Electronic Supplemental Information

Optimizing the formation of 2,6-bis(N-alkyl-benzimidazolyl)pyridine-containing [3]catenates through component design

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Section 1) Materials & Methods.

All solvents, potassium carbonate, sodium bicarbonate, and sodium hydroxide were purchased from Fisher Scientific. Deuterated solvents were purchased from Norell, Inc. Grubbs-Hoveyda Generation II catalyst and all other chemicals and reagents were purchased from Aldrich Chemical Co. Solvents were distilled from suitable drying agents.

Instrumentation

NMR spectra were recorded on a Varian Inova 600 MHz NMR spectrometer (^{13}C NMR = 150.8 MHz) using deuterated solvents (methylene chloride-d_2, chloroform-d or acetonitrile-d_3). Molecular weights of the materials were measured on a Bruker AUTOFLEX III MALDI TOF/TOF mass spectrometer using HABA [2-(4-hydroxyphenylazo)benzoic acid] as the matrix and sodium trifluoroacetate, Na(CF_3COO), as a doping salt.

Modeling

Conformational searches were carried out using the Macrocycle Conformational Sampling routine within MacroModel (version 9.9, Schrödinger, LLC, New York, NY, 2012). Reported structures are based on the lowest energy conformation after 10,000 simulation cycles using the OPLS_2005 force field with a 4r distance-dependent electrostatic treatment. The large-scale low mode (LLMOD) search was disabled. Other options were set as the defaults. Temperature = 300K.

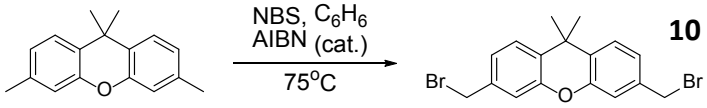
DOSY Experiments

All DOSY-NMR experiments were performed on dilute solutions in 5mm NMR tubes at a constant temperature of 25°C using a Varian Inova 600 MHz spectrometer. A Highland Technology model L700 pulsed gradient driver. The gradient strength was calibrated using an internal TMS standard (1% V/V). The DOSY experiments employed the bipolar pulse-pair

stimulated-echo (Dbppste) pulse sequence was used for acquiring diffusion data with 50 ms diffusion delay, 15 increments for gradient levels and 128 transients. Raw DOSY-NMR data was processed in MestReNova version 5.31-4696 using the Bayesian DOSY transformation algorithm. Before transformation of the array of spectra a phase correction was performed followed by a baseline correction utilizing a Bernstein polynomial fit (polynomial order 3). The processing conditions used for the spectra presented were a resolution factor of 0.90, with 4 repetitions and 256 points in the diffusion dimension. The transformation will fit a monoexponential function to the resonances of the full spectrum. This does not provide a direct measure of how well the data fits to this function. Thus, to provide this description a goodness of fit (R^2 value) was measured for the resonances observed in the aromatic region presented in the main-body of the manuscript and averaged. This was performed by measuring the signal intensities of the various resonances at each increment and graphing these values vs. the gradient strength at each increment. This scatter-plot was then fitted to a mono-exponential function and the R^2 value measured for each resonance.

Section 2) Synthesis of Precursors and Components

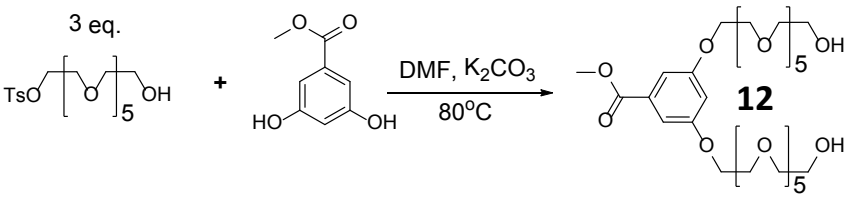
Synthesis of 3,6-bis(bromomethyl)-9,9-dimethyl-*9H*-xanthene



Scheme S1 Synthesis of **10.**

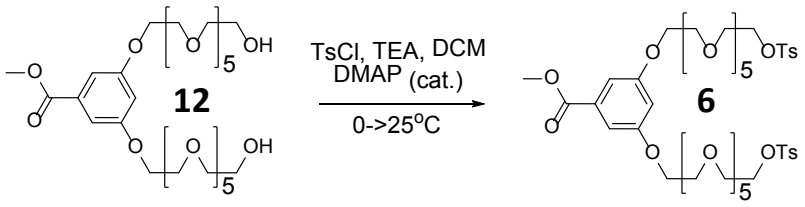
3,6,9,9-tetramethyl-*9H*-xanthene was first prepared according to a literature procedure.[1] 3,6,9,9-tetramethyl-*9H*-xanthene (4.16 g, 0.0175 mol) and *N*-bromosuccinimide (NBS) (6.20 g, 0.0348 mol, 2 eq.) were added to a round bottom flask along with a catalytic amount (20 mg, 0.122 mmol, 0.6 eq.) of azobisisobutyronitrile (AIBN). The round bottom was then equipped with a vigreux column and flushed with argon for a period of three minutes. 100 mL of anhydrous benzene was then cannulated into the round-bottom bringing the concentration of the 3,6,9,9-tetramethyl-*9H*-xanthene to 175 mM. The round-bottom flask was immersed in an oil bath and heated to 75 °C for a period of 18hrs, after which a precipitate was noted. Upon cooling to room temperature an increased amount of precipitate was observed and the reaction filtered. The filtrate was collected and the solvent removed under reduced pressure to yield an oil. Addition of hexanes to this oil leads to the further precipitation of a white solid. This was filtered again and filtrate collected and the solvent again removed under reduced pressure to yield an off white powder. This powder was recrystallized from ethanol to yield the 3,6-bis(bromomethyl)-9,9-dimethyl-*9H*-xanthene in a 38% yield. Melting Point: 138.8-139.8°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.12 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.09 (d, *J* = 1.8 Hz, 2H), 4.48 (s, 4H), 1.61 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.42, 137.41, 130.31, 126.87, 124.05, 117.08, 34.18, 32.98, 32.53. MALDI-MS(matrix: HABA, salt: CF_3COONa): *m/z* 396.0 ($[M]+H^+$).

Synthesis of Macrocycle Precursors



Scheme S2 Synthesis of **12.**

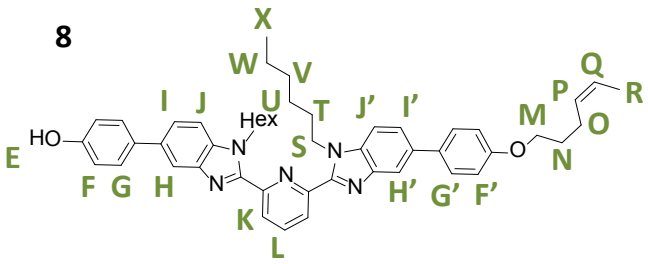
Hexaethylene glycol mono-p-toluenesulfonate was first prepared according to a literature procedure.[2] 0.091 mol (39.72g, 3eq.) of the monotosylate together with 0.030mol (5.04g) of 3,5-dihydroxybenzoate and 0.087mol (12.00g, 3 eq.) of K_2CO_3 are added to a 250 mL round bottom flask equipped with a stir-bar, a Vigreux condenser, and was then flushed with argon. 100 mL dry DMF is then added by cannula and the mixture is heated in an oil-bath to 80 °C and allowed to react for 24hrs. After reaction the DMF is removed under reduced pressure and resulting mixture triturated with $CHCl_3$ and then filtered. The filtrate was then collected and the solvent removed under reduced pressure to yield a yellow-brown oil. The oil was purified by column chromatography (silica gel, ethyl acetate, 3% methanol) to yield the pure diol **12** in a 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (d, *J* = 2.3 Hz, 2H), 6.68 (t, *J* = 2.3 Hz, 1H), 4.12 (t, *J* = 4.8 Hz, 4H), 3.87 (s, 3H), 3.84 (t, *J* = 4.8 Hz, 4H), 3.73 – 3.69 (m, 8H), 3.68 – 3.62 (m, 24H), 3.61 – 3.57 (m, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.91, 159.94, 132.06, 108.21, 107.08, 72.65, 70.95, 70.79, 70.73, 70.67, 70.64, 70.41, 70.31, 70.04, 69.73, 67.92, 61.77, 61.54, 52.39, 29.85. MALDI-MS (matrix: HABA, salt: CF_3COONa): *m/z* 719.0 ($[M]+Na^+$).



Scheme S3 Synthesis of **6.**

4.1 mmol (2.86 g) of **12**, 10.25 mmmol (1.95 g, 2.5 eq.) of p-toluenesulfonyl chloride and a catalytic amount of 4-Dimethylaminopyridine (DMAP) (0.205 mmol, 0.025g, 0.05 mol. %) was added to a 50mL round bottom flask (equipped with a stir bar) followed by 20 mL of dichloromethane (DCM) and 4.5 mL of triethylamine. The reaction was flushed with argon, submerged in an ice bath and stirred for 18hrs. The reaction was then allowed to warm to room temperature at which point the solvent was removed under reduced pressure. The resulting material was triturated with ethyl acetate and filtered. The filtrate was collected and the solvent removed under reduced pressure yielding yellow-brown oil. The resulting material was purified by column chromatography (silica gel, ethyl acetate, 3% methanol) to yield the pure pure ditosylate **6** in a 50% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 4H), 7.17 (d, *J* = 2.4 Hz, 2H), 6.67 (t, *J* = 2.4 Hz, 1H), 4.16 – 4.10 (m, 8H), 3.88 (s, 3H), 3.84 (t, J= 4.8 Hz, 4H), 3.72 – 3.69 (m, 4H), 3.69 – 3.58 (m, 24H), 3.56 (s, 8H), 2.43 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.91, 159.96, 144.97, 133.22, 132.09, 130.02, 128.15, 108.21, 107.06, 71.02, 70.92, 70.80, 70.75, 70.70, 69.77, 69.45, 68.86, 67.95, 52.41, 21.83. MALDI-MS (matrix: HABA, salt: CF_3COONa): *m/z* 1027 ([M]+Na^+).

8

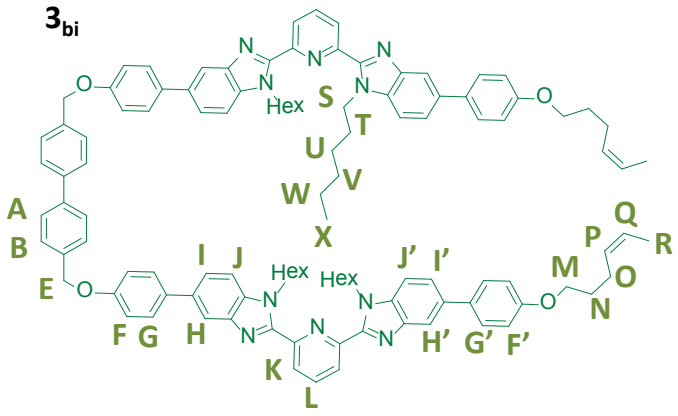


Synthesis of 8

4a (1.547g, 2.33 mmol),[3] tosylate **7**[4] (used crude, >90% purity by NMR, 0.592 g, 2.33 mmol), and K_2CO_3 (1.3 g, 9.11mmol) were added to a 25mL round bottom flask. Dry N,N'-Dimethylformamide (10 mL) was then added and the reaction flushed with argon. The round bottom flask was then immersed in an oil bath at 75°C and the reaction stirred for 18hrs. DMF was then removed under vacuum and the resulting dry material was triturated with chloroform. The resulting heterogeneous mixture was filtered and the organic layer collected and the solvent removed. The remaining solid was purified using column chromatography (silica gel, chloroform, 2% methanol) to yield the desired material in 49% as an off white solid. Melting Point: 91.2-94.1°C ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 0.64 (m, 6H, **X**), 1.05 (m, 8H, **W, V**), 1.10 (m, 4H, **U**), 1.66 (d, 3H, J= 4.8 Hz, **R**), 1.74 (m, 2H, J= 7.2 Hz, **T**), 1.87 (m, 2H, 6.6 Hz, J= 7.2 Hz, **N**), 2.19 (q, 2H, 6.6 Hz, J= 7.2 Hz, **O**), 4.01 (t, 2H, 6.6 Hz, **M**), 4.71 (t, 4H, J=7.2 Hz, **S**), 5.48 (m, 2H, **P & Q**), 6.97 (d, 2H, AB system, J= 8.4 Hz, **F'**), 7.00 (d, 2H, AB system, J= 9.0 Hz, **F**), 7.58-7.41 (m, 8H, **I, I', J, J' and G, G'**), 7.66 (bs, 1H, **E**), 7.97 (s, 1H, **H**), 8.01 (s, 1H, **H'**), 8.06 (t, 1H, J= 7.8 Hz, **L**), 8.32 (dd, 2H, J= 7.8 Hz, J= 1.8 Hz,**K**). δ_C (151 MHz, $CDCl_3$) 158.67, 156.84, 150.73, 150.58, 149.86, 149.78, 143.16, 142.98, 138.62, 137.03, 136.66, 135.42, 135.24, 134.16, 133.30, 130.46, 128.70, 128.54, 125.90, 125.82, 123.53, 123.50, 118.02, 117.86, 116.43, 115.10, 110.70, 110.63, 67.59, 45.27, 31.34, 30.23, 29.30, 29.12, 26.52, 22.54, 18.12, 13.93. MS (MALDI, positive): *m/z 746* ([M]+H^+), 768 ([M]+Na^+).

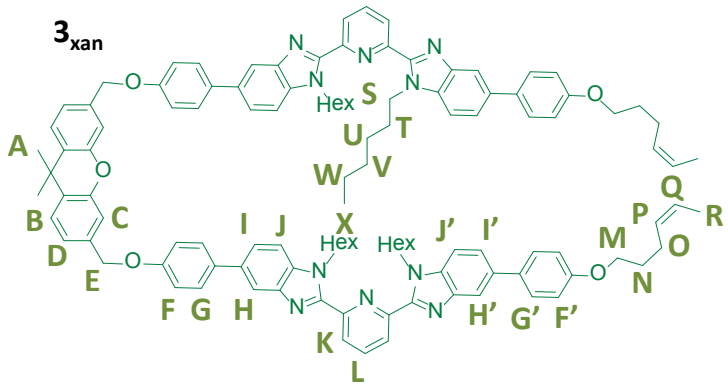
Synthesis of 3_{bi} and 3_{xan}

8 (0.700 g, 0.939 mmol), 3,6-bis(bromomethyl)-9,9-dimethyl-*9H*-xanthene **10** (0.185 g, 0.467 mmol) or 4,4'-Bis(chloromethyl)-1-1'-biphenyl **9** (0.117g, 0.467mmol) and K_2CO_3 (0.500 g, 3.62 mmol) were added to a 8mL conical vial. Dimethylformamide (3 mL) was then added and the reaction flushed with argon. The vial was then immersed in an oil bath at 75°C and stirred for 18hrs. DMF was then removed with vacuum and the solids were stirred with chloroform and filtered. The filtrate was collected and the solvent removed under reduced pressure. The resulting material was purified using column chromatography (alumina, 5:1 hexanes:chloroform, 2:5 and 1:1 in 250 mL increments). The product came off in a 1:1 hexanes:chloroform fraction. Further purification was achieved using silica-prepatory plates eluted with chloroform and 3% methanol to yield the product in 50% ($\mathbf{3_{xan}}$) and 67% ($\mathbf{3_{bi}}$) yields.



***3**$_{bi}$* Melting Point: 106.8-109.3°C. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.33 (d, *J* = 7.8 Hz, 4H, **K**), 8.06 (t, *J* = 7.9 Hz, 2H, **L**), 7.99 (d, *J* = 1.5 Hz, 4H, **H**), 7.97 (d, *J* = 1.5 Hz, 4H, **H'**), 7.69 (d, *J* = 8.1 Hz, 4H, **G**), 7.66 (d, *J* = 8.6 Hz, 4H, **G'**), 7.62 (d, *J* = 8.7 Hz, 4H, **A**), 7.58 (m, 4H, **I, I'**), 7.53 (m, 4H, **J, J'**), 7.12 (d, *J* = 8.6 Hz, 4H, **F**), 7.00 (d, *J* = 8.8 Hz, 4H, **F'**), 5.51 (m, 4H, **P, Q**), 5.20 (s, 4H, **E**),

4.77 (t, *J* = 7.4 Hz, 8H, **S**), 4.02 (t, *J* = 6.5 Hz, 4H, **M**), 2.18 (m, 4H, **O**), 1.86 (m, *J* = 1.9 Hz, 4H, **N**), 1.77 (m, 8H, **T**), 1.67 (d, *J* = 5.3 Hz, 6H, **R**), 1.13 (m, 8H, **U**), 1.08 (m, 16H, **V, W**), 0.65 (t, *J* = 6.9 Hz, 12H, **X**).^{13}C NMR (151 MHz, $CDCl_3$) δ 158.67, 158.31, 150.91, 150.88, 150.67, 150.20, 143.59, 138.37, 136.88, 136.45, 136.32, 135.70, 135.64, 134.86, 134.34, 130.50, 129.85, 128.65, 128.55, 126.76, 125.94, 125.69, 123.35, 122.33, 118.29, 118.23, 115.58, 115.44, 115.13, 110.67, 110.64, 69.76, 67.62, 46.11, 45.25, 34.13, 32.76, 32.08, 31.39, 30.28, 29.34, 29.22, 29.15, 26.55, 22.89, 22.58, 18.15, 14.32, 13.97, 8.82. (MALDI, positive): *m/z* 1670 ([M]+H$^+$), 1693 ([M]+Na).

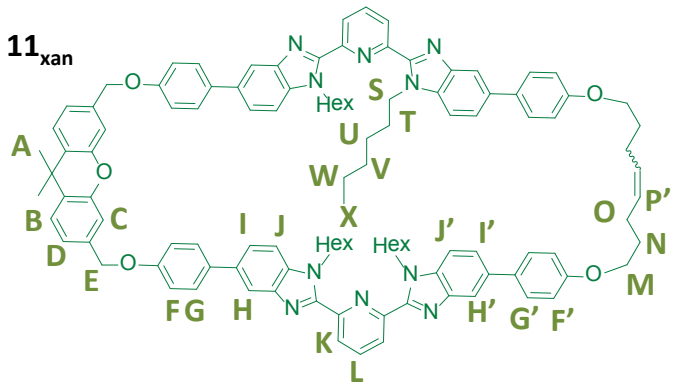


3$_{xan}$ Melting Point: 193.1-195.2°C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.662 (m, 12H, **X**), 1.079 (m, 24H, **U, V, W**), 1.662 (m, 12H, **A, R**), 1.752 (m, 8H, **T**), 1.880 (m, 4H, **N**), 2.188 (m, 4H, **O**), 4.025 (t, 4H, J= 6.6 Hz, **M**), 4.730 (t, 8H, J= 7.2 Hz, **S**), 5.192 (s, 4H, **E**), 5.491 (m, 4H, **P, Q**), 7.014 (d, 4H, J= 8.7 Hz, **F'**), 7.129 (d, 4H, J= 8.7 Hz, **F**), 7.592 (m, 24H, **G, G', I, I', J, J'**), 8.034 (s, 4H, **H, H'**), 8.073 (t, 2H, J= 7.9 Hz, **L**), 8.341 (d, 4H, J= 7.8 Hz, **K**). ^{13}C NMR (150.8 MHz, $CDCl_3$):δ 143.7, 140.7, 138.4, 136.44, 136.41, 136.3, 135.7, 135.68, 134.8, 134.3, 130.544, 128.7, 128.6, 128.3, 127.6, 126.0, 125.7, 128.3, 127.6, 126.0, 123.7, 118.32, 118.27, 115.5, 115.1, 110.7, 110.71, 70.1, 68.8 67.6, 67.5, 45.3, 31.4, 30.3, 29.4, 29.2, 29.18, 29.1, 26.6, 22.7, 18.3, 14.1. (MALDI, positive): *m/z* 1727 ([M]+H$^+$), 1749 ([M]+Na$^+$).

Synthesis of 11_{xan}

Dichloromethane (DCM) was passed over a short plug of alumina and then degassed by directly bubbling argon into the solvent while the stirring for a period of 15 minutes. 9 mL of DCM was added to $\mathbf{3}_{xan}$ (0.103 g, 0.0599 mmol) in a 20mL round bottom flask. Argon was bubbled through this solution for 3 minutes and a vigreux condenser attached to the reaction which was kept under a Argon atmosphere. 30 mol% Hoveyda-Grubbs Generation II metathesis catalyst (0.011g, 0.0180 mmol) was weighed out and placed in a 3mL glass vial. 1 mL of the degassed solvent was used to dissolve the metathesis catalyst and this solution was then injected into the 20 mL round bottom reaction flask, bringing the final concentration to 6mM. The reaction was then flushed again with argon for a period of 3 minutes. Periodically (every 10 minutes for the first hour) the reaction was bubbled with argon for a period of 3-5 minutes. If any change in solution volume was noted additional DCM was added to maintain the initial 6mM concentration. The reaction was stirred at room temperature for 18 hours, after which the solvent was removed and the product purified using a silica gel preparative plate ($CHCl_3$, 3% MeOH) to obtain the product in a 35% yield.

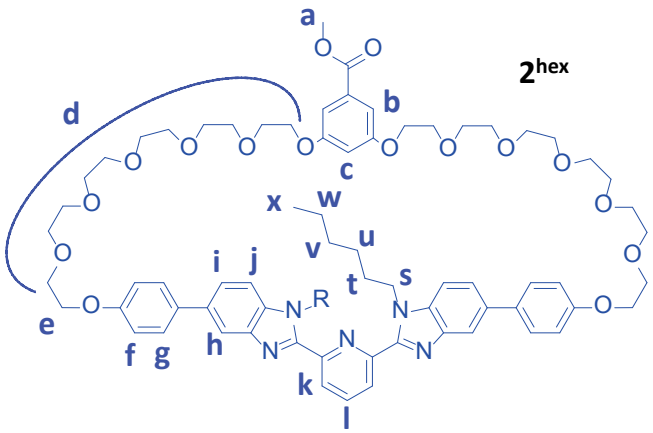
11$_{xan}$



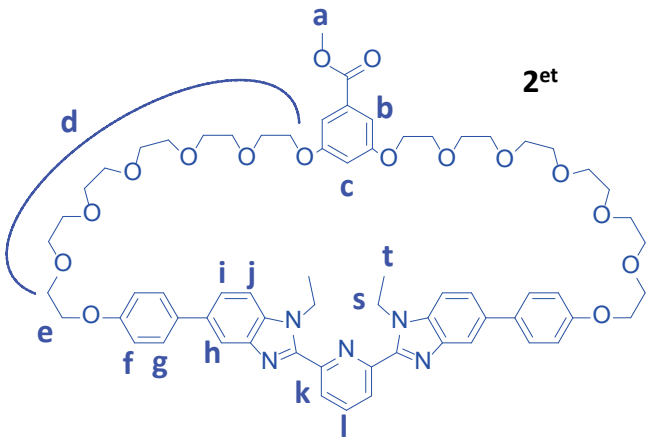
^{1}H NMR (600 MHz, CD_2Cl_2): δ 8.29 (m, 4H, **K**), 7.98 (m, 4H, **L**), 7.92 (s, 2H, **H**), 7.88 (s, 2H, **H'**), 7.56-7.40 (m, 18H, **I, I', J, J', B, G, G'**), 7.33 (m, 2H, **B**), 7.14 (d, J= 7.8 Hz, 2H, **D**), 7.08 (s, 2H, **C**), 6.98 (d, J = 7.0 Hz, 4H, **F**), 6.92 (d, 3H, J = 7.0Hz, **F'**), 6.89 (d, J=7.0Hz, 1H, **F'**), 5.53 (m, 2H, **P'**), 5.26 (m, 4H, **E**), 4.68 (t, J = 7.1Hz, 4H, **S**), 4.62 (m, 4H, **S**), 3.98 (t, J=6.3 Hz, 3H, **M**), 3.86 (t, J=6.1 Hz, 1H, **M**), 2.31 (m, 8H, **U**), 1.88 (m, 3H, **O**), 1.82 (m, 2H, **O**), 1.62 (m, 6H, **A**), 1.27 (m, 4H, **N**), 0.97 (m, 24H, **W, V, U**), 0.58 (m, 12H, **X**). ^{13}C NMR (150.8 MHz, CD_2Cl_2): δ (151 MHz, cd_2cl_2) 159.00, 157.89, 151.20, 151.08, 151.04, 150.68, 144.03, 138.48, 138.13, 136.28, 136.19, 136.12, 135.00, 134.43, 131.06, 130.43, 129.91, 128.77, 128.72, 127.18, 125.87, 123.34, 121.83, 118.26, 118.15, 116.19, 115.39, 115.28, 115.01, 111.12, 111.08, 111.01, 78.12, 77.34, 69.47, 67.30, 62.61, 56.24, 45.53, 45.48, 34.50, 34.40, 32.74, 32.51, 32.26, 31.73, 31.71, 30.57, 30.53, 30.27, 30.09, 29.94, 29.78, 29.68, 29.54, 29.20, 29.04, 28.47, 28.41, 27.18, 26.85, 26.80, 26.70, 25.39, 24.01, 23.27, 23.16, 22.93, 22.91, 15.62, 14.46, 14.35, 14.07. (MALDI, positive): *m/z* 1693 ([M]+Na^+).

Synthesis of 2

2^{hex} and **2**^{et} were prepared by adapting a standard crown ether literature procedure.[5] A 100mL dropping funnel containing the bitosylate **6**[6] (1.000g, 0.995 mmol) and **4** (0.661 g **4a** or 0.549 g **4b**, 0.995 mmol;) in 65 mL of DMF was fitted to a 250 mL round bottom flask containing Cs_2CO_3 (3.000g, 9.2 mmol) and stir bar. The reaction vessel was flushed with argon before anhydrous DMF (100 mL) was added by cannula. The reaction was submerged in an oil bath and heated to 65°C while rapidly stirring to create a suspension of Cs_2CO_3. The dissolved mixture of components in the dropping funnel was slowly added to this suspension over the course of 18 hrs. After complete addition of components the final concentration of the reaction was 6mM. The reaction was allowed to stir at 65°C for three days, after which the solvent was removed and the dry solids triturated with $CHCl_3$. The solids were filtered and the solvent was collect and removed under vacuum. The resulting oil was purified using column chromatography (silica gel, ethyl acetate:methanol gradient 100:0…..86:14) to yield the desired material. Linear components came off in the less polar fractions while the macrocyclic product was obtained as a light yellow oil in the most polar fractions (14% MeOH) in 16% (**2**^{hex}) and 24% (**2**^{et}) yields.



2^{hex}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.8 Hz, 2H, **k**), 8.03 (t, *J* = 7.9 Hz, 1H, **l**), 7.58 (d, *J* = 8.8 Hz, 4H, **g**), 7.55 (dd, *J* = 8.5, 1.7 Hz, 2H, **i**), 7.44 (d, *J* = 8.4 Hz, 2H, **j**), 7.09 (d, *J* = 2.4 Hz, 2H, **b**), 7.07 (d, *J* = 8.8 Hz, 4H, **f**), 6.50 (t, *J* = 2.4 Hz, 1H, **c**), 4.61 (t, *J* = 7.4 Hz, 4H, **s**), 4.26 (m, 4H, **e**), 3.95-3.47 (m, 50H, **d**, **a**), 1.74 (m, 4H, **t**), 1.10 (m, 4H, **u**), 1.04 (m, 8H, **v, w**), 0.65 (m, 6H, **x**). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.79, 159.81, 158.39, 150.87, 150.14, 143.51, 138.20, 136.22, 135.46, 134.64, 131.98, 128.41, 125.24, 123.24, 118.16, 115.80, 110.59, 107.93, 106.92, 71.17, 70.90, 70.79, 70.72, 70.64, 70.60, 70.55, 70.49, 70.14, 69.59, 68.17, 67.57, 67.57, 58.07, 52.32, 46.13, 45.24, 31.36, 30.26, 29.86, 26.53, 22.56, 13.96, 8.78, 8.19. (MALDI, positive): *m/z* 1324 ([M]+H$^+$), *m/z* 1346 ([M]+Na$^+$).



2^{et}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.8 Hz, 2H, **k**), 8.03 (t, *J* = 7.8 Hz, 1H, **l**), 8.00 (s, 2H, **h**), 7.59 (d, *J* = 8.7 Hz, 4H, **g**), 7.56 (dd, *J* = 8.4, 1.5 Hz, 2H, **i**), 7.46 (d, *J* = 8.4 Hz, 2H, **j**), 7.08 (m, 6H, **b, f**), 6.48 (t, *J* = 2.3 Hz, 1H, **c**), 4.72 (q, *J* = 7.2 Hz, 4H, **s**), 4.28 (m, 4H, **e**), 3.94-3.47 (m, 50H, **d, a**), 1.37 (t, *J* = 7.2 Hz, 6H, **t**). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.79, 159.80, 158.43, 150.56, 150.12, 143.67, 138.18, 136.25, 135.21, 134.59, 131.96, 128.40, 125.50, 123.26, 118.19, 115.85, 110.51, 107.90, 106.89, 71.19, 70.93, 70.80, 70.70, 70.63, 70.58, 70.54, 70.47, 70.19, 69.57, 68.19, 67.56, 52.33, 40.14, 15.67. (MALDI, positive): *m/z* 1235 ([M]+Na$^+$).

Section 3) T1 values

T1 values were calculated for all peaks in the aromatic range presented in figures in the main body of the manuscript. The minimum and maximum values are provided to give a description for the range of measured T1 values. In addition, the averages of these values were also presented. These experiments were conducted utilizing the same conditions as the DOSY measurements (i.e. CD_2Cl_2 and dilute concentrations).

Table S1: T1 relaxation values measured for resonances in the aromatic region of the various samples.

sample	T1 (s) shortest	T1 (s) longest
$\mathbf{2}^{hex}$	1.33 ± 0.01	2.58 ± 0.03
$\mathbf{3}_{bi}$	1.56 ± 0.02	3.14 ± 0.02
$\mathbf{1}_{xan}^{et}$	1.38 + 0.04	2.89 + 0.03
$(\mathbf{2}^{hex}\cdot\mathbf{Zn}^{2+})_2\cdot\mathbf{3}_{xan}$	1.02 ± 0.01	2.72 ± 0.08

Section 4) Procedures for the Preparation of [3]metallopseudorotaxanes

$(2^{hex}\cdot Zn^{2+})_2\cdot 3_{bi,}$ $(2^{hex}\cdot Zn^{2+})_2\cdot 3_{xan}$ and $(2^{et}\cdot Zn^{2+})_2\cdot 3_{xan}$

3.40 µmol of **2**^{hex} or **2**^{et} is dissolved in 200-300 µL of deuterated dichloromethane and added to a 178 x 10mm NMR tube then brought to a total volume of 850µL with additional deuterated dichloromethane. 20 µL of a stock solution of either **3**$_{bi}$ or **3**$_{xan}$ (6.47 mM in deuterated dichloromethane) is added to the solution of **2** and the ^{1}H-NMR recorded. This process is repeated until the integrations of the pyridine resonances **K** and **k** are 1:1 (i.e. when there is 2 eq. **2** to 1 eq of **3**). After adjusting the ratio of these two components a metal solution is then prepared using $Zn(ClO_4)_2\cdot 6(H_2O)$ in deuterated acetonitrile (14.5 mM). 20µL of a stock metal ion solution ($Zn(ClO_4)_2\cdot 6(H_2O)$ in deuterated acetonitrile, 14.5 mM) is then added to the solution and the ^{1}H -NMR recorded. In this solvent system the components are in slow exchange and both unbound (e.g. pyridine resonances: **K** (8.34 ppm), **k** (8.23 ppm), **L** (8.08 ppm) and **l** (8.05 ppm) and metal-bound (**K** (8.72 ppm), **k** (8.80 ppm), **L** (9.14 ppm) and **l** (9.03 ppm) species can be observed (See Figure S1). This process is repeated until the unbound pyridine resonances are no longer observed in the ^{1}H-NMR spectrum.

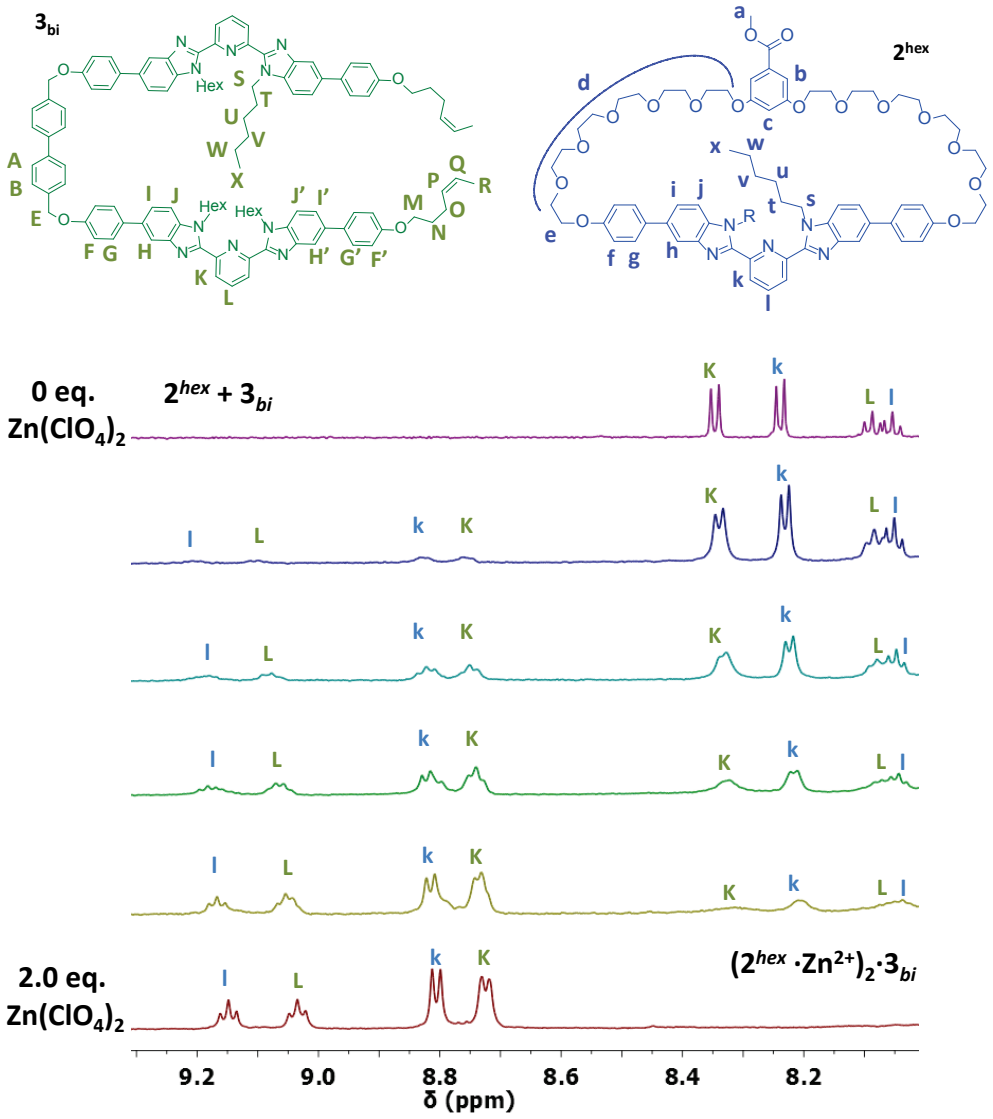


Figure S1: Partial 1H-NMR (CD_2Cl_2 and 0, 2.2, 4.5, 6.6, 8.6, 10% CD_3CN top to bottom) as a small amount of $Zn(ClO_4)_2$ is being added to a mixture of ***2*** ^{Hex} and ***3*** $_{bi}$. Number of equivalents compared to the number of ***3*** $_{bi}$ in solution.

Section 5) Large Scale Synthesis of [3]catenanes

Adopted from a literature procedure.[7] First stock solutions of $Fe(ClO_4)_2$ (43.8 mM) were prepared in acetonitrile (MeCN). Then to a chloroform solution of **2** (62.5mg $\mathbf{2}^{hex}$ or 49.9mg $\mathbf{2}^{et}$, 0.0472 mmol) 0.0472 mmol of the dissolved Fe^{2+} is added to solution. To this 1:1 solution of metal ion and **2**, 0.5 eq. of **3** (39.4 mg $\mathbf{3}_{bi}$ or 40.7 mg $\mathbf{3}_{xan}$, 0.0236 mmol,) is added and the solution is stirred for 5 minutes at which point the solvent is removed. The dry ($\mathbf{(2\cdot Zn^{2+})_2\cdot 3}$) then submitted to the olefin metathesis reaction conditions detailed previously for **11**. Briefly, ($\mathbf{(2\cdot Zn^{2+})_2\cdot 3}$) is dissolved in dried DCM (4mL), transferred to an 8 mL conical vial before 30 mol. % of Hovyeda Grubbs generation II catalyst in DCM to bring the final concentration to 4.7mM. The reaction was flushed periodically with argon and after 20hrs (TLC reveals a new spot that is different than starting materials) additional catalyst (10 mol. %) in DCM is added to the reaction. The reaction is allowed to react for an additional 24 hrs, for a total reaction period of 48hrs, before being quenched with 1mL of ethyl vinyl ether. Following reaction the crude product is demetallated using 1M NaOH under sonication. The time required for this demetallation required optimization, best results were achieved with 10 minutes, so as to reduce any deprotection of the methyl ester moiety on **2**. The organic phase is removed, dried with molecular sieves then solvent removed by vacuum. The crude product is purified using silica gel preparative plate ($CHCl_3$, 6% MeOH) in 38% ($\mathbf{1}_{xan}^{hex}$) and 45% ($\mathbf{1}_{xan}^{et}$) yields. $\mathbf{1}_{xan}^{hex}$ ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.15 (m, 8H), 7.92 (m, 4H), 7.88 (s, 4H), 7.82 (s, 2H), 7.79 (s, 2H), 7.48 (d, J=8.2 Hz, 8H), 7.42 (m, 10H), 7.32 (m, 18H), 7.00 (m, 8H), 6.93 (d, J=8.5 Hz, 8H), 6.87 (d, J=8.4 Hz, 4H), 6.82 (d, J=8.5 Hz, 4H), 6.37 (s, 2H), 5.41 (s, 2H), 5.07 (s, 4H), 4.55 (m, 16H), 4.13 (m, 8H), 3.89 (t, J= 6.6 Hz, 4H), 3.81 (m, 8H), 3.72 (m, 14H), 3.59 (m, 12H), 3.48 (m, 8H), 3.40 (m, 40H), 2.09 (m, 4H), 1.74 (m,4H), 1.67 (m, 12H), 1.48 (s, 6H), 1.01-0.86(m, 42H), 0.64 (m, 12H), 0.58 (m, 12H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ

166.94, 160.24, 158.78, 158.66, 158.06, 151.33, 151.16, 151.00, 150.90, 150.70, 150.64, 144.11, 144.01, 143.94, 138.37, 138.24, 138.01, 136.14, 136.02, 135.92, 134.84, 134.79, 132.49, 130.69, 129.82, 128.71, 128.65, 127.00, 125.71, 125.29, 123.22, 121.90, 118.31, 118.13, 115.97, 115.86, 115.43, 115.34, 115.20, 111.01, 108.17, 106.71, 71.35, 71.11, 71.05, 70.98, 70.95, 70.87, 70.76, 70.30, 69.85, 69.44, 68.38, 67.98, 67.58, 45.56, 45.45, 45.37, 32.66, 31.82, 31.76, 30.64, 30.57, 30.55, 30.26, 29.32, 29.18, 26.91, 26.82, 22.99, 22.93, 14.21, 14.15. (MALDI, positive): *m/z* 4317 ([M]+H^{+1}), *m/z* 4340 ([M]+Na^{+}). $\mathbf{1}_{\boldsymbol{xan}}^{\boldsymbol{et}}$ ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.12 (m, 8H), 7.87 (m, 8H), 7.81 (s, 2H), 7.75 (s, 2H), 7.48 (d, J=7.3 Hz, 8H), 7.40 (m, 10H), 7.32 (m, 18H), 7.21 (m, 4H), 7.03 (d, J=7.9, 4H), 6.99 (m, 7H), 6.94 (d, J= 8.1 Hz, 8H), 6.83 (m, 8H), 6.37 (bs, 2H), 5.42 (bs, 2H), 5.07 (s, 4H), 4.52 (m, 16H), 4.14 (m, 8H), 3.89 (m, 4H), 3.81 (m, 8H), 3.73 (m, 14H), 3.59 (m, 8H), 3.52 (m, 16H), 3.48 (m, 8H), 3.41 (m, 40H), 2.19 (m, 1H), 2.11 (m, 4H), 1.70 (m, 16H), 1.58 (m, 8H), 1.48 (m, 4H), 1.22 (t, J=7.1 Hz, 12H), 0.94 (m, 24H), 0.56 (m, 12H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 166.94, 160.25, 158.79, 158.68, 158.03, 151.18, 150.94, 150.64, 144.19, 144.02, 143.93, 138.35, 138.15, 138.03, 136.13, 136.02, 135.94, 135.64, 134.80, 134.33, 132.51, 130.71, 129.83, 128.63, 127.02, 125.69, 125.44, 123.21, 121.91, 118.30, 118.10, 115.91, 115.42, 115.34, 115.16, 111.00, 110.89, 108.17, 106.72, 71.38, 71.13, 71.06, 70.97, 70.87, 70.77, 70.35, 69.85, 69.43, 68.43, 67.99, 67.58, 52.50, 45.42, 40.45, 32.67, 31.75, 30.55, 29.32, 29.18, 26.81, 22.92, 15.79, 14.14. (MALDI, positive): *m/z* 4117 ([M]+Na^{+}).

Section 6) Additional NMR Spectra Related to the Formation of a [3]pseudorotaxane

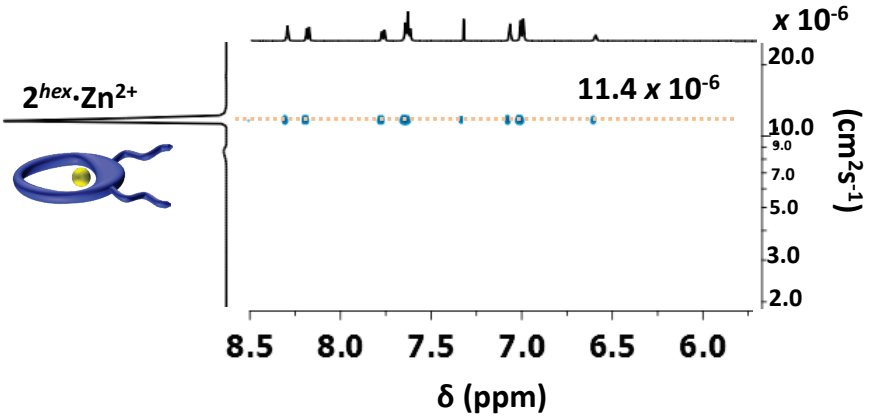


Figure S2: DOSY-NMR (conc. 3.5 mM, CD_2Cl_2) of $\mathbf{2^{hex}\cdot Zn^{2+}}$.

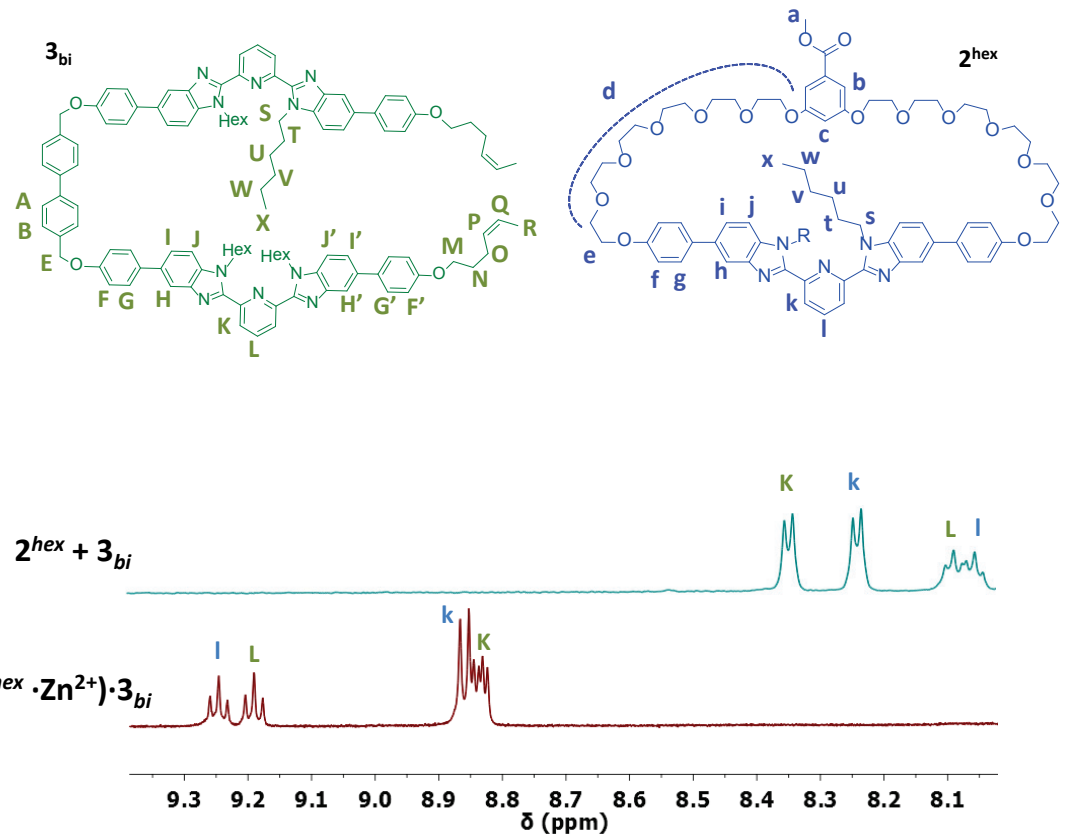


Figure S3: Partial 1H-NMR (600 MHz) comparing a mixture of components $\mathbf{2^{nex} + 3_{bi}}$ (top) and $\mathbf{(2^{hex}\cdot Zn^{2+})\cdot 3_{bi}}$ (bottom) in CD_2Cl_2. With protons labeled and structures.

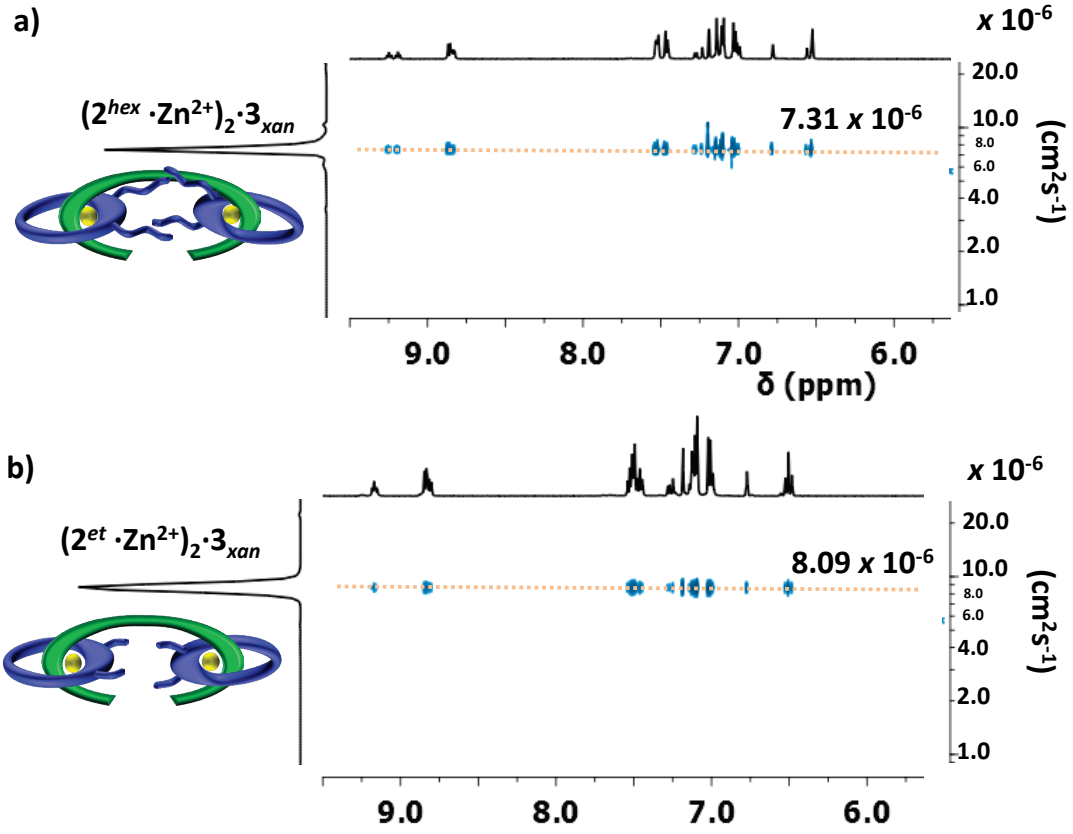


Figure S4: DOSY-NMR (conc. 3.5 mM, CD_2Cl_2) of the targeted [3]pseudorotaxanes **a)** $(2^{hex}\cdot Zn^{2+})_2\cdot 3_{xan}$ and **b**) $(2^{et}\cdot Zn^{2+})_2\cdot 3_{xan}$.

Section 7) Additional NMR Spectra Related to Crude Ring Closing Reactions

COSY CRUDE RING CLOSURE

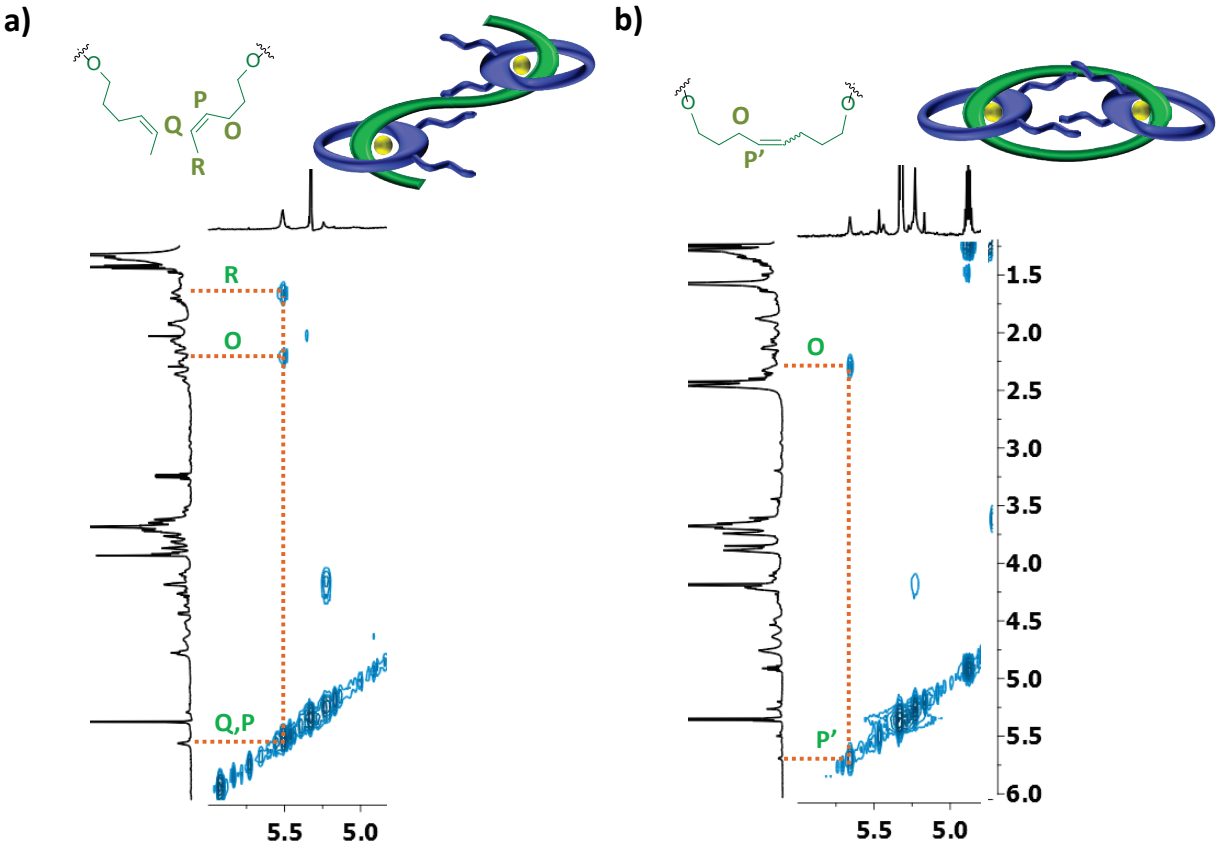


Figure S5: Partial COSY-NMRs (conc. 3.5 mM, CD_2Cl_2) of the [3]metallopseudorotaxane **$(2^{hex}\cdot Zn^{2+})_2\cdot 3_{bi}$** (left) and crude ring-closing reactions of **$(2^{hex}\cdot Zn^{2+})_2\cdot 3_{bi}$** (right) showing the disappearance of the correlation between **Q** and **R** after the olefin metathesis reaction.

MALDI TOF-TOF of the Crude Ring Closing Reactions

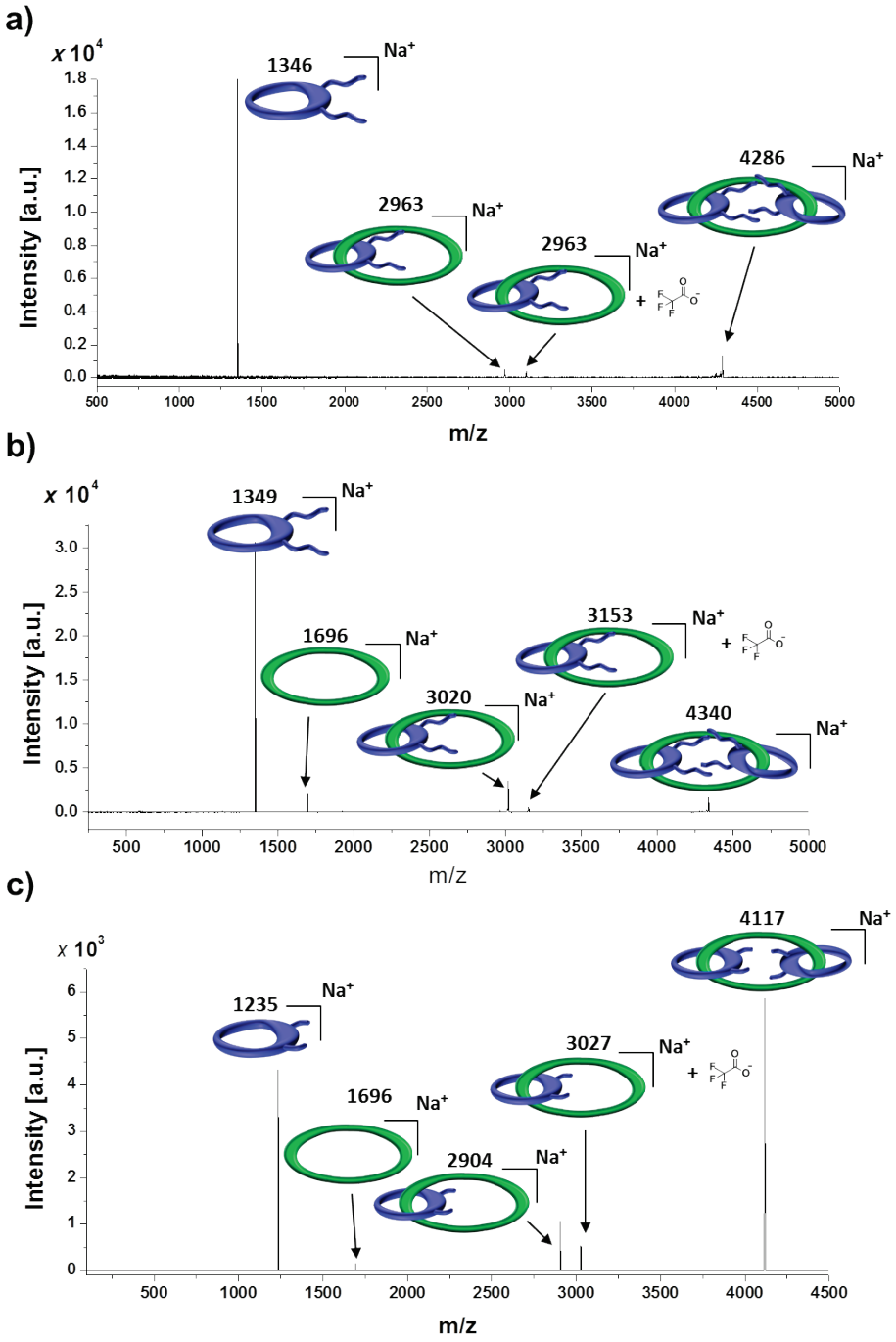


Figure S6: MALDI TOF-TOF using respective parent ion of the [3]catenane yields only fragments consistent with the [2]catenane and the macrocyclic components. **a)** $\mathbf{1}_{bi}^{hex}$, **b)** $\mathbf{1}_{xan}^{hex}$ **c)** $\mathbf{1}_{xan}^{et}$.

Crude 1H-NMR spectrum of Ring Closing Reaction

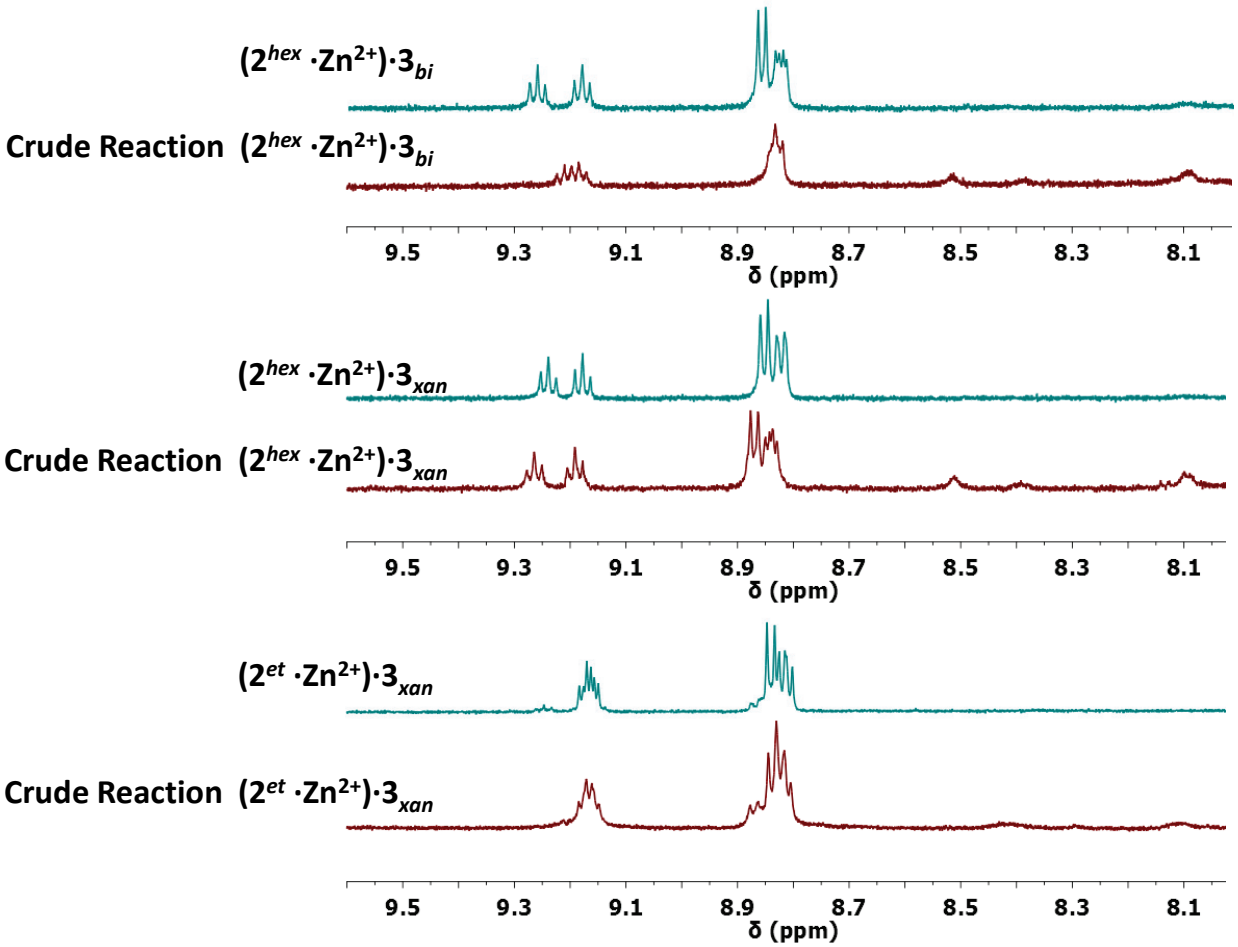


Figure S7: Partial 1H-NMRs (conc. 3.5 mM, CD_2Cl_2) of the crude ring-closing reactions of $(2^{hex}{\cdot}Zn^{2+})_2{\cdot}3_{bi}$, $(2^{hex}{\cdot}Zn^{2+})_2{\cdot}3_{xan}$ and $(2^{et}{\cdot}Zn^{2+})_2{\cdot}3_{xan}$.

Section 8) NMR Characterization of isolated [3]catenanes

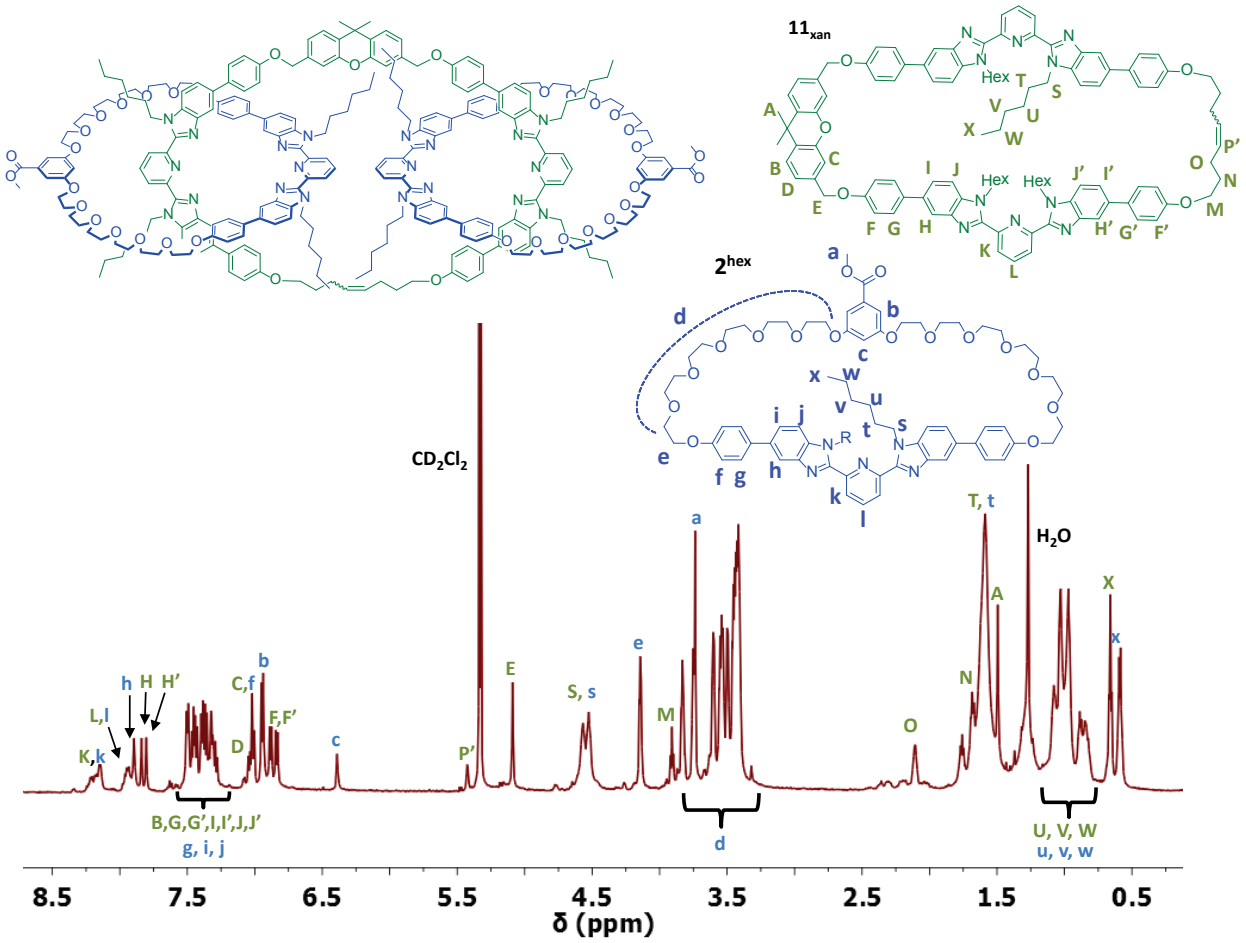


Figure S8: Full ^{1}H-NMR in CD_2Cl_3 of $\mathbf{1}_{xan}^{hex}$.

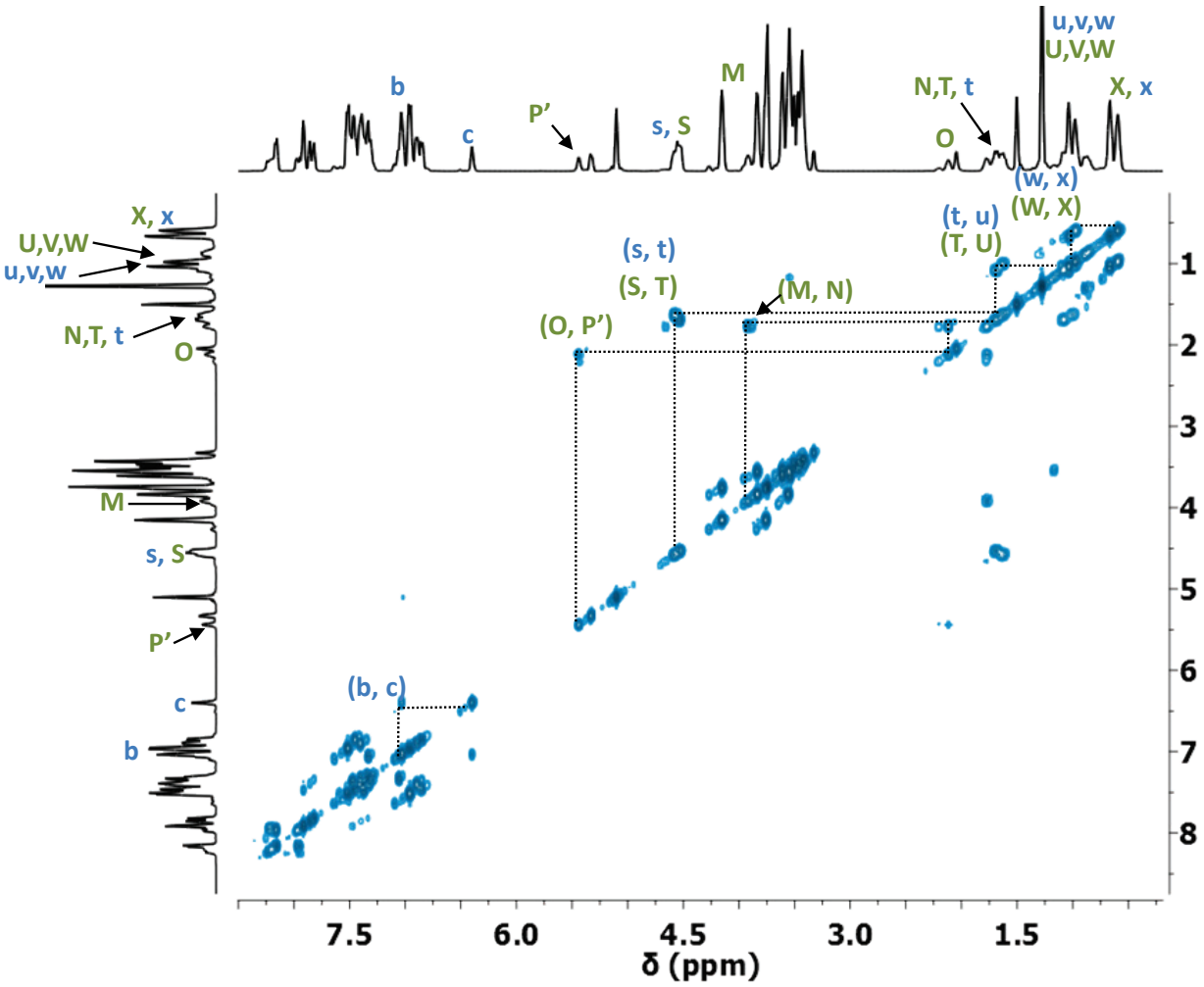


Figure S9: Full COSY in CD_2Cl_2 of $\mathbf{1}_{xan}^{hex}$.

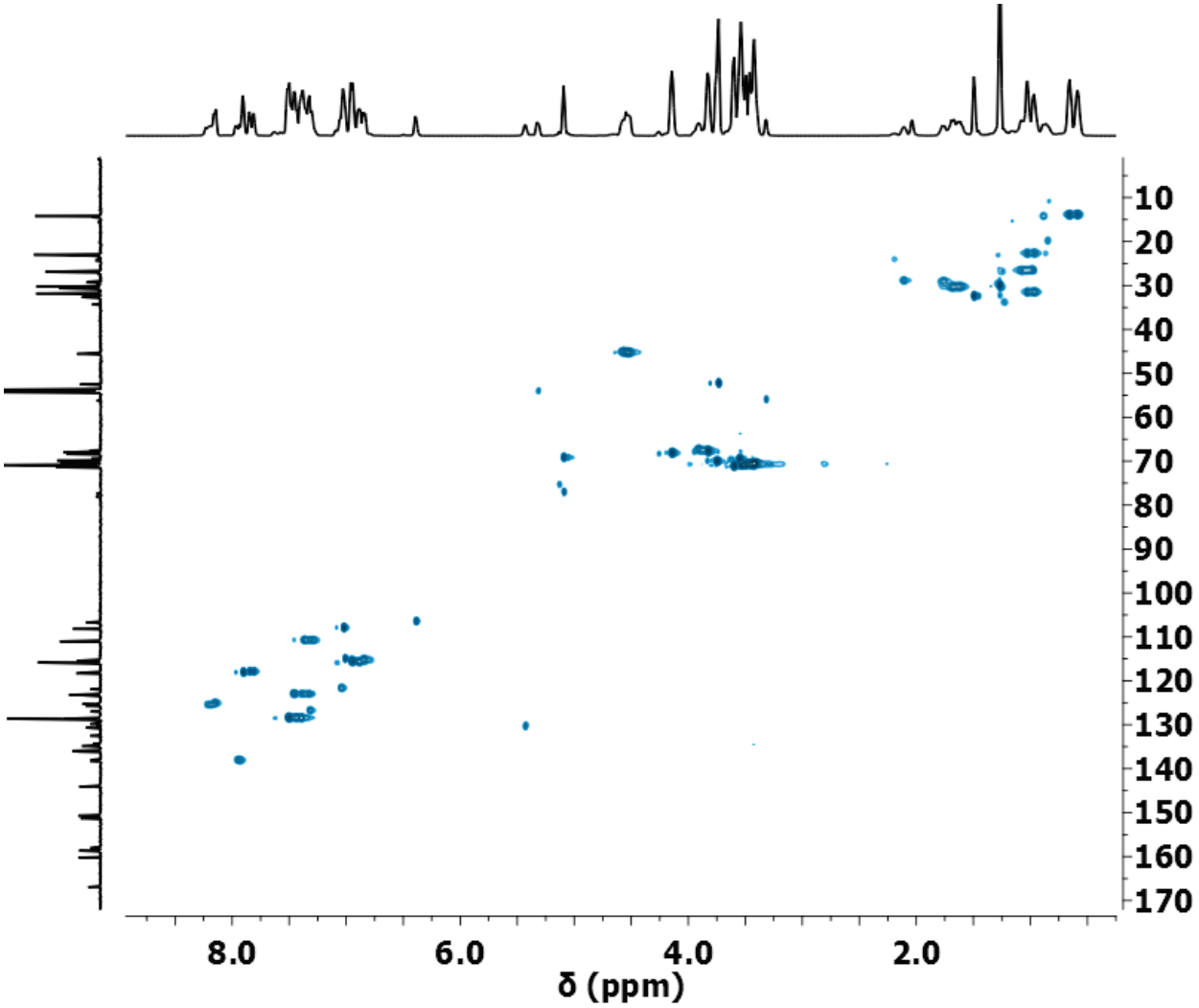


Figure S10: Full HMQC in CD_2Cl_2 of $\mathbf{1}_{xan}^{hex}$.

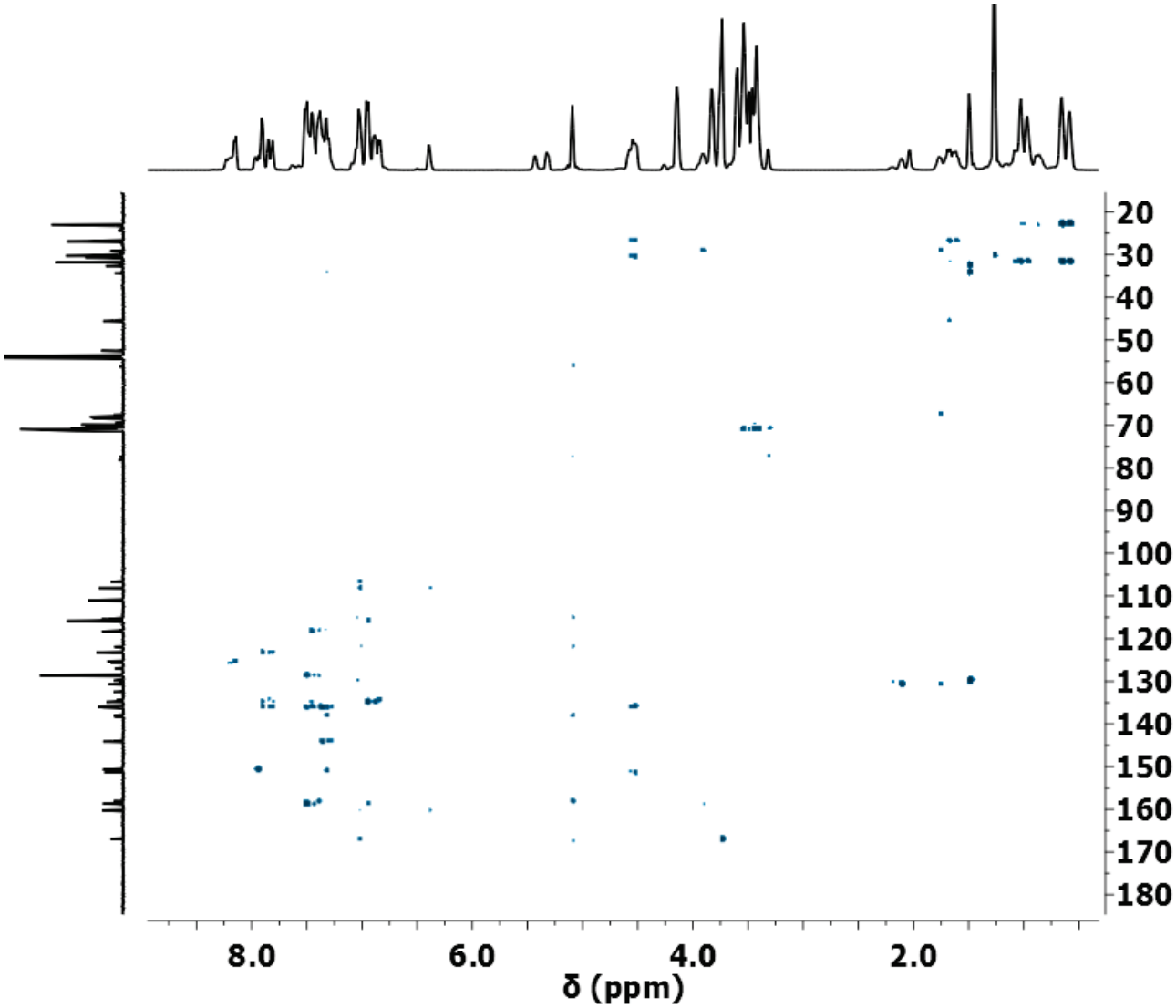


Figure S11: Full HMBC in CD_2Cl_2 of $\mathbf{1}_{xan}^{hex}$.

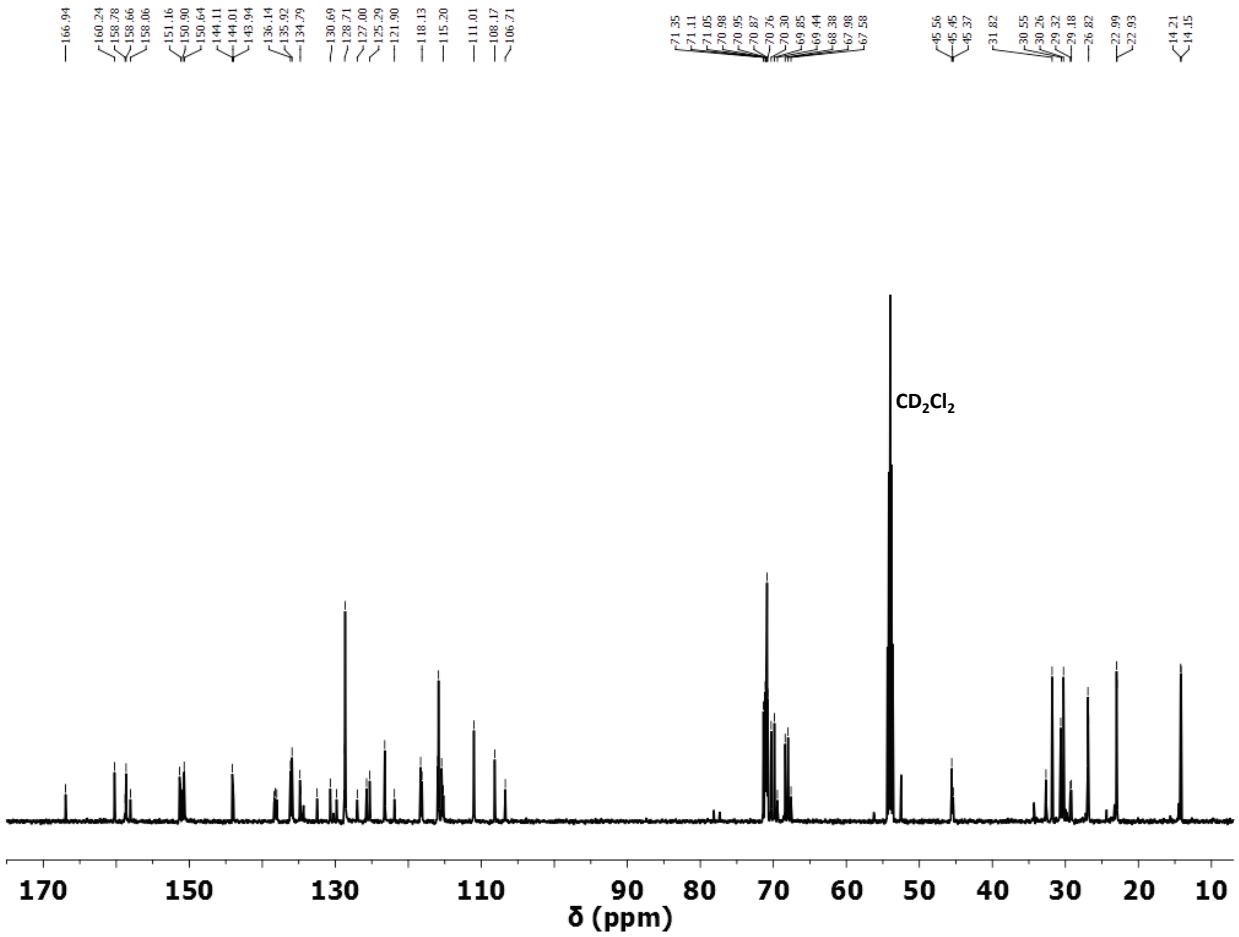


Figure S12: Full ^{13}C-NMR Spectrum in CD_2Cl_2 of $\mathbf{1}_{xan}^{hex}$.

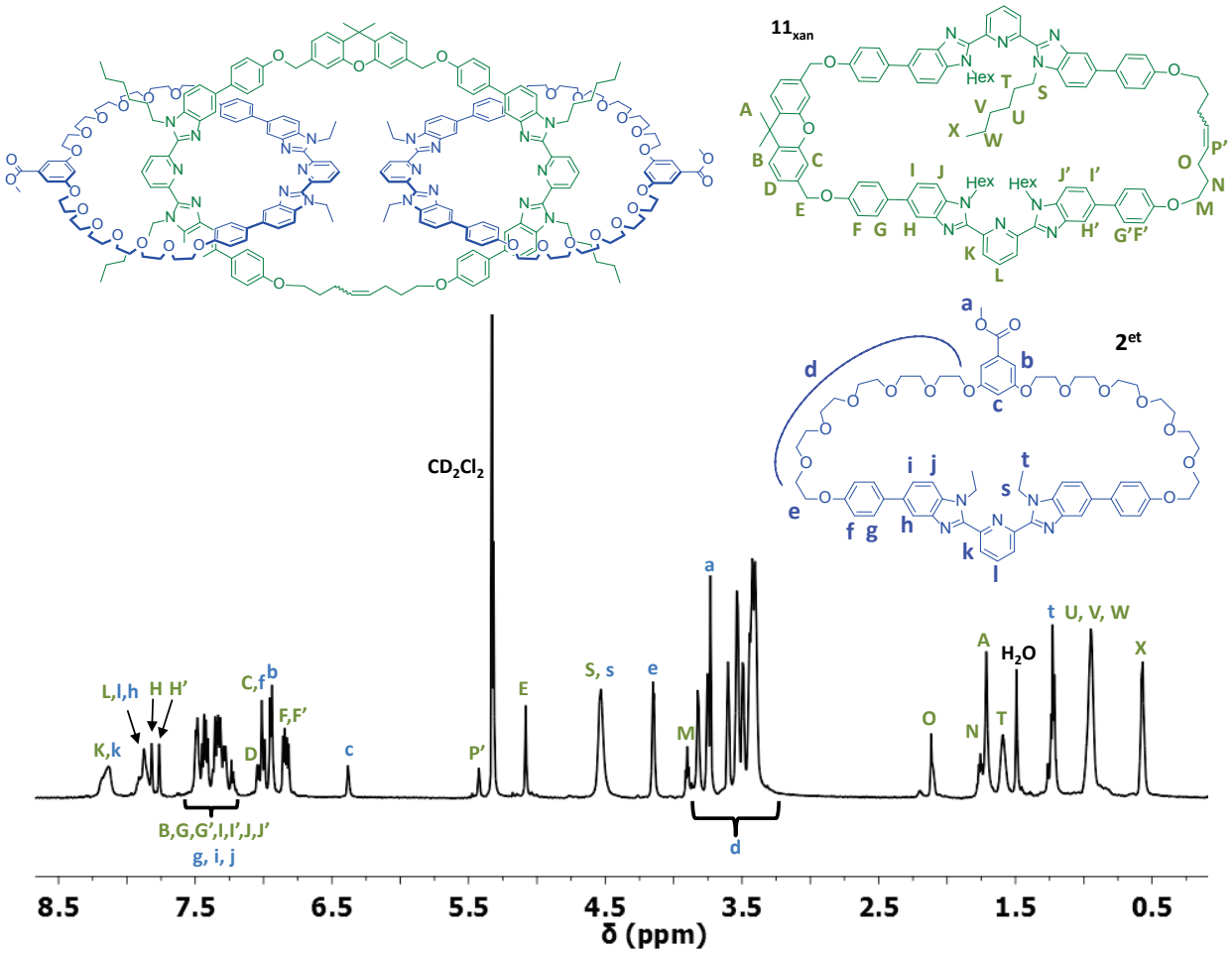


Figure S13: Full ^{1}H-NMR in CD_2Cl_2 of $\mathbf{1}_{xan}^{et}$.

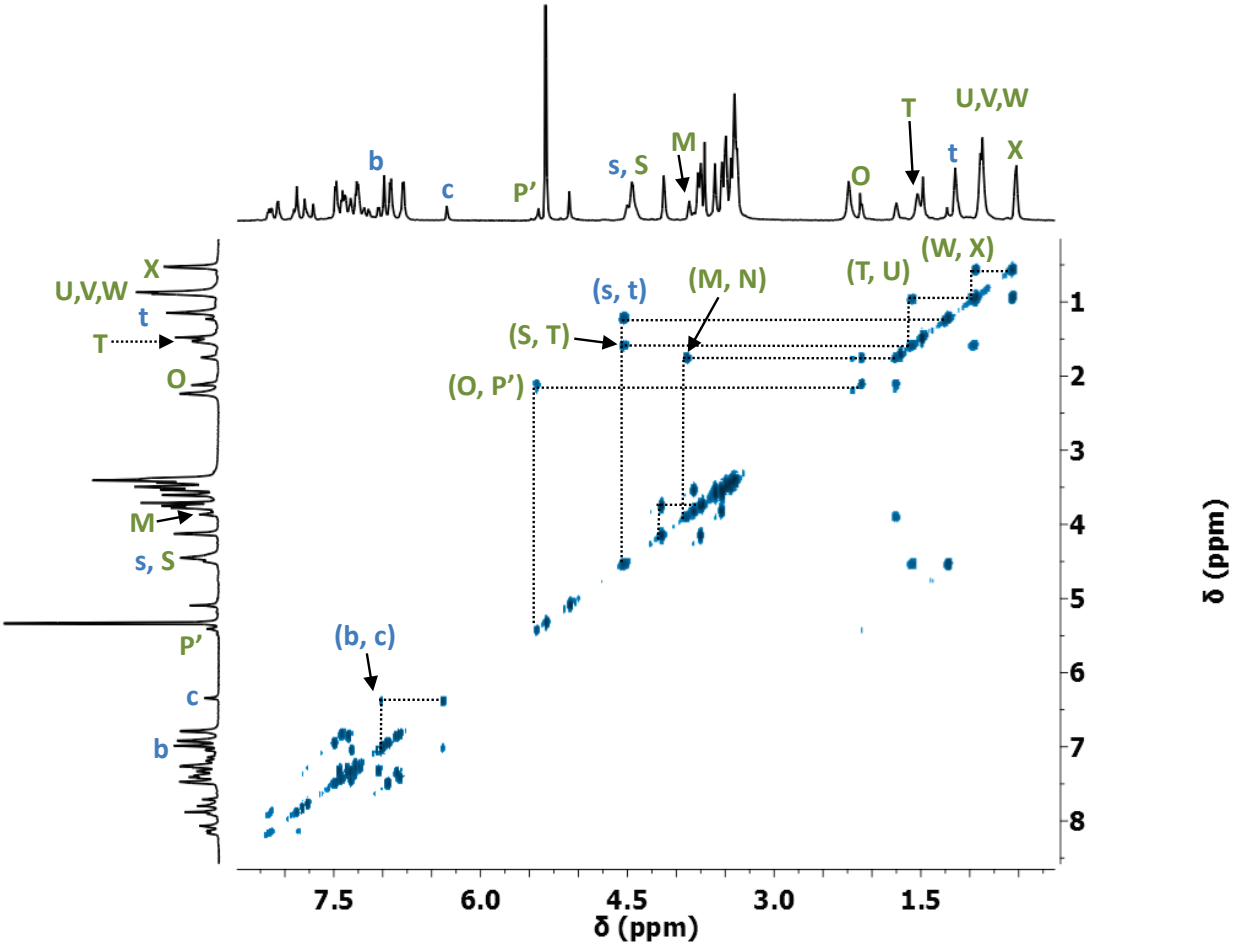


Figure S14: Full COSY in CD_2Cl_2 of $\mathbf{1}_{xan}^{et}$.

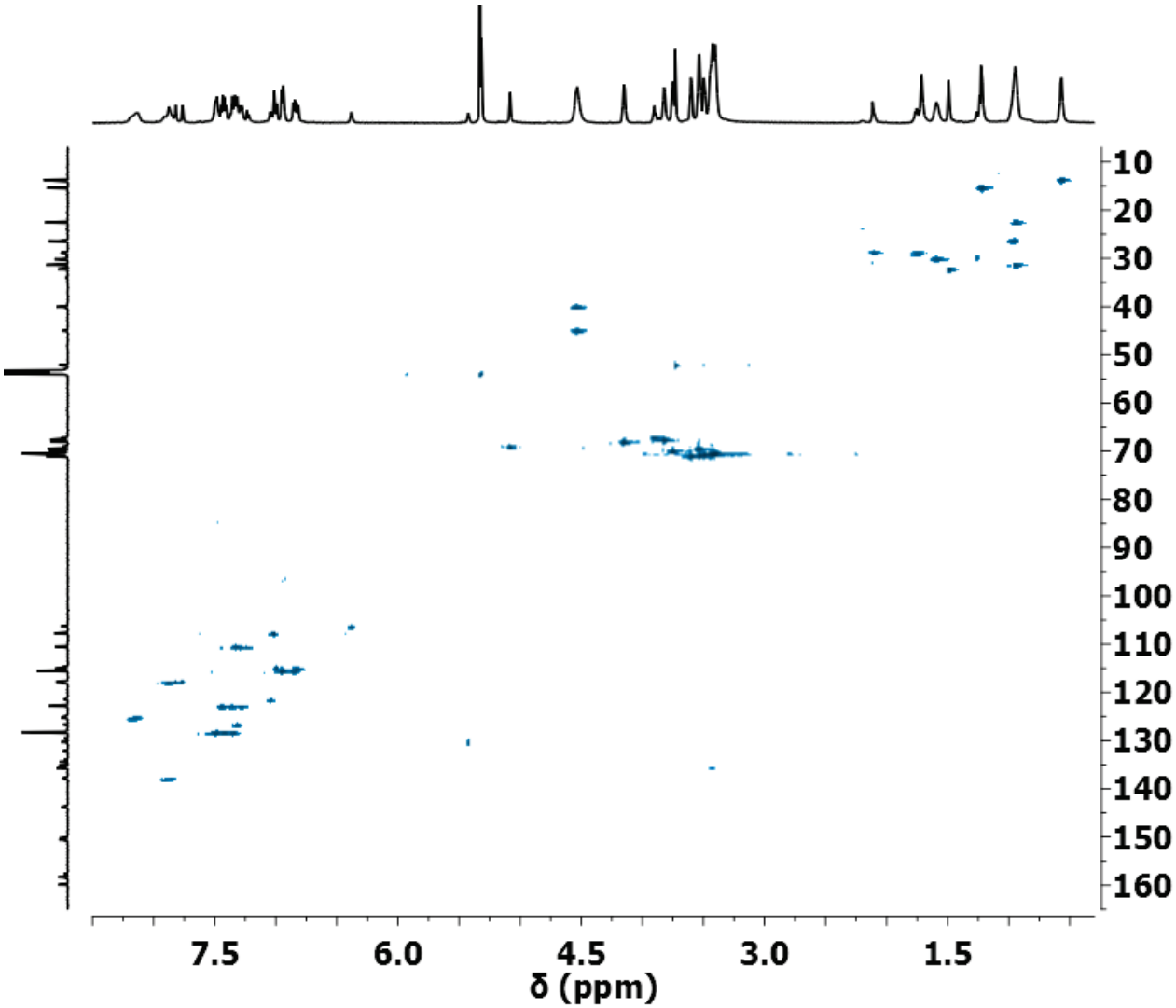


Figure S15: Full HMQC in CD_2Cl_2 of $\mathbf{1}_{xan}^{et}$.

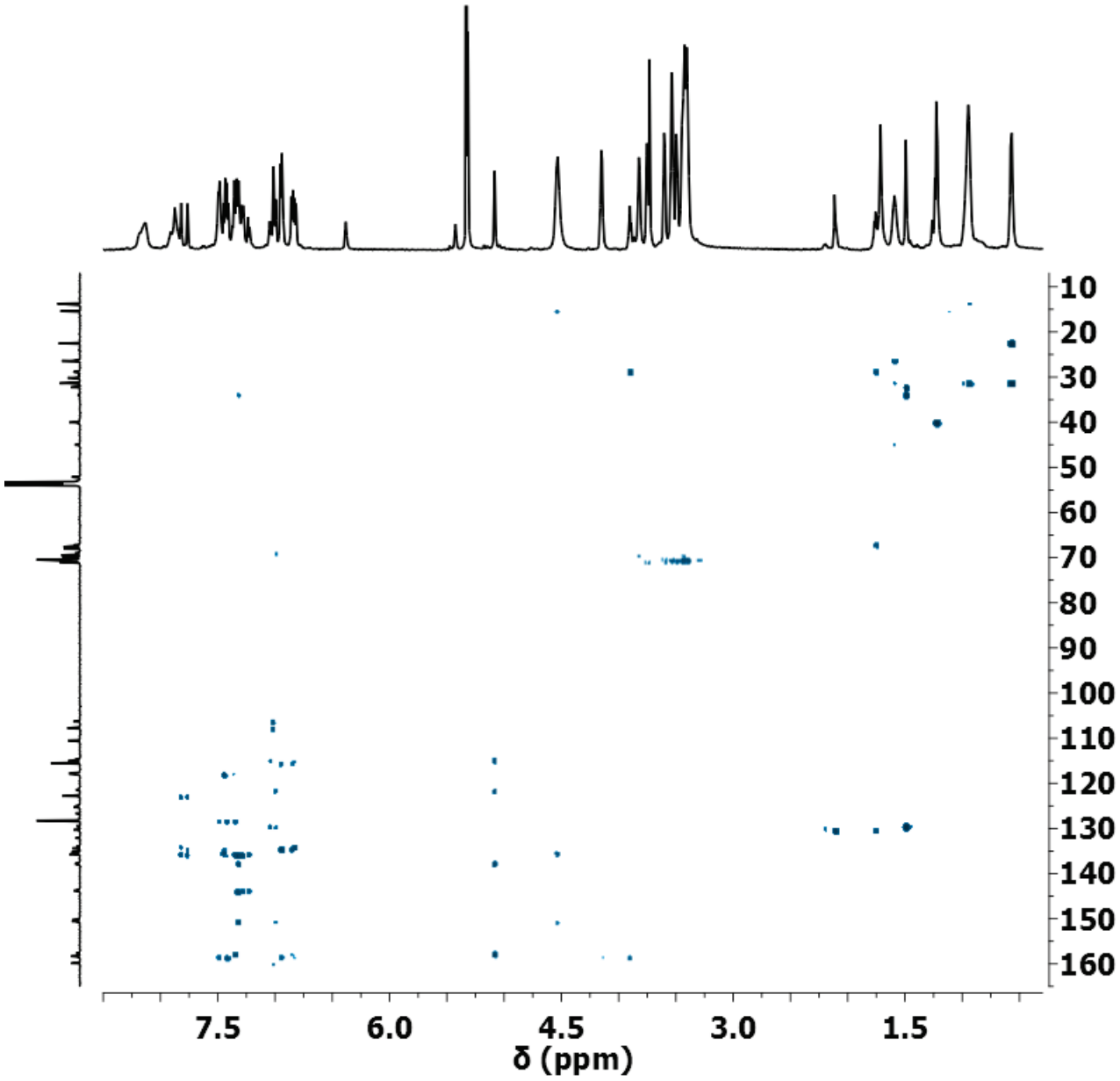


Figure S16: Full HMBC in CD_2Cl_2 of $\mathbf{1}_{xan}^{et}$.

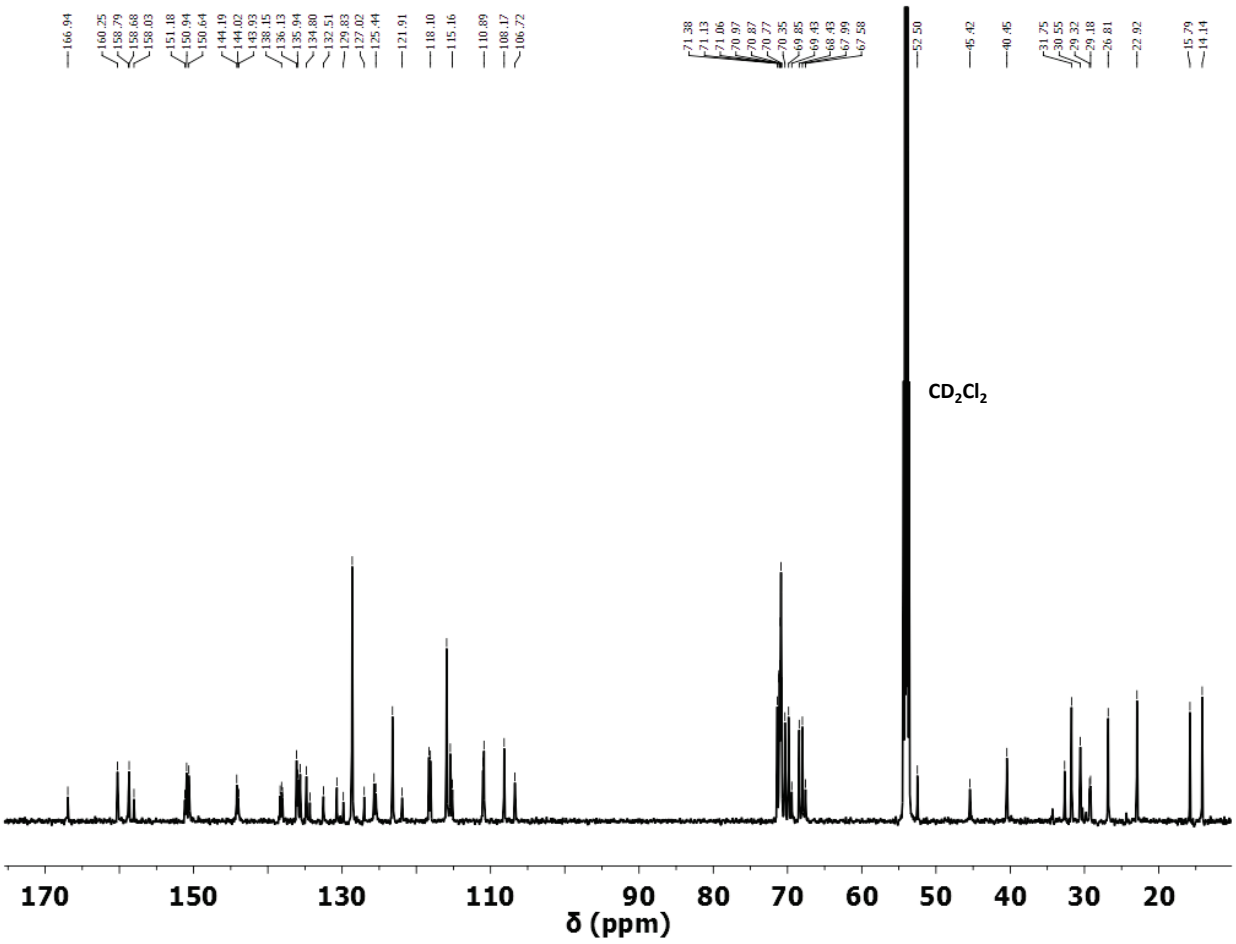


Figure S17: Full ^{13}C-NMR Spectrum in CD_2Cl_2 of $\mathbf{1}_{xan}^{et}$.

Section 9) Modeling Figures

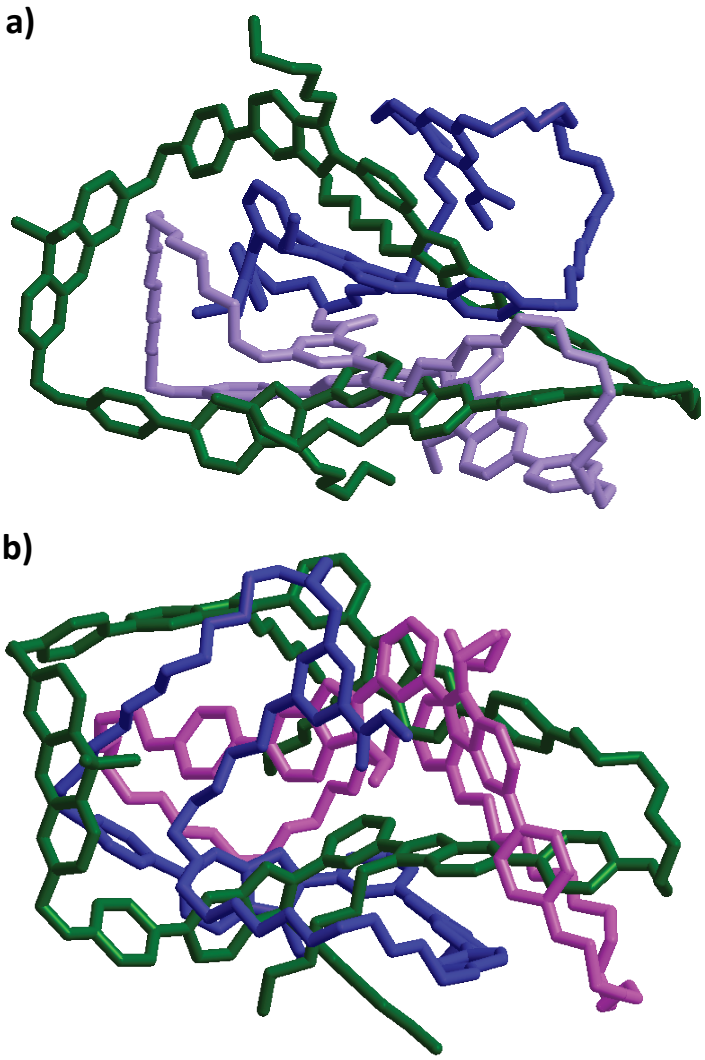


Figure S18: a) a low energy conformation of $\mathbf{1}_{xan}^{et}$ with associated energy 479.72 kJ/mol. **b**) Another low energy conformation of $\mathbf{1}_{xan}^{et}$ with similar associated energy 484.73 kJ/mol. The green colored molecule corresponds to the macrocycle $\boldsymbol{11}_{xan}$. The blue and pink colored molecules correspond to component $\boldsymbol{2}^{et}$. Hydrogens have been omitted for clarity.

Section 10) NOESY $\mathbf{1}_{xan}^{hex}$

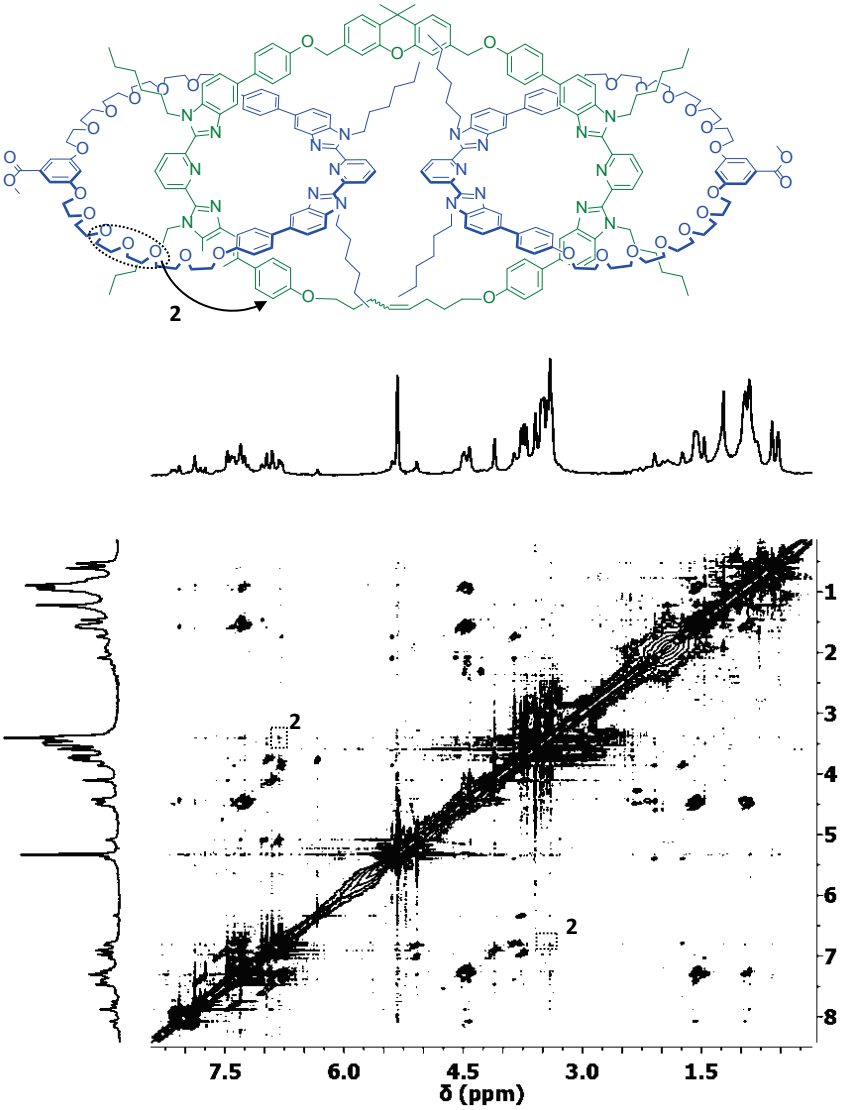


Figure S19: 1H-NOESY Spectrum in CD_2Cl_2 of $\mathbf{1}_{xan}^{hex}$ taken at -17°C.

Section 11) References

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