Electronic Supplementary Information

Template-directed synthesis of π-conjugated porphyrin [2]rotaxanes and a [4]catenane based on a six-porphyrin nanoring

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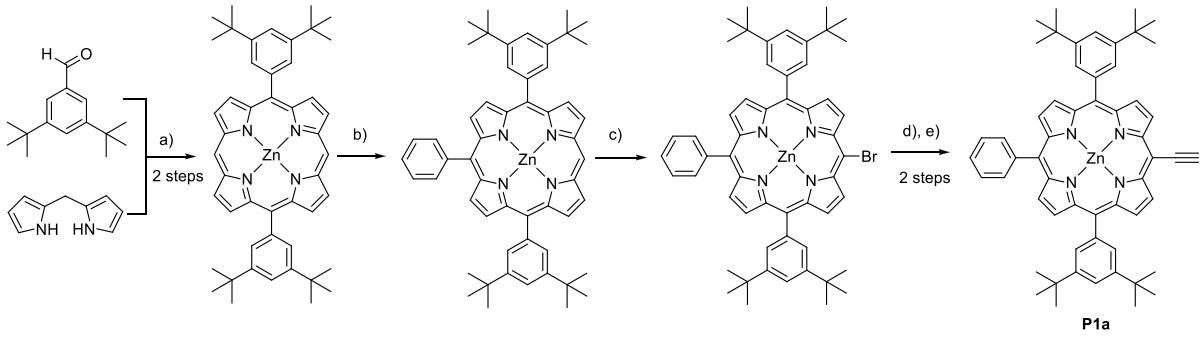
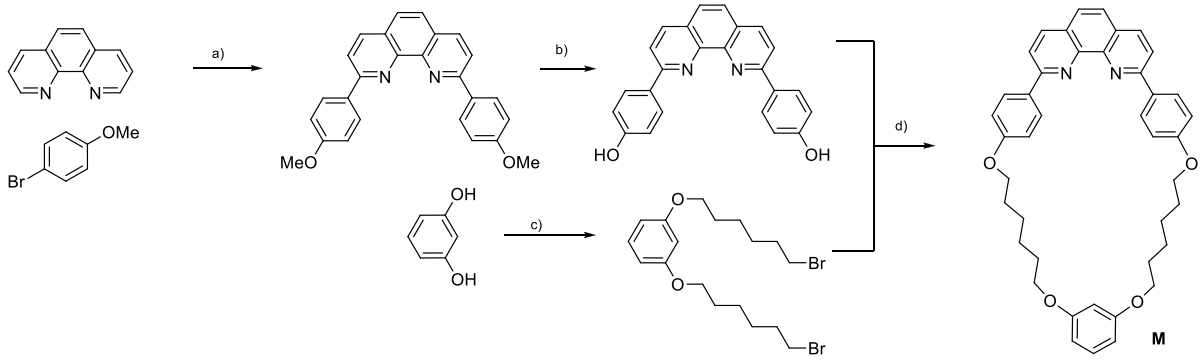
Section 1) Materials and Methods.

All reagents were purchased from commercial sources. Air/water sensitive materials were handled using standard high vacuum techniques. Column chromatography was carried out on Merck® silica gel 60 under a positive pressure of nitrogen. Where mixtures of solvents were used, ratios reported are by volume. NMR spectra were recorded on Bruker instruments AVIII 700 with cryoprobe, AVII 500 with cryoprobe (500 MHz) or DPX400 (400 MHz). ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) relative to the signal of the solvent, coupling constants (*J*) are given in Hertz. UV-vis spectra were recorded on a Perkin-Elmer Lambda 20 spectrometer. UV-vis titrations were analysed by fitting the experimental data to the theoretical curve using Origin™ software. Fluorescence spectra were recorded on a J-Y Spex Fluoromax 2 fluorimeter. MALDI-TOF mass spectrometry was carried out in positive reflectron or positive linear mode using a Micromass MALDI micro MX spectrometer with dithrinol (1,8-dihydroxyanthrone) as the matrix, or with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malonitrile (DCTB) matrix by the EPSRC Mass Spectrometry Service, Swansea, UK. Only molecular ions and major peaks are reported.

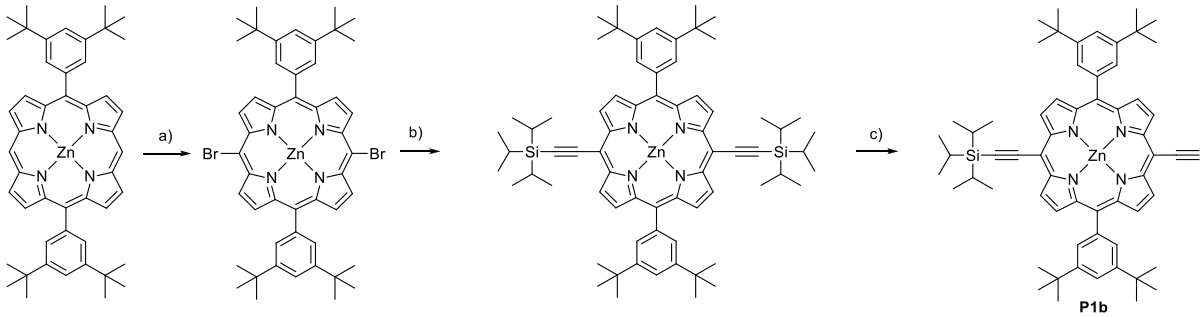
Section 2) Reaction Schemes



Scheme S1. Synthesis of porphyrin monomer **P1a**. Reaction conditions: a) TFA then DDQ then $Zn(OAc)_2 \cdot 2H_2O$, 56%;[1] b) PhLi, 89%;[2] c) NBS, 82%;[1] d) Triisopropylsilylacetylene, $Pd_2(dba)_3$, CuI, PPh_3, 72%;[3] h) TBAF, 90%.[4] 3,5-Bis(*tert*-butyl)benzaldehyde[5] and dypyrromethane[6] were prepared according to published procedures.

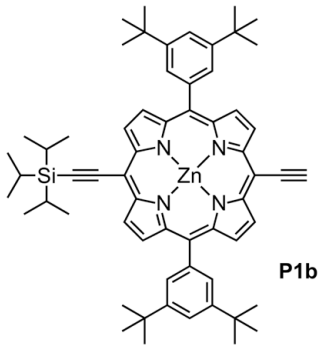


Scheme S2. Synthesis of macrocycle **M**. Reaction conditions: a) 4-Bromoanisole, *t*-BuLi, then phenanthroline, 53%;[7] b) pyridine, HCl, 83%;[7] c) 1,6-dibromohexane, K_2CO_3, 66%;[8] d) K_2CO_3, 53%.[8]



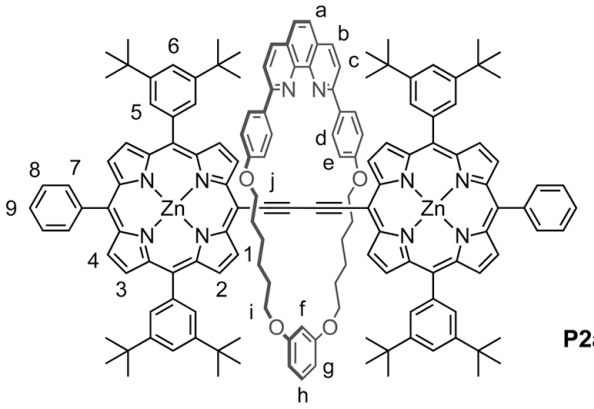
Scheme S3. Synthesis of porphyrin monomer **P1b.** Reaction conditions: a) NBS, pyridine 85%;[1] b) triisopropylsilylacetylene, $Pd_2(dba)_3$, CuI, PPh_3, 50%;[3] c) TBAF, 33%.[4]

Section 3) Experimental Synthetic Procedures



P1b

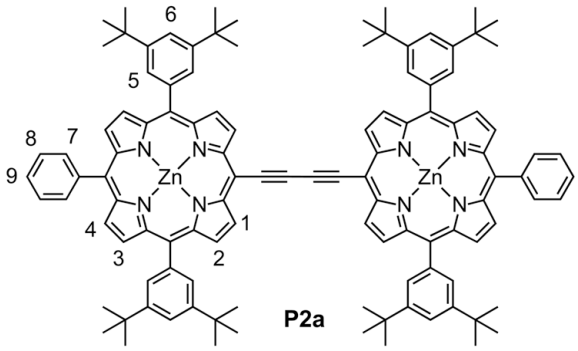
Zinc 5,15-bis-(3,5-bis-*tert*-butyl-phenyl)-10-ethynyl-20-triisopropylsilylethynyl-porphyrin, P1b. This compound was prepared using an adapted literature procedure.[9] Zinc 5,15-bis-(3,5-di-*tert*-butyl-phenyl)-10,20-bis-triisopropylsilylethynyl-porphyrin (0.670 g, 0.605 mmol) was placed in a dry flask under N_2 and dissolved in a mixture of CH_2Cl_2 (29 mL) and $CHCl_3$ (14 mL). Through a septum tetrabutylammonium fluoride (1.0 M in THF, 0.665 mL, 0.665 mmol) was added. The reaction was monitored by TLC (PE 40-60/EtOAc/pyridine = 10/1/1) until an optimal product mixture was reached after 1.5 hrs. The crude solution was immediately passed directly over a silica plug (CH_2Cl_2). Recrystallisation from $CHCl_3$/MeOH gave the product (0.186 g, 32%) as a green solid. ^{1}H NMR (400 MHz, $CDCl_3$ + 1% C_5D_5N) δ_H 9.69 (d, J = 4.4 Hz, 2H, H_β), 9.65 (d, J = 4.8 Hz, 2H, H_β), 8.88 (m, 4H, H_β), 7.98 (d, 1.8 Hz, 4H, Ar-H_{ortho}), 7.78 (t, J = 1.8 Hz, 2H, Ar-H_{para}), 4.13 (s, 1H, $H_{acetylene}$), 1.53 (s, 36H, $H_{t\text{-}butyl}$), 1.43 (s, 18H, $H_{TIPS\text{-}Me}$), 1.41 (s, 3H, $H_{TIPS\text{-}CH}$). ^{13}C NMR (125 MHz, $CDCl_3$ + 1% C_5D_5N) δ_C 152.1, 152.1, 148.3, 141.7, 132.8, 132.7, 130.7, 130.5, 129.6, 123.7, 120.8, 110.2, 101.1, 98.7, 97.2, 86.9, 83.0, 35.0, 31.7, 19.1, 12.1, 11.9, 11.7. *m/z* (MALDI TOF MS+) 952.99 ($C_{61}H_{72}N_4SiZn$); $[M]^+$ requires 952.48.



P2a⊂M

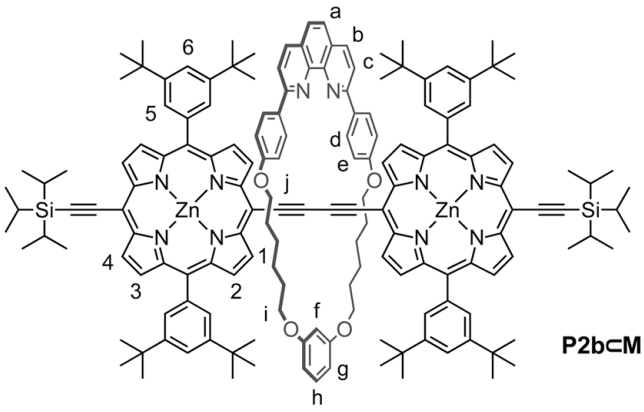
Rotaxane P2a⊂M. This compound was prepared using an adapted literature procedure.[10] To a solution of macrocycle **M** (36.8 mg, 0.057 mmol) in CH_2Cl_2 (1.5 mL), was added a solution of CuI (7.3 mg, 0.039 mmol) in acetonitrile (0.5 mL) and stirred at room temperature for 1.5 hrs. The solvent was removed and the resulting dark red residue was redissolved in a 1:1 mixture of toluene and THF (2 mL). The solution was added to a solution of [5-ethynyl-10,20-bis-(3,5-di-*tert*-butylphenyl)-15-

phenylporphyrinato]-zinc(II) **P1b** (65.3 mg, 0.077 mmol) in toluene (1.5 mL). Iodine (4.9 mg, 0.039 mmol) and potassium carbonate (21.2 mg, 0.154 mmol) was added and the reaction stirred for 5 days at 60 °C under N_2. The reaction mixture was cooled to room temperature, diluted with acetonitrile (3 mL) and CH_2Cl_2 (3 mL) and a solution of potassium cyanide (19.1 mg, 0.293 mmol) in water (2 mL) was added. The mixture was stirred for 14 hrs. Further CH_2Cl_2 (5 mL) was added and the organic fraction was collected and washed with water (10 mL). The solvent was removed and the crude was passed over a silica gel plug (CH_2Cl_2, 1% pyridine). The residue was dissolved in THF and passed through a size exclusion column to remove unthreaded macrocycle **M**. The unthreaded dimer **P2a** and rotaxane **P2a⊂M** were not separated by SEC, but **P2a⊂M** eluted second when the residue was passed through a silica gel column (CH_2Cl_2/PE 40-60 1:1, 1% pyridine). The product was precipitated from CH_2Cl_2/MeOH to yield **P2a⊂M** (38 mg, 42%). ^{1}H NMR (700 MHz, $CDCl_3$ + 1% C_5D_5N) δ_H 9.97 (d, J = 4.4 Hz, 4H, H_1), 8.82 (d, J = 4.4 Hz, 4H, H_2), 8.76 (d, J = 4.4 Hz, 4H, H_3), 8.74 (d, J = 4.4 Hz, 4H, H_4), 8.66 (d, J = 8.9, 4H, H_d), 8.20 (d, J = 8.5, 2H, H_b), 8.16 (m, 4H, H_7), 8.00 (d, J = 8.5 Hz, 2H, H_c), 7.97 (d, J = 1.7 Hz, 8H, H_5), 7.73 (t, J = 1.7 Hz, 4H, H_6), 7.72–7.67 (m, 8H, $H_{8, 9, a}$), 7.47 (t, J = 2.3 Hz, 1H, H_f), 7.32 (d, J = 8.9 Hz, 4H, H_e), 6.82 (t, J = 8.2 Hz, 1H, H_h), 6.30 (dd, J_1 = 8.2 Hz, J_2 = 2.3 Hz, 2H, H_g), 4.15 (t, J = 6.4 Hz, 4H, H_i), 3.83 (t, J = 6.9 Hz, 4H, H_j), 1.69–1.37 (m, 16H, H_{alkyl}), 1.47 (s, 72H, $H_{t\text{-}butyl}$). ^{13}C NMR (125 MHz, $CDCl_3$ + 1% C_5D_5N) δ_C 160.7, 160.5, 156.5, 153.5, 150.8, 149.8, 148.2, 146.1, 143.4, 141.9, 136.3, 134.2, 133.4, 132.0, 131.6, 130.8, 129.8, 129.4, 129.2, 129.0, 128.2, 127.2, 127.1, 126.2, 123.6, 122.9, 120.5, 118.9, 114.9, 107.2, 100.3, 97.3, 89.1, 82.1, 67.9, 67.6, 34.9, 31.7, 29.5, 28.9, 25.8, 25.7 *m/z* (MALDI TOF MS+) 2337.58, ($C_{154}H_{152}N_{10}O_4Zn_2$); $[M]^+$ requires 2337.06. UV-Vis ($CHCl_3$) λ / nm (ε / M^{-1} cm^{-1}) 286 (0.5 × 10^5), 452 (1.8 × 10^5), 484 (1.5 × 10^5), 568 (0.2 × 10^5), 641 (0.5 × 10^5), 690 (0.3 ×10^5).

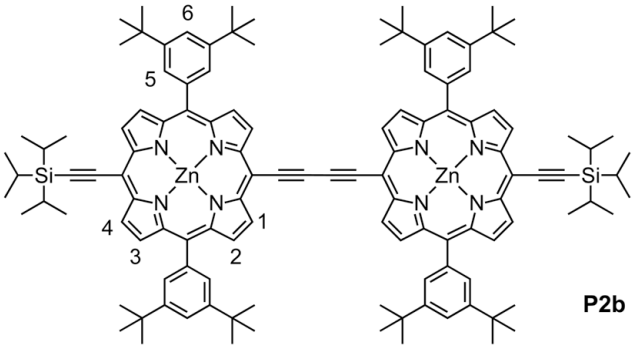


P2a

P2a is formed as a by-product during the synthesis of **P2a⊂M** (19.7 mg, 30 %). ^{1}H NMR (400 MHz, $CDCl_3$ + 1% C_5D_5N) δ_H 9.95 (d, J = 4.7 Hz, 4H, H_1), 9.05 (d, J = 4.7 Hz, 4H, H_2), 8.83 (d, J = 4.5 Hz, 4H, H_3), 8.79 (d, J = 4.5 Hz, 4H, H_4), 8.19 (dd, J_1 = 7.7 Hz, J_2 = 1.8 Hz, 4H, H_8), 8.07 (d, 1.8 Hz, 8H, H_5), 7.79 (t, J = 1.8 Hz, 4H, Ar-H_6), 7.72 (m, 6H, Ph-$H_{7,9}$), 1.55 (s, 72H, $H_{t\text{-}butyl}$). UV-Vis ($CHCl_3$) λ / nm (ε / M^{-1} cm^{-1}) 452 (2.7 × 10^5), 484 (2.0 × 10^5), 568 (0.2 × 10^5), 641 (0.4 × 10^5), 690 (0.6 × 10^5).

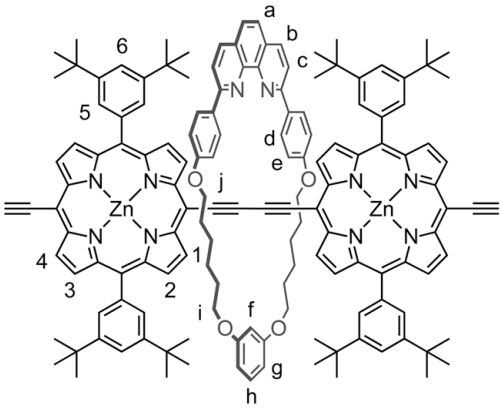


Rotaxane P2b⊂M. To a solution of macrocycle **M** (34.4 mg, 0.054 mmol) in CH_2Cl_2 (1.5 mL), was added a solution of CuI (6.8 mg, 0.036 mmol) in acetonitrile (0.5 mL) and stirred at room temperature for 1.5 hrs. The solvent was removed and the resulting dark red residue was redissolved in a 1:1 mixture of toluene and THF (2 mL). The solution was added to a solution of zinc 5,15-bis-(3,5-di-*tert*-butyl-phenyl)-10-ethynyl-20-triisopropylsilylethynyl-porphyrin **P1b** (68.5 mg, 0.072 mmol) in toluene (2 mL). Iodine (4.6 mg, 0.036 mmol) and potassium carbonate (19.9 mg, 0.154 mmol) was added and the reaction stirred for 5 days at 60 °C. The reaction mixture was cooled to room temperature, diluted with acetonitrile (3 mL) and CH_2Cl_2 (3 mL) and a solution of potassium cyanide (19.9 mg, 0.27 mmol) in water (2 mL) was added. The mixture was stirred for 14 hrs. Further CH_2Cl_2 (5 mL) was added and the organic fraction was collected and washed with water (10 mL). The solvent was removed and the crude was passed over a silica gel plug (CH_2Cl_2, 1% pyridine). The residue was dissolved in THF and passed through a size exclusion column to remove unthreaded macrocycle **M**. The unthreaded dimer **P2b** and rotaxane **P2a⊂M** were not separated by SEC, but **P2b⊂M** eluted second when the residue was passed through a silica gel column (CH_2Cl_2/PE 40-60 1:1, 1% pyridine). The solvent was removed and the product was precipitated from CH_2Cl_2 / MeOH to yield rotaxane **P2b⊂M** (56 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$ + 1% C_5D_5N) δ_H 9.92 (d, J = 4.6 Hz, 4H, H_1), 9.61 (d, J = 4.4 Hz, 4H, H_4), 8.84 (d, J = 4.4 Hz, 4H, H_3), 8.76 (d, J = 4.6 Hz, 4H, H_2), 8.62 (d, J = 8.7, 4H, H_d), 8.17 (d, J = 8.5, 2H, H_b), 7.97 (d, J = 8.5 Hz, 2H, H_c), 7.93 (d, J = 1.7 Hz, 8H, H_5), 7.74 (t, J = 1.7 Hz, 4H, H_6), 7.67 (s, 2H, H_a), 7.40 (t, J = 2.2 Hz, 1H, H_f), 7.29 (m, 4H, H_e), 6.77 (t, J = 8.1 Hz, 1H, H_h), 6.25 (dd, J_1 = 8.1 Hz, J_2 = 2.2 Hz, 2H, H_g), 4.10 (t, J = 6.0 Hz, 4H, H_i), 3.75 (t, J = 6.5 Hz, 4H, H_j), 1.64–1.35 (m, 16H, H_{alkyl}), 1.47 (s, 72H, $H_{t\text{-}butyl}$), 1.41 (s, 36H, $H_{TIPS\text{-}Me}$), 1.40 (s, 6H, $H_{TIPS\text{-}CH}$). ^{13}C NMR (125 MHz, $CDCl_3$ + 1% C_5D_5N) δ_C 160.6, 160.5, 156.4, 153.0, 152.0, 150.5, 150.1, 148.3, 146.1, 141.6, 136.3, 133.3, 132.6, 132.0, 130.9, 130.6, 129.5, 129.4, 129.1, 127.2, 125.2, 124.2, 120.7, 118.9, 114.9, 110.3, 107.1, 101.5, 100.9, 99.0, 97.3, 89.2, 82.5, 67.9, 67.5, 34.9, 31.7, 29.5, 28.8, 25.8, 25.7. *m/z* (MALDI TOF MS+) 2546.70, ($C_{164}H_{184}N_{10}O_4Si_2Zn_2$); $[M]^+$ requires 2546.26. UV-Vis ($CHCl_3$) λ / nm (ε / M^{-1} cm^{-1}) 289 (4.6×10^5), 452 (3.3×10^5), 494 (1.8×10^5), 674 (3.6×10^5), 690 (1.4×10^5).



P2b

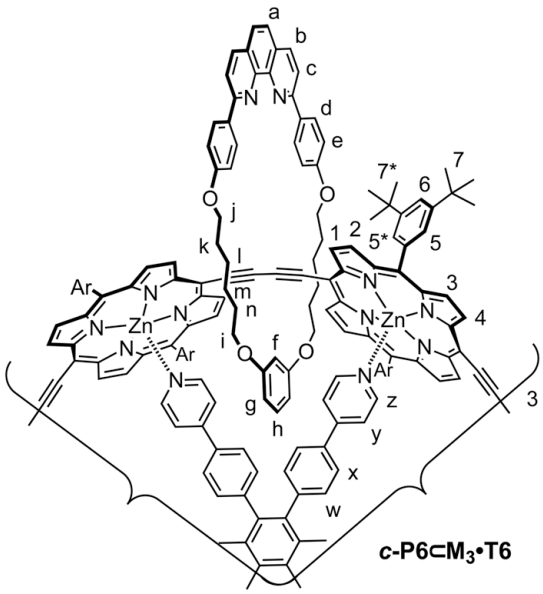
P2b is formed as a by-product during the synthesis of **P2c⊂M** (5 mg, 7%). ^{1}H NMR (500 MHz, $CDCl_3$ + 1% C_5D_5N) δ 9.87 (d, J = 4.6 Hz, 4H, H_1), 9.69 (d, J = 4.6 Hz, 4H, H_4), 8.97 (d, J = 4.4 Hz, 4H, H_3), 8.89 (d, J = 4.4 Hz, 4H, H_2), 8.02 (d, J = 1.9 Hz, 4H, H_5), 7.80 (t, J = 1.9 Hz, 4H, H_6), 1.56 (s, 72H, $H_{t\text{-}butyl}$), 1.41 (s, 36H, $H_{TIPS\text{-}Me}$), 1.40 (s, 6H, $H_{TIPS\text{-}CH}$). *m/z* (MALDI TOF MS+) 1906.77, ($C_{122}H_{142}N_8Si_2Zn_2$); $[M]^+$ requires 1906.95.



P2c⊂M

Rotaxane P2c⊂M. The TIPS-protected rotaxane **P2b⊂M** (20 mg, 0.0079 mmol) was placed in a dry flask under N_2 and dissolved in CH_2Cl_2 (3.0 mL). Through a septum tetrabutylammonium fluoride (1.0 M in THF, 0.023 mL, 0.023 mmol) was added. The reaction mixture was stirred for 30 min then the solvent removed. The crude was passed over a silica plug (CH_2Cl_2 + 1% pyridine). Recrystallisation from CH_2Cl_2/MeOH gave **P2c⊂M** as a green solid (15 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$ + 1% C_5D_5N) δ_H 9.88 (d, J = 4.7 Hz, 4H, H_1), 9.63 (d, J = 4.4 Hz, 4H, H_4), 8.82 (d, J = 4.4 Hz, 4H, H_3), 8.73 (d, J = 4.4 Hz, 4H, H_2), 8.61 (d, J = 8.8 Hz, 4H, H_d), 8.17 (d, J = 8.5 Hz, 2H, H_b), 7.97 (d, J = 8.5 Hz, 2H, H_c), 7.92 (d, J = 1.8 Hz, 8H, H_5), 7.72 (t, J = 1.8 Hz, 4H, H_6), 7.67 (s, 2H, H_a), 7.40 (t, J = 2.2 Hz, 1H, H_f), 7.29 (m, 4H, H_e), 6.76 (t, J = 8.2 Hz, 1H, H_h), 6.25 (dd, J_1 = 8.2 Hz, J_2 = 2.2 Hz, 2H, H_g), 4.12 (s, 2H, $H_{acetylene}$), 4.09 (t, J = 6.2 Hz, 4H, H_i), 3.79 (t, J = 6.9 Hz, 4H, H_j), 1.64–1.33 (m, 16H, H_{alkyl}), 1.47 (s, 72H, $H_{t\text{-}butyl}$). ^{13}C NMR (125 MHz, $CDCl_3$ + 1% C_5D_5N) δ_C 160.7, 160.5, 156.4, 153.0, 151.9, 150.6, 150.3, 146.1, 141.5, 136.3, 133.4, 132.8, 132.05, 131.0, 130.6, 129.8, 129.4, 129.2, 127.2, 125.3, 124.2, 120.8, 118.9, 115.0, 107.1, 101.0, 99.5 99.3, 89.2,

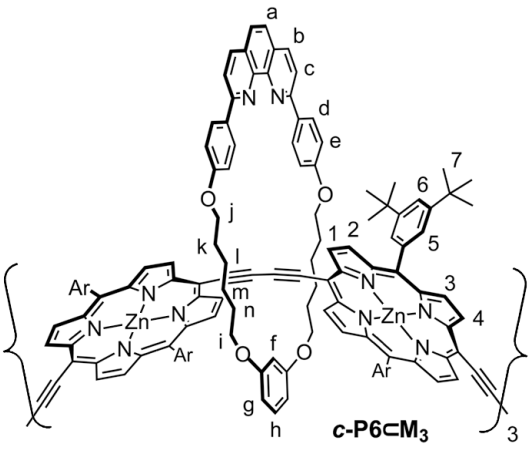
86.9, 83.2, 82.6, 67.9, 67.5, 35.0, 31.7, 29.7, 29.4, 28.8, 25.9, 25.7. *m/z* (MALDI TOF MS+) 2232.83, ($C_{146}H_{144}N_{10}O_4Zn_2$); $[M]^+$ requires 2233.15.



***c*-P6⊂M$_3$•T6**

[4]Catenane-Template Complex *c*-P6⊂M$_3$·T6. Hexadentate-template **T6**[11] (1.34 mg, 1.04 μmol) and **P2c⊂M** (8.99 mg, 4.02 μmol) were dissolved in a mixture of chloroform (1.80 mL) and diisopropylamine (0.10 mL) and sonicated (bath sonicator) for 2 hrs. A catalyst solution was prepared by dissolving dichlorobis(triphenylphosphine)-palladium(II) (0.85 mg, 1.2 μmol), copper(I) iodide (2.3 mg, 12.1 μmol) and benzoquinone (1.74 mg, 1.6 μmol) in a mixture of $CHCl_3$ (1.80 mL) and diisopropylamine (0.10 mL). The catalyst solution was added to the solution of hexadentate template and rotaxane **P2c⊂M** and the reaction mixture was stirred at room temperature for 5 hrs under N_2. The mixture was passed directly through an alumina plug ($CHCl_3$) and the solvent removed. Preparative size exclusion chromatography in toluene afforded ***c*-P6⊂M$_3$·T6** as a brownish-red solid (6.4 mg, 62%). ***c*-P12⊂M$_6$·(T6)$_2$** was also isolated as a orange solid (0.4 mg, 7%). ^{1}H NMR of ***c*-P6⊂M$_3$·T6** (500 MHz, $CDCl_3$ + 1% C_5D_5N) δ_H 9.61 (d, J = 4.4 Hz, 12H, H_1), 9.52 (d, J = 4.4 Hz, 12H, H_4), 8.73 (d, J = 4.4 Hz, 12H, H_3), 8.67 (d, J = 8.2 Hz, 12H, H_d), 8.50 (d, J = 4.4 Hz, 12H, H_2), 8.30 (d, J = 8.5 Hz, 6H, H_b), 8.02 (m, 6H, *overlapped* H_c), 8.02 (s, 12H, H_5), 7.80 (s, 6H, H_a), 7.72 (m, 12H, H_{5*}), 7.69 (m, 18H, H_6), 7.23 (m, 3H, H_f), 7.08 (d, J = 8.2 Hz, 12H, H_e), 6.83 (t, J = 8.2 Hz, 3H, H_h), 6.25 (dd, J_1 = 8.2 Hz, J_2 = 2.0 Hz, 6H, H_g), 5.62 (d, J = 8.8 Hz, 12H, H_w), 5.54 (d, J = 8.8 Hz, 12H, H_x), 5.03 (d, J = 7.0 Hz, 12H, H_y), 3.79 (t, J = 6.5 Hz, 12H, H_i), 3.34 (t, J = 7.3 Hz, 12H, H_j), 2.33 (d, J = 7.0 Hz, 12H, H_z), 1.52 (s, 108H, H_7), 1.36 (s, 108H, H_{7*}), 0.89 (m, 12H, H_n), 0.66 (m, 24H, $H_{k,m}$), 0.37 (m, 12H, H_l). ^{13}C NMR (125 MHz, $CDCl_3$ + 1% C_5D_5N) δ_C 160.5, 160.1, 156.4, 151.4, 151.1, 150.1, 150.0, 148.9, 148.2, 146.3, 142.9, 141.1, 140.1, 138.9, 136.5, 133.1, 132.6, 132.3, 132.2, 130.7, 130.6, 130.5, 130.2, 129.6, 129.2, 129.0, 127.4, 125.4, 125.3, 125.2, 124.0, 120.8, 119.0, 118.9, 114.9, 107.3, 100.9, 99.9, 99.4, 97.3, 96.7, 89.3, 89.0, 67.7, 67.2, 34.9, 28.8, 28.2, 25.0, 24.8, 22.3 (one signal missing, presumably due to overlap). *m/z* (MALDI TOF MS+) 7692.5,

($C_{510}H_{474}N_{36}O_{12}Zn_6$); $[M]^+$ requires 7691.3. UV-Vis ($CHCl_3$) λ / nm (ε / M^{-1} cm^{-1}) 291 (3.3×10^5), 482 (5.5×10^5), 773 (3.7×10^5), 808 (4.9×10^5), 851 (4.1×10^5). The ^{1}H NMR of ***c*-P12⊂M$_6$·(T6)$_2$** (700 MHz, $CDCl_3$) is shown in Figure S6b. MALDI-TOF analysis of ***c*-P12⊂M$_6$·(T6)$_2$** is shown in Figure S15. UV-Vis ($CHCl_3$) λ / nm (ε / M^{-1} cm^{-1}) 497 (5.7×10^5), 767 (2.2×10^5), 804 (2.8×10^5), 837 (4.3×10^5), 879 (4.6×10^5).



[4]Catenane *c*-P6⊂M$_3$. [4]Catenane template complex ***c*-P6⊂M$_3$·T6** (7.0 mg, 0.91 mmol) was passed through a size exclusion column (Biobeads SX-1) containing a 50 mg mL^{-1} solution of 1,4-diazabicyclo[2.2.2]octane (DABCO) in THF. Recrystallisation from $CHCl_3$/MeOH gave ***c*-P6⊂M$_3$** (5.4 mg, 89%) as a brown solid. ^{1}H NMR (500 MHz, $CDCl_3$ + 1% C_5D_5N) δ_H 9.59 (d, J = 4.5 Hz, 12H, H_1), 9.58 (d, J = 4.5 Hz, 12H, H_4), 8.73 (d, J = 4.5 Hz, 12H, H_3), 8.53 (d, J = 8.5, 12H, H_d), 8.50 (d, J = 4.5 Hz, 12H, H_2), 7.89 (d, J = 8.2, 6H, H_b), 7.80 (d, J = 1.2 Hz, 24H, H_5), 7.77 (m, J = 8.2 Hz, 6H, H_c), 7.68 (m, 12H, H_6), 7.67 (s, 6H, H_a), 7.22 (d, J = 8.5, 12H, H_e), 6.45 (m, 3H, H_f), 5.80 (t, J = 8.2 Hz, 3H, H_h), 5.39 (dd, J_1 = 8.2 Hz, J_2 = 1.8 Hz, 6H, H_g), 3.60 (t, J = 6.5 Hz, 12H, H_i), 3.41 (t, J = 7.3 Hz, 12H, H_j), 1.42 (s, 216H, H_7), 1.62–0.75 (m, 48H, H_{alkyl}). Free rotation of the porphyrins means H_5 is equivalent to H_{5*}, and H_7 is equivalent to H_{7*}. (It was not possible to record a good quality ^{13}C NMR spectrum of this compound due to the poor solubility.) *m/z* (MALDI TOF MS+) 6695.0 ($C_{438}H_{426}N_{30}O_{12}Zn_6$); $[M]^+$ requires 6695.0. UV-Vis ($CHCl_3$ / 1% pyridine) λ / nm (ε / M^{-1} cm^{-1}), 482 (5.1×10^5), 759 (3.1×10^5), 798 (3.9×10^5), 846 (4.3×10^5).

Section 4) NMR Spectra

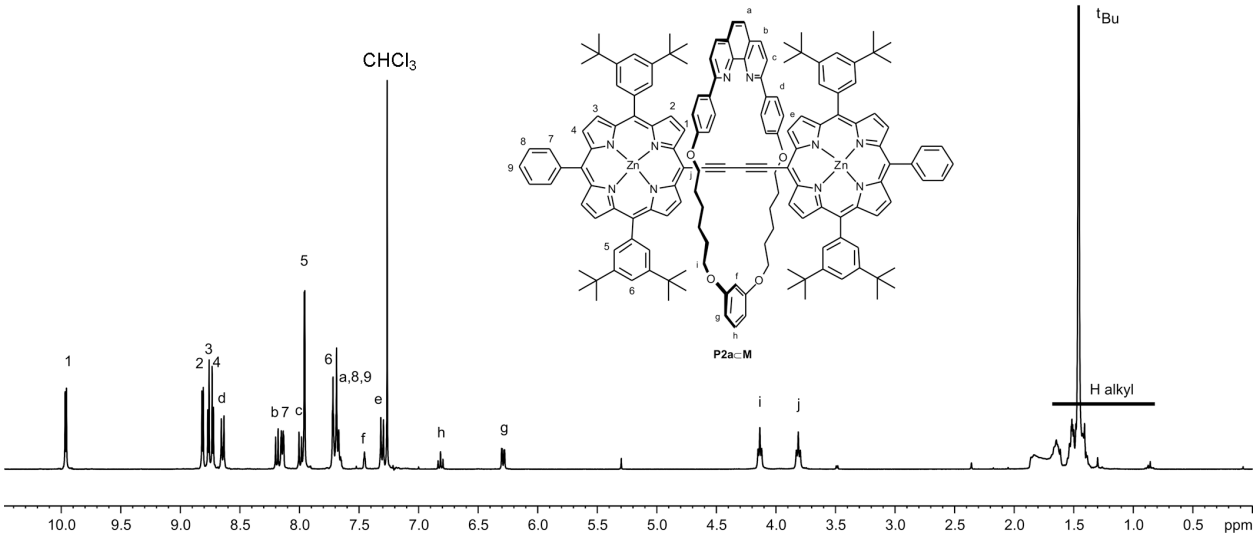


Figure S1. ^{1}H NMR spectrum of **P2a⊂M** (700 MHz, $CDCl_3$ containing 1% C_5D_5N).

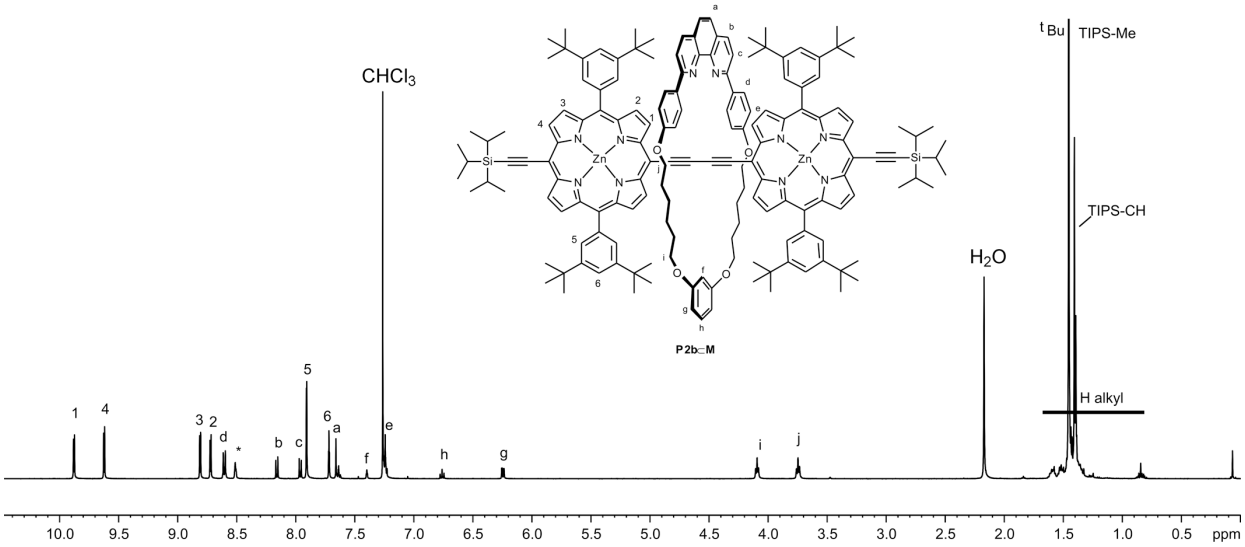


Figure S2. ^{1}H NMR spectrum of [2]rotaxane **P2b⊂M** (500 MHz, $CDCl_3$ containing 1% C_5D_5N; * indicated a peak due to d_5-pyridine).

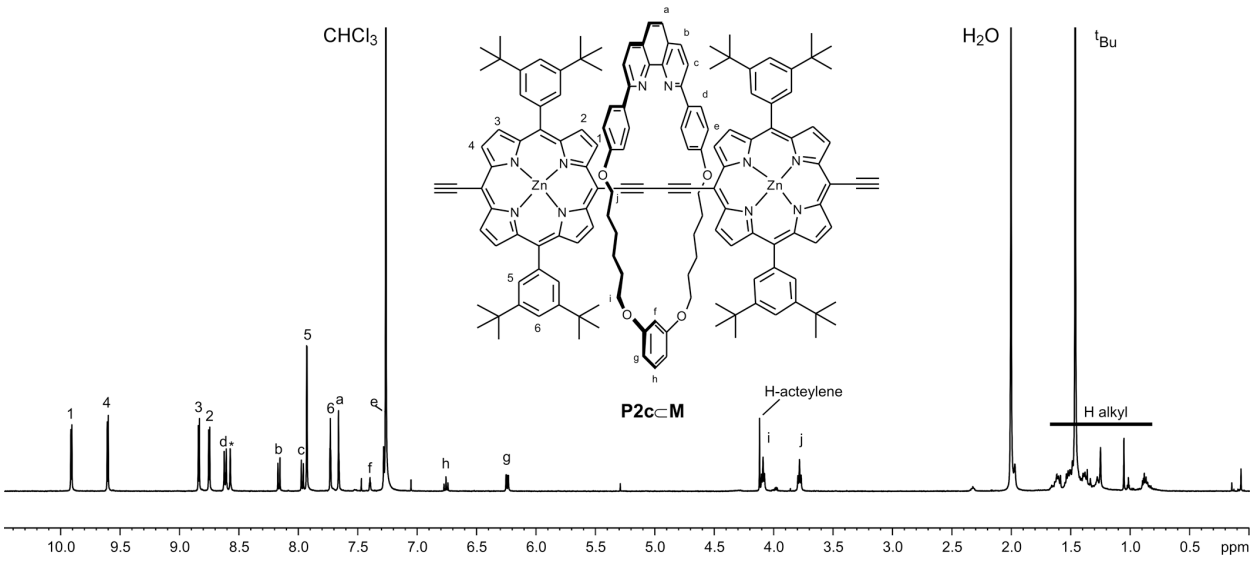


Figure S3. ^{1}H NMR spectrum of [2]rotaxane **P2c⊂M** (400 MHz, $CDCl_3$ containing 1% C_5D_5N; * indicated a peak due to d_5-pyridine).

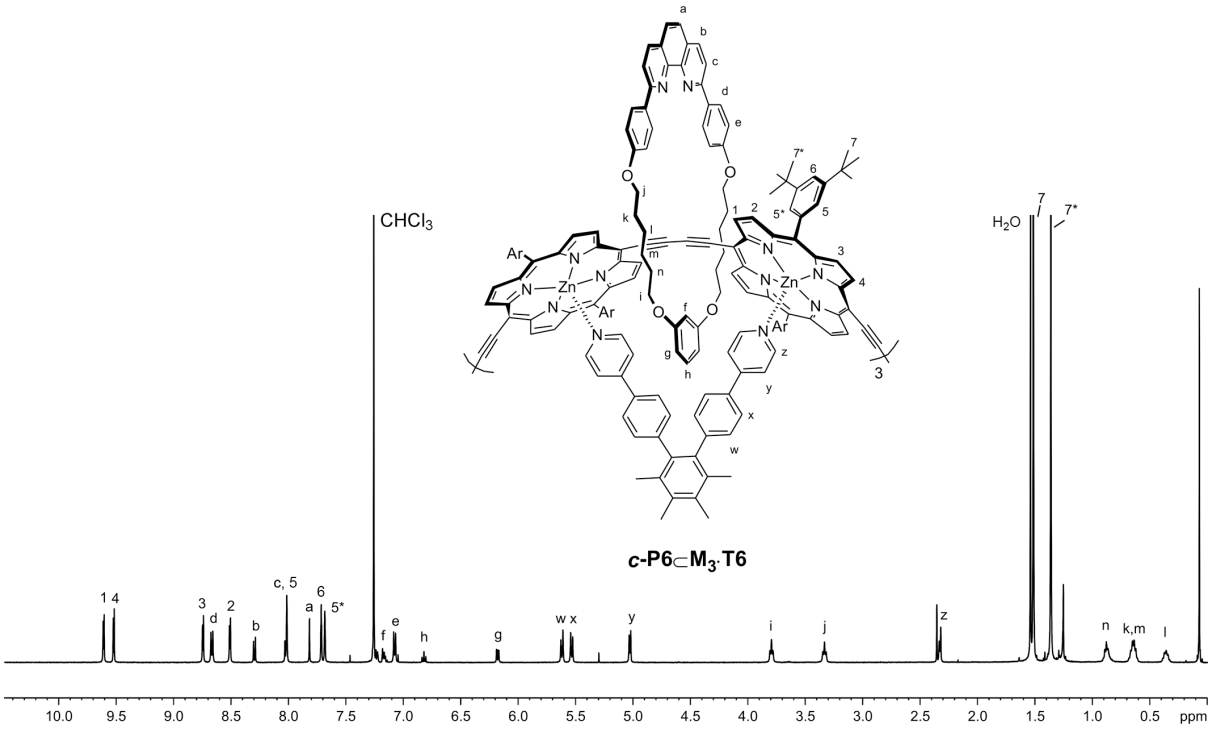


Figure S4. ^{1}H NMR spectrum of [4]catenane ***c*-P6⊂M$_3$·T6** (500 MHz, $CDCl_3$ containing 1% C_5D_5N).

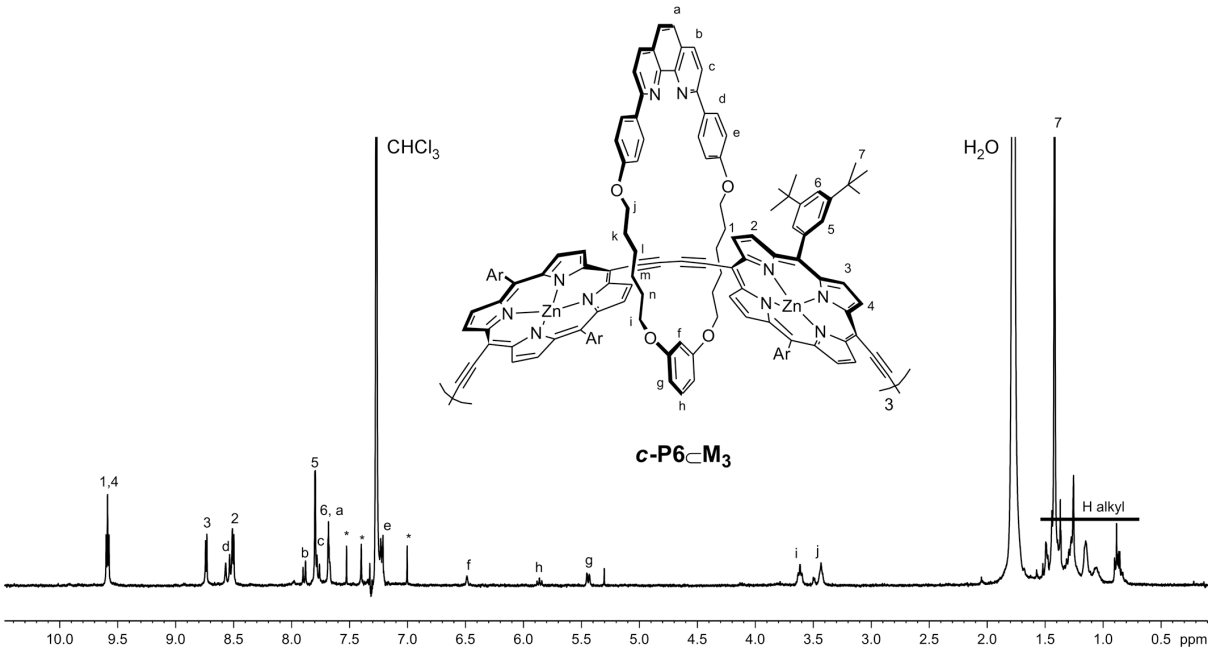


Figure S5. ^{1}H NMR spectrum of [4]catenane ***c*-P6⊂M$_3$** (400 MHz, $CDCl_3$ containing 1% C_5D_5N; solvent signals are denoted by *).

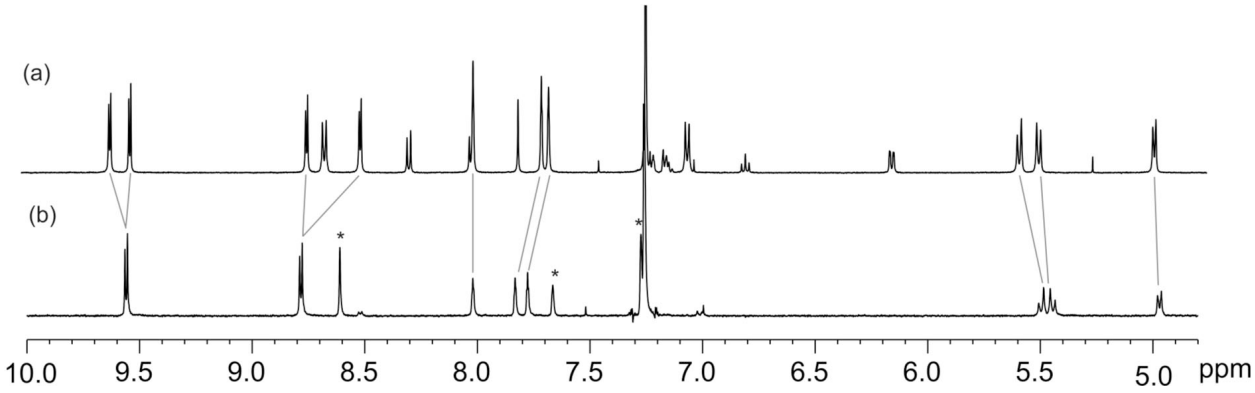
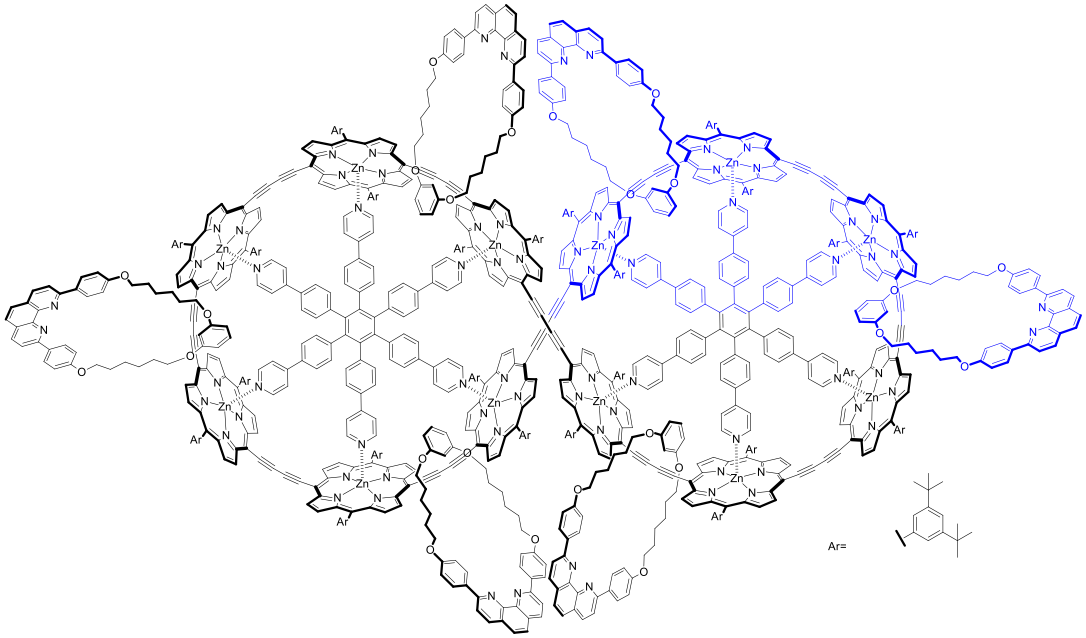


Figure S6. Comparison of the ^{1}H NMR spectra of (a) [4]catenane ***c*-P6⊂M$_3$·T6** and (b) non-catenated ***c*-P6·T6**[11] (500 MHz, $CDCl_3$ containing 1% C_5D_5N; * denotes pyridine signals).

Section 5) NMR Characterisation of [7]catenane complex *c*-P12⊂M_6·$(T6)_2$



As a result of the D_2 symmetry it is sufficient to consider only one quarter of the molecule for interpretation of the NMR spectrum. Comparison with the previously reported "figure-of-8" complex[12] ***c*-P12·$(T6)_2$,** identical to ***c*-P12⊂M_6·$(T6)_2$** minus the 6 interlocked macrocycles, allows for assignment of some of the characteristic signals.

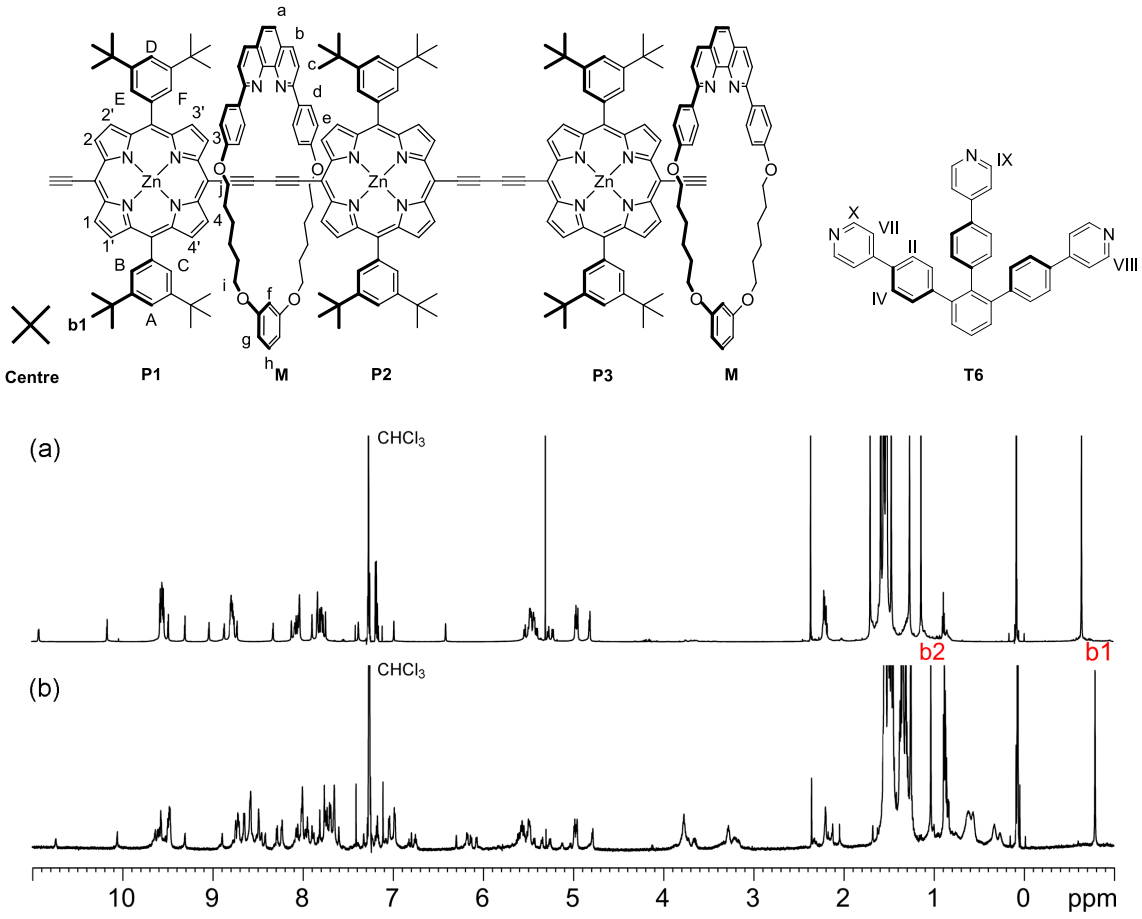


Figure S7. a) ^{1}H NMR spectrum of non-catenated 'figure-of-8' complex ***c*-P12·(T6)$_2$** (700 MHz, $CDCl_3$). b) ^{1}H NMR spectrum of [7]catenane complex ***c*-P12⊂M$_6$·(T6)$_2$** (700 MHz, $CDCl_3$).

All 9 protons on each *t*-butyl group are equivalent, and on each quarter the 12 *t*-butyl groups are non-equivalent. The *t*-butyl groups pointing inwards at the crossover point (protons b1 and b2) can be identified as the signals at a characteristic resonance of –0.79 ppm and 1.04 ppm, shielded by interaction with ring currents from the adjcent porphyrin. The close proximity of the porphyrins at the cross-over point leads to unusual shifts for the eight *β*-pyrrole protons from porphyrin P1. These could be assigned as shown in Figure S8.

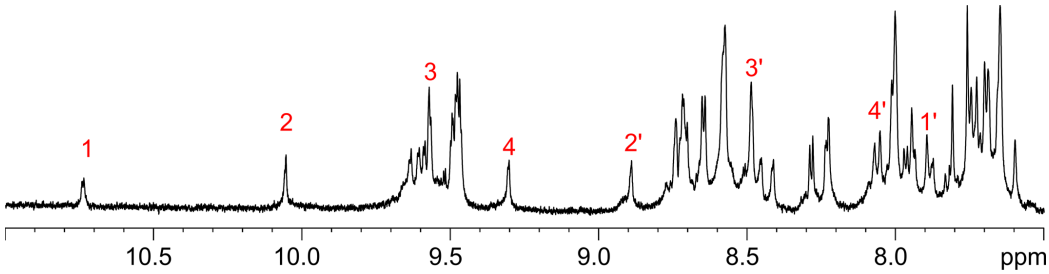


Figure S8. *β*-Pyrrole protons of porphyrin P1 of "figure-of-8" [7]catenane complex ***c*-P12⊂M$_6$·(T6)$_2$**.

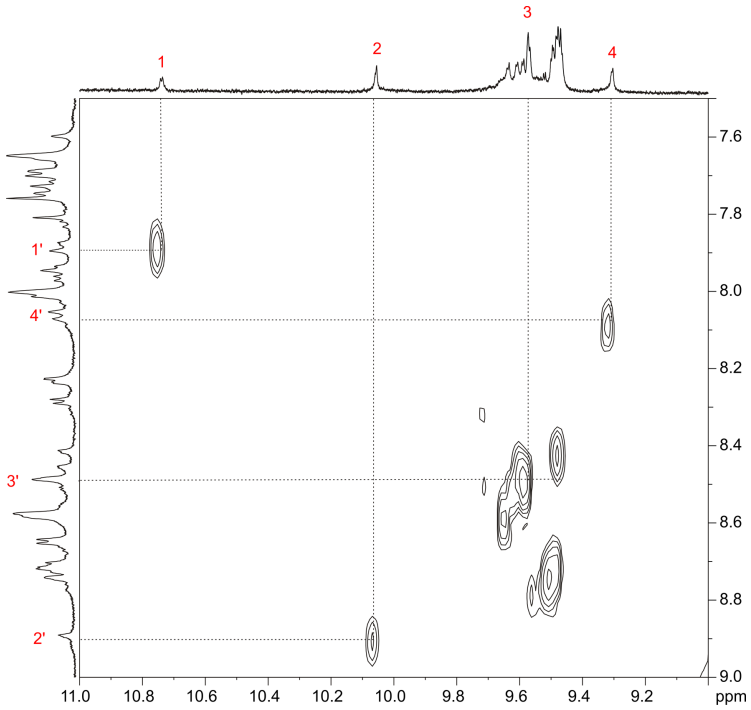


Figure S9. Part of the ^{1}H-^{1}H COSY spectrum showing coupling of *β*-pyrrole protons of "figure-of-8" [7]catenane complex ***c*-P12⊂M$_6$·(T6)$_2$** (700 MHz, $CDCl_3$, 298 K).

The signals from the template are consistant with those from the non-catenated complex and are observed in the region 5.7–4.7 ppm, and at 2.2 ppm. As with previously reported nanoring-template complexes, the pyridyl and phenyl proptons of the template are expected to be shielded by the porphyrin. This effect is greatest for protons VIII–X, and these resonate at 2.2 ppm. Protons X and VII, which show coupling in the COSY spectrum, are tentatively assigned to the arm of the template coordinating to porphyrin P1 due to the usual shifts arising from the crowded centre at the cross over point.

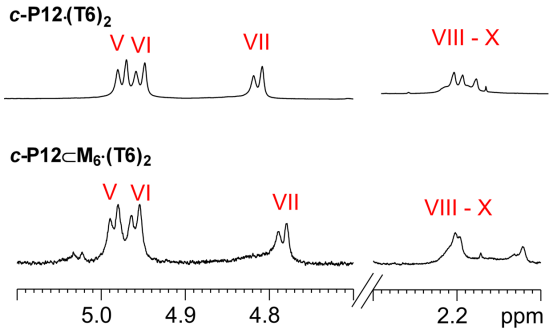


Figure S10. Region of the ^{1}H NMR spectrum showing signals of the template protons of ***c*-P12⊂M$_6$·(T6)$_2$** (700 MHz, $CDCl_3$, 298 K). The related uncatenated "figure-of-8" ***c*-P12·(T6)$_2$** is shown above for comparison.

The macrocycle signals in the aromatic region overlap with many of the porphrin peaks, however some could be assigned and clearly identified. All identifiable signals are split into two, integrating in a 2:1 ratio, which is consistant with the two macrocycle environments in the complex (Figure S11).

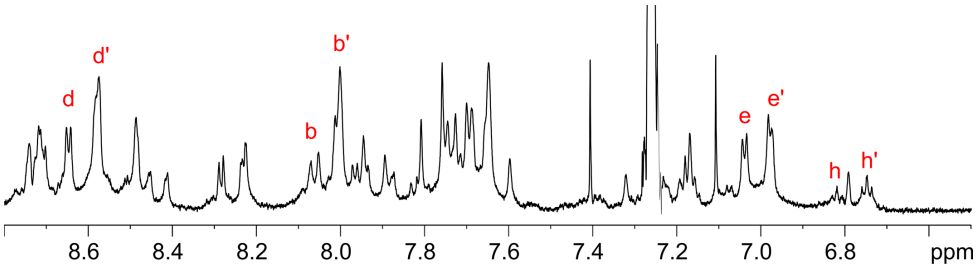


Figure S11. Partial assignment of signals from macrocycle **M** of ***c*-P12⊂M$_6$·(T6)$_2$**. Signals from the four equivalent macrocycles furthest from the cross over point are b', d', e' and h'.

Having identified and assigned some of the protons on porphyrin P1, the macrocycles **M** and the template **T6**, the NOESY spectrum can be used to confirm the interlocked nature of the macrocyles. NOEs are observed between the macrocyle proton d and both *t*-butyl protons b1 and b2. Ethylene glycol protons i and j of the macrocycle show NOEs with template protons V–VII (Figure S11). Protons VII only interact with protons from the macrocycles nearest to the crossover point (denoted by i* and j*), confirmimg the assigment of proton VII.

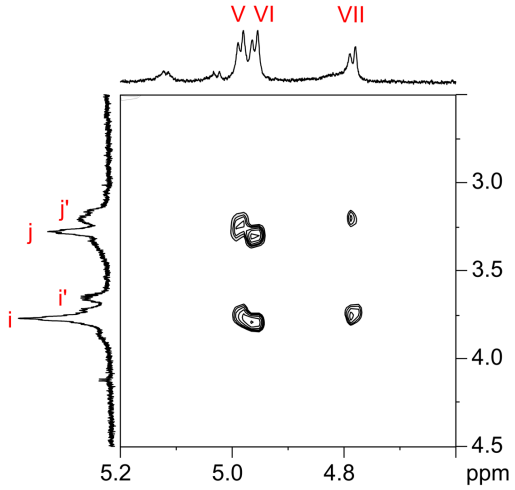


Figure S12. Part of the NOESY spectrum showing NOEs between the macrocycle and the template (700 MHz, $CDCl_3$, 298 K).

As with the non-catenated "figure-of-8" previously reported, NOESY data give good structural evidence for formation of the "figure-of-8" using correlations between different porphyrin units in the centre of the molecule (Figure S12). We observe NOEs between *t*-butyl protons b1 and b2 with *β*-pyrrole protons 1' and 4' of porphyrin unit P1 as expected due to their close proximity (3–4 Å). We also observe an NOE between *t*-butyl protons b1 and b2 and the *β*-pyrrole protons 2' and 2 respectively, on the opposite side of P1. This is too far to observe an NOE signal (>8 Å) and so the interaction must be between the two different but symmetry related porphyrins P1 at the cross-over

point. As with the previously reported "figure-of-8", this is good evidence to confirm the structure of this complex. An NOE is also observed between *t*-butyl protons b1 and b2 with proton d on the adjacent macrocycle.

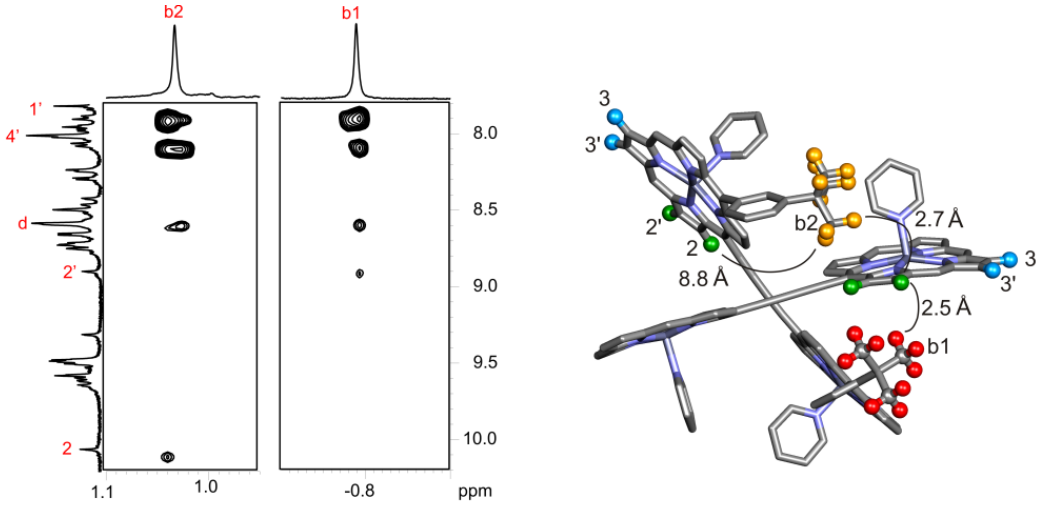


Figure S13. Interporphyrin NOEs between *β*-pyrrole and *t*Bu protons and model of the crossover point of ***c*-P12⊂M$_6$·(T6)$_2$**.

Section 6) MALDI-TOF Mass Spectra

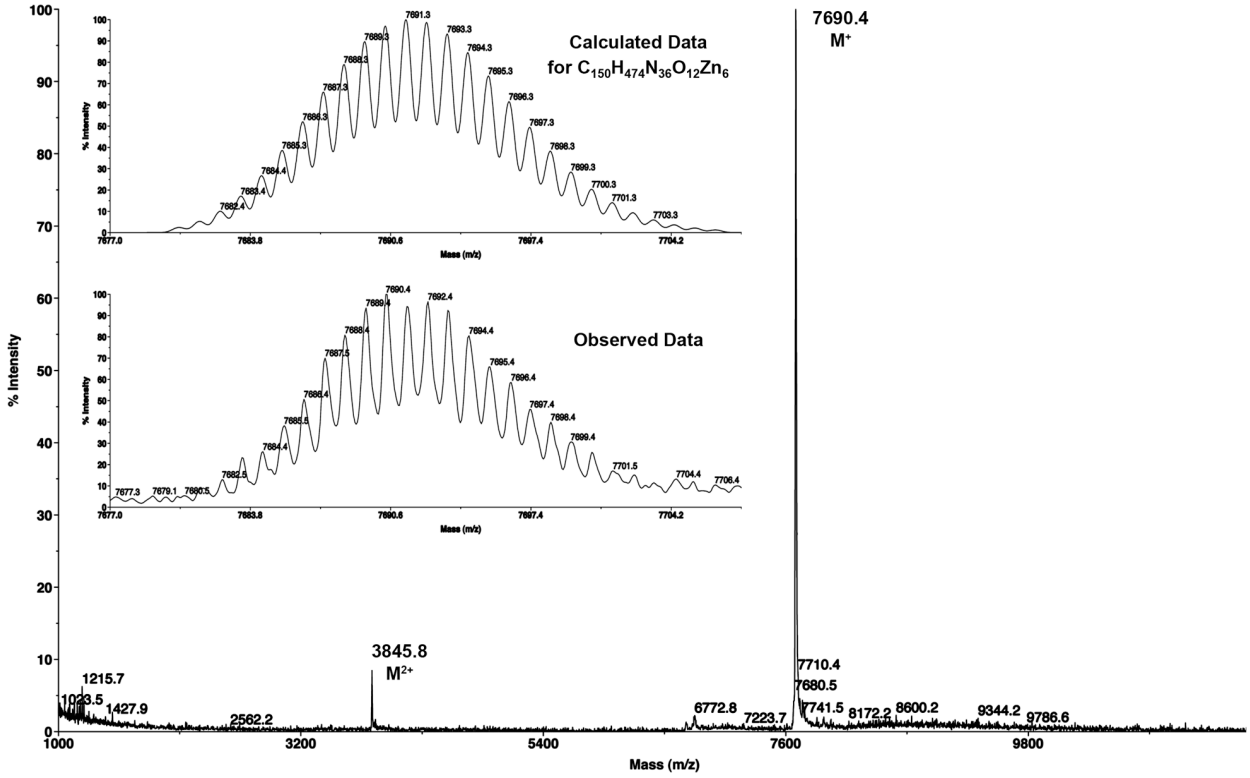


Figure S14. MALDI-TOF analysis of ***c*-P6⊂M$_3$·T6** (*m/z* 7690.4 $C_{510}H_{474}N_{36}O_{12}Zn_6$; expected 7691.3). Expansion inset: Theoretical and observed isotope patterns.

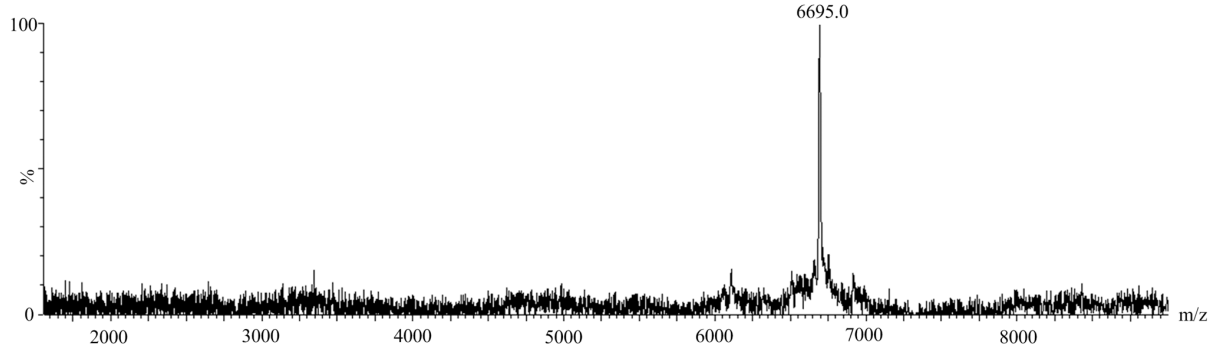


Figure S15. MALDI-TOF analysis of ***c*-P6⊂M$_3$** (*m/z* 6695.0 $C_{438}H_{426}N_{30}O_{12}Zn_6$, expected 6695.0).

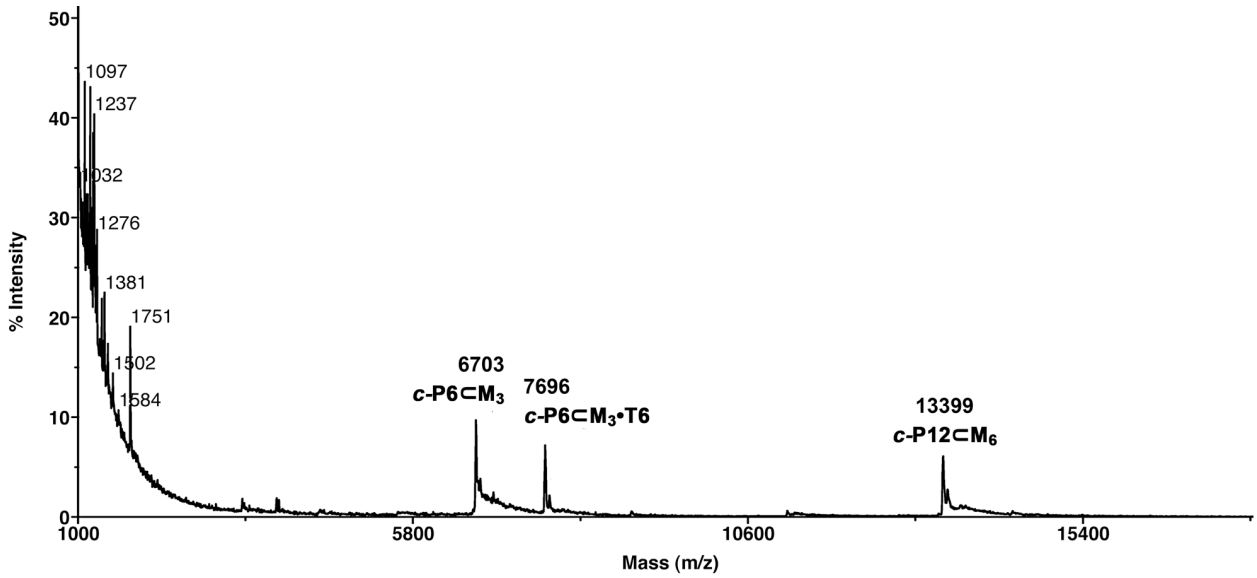


Figure S16. MALDI-TOF analysis of ***c*-P12⊂M$_6$·(T6)$_2$** ($C_{1020}H_{948}N_{72}O_{24}Zn_{12}$, expected 15389). The "figure-of-8" complex dissociates, losing the two **T6** template molecules: (*m/z* 13399 $C_{948}H_{900}N_{66}O_{24}Zn_{12}$; expected 13388). Also observed is the impurity ***c*-P6⊂M$_3$·T6** (*m/z* 7696; expected 7690) which dissociates to form ***c*-P6⊂M$_3$** (*m/z* 6703; expected 6694)

Section 7) Vis-NIR Titration of *c*-P6⊂M_3·T6 with Quinuclidine

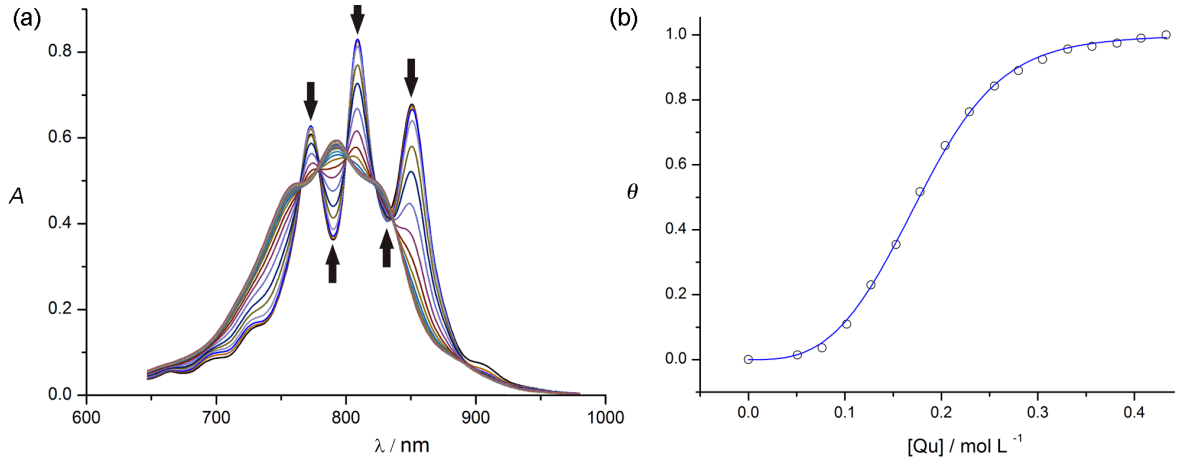


Figure S17. (a) Vis-NIR titration spectra and (b) binding curve for titration of ***c*-P6⊂M_3·T6** with quinuclidine in $CHCl_3$ at 298 K (*A* is absorption; θ is fraction bound; [***c*-P6⊂M_3·T6**] = 3.2 μM; arrows indicate regions of increasing and decreasing absorption during the titration). The fit to the binding curve gives an equilibrium constant for the displacement reaction of $K_b = 5.2 \times 10^{-2}$ M^{-5}. In combination with a single-site monomer binding constant for quinuclidine of $K_{Qu} = 3.9 \times 10^5$ M^{-1}, this corresponds to a formation constant of $\log K_f = 35 \pm 1$, calculated using the equation $K_f = (K_{Qu})^6/K_b$.[11] The analogous non-catenated complex ***c*-P6·T6** gives $K_b = 2.7 \times 10^{-3}$ M^{-5} and $\log K_f = 36 \pm 1$.

Section 8) Absorption and Fluorescence Spectra

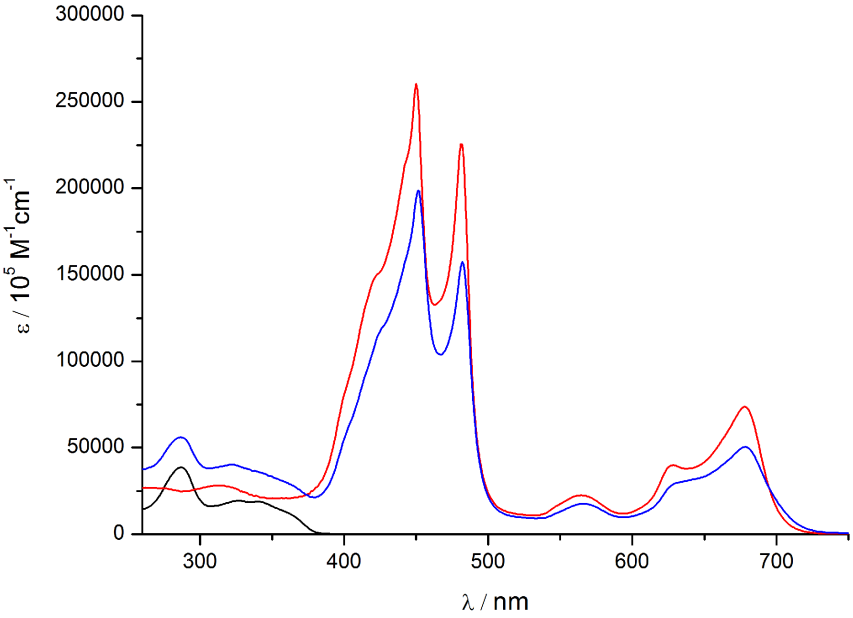


Figure S18. Absorption spectra ($CHCl_3$) of macrocycle **M** (black line), rotaxane **P2a⊂M** (blue line) and non-interlocked porphyrin dimer **P2a** (red line).

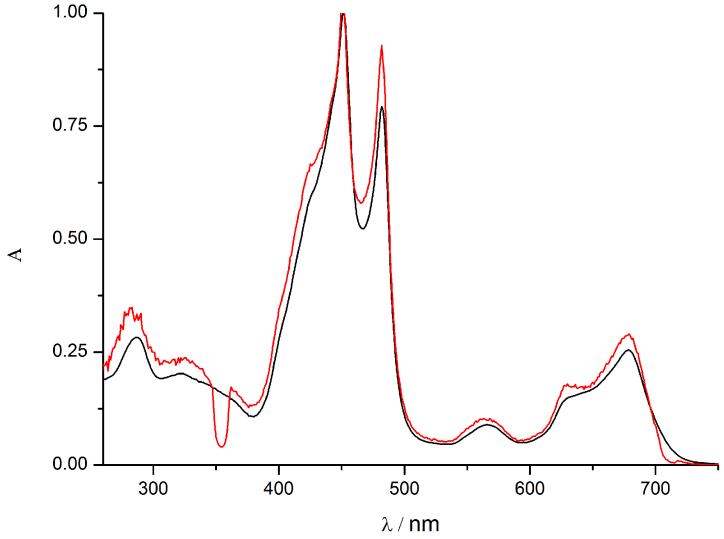


Figure S19. Absorption spectrum (black line) and fluorescence excitation spectrum (red line, detection at 715 nm) of rotaxane **P2a⊂M**, recorded in $CHCl_3$. The excitation spectrum was corrected for varying light intensity by multiplication by the ratio of the absorption and excitation spectra of the non-interlocked porphyrin dimer **P2a**. The discontinuity at half the detection wavelength (358 nm) is due to scattering.

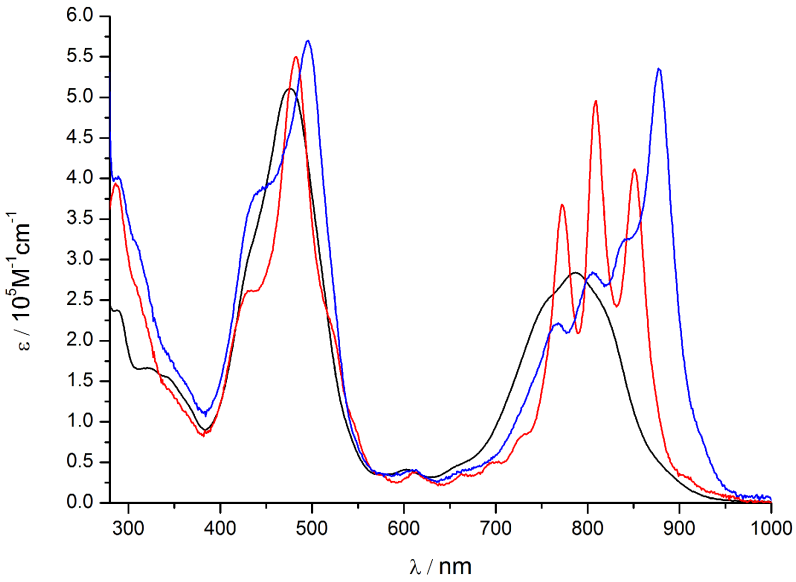


Figure S20. Absorption spectra of ***c*-P6⊂M$_3$·T6** (red line), ***c*-P6⊂M$_3$** (black line) and ***c*-P12⊂M$_6$·(T6)$_2$** (blue line), recorded in $CHCl_3$.

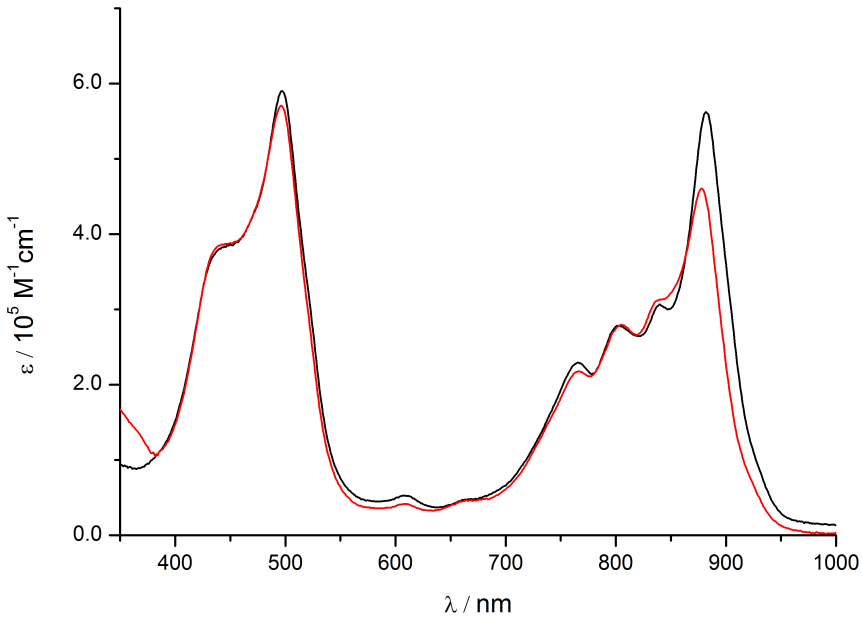


Figure S21. Comparison of the absorption spectra of "figure-of-8" [7]catenane ***c*-P12⊂M$_6$·(T6)$_2$** (red line) and non-catenated ***c*-P12·(T6)$_2$**[12] (black line), recorded in $CHCl_3$.

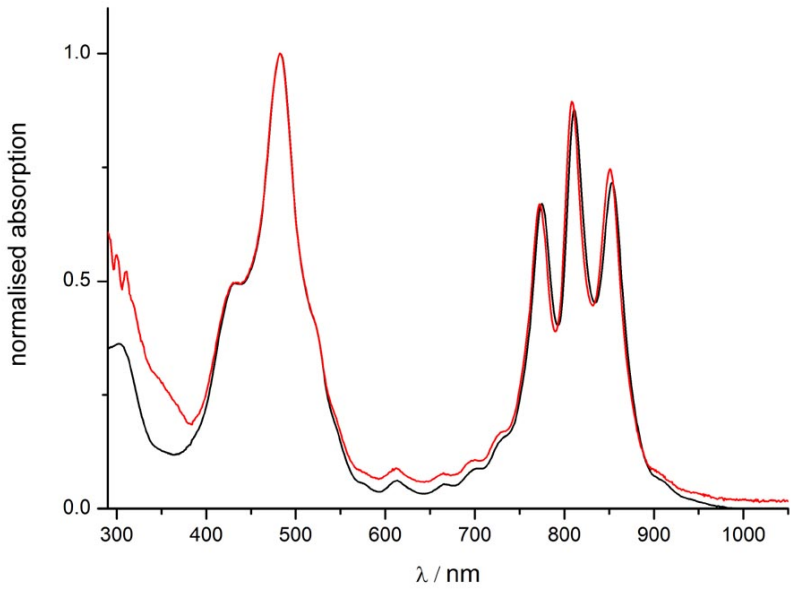


Figure S22. Comparison of the absorption spectra of [4]catenane-template complex ***c*-P6⊂M$_3$·T6** (red line) and non-catenated ***c*-P6·T6**[11] (black line), recorded in $CHCl_3$.

Section 10) GPC Analysis

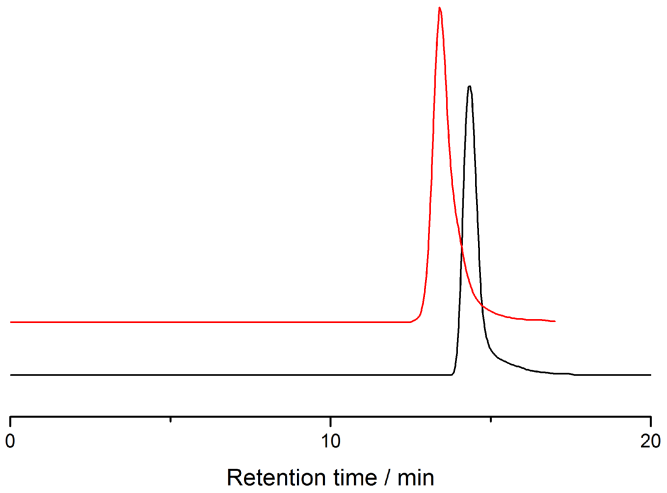


Figure S23. Analytical gel permeation chromatogram of ***c*-P6⊂M$_3$·T6** (black line) and ***c*-P12⊂M$_6$·(T6)$_2$** (red line). PLgel 3 µm mixed-E columns; length: 2 × 300 mm, diameter: 7.5 mm; flow rate 1.0 mL / min; detection: absorbance at 480 nm; solvent: toluene.

Section 11) References

1. S. G. DiMagno, V. S.-Y. Lin and M. J. Therien, *J. Org. Chem.,* 1993, **58**, 5983-5993.
2. M. O. Senge and X. Feng, *J. Chem. Soc., Perkin Trans. 1*, 2000, 3615-3621.
3. M. J. Plater, S. Aiken and G. Bourhill, *Tetrahedron*, 2002, **58**, 2415-2422.
4. S. M. Kuebler, R. G. Denning and H. L. Anderson, *J. Am. Chem. Soc.*, 1999, **122**, 339-347.
5. M. S. Newman and L. F. Lee, *J. Org. Chem.*, 1972, **37**, 4468-4469.
6. B. J. Littler, M. A. Miller, C.-H. Hung, R. W. Wagner, D. F. O'Shea, P. D. Boyle and J. S. Lindsey, *J. Org. Chem.*, 1999, **64**, 1391-1396.
7. H. Yang and H. F. Sleiman, *Angew. Chem. Int. Ed.*, 2008, **47**, 2443-2446.
8. S. Saito, K. Nakazono and E. Takahashi, *J. Org. Chem.*, 2006, **71**, 7477-7480.
9. M. U. Winters, E. Dahlstedt, H. E. Blades, C. J. Wilson, M. J. Frampton, H. L. Anderson and B. Albinsson, *J. Am. Chem. Soc.*, 2007, **129**, 4291-4297.
10. S. Saito, E. Takahashi and K. Nakazono, *Org. Lett.*, 2006, **8**, 5133-5136.
11. M. Hoffmann, J. Kärnbratt, M.-H. Chang, L. M. Herz, B. Albinsson and H. L. Anderson, *Angew. Chem. Int. Ed.*, 2008, **47**, 4993-4996.
12. M. C. O' Sullivan, J. K. Sprafke, D. V. Kondratuk, C. Rinfray, T. D. W. Claridge, A. Saywell, M. O. Blunt, J. N. O' Shea, P. H. Beton, M. Malfois and H. L. Anderson, *Nature*, 2011, **469**, 72-75.