Supporting Information

Polyyne Rotaxanes: Stabilization by Encapsulation

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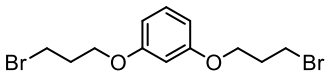
A. General Experimental Procedures

Unless stated otherwise, all reagents and solvents were used as commercially supplied, without further purification. Dry THF was obtained by passing through alumina under nitrogen pressure or was distilled from sodium/benzophenone. Dry CH_3CN and CH_2Cl_2 were distilled from CaH_2 or were obtained by passing through alumina under nitrogen pressure. Column chromatography was carried out using Silica 60A (particle size 35–70 μm, Fisher, UK) as the stationary phase. Size-exclusion chromatography was carried out using polystyrene beads (Bio-Beads-S-X3, operating range 2000 Da and Bio-Beads-S-X1, operating range 10 kDa). Where mixtures of solvents were used, ratios reported are by volume. TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F254, Merck, Germany) and visualized under UV light (254 nm). NMR spectra were recorded at 500 MHz using Bruker AVII 500 or at 400 MHz using Bruker DPX 400 and Bruker Avance 400 MHz instruments at 298 K. Chemical shifts are reported in parts per million (ppm) from low to high frequency and referenced to the residual solvents resonances (CD_2Cl_2: ^{1}H NMR - 5.32 and ^{13}C NMR- 53.8, $CDCl_3$: ^{1}H NMR - 7.26 and ^{13}C NMR - 77.2). For simplicity, the coupling constants of the aryl protons for para-substituted aryl groups have been reported as pseudo first-order (i.e., doublets), even though they are second-order (AA'XX') spin systems. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, dd = double doublets, t = triplet, q = quartet, m = multiplet. Proton peaks are assigned by COSY, NOESY and ROESY spectra. MALDI-TOF mass spectrometry was carried out in positive reflectron mode using a Micromass MALDI micro MX and Bruker 9.4T Apex-Qe FTICR spectrometers with dithranol (1,8-dihydroxyanthrone) as a matrix. ESI/APPI spectrometry was carried out using Agilent 6220 and Agilent 6120 Series, or a Bruker micrOTOF II focus LC/MS Trap instruments. UV-vis spectra were recorded at ambient temperature on Perkin-Elmer Lambda 20, Lambda 25, or a Varian Cary 5000 UV-vis-NIR spectrometers with 1 nm resolution; λ in nm (ε in $M^{-1}\cdot cm^{-1}$). IR spectra of solids were recorded on a Varian 660-IR spectrometer with ATR-module. Melting points (Mp) were determined by pair of microscope cover glasses on Leica Galen III melting point microscope or measured with an Electrothermal 9100 instrument.

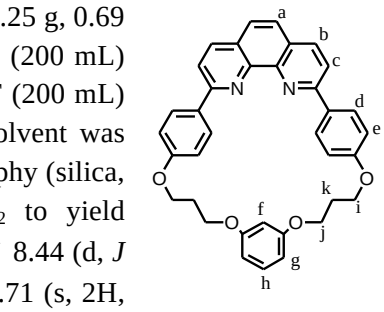
B. Synthetic Procedures

Terminal polyynes **1a–f**,[S1] porphyrin **3**,[S2] macrocycles **M1**,[S3] **M4**,[S3] **M7**,[S3b] and **M8**[S4] were synthesized according to published procedures. The synthesis of rotaxanes **2b·M1**, **2c·M1** and **2e·M1** have been reported before.[S5]

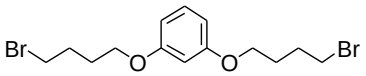
***m*-Bis[(3-bromopropyl)oxy]benzene**:[S6] Resorcinol (6.00 g, 54.5 mmol), 1,3-dibromopropane (16.7 mL, 163 mmol) and K_2CO_3 (19.1 g, 138 mmol) were dissolved in acetone (250 mL). The mixture was refluxed for 7 h at 65 °C, then water was added (50 mL) and the mixture was stirred for 1 h at the same temperature. The reaction mixture was cooled, water (100 mL) was added and the organic phase was extracted with EtOAc (3 × 150 mL). Organic fractions were combined and solvent was removed. The crude product was purified by flash column chromatography (silica, hexane/EtOAc 15:1) followed by recrystallization from EtOAc affording the product (4.8 g, 25%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (t, J = 8.2 Hz, 1H), 6.54–6.47 (m, 3H), 4.09 (t, J = 5.8 Hz, 4H), 3.60 (t, J = 6.5 Hz, 4H), 2.31 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 130.1, 107.1, 101.7, 65.4, 32.5, 30.2.



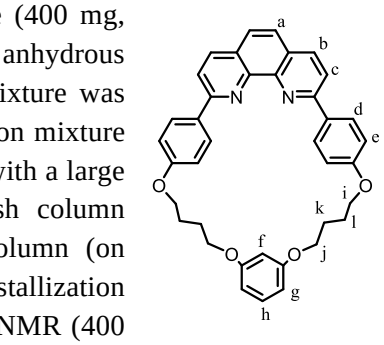
Macrocycle M2: A solution of 2,9-bis(4-hydroxyphenyl)-1,10-phenanthroline (0.25 g, 0.69 mmol)[S3] and *m*-bis[(3-bromopropyl)oxy]benzene (0.24 g, 0.69 mmol) in DMF (200 mL) was dropped over 2 h into a suspension of Cs_2CO_3 (1.35 g, 4.12 mmol) in DMF (200 mL) heated at 75 °C, and stirred for 4 h. The reaction mixture was cooled and solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (silica, CH_2Cl_2 + 1% CH_3OH) followed by recrystallization from CH_3OH/CH_2Cl_2 to yield macrocycle **M2** (210 mg, 55%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, J = 8.9 Hz, 4H H_d), 8.23 (d, J = 8.4 Hz, 2H, H_c), 8.07 (d, J = 8.4 Hz, 2H, H_b), 7.71 (s, 2H, H_a), 7.21 (m, 5H, H_e,H_h), 6.70 (t, J = 2.3 Hz, 1H, H_f), 6.53 (dd, J = 8.2, 2.4 Hz, 2H, H_g), 4.48 (t, J = 6.9 Hz, 4H), 4.11 (t, J = 5.4 Hz, 4H), 2.50–2.03 (m, 4H, H_k). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 160.2, 146.0, 136.8, 132.4, 130.3, 129.2, 127.5, 125.6, 119.0, 115.8, 105.2, 104.4, 65.6, 63.9, 53.6, 29.4. LRMS (ESI) calcd for $[C_{36}H_{30}N_2O_4 + H]^+$ 555.6, found 555.2.



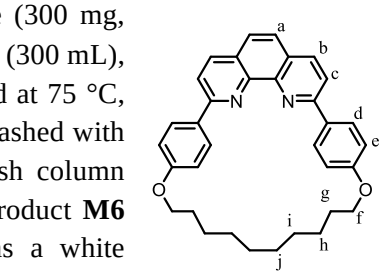
***m*-Bis[(4-bromobutyl)oxy]benzene**:[S7] Resorcinol (300 mg, 2.72 mmol), 1,4-dibromobutane (2.60 mL, 4.68 g, 21.6 mmol) were dissolved in acetone (100 mL) and K_2CO_3 (19.0 g, 13.8 mmol) was added. The reaction mixture was refluxed for 3 d and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, $PE_{40/60}/CH_2Cl_2$ 2:3) to give the product (710 mg, 68%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (t, J = 8.2 Hz, 1H), 6.49 (dd, J_1 = 2.4 Hz, J_2 = 5.8 Hz, 2H), 6.44 (t, J = 2.4 Hz), 3.97 (t, J = 6.1 Hz, 4H), 3.49 (t, J = 6.6 Hz, 4H), 2.10–2.02 (m, 4H), 1.97–1.90 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 160.2, 130.0, 106.9, 101.6, 66.9, 33.6, 29.6, 28.0.



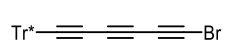
Macrocycle M3: To a solution of 2,9-bis(hydroxyphenyl)-1,10-phenanthroline (400 mg, 1.10 mmol) and 1,3-bis(4-bromobutyloxy)benzene (416 mg, 1.10 mmol) in anhydrous DMF (500 mL), K_2CO_3 (902 mg, 6.54 mmol) was added and the reaction mixture was stirred for 24 h at 75 °C under a slight positive pressure of nitrogen. The reaction mixture was cooled and solvent was removed *in vacuo*. The crude mixture was washed with a large excess of water and filtered, then the crude product was purified by flash column chromatography (silica, THF/CH_2Cl_2 10:1), then by using size-exclusion column (on Biobeads-S-X3) in THF to remove larger macrocyclic molecules. The final recrystallization from CH_2Cl_2/hexane gave the product **M3** (300 mg, 47%) as a white solid. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.34 (d, J = 8.9 Hz, 4H, H_d), 8.29 (d, J = 8.4 Hz, 2H, H_b), 8.07 (d, J = 8.4 Hz, 2H, H_c), 7.77 (s, 2H, H_a), 7.18–7.13 (m, 5H, $H_{h,e}$), 6.58 (t, J = 2.4 Hz, 1H, H_f), 6.52 (dd, J_1 = 8.2 Hz, J_2 = 2.4 Hz, 2H, H_g) 4.28 (t, J = 7.2 Hz, 4H, H_i), 4.06 (t, J = 5.9 Hz, 4H, H_j), 2.08 (m, 4H, H_l), 1.98 (m, 4H, H_k): ^{13}C NMR (100 MHz, CD_2Cl_2, 298 K): δ 160.8, 160.5, 156.5, 146.4, 137.0, 132.7, 130.2, 129.3, 127.8, 125.9, 119.6, 115.6, 106.8, 102.3, 68.6, 68.4, 27.0, 26.3. (MALDI TOF MS+) requires 583.26, calcd for $C_{38}H_{34}N_2O_4$, $(M)^+$, found 583.33.



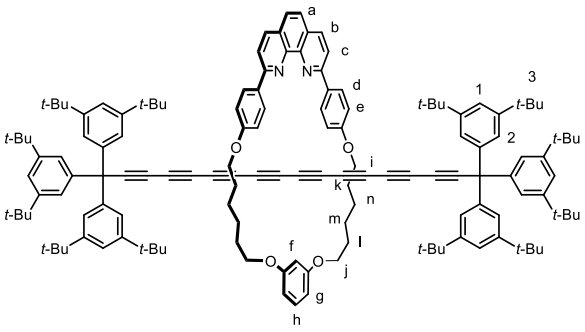
Macrocycle M6: To a solution of 2,9-bis(hydroxyphenyl)-1,10-phenanthroline (300 mg, 0.823 mmol) and 1,10-dibromodecane (245 mg, 0.816 mmol) in anhydrous DMF (300 mL), K_2CO_3 (3.0 g, 22 mmol) was added and the reaction mixture was stirred for 2 d at 75 °C, under nitrogen. The solvent was removed *in vacuo* and the crude mixture was washed with a large excess of water, filtered, then the crude mixture was purified by flash column chromatography (silica, CH_2Cl_2, gradually adding EtOAc 0–15%). The pure product **M6** (119 mg, 29%) was obtained after recrystallization from CH_2Cl_2/CH_3OH as a white solid.^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.36 (d, J = 8.8, Hz, 4H, H_d), 8.29 (d, J = 8.2 Hz, 2H, H_b), 8.07 (d, J = 8.5 Hz, 2H, H_c), 7.77 (s, 2H, H_a), 7.11 (d, J = 8.8 Hz, 4H, H_e), 4.25 (t, J = 8.2 Hz, 4H,



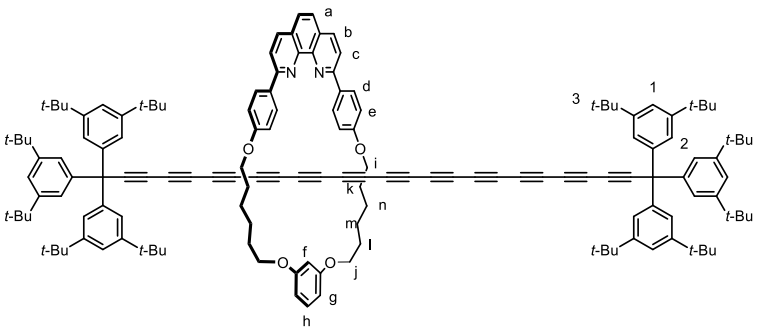
H_f), 1.81 (m, 4H, H_g), 1.42–1.40 (m, 12H, $H_{h,j,k}$). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K): δ 159.9, 156.5, 146.4, 137.0, 132.5, 129.4, 127.8, 125.9, 119.5, 115.9, 68.3, 29.7, 29.4, 28.1, 25.6. (MALDI TOF MS+) requires 503.7, calcd for $C_{34}H_{35}N_2O_2$ ($[M + H]^+$), found 504.8.



1-Bromo-triyne 3:[S8] *N*-bromosuccinimide (98 mg, 0.55 mmol) and $AgNO_3$ (16 mg, 0.092 mmol) were added to a solution of **1c** (300 mg, 0.46 mmol) in acetone (30 mL). After stirring at 20 °C for 6 h the reaction mixture was quenched by adding water (10 mL) and then extracted with a CH_2Cl_2 (3 × 50 mL). The organic layers were combined, washed with brine (20 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product purified by passing through a silica plug (CH_2Cl_2/hexanes 1:5) to yield **3** (330 mg, 95%) as a slightly yellow solid. R_f = 0.4 (hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, J = 2 Hz, 3H), 6.91 (d, J = 2 Hz, 6H), 1.19 (s, 54H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 143.6, 123.7, 120.3, 84.5, 68.5, 66.4, 62.4, 60.0, 57.1, 40.0, 34.8, 31.4.



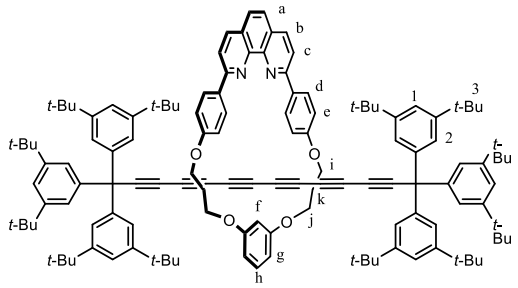
Rotaxane 2d·M1: A solution of CuI (5.7 mg, 30 μmol) in CH_3CN (dry, 2 mL) was added to a solution of the macrocycle **M1** (18.8 mg, 29.5 μmol) in CH_2Cl_2 (dry, 5 mL) and the mixture was stirred at 20 °C for 1 h. The solvent was removed *in vacuo* and the Cu·**M1** complex dissolved in dry THF (3 mL). Tetrayne **1d** (50 mg, 74 μmol) was dissolved in THF (2 mL) in a Schlenk tube, iodine (8.0 mg, 31 μmol), K_2CO_3 (16.6 mg, 120 μmol), and the solution of the Cu·**M1**complex in THF were added. The mixture was stirred at 60 °C in the dark for 40 h. The reaction mixture was cooled to 20 °C, CH_3CN (3 mL), CH_2Cl_2 (4 mL), and an aqueous KCN solution (30.0 mg, 450 μmol, in 3 mL H_2O) were added and the mixture was stirred at 20 °C for 1 h. CH_2Cl_2 (25 mL) was added, the organic layer was separated and washed with water (3 × 10 mL). The organic phase was dried ($MgSO_4$) and the solvent was removed. The crude product was purified by flash column chromatography (silica, hexane/EtOAc 30:1 → 20:1) to yield **2d·M1** (14 mg, 23%) as a beige solid. Mp 285–290 °C (decomp). R_f = 0.29 (hexanes/EtOAc 6:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.44 (d, J = 8.8 Hz, 4H, H_d), 8.27 (d, J = 8.5 Hz, 2H, H_b), 8.09 (d, J = 8.5 Hz, 2H, H_c), 7.75 (s, 2H, H_a), 7.29 (t, J = 1.7 Hz, 6H, H_1), 7.14–7.07 (m, 5H, $H_{e,h}$), 6.53 (t, J = 2.2 Hz, 1H, H_f), 6.46 (dd, J_1 = 8.2 Hz, J_2 = 2.3 Hz, 2H, H_g), 4.13 (t, J = 7.0 Hz, 4H, H_j), 4.00 (t, J = 6.4 Hz, 4H, H_i), 1.94–1.83 (m, 8H, $H_{k,l}$), 1.63–1.61 (m, 8H, $H_{m,n}$), 1.18 (s, 108H, H_3). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 160.98, 160.96, 156.3, 150.8, 146.5, 143.5, 136.9, 132.2, 130.0, 129.2, 127.8, 125.8, 123.9, 121.1, 119.2, 115.2, 107.5, 100.8, 87.0, 69.3, 68.5, 68.2, 64.0, 63.7, 63.6, 63.0, 62.9, 62.5, 57.8, 35.1, 31.5, 30.0, 29.5, 26.32, 26.28. ESI HRMS (MeCN/$CHCl_3$) requires 1990.3077 calcd for $C_{144}H_{169}N_2O_4$ ($[M + H]^+$), found 1990.3056. UV-vis (CH_2Cl_2) λ_{max} / nm (ε / M^{-1} cm^{-1}) 354 (322000), 331 (264000), 311(150000) 293 (103000). IR (ATR) 2957 (m), 2865 (w), 2201 (w), 2120 (m), 1589 (m), 1473 (m), 1362 (m), 1249 (s), 1173 (s) cm^{-1}.



Rotaxane 2f·M1: To a solution of CuI (5.1 mg, 27 μmol) in CH_3CN (1 mL) was added a solution of the macrocycle **M1** (17.0 mg, 27.0 μmol) in CH_2Cl_2 (1 mL). The mixture was stirred for 1.5 h at 20 °C and the solvent was removed *in vacuo* to give the Cu·**M1** complex. The complex was redissolved in THF (2 mL) and added to a mixture of the hexayne **1f** (49.0 mg, 67.0 μmol), K_2CO_3 (14 mg, 0.10 mmol)

and I_2 (6.8 mg, 27 μmol) in THF (2 mL). The reaction mixture was then flushed with N_2 and stirred at 60 °C in the dark for 16 h. CH_2Cl_2 (2 mL), CH_3CN (2 mL), and KCN (20.0 mg, 30.0 mmol in 1 mL H_2O) were added, and the mixture was stirred at 20 °C for 3 h. CH_2Cl_2 (10 mL) was added, the organic phase separated, washed with H_2O (3 x 10 mL), and the solvent removed under reduced pressure. Column chromatography (silica, hexanes/EtOAc 20:1) followed by size exclusion chromatography (Bio Beads SX-3, $CHCl_3$) afforded **2f·M1** (6.2 mg, 11%) as a yellow-orange solid. Mp (decomp) 190 °C. R_f = 0.34 (hexanes/EtOAc 6:1). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.44 (d, J = 8.8, Hz, 4H, H_d), 8.28 (d, J = 8.4 Hz, 2H, H_b), 8.10 (d, J = 8.4 Hz, 2H, H_c), 7.76 (s, 2H, H_a), 7.30 (t, J = 1.6 Hz, 6H, H_1), 7.12-7.09 (m, 5H, $H_{e,h}$), 6.92 (d, J = 1.6 Hz, 12H, H_2), 6.51 (t, J = 2.2 Hz, 1H, H_f), 6.46 (dd, J_1 = 8.1 Hz, J_2 = 2.3 Hz, 2H, H_g), 4.12 (t, J = 6.9 Hz, 4H, H_j), 3.99 (t, J = 6.3 Hz, 4H, H_i), 1.93-1.83 (m, 8H, $H_{k,l}$), 1.61 (m, 8H, $H_{m,n}$), 1.19 (s, 108H, H_3): ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K): δ 160.9, 156.2, 150.9, 146.5, 143.5, 136.9, 132.2, 130.0, 129.2, 127.9, 125.9, 123.9, 121.1, 119.2, 115.1, 107.4, 100.9, 87.4, 69.2, 68.5, 68.1, 64.3, 64.0 (two signals are overlapped), 63.8, 63.5, 63.2, 62.9, 62.7, 62.5, 62.2, 57.8, 35.1, 31.5, 29.9, 29.5, 26.3, 26.3; *m/z* (MALDI TOF MS+) requires 2087.03, calcd for $C_{152}H_{168}N_2O_4$ $(M)^+$ requires 2087.0; UV-vis (CH_2Cl_2) λ_{max} / nm (ε / M^{-1} cm^{-1}) 407 (296500), 380 (285000), 359 (212000), 337 (127000) 320 (84300) 289 (96600) 279 (75700) 267 (59800) 254 (47600); UV-vis (THF) λ_{max} / nm (ε / M^{-1} cm^{-1}) 407 (291700), 380 (273000), 356 (205000), 336 (119000) 319 (80100) 288 (94800) 279 (79400) 267 (61200) 255 (48000). IR (ATR) 3064 (w), 2954 (m), 2863 (m), 2195 (m), 2152 (m), 2037 (m), 1590 (s), 1474 (m), 1361 (m), 1247 (s), 1173 (m) cm^{-1}.

Rotaxane 2c·M2

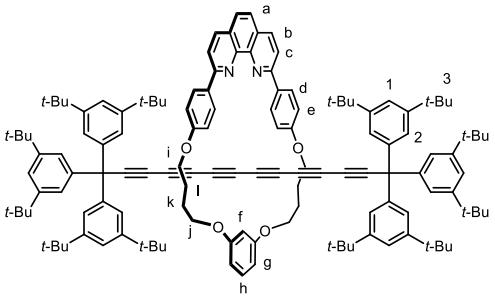


Via homo-coupling: To a solution of CuI (3.82 mg, 20.0 μmol) in CH_3CN (1 mL) was added a solution of the macrocycle **M2** (11.1 mg, 20.0 μmol) in CH_2Cl_2 (1 mL). The mixture was stirred for 1.5 h at 20 °C and the solvent was removed *in vacuo* to give the Cu·**M2** complex. The complex was redissolved in THF (2 mL) and added to a mixture of the triyne **1c** (33 mg, 50 μmol), K_2CO_3 (11.4 mg, 82.4 μmol) and I_2 (6.14 mg, 24.0 μmol) in THF (3 mL). The reaction mixture was then flushed with N_2 and stirred at 60 °C for 50 h. CH_2Cl_2 (2 mL), CH_3CN (2 mL), and ETDA (23.4 mg, 80.0 μmol in 2 mL H_2O) were added, and the mixture was stirred at 20 °C for 1 h. CH_2Cl_2 (5 mL) was added, the organic phase separated, washed with H_2O (3 x 10 mL), and the solvent removed. Column chromatography (silica gel, hexanes/EtOAc 20:1) afforded **2c·M2** (2 mg, 5%) as a yellow solid.

Via cross-coupling: To a solution of macrocycle **M2** (11 mg, 20 μmol) in CH_2Cl_2 (3.0 mL) a solution of CuI (3.8 mg, 20 μmol) in CH_3CN (2.0 mL) was added and the mixture stirred at 20 °C for 1.5 h. The mixture was dried *in vacuo* and re-dissolved in dry THF (2.0 mL) (macrocycle-Cu complex solution). Triyne **1c** (16 mg, 24 μmol), bromotriyne **3** (22 mg, 30 μmol) were added to the solution of CuI·**M2** complex and Cs_2CO_3 (26 mg, 80 μmol) was added. The reaction mixture was degassed through three cycles of freeze-pump-thaw, flushed with nitrogen gas and stirred in dark at 60 °C for 11 h. After cooling to 20 °C, the reaction was quenched by adding KCN (10 mg, 0.15 mmol in 1.0 mL water), then CH_3CN (1.0 mL) and CH_2Cl_2 (4.0 mL) were added. The organic phase was extracted by CH_2Cl_2 (3 x 5 mL), fractions were combined, washed with H_2O (10.0 mL), brine (10 mL) and solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, hexane/EtOAc 20:1) followed by recrystallization from CH_2Cl_2/CH_3OH affording **2c·M2** (8 mg, 21%) as a yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.26 (d, J = 8.3 Hz, 2H, H_c), 8.19 (d, J = 8.5 Hz, 4H, H_d), 7.99 (d, J = 8.4 Hz, 2H, H_b), 7.77 (s, 2H, H_a), 7.26 (t, J = 1.8 Hz, 6H, H_1), 7.13 (d, J = 8.8 Hz, 4H, $H_{e,}$), 7.09 (t, J = 8.2 Hz, 1H, $H_{h,}$), 6.88 (d, J = 1.8 Hz, 12H, H_2), 6.74 (t, J = 2.4 Hz, 1H, H_f), 6.48 (dd, J_1 = 8.2, J_2 = 2.4 Hz, 2H, H_g), 4.36 (t, J = 6.8 Hz, 4H, H_i), 4.14 (t, J = 6.0 Hz, 4H, H_j), 2.45–2.00 (m, 4H, H_k), 1.15 (s, 108 H, H_3). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 160.6, 160.6, 157.4, 150.7, 146.7, 143.7, 136.5, 133.9, 130.0, 129.7, 128.5, 127.6, 125.8, 123.9, 121.0, 119.8, 116.0, 106.3, 104.5, 86.2, 69.5, 66.8, 65.3, 64.0, 63.7, 63.5, 63.3, 57.7, 35.1, 31.5, 30.0. (MALDI TOF MS+) requires 1859.22 calcd for $C_{134}H_{157}N_2O_4$ $[M + H]^+$

found 1860.18. UV-vis (CH_2Cl_2) λ_{max} / nm (ε / M^{-1} cm^{-1}) 317 (210000), 297 (171000), 281 (126000); UV-vis (THF) λ_{max} / nm (ε / M^{-1} cm^{-1}) 316 (244000), 296 (187000), 281 (141000).

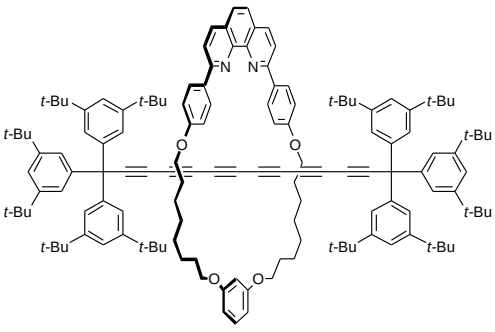
Rotaxane 2c·M3



Via homo-coupling: To a solution of CuI (6.7 mg, 35 μmol) in CH_3CN (1 mL) was added a solution of the macrocycle **M3** (201 mg, 35.0 μmol) in CH_2Cl_2 (1 mL). The mixture was stirred for 1.5 h at 20 °C and the solvent was removed *in vacuo* to give the CuI·**M3** complex. The complex was redissolved in THF (2 mL) and added to a mixture of the triyne **1c** (57 mg, 88 μmol), K_2CO_3 (19.3 mg, 140 μmol) and I_2 (9.0 mg, 35 μmol) in THF (3 mL). The reaction mixture was then flushed with nitrogen gas and stirred at 60 °C for 2 d. CH_2Cl_2 (2 mL), CH_3CN (2 mL), and KCN (20 mg, 30 mmol in 1 mL H_2O) were added, and the mixture was diluted with CH_2Cl_2 (10 mL), the organic phase separated, washed with H_2O (10 mL), and the solvent removed. Flash column chromatography (silica, $PE_{40/60}$/EtOAc 30:1 → 20:1) followed by recrystallization from CH_2Cl_2/CH_3OH afforded **2c·M3** (19.6 mg, 28%) as a yellow solid.

Via cross-coupling: CuI (4.53 mg, 23.7 μmol) in CH_3CN (2 mL) was added to a solution of macrocycle **M3** (13.8 mg, 23.7 μmol) in CH_2Cl_2 (3 mL) and the mixture was stirred at 20 °C for 2 h. The solvent was removed *in vacuo* and the residue dissolved in THF (2 mL). This solution was then added to triyne **1c** (17 mg, 26 μmol), bromotriyne **3** (26 mg, 36 μmol), and K_2CO_3 (13 mg, 95 μmol) in THF (2 mL), the mixture was degassed and stirred at 60 °C for 8 h. After cooling to 20 °C, the reaction was quenched by the addition of KCN (6.5 mg, 0.10 mmol, in 1 mL H_2O), CH_2Cl_2 (2 mL), CH_3CN (2 mL), and stirred at 20 °C for 1 h. CH_2Cl_2 (10 mL) was added, the organic phase separated, washed with H_2O (5 mL), brine (5 mL), and the solvent was removed under reduced pressure. Flash column chromatography (silica, hexanes/EtOAc 20:1 → 10:1) followed by recrystallization from CH_2Cl_2/CH_3OH afforded **2c·M3** (19 mg, 43%) as a yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.44 (d, J = 8.8, Hz, 4H, H_d), 8.28 (d, J = 8.4 Hz, 2H, H_b), 8.10 (d, J = 8.4 Hz, 2H, H_c), 7.76 (s, 2H, H_a), 7.30 (t, J = 1.6 Hz, 6H, H_1), 7.12–7.09 (m, 5H, $H_{e,h}$), 6.92 (d, J = 1.6 Hz, 12H, H_2), 6.51 (t, J = 2.2 Hz, 1H, H_f), 6.46 (dd, J_1 = 8.1 Hz, J_2 = 2.3 Hz, 2H, H_g), 4.12 (t, J = 6.9 Hz, 4H, H_j), 3.99 (t, J = 6.3 Hz, 4H, H_i), 1.93–1.83 (m, 8H, $H_{k,l}$), 1.61 (m, 8H, $H_{m,n}$), 1.19 (s, 108H, H_3): ^{13}C NMR (125 MHz, CD_2Cl_2): δ 160.5, 160.3, 156.1, 150.4, 146.2, 143.2, 136.5, 132.3, 129.7, 128.9, 127.4, 125.5, 123.5, 120.7, 119.0, 115.2, 107.4, 102.0, 86.3, 69.0, 68.3, 67.8, 63.6, 63.4, 62.9, 62.7, 57.4, 34.7, 31.1, 26.4, 26.0; *m/z* (MALDI TOF MS+) requires 1887.24 calcd for $C_{152}H_{169}N_2O_4$; $[M + H]^+$, found 1887.07. UV-vis (CH_2Cl_2) λ_{max} / nm (ε / M^{-1} cm^{-1}) 318 (234000), 298 (195000), 282 (144000); UV-vis (THF) λ_{max} / nm (ε / M^{-1} cm^{-1}) 317 (267900), 297 (220000), 281 (163000).

Rotaxane 2c·M4

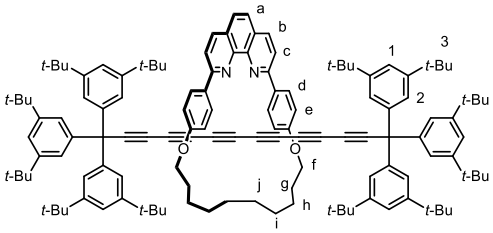


Via homo-coupling: CuI (12 mg, 61 μmol) in MeCN (3 mL) was added to a solution of macrocycle **M4** (43 mg, 61 μmol) in CH_2Cl_2 (6 mL) and stirred at 20 °C for 1.5 h. The solvent was removed *in vacuo* and the residue redissolved in THF (5 mL). This solution was then added to triyne **2c** (0.10 g, 0.15 mmol), K_2CO_3 (34 mg, 0.24 mmol), and iodine (20 mg, 77 μmol) in THF (10 mL) and the mixture was stirred at 60 °C for 45 h. After cooling to 20 °C, the reaction was quenched by the addition of CH_2Cl_2 (3 mL), MeCN (3

mL), and aq. KCN (50 mg, 1 mL H_2O) and stirred at 20 °C for 2 h. CH_2Cl_2 (20 mL) was added, the organic phase separated, washed with H_2O (10 mL), brine (10 mL), and the solvent was removed under reduced pressure. Column chromatography (silica, hexanes/EtOAc 20:1 → 10:1) followed by recrystallization from CH_2Cl_2/MeOH afforded **2c·M4** (11 mg, 9%) as a yellow solid.

Via cross-coupling: CuI (16 mg, 82 μmol) in CH_3CN (3 mL) was added to a solution of macrocycle **M4** (57 mg, 82 μmol) in CH_2Cl_2 (9 mL) and the mixture was stirred at 20 °C for 2 h. The solvent was removed *in vacuo* and the residue redissolved in THF (4 mL). This solution was then added to triyne **1c** (64 mg, 98 μmol), bromotriyne **3** (72 mg, 98 μmol), and K_2CO_3 (45 mg, 0.33 mmol) in THF (4 mL) and the mixture was stirred at 50 °C for 17 h. After cooling to 20 °C, the reaction was quenched by the addition of KCN (50 mg, 0.77 mmol, 1 mL H_2O), CH_2Cl_2 (2 mL), CH_3CN (2 mL), and stirred at 20 °C for 3 h. CH_2Cl_2 (20 mL) was added, the organic phase separated, washed with H_2O (10 mL), brine (10 mL), and the solvent was removed. Flash column chromatography (silica, hexanes/EtOAc 20:1 → 10:1) followed by recrystallization from CH_2Cl_2/CH_3OH afforded **2c·M4** (68 mg, 41%) as a yellow solid. Mp 228–230 °C (decomp). R_f = 0.56 (hexanes/EtOAc 6:1). IR (ATR) 2951 (m), 2863 (w), 2181 (w), 2163 (w), 1589 (m), 1472 (m), 1361 (m), 1246 (s), 1173 (s) cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.43 (d, J = 8.8 Hz, 4H), 8.28 (d, J = 8.5 Hz, 2H), 8.10 (d, J = 8.5 Hz, 2H), 7.77 (s, 2H), 7.28 (t, J = 1.7 Hz, 6H), 7.15 (d, J = 8.9 Hz, 4H), 7.07 (t, J = 8.2 Hz, 1H), 6.92 (d, J = 1.7 Hz, 12H), 6.55 (t, J = 2.2 Hz, 1H), 6.45 (dd, J = 8.2, 2.3 Hz, 2H), 4.11 (t, J = 6.9 Hz, 4H), 3.99 (t, J = 6.6 Hz, 4H), 1.91–1.78 (m, 8H), 1.58–1.47 (m, 16H), 1.16 (s, 108H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 161.1, 161.0, 156.4, 150.8, 146.5, 143.7, 136.9, 132.2, 129.9, 129.1, 127.9, 125.9, 123.9, 121.0, 119.4, 115.2, 107.6, 100.7, 86.5, 69.4, 68.6, 68.3, 63.4, 63.3, 63.1, 62.9, 57.7, 35.1, 31.5, 29.8, 26.3 (four signals coincident or not observed). APPI HRMS (THF/Toluene) requires 1998.370289 calcd for $C_{144}H_{177}N_2O_4$ ($[M + H]^+$), found 1998.371121. UV-vis (CH_2Cl_2) λ_{max} / nm (ε / M^{-1} cm^{-1}), 316 (240000), 297 (203000), 281 (139000).

Rotaxane 2c·M6

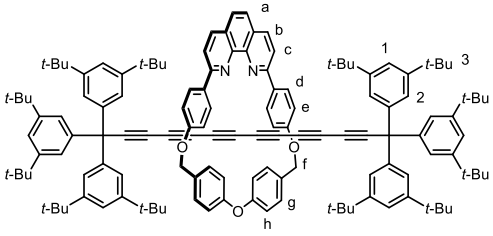


Via homo-coupling: To a solution of macrocycle **M6** (19 mg, 37 μmol) in CH_2Cl_2 (1.5 mL) a solution of CuI (7.0 mg, 37 μmol) in CH_3CN (1.0 mL) was added and the mixture stirred at 20 °C for 1.5 h. The mixture was then dried *in vacuo* and redissolved in dry THF (5.0 mL) (CuI·**M6** complex solution). Triyne **1c** (60 mg, 0.092 mmol) was dissolved in THF (2.0 mL) in a dry Schlenk tube and iodine (11.8 mg, 115 μmol), K_2CO_3 (21 mg, 0.15 mmol) and the THF solution of CuI·**M6** complex were added. The reaction mixture was flushed with nitrogen gas and stirred at 60 °C for 24 h. The progress of the reaction was monitored by TLC ($PE_{40/60}$/CH_2Cl_2 1:1). After stirring for 24 h, iodine (2.5 mg, 10 μmol) and K_2CO_3 (6.0 mg, 43 μmol) were added and the mixture stirred additionally for 24 h. Then the reaction mixture was cooled to 20 °C; CH_3CN (1.5 mL), CH_2Cl_2 (1.5 mL) and KCN (13 mg, 0.20 mmol in 1.0 mL H_2O) were added and the mixture was diluted with CH_2Cl_2 (5.0 mL), the organic fraction was separated, washed with H_2O (10 mL) and solvents were removed. Flash column chromatography of the crude mixture (silica, $PE_{40/60}$/CH_2Cl_2 1:1, gradually adding EtOAc 0 – 15%) afforded **2c·M6** (11.7 mg, 17%) as a yellow solid.

Via cross-coupling: CuI (3.82 mg, 20.0 μmol) in CH_3CN (2 mL) was added to a solution of macrocycle **M6** (10.4 mg, 20.0 μmol) in CH_2Cl_2 (2 mL) and the mixture was stirred at 20 °C for 2 h. The solvent was removed *in vacuo* and the residue redissolved in THF (2 mL). This solution was then added to triyne **1c** (15.3 mg, 23.4 μmol), bromotriyne **3** (24.8 mg, 34.0 μmol), and K_2CO_3 (11.4 mg, 82.5 μmol) in THF (3 mL), the mixture was

degassed and stirred at 60 °C for 6 h. After cooling to 20 °C, the reaction was quenched by the addition of ETDA (23.3 mg, 80.0 μmol, in 1 mL H_2O), CH_2Cl_2 (2 mL), CH_3CN (2 mL), and stirred at 20 °C for 1 h. CH_2Cl_2 (5 mL) was added, the organic phase separated, washed with H_2O (5 mL), brine (5 mL), and the solvent was removed. Flash column chromatography (silica, hexanes/EtOAc 20:1 → 5:1) followed by recrystallization from CH_2Cl_2/CH_3OH afforded **2c·M6** (9.4 mg, 26%) as a yellow solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.36 (d, J = 8.9, 4H, H_d), 8.26 (d, J = 8.4, 2H, H_c), 8.03 (d, J = 8.36, 2H, H_b), 7.76 (s, 2H, H_a), 7.25 (t, J = 1.7, 6H, H_1), 7.13 (d, J = 8.9, 4H, H_e), 6.87 (d, J = 1.7, 12H, H_2), 4.20 (t, J = 1.0, 4H, H_f), 1.85 (m, 8H, $H_{k,l}$), 1.81 (m, 4H, H_g) 1.44–1.1.3(m, 12H, $H_{i/h}$), 1.14 (s, 108H, H_3). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 159.7, 156.9, 146.8, 143.6, 136.7, 132.9, 129.6, 127.8, 125.8, 123.9, 121.0, 119.5, 86.7, 69.3, 68.7, 64.3, 63.8, 63.8, 63.4, 57.7, 35.1, 31.4, 30.1, 29.6, 29.4, 28.8, 26.1: (MALDI TOF MS+) requires 1808.28 calcd for $C_{132}H_{161}N_2O_2$, $[M + H]^+$, found 1808.60. UV-vis (CH_2Cl_2) λ / nm (ε / M^{-1} cm^{-1}), 317 (234500), 298(164000), 282 (118000), 267 (66500), UV-vis (THF) λ / nm (ε / $M^{-1}cm^{-1}$) 316 (180000), 297 (139000), 280 (81000), 248 (30000).

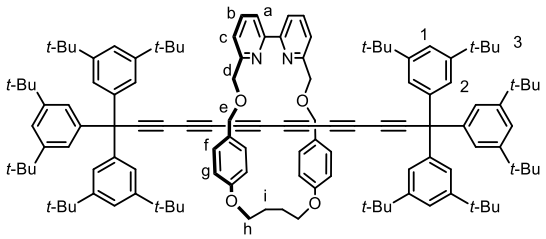
Rotaxane 2c·M7



Via homo-coupling: To a solution of CuI (5.9 mg, 30 μmol) in CH_3CN (1 mL) was added a solution of the macrocycle **M7** (17.1 mg, 30 μmol) in CH_2Cl_2. The mixture was stirred for 2.5 h at 20 °C and the solvent was removed *in vacuo* and redissolved in THF (2 mL) (CuI·**M7** complex solution) and added to a mixture of the triyne **1c** (50 mg, 76 μmol), K_2CO_3 (17 mg, 0.12 mmol) and I_2 (8.6 mg, 33 μmol) in THF (2 mL). The reaction mixture was then flushed with N_2 and stirred at 60 °C in the dark for 62 h, Then, the mixture was cooled to 20 °C, CH_2Cl_2 (2 mL), MeCN (2 mL), and KCN (20 mg in 1 mL H_2O) were added and the solution was stirred for 6 h at 20 °C. CH_2Cl_2 (5 mL) was added, the organic phase was separated and washed with H_2O (5 mL). The solvent was removed, and the crude product was purified by flash column chromatography (silica, hexane/EtOAC 20:1) followed by recrystallization from CH_2Cl_2/MeOH affording **2c·M7** (16.2 mg, 23%) as a yellow solid.

Via cross-coupling: CuI (10.3 mg, 53.7 μmol) in CH_3CN (2 mL) was added to a solution of macrocycle **M7** (30.0 mg, 53.7 μmol) in CH_2Cl_2 (3 mL) and the mixture was stirred at 20 °C for 1 h. The solvent was removed *in vacuo* and the residue redissolved in THF (4 mL). This solution was then added to triyne **1c** (42.0 mg, 64.5 μmol), bromotriyne **3** (67.1 mg, 91.9 μmol), and K_2CO_3 (29.2 mg, 214 μmol) in THF (4 mL), the mixture was degassed and stirred at 60 °C for 12 h. After cooling to 20 °C, the reaction was quenched by the addition of KCN (13 mg, 0.20 mmol, in 2 mL H_2O), CH_2Cl_2 (5 mL), CH_3CN (5 mL), and stirred at 20 °C for 1 h. CH_2Cl_2 (15 mL) was added, the organic phase separated, washed with H_2O (10 mL), brine (10 mL), and the solvent was removed. Flash column chromatography (silica, hexanes/EtOAc 20:1) followed by recrystallization from CH_2Cl_2/CH_3OH afforded **2c·M7** (54 mg, 54%) as a yellow solid. Mp 259–262 °C (decomp). R_f = 0.46 (hexanes/EtOAc 6:1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.23 (d, J = 8.3 Hz, 2H, H_c), 7.89–7.85 (m, 6H, $H_{b,d}$), 7.75 (s, 2H, H_a), 7.29-7.27 (m, 10H, H1,$_g$), 7.19 (d, J = 8.6 Hz, 4H, H_h), 6.92 (d, J = 1.8 Hz, 12H, H_2), 6.89 (d, J = 8.8 Hz, 4H, H_e), 5.27 (s, 4H, H_f), 1.17 (s, 108H, H_3): ^{13}C NMR (100 MHz, CD_2Cl_2): δ 159.5, 158.4, 158.2, 150.7, 146.9, 143.8, 136.4, 134.4, 134.3, 130.0, 127.7, 127.6, 125.9, 123.9, 122.2, 121.0, 120.8, 116.3, 85.8, 70.4, 69.7, 63.9, 63.63, 63.59, 62.6, 57.7, 35.1, 31.5. (MALDI TOF MS+) requires 1862.7 calcd for $C_{136}H_{152}N_2O_3$, $(M)^+$; found 1863.50. UV-vis (CH_2Cl_2) λ_{max} /nm (ε / M^{-1} cm^{-1}), 317 (211000), 297(161000), 281 (115000), 267 (61000), 241 (43000); UV-vis (THF) λ_{max} /nm (ε / $M^{-1}cm^{-1}$) 316 (233800), 297 (179000); 281 (120000), 267 (70000).

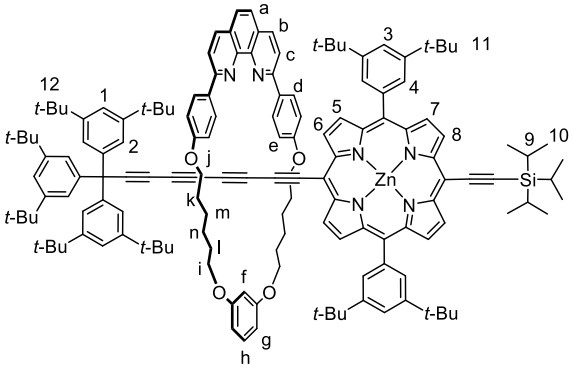
Rotaxane 2c·M8



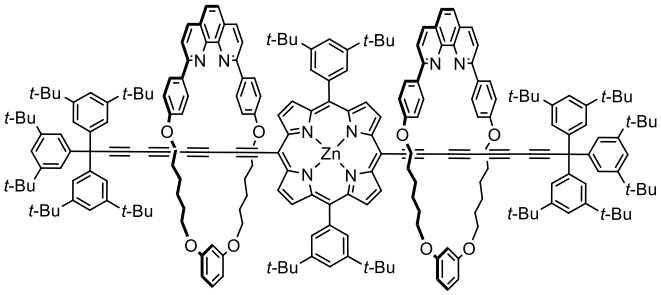
Via homo-coupling: To a solution of macrocycle **M**8 (10 mg, 21 μmol) in CH_2Cl_2 (1.0 mL) a solution of CuI (4.1 mg, 21 μmol) in CH_3CN (1.0 mL) was added and the mixture was stirred at 20 °C for 1.5 h. The mixture was then dried *in vacuo* and re-dissolved in dry THF (2.0 mL) (CuI·**M8** complex solution). The triyne **1c** (35 mg, 54 μmol) was dissolved in THF (2.0 mL) in a dry Schlenk tube and iodine (5.5 mg, 21 μmol), K_2CO_3 (12 mg, 86 μmol) and the THF solution of CuI·**M8** complex were added. The reaction mixture was flushed with nitrogen gas and stirred at 60 °C for 24 h. The progress of reaction was monitored by TLC ($PE_{40/60}$/EtOAc 6:1). After stirring for 24 h, iodine (5.0 mg, 19 μmol) and K_2CO_3 (12 mg, 86 μmol) were added and the mixture stirred additionally for 24 h. Then the reaction mixture was cooled to 20 °C, CH_3CN (1.5 mL), CH_2Cl_2 (2.0 mL) and KCN (20.0 mg, 310 μmol in 1.0 mL H_2O) were added and the mixture was diluted with CH_2Cl_2 (5 mL). The organic fraction was separated, washed with water (3 × 5.0 mL) and solvent was removed under reduced pressure. Flash column chromatography of the crude mixture (silica, $PE_{40/60}/CH_2Cl_2$ 1:1, gradually adding EtOAc 0–10%) afforded **2c·M8** (9.0 mg, 23%) as a yellow solid.

Via cross-coupling: CuI (5.73 mg, 30.0 μmol) in CH_3CN (2 mL) was added to a solution of macrocycle **M8** (14.5 mg, 30.0 μmol) in CH_2Cl_2 (2 mL) and the mixture was stirred at 20 °C for 1 h. The solvent was removed *in vacuo* and the residue redissolved in THF (2 mL). This solution was then added to triyne **1c** (19.6 mg, 30.0 μmol), bromotriyne **3** (26.3 mg, 36.0 μmol), and K_2CO_3 (16.6 mg, 120 μmol) in THF (2 mL), the mixture was degassed and stirred at 60 °C for 4 h. After cooling to 20 °C, the reaction was quenched by the addition of KCN (7.8 mg, 0.12 mmol, in 1 mL H_2O), CH_2Cl_2 (2 mL), CH_3CN (2 mL), and stirred at 20 °C for 1 h. CH_2Cl_2 (5 mL) was added, the organic phase separated, washed with H_2O (5 mL), brine (5 mL), and the solvent was removed under reduced pressure. Flash column chromatography (silica, hexanes/EtOAc 20:1 → 5:1) followed by recrystallization from CH_2Cl_2/CH_3OH afforded **2c·M8** (14 mg, 26%) as a yellow solid. Mp 103 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.87 (d, J = 7.57, 2H, H_a), 7,56 (t, J = 7.88, 2H, H_b), 7.37–7.35 (m, 8H, $H_{c,1}$), 7.07 (d, J = 8.51, 2H, H_f), 7.03 (d, J = 1.89, 12H, H_2), 6.67 (d, J = 8.51, 2H, H_g), 4.62 (s, 4H, H_e), 4.53 (s, 4H, H_d), 3.87 (t, J = 6.62, 4H, H_h), 1.83 (m, 4H, H_i), 1.26 (s, 108H, H_3): ^{13}C NMR (125 MHz, CD_2Cl_2): δ 159.2, 158.9, 155.7, 150.8, 143.9, 136.9, 130.4, 129.9, 124.0, 121.1, 120.9, 119.8, 115.1, 85.6, 77.9, 72.6, 71.6, 69.9, 67.1, 63.6, 62.7, 62.3, 62.3, 57.8, 35.2, 31.5, 25.2: (MALDI TOF MS+) requires 1785.2 calcd for $C_{128}H_{156}N_2O_4$, $(M)^+$; found 1784.78. UV-vis ($CHCl_3$) λ_{max} /nm (ε / M^{-1} cm^{-1}), 317 (211000), 297(161000), 281 (115000), 267 (61000), 241 (43000); UV-vis (THF) λ_{max} /nm (ε / $M^{-1}cm^{-1}$) 316 (180000), 297 (139000); 280 (81000), 248 (30000).

Rotaxane 5a·M1: To a solution of macrocycle **M1** (14.7 mg, 23.0 μmol) in CH_2Cl_2 (1.5 mL) a solution of CuI (4.4 mg, 23 μmol) in CH_3CN (1.5 mL) was added and the mixture was stirred for 1 h at 20 °C. The solvent was removed *in vacuo* and the residue redissolved in a 1:1 mixture of THF and toluene (2 mL). This solution was then added to a mixture of porphyrin **4** (22 mg, 23 μmol), bromotriyne **3** (25 mg, 35 μmol), and K_2CO_3 (13 mg, 92 μmol) in toluene (2 mL), degassed through freeze-pump-thaw cycles, flushed with nitrogen, and stirred at

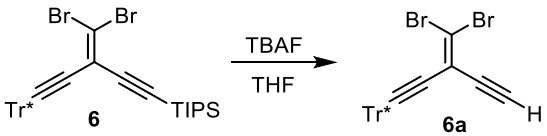


60 °C for 3 d. After cooling to 20 °C, the reaction was quenched by the addition of KCN (20 mg, 0.30 mmol, in 1 mL H_2O), diluted with CH_2Cl_2 (1 mL), CH_3CN (1 mL), and stirred at 20 °C for 2 h. CH_2Cl_2 (10 mL) was added, the organic phase separated, washed with H_2O (10 mL), brine (10 mL), and the solvents were removed. Flash column chromatography (silica, hexane/EtOAc/pyridine 100:1:1 → 10:1:1) followed by recrystallization from CH_2Cl_2/CH_3OH afforded **5a·M1** (10.0 mg, 19%) as a green solid. Mp 130–131 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 9.63 (d, J = 4.5 Hz, 2H, H_6), 9.35 (d, J = 4.6 Hz, 2H, H_8), 8.79 (d, J = 4.5 Hz, 2H, H_5), 8.60 (d, J = 4.6 Hz, 2H, H_7), 8.53 (d, J = 8.8 Hz, 4H, H_d), 8.09 (d, J = 8.4 Hz, 2H, H_b), 7.98 (d, J = 8.4 Hz, 2H, H_c), 7.91 (d, J = 1.8 Hz, 4H, H_4), 7.80 (t, J = 1.8 Hz, 2H, H_3), 7.53 (s, 2H, H_a), 7.29 (t, J = 1.7 Hz, 3H, H_1), 7.25 (d, J = 8.7 Hz, 4H, H_e), 6.99 (d, J = 1.7 Hz, 6H, H_2), 6.95 (t, J = 8.2 Hz, 1H, H_h), 6.91 (t, J = 2.3 Hz, 1H, H_f), 6.38 (dd, J = 8.2 Hz, 2.3 Hz, 2H, H_g), 4.14–4.02 (m, 8H, $H_{j,i}$), 1.87–1.52 (m, 16H, $H_{k,l,m,n}$), 1.49 (s, 36H, H_{11}), 1.43–1.39 (m, 21H, $H_{9,10}$), 1.17 (s, 54H, H_{12}). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 161.03, 160.96, 156.0, 153.9, 152.1, 151.2, 150.6, 150.4, 149.0, 146.2, 143.9, 141.6, 136.6, 133.8, 133.0, 132.1, 131.2, 130.6, 129.9, 129.8, 129.2, 127.5, 125.5, 124.9, 123.9, 121.4, 120.9, 119.0, 115.3, 110.2, 107.6, 102.8, 100.6, 98.7, 96.2, 87.8, 82.5, 81.7, 71.1, 70.0, 68.3, 68.2, 66.9, 64.0, 63.7, 57.8, 35.2, 35.1, 31.8, 31.4, 29.9, 29.4, 26.20, 26.19, 19.2, 12.2. *m/z* (MALDI TOF MS+) requires 2244.3 calcd for $C_{152}H_{176}N_6O_4SiZn$, [M + H]; found 2244.3. UV-vis (THF) λ_{max} / nm (ε / M^{-1} cm^{-1}) 285 (94000), 320 (57000), 456 (542000), 607 (14000), 661 (129000). UV-vis (CH_2Cl_2) λ_{max} / nm (ε / M^{-1} cm^{-1}) 285 (95500), 319 (64500), 456 (435000), 661 (84100).

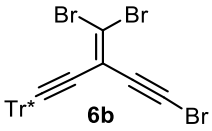


5c·(M1)$_2$. TIPS-protected porphyrin rotaxane **5a·M1** (41 mg, 18.3 μmol) was dissolved in the mixture of CH_2Cl_2 (20 mL) and $CHCl_3$ (5 mL) and TBAF (1.0 M solution in THF, 36.6 μL, 36.6 μmol) was added at 40 °C and the reaction mixture stirred for 3 h. After complete consumption of starting materials monitored by TLC (Py/EtOAc/$PE_{40/60}$ 1:1:10) the reaction mixture was passed through a short silica plug (CH_2Cl_2 + 5% Py) and solvent was removed *in vacuo* resulting in **5b·M1** deprotected rotaxane (37 mg, 18 μmol). To a solution of macrocycle **M1** (11.3 mg, 17.8 μmol) in CH_2Cl_2 (1.5 mL) a solution of CuI (3.4 mg, 18 μmol) in CH_3CN (1.5 mL) was added and the mixture was stirred for 1 h at 20 °C. The solvent was removed *in vacuo* and the residue re-dissolved in a 1:1 mixture of THF and toluene (9 mL). This solution was then added to a mixture of **5b·M1** rotaxane, bromotriyne **3** (18 mg, 25 μmol), and K_2CO_3 (9.8 mg, 71 μmol). The reaction mixture was degassed through freeze-pump-thaw cycles, flushed with nitrogen, and stirred at 70 °C for 2 d. After cooling to 20 °C, the reaction was quenched by the addition of ETDA (21 mg, 0.71 mmol, in 1 mL H_2O), diluted with CH_2Cl_2 (2 mL), CH_3CN (1 mL) and stirred at 20 °C for 2 h. Additional CH_2Cl_2 (10 mL) was added, the organic phase separated, washed with H_2O (10 mL), brine (10 mL) and solvents were removed under reduced pressure. Column chromatography (silica, hexane/EtOAc/pyridine 100:1:1 → 5:1:1) followed by SEC column (Bio-Beads-S-X, $CHCl_3$ + 1% Py, to remove traces of unreacted rotaxane) and recrystallization from CH_2Cl_2/CH_3OH afforded **5c·(M1)$_2$** (11 mg, 23%) as a green solid. Mp 150–152 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 9.15 (d, J = 6.1 Hz, 4H), 8.40 (d, J = 8.7 Hz, 8H), 8.37 (d, J = 4.6 Hz, 4H), 7.79–7.77 (m, 6H), 7.63 (d, J = 8.4 Hz, 4H), 7.45 (d, J = 8.4 Hz, 4H), 7.30 (t, J = 1.7 Hz, 6H), 7.26 (d, J = 8.8 Hz, 8H), 7.0 (d, J = 1.7 Hz, 8H), 6.77–6.71 (m, 8H), 6.20 (dd, J_1 = 8.12 Hz, J_2 = 2.3 Hz, 4H), 4.28 (m, 4H), 4.16 (m, 4H), 4.07–3.97 (m, 8H), 1.90 (m, 8H), 1.83–1.60 (m, 32H), 1.51 (s, 36H), 1.43–1.39 (m, 12H), 1.19 (s, 108H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 160.9, 160.9, 155.2, 153.0, 150.8, 150.7, 150.4, 149.2, 145.2, 143.9, 141.0, 135.8, 133.3, 132.0, 130.9, 129.8, 129.7, 129.2, 128.3, 126.5, 124.8, 124.5, 124.0, 121.6, 121.0, 120.9, 118.2, 115.3, 107.5, 100.6, 98.4, 88.2, 82.8, 81.5, 71.7, 69.9, 68.4, 68.3, 67.5, 63.7, 63.6, 59.9, 57.9, 35.3, 35.1, 31.9, 31.5, 29.9, 29.4, 26.3, 26.3, 25.4. *m/z* (MALDI

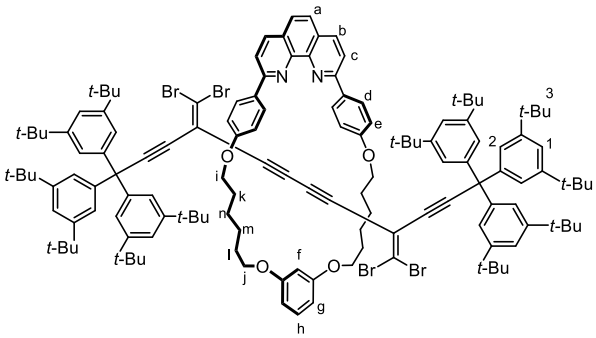
TOF MS+) requires 3378.96 calcd for $C_{234}H_{260}N_8O_8Zn$; (M^+), found 3378.48. UV-vis (THF) λ_{max} / nm (ε / M^{-1} cm^{-1}) 288 (129000), 320 (57000), 466 (452000), 651 (155000), 661 (129000). UV-vis (CH_2Cl_2) λ_{max} / nm (ε / M^{-1} cm^{-1}) 288 (126000), 467 (361000), 689 (115000).



6a: To a solution of TIPS protected precursor **6**[S1] (400 mg, 0.413 mmol) in THF (25 mL) water was added (15 μL) and the mixture cooled down to 0 °C. TBAF (1.0 M in THF, 0.5 mL, 0.5 mmol) was added dropwise and reaction mixture was allowed to warm up to 20 °C. After 30 min stirring the reaction was quenched by adding saturated NH_4Cl(aq) (10 mL). The organic layer was separated, washed with water (50 mL), brine (50 mL) and solvents were removed. The product was obtained by passing the crude mixture through a silica plug (hexanes/CH_2Cl_2 5:1) affording **6a** (340 mg, 100%) as a pale yellow solid. R_f = 0.5 (CH_2Cl_2/hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (overlap with solvent residual signal), 6.98 (d, J = 2 Hz, 6H), 3.42 (s, 1H), 1.20 (s, 54H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 144.2, 123.9, 120.0, 114.1, 104.4, 83.4, 80.7, 80.3, 57.2, 34.9, 31.5.

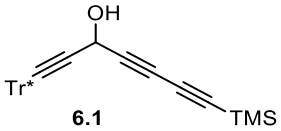


6b:[S8] To a mixture of **6a** (150 mg, 370 μmol) in acetone (15 mL) was added *N*-bromosuccinimide (39.8 mg, 450 μmol) and $AgNO_3$ (6.2 mg, 74 μmol) and the reaction mixture was stirred at 20 °C in darkness for 12 h. The reaction was quenched by adding water (10 mL), then extracted with hexanes (100 mL). The organic layer was washed with brine (50 mL) and dried over Mg_2SO_4. The solvent was removed and the crude product was purified by passing through a silica plug (CH_2Cl_2/hexanes 1:10) to yield **6b** (158 mg, 96%) as a white solid: R_f = 0.52 (CH_2Cl_2/hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (t, J = 2 Hz, 3H), 6.96 (d, J = 2 Hz, 6H), 1.19 (s, 54H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 144.1, 123.9, 120.0, 114.5, 107.5, 104.4, 80.5, 77.3, 57.3, 57.2, 34.9, 31.4.



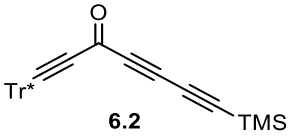
Rotaxane 7a·M1: To a solution of macrocycle **M1** (29.8 mg, 46.7 μmol) in CH_2Cl_2 (1.5 mL) a solution of CuI (8.9 mg, 46.7 μmol) in CH_3CN (1.5 mL) was added and the mixture was stirred for 1 h at 20 °C. The solvent was removed *in vacuo* and the residue re-dissolved in THF (2 mL). This solution was then added to a mixture of dibromoolefin **6a** (38 mg, 47 μmol), dibromoolefin bromide **6b** (50 mg, 56 μmol) K_2CO_3 (25.8 mg, 187 μmol) in THF (2 mL). The mixture was flushed with nitrogen, and stirred at 60 °C for 2 d. After cooling to 20 °C, the reaction was quenched by the addition of KCN (12 mg, 0.19 mmol, in 1 mL H_2O), diluted with CH_2Cl_2 (1 mL), MeCN (1 mL), and stirred at 20 °C for 1 h. More CH_2Cl_2 (5 mL) was added, the organic phase separated, washed with H_2O and the solvents were removed. Flash column chromatography (silica, hexanes/EtOAc 25:1) afforded **7a·M1** (6 mg, 9%) as a yellow solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.55 (d, J = 8.6 Hz, 4H, H_d), 8.30 (br. s, 2H, H_b), 8.14 (d, J = 8.2 Hz, 2H, H_b), 7.78 (s, 2H, H_a), 7.23 (s, 6H, H_1), 7.16 (d, J = 8.8 Hz, 4H, H_e), 7.0 (t, J = 8.2 Hz, 1H, H_h), 6.92 (t, J = 1.5 Hz, 12H, H_2), 6.58 (br. t, J = 1.7 Hz, 1H, H_f), 6.41 (dd, J_1 = 2.2 Hz, J_2 = 6.0 Hz, 2H, H_g), 4.15 (t, J = 7.2 Hz, 4H, H_i), 4.0 (t, J = 6.6 Hz, 4H, H_j), 1.92 (m, 4H, H_k), 1.84 (m, 4H, H_l), 1.61 (m, 8H, $H_{m,n}$), 1.14 (s, 108H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 161.1, 160.9, 156.0, 150.6, 146.3, 144.3, 130.0, 129.4, 127.9, 125.9, 125.3, 124.0, 120.7, 115.2, 114.7, 113.2, 107.9, 105.7, 100.4, 80.1, 79.4, 75.3, 70.1, 68.6, 68.2, 65.4, 57.7, 35.1, 31.5, 30.1, 29.6, 26.4, 26.3. *m/z* (MALDI TOF MS+) requires 2262.97 calcd for $C_{140}H_{168}N_2O_4Br_4$ $((M))^+$, found 2261.93, calcd for $C_{140}H_{168}N_2O_4Br_3$ ($[M–Br]^+$) 2182.06, found 2182.03, calcd for

$C_{140}H_{168}N_2O_4Br_2$ ([M–2Br]$^+$) 2102.14, found 2101.99. UV-vis (THF) λ_{max} / nm (ε / M^{-1} cm^{-1}) 286 (74000), 327 (40000). UV-vis (CH_2Cl_2) λ_{max} / nm (ε / M^{-1} cm^{-1}) 286 (69100), 327 (38800).



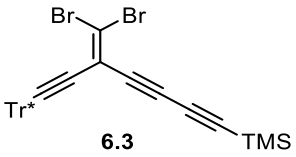
6.1

6.1:[S8] To a solution of 1,4-bis(trimethylsilyl)butadiyne (410 mg, 2.11 mmol) in THF (10 mL) cooled to 0 °C under N_2 atmosphere was added MeLi (1.33 mL, 1.6 M in Et_2O, 2.13 mmol) and the mixture was stirred for 30 min. at 20 °C. To this mixture was added a solution of Tr*C≡CCHO aldehyde[S1,8] (1.25 g, 1.98 mmol) in THF (15 mL) at 0 °C and the reaction stirred at 20 °C for 12 h. The reaction was quenched with saturated aqueous NH_4Cl (20 mL), the aqueous phase was extracted with hexanes (3 × 30 mL). The organic phase was washed with brine (2 × 50 mL) and dried over $MgSO_4$. The solvent was removed and the crude product was purified by column chromatography (silica, gradient with hexanes/EtOAc 50:1 to 20:1) to yield **6.1** (1.0 g, 67%) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, J = 1.8 Hz, 3H), 6.95 (d, J = 1.8 Hz, 6H), 5.26 (d, J = 8.8Hz, 1H), 2.20 (d, J = 8.3 Hz, 1H), 1.21 (s, 54H), 0.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 144.5, 123.9, 120.1, 93.1, 88.7, 87.2, 79.6, 74.6, 69.3, 56.3, 53.2, 35.0, 31.6, 0.4.



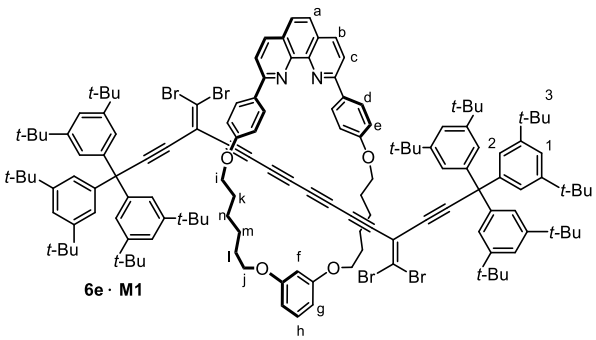
6.2

6.2: To a solution of **6.1** (300 mg, 0.409 mmol) in CH_2Cl_2 (25 mL) was added celite (0.352 g), molecular sieves (0.352 g), and PCC (176 mg, 0.918 mmol) in that order and the reaction stirred at 20 °C under a N_2 atmosphere for 1 d. The mixture was filtered through a plug of silica with CH_2Cl_2 and the solvent removed *in vacuo* to yield **6.2** (286 mg, 93%) as an orange-brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, J = 2.1 Hz, 3H), 6.95 (d, J = 1.8 Hz, 6H), 1.23 (s, 54H), 0.25 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 150.4, 143.0, 123.9, 120.7, 102.7, 98.7, 86.1, 84.7, 75.4, 74.5, 57.0, 35.0, 31.5, 0.6. FTIR (ATR) 2952, 2900 (w), 2866 (w), 2198(m), 2098 (m), 1634(s), 1593(m) cm^{-1}. LRMS ESI *m/z* 681.3 ([M – TMS]$^+$).



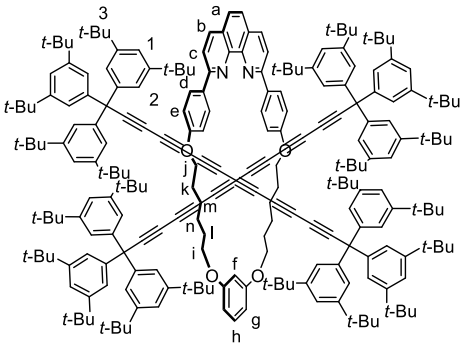
6.3

6.3: To a solution of CBr_4 (243 mg, 0.746 mmol) in CH_2Cl_2 (5 mL) was added PPh_3 (391 mg, 1.49 mmol) and the resulting mixture stirred at 20 °C under a N_2 atmosphere for 3 h. A solution of **6.2** (280 mg, 0.373 mmol) in CH_2Cl_2 (5 mL) was added and the reaction was stirred for 18 h. The reaction mixture was concentrated by removing the solvent and hexanes were added to precipitate the phosphine salts as a white solid along with an oily residue. The supernatant was decanted and filtered through a pad of silica gel (hexane). The oily residue left in the flask was dissolved in minimal CH_2Cl_2 and hexane was added; the heterogeneous mixture was then decanted and the supernatant filtered through silica gel (this procedure was repeated three times). The filtrate was passed through silica plug until the filtrate remained a clear dark yellow solution. The solvent was removed yielding **6.3** (206 mg, 61%) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, J = 1.7 Hz, 3H), 6.98 (d, J = 1.5 Hz, 6H), 1.22 (s, 54H), 0.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 144.2, 124.0, 120.1, 114.1, 109.2, 105.0, 94.7, 87.5, 80.3, 80.0, 73.0, 57.4, 36.0, 31.6, -0.4. FTIR (ATR) 2947, 2867, 2362 (vw), 2108 (w), 1461 cm^{-1}.

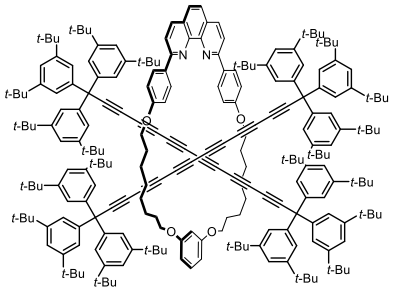


7b·M1: To a solution of **6.3** (270 mg, 297 μmol) in THF (30 mL) and MeOH (30 mL) was added K_2CO_3 (45 mg, 3.3 mmol). After stirring for 1 h, the solvent was removed and the crude product was purified by passing through silica plug (hexane/CH_2Cl_2 20:1) to yield deprotected **6c** as a white solid (240 mg, 97%). The product was immediately proceeded for the next step. To a solution of macrocycle **M1** (63.8 mg, 100 μmol) in CH_2Cl_2 (5 mL) a solution of CuI

(19.1 mg, 100 μmol) in CH_3CN (5 mL) was added and the mixture was stirred for 1 h at 20 °C. The solvent was removed *in vacuo* and the residue re-dissolved in THF (5 mL). This solution was then added to a mixture of **6c** (230 mg, 275 μmol), K_2CO_3 (55.2 mg, 400 μmol) and I_2 (33.3 mg, 130 μmol) in THF (3 mL). The reaction mixture was flushed with nitrogen, and stirred at 60 °C for 15 h. After cooling to 20 °C, the reaction was quenched by the addition of KCN (26 mg, 0.40 mmol, in 3 mL H_2O), diluted with CH_2Cl_2 (5 mL), CH_3CN (3 mL), and stirred at 20 °C for 2 h. More CH_2Cl_2 (5 mL) was added, the organic phase separated, washed with H_2O (10 mL) and the solvents were removed. Column chromatography (silica, hexane/EtOAc 25:1) followed by recrystallization from CH_2Cl_2/MeOH afforded the product **7b·M1** (180 mg, 78%) as a yellow solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.55 (d, J = 8.3 Hz, 4H, H_d), 8.30 (br. s, 2H, H_b), 7.98 (d, J = 8.2 Hz, 2H, H_c), 7.78 (s, 2H, H_a), 7.23 (br. s, 6H, H_1), 7.16 (d, J = 8.8 Hz, 4H, H_e), 7.0 (t, J = 8.2 Hz, 1H, H_h), 6.93 (d, J = 1.5 Hz, 12H, H_2), 6.58 (br. s, 1H, H_f), 6.41 (dd, J_1 = 2.2 Hz, J_2 = 6.0 Hz, 2H, H_g), 4.13 (t, J = 7.3 Hz, 4H, H_j), 4.0 (t, J = 6.7 Hz, 4H, H_i), 1.93–1.84 (m, 8H, $H_{k,l,}$), 1.61 (br. s, 8H, $H_{m,n}$), 1.14 (s, 108H, H_3). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 160.9, 156.0, 150.6, 146.3, 144.3, 137.1, 131.7, 130.0, 129.4, 127.9, 125.9, 125.3, 124.0, 120.6, 119.2, 115.2, 110.2, 114.7, 113.2, 107.9, 105.7, 100.4, 80.1, 79.4, 75.3, 70.1, 68.6, 68.2, 65.4, 57.7, 35.1, 31.5, 30.1, 29.6, 26.4, 26.3. *m/z* (MALDI TOF MS+) requires 2311.97 calcd for $C_{144}H_{169}N_2O_4Br_4$ ($[M + H]^+$), found 2311.93, calcd for $C_{140}H_{168}N_2O_4Br_2$ ($[M - 2Br]^+$) 2151.06, found 2152.03, for $C_{140}H_{168}N_2O_4Br$ ($[M - 3Br]^+$) 2072.14, found 2071.99. UV-vis (THF) λ_{max} / nm (ε / M^{-1} cm^{-1}) 286 (92000), 340 (52000), 361 (38300), 389 (27000), 421 (18500). UV-vis (CH_2Cl_2) λ_{max} / nm (ε / M^{-1} cm^{-1}) 286 (156000), 340 (88100), 361 (64700), 389 (45500), 421 (22000).



Rotaxane (**2c**)$_2$**·M1:** To a solution of rotaxane **2c·M1** (60 mg, 31 mmol) in CH_2Cl_2 (4.0 mL) a solution of CuI (5.9 mg, 31 mmol) in CH_3CN (1.0 mL) was added and the mixture stirred at 20 °C for 1.5 h. The mixture was then dried under vacuum and re-dissolved in dry THF (5.0 mL) (CuI·**2c·M1** complex solution). Bromotriyne **3** (35.6 mg, 48.8 mmol) was added to the solution with **1c** (23.8 mg, 36.6 mmol) and K_2CO_3 (20 mg, 0.14 mmol). The reaction mixture was degassed through three time freeze-pump-thaw cycles, flushed with nitrogen gas and stirred in dark at 60 °C for 36 h. The progress of reaction was monitored by TLC ($PE_{40/60}$/EtOAc 6:1). After cooling to 20 °C the reaction was quenched by adding CH_3CN (1.0 mL), CH_2Cl_2 (2.0 mL) and KCN (10.0 mg, 0.15 mmol in 1.0 mL water). The mixture was diluted with CH_2Cl_2 (4.0 mL), the organic fraction was separated, washed with water (3 × 5.0 mL) and solvents were removed. The residue was purified by flash column chromatography (silica, PE $_{40/60}$/EtOAc 30:1) and followed by size-exclusion chromatography (on Biobeads-S-X1) in CH_2Cl_2 to afford (**2c**)$_2$**·M1** (5.9 mg, 6%) as a yellow solid. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.23 (d, J = 4.4, 2H, H_c), 8.19 (d, J = 4.1, 4H, $H4_d$), 7.95 (d, J = 4.0, 2H, H_b), 7.74 (s, 2H, H_a), 7.23 (t, J = 3.6, 12H, H_1), 7.07 (d, J = 4.1, 4H, $H_{e,}$), 6.98 (t, J = 3.5, 1H, $H_{h,}$), 6.88 (d, J = 3.4, 24 H, H_2), 6.59 (t, J = 3.3, 1H, H_f), 6.36 (dd, J_1 = 6.2 Hz, J_2 = 3.2, 2H, H_g), 4.04 (t, J = 4.0, 4H, H_i), 3.99 (t, J = 3.9, 4H, H_j), 1.82–1.76 (m, 8H, $H_{k,l}$), 1.61 (m, 8H, $H_{m,n}$), 1.12 (s, 216H, H_3). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K): δ 161, 160.6, 157.6, 150.5, 146.9, 143.8, 136.5, 133.0, 129.6, 129.5, 127.7, 125.7, 123.9, 120.9, 120.2, 115.4, 108, 101.2, 86.1, 69.8, 68.5, 68.2, 64.7, 64.3, 63.6, 63.6, 57.7, 35.5, 31.4, 30.4, 30.0, 26.4, 26.4; *m/z* (MALDI TOF MS+) requires 3244.8 calcd for $C_{238}H_{394}N_2O_4$ $(M)^+$, found 3244.3. Uv-vis(THF) λ_{max} / nm (ε / M^{-1} cm^{-1}) 317 (391000), 298 (366000), 285 (317000), 267 (192000). UV-vis (CH_2Cl_2) λ_{max} / nm (ε / M^{-1} cm^{-1}) 317 (417000), 298 (38300), 282 (262000), 267 (154000).



Rotaxane (**2c**)$_2$·**M4:** CuI (2.8 mg, 15 μmol) in CH_3CN (2.5 mL) was added to a solution of rotaxane **2c**·**M4** (20 mg, 15 μmol) in CH_2Cl_2 (9 mL) and the mixture was stirred at 20 °C for 1.5 h. The solvent was removed *in vacuo* and the residue redissolved in THF (5 mL). This solution was then added to triyne **1c** (16 mg, 22 μmol), bromotriyne **3** (16 mg, 22 μmol), and K_2CO_3 (8.2 mg, 59 μmol) in THF (3 mL) and the mixture was stirred at 60 °C for 18 h. After cooling to 20 °C, the reaction was quenched by the addition of CH_2Cl_2 (2 mL), CH_3CN (2 mL), and KCN (30 mg, 0.46 mmol, in 1 mL H_2O) and stirred at 20 °C for 4 h. CH_2Cl_2 (20 mL) was added, the organic phase separated, washed with H_2O (10 mL), brine (10 mL), and the solvent was removed *in vacuo*. Flash column chromatography (silica, hexanes/EtOAc 20:1 → 10:1 and then second column, silica, hexanes/CH_2Cl_2 1:1 → hexanes/CH_2Cl_2 1:2 + 1% EtOAc) followed by recrystallization from CH_2Cl_2/ CH_3OH afforded (**2c**)$_2$·**M4** (9 mg, 18%) as a yellow solid. R_f = 0.51 (hexanes/EtOAc 6:1). Mp 264–266 °C (decomp). IR (ATR) 2954 (s), 2904 (m), 2864 (m), 2189 (w), 2168 (w), 1589 (s), 1475 (m), 1361 (m), 1248 (s), 1174 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.9 Hz, 4H), 8.18 (d, *J* = 8.5 Hz, 2H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.67 (s, 2H), 7.18 (t, *J* = 1.7 Hz, 12H), 7.09 (d, *J* = 8.9 Hz, 4H), 7.00 (t, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 1.7 Hz, 24H), 6.56 (t, *J* = 2.1 Hz, 1H), 6.40 (dd, *J* = 8.2, 2.3 Hz, 2H), 4.02 (t, *J* = 7.6 Hz, 4H), 3.94 (t, *J* = 7.0 Hz, 4H), 1.76–1.71 (m, 8H), 1.44–1.34 (m, 16H), 1.10 (s, 216H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 161.1, 161.0, 156.5, 150.6, 146.5, 143.7, 136.7, 131.8, 129.6, 129.0, 127.7, 125.6, 123.9, 120.8, 119.2, 115.2, 107.9, 100.2, 86.1, 69.7, 68.5, 68.2, 63.7, 63.4, 63.34, 63.26, 57.7, 35.0, 31.5, 30.13, 30.06, 30.03, 29.99, 26.24, 26.18. *m/z* APPI HRMS (in toluene) requires 3300.3484 calcd for $C_{242}H_{302}N_2O_4$, (M^+), found 3300.3480.

C. Attempted Carbenoid Rearrangement in 6e·M1 Rotaxane

The synthesis of octayne rotaxane **2d**·**M1** from the **7b**·**M1** rotaxane via carbenoid rearrangement was attempted according to the published procedure.[S9]

In a typical procedure, rotaxane **7b**·**M1** (10 mg, 4.3 μmol) was dissolved in dry solvent (toluene or methylcyclohexane, 5 mL, passed through active Al_2O_3 and kept over molecular sieves) in a two-neck flask. The solution was degassed by three freeze-pump-thaw cycles. Then the corresponding reagent was added at low temperature and the reaction mixture was allowed to warm up over 20–30 min. The reaction mixture was quenched at various temperatures and the resulting crude product was analyzed by UV-Vis absorption, MALDI and NMR spectra. The table below summarizes the results of experiments.

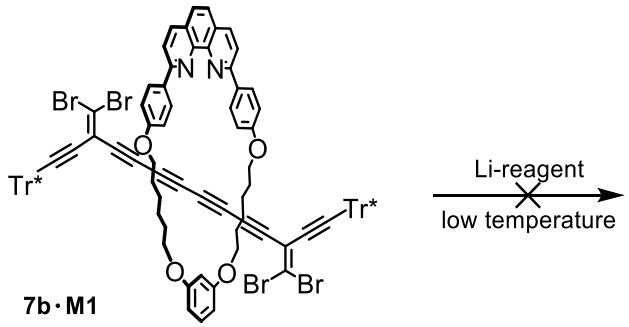


Table S1. Summary of FBW reaction conditions for rotaxane **7b·M1**.

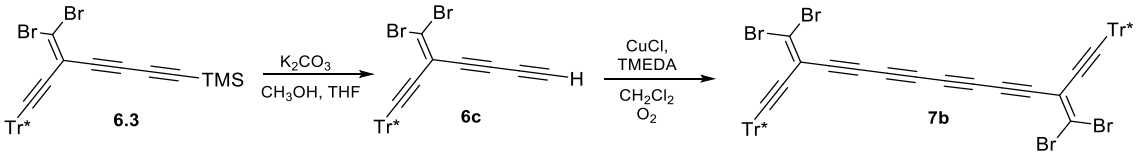
reagent	***solvent***	***Reaction temperature***	***Quench temperature***	***yield***
t-BuLi (2.4 equiv)	toluene	–40 °*C*	0 °*C*	-
	toluene	–78 °*C*	–70 °*C*	-
sec-BuLi (2.4 equiv)	MCH	–78 °*C*	–20 °*C*	-
n-BuLi (2.4 equiv)	toluene	–78 °*C*	–70 °*C*	-
	toluene	–78 °*C*	–40 °*C*	-
	toluene	–78 °*C*	–20 °*C*	-
	MCH	–78 °*C*	0 °*C*	-
PhLi (2.5 equiv.)	toluene	–78 °*C*	–5 °*C*	-

Disappointingly, we never detected the formation of the expected product **2d·M1**: Quenching the reaction at different temperatures (–70, –40, –20, 0 °C) or repeating the experiment with more concentrated 10 mM solution of the **7b·M1** (45 mg in 2 mL MCH) were equally futile. During the reaction the starting rotaxane **7b·M1** was completely consumed giving a complex mixture of by-products and farther separation and characterization of crude products was not pursued. Additionally, the rearrangement reaction was tested by refluxing the toluene solution of the rotaxane with activated Zn dust, however, after 2 h heating the UV-Vis spectra indicated no reaction and the starting material was recovered.

It was thought that perhaps the threaded macrocycle reacts with intermediate carbene and prevents the rearrangement to take place. To check this hypothesis we tested separately the reactivity of the free macrocycle and unthreaded polyyne dumbbell with *n*-BuLi.

To a dry, degassed solution of macrocycle **M1** (10 mg, 16 μmol) in toluene (5 mL) *n*-BuLi (2.5 M in hexane, 6.3 μL, 16 μmol) was added at –78 °C. The reaction mixture was allowed to warm up to 20 °C and after quenching and the workup of the crude mixture the starting macrocycle was recovered almost quantitatively. The reaction product structure was confirmed by ^{1}H NMR spectroscopy.

The free dumbbell **7b** was synthesized via Hay coupling according the scheme given below.



To a solution of **6.3** (33.0 mg, 35.9 μmol) in a mixture of THF (2 mL) and CH_3OH (2 mL) K_2CO_3 (5 mg, 35.9 μmol) was added and the reaction mixture was stirred for 3 h at 20 °C. The solvent was removed in vacuo and the crude product was purified by passing through silica plug (hexanes) to yield deprotected **6c**. To a solution of TMEDA (16 μL, 0.11 mmol) in CH_2Cl_2 (6 mL) CuCl (3.6 mg, 36 μmol) was added and oxygen was bubbled into the solution for 5 min. The deprotected **6c** was dissolved in CH_2Cl_2 (4 mL) and the solution was transfer to the CuCl·TMEDA mixture. After 5 min stirring (TLC monitoring, hexanes + 10% CH_2Cl_2) the reaction mixture was passed through silica plug (CH_2Cl_2) and the solvent was removed affording the product **7b** (29.0 mg, 99%) as a yellow solid. R_f = 0.78 (hexanes + 10% CH_2Cl_2). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.32 (t, J = 1.9 Hz, 6H), 7.0 (d, J = 1.8 Hz, 12H), 1.22 (s, 108H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 150.7, 144.3, 124.1, 120.8, 113.7, 112.5, 106.0, 80.4, 79.9, 74.8, 70.3, 64.7.0, 57.8, 35.3, 31.6. Uv-vis (THF) λ_{max} / nm (ε / M^{-1} cm^{-1}) 417 (18000), 387 (27000), 358 (27000), 337 (52000), 315 (45000), 301 (48000), 255 (48000).

The rearrangement of **7b** (15 mg, 9.0 μmol) was carried out in dry, degassed MCH (2 mL) by adding *n*-BuLi (1.6M in hexane, 13.4 μL, 21.4 μmol) at –78 °C and slowly warming the temperature to –20 °C over 20 minutes and the reaction mixture was quenched by aqueous NH_4Cl. After the workup and silica column chromatography (hexane/EtOAc 50:1) the octayne **2d** was isolated in 11% yield (calculated from the extinction coefficient in hexane). This experiment suggested that, the FBW rearrangement of supertrityl-capped dumbbell is achievable despite the low yield.

D. Selected NMR spectra

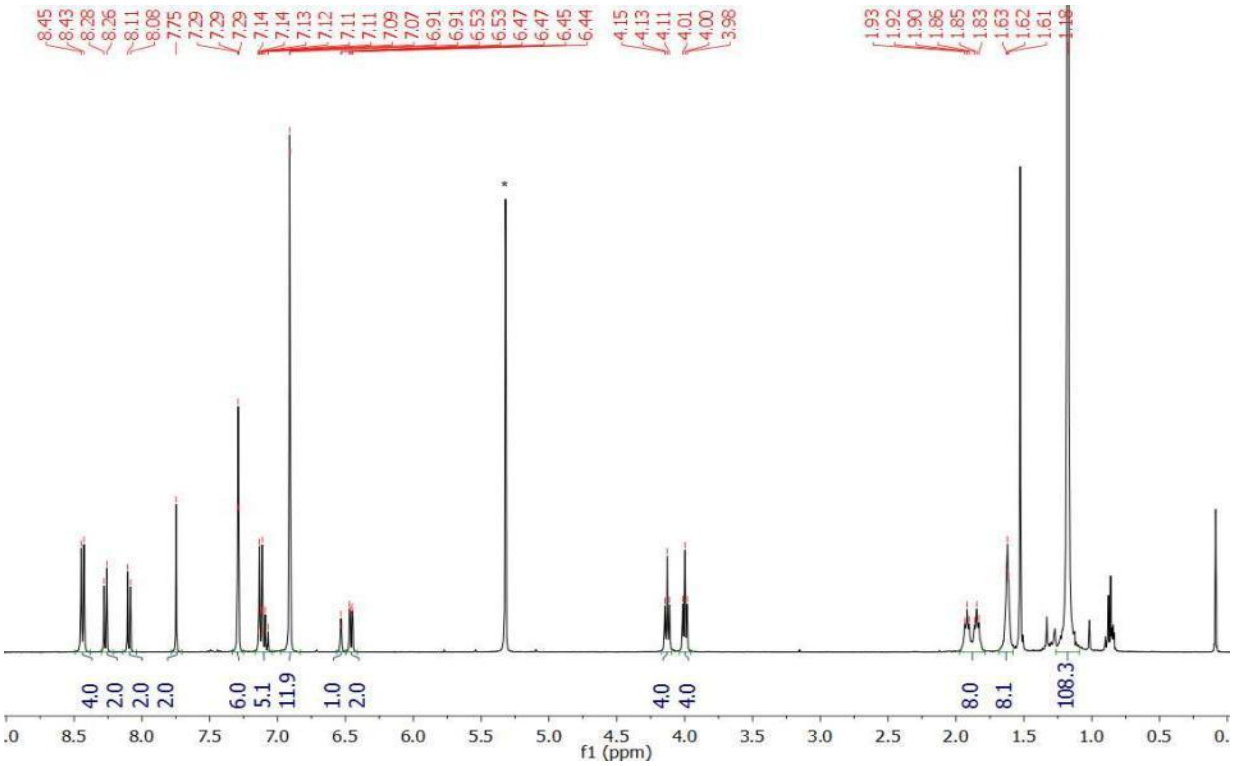


Figure S1. ^{1}H NMR spectrum of **2d·M1** rotaxane (400 MHz, 298 K, CD_2Cl_2).

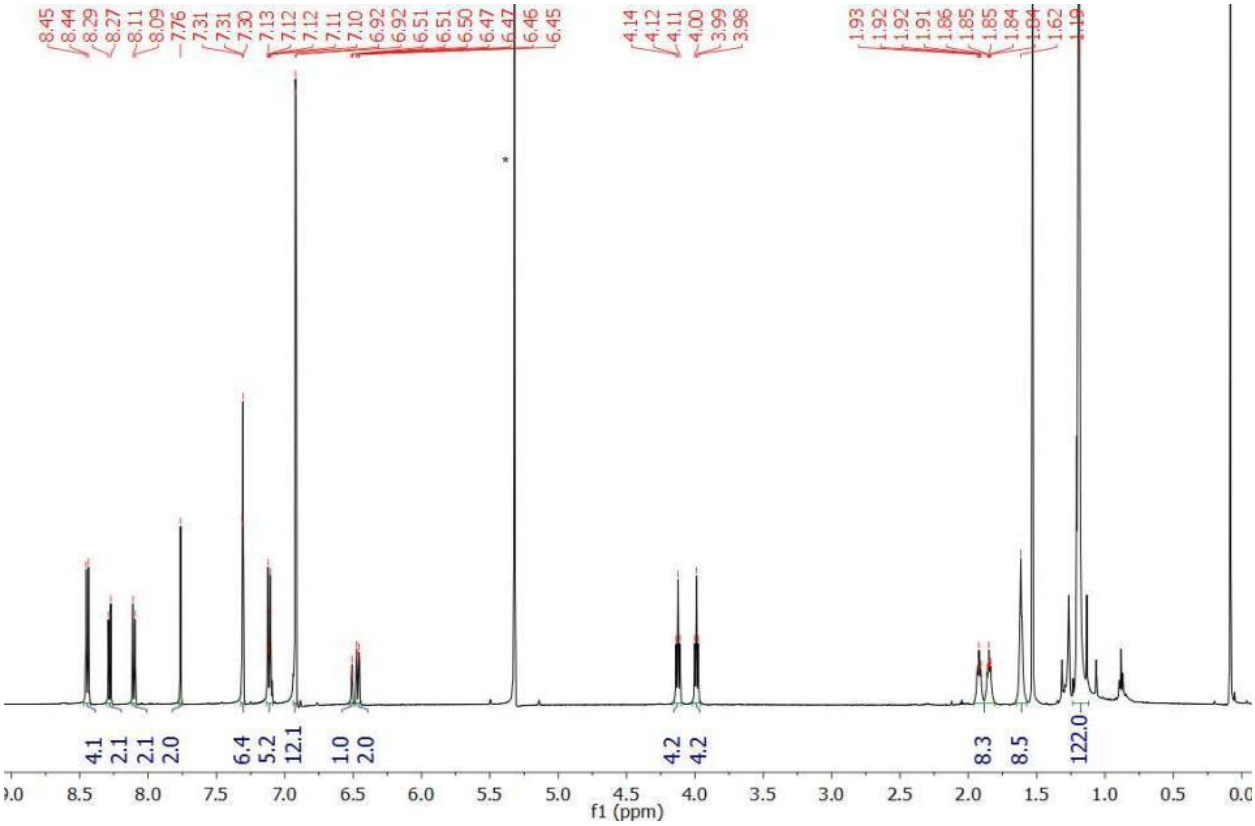


Figure S2. ^{1}H NMR spectrum of **2f·M1** rotaxane (500 MHz, 298 K, CD_2Cl_2).

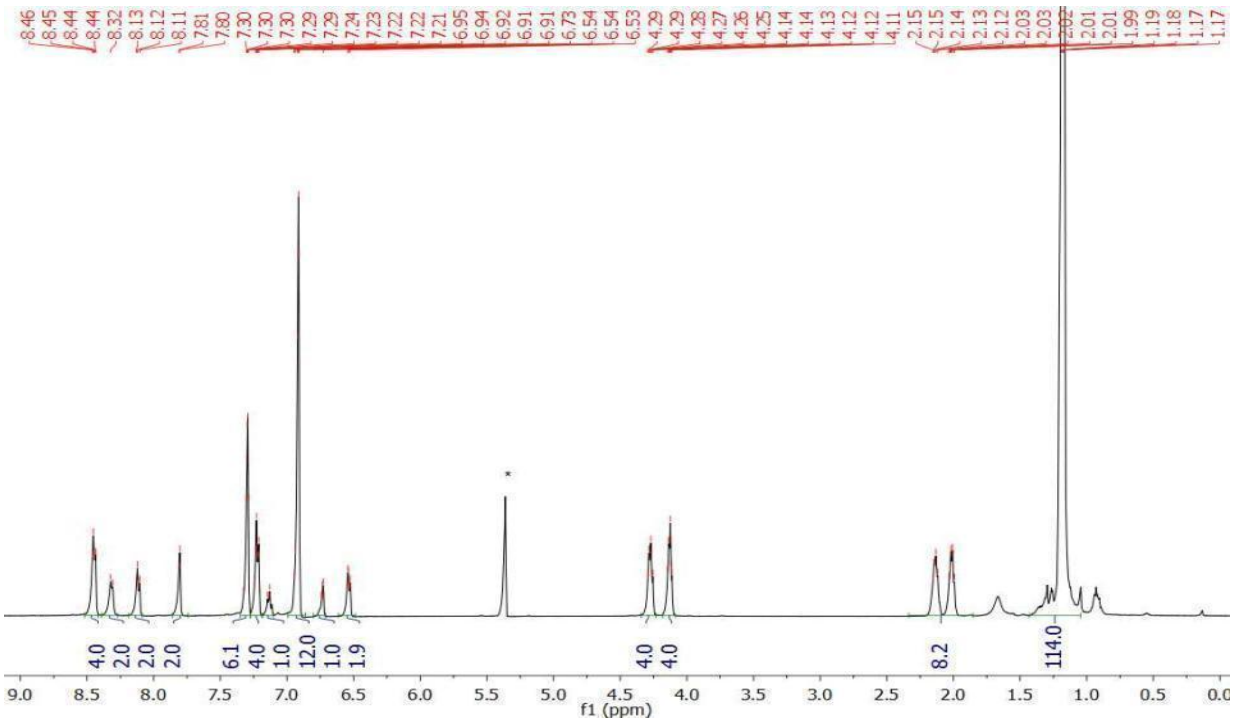


Figure S3. ^{1}H NMR spectrum of **2c**·**M2** rotaxane (500 MHz, 298 K, CD_2Cl_2).

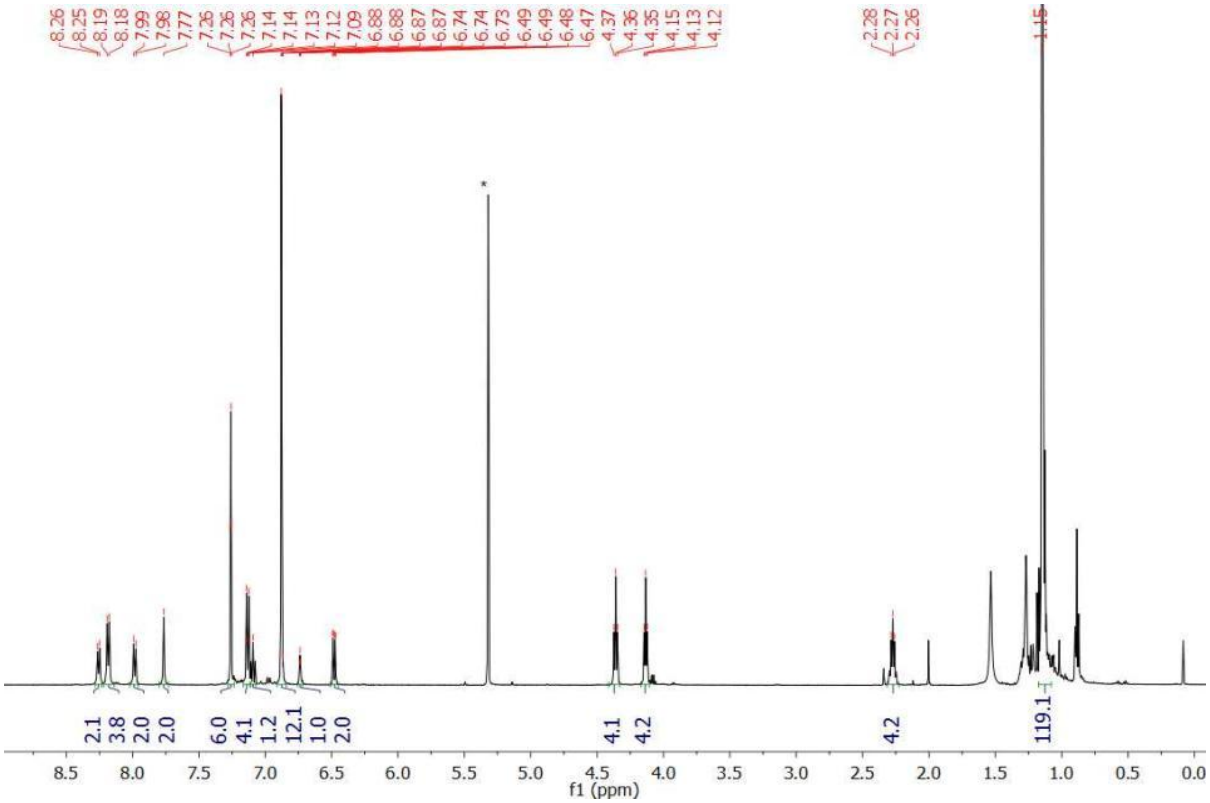


Figure S4. ^{1}H NMR spectrum of **2c**·**M3** rotaxane (500 MHz, 298 K, CD_2Cl_2).

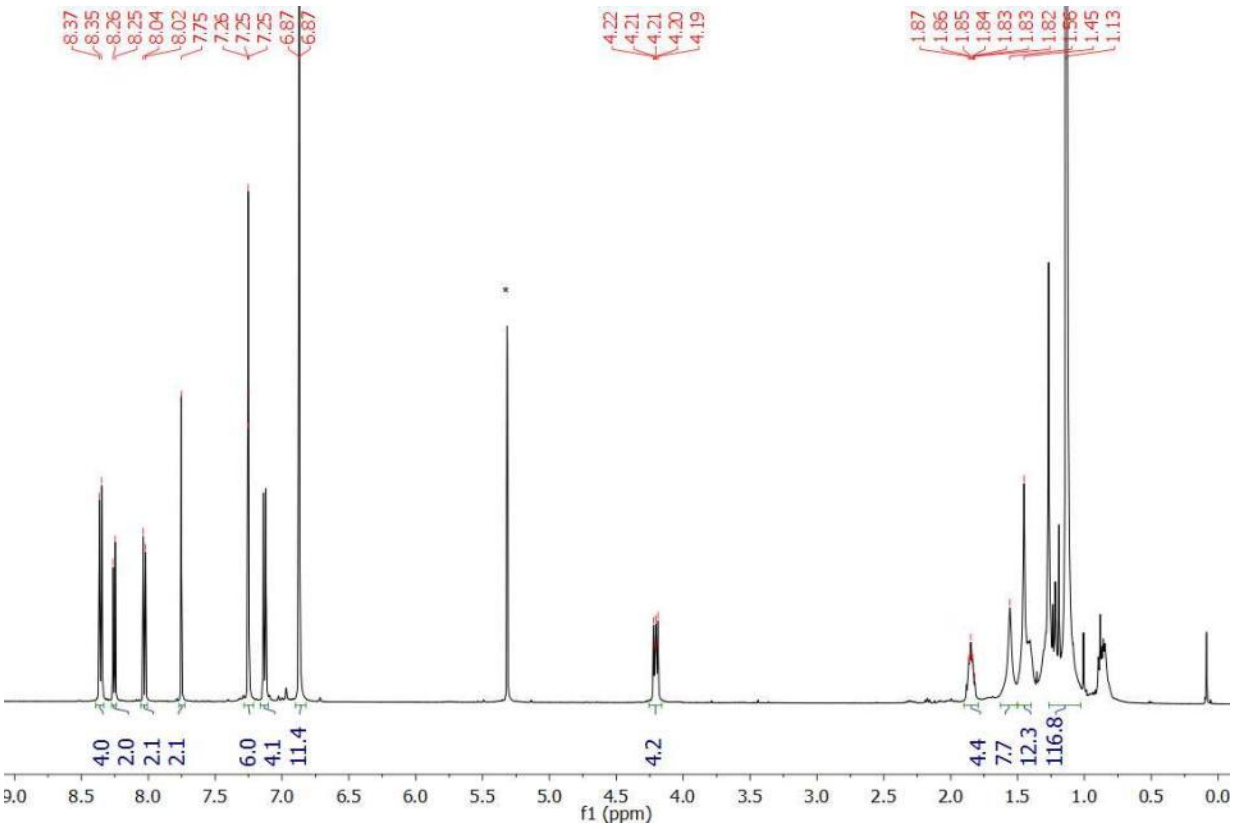


Figure S5. ^{1}H NMR spectrum of **2c**·**M6** rotaxane (500 MHz, 298 K, CD_2Cl_2).

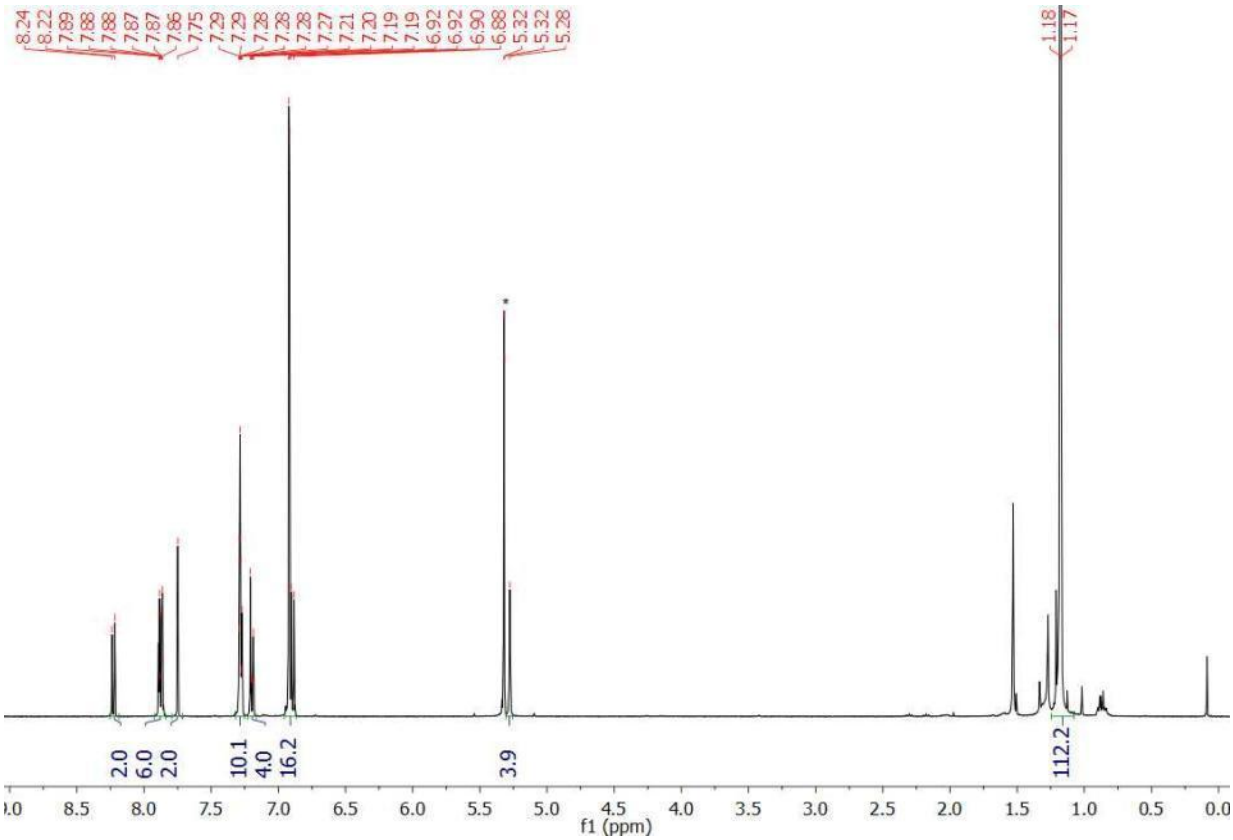


Figure S6. ^{1}H NMR spectrum of **2c**·**M7** rotaxane (500 MHz, 298 K, CD_2Cl_2).

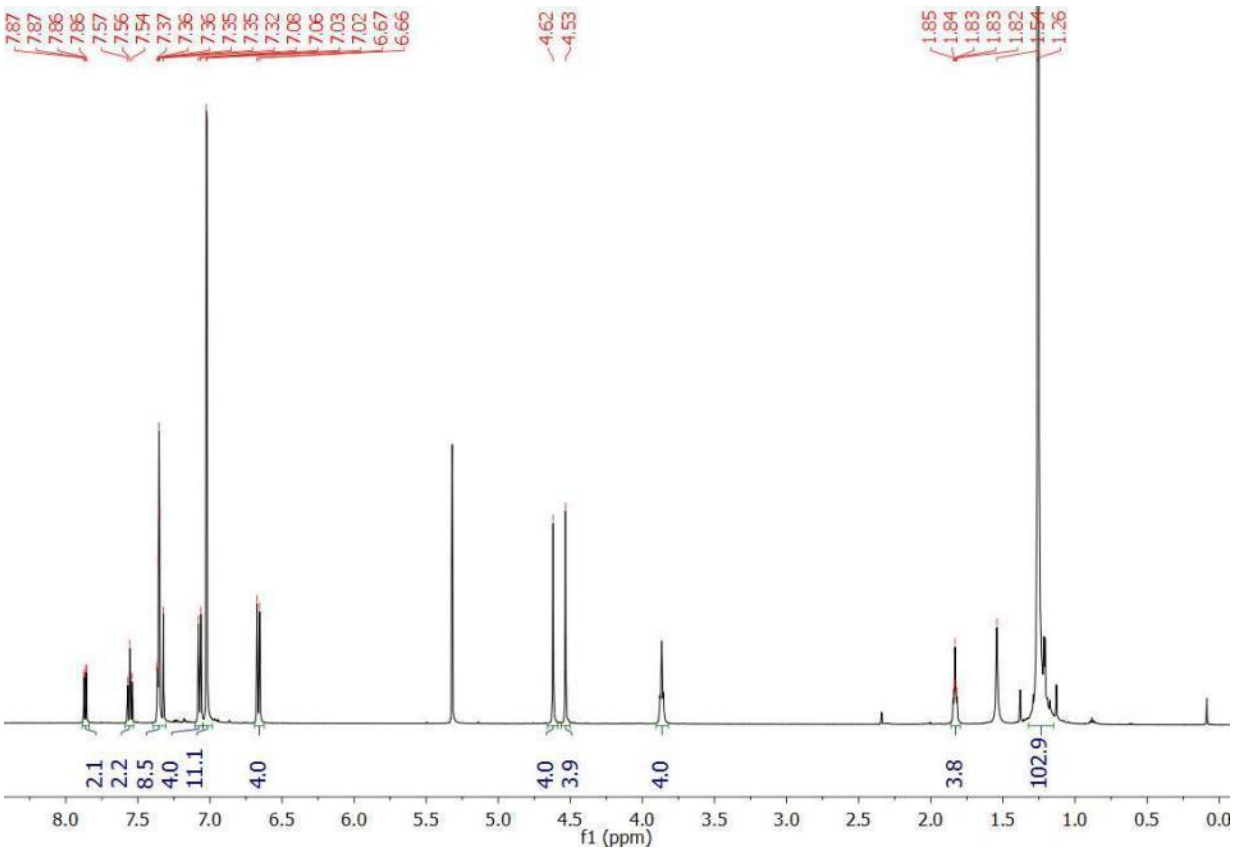


Figure S7. ^{1}H NMR spectrum of **2c**·**M8** rotaxane (500 MHz, 298 K, CD_2Cl_2).

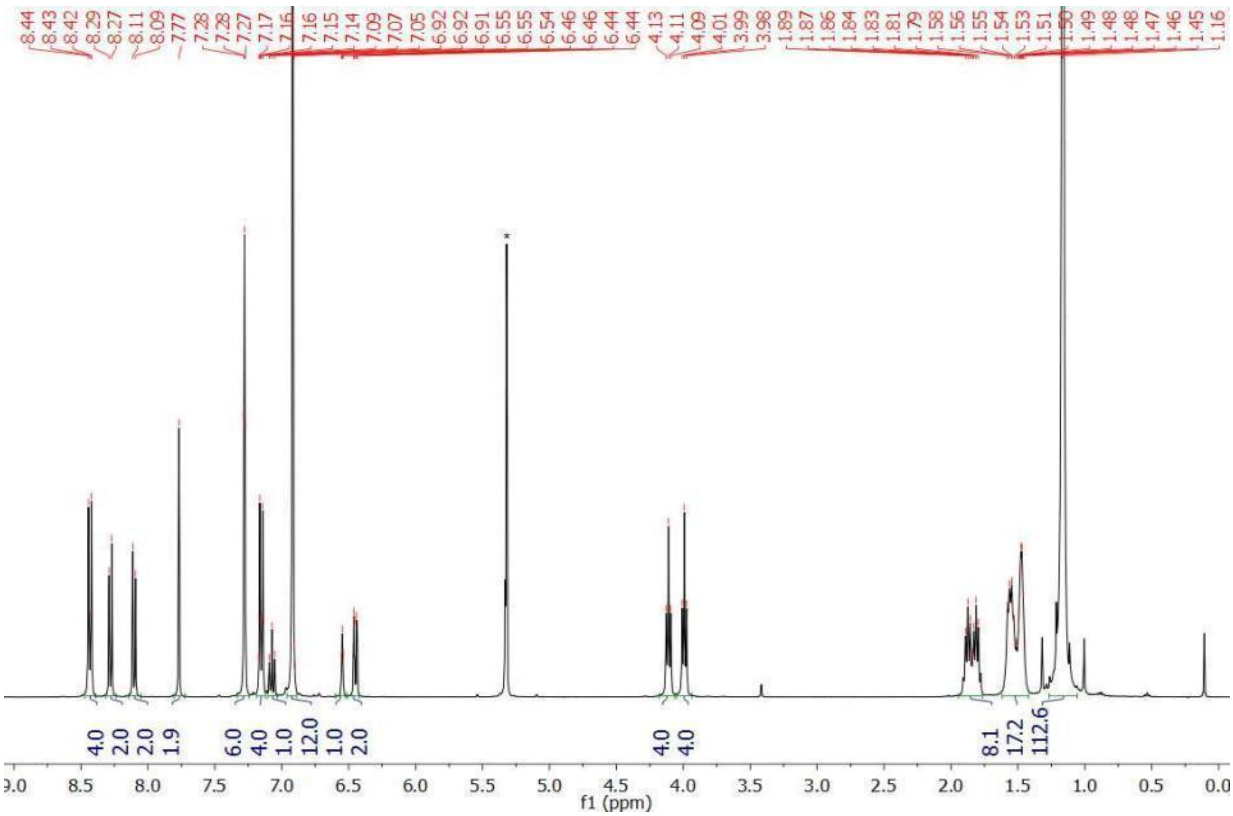


Figure S8. ^{1}H NMR spectrum of **2c**·**M4** rotaxane (400 MHz, 298 K, CD_2Cl_2).

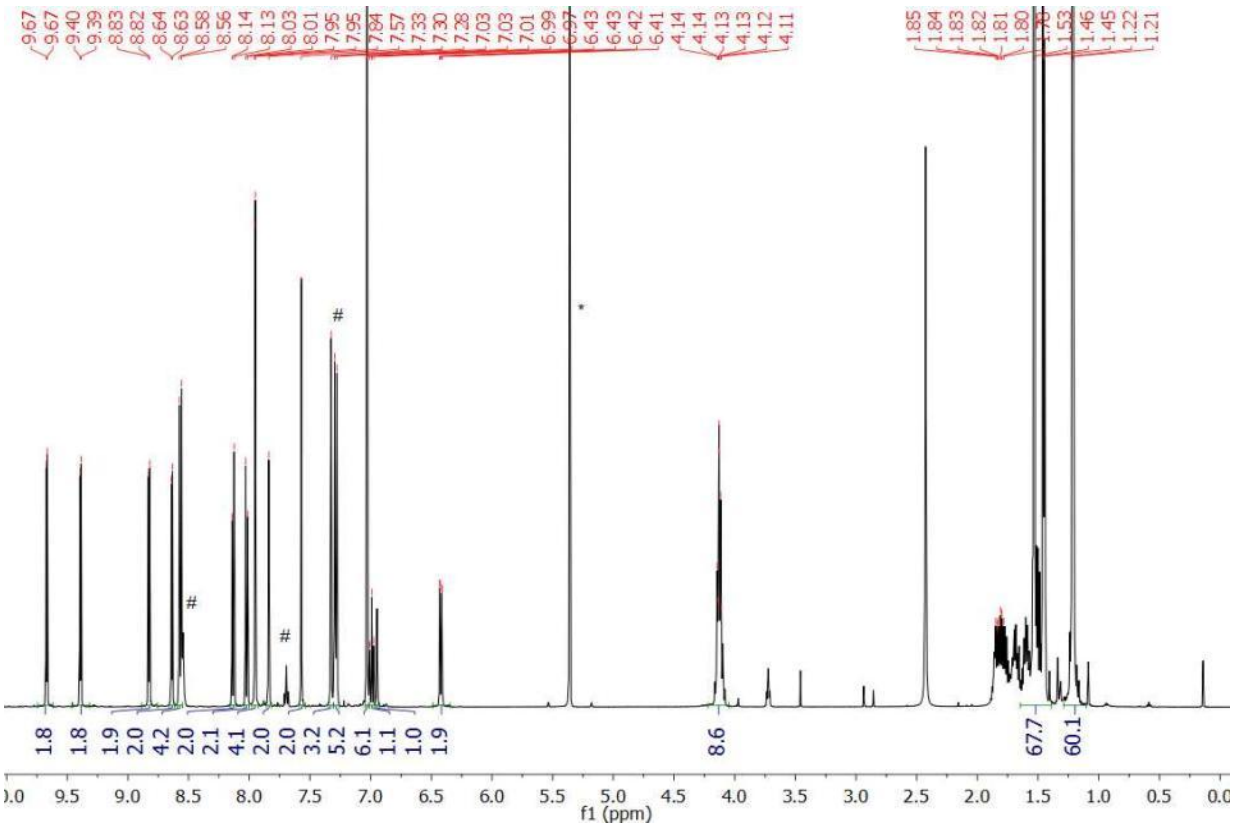


Figure S9. ^{1}H NMR spectrum of **5a·M1** rotaxane (500 MHz, 298 K, CD_2Cl_2). # denotes pyridine-*d5* residual peaks.

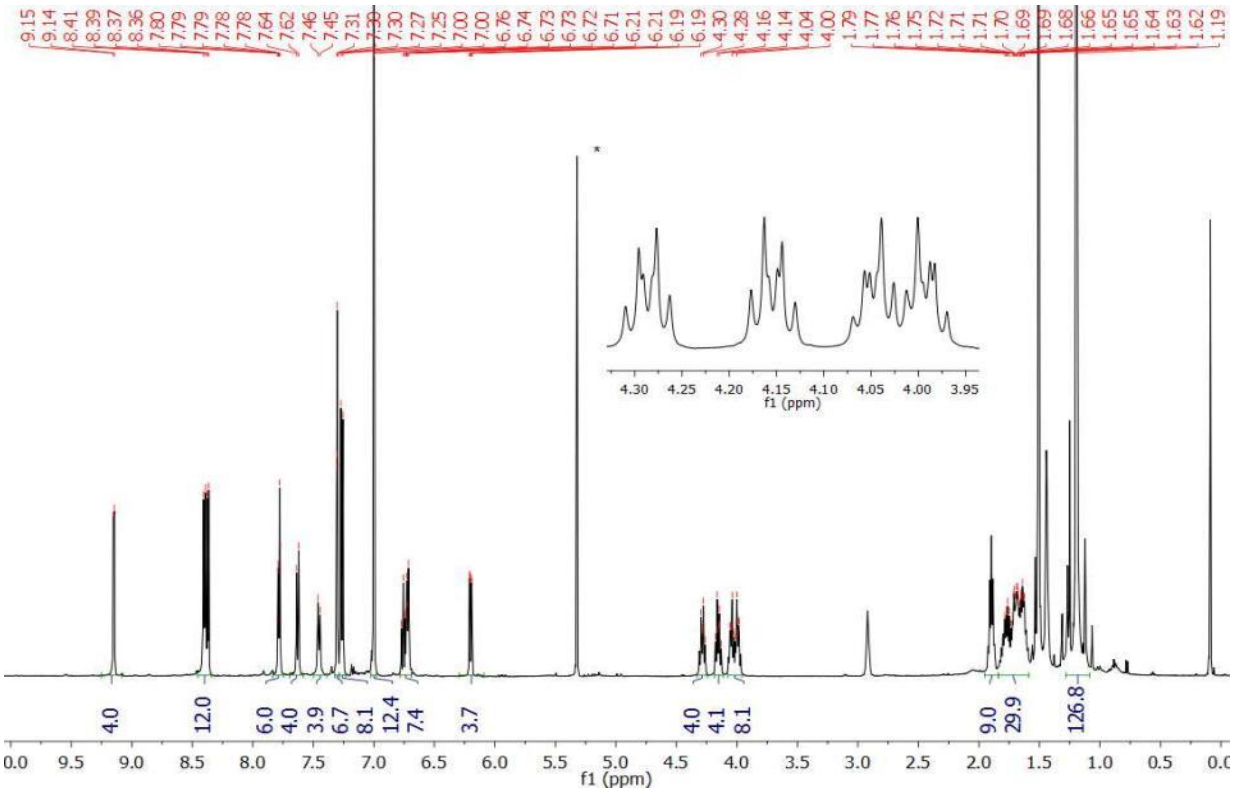


Figure S10. ^{1}H NMR spectrum of **5c·2(M1)** rotaxane (500 MHz, 298 K, CD_2Cl_2). The expansion shows the splitting of the resonances of CH_2 protons of the macrocycle due to desymmetrized rotaxane axle.

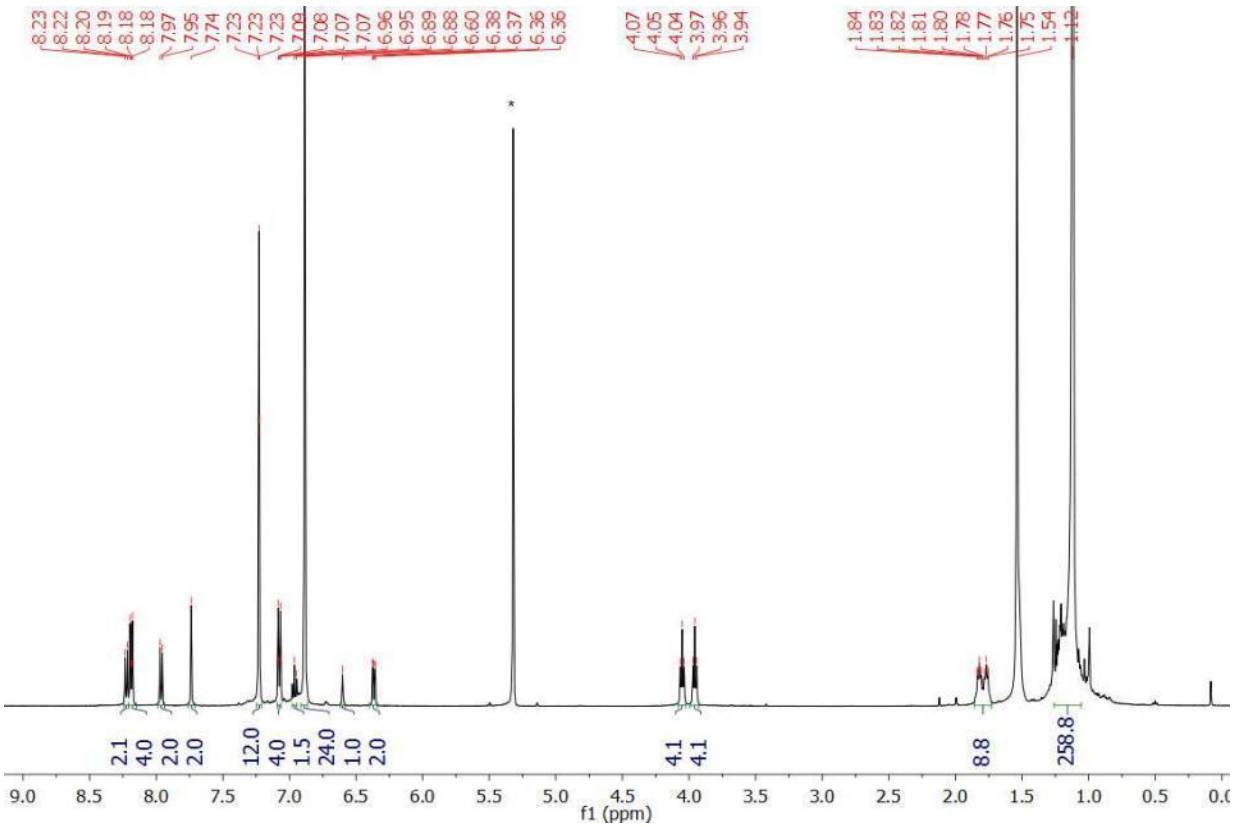


Figure S11. ^{1}H NMR spectrum of (**2c**)$_2$·**M1** rotaxane (500 MHz, 298 K, CD_2Cl_2).

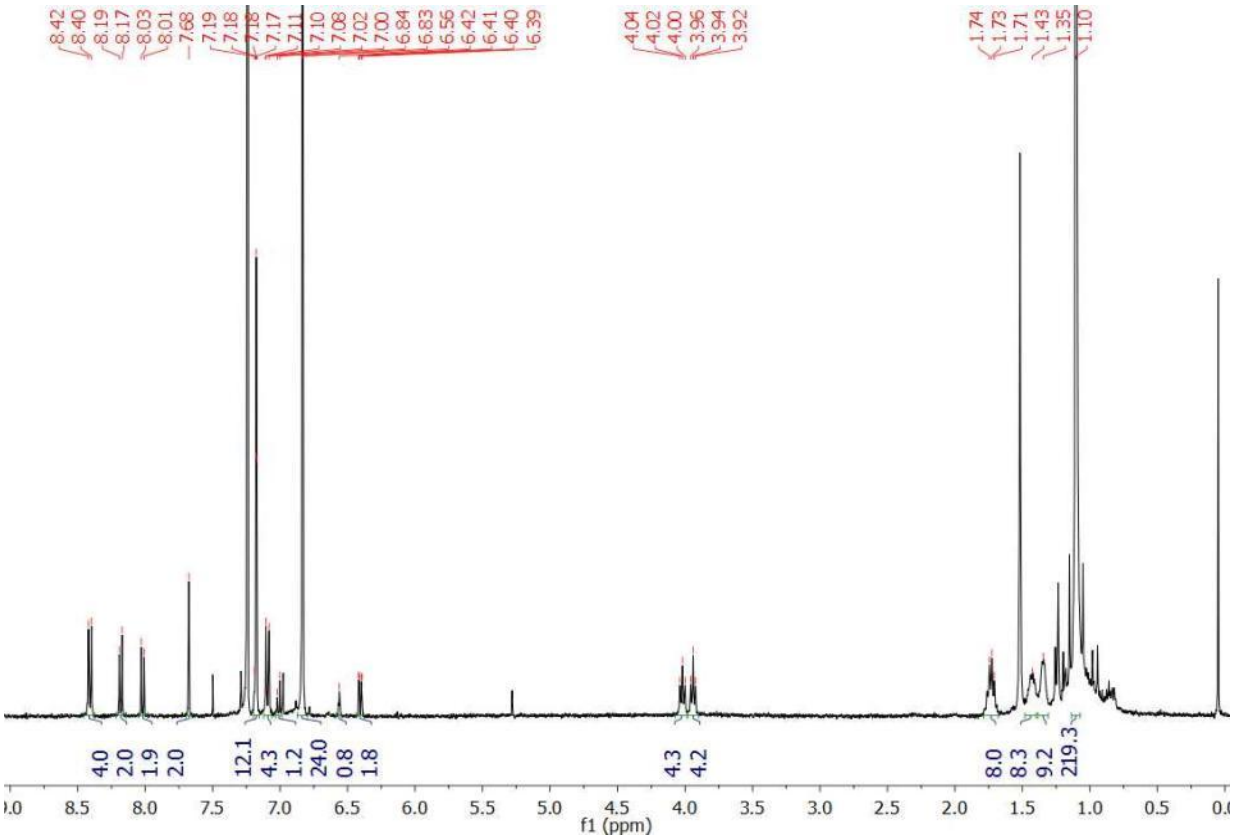


Figure S12. ^{1}H NMR spectrum of (**2c**)$_2$·**M4** rotaxane (400 MHz, 298 K, $CDCl_3$).

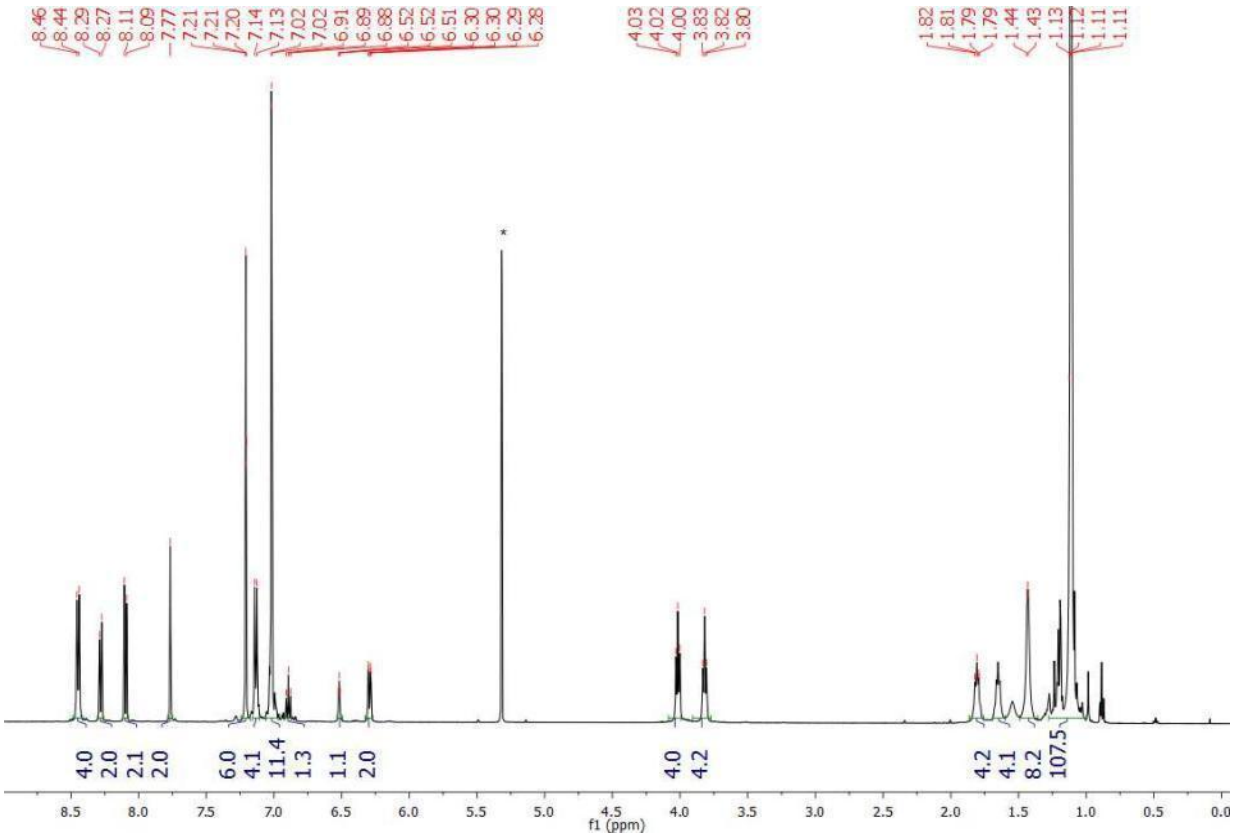


Figure S13. ^{1}H NMR spectrum **7a·M1** rotaxane (500 MHz, 298 K, CD_2Cl_2).

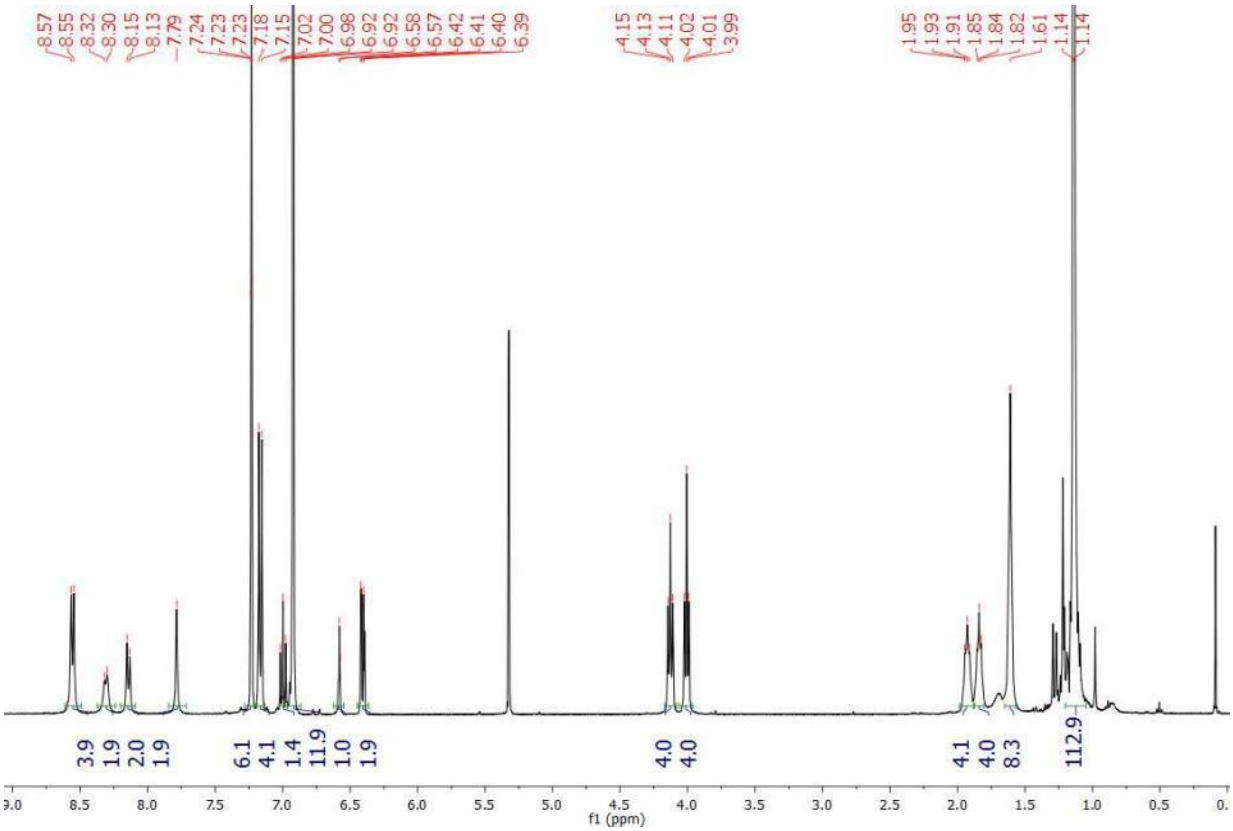


Figure S14. ^{1}H NMR spectrum **7b·M1** rotaxane (500 MHz, 298 K, CD_2Cl_2).

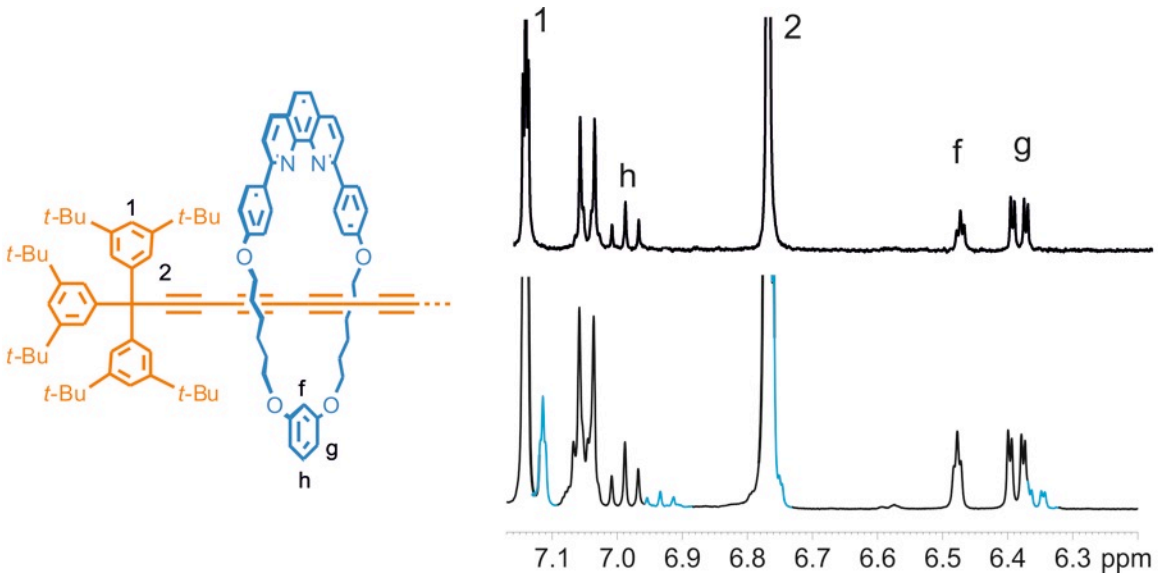


Figure S15. The ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectra of hexayne rotaxane **2c·M1** (top) compared to the product mixture from the cross-coupling reaction (bottom). The blue colored peaks belong to the pentayne rotaxane.

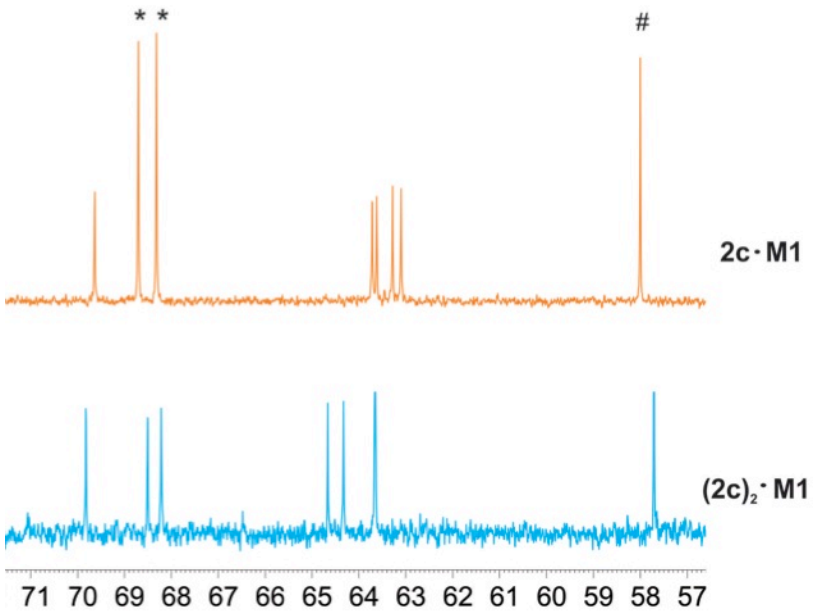


Figure S16. ^{13}C NMR spectra of **2c·M1** (orange) and **(2c)$_2$·M1** (blue) rotaxanes (125 MHz, CD_2Cl_2, 298 K), showing the region containing resonances of the polyyne *sp* carbons. Signals designated with * belong to the macrocycle and the another one with # comes from quarterly carbon of Tr* group.

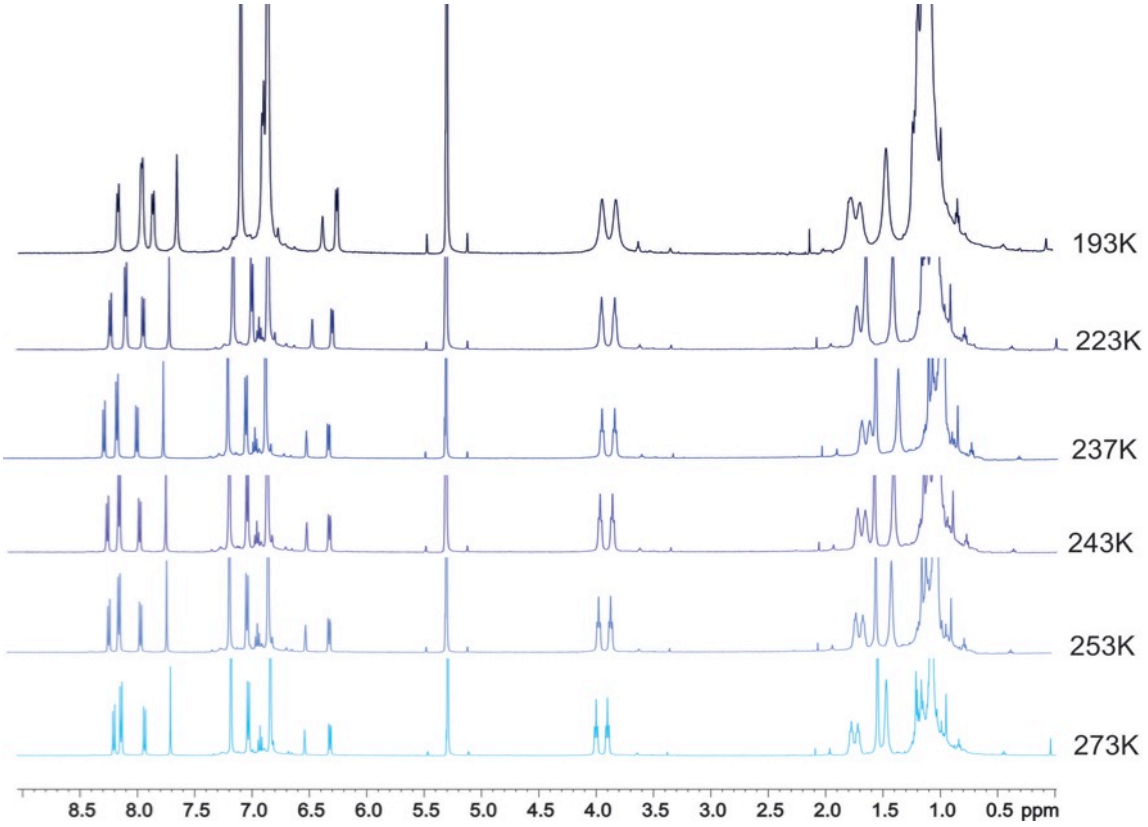


Figure S17. VT ^{1}H NMR spectra of **(2c)$_2$·M1** rotaxane (500 MHz, CD_2Cl_2).

E. X-ray Crystallography

For all crystals except **2c·M7**, single crystal X-ray diffraction data were collected at 100 K using synchrotron radiation at the Diamond Light Source, beamline I19(EH1).[S10] In general, raw frame data were collected using CrystalClear and reduced using CrysAlisPro. The structures were solved using charge flipping[S11] with SuperFlip[S12] and refined using full-matrix least-squares within CRYSTALS.[S13] In some cases, the structure contained large solvent-accessible voids comprising diffuse electron density. In these cases the discrete Fourier transforms of the void regions were treated as contributions to the A and B parts of the calculated structure factors using PLATON/SQUEEZE SQUEEZE[S14] to leave a void from which the electron density had been effectively removed. Hydrogen atoms were positioned geometrically and refined separately with soft restraints within *CRYSTALS*.[S15] The diffraction data for **2c·M7** were collected at 173 K using an Oxford Diffraction/Agilent SuperNova (Cu) X-ray Source. The structure was solved with ShelXS[S16] using Direct Methods and refined with ShelXL[S16] by full-matrix least-squares within OLEX2.[S17] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1437276–1437283) and copies of these data can be obtained free of charge via www. ccdc.cam.ac.uk/data_request/cif.

The error propagation in the calculation of BLA values for **(2c)$_2$·M1** rotaxane was done using the following equation.

$$\delta R = \sqrt{(\delta X)^2 + (\delta Y)^2 + \cdots}$$

where δX, δY are uncertainties of X and Y, respectively.

We have investigated the distribution of intermolecular aromatic CH/π_{sp} interactions by searching the Cambridge Structural Database (CSD). Mean values of C–H/C$_{sp}$ distances are calculated by measuring the distance between carbon atom of polyyne and proton of the interaction aromatic CH group. We considered only polyynes with four or more triple bonds, in accordance with the structure of rotaxanes. The table below and Figure S18 summarize the results. From the graph it seems that number of molecules form short contacts at the distance of 2.71 Å. In rotaxanes **2d·M1** (d = 2.738 Å), **2c·M6** (d = 2.670 Å) and **2c·M2** (d = 2.625, 2.576 Å) there are several CH/C$_{sp}$ short contacts with distances distributed around 2.71 Å.

	N total	Mean (Å)	St. Deviation	Minimum (Å)	Median (Å)	Maximum (Å)
***aromatic* CH/C$_{sp}$**	120	2.816	0.067	2.629	2.829	2.899

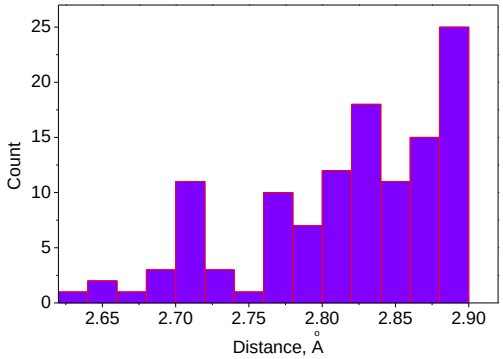


Figure S18. Distance distribution of aromatic CH/C$_{sp}$ short contacts (< sum of van der Waals radii) found in CSD for tetraynes and longer polyynes.

Crystal Packing

2d·M1: Crystals suitable for X-ray diffraction studies were grown by liquid diffusion of overlaid CH_3OH into solution of the compound in THF at 20 °C. The rotaxane **2d·M1** crystallizes in P-1 space group and the asymmetric unit contains one molecule of **2d·M1**. In the crystal lattice *t*-Bu moieties of neighboring supertrityl end groups of the rotaxane **2d·M1** interact with each other via dispersion interactions. In addition, *t*-Bu groups interact with π system of macrocycle (C–H/π_{arene}) and octayne (C–H/π_{sp} and C/π_{sp}). There is also π–π stacking between two phenanthrolines. Distances for all mentioned short contacts are listed below and the crystal packing is shown in Figure S19.

π–π stacking (Å)	C_{sp3}–H/C_{arene} (Å)	C_{sp3}–H/C_{sp} (Å)	C_{sp3}/C_{sp} Å)
3.393	2.813, 2.812	2.713	3.275
	2.842, 2.745	2.835	3.378
	2.729, 2.862	2.830	

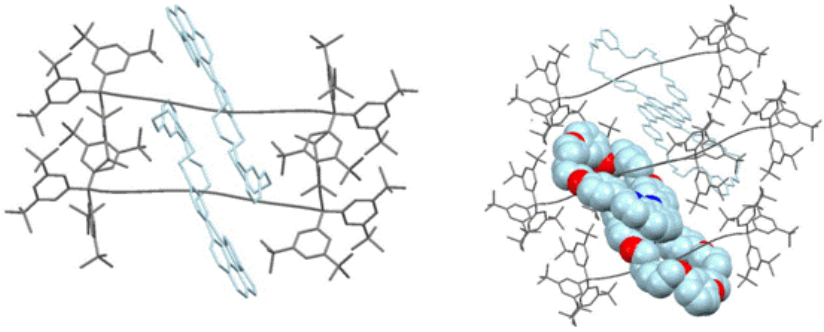


Figure S19. The crystal packing of **2d·M1** rotaxane viewed down to crystallographic *b* axis (left) and highlighting π-π stacking between two phenanthrolines (right). Hydrogen atoms are omitted for clarity.

2c·M6: Crystals of **2c·M6** suitable for X-ray diffraction studies were grown from slow diffusion of CH_3OH vapor into solution of the compound (*c* = 1.5 mg/mL) in THF at 20 °C. The asymmetric unit contains one molecule of **2c·M6** and one CH_3OH molecule, and the space group is P-1. In the crystalline rotaxane **2c·M6** there is a plethora of various type of non-covalent interactions. Macrocycles form π-π stacking involving phenanthroline part of the molecule and weak hydrogen bonds between neighboring hexayne π system and decyl strap. *t*-Bu moieties of the supertrityl groups in addition to dispersion interactions between themselves, become involved in CH/π_{arene}, CH/O and C_{sp3}/π_{arene} type interactions. All non-covalent bonds are listed below with corresponding distances and the crystal packing diagram is given in Figure S20.

π-π stacking (Å)	C_{sp3}–H/C_{arene} (Å)	C_{sp3}–H/C_{sp} (Å)	C_{sp3}/C_{arene} (Å)	C_{sp3}–H/O (Å)	C_{arene}–H/C_{sp3} (Å)	C_{arene}–H/C_{arene} (Å)
3.494	2.736	2.863	2.940	2.665	2.410	2.842
	2.171		3.434			2.688
	2.805					
	2.724					

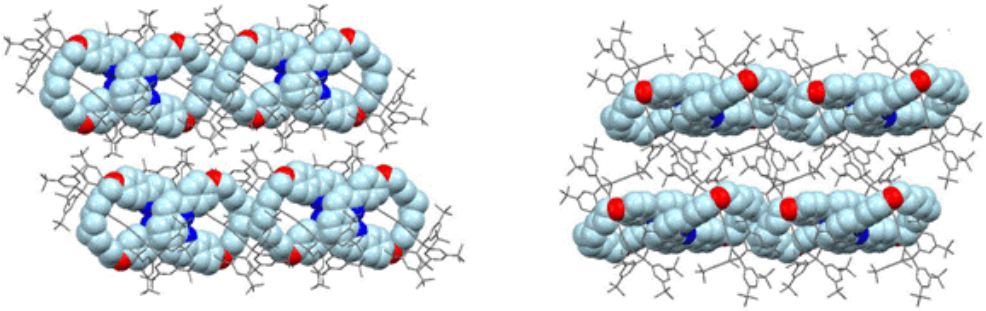


Figure S20. The crystal packing of **2c·M6** rotaxane viewed down to crystallographic *b* (left) and *a* (right) axes. Hydrogen atoms and solvent molecules are omitted for clarity.

2c·M7: Crystals of **2c·M7** suitable for X-ray diffraction studies were grown from slow diffusion of CH_3OH vapor into solution of the compound (c = 1.5 mg/mL) in THF at 20 °C. The space group is $P2_1/c$ and asymmetric unit contains one molecule of **2c·M7**. In the crystal, neighboring molecules of rotaxane form various type of none-covalent interaction, such as π–π stacking, CH/π_{sp} and CH/O hydrogen bonds. It worth to mention that in π–π stacking takes place between aryl side groups of two adjacent macrocycles. The crystal packing of the molecule is shown in Figure S21 and the short contacts are listed in the table below.

π-π stacking (Å)	C_{sp3}–H/C_{sp} (Å)	C_{arene}–H/O (Å)	C_{arene}–H/C_{sp} (Å)	C_{arene}–H/C_{sp3} (Å)
3.185	2.822	2.653	2.851	2.858
	2.713	2.605		

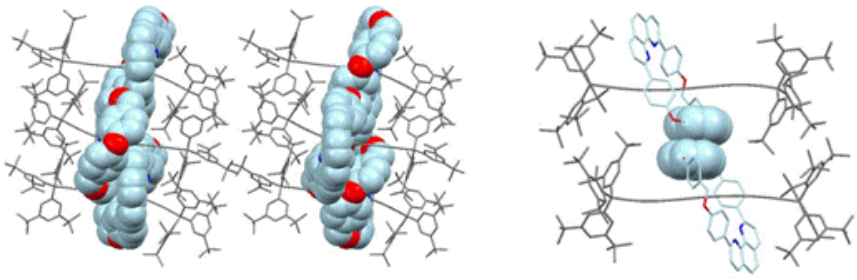


Figure S21. The crystal packing of **2c·M7** rotaxane viewed down to crystallographic *b* axis (left. The figure in right shows the packing of the molecules with highlighted (with space-filling model) π–π stacking. Solvent molecules and hydrogen atoms are omitted for clarity.

2c·M2: Crystals suitable for X-ray diffraction studies were grown from slow diffusion of CH_3OH vapor into solution of the compound (c = 2 mg/mL) in CH_2Cl_2 at 20 °C. The space group is $P2_1$, asymmetric unit contains one molecule of **2c·M2**, 0.15 dichloromethane and 0.85 methanol. Number of as CH/π and CH/O weak interactions between neighboring rotaxane molecules are involved in crystal packing. In crystal, the rotaxane molecules are packed in lamellar fashion, where two distinctive layers of hexaynes are twisted over each other. Figure S22 depicts the crystal packing of the molecule and the table below summarizes the non-covalent contacts.

C_{sp3}–H/C_{arene} (Å)	C_{sp3}–H/O (Å)	C_{arene}–H/C_{sp} (Å)	C_{arene}–H/C_{arene} (Å)
2.789	2.625	2.878	2.858
2.816		2.753	
		2.625	
		2.576	

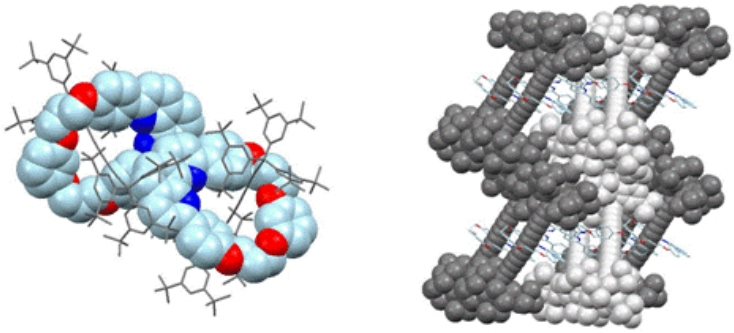


Figure S22. The crystal packing of **2c·M2** rotaxane viewed down to crystallographic *c* (left) and *a* axes (right). On the right picture two layers of polyynes are colored differently for visual assistance. Solvent molecules and hydrogen atoms are omitted for clarity.

7a·M1: Crystals suitable for X-ray diffraction studies were grown from slow diffusion of CH_3OH vapor into solution of the compound (c = 2 mg/mL) in CH_2Cl_2 at 20 °C. The crystals are assigned to the P-1 space group, the asymmetric unit contains one molecule of **7a·M1**, one CH_2Cl_2 and seven CH_3OH molecules.

For the macrocycle-nested dibromoolefin part, the ∠Br–C(sp^2)–Br angle is 114.8°, and for the second dibromoolefin moiety the ∠Br–C(sp^2)–Br angle is 116.3° (Figure S23).

In the crystal, the macrocycle interacts with its thread through couple of CH/π_{sp} contacts formed between π system of the polyyne and alkyl chain of the macrocycle. Bromine atoms also interact with neighboring macrocycle molecule through Br-C_{arene} interactions, mentioned below. Non-covalent interactions contribution to the crystal packing of the rotaxane molecules are summarized in the table below and the crystal packing is shown in Figure S23.

C_{arene}/Br (Å)	C_{sp3}–H/Br (Å)	C_{arene}–H/C_{sp} (Å)	C_{arene}/C_{sp3} (Å)
3.308	3.038	2.872	3.331
3.414		2.736	
3.489			

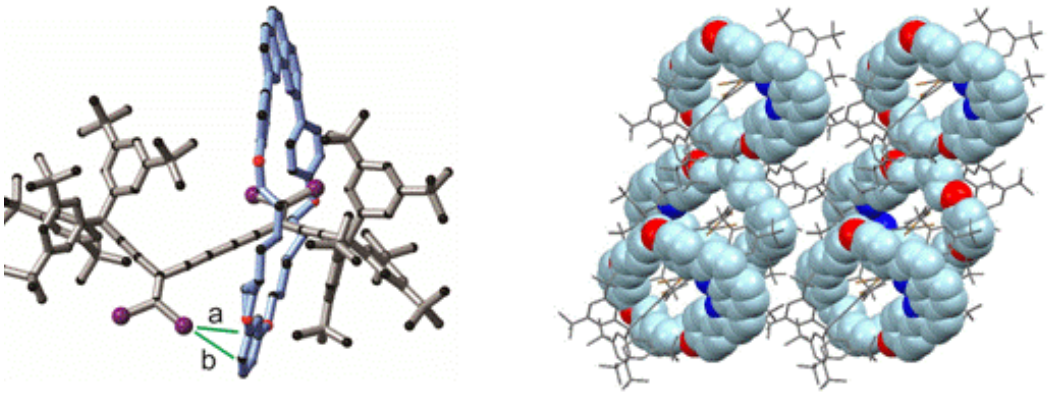


Figure S23. X-ray crystal structure of **7a·M1** with highlighted C_{aryl}/Br short contacts: a: 3.33 Å; b: 3.37 Å (left). The crystal packing of **7a·M1** viewed down to crystallographic *c* axis (right). Solvent molecules and hydrogen atoms are omitted for clarity.

5a·M1: Crystals suitable for X-ray diffraction studies were grown by liquid diffusion of CH_3OH layer into solution of the compound (*c* = 1.5 mg/mL) in CH_2Cl_2 at 20 °C. The crystals are assigned to the P 2_1/c space group, and the asymmetric unit contains one molecule of **5a·M1**, one dichloromethane molecule and three molecules of methanol, one of which is coordinated to the Zn centre of the porphyrin (Figure S24). The distance (*r*) between the Zn and O atom of the methanol is 2.106 Å. The Cambridge Structural Database revealed numerous Zn porphyrin structures with fifth-coordinated methanol with similar *r* (Zn-O) distances. The tetrayne chain is slightly bent in an arc-shaped fashion with average ∠C–C≡C angle equal to 176.3 ± 1.3°. Average C≡C and C–C bond lengths are 1.213 ± 0.007 Å and 1.354 ± 0.011 Å, respectively. The Tr* and TIPS groups are in staggered conformation with respect to each other. The TIPS- acetylene chain is deviated from linearity and the ∠Si–C≡C angle is 173.5°.

Macrocycle is distorted and the resorcinol part possesses two conformations. In both conformations, it interacts weakly with porphyrin π system. The rotaxane molecules form pairs through *π*-*π* interactions between vicinal phenanthroline moieties. The distance between phenanthroline planes is 3.523 Å. In the **5a·M1** molecular pairs, two dumbbells are aligned opposite each other in a head-to-tail way (Figure S24)

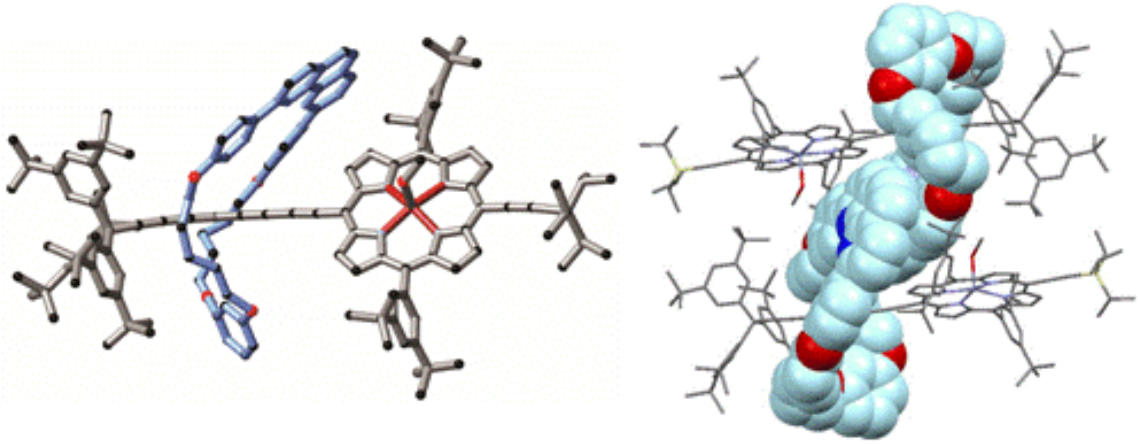


Figure S24. X-ray crystal structure of rotaxane **5a·M1** (left). Crystal packing of the rotaxane **5a·M1** viewed down the crystallographic *c* axis showing the *π*-*π* stacking of adjacent phenanthrolines. Only one conformation of the macrocycle is shown. Hydrogen atoms and free solvent molecules are omitted for clarity.

5c·(**M1**)$_2$: Crystals suitable for X-ray diffraction studies were grown from slow diffusion of CH_3OH vapor into solution of the compound (c = 1.5 mg/mL) in THF at 20 °C. The crystals are assigned to the P -1 space group, the asymmetric unit contains one molecule of **5c**·(**M1**)$_2$ and six molecules of methanol one of which is coordinated to the Zn centre of the porphyrin (Figure S25). The distance (r) between the Zn and O atom of the methanol is 2.094 Å, and the Zn atom is slightly out of the porphyrin plane (0.368 Å), similar to the **5a**·**M1**. The tetrayne chains are slightly bent in an arc-shaped fashion and average C≡C and C–C bond lengths are identical (within error) for both tetrayne chains (1.198 ± 0.017 Å (triple bond) and 1.369 ± 0.019 Å (single bond). The 3,5-di(*t*-butyl)phenyl (Ar') substituent of the porphyrin moiety are twisted regarding the porphyrin plane (~61°). The torsion angle (ϕ) between two Ar' planes is 52.8°. Two Tr* end-groups are in staggered position in respect to each other.

In the crystal, one of the macrocycles interacts with the polyyne chain (d(C/C$_{sp}$) = 3.358 Å) as well as with porphyrin (CH/π_{arene}, d(C$_{porph}$H/C$_{arene}$) = 2.817 Å). In crystal, **5c**·(**M1**)$_2$ molecules interact via CH/π_{sp} short contacts (2.639 and 2.519 Å) and form a layer. Molecular layers are also separated from each other forming a multilayer 3D structure (Figure S25).

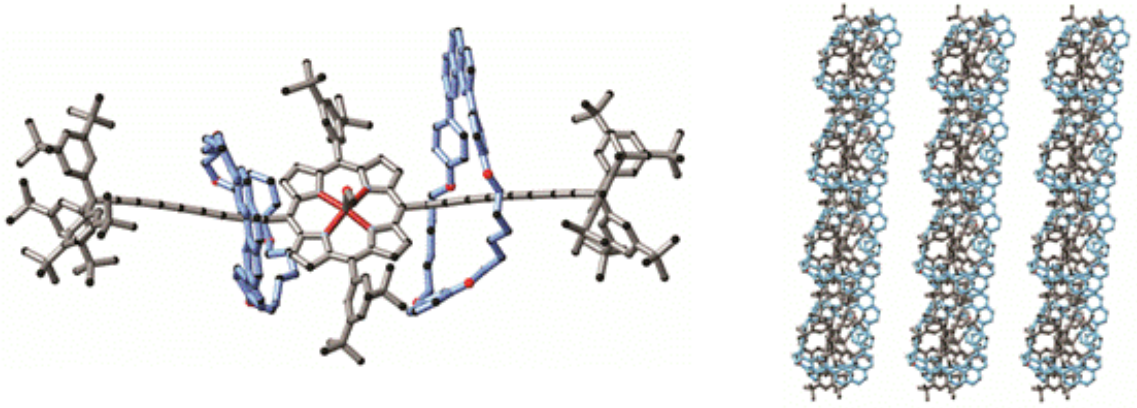


Figure S25. The crystal structure the [3]rotaxane **5c**·**(M1)$_2$** (left) and the side view of crystal packing. Hydrogen atoms and free solvent molecules are omitted for clarity.

(**2c**)$_2$·**M1:** Crystals suitable for X-ray diffraction studies were grown by diffusion of CH_3OH layer into solution of the compound (c = 2.5 mg/mL) in THF at 20 °C. The asymmetric unit contains one molecule of (**2c**)$_2$·**M1**, and the crystal belongs to the P-1 space group. Rotaxane molecules interact through dispersion forces between *t*-butyl groups of the Tr* moiety. Similar interactions exist between two identical hexayne chains locked inside the macrocycle. The crystal packing is shown in Figure S26.

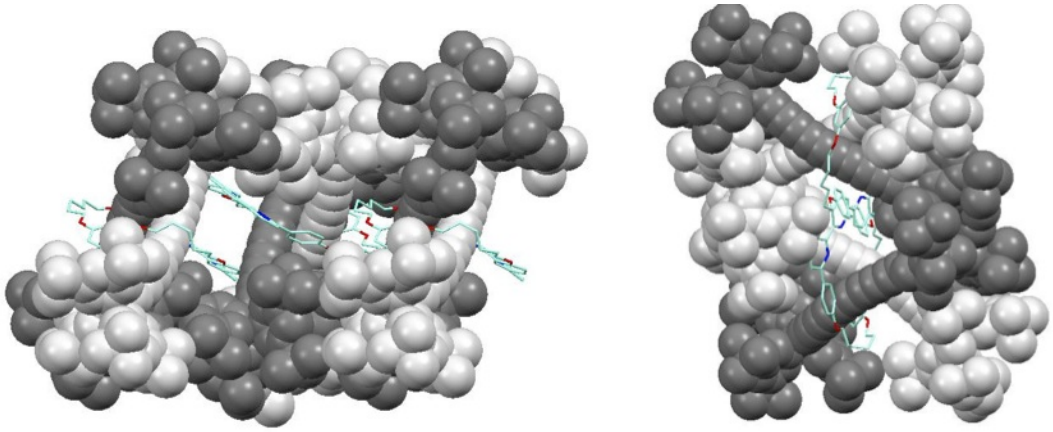


Figure S26. The crystal packing the [3]rotaxane **(2c)$_2$·M1** viewed down to crystallographic *a* (left) and *b* axes. The A and B chains of hexayne are colored differently. Hydrogen atoms are omitted for clarity.

F. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo TGA/ STDA 851e/1100/SF instrument using aluminum plate as a reference.

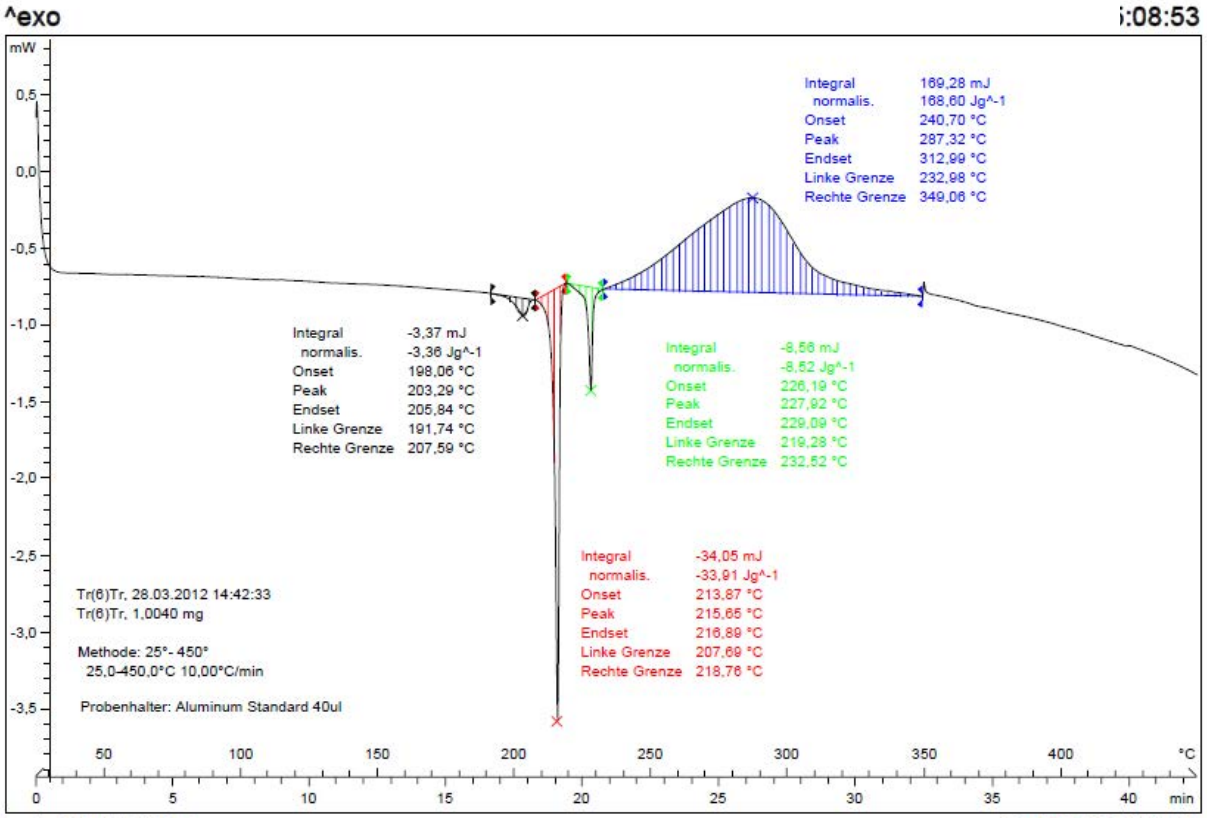


Figure S27. DSC trace of **2c·M1**. We assign the peak at 216 °C to the melting of the compound (from measuring the melting points by conventional method). The peaks at 203 and 228 °C are attributed to the phase transitions.

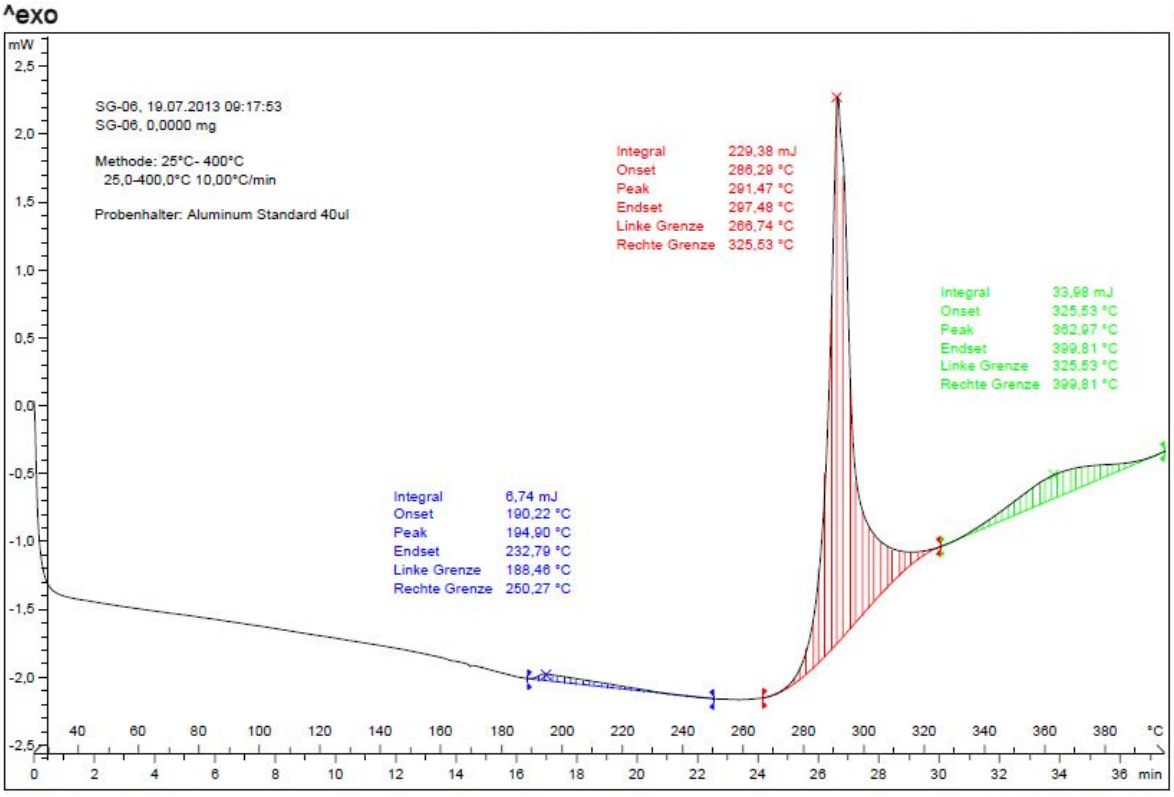


Figure S28. DSC trace of **2d·M1**.

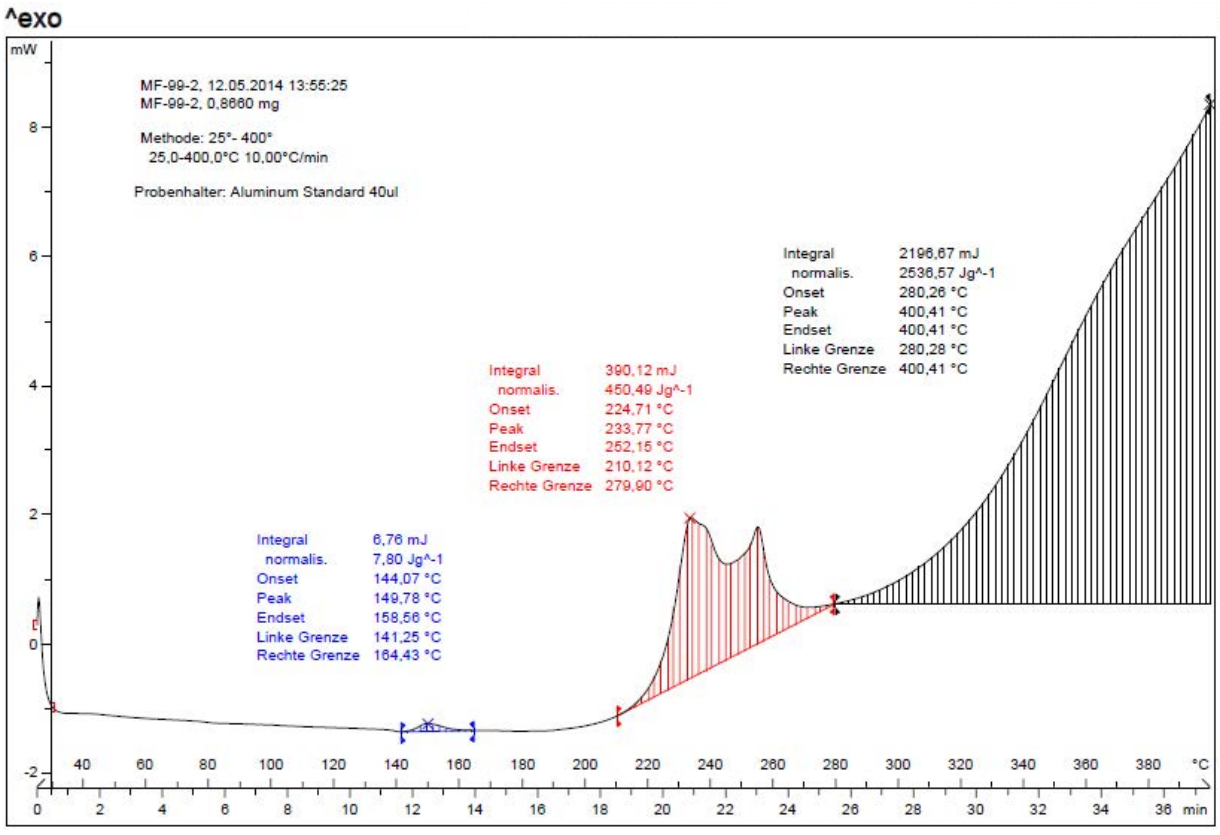


Figure S29. DSC trace of **2e·M1**.

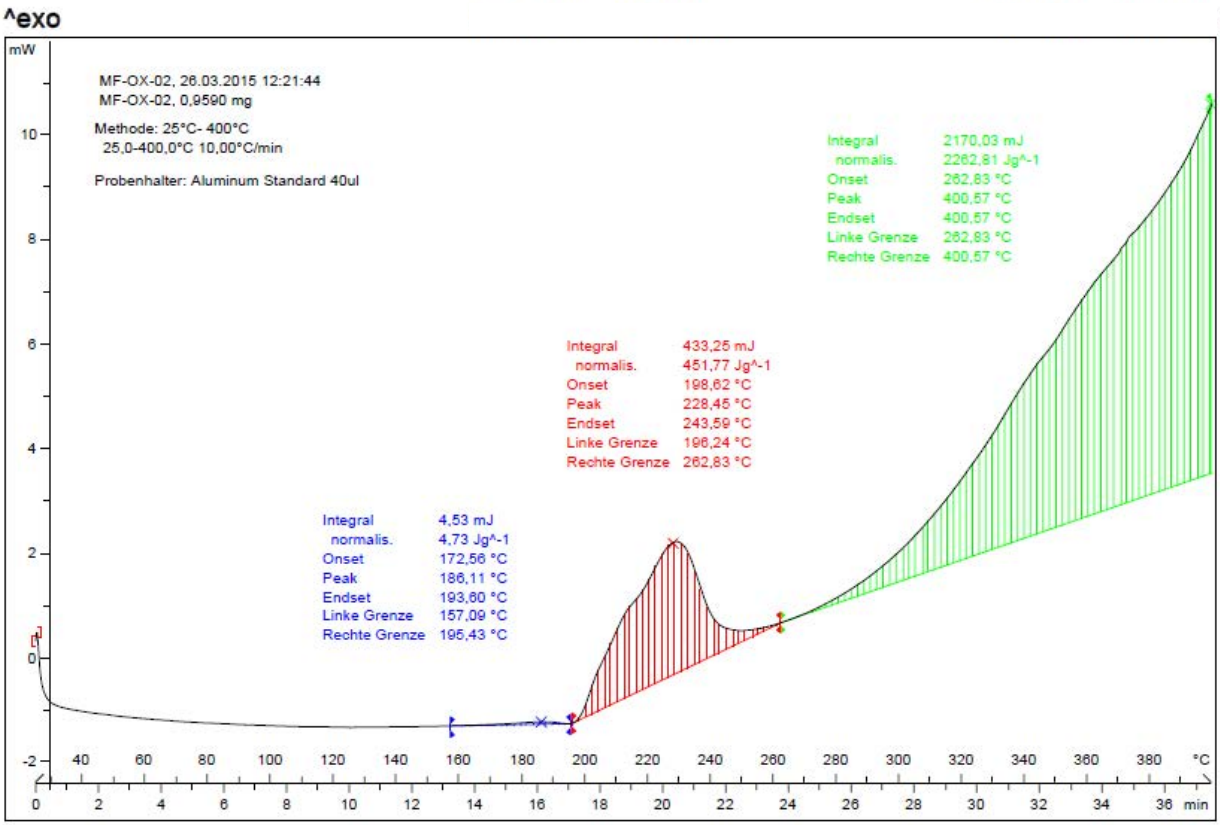


Figure S30. DSC trace of **2f·M1**.

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