixture was stirred overnight. The insoluble material was then removed by filtration and the remaining solution was washed with sat. KI (15 mL) and H_2O (3 x 15 mL). The organic layer was dried over Na_2SO_4 and the solvent removed *in vacuo*. The product was purified via column chromatography using CH_2Cl_2/0.5%MeOH as the eluent followed by crystallisation from CH_2Cl_2/MeOH to give a bright red solid (17 mg, 70%), m.p. 242-244 °C; m/z (ESI-MS) $[M]^+$ 1228.3275 $C_{62}H_{70}N_4O_8RhI$ (calc. 1228.3293); ^1H NMR (300 MHz, $CDCl_3$) δ 10.12 (2H, s, 1), 7.69 (2H, t, *J* 8, 13), 7.51 (2H, d, *J* 6, 11), 7.15-7.26 (4H, m, 12, 14), 5.22 (4H, s, HQ), 4.13-4.16 (4H, m, 16), 3.85-4.04 (8H, m, 4), 3.27-3.31 (4H, m, 17), 2.57-2.60 (4H, m, 21), 2.54 (12H, s, 17), 2.26-2.48 (4H, m, 20), 2.27 (8H, m, 18, 19), 1.73-1.78 (12H, t, *J* 7, 5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 151.4, 145.0, 141.2, 140.0, 138.0, 135.6, 132.2, 129.9, 121.2, 115.9, 111.7, 98.6, 69.6, 69.5, 69.1, 68.6, 68.2, 67.7, 20.1, 17.8, 14.5; UV (λnm (ε $M^{-1}cm^{-1}$), CH_2Cl_2) 414 (1.49 x 10^5), 527 (1.86 x 10^4), 558 (1.39 x 10^4).

Isonicotinic acid 4-[tris-(4-*tert*-butyl-phenyl)-methyl]-phenyl ester (2.10)



4-[Tris-(4-*tert*-butyl-phenyl)-methyl]-phenol[5] (1.11 g, 2.20 mmol), isonicotinic acid (0.307 g, 2.49 mmol), EDC (0.432 g, 2.25 mmol) and HOBT (0.367 g, 2.71 mmol) were dissolved in dry, degassed DMF (100 mL) and stirred at room temp under N_2 for 7 days. The solvent was then removed *in vacuo* and the residue was taken up in CH_2Cl_2 (50 mL) and washed with water (30 mL). The organic layer was then dried over Na_2SO_4 and the solvent evaporated. Purification via column chromatography (SiO_2) using CH_2Cl_2/10%Hexane as the eluent yielded the pure product as a white solid (100 mg, 7%), m.p 297-299 °C; m/z (EI-MS) $[M]^+$ 609.3602 $C_{43}H_{47}NO_2$ (calc. 609.3607); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (2H, d, *J* 6, py Ar-H), 8.01 (2H, d, *J* 6, py Ar-H), 7.27-7.33 (8H, m, Ar-H), 7.04-7.16 (8H, m, Ar-H), 1.34 (27H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 150.8, 148.6, 148.3, 145.6, 143.6, 137.0, 132.4, 130.7, 124.2, 123.2, 119.9, 63.4, 34.3, 31.4.

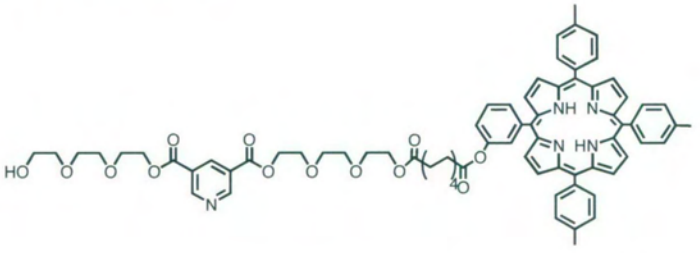
[2,8,12,18-tetrahexyl-3,7,13,17-tetramethyl-5,15{2,2'-[2-{2-[2-(1,5-napthoxy)ethoxy]ethoxy}ethoxy]diphenyl}porphyrinatorhodium(III) chloride (2.15)



This compound was prepared using a variant of published procedures.[6] A mixture of free base porphyrin (35 mg, 0.027 mmol), and $[Rh(CO)_2Cl]_2$ (15 mg, 0.038 mmol) was

evacuated under high vacuum and then purged with N_2. Degassed, dry toluene (10 mL) was then cannulated in and the mixture was stirred under N_2 for 12 hours. The mixture was opened to the air and heated at approximately 60 °C with vigorous stirring for 4 hours to oxidise the rhodium. The insoluble material was then removed by filtration and the solvent was removed *in vacuo*. The mixture was taken up in 2%MeOH/CH_2Cl_2 to form the methanol complex and again the solvent was removed. The product was purified via column chromatography using CH_2Cl_2 as the eluent followed by crystallisation from CH_2Cl_2/MeOH to give a bright red solid (25 mg, 64%), m.p. 153-155 °C; m/z (ESI-MS) $[M]^+$ 1410.6632 $C_{82}H_{104}N_4O_8RhCl$ (calc. 1410.6598); ^1H NMR (300 MHz, $CDCl_3$) δ 10.35 (2H, s, 1), 7.78 (2H, t, *J* 8, 13), 7.64 (2H, br d, 11), 7.30-7.39 (4H, m, 12, 14), 7.04 (2H, d, *J* 8, γ), 6.53 (2H, br t, β), 5.65 (2H, d, *J* 8, α), 4.22 (4H, m, 16), 4.02 (8H, m, 4), 3.54 (4H, m, 17), 3.32 (8H, m, 20, 21), 2.80 (8H, m, 18, 19), 2.64 (12H, s, 7), 2.28-2.30 (8H, m, 5), 1.83-1.90 (8H, m, 6'), 1.44-1.62 (16H, m, 7', 8'), 0.97-1.02 (12H, m, 9'); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 153.1, 143.5, 140.8, 140.1, 138.2, 135.9, 132.2, 130.0, 126.1, 124.3, 121.3, 115.0, 113.9, 111.1, 105.6, 98.4, 69.9, 69.5, 69.2, 68.9, 67.8, 66.9, 33.6, 32.0, 30.3, 27.2, 22.8, 14.7, 14.2; UV (λnm (ε $M^{-1}cm^{-1}$), CH_2Cl_2) 413 (2.01 x 10^5), 527 (2.04 x 10^4), 559 (1.48 x 10^4).

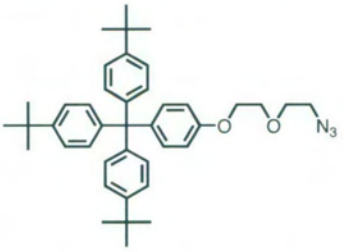
Pyridine-3,5-dicarboxylic acid 3-{2-[2-(2-hydroxy-ethoxy)-ethoxy]-ethyl} ester 5-{2-[2-(2-{9-[3-(10,15,20-tri-*p*-tolyl-porphyrin-5-yl)-phenoxycarbonyl]-nonanoyloxy}-ethoxy)-ethoxy]-ethyl} ester (3.11)



Sebacic acid tetra tolyl porphyrin **3.9**[7] (210 mg, 0.25 mmol) was dissolved in excess oxalyl chloride (5 mL) and the mixture was stirred at room temperature under N_2 for 2 hours. The reaction mixture was then pumped dry, solubilized in 1 mL $CHCl_3$, and pumped dry. This procedure was repeated 4 times to remove all excess oxalyl chloride. The produced acid chloride porphyrin **3.10** (quantitative yield) in dry $CHCl_3$ (10 mL) was then added dropwise over 30 minutes to a solution of excess pyridine thread **3.6** (600 mg,

1.38 mmol) in dry $CHCl_3$ (30 mL). The reaction mixture was then stirred at room temperature under N_2 for 48 hours. After this time the mixture was diluted with $CHCl_3$ (30 mL) and washed with sat. $NaHCO_3$ (20 mL) and H_2O (20 mL). The crude product was purified by chromatatron (2mm silica plate) using CH_2Cl_2/5%MeOH as the eluent before final crystallisation from CH_2Cl_2/MeOH to yield the pure product as a purple solid (175 mg, 56%); m.p 128-130 °C; m/z (ESI-MS) $[M+H]^+$ 1270.5764 $C_{76}H_{80}N_5O_{13}$ (calc. 1270.5674); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.39 (2H, s, py *ortho* H), 8.88 (9H, m, Ar-H, py *para* H), 8.11 (7H, m, Ar-H), 7.99 (1H, s, Ar-H), 7.76 (1H, t, *J* 7, Ar-H), 7.56 (7H, m, Ar-H), 4.51-4.55 (4H, m, OCH_2), 4.18-4.21 (2H, m, OCH_2), 3.82-3.84 (4H, m, OCH_2), 3.58-3.71 (14H, m, OCH_2), 2.73 (9H, s, CH_3), 2.64-2.68 (2H, m, CH_2), 2.27-2.32 (2H, m, CH_2), 1.81 (2H, m, CH_2), 1.61 (2H, m, CH_2), 1.33-1.41 (8H, m, CH_2), -2.76 (2H, s, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ173.7, 172.4, 164.4, 154.3, 149.3, 144.7, 139.2, 138.2, 137.4, 134.5, 132.1, 131.2, 127.9, 127.4, 126.0, 120.9, 120.5, 120.3, 118.3, 72.5, 70.7, 70.6, 70.4, 69.3, 69.0, 64.8, 63.2, 61.8, 45.8, 34.5, 34.1, 29.1, 24.9, 21.5; UV (λnm (ε $M^{-1}cm^{-1}$), CH_2Cl_2) 419 (3.70×10^5), 515 (1.74×10^4), 551 (8.77×10^3), 591 (5.44×10^3), 646 (4.38×10^3).

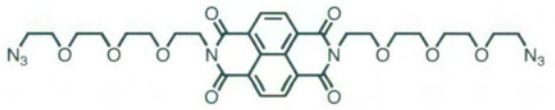
2-(2-{4-[Tris-(4-*tert*-butyl-phenyl)-methyl]-phenoxy}-ethoxy)-ethylazide (3.15)



2-(2-{4-[Tris-(4-*tert*-butyl-phenyl)-methyl]-phenoxy}-ethoxy)-ethyltosylate[5] (0.99 g, 1.32 mmol) and NaN_3 (0.86 g, 13.2 mmol) were suspended in dry, degassed DMF (10 mL). The mixture was stirred under N_2 at room temperature for 3 days, before being diluted with H_2O (50 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The organic layers were combined and washed with brine (50 mL), dried over anhydrous Na_2SO_4 and the solvent removed *in vacuo*. The compound was purified by chromatotron (2 mm silica plate) using 20% Hexane/CH_2Cl_2 as the eluent to give the pure product as a white solid (513 mg, 63%); m.p 208-210 °C; m/z (FAB-MS) $[M + H]^+$ 617.3991 $C_{41}H_{52}N_3O_2$ (calc. 617.3981); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25-7.28 (6H, m, Ar-H), 7.10-7.13 (8H, m,

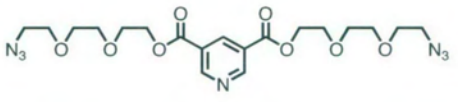
Ar-H), 6.82 (2H, d, *J* 6, OAr-H), 4.14-4.17 (2H, m, OCH_2), 3.87-3.90 (2H, m, OCH_2), 3.76-3.79 (2H, m, OCH_2), 3.42-3.45 (2H, m, N_3CH_2), 1.34 (27H, s, *t*-but); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.5, 148.3, 144.2, 139.9, 132.4, 130.8, 124.1, 113.2, 70.3, 69.9, 67.3, 63.1, 50.8, 34.4, 31.5.

2,7-Bis-(2-{2-[2-(2-azide-ethoxy)-ethoxy]-ethoxy}-ethyl)benzo[*lmn*][3,8] phenanthroline -1,3,6,8-tetraone (3.17)



2,7-Bis-(2-{2-[2-(2-tosyl-ethoxy)-ethoxy]-ethoxy}-ethyl)benzo[*lmn*][3,8]phenanthroline -1,3,6,8-tetraone[8] (1.12 g, 1.21 mmol) and NaN_3 (1.56 g, 24.0 mmol) were suspended in dry, degassed DMF (30 mL). The mixture was stirred under N_2 at room temperature for 4 days, before being diluted with H_2O (100 mL) and extracted with CH_2Cl_2 (3 x 60 mL). The organic layers were combined and washed with brine (100 mL), dried over anhydrous Na_2SO_4 and the solvent removed *in vacuo*. The compound was purified by chromatotron (2 mm silica plate) using 5% $MeOH/CH_2Cl_2$ as the eluent to give the pure product as an orange solid (671 mg, 83%); m.p 57-59 °C; m/z (ESI-MS) $[M + Na]^+$ 691.2422 $C_{30}H_{36}N_8O_{10}Na$ (calc. 691.2452); ^1H NMR (300 MHz, $CDCl_3$) δ 8.59 (4H, s, NDI-H), 4.34-4.37 (4H, m, OCH_2), 3.76-3.79 (4H, m, OCH_2), 3.63-3.64 (4H, m, OCH_2), 3.53-3.58 (16H, m, OCH_2), 3.26-3.29 (4H, m, N_3CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6, 130.8, 126.4, 70.6, 70.5, 70.0, 69.9, 67.7, 50.6, 39.5.

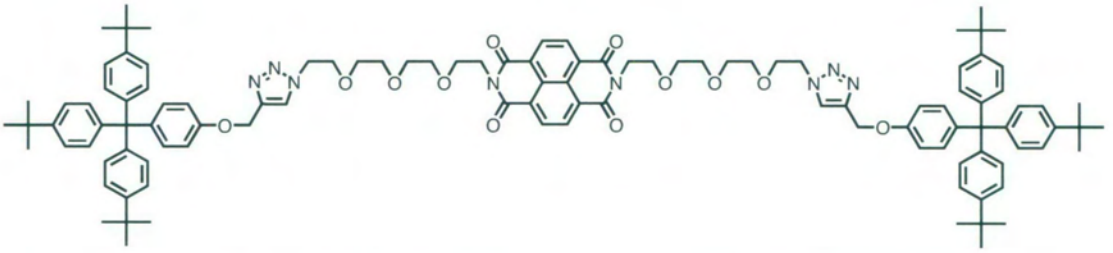
Pyridine-3,5-dicarboxylic acid bis-{2-[2-(2-azide-ethoxy)-ethoxy]-ethyl} ester (3.18)



Pyridine-3,5-dicarboxylic acid bis-{2-[2-(2-hydroxy-ethoxy)-ethoxy]-ethyl} ester **3.6** (1.2 g, 2.74 mmol) and Et_3N (650 µL) was dissolved in dry $CHCl_3$ (40 mL) under N_2 and stirred in an ice/salt bath. Tosyl chloride (1.06 g, 5.6 mmol) and Et_3N (475 µL) in dry $CHCl_3$ was added dropwise over 30 minutes. The mixture was then refluxed under N_2 for 7 days before being diluted with cold water (100 mL). The organic layer was separated, washed with H_2O (100 mL), dried over anhydrous Na_2SO_4 and the solvent removed. The

crude tosylate was then added to a suspension of NaN_3 in dry, degassed DMF (20 mL) and stirred at room temperature under N_2 for a further 4 days. The reaction mixture was again diluted with H_2O (100 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The organic layers were combined and then were washed with brine (50 mL), dried over anhydrous Na_2SO_4 and the solvent removed *in vacuo*. The product was purified by chromatatron (2 mm silica plate) using 2% MeOH/CH_2Cl_2 as the eluent to give the pure product as yellow oil (180 mg, 13%); m/z (FAB-MS) $[M + H]^+$ 482.2012 $C_{19}H_{28}N_7O_8$ (calc. 482.1999); ^1H NMR (300 MHz, $CDCl_3$) δ 9.39 (2H, s, py *ortho*-H), 8.89 (1H, s, py *para*-H), 4.54-4.57 (4H, m, OCH_2), 3.86-3.89 (4H, m, OCH_2), 3.67-3.71 (12H, m, OCH_2), 3.36-3.40 (4H, m, N_3CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 154.3, 138.2, 126.0, 77.2, 70.7, 70.1, 69.1, 64.8, 50.7.

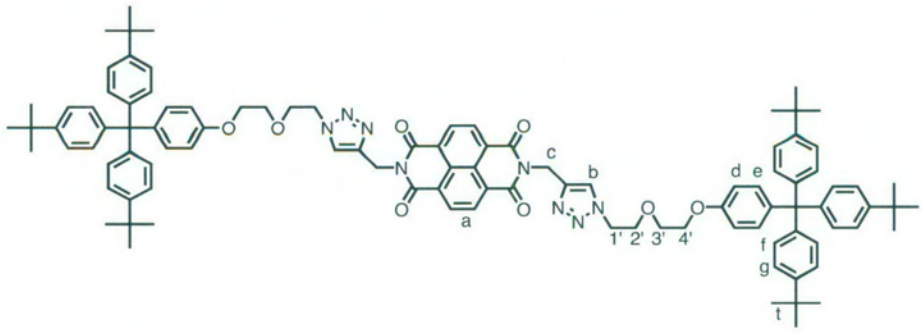
2,7-Bis-{1-[2-(2-{4-[tris-(4-*tert*-butyl-phenyl)-methyl]-phenoxymethyl}-1*H*-[1,2,3] triazo l-4-ylethoxy}-ethoxy)-ethoxy]-ethyl-benzo[*lmn*][3,8] phenanthroline-1,3,6,8-tetraone (3.20)



2,7-Bis-(2-{2-[2-(2-azide-ethoxy)-ethoxy]-ethoxy}-ethyl)benzo[*lmn*][3,8] phenanthroline -1,3,6,8-tetraone **3.17** (13 mg, 0.02 mmol), 4-[Tris-(4-*tert*-butyl-phenyl)-methyl]-propargyl ether[9] (23 mg, 0.04 mmol), DIPEA (6 mg, 0.05 mmol) and $Cu(MeCN)_4BF_4$ (2 mg, 0.006 mmol) were dissolved in dry degassed toluene (5 mL) and the mixture was stirred under N_2 for 4 days. The reaction mixture was then diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (30 mL). The organic layer was dried over anhydrous Na_2SO_4, and the solvent removed. The product was purified by chromatotron (2 mm silica plate) using CH_2Cl_2/3% MeOH as the eluent and then crystallised from CH_2Cl_2/MeOH to give the pure product as a pale yellow solid (31 mg, 90%); m.p 197-198 °C; m/z (ESI-MS) $[M + H]^+$ 1753.9776 $C_{110}H_{129}N_8O_{12}$ (calc. 1753.9730); ^1H NMR (300 MHz, $CDCl_3$) δ 8.73 (4H, s, NDI-H), 7.84 (2H, s, triazole H), 7.19-7.31 (16H, m, Ar-H), 7.09-7.16 (12H, m, Ar-H) 6.88 (4H, d, *J* 6, OAr-H), 5.19 (4H, s, OCH_2-triazole), 4.54-4.57 (4H, m, CH_2-triazole), 4.46-4.48 (4H, m, NDI-CH_2), 3.83-3.90 (8H, m, OCH_2), 3.69-3.72 (4H, m, OCH_2), 3.57-

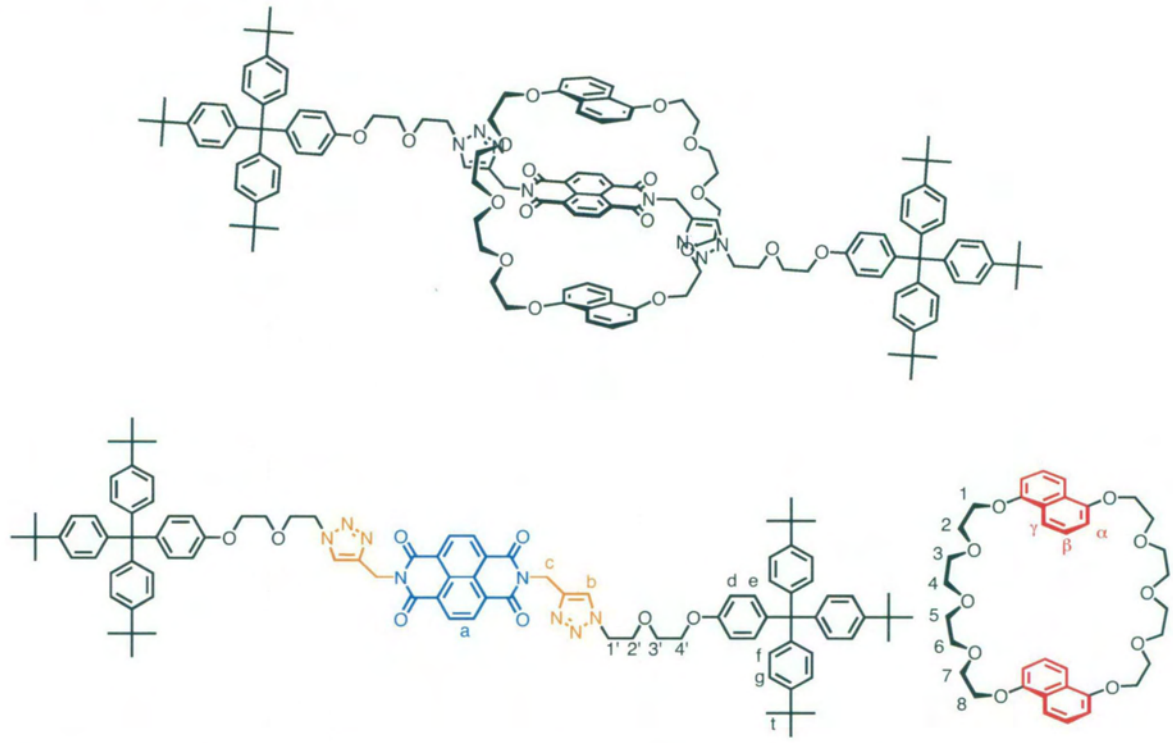
3.61 (12H, m, OCH_2), 1.33 (54H, s, *t*-but); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 156.2, 148.4, 144.1, 140.1, 132.3, 131.0, 130.7, 126.6, 124.0, 123.9, 113.3, 70.6, 70.5, 70.1, 69.4, 67.8, 63.1, 62.0, 50.3, 39.6, 34.3, 31.4.

2,7-Bis-{1-[2-(2-{4-[tris-(4-*tert*-butyl-phenyl)-methyl]-phenoxy}-ethoxy)-ethyl]-1*H*-[1,2,3]triazo l-4-ylmethyl}-benzo[*lmn*][3,8]phenanthroline-1,3,6,8-tetraone (3.22)



2,7-Di-prop-2-ynyl-benzo[*lmn*][3,8]phenanthroline-1,3,6,8-tetraone[10] (8 mg, 0.025 mmol), 2-(2-{4-[Tris-(4-*tert*-butyl-phenyl)-methyl]-phenoxy}-ethoxy)-ethylazide **3.15** (30 mg, 0.05 mmol), DIPEA (6 mg, 0.05 mmol) and $Cu(MeCN)_4BF_4$ (2 mg, 0.006 mmol) were dissolved in dry degassed toluene (5 mL) and the mixture was stirred under N_2 for 8 days. The reaction mixture was then diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (30 mL). The organic layer was dried over anhydrous Na_2SO_4, and the solvent removed. The product was purified by crystallisation from CH_2Cl_2/MeOH to give the pure product as a pale yellow solid (32 mg, 80%); m.p 204-207 °C; m/z (ESI-MS) $[M + H]^+$ 1577.8690 $C_{102}H_{113}N_8O_8$ (calc. 1577.8681); ^1H NMR (300 MHz, $CDCl_3$) δ 8.74 (4H, s, a), 7.87 (2H, s, b), 7.24-7.29 (12H, m, g), 7.09-7.16 (16H, m, e,f) 6.80 (4H, d, *J* 6, d), 5.50 (4H, s, c), 4.52-4.55 (4H, m, 1'), 4.07-4.10 (4H, m, 4'), 3.91-3.95 (4H, m, 2'), 3.79-3.81 (4H, m, 2'), 1.32 (54H, s, t); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.4, 156.4, 148.4, 144.1, 142.7, 140.1, 132.3, 131.2, 130.7, 126.8, 136.6, 124.5, 124.1, 113.1, 69.9, 69.6, 67.1, 63.1, 50.3, 35.6, 34.3, 31.4.

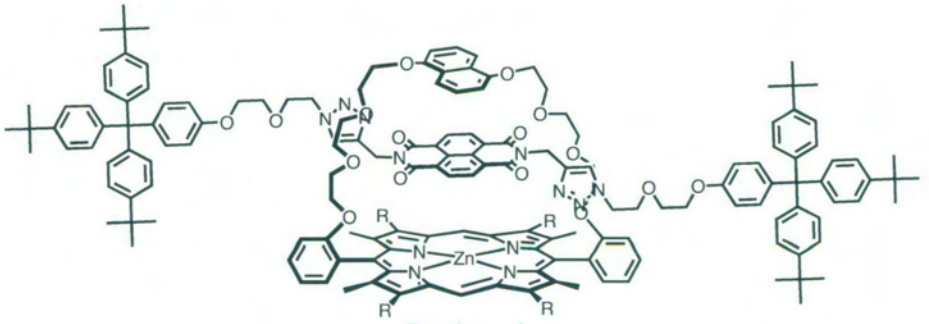
Crown rotaxane (3.23)

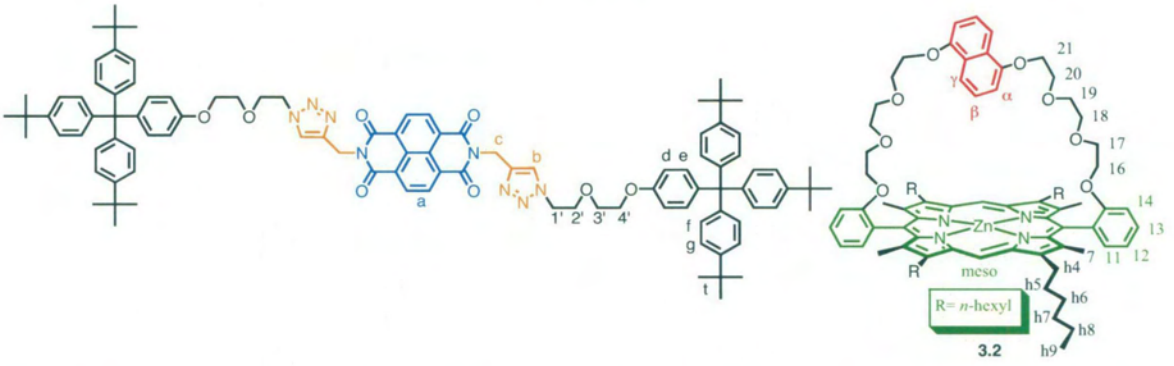


2,7-Di-prop-2-ynyl-benzo[*lmn*][3,8]phenanthroline-1,3,6,8-tetraone[10] (8 mg, 0.025 mmol), 2-(2-{4-[Tris-(4-*tert*-butyl-phenyl)-methyl]-phenoxy}-ethoxy)-ethylazide **3.15** (30 mg, 0.05 mmol), dinaphthocrown **3.16** (16 mg, 0.025 mmol) and DIPEA (6 mg, 0.05 mmol) were dissolved in dry degassed toluene (5 mL) and the mixture was stirred under N_2 for 1 hour to allow solubilisation of the diimide. After this time $Cu(MeCN)_4BF_4$ (2 mg, 0.006 mmol) was added and the mixture was stirred at room temperature under N_2 for 3 days. The reaction mixture was then diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (30 mL). The organic layer was dried over anhydrous Na_2SO_4, and the solvent removed. The product was purified by chromatotron (2 mm silica plate) using 5% $MeOH/CH_2Cl_2$ as the eluent yielding dumbbell **3.22** (18 mg, 46%) and crown rotaxane products. The crown rotaxane was then crystallised from EtOAC/Hexane to give the pure crown rotaxane as a pale pink solid (22 mg, 43%); m.p 181-184 °C; m/z (ESI-MS) $[M + H]^+$ 2214.1600 $C_{138}H_{157}N_8O_{18}$ (calc. 2214.1616); ^1H NMR (300 MHz, $CDCl_3$) δ 8.31 (4H, s, a), 8.08 (2H, s, b), 7.24-7.29 (12H, m, g), 7.08-7.11 (16H, m, e,f), 6.76-6.79 (8H, d, *J 6*, d, γ), 6.26 (4H, t, *J 8*, β), 5.90 (4H, d, *J 6*, α), 5.41 (4H, s, c), 4.64-4.67 (4H, m, 1'), 3.99-4.07 (16H, m, OCH_2), 3.87-3.92 (24H, m, OCH_2), 3.78-3.81 (4H, m, OCH_2), 1.32 (54H, s, t); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6, 156.3, 152.9, 148.4, 144.1, 143.2, 140.0, 132.3,

130.7, 125.5, 125.0, 124.7, 124.0, 123.5, 114.1, 113.1, 103.5, 77.2, 71.4, 71.2, 69.9, 69.8, 67.3, 67.1, 63.1, 50.4, 34.6, 34.3, 31.4; UV (λnm (ε $M^{-1}cm^{-1}$), CH_2Cl_2) 500 (745).

Zinc porphyrin rotaxane (3.24)

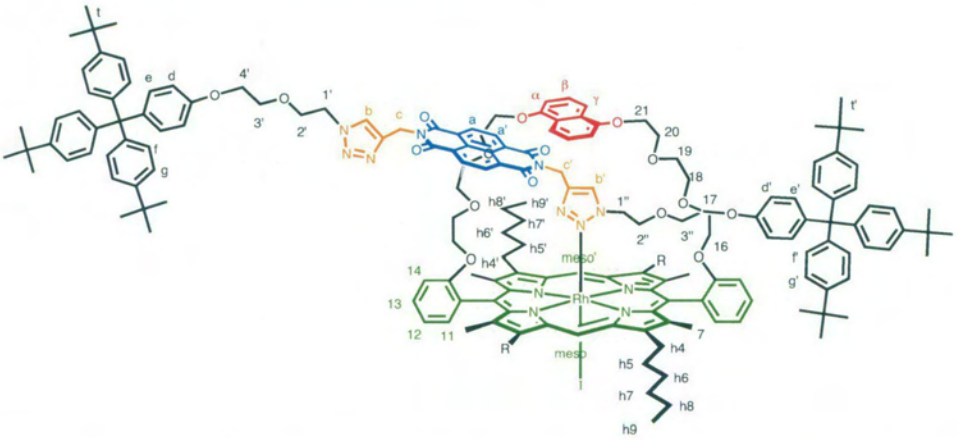




2,7-Di-prop-2-ynyl-benzo[*lmn*][3,8]phenanthroline-1,3,6,8-tetraone[10] (8 mg, 0.025 mmol), 2-(2-{4-[Tris-(4-*tert*-butyl-phenyl)-methyl]-phenoxy}-ethoxy)-ethylazide **3.15** (30 mg, 0.05 mmol), strapped porphyrin **3.2** (33 mg, 0.025 mmol) and DIPEA (6 mg, 0.05 mmol) were dissolved in dry degassed toluene (5 mL) and the mixture was stirred under N_2 for 1 hour to allow solubilisation of the diimide. After this time $Cu(MeCN)_4BF_4$ (2 mg, 0.006 mmol) was added and the mixture was stirred at room temperature under N_2 for 3 days. The reaction mixture was then diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (30 mL). The organic layer was dried over anhydrous Na_2SO_4, and the solvent removed. The product was purified by chromatotron (2 mm silica plate) using 2% MeOH/CH_2Cl_2 as the eluent, yielding dumbbell **3.22** (21 mg, 55%) and porphyrin rotaxane products. The porphyrin rotaxane was then crystallised from EtOAC/Hexane to give the pure porphyrin rotaxane as a purple solid (11 mg, 20%); m.p 145-148 °C; m/z (ESI-MS) $[M]^+$ 2913.5612 $C_{184}H_{216}N_{12}O_{16}Zn$ (calc. 2913.5749); ^1H NMR (300 MHz, $CDCl_3$) δ 9.78 (2H, s, *meso*), 7.78 (2H, s, b), 7.70 (2H, t, *J 7*, 13), 7.36 (2H, d, *J 8*, 14), 7.25-7.29 (16H, m, e, g), 7.09-7.16 (14H, m, f, 12), 6.94 (2H, t, *J 6*, 11), 6.74 (4H, d, *J 6*,

d), 6.42 (4H, s, a), 5.86 (2H, d, *J* 6, γ), 5.25 (2H, t, *J* 8, β), 5.12 (4H, s, c), 4.87 (4H, m, 16), 4.66 (2H, d, *J* 6, α), 4.46 (4H, m, 1'), 4.22 (4H, m, 17), 4.08 (4H, m, h4), 3.95 (4H, m, 4'), 3.80-3.85 (12H, m, h4, 19, 2') 3.72 (4H, m, 18), 3.62 (4H, m, 3'), 3.54 (4H, m, 20), 3.29 (4H, m, 21), 2.58 (12H, s, 7), 2.14 (8H, m, h5), 1.76 (8H, m, h6), 1.45-1.57 (16H, m, h7, h8), 1.34 (54H, s, t), 0.92 (12H, m, h9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 157.8, 156.3, 151.9, 148.4, 148.1, 145.5, 144.1, 143.1, 142.8, 140.0, 137.9, 135.9, 132.8, 132.3, 130.7, 129.5, 126.9, 125.6, 124.1, 123.7, 122.6, 120.8, 120.6, 119.7, 115.4, 113.0, 110.7, 102.9, 96.2, 71.1, 70.3, 69.7, 69.6, 67.6, 67.1, 65.6, 63.1, 50.2, 34.3, 33.4, 32.0, 31.4, 30.1, 27.0, 22.7, 14.2; UV (λnm (ε $M^{-1}cm^{-1}$), CH_2Cl_2) 417 (2.48 x 10^5), 537 (1.57 x 10^4), 570 (9.76 x 10^3).

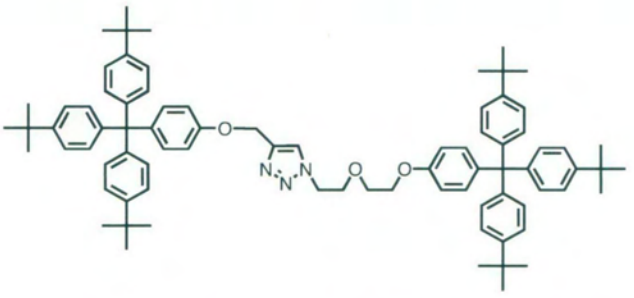
Rhodium porphyrin rotaxane (3.27)



Free base porphyrin rotaxane **3.26** (13 mg, 0.005 mmol), anhydrous sodium acetate (4 mg, 0.05 mmol) and $[Rh(CO)_2Cl]_2$ (3 mg, 0.008 mmol) were dissolved in dry degassed DCM and the reaction mixture was stirred at room temperature under N_2 for 5 hours. Solid I_2 (4 mg, 0.02 mmol) was then added and the mixture stirred under N_2 overnight at room temperature. The solution was then diluted with CH_2Cl_2 (30 mL), washed with sat. $KI_{(aq)}$ (20 mL) and H_2O (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent removed *in vacuo*. The product was purified by preparative TLC (2 mm silica plate) using 2% MeOH/CH_2Cl_2 as the eluent. The product was then crystallised from EtOAC/Hexane to give the pure porphyrin rotaxane as a red solid (5 mg, 40%); m.p 151-152 °C; m/z (ESI-MS) $[M + H]^+$ 3080.4540 $C_{184}H_{217}N_{12}O_{16}RhI$ (calc.3080.4635); ^{1}H NMR (300 MHz, $CDCl_3$ at –20 °C) δ 10.30 (1H, s, 1), 10.21 (1H, s, 1'), 8.30 (2H, d, *J* 8, a), 7.97 (1H, s, b), 7.86-7.90 (4H, m, a', 11), 7.70 (2H, t, *J* 7, 12), 7.36 (2H, t, *J* 8, 13),

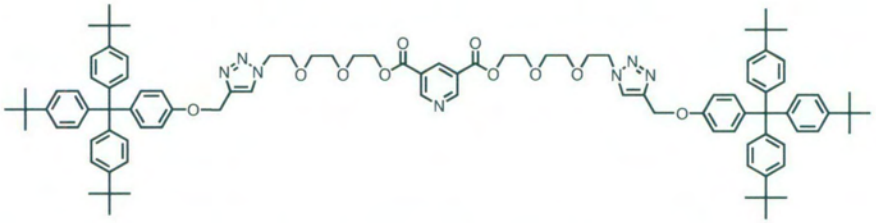
7.23-7.29 (16H, m, e, g), 7.07-7.15 (14H, m, f, 12), 6.81 (2H, d, *J* 6, d), 6.63 (2H, d, *J* 6, d'), 6.57 (2H, d, *J* 6, γ), 6.01-6.04 (4H, m, β, α), 5.43 (2H, s, c), 5.02 (1H, s, b'), 4.56 (2H, m, 1'), 3.50-4.21 (24H, m, 16,17,20,21,h4,h4'), 3.40 (4H, m, 2',3'), 3.20 (4H, m, 19), 2.90-3.11 (4H, m, 4'',3''), 2.78 (4H, m, 18), 2.50 (16H, m, 7, 1'', 2'') 2.23 (8H, m, h5, h5'), 1.44-1.87 (20H, m, h6,h6',h7,h7',h8), 1.30 (54H, s, t,t'), 0.89-1.00 (10H, m, h9,h8'), 0.37 (6H, m, h9'), 0.11 (2H, s, c'); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3, 156.3, 153.5, 148.4, 144.1, 143.6, 140.0, 136.3, 133.3, 132.3, 132.0, 130.7, 130.2, 129.7, 125.4, 124.0, 121.6, 114.9, 113.5, 113.3, 113.0, 105.6, 98.1, 70.5, 70.2, 69.5, 68.7, 68.0, 67.9, 66.9, 63.1, 34.3, 33.9, 32.1, 31.4, 30.1, 30.0, 29.8, 27.1, 22.7, 14.9, 14.1; UV (λnm (ε $M^{-1}cm^{-1}$), CH_2Cl_2) 423 (1.40 x 10^5), 534 (1.94 x 10^4), 564 (9.41 x 10^3).

1-[2-(2-{4-[Tris-(4-*tert*-butyl-phenyl)-methyl]-phenoxy}-ethoxy)-ethyl]-4-{4-[tris-(4-*tert*-butyl-phenyl)-methyl]-phenoxymethyl}-1*H*-[1,2,3]triazole (3.28)



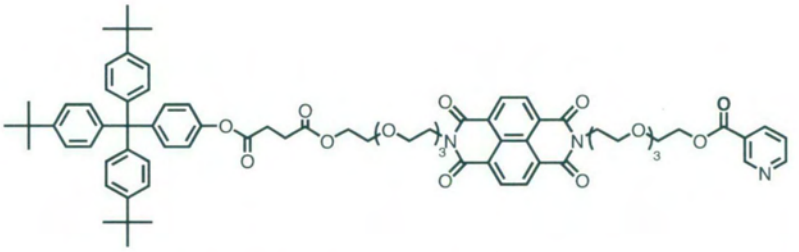
4-[Tris-(4-*tert*-butyl-phenyl)-methyl]-propargyl ether[9] (20 mg, 0.04 mmol), 2-(2-{4-[Tris-(4-*tert*-butyl-phenyl)-methyl]-phenoxy}-ethoxy)-ethylazide **3.15** (23 mg, 0.04 mmol), DIPEA (5 mg, 0.04 mmol) and $Cu(MeCN)_4BF_4$ (1.2 mg, 0.004 mmol) were dissolved in dry degassed toluene (5 mL) and the mixture was stirred under N_2 for 4 days. The reaction mixture was then diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (30 mL). The organic layer was dried over anhydrous Na_2SO_4, and the solvent removed. The product was purified by chromatotron (2 mm silica plate) using CH_2Cl_2 as the eluent to give the pure product as a white solid (30 mg, 71%); m.p 264-265 °C; m/z (ESI-MS) $[M + H]^+$ 1160.7576 $C_{81}H_{98}N_3O_3$ (calc. 1160.7608); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (1H, s, triazole), 7.21-7.24 (12H, m, Ar-H), 7.04-7.09 (16H, m, Ar-H), 6.73-6.80 (4H, m, OAr-H), 5.13 (2H, s, OCH_2triazole), 4.56-4.60 (2H, m, OCH_2), 4.03-4.06 (2H, m, OCH_2), 3.94-3.97 (2H, m, OCH_2), 3.78-3.81 (2H, m, OCH_2), 1.30 (54H, s, t); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 156.1, 148.3, 144.1, 140.1, 132.3, 130.7, 126.7, 113.3, 113.0, 69.9, 69.6, 67.0, 63.1, 61.9, 34.3, 31.4.

Pyridine-3,5-dicarboxylic acid bis-(2-{2-[2-(4-{4-[tris-(4-*tert*-butyl-phenyl)-methyl]-phenoxymethyl}-[1,2,3]triazol-1-yl)-ethoxy]-ethoxy}-ethyl) ester (3.30)



4-[Tris-(4-*tert*-butyl-phenyl)-methyl]-propargyl ether[9] (27 mg, 0.05 mmol), Pyridine-3,5-dicarboxylic acid bis-{2-[2-(2-azide-ethoxy)-ethoxy]-ethyl} ester **3.18** (12 mg, 0.025 mmol), DIPEA (6 mg, 0.05 mmol) and $Cu(MeCN)_4BF_4$ (2 mg, 0.005 mmol) were dissolved in dry degassed toluene (5 mL) and the mixture was stirred under N_2 for 2 days. The reaction mixture was then diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (30 mL). The organic layer was then dried over anhydrous Na_2SO_4, and the solvent removed. The product was purified by preparative TLC (2 mm silica plate) using 2%MeOH/CH_2Cl_2 as the eluent followed by recrystallisation from EtOAc/Hexane to give the pure product as a white solid (25 mg, 70%); m.p 207-209 °C; m/z (ESI-MS) $[M + H]^+$ 1566.9073 $C_{99}H_{120}N_7O_{10}$ (calc. 1566.9097); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.40 (2H, s, py *ortho*-H), 8.89 (1H, s, py *para*-H), 7.80 (2H, s, triazole), 7.23-7.26 (12H, m, Ar-H), 7.10-7.13 (16H, m, Ar-H) 6.87 (4H, d, *J* 6, OAr-H), 5.19 (4H, s, OCH_2triazole), 4.51-4.57 (8H, m, OCH_2), 3.89-3.92 (4H, m, OCH_2), 3.78-3.81 (4H, m, OCH_2), 3.64 (8H, m, OCH_2), 1.32 (54H, s, t); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 156.2, 154.3, 148.4, 144.2, 140.2, 132.3, 130.7, 124.0, 123.8, 113.3, 70.6, 69.5, 69.0, 64.7, 63.1, 62.0, 50.3, 34.3, 31.4.

Succinic acid 2(2-[2-(2-{1,3,6,8-tetraoxo-7-[2-(2-{2-[2-(pyridine-3-carbonyloxy)-ethoxy]-ethoxy}-ethoxy)-ethyl]-3,6,7,8-tetrahydro-1*H*-benzo[*lmn*][3,8]phenanthrolin-2-yl} ethoxy)-ethoxy]-ethoxy)-ethyl ester 4-[tris-(4-*tert*-butyl-phenyl)-methyl]-phenyl ester (4.5)

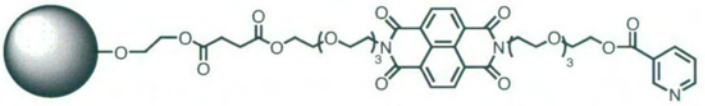


Succinic acid mono-(2-{2-[2-(2-{1,3,6,8-tetraoxo-7-[2-(2-{2-[2-(pyridine-3-carbonyloxy)-ethoxy]-ethoxy}-ethoxy)-ethyl]-3,6,7,8-tetrahydro-1*H*-benzo[*lmn*][3,8]phenanthrolin-2-yl}-ethoxy)-ethoxy]-ethoxy}-ethyl) ester **3.6**[7] (50 mg, 0.06 mmol) was dissolved in toluene (5 mL) and excess oxalyl chloride (2 mL) was added. The mixture was stirred at room temperature under N_2 for 4 hours. The reaction mixture was then pumped dry, solubilized in 1 mL $CHCl_3$, and pumped dry. This procedure was repeated 4 times to remove all excess oxalyl chloride. The produced acid chloride diimide thread (quantitative yield) in dry $CHCl_3$ (10 mL) was then added to a solution of stopper **4.4** (34 mg, 0.06 mmol) in dry $CHCl_3$ (30 mL). The reaction mixture was then stirred at room temperature under N_2 for 12 hours. After this time the mixture was diluted with $CHCl_3$ (30 mL) and washed with sat. $NaHCO_3$ (20 mL) and H_2O (20 mL). The crude product was purified by chromatatron (2mm silica plate) using 5%MeOH/ CH_2Cl_2 as the eluent to give the pure product as a yellow solid (66 mg, 81%); m.p 168-170 °C; m/z (ESI-MS) $[M+H]^+$ 1310.6165 $C_{77}H_{88}N_3O_{16}$ (calc. 1310.6086); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.24 (1H, s, py-H), 8.76 (5H, s, py-H, NDI), 8.35 (1H, d, *J 8*, py-H), 7.45 (1H, t, *J 6*, py-H), 7.18-7.28 (8H, m, Ar-H), 7.08-7.11 (6H, m, Ar-H) 6.97 (2H, d, *J 6*, OAr-H), 4.45-4.52 (8H, m, OCH_2), 4.24-4.27 (2H, m, OCH_2), 3.84-3.87 (8H, m, OCH_2), 3.60-3.72 (14H, m, OCH_2), 2.86 (2H, m, CH_2), 2.77 (2H, m, CH_2), 1.31 (27H, s, t); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 170.8, 165.1, 162.8, 153.1, 150.7, 148.5, 145.0, 143.7, 137.3, 132.2, 131.0, 130.7, 126.8, 126.6, 124.1, 119.9, 70.7, 70.6, 70.1, 69.0, 67.8, 64.5, 63.9, 63.4, 39.6, 34.3, 31.4, 29.3, 29.1.

General Bead Attachment Procedure

ArgoGel-OH beads* (50 mg) and monocarboxylic acid component(s) (300 μmol) were stirred at room temperature under nitrogen with 5 mL $CHCl_3$. Triethylamine (62 μL, 450 μmol) was added to the mixture via a syringe, followed by HOBT (81 mg, 600 μmol) and EDC (115 mg, 600 μmol). The mixture was heated to 50 °C and stirred for 7 days under N_2. Then the beads were filtered and washed successively with $CHCl_3$ (5 mL), acetone (5 mL), water (5 mL), 2M $HCl_{(aq)}$ (5 mL), sat. sodium bicarbonate (5 mL), water (5 mL) acetone (5 mL), pet. spirits (5 mL) and $CHCl_3$ (5 mL). The beads were then dried under high vacuum.

ArgoGel™-OH bound 2-[2-(2-{2-[2-nicotinoyloxy-ethoxy]-ethoxy}-ethoxy)-ethyl],7-[2-(2-{2-[2-(3-carboxy-propionyloxy)-ethoxy]-ethoxy}-ethoxy)-ethyl]benzo[lmn]-[3,8]phenanthroline-1,3,6,8-tetraone (4.10)



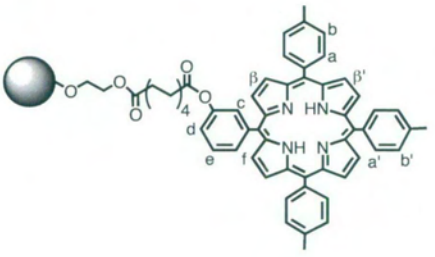
The general bead attachment procedure was followed reacting 2-[2-(2-{2-[2-nicotinoyloxy-ethoxy]-ethoxy}-ethoxy)-ethyl],7-[2-(2-{2-[2-(3-carboxy-propionyloxy)-ethoxy]-ethoxy}-ethoxy)-ethyl]benzo[lmn]-[3,8]phenanthroline-1,3,6,8-tetraone[7] (337 mg, 409 μmol) with ArgoGel-OH beads (50 mg). The resulting component-attached beads were coloured yellow. ^{1}H NMR (400 MHz, 2%MeOD/$CDCl_3$) δ 9.16 (1H, d, Ar-H), 8.72 (5H, s, Ar-H), 8.28 (1H, dd, Ar-H), 7.39 (1H, dd, Ar-H), 4.43 (4H, m, OCH_2), 4.19 (8H, m, OCH_2), 3.44-3.79 (20H, m, OCH_2), 2.60 (4H, s, CH_2). This compound was also attached to TentaGel resin beads giving an identical HR MAS NMR spectrum.

* This same procedure was used for attaching the same components to TentaGel beads.

TentaGel-OH bound 1(2,6)-(3-carboxynaphthalena) 15(1,5)-naphthalena-2,5,8,11,14,16,19,22,25,28-decaoxacyclo-octacosaphane (4.15)

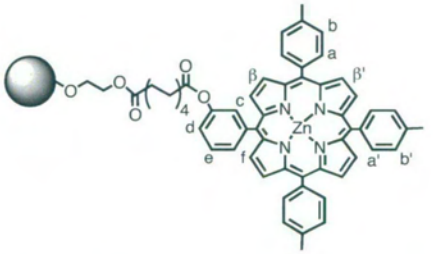
The general bead attachment procedure was followed reacting 1(2,6)-(3-carboxynaphthalena) 15(1,5)-naphthalena-2,5,8,11,14,16,19,22,25,28-decaoxacyclo-octacosaphane[7] (250 mg, 367 μmol) with TentaGel-OH beads (50 mg). The resulting component-attached beads were coloured off-white. ^{1}H NMR (400 MHz, 2%MeOD/$CDCl_3$) δ 8.08 (1H, s, Ar-H), 7.72 (1H, dd, Ar-H), 7.33 (1H, d, Ar-H), 7.29 (1H, d, Ar-H), 7.10 (1H, dd, Ar-H), δ 7.03 (2H, dd, Ar-H), δ 6.94 (2H, m, Ar-H), δ 6.46 (2H, dd, Ar-H), δ 4.44 (2H, m, OCH_2), δ 4.15 (2H, m, OCH_2), δ 3.42-3..99 (28H, m, OCH_2). This compound was also attached to ArgoGel beads but the synthesis was performed by Dilip Nath.[11]

ArgoGel™-OH tethered free base 5-[3-(9-carboxy-nonionyloxy)-phenyl]10,15,20-*tris*-[*p*-tolyl] porphyrin (4.18)



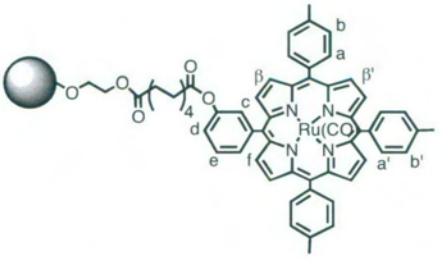
The general bead attachment procedure was followed reacting free base 5-[3-(9-carboxy-nonionyloxy)-phenyl]10,15,20-*tris*-[*p*-tolyl] porphyrin[7] (260 mg, 304 μmol) with ArgoGel-OH beads (40 mg). The resulting purple coloured beads were then dried under water pump vacuum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (8H, dd, β-H), 8.04 (7H, d, Ar-H), 7.92 (1H, s, Ar-H), 7.70 (1H, s, Ar-H), 7.51 (7H, s, Ar-H), 2.81 (2H, m, CH_2), 2.63 (2H, m, CH_2), 2.19 (4H, m, CH_2), 1.71 (2H, m, CH_2), 1.54 (2H, m, CH_2), 1.24 (8H, m, CH_2).

ArgoGel™-OH tethered zinc 5-[3-(9-carboxy-nonionyloxy)-phenyl]10,15,20-*tris*-[*p*-tolyl] porphyrin (4.19)



Zinc was inserted into the free base porphyrin beads **3.18** by gently stirring the beads in a solution of DCM followed by addition of a solution of methanol saturated with zinc acetate. The mixture was stirred at room temperature overnight before filtering the beads. The beads were then washed with water (3 x 10 mL) to remove any excess zinc acetate, acetone (5 mL) and $CHCl_3$ (5 mL). The resulting purple coloured beads were then dried under water pump vacuum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (8H, d, β-H), 8.03 (7H, d, Ar-H), 7.90 (1H, dd, Ar-H), 7.50 (7H, d, Ar-H), 2.83 (2H, m, CH_2), 2.65 (2H, m, CH_2), 2.18 (4H, m, CH_2), 1.70 (2H, m, CH_2), 1.55 (2H, m, CH_2), 1.23 (8H, m, CH_2).

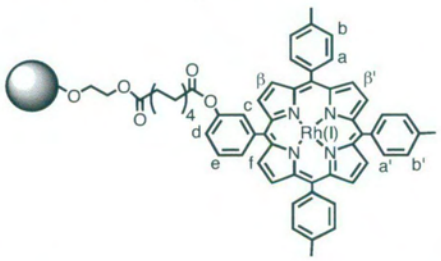
ArgoGel™-OH tethered ruthenium carbonyl 5-[3-(9-carboxy-nonionyloxy)-phenyl]10,15,20-*tris*-[*p*-tolyl] porphyrin (4.20)



ArgoGel-OH beads (40 mg), ruthenium carbonyl 5-[3-(9-carboxy-nonionyloxy)-phenyl]10,15,20-*tris*-[*p*-tolyl] porphyrin[7] (256 mg, 258 μmol) and pyridine (60 mg, 810 μmol) were stirred at room temperature under nitrogen with 5 mL $CHCl_3$. Triethylamine (61 μL, 456 μmol) was added to the mixture via a syringe, followed by HOBT (78 mg, 644 μmol) and EDC (111 mg, 644 μmol). The mixture was heated to 50 °C and stirred for 7 days. Then the beads were filtered and washed successively with $CHCl_3$ (5 mL), acetone (5 mL), 2 M HCl (5 mL), water (5 mL), sat. sodium bicarbonate (5 mL), water (5 mL), acetone (5 mL), pet. spirits (5 mL) and $CHCl_3$ (5 mL). The resulting red coloured beads were then dried under water pump vacuum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85

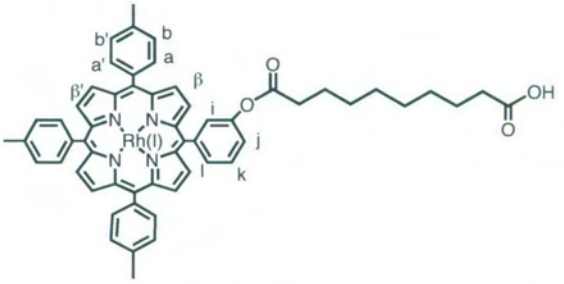
(8H, d, β-H), 8.06 (6H, d, Ar-H), 7.70 (1H, dd, Ar-H), 7.53 (6H, d, Ar-H), δ 7.23 (1H, dd, Ar-H), δ 2.25 (4H, m, CH_2), δ 1.54 (4H, m, CH_2), δ 1.23 (8H, m, CH_2).

ArgoGel™-OH tethered rhodium iodide 5-[3-(9-carboxy-nonionyloxy)-phenyl]10,15,20-*tris*-[*p*-tolyl] porphyrin (4.21)



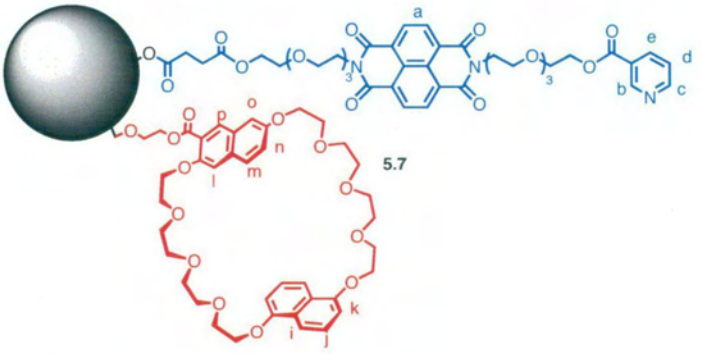
ArgoGel-OH beads (50 mg), rhodium iodide 5-[3-(9-carboxy-nonionyloxy)-phenyl]10,15,20-*tris*-[*p*-tolyl] porphyrin **5.6** (283 mg, 260 μmol) and pyridine (60 mg, 810 μmol) were stirred at room temperature under nitrogen with 5 mL $CHCl_3$. Triethylamine (61 μL, 456 μmol) was added to the mixture via a syringe, followed by HOBT (78 mg, 644 μmol) and EDC (111 mg, 644 μmol). The mixture was heated to 50 °C and stirred for 7 days. Then the beads were filtered and washed successively with $CHCl_3$ (5 mL), acetone (5 mL), 2 M HCl (5 mL), water (5 mL), sat. sodium bicarbonate (5 mL), water (5 mL), acetone (5 mL), pet. spirits (5 mL) and $CHCl_3$ (5 mL). The resulting red coloured beads were then dried under water pump vacuum.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (8H, d, β-H), 8.06 (5H, d, Ar-H), 7.97 (4H, dd, Ar-H), 7.69 (1H, dd, Ar-H), 7.49 (6H, d, Ar-H), 2.29 (4H, m, CH_2), 1.56 (4H, m, CH_2), 1.23 (8H, m, CH_2). This compound was also attached to TentaGel resin beads giving a similar HR MAS NMR spectrum.

5-[3-(9-carboxy-nonionyloxy)-phenyl]10,15,20-*tris*-[*p* tolyl]porphyrinatio rhodium (III) iodide (5.6)



Rhodium iodide was inserted into 5-[3-(9-carboxy-nonionyloxy)-phenyl]10,15,20-*tris*-[*p*-tolyl] porphyrin (320 mg, 0.35 mmol) using the same procedure as for porphyrins **2.6** and **2.7**, then subjected to column chromatography (SiO_2: DCM to 2% MeOH/DCM) and final crystallisation from CH_2Cl_2/MeOH to afford 282 mg (78 %) of the deep red solid product, m.p. 163-165 °C; m/z (ESI-MS) $[M]^+$ 957.2851 $C_{57}H_{50}N_4O_4{}^{96}Rh$ (calc. 957.2887); ^1H NMR (300 MHz, $CDCl_3$) δ 8.89 (8H, s, β, β'), 8.06-8.10 (7H, m, a, a', j), 7.91 (1H, s, i), 7.74 (1H, br t, k), 7.58 (6H, d, *J* 9, b, b'), 7.46 (1H, br d, l), 2.56 (2H, m, CH_2), 1.96 (2H, m, CH_2), 1.76 (2H, m, CH_2), 1.50 (2H, m, CH_2), 1.38 (2H, m, CH_2), 1.29 (2H, m, CH_2), 1.11 (2H, m, CH_2), 0.98 (2H, m, CH_2), 0.86 (2H, m, CH_2), -0.76 (1H, br s, COOH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.8, 178.4, 172.6, 143.7, 143.4, 143.2, 139.0, 137.4, 134.5, 133.7, 132.9, 132.6, 132.3, 131.2, 128.0, 122.6, 121.0, 120.8, 53.5, 46.9, 34.4, 33.5, 33.1, 28.8, 24.9, 24.1, 22.1; UV (λnm (ε $M^{-1}cm^{-1}$), CH_2Cl_2) 421 (1.71 x 10^5), 531 (2.11 x 10^4), 568 (7.76 x 10^3).

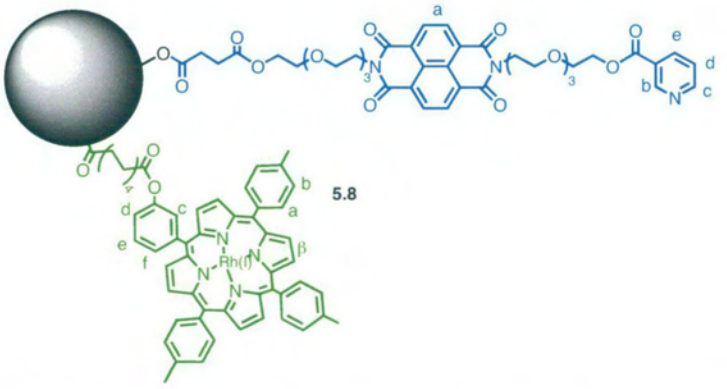
Synthesis of crown-diimide functionalised TentaGel beads (5.7)



TentaGel beads (50 mg), 2-[2-(2-{2-[2-nicotinoyloxy-ethoxy]-ethoxy}-ethoxy)-ethyl],7-[2-(2-{2-[2-(3-carboxy-propionyloxy)-ethoxy]-ethoxy}-ethoxy)-ethyl]benzo[lmn]-[3,8]phenanthroline-1,3,6,8-tetraone (154 mg, 186 μmol), 1(2,6)-(3-carboxynaphthalena)

15(1,5)-naphthalena-2,5,8,11,14,16,19,22,25,28-decaoxacyclo-octacosaphane (126 mg, 185 μmol) and LiI (230 mg, 172 mmol) were stirred at room temperature under N_2 in dry $CDCl_3$ (5 mL). Triethylamine (76 μL, 568 μmol) was added to the mixture via a syringe, followed by HOBT (104 mg, 858 μmol) and EDC (153 mg, 887 μmol). The mixture was heated to 50 °C and stirred for 7 days. The beads were then filtered and washed successively with $CHCl_3$ (5 mL), acetone (5 mL), 2 M HCl (5 mL), water (5 mL), sat. sodium bicarbonate (5 mL), water (5 mL), acetone (5 mL), pet. spirits (5 mL) and $CHCl_3$ (5 mL). The resulting orange coloured beads were then dried under water pump vacuum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (1H, s, b), 8.68 (5H, s, a, c), 8.28 (1H, s, e), 7.37 (1H, s, d), 4.44 (4H, m, OCH_2), 4.21 (8H, m, OCH_2), 3.45-3.79 (20H, m, OCH_2), 2.62 (4H, s, CH_2).

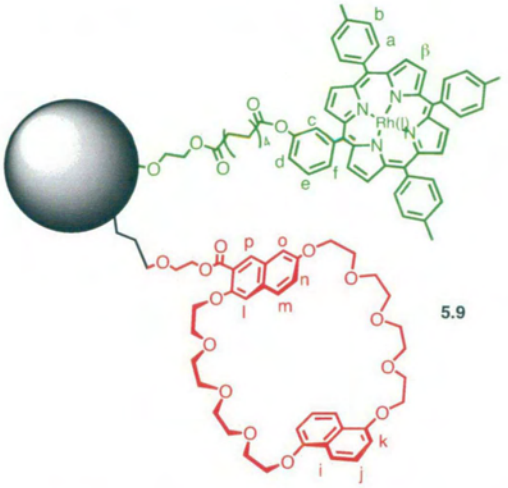
Synthesis of porphyrin-diimide functionalised TentaGel beads (5.8)



TentaGel beads (50 mg), 2-[2-(2-{2-[2-nicotinoyloxy-ethoxy]-ethoxy}-ethoxy)-ethyl],7-[2-(2-{2-[2-(3-carboxy-propionyloxy)-ethoxy]-ethoxy}-ethoxy)-ethyl]benzo[lmn]-[3,8]phenanthroline-1,3,6,8-tetraone (107 mg, 129 μmol), and rhodium iodide 5-[3-(9-carboxy-nonionyloxy)-phenyl]10,15,20-*tris*-[*p*-tolyl] porphyrin (143 mg, 131 μmol) were stirred at room temperature under N_2 in dry $CDCl_3$ (5 mL). Triethylamine (55 μL, 411 μmol) was added to the mixture via a syringe, followed by HOBT (73 mg, 602 μmol) and EDC (106 mg, 614 μmol). The mixture was heated to 50 °C and stirred for 7 days. Then the beads were filtered and washed successively with $CHCl_3$ (5 mL), acetone (5 mL), 2 M HCl (2 x 5 mL), water (5 mL), 2 M HCl (2 x 5 mL), water (5 mL), sat. sodium bicarbonate (2 x 5 mL), water (5 mL), acetone (5 mL), pet. spirits (5 mL) and $CHCl_3$ (5 mL). The resulting red coloured beads were then dried under water pump vacuum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (1H, s, b), 8.85 (8H, d, β), 8.71 (4H, s, a), 8.68 (5H, s, a',

c), 8.28 (1H, s, e), 8.07 (7H, s, Ar-H), 7.94 (1H, s, Ar-H), 7.69 (1H, s, Ar-H), 7.49 (6H, d, Ar-H), 7.37 (1H, s, d), 6.67 (1H, s, e'), 5.25 (1H, s, d'), 4.43 (4H, m, OCH_2), 4.19 (8H, m, OCH_2), 3.45-3.79 (20H, m, OCH_2), 2.79 (2H, m, CH_2), 2.62 (4H, s, CH_2), 2.28 (4H, m, CH_2), 1.58 (4H, m, CH_2), 1.28 (8H, m, CH_2).

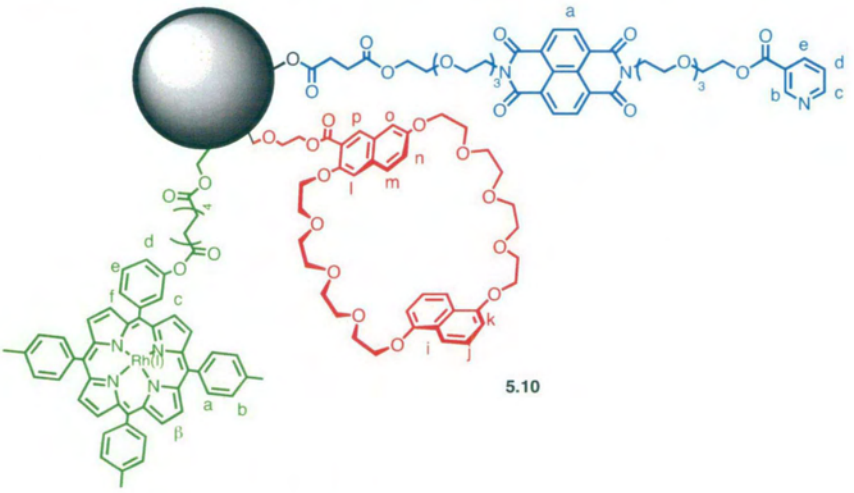
Synthesis of crown-porphyrin functionalised TentaGel beads (5.9)



5.9

TentaGel beads (50 mg), 1(2,6)-(3-carboxynaphthalena) 15(1,5)-naphthalena-2,5,8,11,14, 16,19,22,25,28-decaoxacyclo-octacosaphane (90 mg, 132 µmol), rhodium iodide 5-[3-(9-carboxy-nonionyloxy)-phenyl]10,15,20-*tris*-[*p*-tolyl] porphyrin (143 mg, 131 µmol), 2,7-*Bis*-[2-(2-{2-[2-nicotinoyloxyethoxy]ethoxy}ethoxy)ethyl]benzo[lmn]-[3,8] phenanthroline-1,3,6,8-tetraone (55 mg, 67 µmol) and LiI (185 mg, 138 mmol) were stirred at room temperature under N_2 in dry $CDCl_3$ (5 mL). Triethylamine (56 µL, 418µmol) was added to the mixture via a syringe, followed by HOBT (79 mg, 651 µmol) and EDC (106 mg, 618 µmol). The mixture was heated to 50 °C and stirred for 7 days. The beads were then filtered and washed successively with $CHCl_3$ (5 mL), acetone (5 mL), 2 M HCl (2 x 5 mL), water (5 mL), 2 M HCl (2 x 5 mL), water (5 mL), sat. sodium bicarbonate (2 x 5 mL), water (5 mL), acetone (5 mL), pet. spirits (5 mL) and $CHCl_3$ (5 mL). The resulting red coloured beads were then dried under water pump vacuum. ^1H NMR (400 MHz, $CDCl_3$) δ 8.84 (8H, d, β-H), 8.07 (7H, s, Ar-H), 7.98 (1H, s, Ar-H), 7.73 (1H, dd, Ar-H), 7.49 (6H, m, Ar-H), 2.66 (2H, m, CH_2), 2.29 (4H, m, CH_2), 1.59 (4H, m, CH_2), 1.28 (8H, m, CH_2).

Synthesis of diimide- crown-porphyrin functionalised TentaGel beads (5.10)



TentaGel beads (50 mg), 2-[2-(2-{2-[2-nicotinoyloxy-ethoxy]-ethoxy}-ethoxy)-ethyl],7-[2-(2-{2-[2-(3-carboxy-propionyloxy)-ethoxy]-ethoxy}-ethoxy)-ethyl]benzo[lmn]-[3,8]phenanthroline-1,3,6,8-tetraone (94 mg, 113 μmol), 1(2,6)-(3-carboxynaphthalena) 15(1,5)-naphthalena-2,5,8,11,14, 16,19,22,25,28-decaoxacyclo-octacosaphane (78 mg, 114 μmol), rhodium iodide 5-[3-(9-carboxy-nonionyloxy)-phenyl]10,15,20-*tris*-[*p*-tolyl] porphyrin (125 mg, 114 μmol), and LiI (146 mg, 108 mmol) were stirred at room temperature under N_2 in dry $CDCl_3$ (5 mL). Triethylamine (71 μL, 529 μmol) was added to the mixture via a syringe, followed by HOBT (93 mg, 766 μmol) and EDC (134 mg, 781 μmol). The mixture was heated to 50 °C and stirred for 7 days. The beads were then filtered and washed successively with $CHCl_3$ (5 mL), acetone (5 mL), 2 M HCl (2 x 5 mL), water (5 mL), 2 M HCl (2 x 5 mL), water (5 mL), sat. sodium bicarbonate (2 x 5 mL), water (5 mL), acetone (5 mL), pet. spirits (5 mL) and $CHCl_3$ (5 mL). The resulting red coloured beads were then dried under water pump vacuum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (1H, s, b), 8.85 (8H, d, β), 8.71 (4H, s, a), 8.67 (5H, s, a', c), 8.27 (1H, s, e), 8.06 (7H, s, Ar-H), 7.94 (1H, s, Ar-H), 7.69 (1H, s, Ar-H), 7.49 (6H, d, Ar-H), 7.35 (1H, s, d), 6.65 (1H, s, e'), 5.27 (1H, s, d'), 4.44 (4H, m, OCH_2), 4.20 (8H, m, OCH_2), 3.44-3.80 (20H, m, OCH_2), 2.62 (4H, s, CH_2), 2.29 (4H, m, CH_2), 1.54 (4H, m, CH_2), 1.28 (8H, m, CH_2).

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APPENDIX 2

Supplementary material for Chapter 2. This appendix includes selected COSY, NOESY and ROESY spectrum typical of the NMRs obtained for use in characterisation of the compounds and binding geometries discussed in Chapter 2.

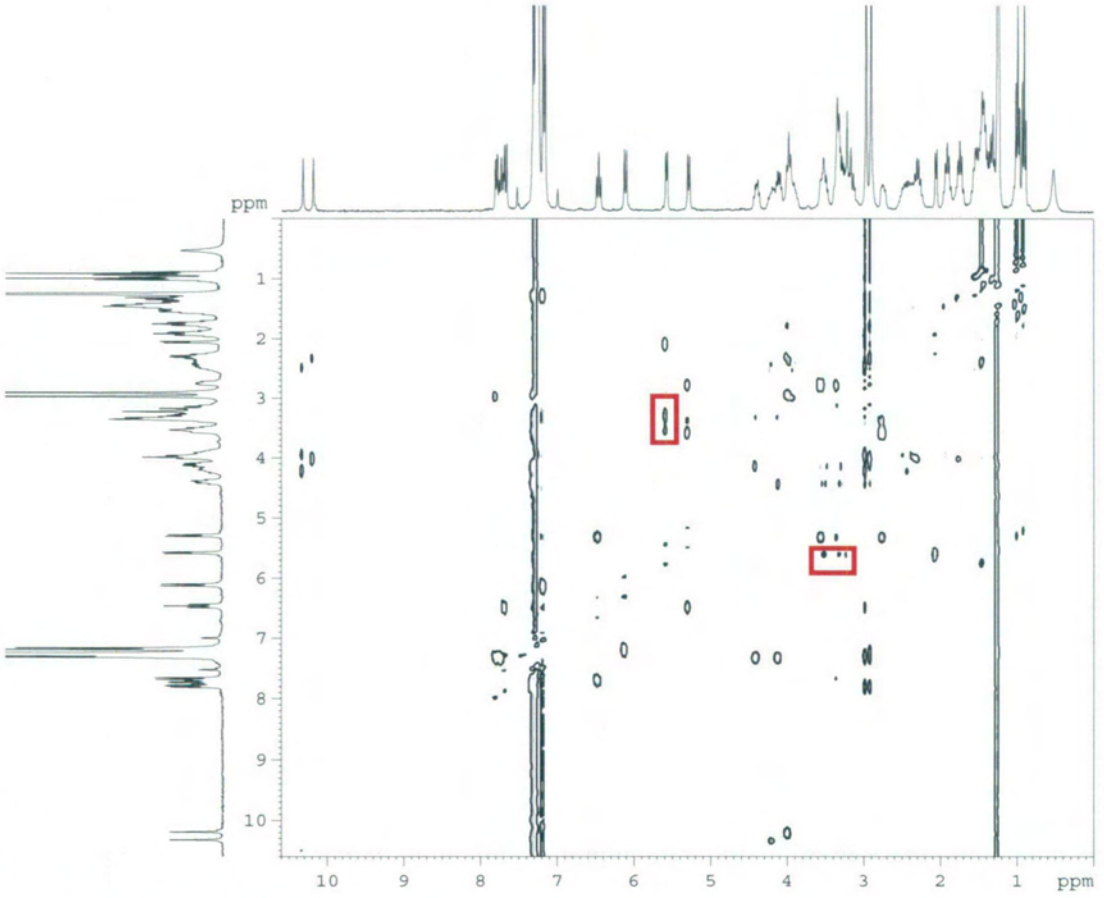


Figure A2.1:- ROESY spectra of a 1:1 mixture of ruthenium porphyrin **2.5** with pyridine ligand **2.10**. Red boxes indicate near in space correlations of the pyridine ligands with the strap of the porphyrin indicating "inside" coordination.

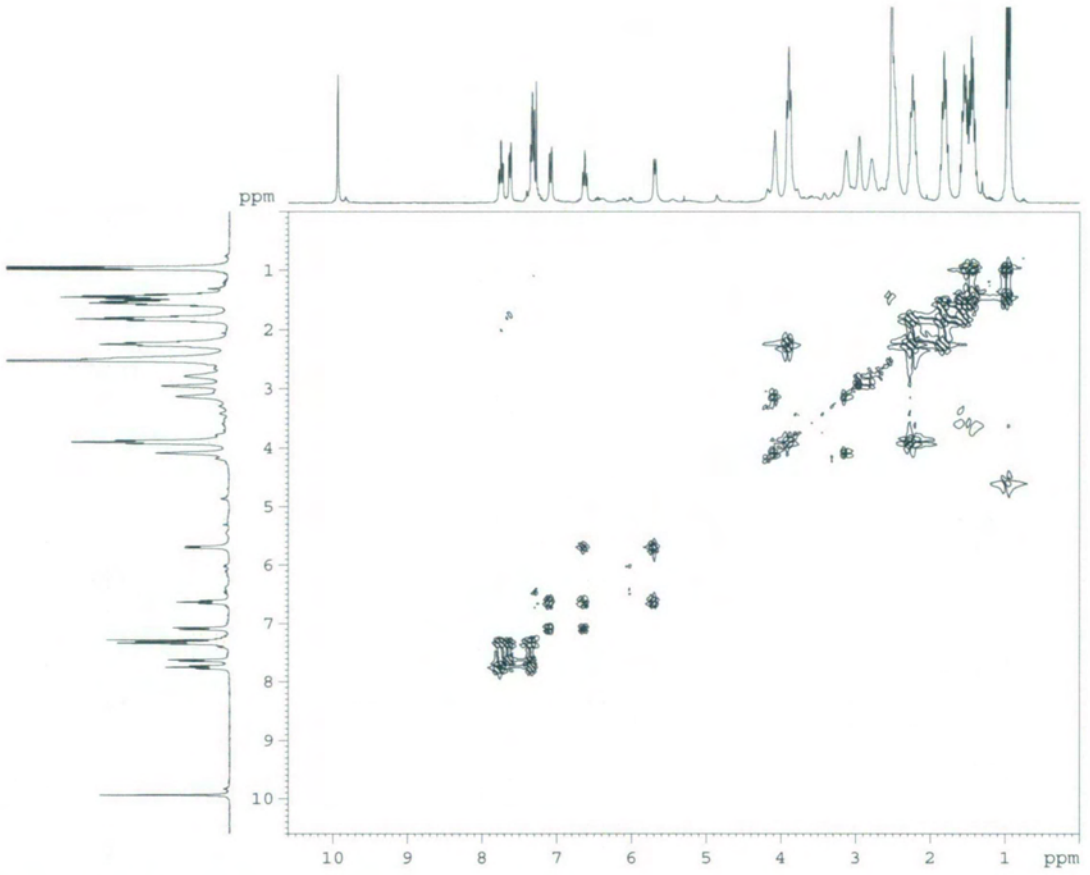


Figure A2.2:- COSY of ruthenium strapped porphyrin **2.5.**

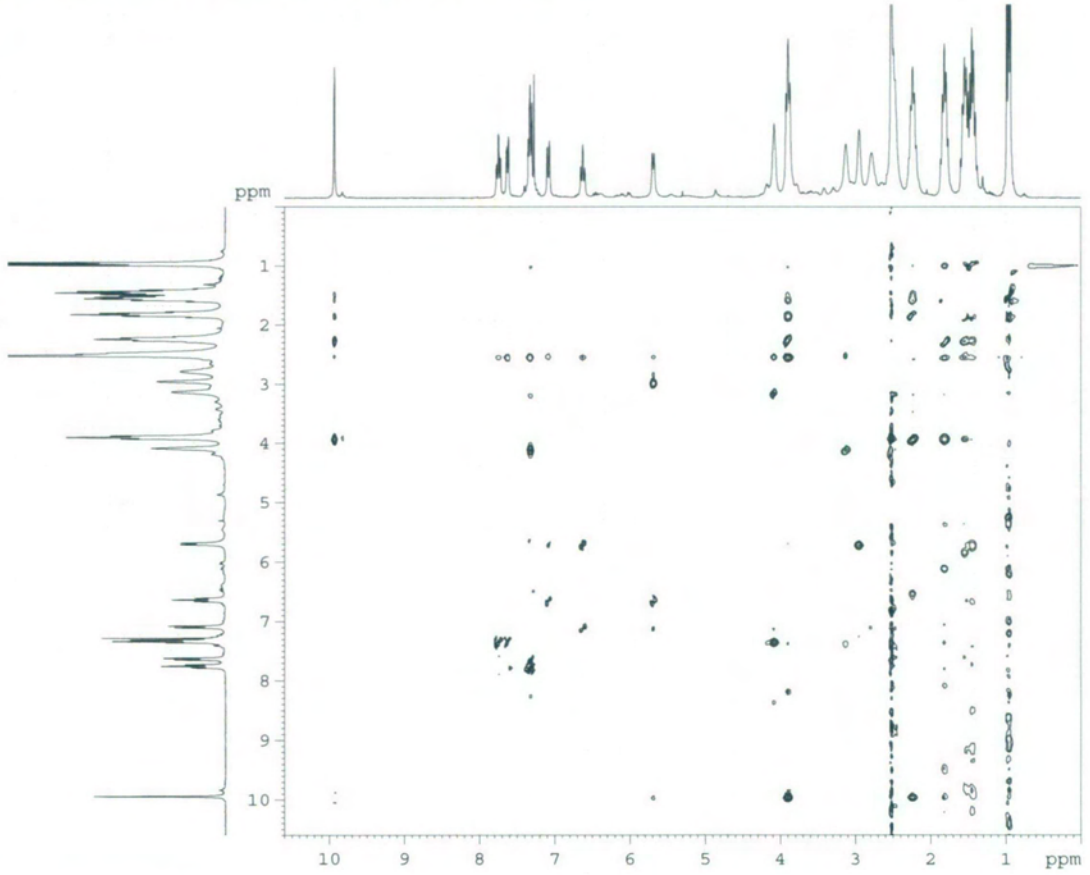


Figure A2.3:- NOESY spectrum of ruthenium strapped porphyrin **2.5.**

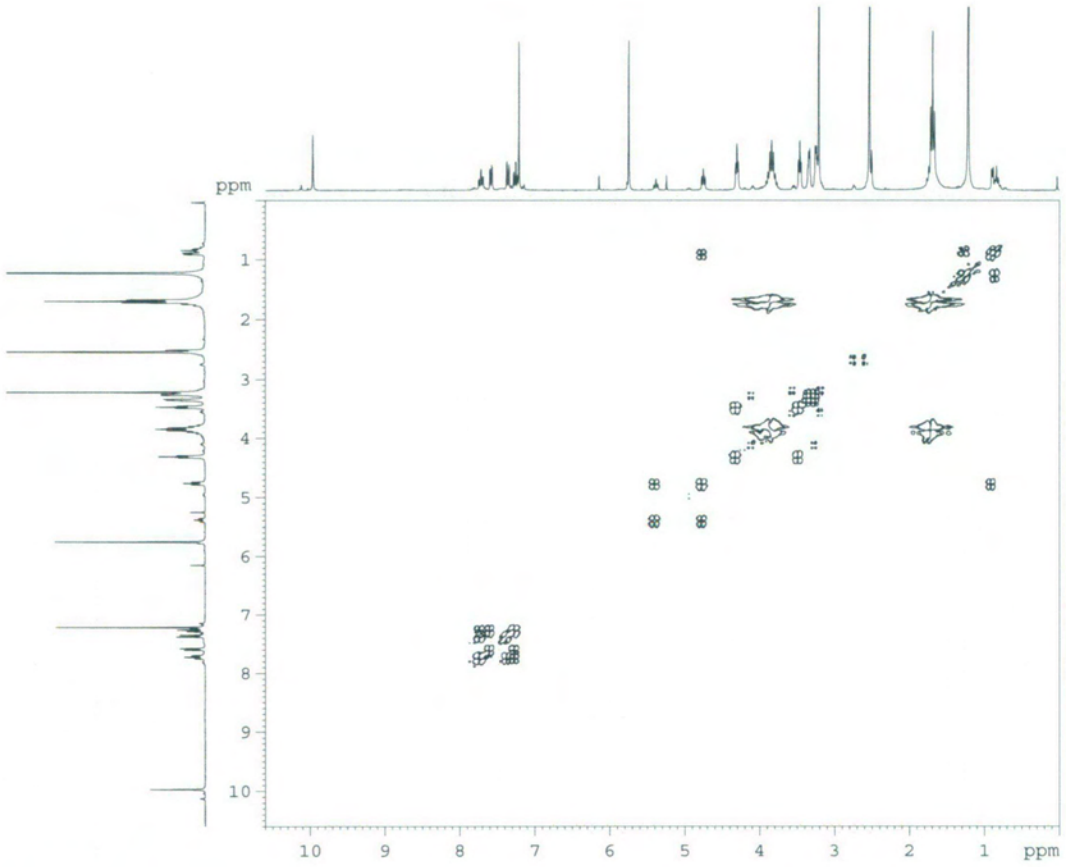


Figure A2.4:- COSY of a 1:1 mixture of rhodium porphyrin **2.7** and pyridine.

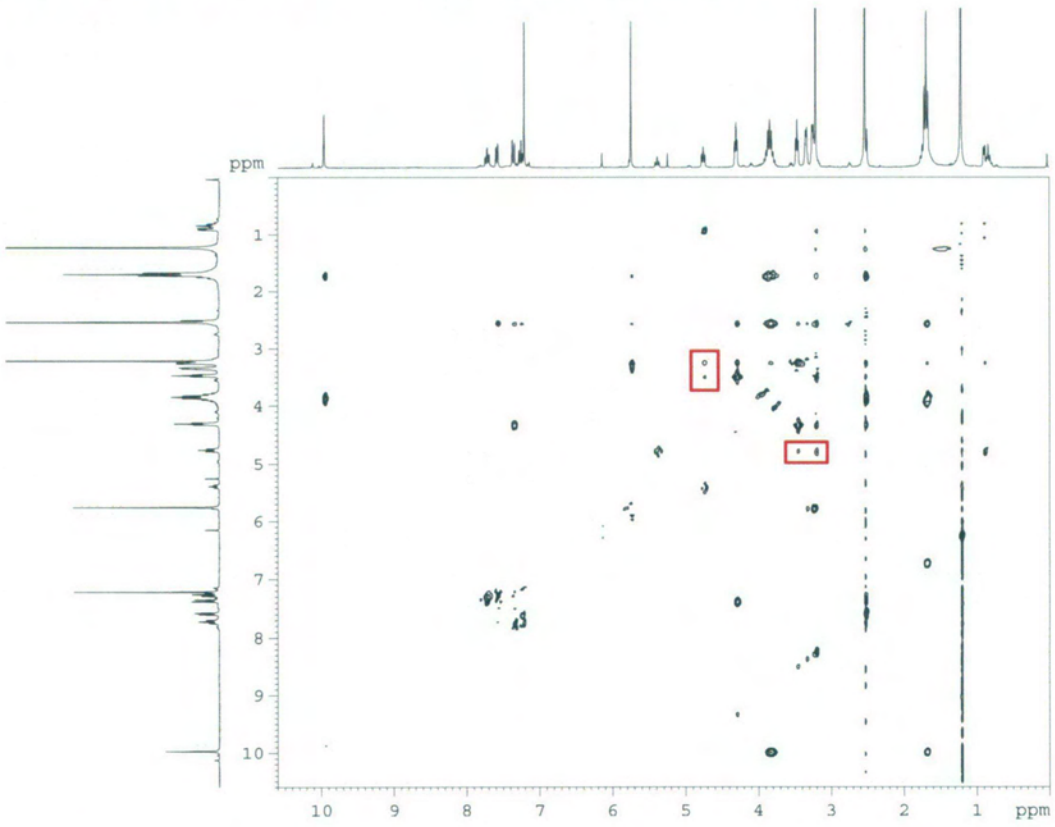


Figure A2.5:- NOESY of a 1:1 mixture of rhodium porphyrin **2.7** with pyridine. Red boxes indicate near in space interactions between pyridine and the strap of the porphyrin indicating "inside" coordination.

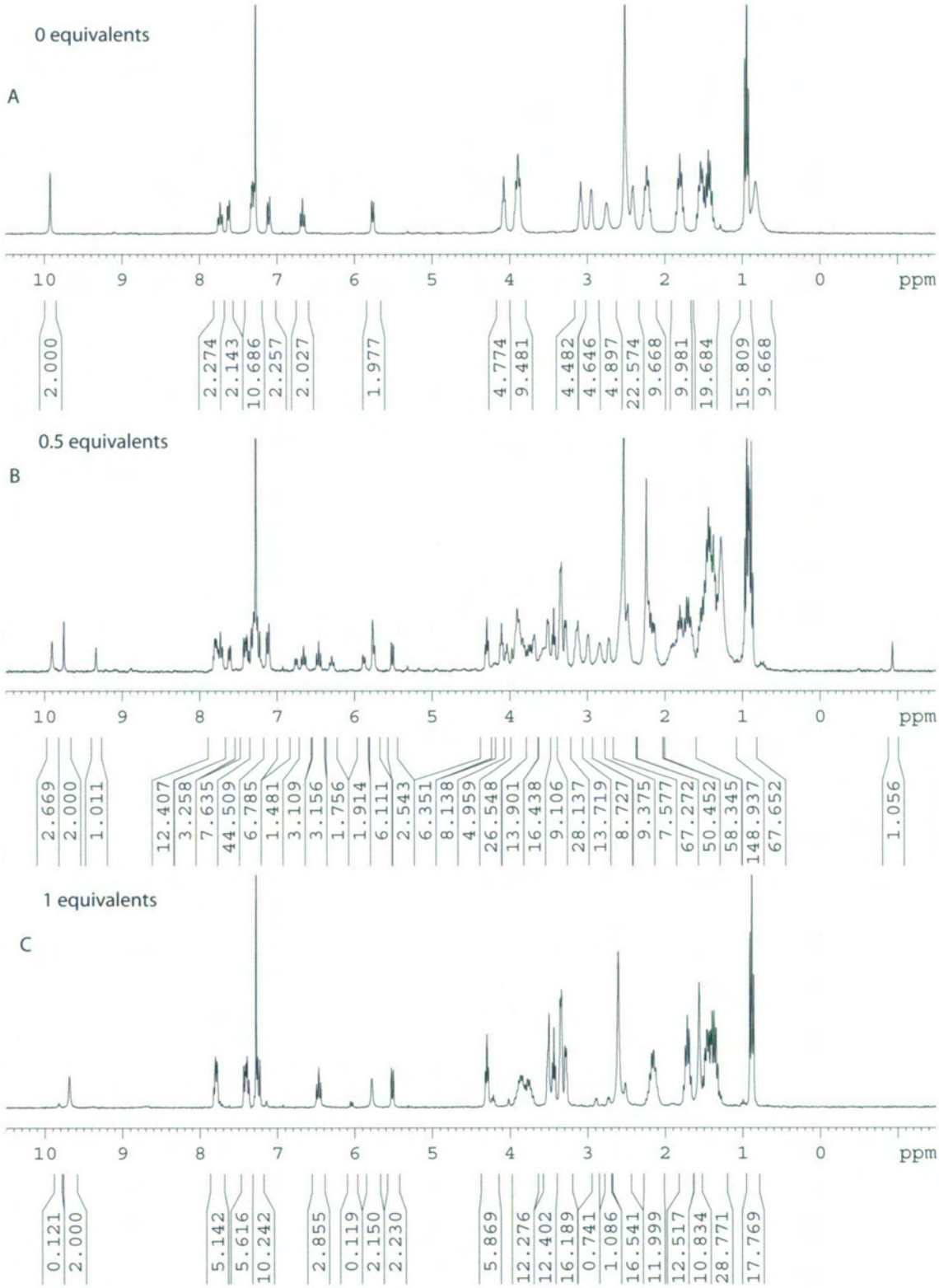


Figure A2.6:- NMR titration of Ru porphyrin **2.5** with increasing number of pyrazine equivalents (See Figure 2.11) with integration.

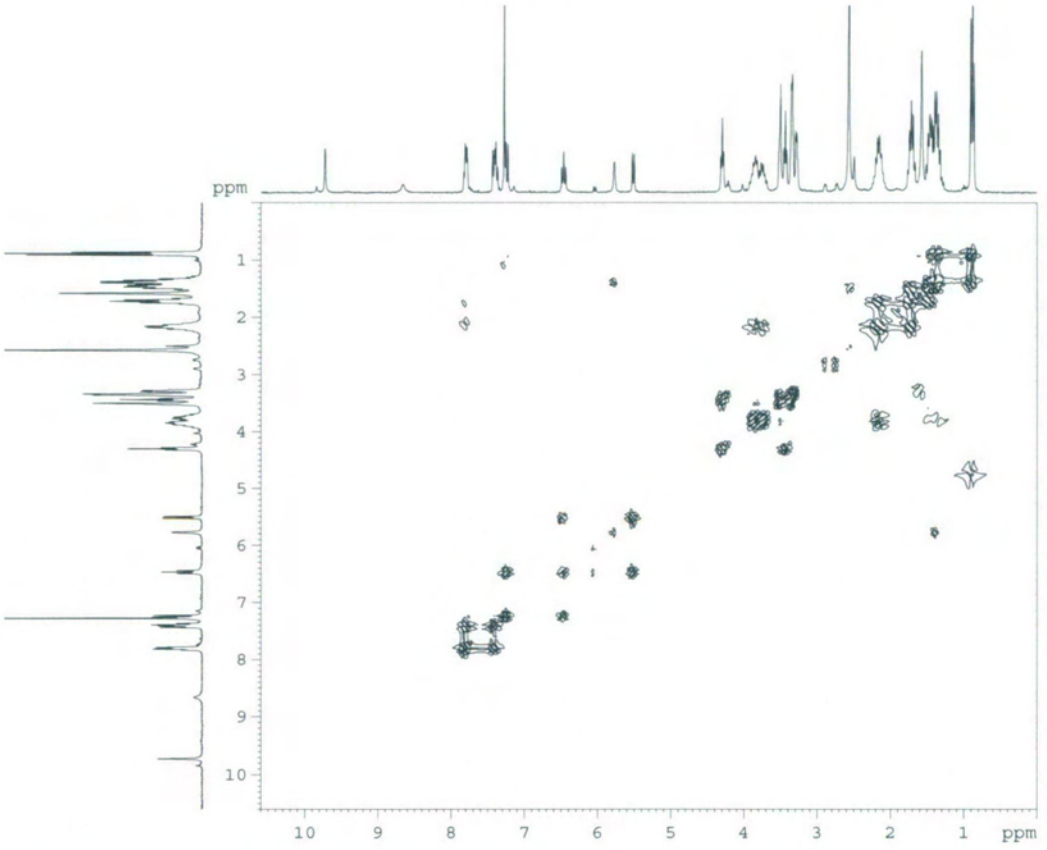


Figure A2.7:- COSY spectrum of a mixture of ruthenium porphyrin **2.5** with 1.5 equiv. of pyrazine.

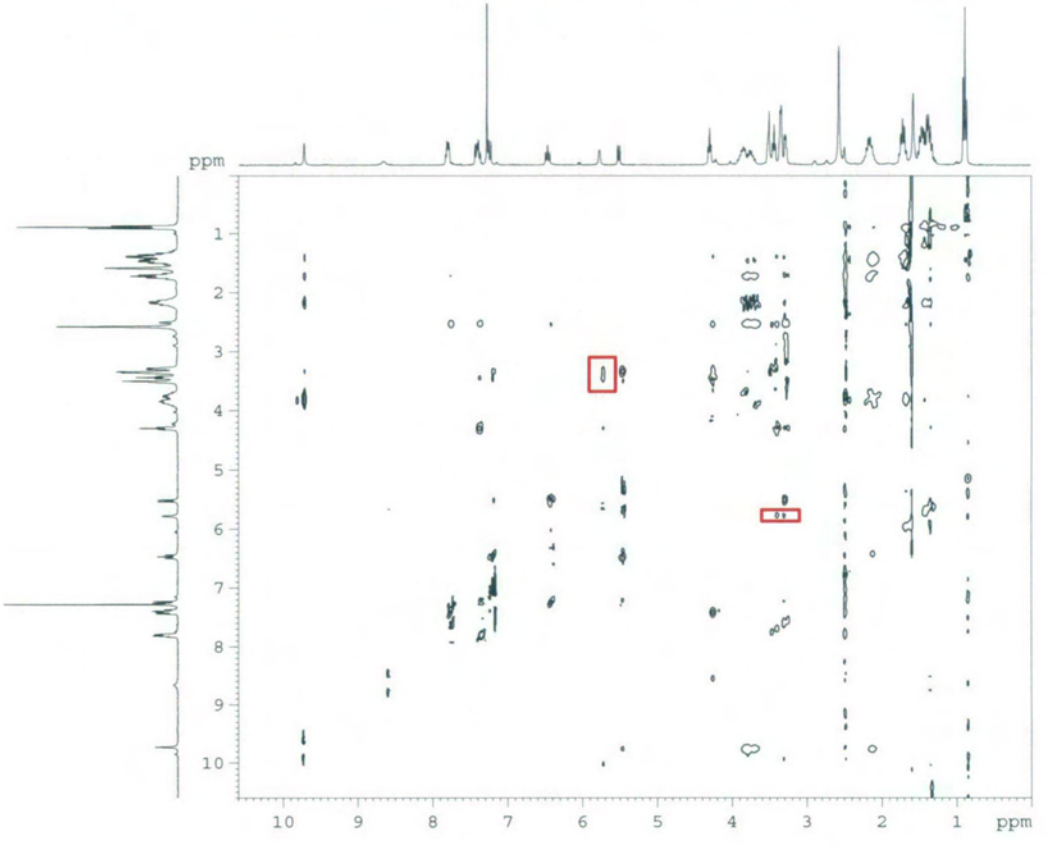


Figure A2.8:- NOESY spectrum of a mixture of ruthenium porphyrin **2.5** with 1.5 equivalents of pyrazine. Red boxes show near in space interactions between pyrazine and the porphyrin strap indicating pyrazine adopting an "inside" coordination.

APPENDIX 3

Supplementary material for Chapter 3. This appendix includes selected mass spectral data as well as COSY, NOESY and ROESY spectrum typical of the NMR spectra obtained for use in characterisation of the rotaxanes discussed in Chapter 3.

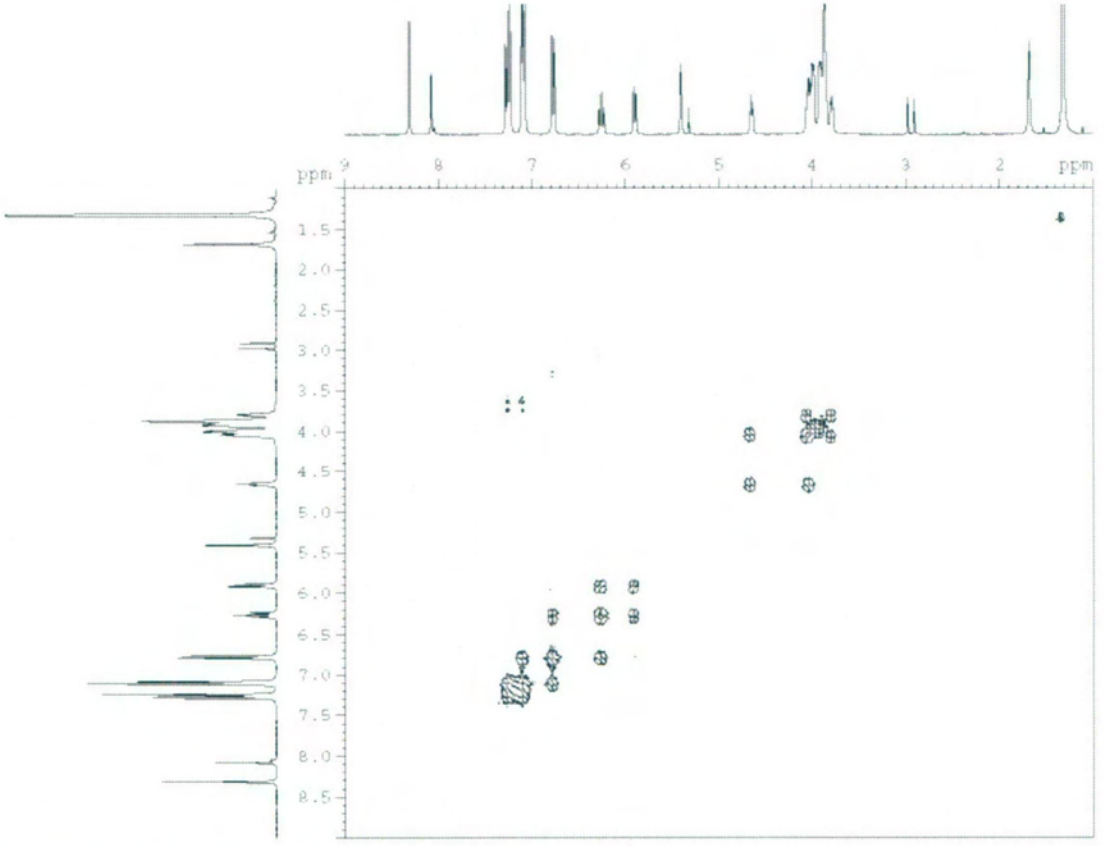


Figure A3.1:- COSY NMR spectrum of crown rotaxane **3.23**.

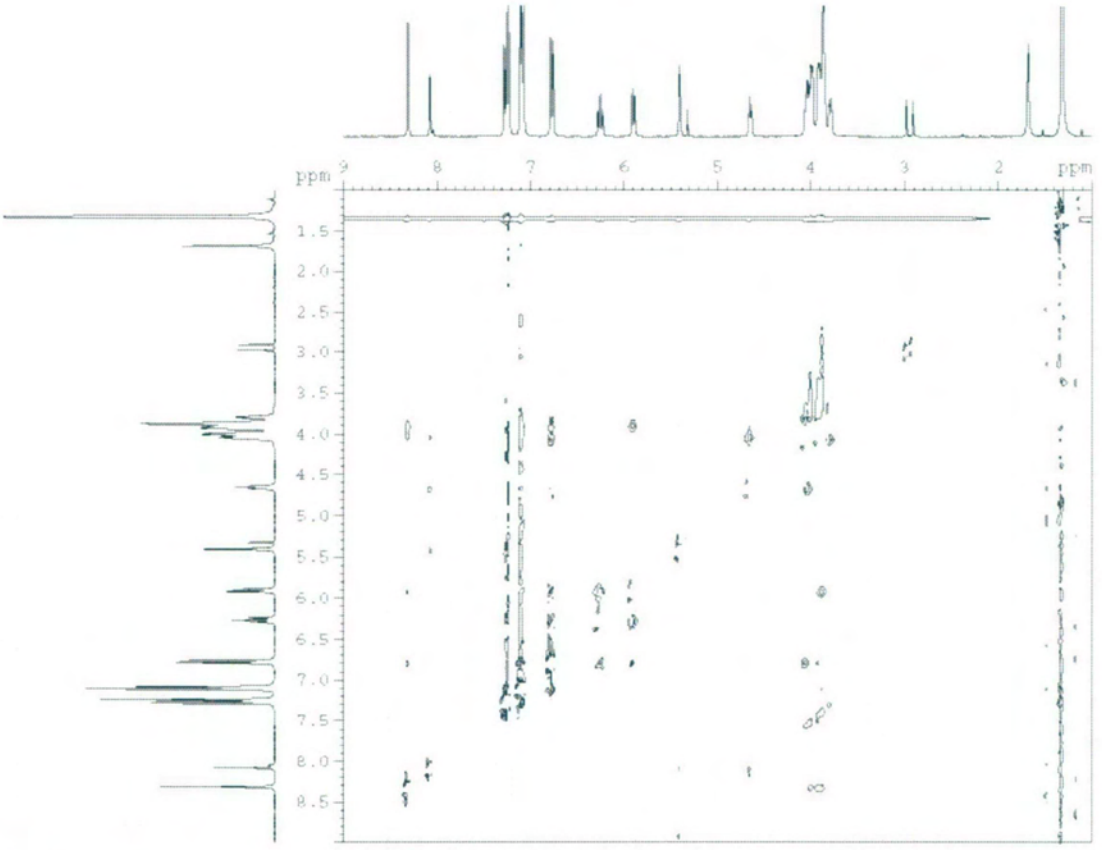


Figure A3.2:- NOESY spectrum of crown rotaxane **3.23**.

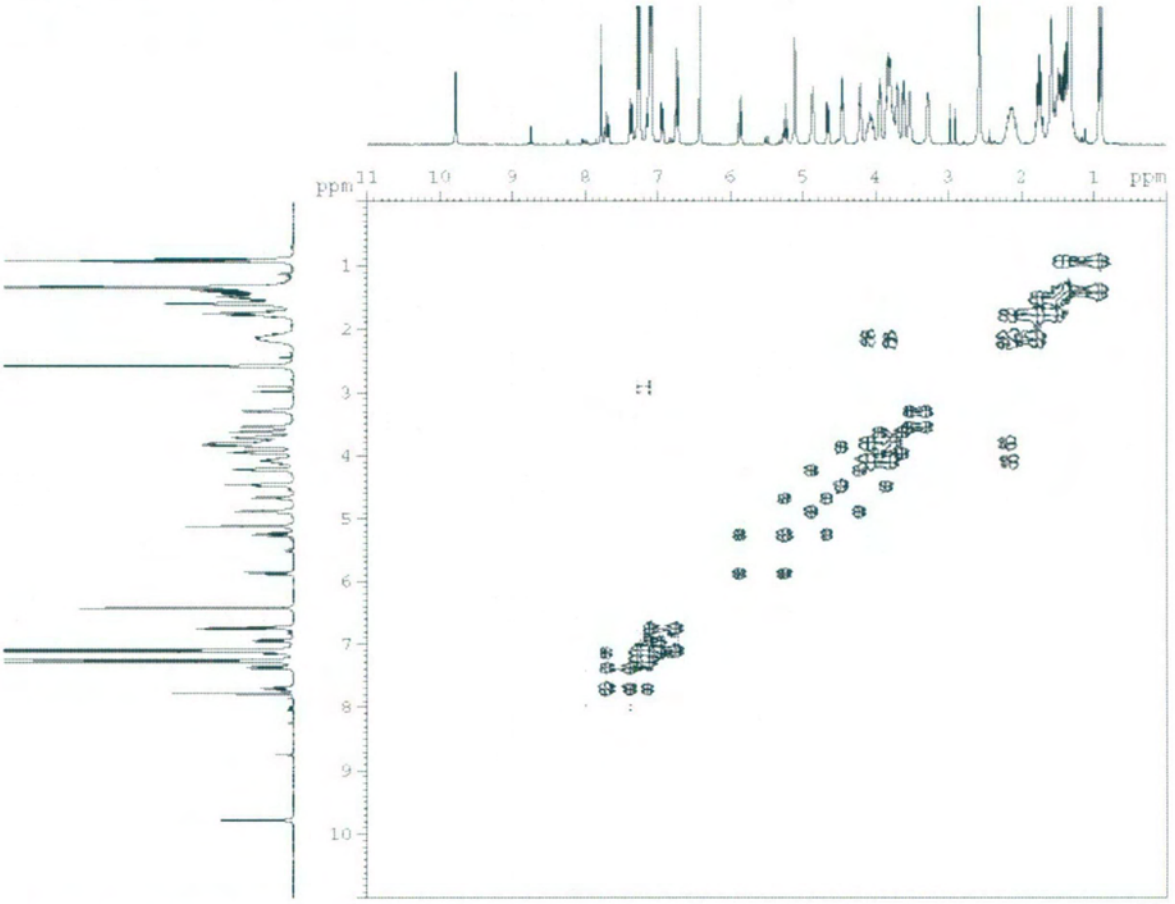


Figure A3.3:- COSY spectrum of zinc porphyrin rotaxane **3.24**.

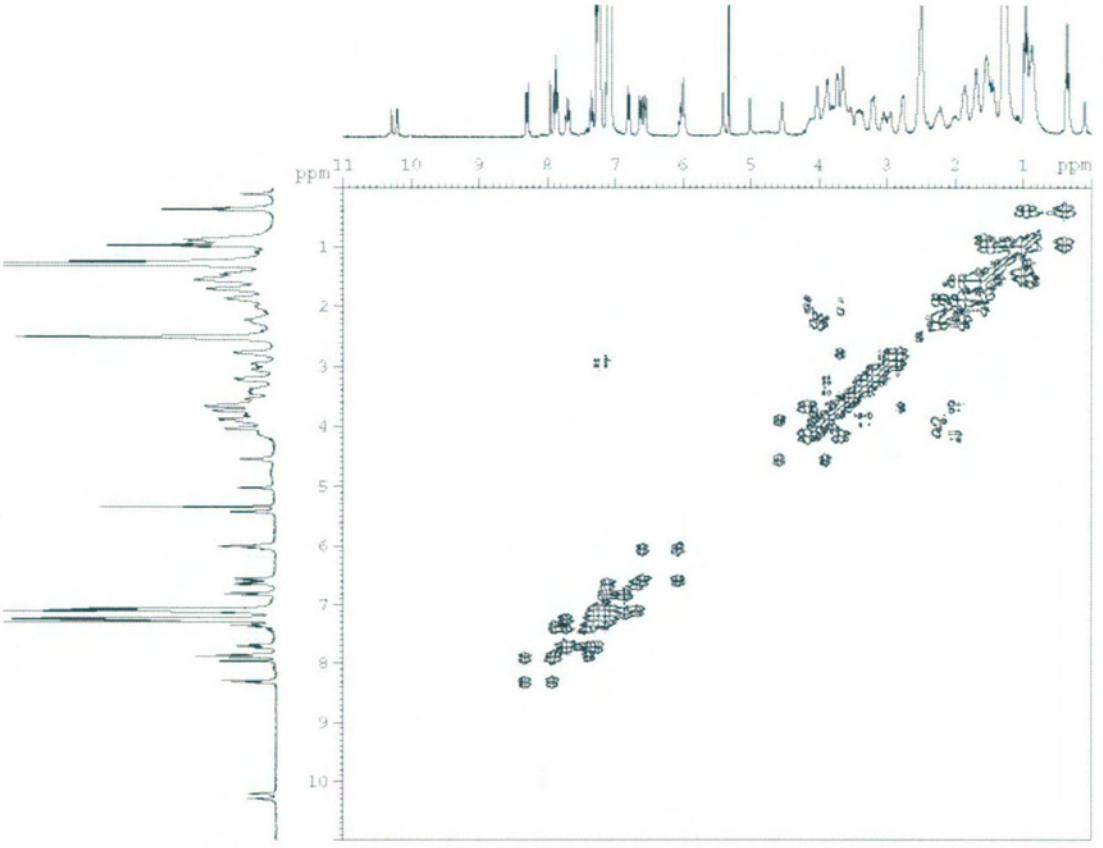


Figure A3.4:- COSY spectrum of rhodium porphyrin rotaxane **3.27** at –20 °C.

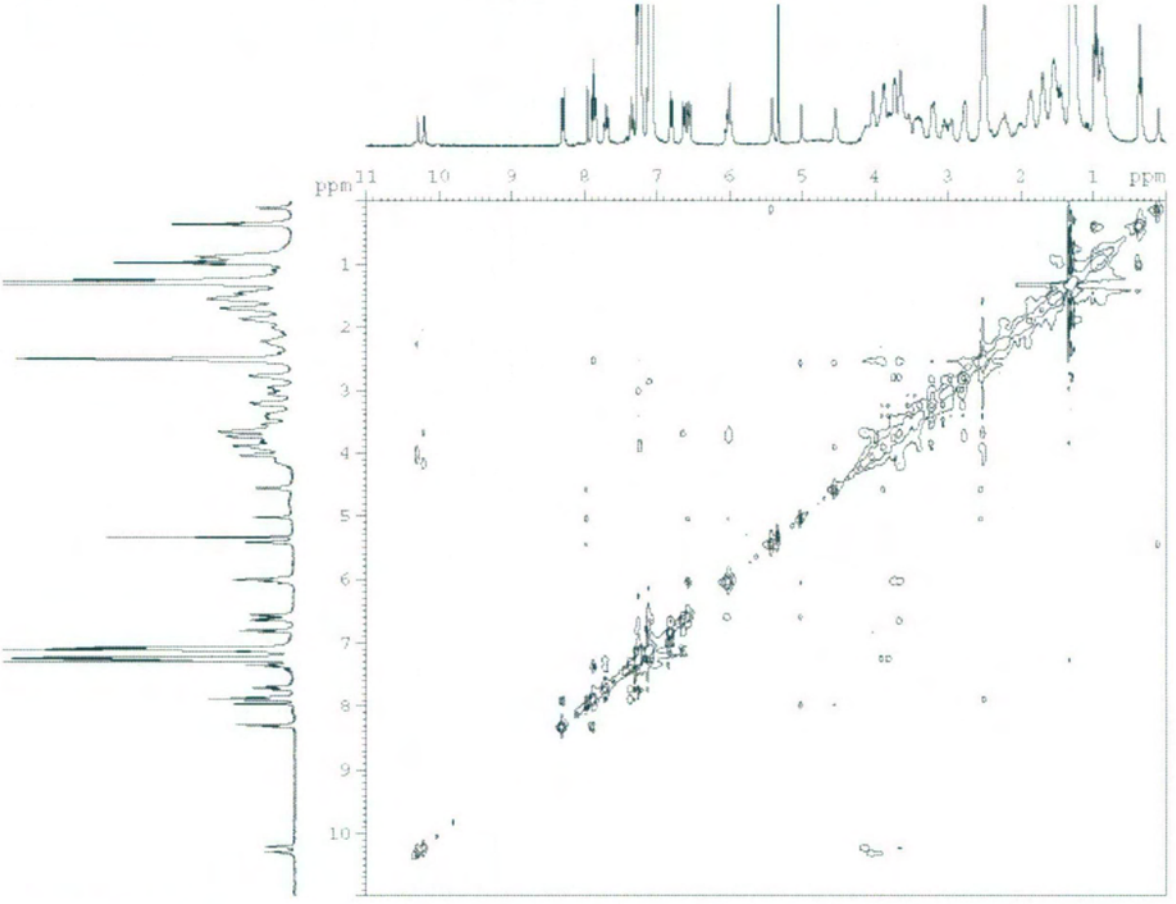


Figure A3.5:- NOESY spectrum of rhodium porphyrin rotaxane **3.27** at –20 °C.

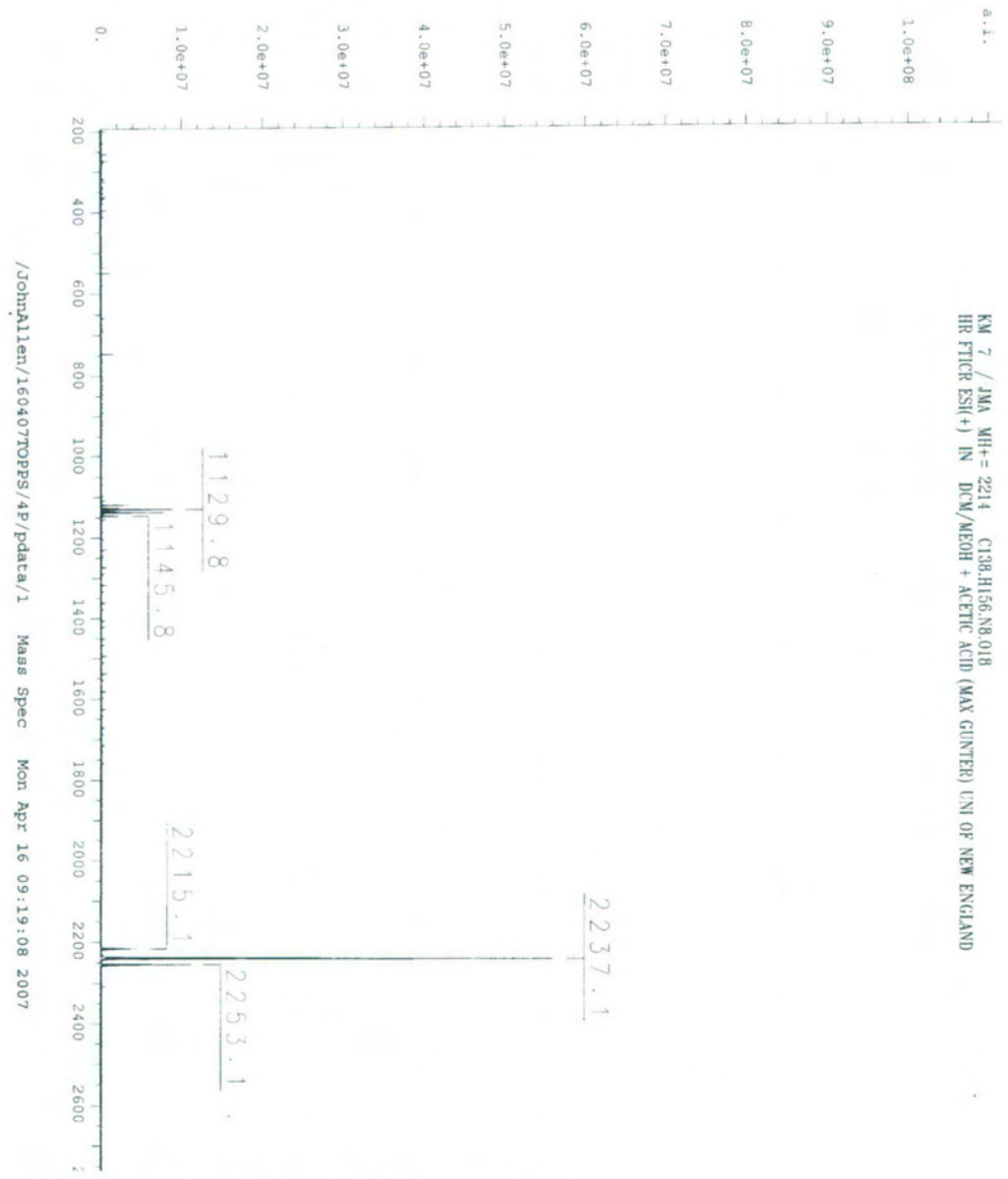


Figure A3.6:- Mass spectrum obtained for crown rotaxane **3.23**.

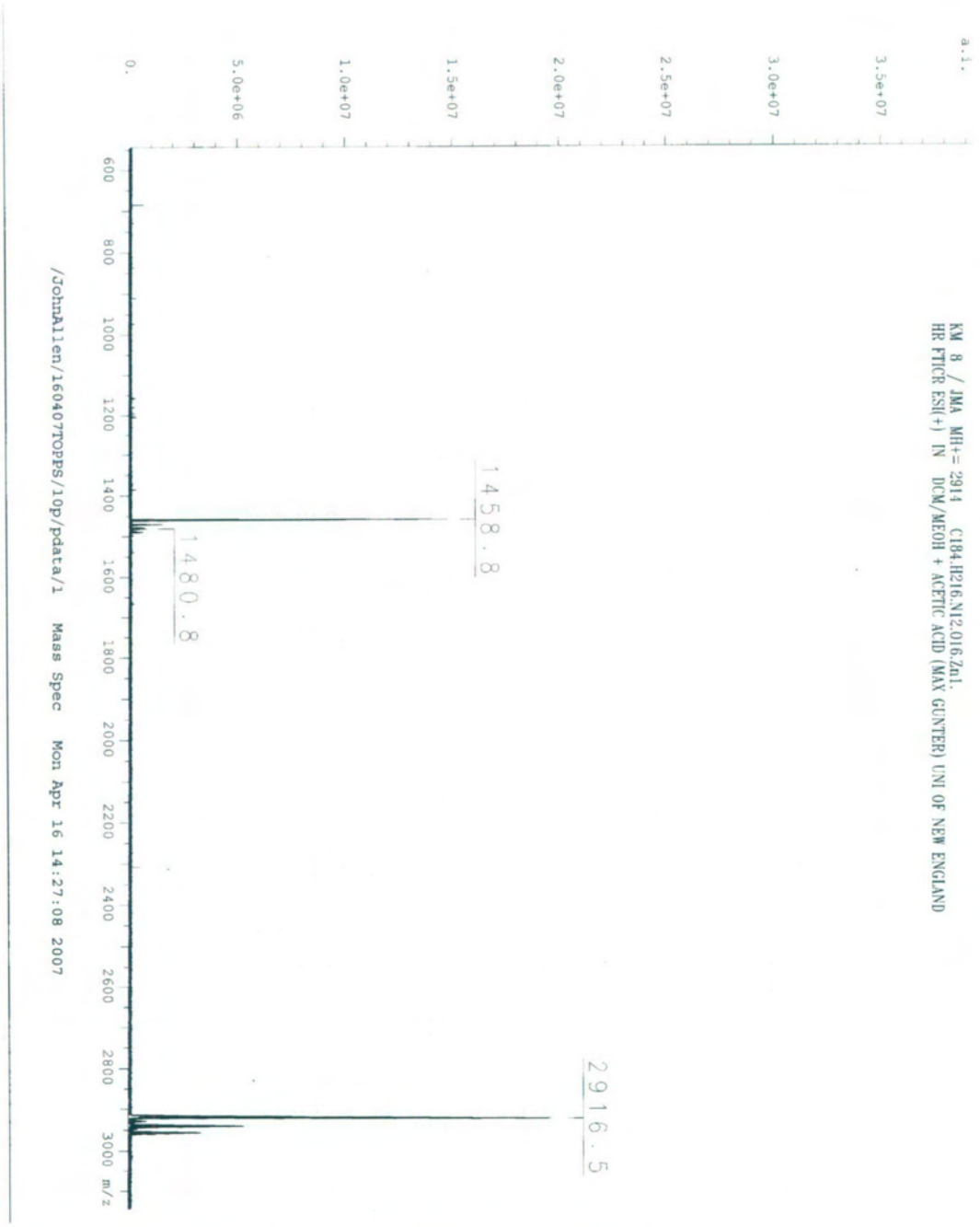


Figure A3.7:- Mass spectrum obtained for porphyrin rotaxane **3.24**.

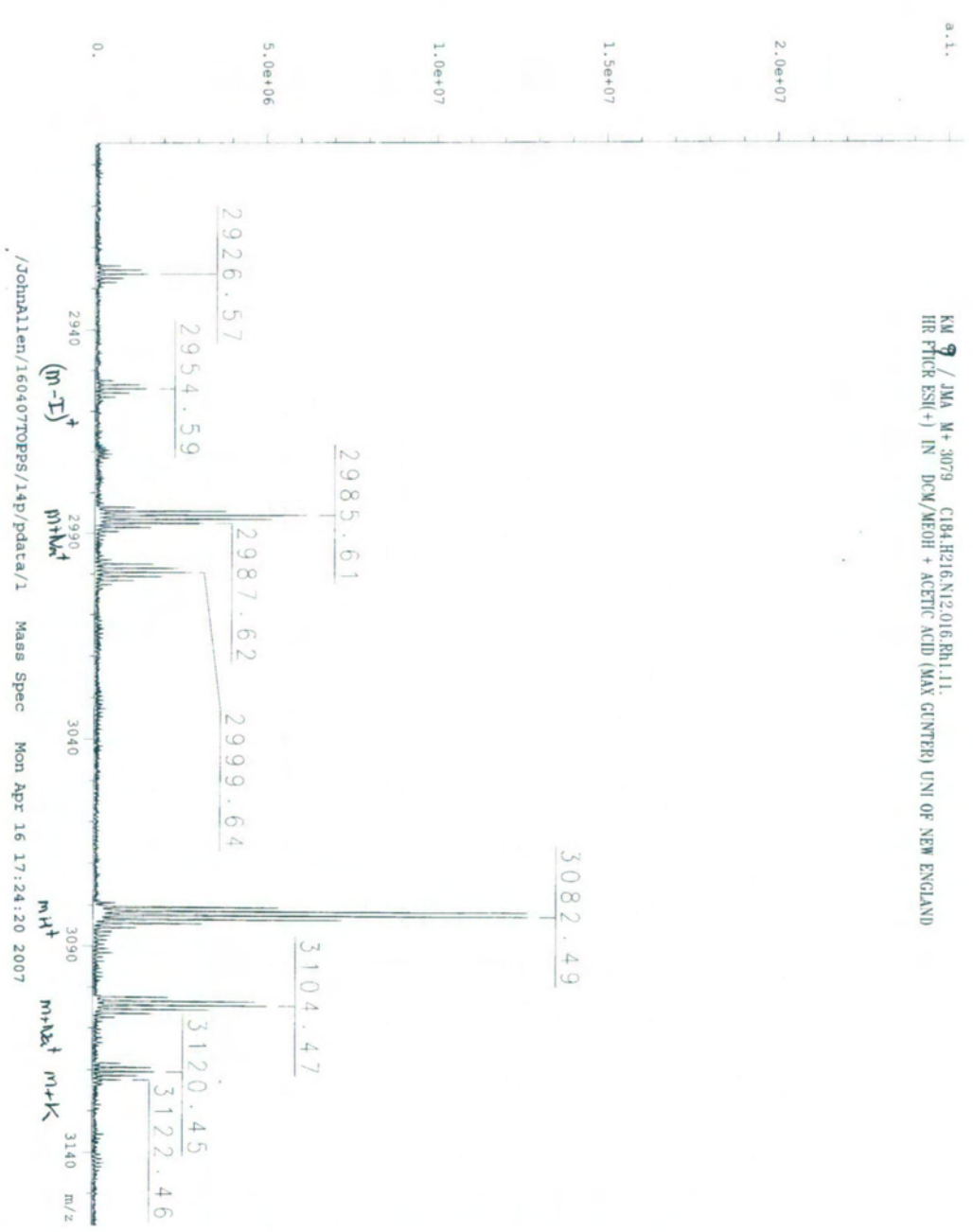
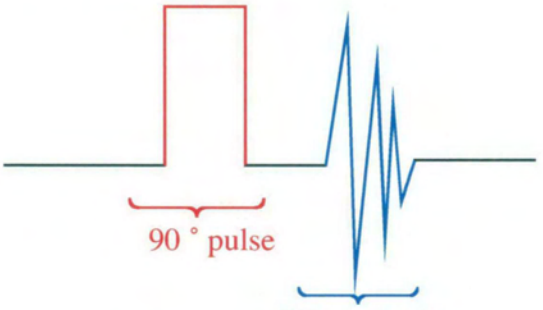


Figure A3.8:- Mass spectrum obtained for rhodium porphyrin rotaxane **3.27**.

APPENDIX 4

PULSE PROGRAMS USED IN HR MAS NMR STUDIES

Basic proton 1d pulse sequence



1d proton MAS
avance-version

"p2=p1*2"

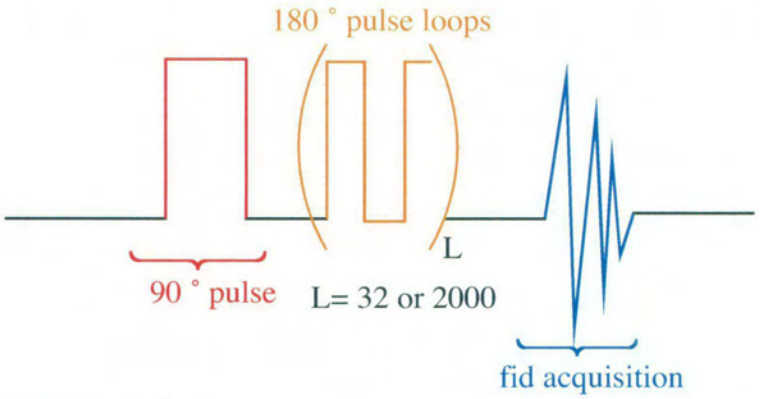
```
1 ze
2 p1  ph1                    Basic 1d pulse sequence (90 ° pulse)
  go=2  ph31
  d11  wr  #0
exit
```

```
ph1=0  0  2  2  1  1  3  3
ph2=1  3  1  3  0  2  0  2
ph29=0
ph31=0  0  2  2  1  1  3  3
```

pl1 : f1 channel – power level for pulse (default)
p1 : f1 channel – 90 degree high power pulse
p2 : f1 channel – 180 degree high power pulse
d11: delay for disk I/O [30 msec]
d20: fixed echo time to allow elimination of diffusion and J-mod. Effects [1-2 msec]

CPMG 1D pulse sequence

This CPMG pulse program filters out broad peaks in the NMR spectrum using T2 editing.



Avance version

T2 measurement using Carr-Purcell-Meiboom-Gill Sequence

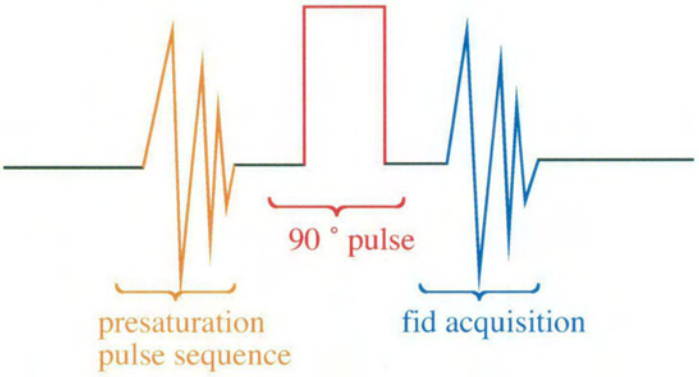
"p2=p1*2"
"d11=30m"

```
1 ze
2 d1                    relaxation delay between scans
  p1  ph1               90 ° pulse
3 d20
  p2  ph2               180 ° pulse
  d20
  lo to 3 times L1      loop counter for T2 editing (standard to run 32 and 2000 loops)
  go=2  ph31
  d11  wr  #0
exit
```

```
ph1=0  0  2  2  1  1  3  3
ph2=1  3  1  3  0  2  0  2
ph31=0  0  2  2  1  1  3  3
```

pl1 : f1 channel – power level for pulse (default)
p1 : f1 channel – 90 degree high power pulse
p2 : f1 channel – 180 degree high power pulse
d1 : relaxation delay; 1-5 * T1
d11: delay for disk I/O [30 msec]
d20: fixed echo time to allow elimination of diffusion and J-mod. Effects

Presaturation 1d proton pulse sequence



avance-version
Yiu-Fai Ng

"p2=p1*2"
"d13=30m"
"d12=20u"

```
1 ze
2 d12
  d12  p19:f1
  d1  cw:f1  ph29
  d13  do:f1
  d12  pl1:f1
  p1  ph1
  go=2  ph31
  d11  wr  #0
exit
```

Presaturation pulses set to polyethylene glycol peak

Basic 1d pulse sequence (90 ° pulse)

```
ph1=0  0  2  2  1  1  3  3
ph2=1  3  1  3  0  2  0  2
ph29=0
ph31=0  0  2  2  1  1  3  3
```

pl1 : f1 channel – power level for pulse (default)
p1 : f1 channel – 90 degree high power pulse
p2 : f1 channel – 180 degree high power pulse
d1 : relaxation delay; 1-5 * T1
d12: delay for power switching
d13: delay for disk I/O [30 msec]
d20: fixed echo time to allow elimination of diffusion and J-mod. Effects [1-2 msec]

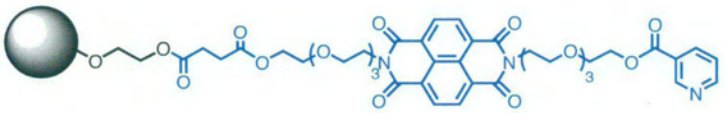
APPENDIX 5

QUANTITATION IN THE SOLID TETHERED SYSTEMS USING HR MAS NMR

One of the significant disadvantages of using HR MAS NMR to analyse solid-supported supramolecular systems, is the lack of available quantitation methods. This is due to two main factors; firstly, that the HR MAS NMR spectrum cannot be integrated as with standard ^{1}H NMR, due to the application of the CPMG pulse sequences used. While the CPMG pulse loops successfully filter out any broad resonances due to the bead core, this is indiscriminate and signals arising from the tethered components can also be affected, depending on their relaxation properties. Signals broadened by relaxation or exchange processes are particularly affected, sometimes to such an extent that they are not observable in the filtered spectrum. Even relative integrations of individual protons within a single molecule, which are affected by the CPMG pulse sequences, can be anomalous. For example in the tethered pyridyl diimide tethered thread **4.10**, the four pyridine protons are filtered to varying degrees, and therefore do not have the expected 1:1:1:1 integration. Thus integration cannot be relied upon as an accurate indication of the relative loading of different components, and even strategies that might be used which incorporate an 'internal standard' marker proton resonance are not feasible. A more reliable internal comparison of relative integrations can be obtained from the unfiltered spectrum, but this is only feasible for those signals which are not obscured by the large and broad residual peaks arising from the structural components of the beads.

The second factor that renders any quantitation difficult, is that the loading of the tethered component on the bead is difficult to ascertain. The average percentage of functional sites on the beads is given by the manufacturer (around 0.46% mmol OH/g for ArgoGel beads), however, it cannot be assumed that the tethering reaction is 100% effective, either through incomplete reaction in the heterogeneous system, or restricted access (especially of larger reactants such as porphyrins) to available sites on the beads. Thus other indirect methods to determine the loading of components on the beads were investigated.

One such indirect method was by a UV Vis spectroscopic approach.



4.10

By comparing the UV Vis spectrum of a solution of known concentration of rhodium porphyrin before and after the addition of a known quantity of beads, it would be possible to estimate the amount of porphyrin coordinated to the terminal pyridyl groups on the tethered diimide thread, as any coordinated metalloporphyrin would be effectively removed from solution by absorption on the beads. Preliminary investigations indeed showed that the addition of beads to a solution of porphyrin of known concentration decreased the initial rhodium porphyrin UV absorption intensity. However, this decrease was found to be concentration dependent, and the relative decrease in porphyrin absorbance varied with the initial concentration of porphyrin solution. Control experiments showed that the addition of unfunctionalised beads to a solution of rhodium porphyrin of known concentration also resulted in a decrease in the expected porphyrin absorbance. This indicates some additional interaction between the porphyrin and the bead surface, which could be due to π-π stacking between the porphyrin and the polystyrene aromatics, or even by rhodium coordination to the exposed hydroxyl or ether groups of the beads (albeit weaker than with the nitrogenous ligands of the attached thread). Thus, alternative strategies to determine the loading were needed.

The first revised method chosen was to take two solutions of rhodium porphyrin of identical concentration. To one solution were added unfunctionalised beads, and to the other, the diimide thread functionalised beads **4.10**. The difference between the absorbance of the rhodium porphyrin between these two solutions would thus give an approximation for the amount of porphyrin coordinated to the pyridine group in the diimide tethered beads, compared to the concentration of porphyrin absorbed by the bead core. The loading of the porphyrin on the beads using this method was determined to be 0.22 mmol/g based on dry bead weight, and this value could be obtained reproducibly with varying porphyrin concentration

A converse method was also investigated. In this case the diimide thread-attached beads **4.10** and the unfunctionalised beads that had been pre-soaked in a concentrated porphyrin solution were filtered and both sets of beads were washed thoroughly and repeatedly (with CH_2Cl_2 and hexane, which causes alternate shrinking and swelling of the beads) with identical amounts of solvent until no colour remained on the unfunctionalised beads. The diimide beads **4.10** retained a red colouration due to the strong coordination of the rhodium porphyrin to the terminal pyridyl groups of the thread. These beads were then washed with an excess of pyridine/CH_2Cl_2 solution until all coordinated porphyrin was removed from the beads, and the filtrate made up to a standard volume. The UV Vis absorptivity of this solution was then recorded to determine the amount of rhodium porphyrin displaced from the diimide thread. The loading of the porphyrin on the beads using this method was determined to be 0.21 mmol/g.

Although these two UV Vis experiments gave consistent values for the loading of the diimide thread on the beads, confirmation of these results by elemental analysis would also add confidence to the methods. Elemental analysis for the nitrogen content in the diimide tethered beads **4.10** was 0.56 % (average of 2 combustion experiments) which converted to a bead loading of 0.13 mmol/g, with an associated error, as calculated as the standard deviation between runs, of 20%. This loading is lower than that calculated by UV Vis methods, and this could be due to problems in the purification of solid supported systems; for example dust and other solid particulates cannot be removed from the bead sample, and this could result in lower nitrogen content readings. Thorough drying of the beads is also somewhat problematic, as residual solvent and moisture is strongly adsorbed. Nevertheless it can be said that the loading of the naphthodiimide tethered beads **4.10** is approximately 0.19 mmol/g (taken as an average of the three methods) which is approximately 40% of the estimated functional group loading (0.46 mmol/g) reported by the manufacturer.

The lower measured loading of the diimide component on the beads, as compared to the available hydroxyl sites for tethering is intuitively reasonable, given the expected reduced yields for the heterogeneous system, and the possibility of steric interference from adjacent sites and inaccessibility of others. Nevertheless it is clear that these loadings are

adequate for HR MAS NMR analysis yielding good quality spectra under these conditions.

A further hindrance to accurate quantitation in this methodology is a function of the technique itself. In the measurement process, small quantities of dried beads are loaded into the rotor. Although the initial precise weight of added beads could be obtained, in the next stage where these beads are swollen by adding excess solvent or solution inside the rotor and the cap is inserted, inevitably some unknown quantity of excess beads are squeezed from the sample cavity. Likewise, there is no simple means by which a measured volume of known concentration of surrounding solution can be ascertained with certainty, as in the swelling and capping process, an unknown portion of this solution is invariably ejected and lost. Irreproducible packing of the swollen beads inside the sample cavity also means that the volume occupied by the surrounding solution is variable from one sample to the next. Nevertheless, an element of reproducibility can be obtained by a consistent approach using similar quantities and concentrations of swelling solution, and an estimated similar bead sample size.

For those experiments where sequential addition of reagents are needed, it is impractical to add the second reagent to already swollen beads within the cavity of the rotor (since the beads and solvent are tightly confined within the tiny internal space of the rotor, and this is accessible only through a small orifice). Furthermore, the swelling process itself is a necessary function to maximise reagent access to the bead functionalised sites, and it is not feasible to remove, shrink, and re-swell beads from the cavity. Thus, in those cases where sequential or multiple reagent addition is required, separate samples must be made, one with the added first reagent, and the next with both reagents added concurrently in the surrounding solution (this can of course only be successful in systems such as those used in this study where all solid-phase and solution components are in equilibrium). A certain degree of subjectivity must then be exercised in the comparison of the two different samples, as the signal strength of both bead-attached and solution-phase components cannot be compared directly.