Electronic Supplementary Information

The effect of thread-like monomer structure on the synthesis of poly[*n*]catenanes from metallosupramolecular polymers

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Materials /Methods/ Experimentation

Materials

Dichloromethane (DCM) was purchased from Acros Organics and distilled over CaH_2 under argon atmosphere before using. Dimethylformamide (DMF, anhydrous) was purchased from Fisher Chemical and was stored over molecular sieves. Deuterated solvents were purchased from Sigma Aldrich (with d-chloroform containing tetramethylsilane (TMS) as an internal standard). Zinc di[bis(trifluoromethylsulfonyl)imide] was purchased from Strem Chemicals and stored in a nitrogen desiccator. All other chemicals were purchased from Sigma-Aldrich and used without further purification unless otherwise mentioned.

Instruments and Methods

All silica column chromatography was performed on a Buchi Reveleris X2 Flash Chromatography System. Size exclusion chromatography was performed on a hand loaded column with Bio-Beads S-X1 gel and a mixture of 25% HPLC grade dimethylformamide (DMF) and 75% HPLC grade tetrahydrofuran (THF) as mobile phase. Silica preparatory plates were purchased from Analtech with a thickness of 1000 μm and a pore size of 6.0 Å.

NMR data was acquired on either a 400 MHz Bruker DRX spectrometer equipped with a BBO probe, using Topspin 1.3; or a 500 MHz Bruker Avance-II+ spectrometer equipped with a $^{1}H\{^{19}F, ^{13}C, ^{31}P\}$ QNP probe, using Topspin 2.1. Chemical shifts were calibrated with TMS for all measurements. Diffusion measurements were obtained using the 2D Bruker pulse program stebpgp1s, which includes a stimulated echo, bipolar gradient pulses, and one spoil gradient. The corresponding 1D pulse sequence stebpgp1s1d was used to optimize the parameters D20 ("big delta", the major diffusion delay) and P30 ("little delta", the diffusion gradient length), in accord with manufacturer-recommended methods.[1] The 2D data were acquired with a linear array of 32 diffusion gradient strengths (GPZ6 values) from 5% to 95%. ^{1}H T_1 measurements were taken using the standard Bruker inversion-recovery experiment "t1ir" with a relaxation delay D1 = 30 seconds and 16 interpulse recovery delays ranging from 0.001 to 16.0 seconds. T_1 values were obtained by fitting data to a recovery function using MestReNova software. All 1D and 2D NMR spectra were processed by either MestReNova software or Bruker Topspin 4.0.6. Diffusion coefficients were determined using the Bruker Topspin 4.0.6 direct exponential curve resolution algorithm (DECRA) plotting method.

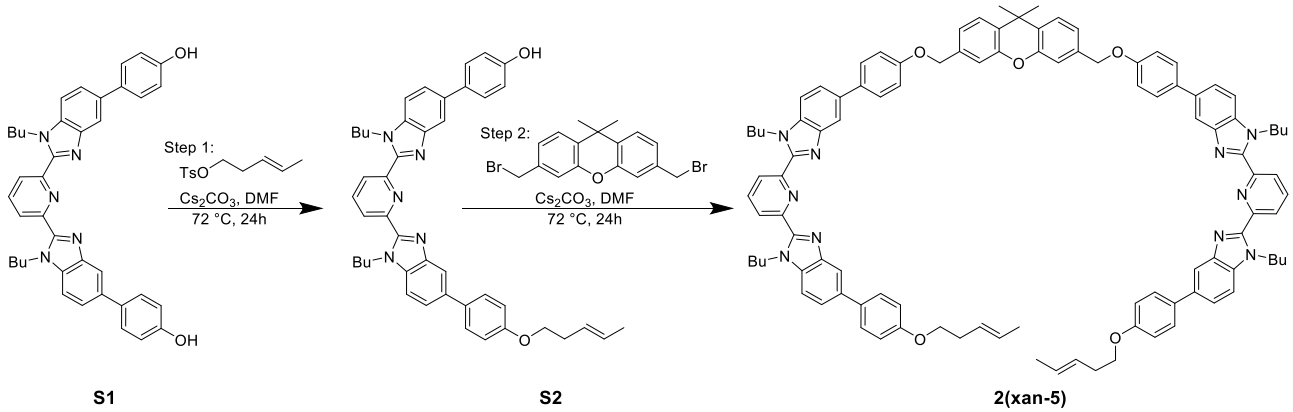
Analytical SEC was performed on a Shimadzu Prominance LC system with PLgel Mixed-D columns using a mixture of 25% HPLC grade DMF and 75% HPLC grade THF as the eluent (1mL/min) at 25 °C. Characterization of the eluent occurred using Wyatt Dawn Helios MALS (658 nm laser) and Wyatt Optilab T-rEX refractive index (RI) detectors. The *dn*/*dc* values for each new poly[*n*]catenane material were measured by injecting a series of diluted crude samples of each material (**4(xan-5)**, **4(nap-5)**, or **4(nap-6)**) in 25% DMF/THF solution (concentration: 0.25, 0.5, 1.0, and 2.0 mg/mL) subsequently into the RI detector until receiving stable signal for each concentration. The data collected was processed by Wyatt Astra software, which plots the dRI value vs. the concentration, giving the slope as the *dn*/*dc* value for a given substance. The following *dn*/*dc* values were obtained: 0.2042 for **4(xan-5)**, 0.1920 for **4(nap-5)**, and 0.1829 for **4(nap-6)**. The *dn*/*dc* value for the previously published material (0.2125), **4(xan-6)**, had been determined

prior to this work.[2] Using these *dn*/*dc* values the molar mass was obtained by the software using the relationship between the RI and *dn*/*dc*.

MALDI-TOF was measured by a Bruker Ultraflextreme MALDI TOF-TOF spectrometer using dithranol as the matrix and sodium trifluoroacetate as ionizer (when necessary).

Experimental Procedures

Synthesis of **2(xan-5)**

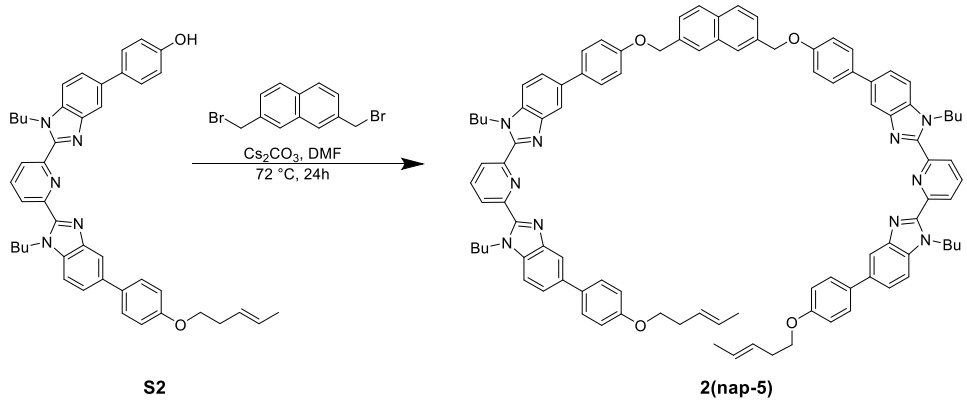


Step 1: 2.0 g (3.29 mmol) of a 2,6-bisbenzimidazolylpyridine (Bip) derivative (**S1**) (prepared using literature procedures)[3], 0.554 g (3.29 mmol, 1 eq.) pent-3-en-1-yl 4-methylbenzenesulfonate (prepared using literature procedures)[4] and 3.2 g (9.82 mmol, 3 eq.) of anhydrous Cs_2CO_3 were added into a 50 mL round bottom flask equipped with stir bar. The flask was flushed with argon and then 22 mL anhydrous DMF was added by cannula. The reaction mixture was stirred at 72 °C for 24 hours. DMF was then removed under vacuum and the solid was stirred with chloroform and filtered. The filtrate was collected and the solvent removed under reduced pressure. The product was purified via flash column chromatography on silica gel (120 g) with a chloroform/methanol gradient from 100/0 to 97/3 (v/v) as the mobile phase (85 mL/min, 1 hour) followed by recrystallization in a mixture of chloroform and methanol. **S2** was isolated as yellow crystals in 36% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.34 (d, J = 7.9 Hz, 2H), 8.07 (t, J = 7.9 Hz, 1H), 8.02 (dd, J = 8.0, 1.6 Hz, 2H), 7.65 – 7.53 (m, 6H), 7.50 (dd, J = 8.5, 1.6 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 5.69 – 5.49 (m, 2H), 4.76 (t, J = 7.3 Hz, 4H), 4.03 (t, J = 6.9 Hz, 2H), 2.51 (q, J = 6.7 Hz, 2H), 1.76 (q, J = 7.5 Hz, 4H), 1.71 (dd, J = 5.9, 1.3 Hz, 3H), 1.15 (h, J = 7.4 Hz, 4H), 0.73 (t, J = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C (ppm) 158.4, 156.3, 150.6, 150.5, 149.8, 149.7, 143.1, 142.9, 138.4, 136.7, 136.4, 135.3, 135.2, 134.1, 133.5, 128.6, 128.4, 127.8, 126.8, 125.7, 123.3, 117.9, 117.8, 116.2, 115.0, 110.6, 68.0, 44.8, 32.6, 32.2, 19.9, 18.1, 13.5. MALDI-TOF MS: m/z 676 ($[M]H^+$).

Step 2: To a 10 mL round bottom flask equipped with stir bar, 500 mg (0.74 mmol) of **S2**, 146 mg (0.37 mmol, 0.5 eq.) of 3,6-bis(bromomethyl)-9,9-dimethyl-9H-xanthene (synthesized by literature procedure)[5] and 352 mg (1.08 mmol, 1.5 eq.) of anhydrous cesium carbonate was added, followed by flushing with argon. Then 3 mL anhydrous DMF was injected into the reaction. The mixture was stirred at 72 °C for 24 hours. DMF was then removed under vacuum and the solid was stirred with chloroform and filtered. The filtrate was collected and the solvent removed under

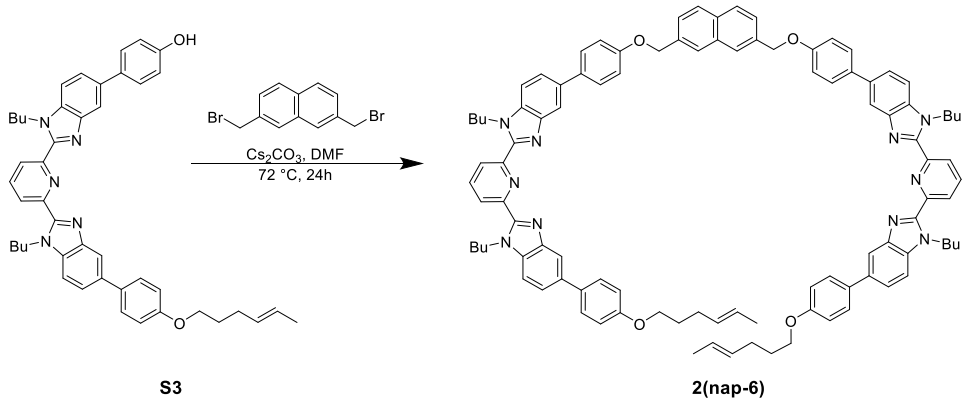
reduced pressure. The product purified by flash column chromatography on silica gel (80 g) with a chloroform/methanol gradient from 99.5/0.5 to 99/1 (v/v) as the mobile phase (60 mL/min, 30 minutes), followed by recrystallization in a mixture of chloroform and methanol. Yield of **2 (xan-5)**: 38% as an off-white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.35 (d, J = 7.9 Hz, 4H), 8.07 (t, J = 7.9 Hz, 2H), 8.03 (dd, J = 3.8, 1.6 Hz, 4H), 7.67 – 7.54 (m, 12H), 7.54 – 7.43 (m, 6H), 7.20 (dd, J = 6.3, 1.9 Hz, 4H), 7.12 (d, J = 8.9 Hz, 4H), 7.02 (tt, J = 8.7, 7.0, 6.6 Hz, 4H), 5.69 – 5.48 (m, 4H), 5.12 (s, 4H), 4.76 (t, J = 7.3 Hz, 8H), 4.03 (t, J = 6.8 Hz, 4H), 2.56 – 2.46 (m, 4H), 1.75 (p, J = 8.7, 7.5, 6.5 Hz, 8H), 1.71 (d, J = 5.5 Hz, 6H), 1.15 (h, J = 7.4 Hz, 8H), 0.73 (t, J = 7.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C (ppm) 157.3, 157.1, 149.71, 149.68, 149.5, 149.0, 142.4, 137.2, 135.7, 135.2, 135.1, 134.5, 134.5, 133.6, 133.2, 128.6, 127.4, 127.3, 126.7, 125.7, 125.6, 124.5, 122.1, 122.1, 121.1, 117.1, 117.0, 114.4, 114.2, 113.9, 109.5, 109.4, 68.5, 66.9, 43.8, 32.9, 31.5, 31.2, 18.9, 17.1, 12.5. MALDI-TOF MS: m/z 1586 ([M]H$^+$).

Synthesis of **2(nap-5)**



To a 10 mL round bottom flask equipped with stir bar, 500 mg (0.74 mmol) of **S2**, 116 mg (0.37 mmol, 0.5 eq.) of 2,7-bis(bromomethyl) naphthalene (synthesized by literature procedure[6]) and 689 mg (1.08 mmol, 1.5 eq.) of anhydrous cesium carbonate was added, followed by flushing with argon. Then 3 mL anhydrous DMF was injected into the reaction. The mixture was stirred at 72 °C for 24 hours. DMF was then removed under vacuum and the solid was stirred with chloroform and filtered. The filtrate was collected and the solvent removed under reduced pressure. The product purified via flash column chromatography on silica gel (80 g) with a chloroform/methanol gradient from 100/0 to 98/2 (v/v) as the mobile phase (60 mL/min, 35 minutes), followed by recrystallization in a mixture of chloroform and methanol. Yield of **2(nap-5)**: 36%, as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.35 (d, J = 7.9 Hz, 4H), 8.07 (t, J = 7.8 Hz, 2H), 8.03 (d, J = 2.8 Hz, 4H), 7.96 (s, 2H), 7.91 (d, 8.3 Hz, 2H), 7.65-7.56 (overlapped, 14H), 7.50 (dd, J = 3.5 Hz, 4H), 7.14 (d, J = 8.6 Hz, 4H), 7.01 (d, J = 8.6 Hz, 4H), 5.58 (m, J = 6.3 Hz, 4H), 5.32 (s, 4H), 4.76 (t, J = 7.3 Hz, 8H), 4.03 (t, J = 6.8 Hz, 4H), 2.51 (q, J = 6.6 Hz, 4H), 1.75 (p, J = 7.3 Hz, 8H), 1.70 (d, J = 5.9 Hz, 6H) 1.15 (h, J = 7.5 Hz, 8H), 0.73 (t, J = 7.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C (ppm) 158.5, 158.3, 150.9, 150.8, 150.2, 150.1, 143.6, 138.3, 136.4, 136.2, 135.7, 135.6, 135.2, 134.8, 134.3, 133.4, 132.9, 128.6, 128.5, 128.5, 127.9, 126.9, 126.5, 125.7, 125.6, 123.3, 123.2, 118.3, 118.2, 115.5, 115.1, 110.7, 110.6, 70.4, 68.1, 44.9, 32.7, 32.32, 20.0, 18.2, 13.7. MALDI-TOF MS: m/z 1504 ([M]2H$^+$).

Synthesis of **2(nap-6)**



To a 10 mL round bottom flask equipped with stir bar, 500 mg (0.74 mmol) of 2,6-bisbenzimidazolylpyridine (Bip) containing compound **S3** (prepared using previously published literature protcols[3]), 113 mg (0.37 mmol, 0.5 eq.) of 2,7-bis(bromomethyl) naphthalene (synthesized using literature procedures[6]) and 352 mg (1.08 mmol, 1.5 eq.) of anhydrous cesium carbonate was added, followed by flushing with argon. Then 3 mL anhydrous DMF was injected into the reaction. The mixture was stirred at 72 °C for 24 hours. DMF was then removed under vacuum and the solid was stirred with chloroform and filtered. The filtrate was collected and the solvent removed under reduced pressure. The product purified via column chromatography on silica gel (80 g) with a chloroform/methanol gradient from 100/0 to 97/3 (v/v) as the mobile phase (60 mL/min, 40 minutes), followed by recrystallization in a mixture of chloroform and methanol. Purified yield of **2(nap-6)**: 33% as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 7.9 Hz, 4H), 8.07 (t, J = 7.9 Hz, 2H), 8.03 (d, J = 1.3 Hz, 4H), 7.96 (s, 2H), 7.91 (d, 8.4 Hz, 2H), 7.65-7.56 (overlapped, 14H), 7.50 (dd, J = 3.4 Hz, 4H), 7.14 (d, J = 8.7 Hz, 4H), 7.01 (d, J = 8.7 Hz, 4H), 5.50 (m, J = 3.4 Hz, 4H), 5.31 (s, 4H), 4.76 (t, J = 7.3 Hz, 8H), 4.02 (t, J = 6.5 Hz, 4H), 2.19 (q, J = 6.5 Hz, 4H), 1.88 (p, J = 6.9 Hz, 4H), 1.74 (p, J = 7.3 Hz, 8H), 1.66 (d, J = 4.3 Hz, 6H) 1.15 (h, J = 7.5 Hz, 8H), 0.73 (t, J = 7.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 158.2, 150.9, 150.8, 150.2, 150.1, 143.5, 138.3, 136.3, 136.2, 135.7, 135.6, 135.2, 134.8, 134.2, 133.3, 132.9, 130.4, 128.6, 128.5, 128.4, 126.5, 125.8, 125.6, 125.6, 123.2, 118.2, 118.2, 110.6, 110.5, 70.3, 67.5, 44.9, 32.3, 29.2, 29.1, 20.0, 18.1, 13.6. MALDI-TOF MS: m/z 1532 ([M]2H$^+$).

Synthesis of RC Materials (3)

In a 250 mL round bottom flask equipped with stir bar and water condenser, 250 mg (0.158 mmol) of **2(xan-5)** was dissolved in 50 mL of DCM. The solution was stirred and heated to reflux followed by bubbling argon for 30 minutes to degas the solvent. The Hoveyda-Grubbs catalyst (12.6 mg) was injected in additional solvent to return the solution to the initial concentration (to account for any solvent lost during the initial bubbling step, approximately 2 mL of DCM). After the catalyst, a second degassing argon bubbling step was carried out for approximately 30 minutes. After 24 hours, a second catalyst addition step was carried out (following the same degassing and addition procedure as before). When purging is stopped, the evaporation of DCM is negligible and

the total concentration of **2(xan-5)** remains approximately constant (ca. 2.5 mM) through the entire reaction. The reaction solution was kept at reflux for another 24 hours. At which point the solution was cooled to room temperature followed by the addition of excess ethyl vinyl ether (~1mL) to deactivate the catalyst. The solvent was removed under vacuum and the product purified by repeated gravity column chromatography with triethylamine neutralized silica gel and a chloroform/methanol gradient from 100/0 to 98/2 (v/v) as the mobile phase (one hour at 100/0, 45 minutes at 99.5/0.5, 45 minutes at 99/1, 45 minutes at 98/2). The resulting product was precipitated in a mixture of chloroform and methanol.

3(xan-5): Crude ^{1}H NMR Yield: 35% Isolated yield: 5% as a white waxy solid that is a mixture of *cis* and *trans* isomers. ^{1}H NMR (400 MHz, $CDCl_3$, *cis/trans* isomers are partially overlapped) δ_H (ppm) 8.30 (dd, J = 7.8, 3.7 Hz, 4H), 8.05 – 7.95 (m, 4H), 7.93 (s, 2H), 7.54 – 7.44 (m, 12H), 7.44 – 7.35 (m, 6H), 7.16 – 7.06 (m, 4H), 7.01 – 6.88 (m, 8H), 5.74 – 5.66 (m, 2H), 5.25 (s, 4H), 4.66 (p, J = 14.8, 7.3 Hz, 8H), 4.06 (t, J = 5.9 Hz, 4H), 2.58 – 2.43 (m, 4H), 1.72 – 1.60 (m, 16H), 1.10 – 1.02 (m, 8H), 0.68 – 0.57 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, *cis/trans* isomers are partially overlapped) δ_C (ppm) 158.65, 157.61, 150.74, 150.68, 150.61, 150.16, 143.54, 143.47, 138.23, 137.62, 136.33, 136.28, 135.58, 134.57, 134.28, 129.37, 129.26, 128.52, 128.42, 126.81, 125.59, 123.35, 121.26, 118.14, 115.77, 115.48, 115.20, 114.63, 110.56, 69.29, 68.05, 44.81, 33.97, 32.70, 32.61, 32.27, 29.86, 22.85, 19.96, 14.27, 13.63, 13.62. MALDI-TOF MS: m/z 1530 ($[M]H^+$).

3(nap-5): This compound was synthesized in the same way as **3(xan-5)** with 472 mg of **2(nap-5)** (0.308 mmol) dissolved in 123 mL of DCM with 24.6 mg of catalyst in 4 mL DCM for each addition. The product purified by repeated gravity column chromatography with triethylamine neutralized silica gel and a chloroform/methanol gradient from 100/0 to 99/1 (v/v) as the mobile phase (one hour at 100/0, 45 minutes at 99.5/0.5, one hour at 99/1) and repeated precipitation with a mixture of chloroform and methanol. Crude ^{1}H NMR Yield: 27% Isolated yield: 4% as a white waxy solid that is a mixture of *cis* and *trans* isomers. ^{1}H NMR (400 MHz, $CDCl_3$, *cis/trans* isomers are partially overlapped) δ_H (ppm) 8.32 – 8.25 (m, 4H), 8.07 – 7.95 (m, 4H), 7.93 – 7.90 (m, 2H), 7.88 – 7.79 (m, 4H), 7.57 – 7.38 (m, 16H), 7.34 (d, J = 8.5 Hz, 2H), 7.01 (d, J = 8.6 Hz, 4H), 6.91 (d, J = 8.4 Hz, 4H), 5.71 (d, J = 4.5 Hz, 2H), 5.43 (s, 4H), 4.63 (dt, J = 16.1, 7.2 Hz, 8H), 4.14 – 3.98 (m, 4H), 2.69-2.45 (m, 4H), 1.72 – 1.59 (m, 8H), 1.11 – 0.97 (m, 8H), 0.68 – 0.57 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, *cis/trans* isomers are partially overlapped)) δ_C (ppm) 158.67, 157.69, 150.70, 150.16, 143.46, 138.22, 136.32, 136.16, 135.94, 135.55, 134.62, 134.34, 134.25, 133.44, 129.30, 128.64, 128.53, 128.48, 128.40, 128.34, 125.57, 124.65, 123.34, 118.11, 118.08, 115.98, 115.49, 115.22, 110.58, 110.52, 70.16, 68.09, 67.59, 44.82, 32.60, 32.25, 32.08, 29.86, 22.84, 19.95, 14.27, 13.62. MALDI-TOF MS: m/z 1448 ($[M]H^+$).

3(nap-6): This compound was synthesized in the same way as **3(xan-5)** with 350 mg of **2(nap-5)** (0.233 mmol) dissolved in 93 mL of DCM with 18.6 mg of catalyst in 3 mL DCM for each addition. The product purified by repeated gravity column chromatography with triethylamine neutralized silica gel and a chloroform/methanol gradient from 100/0 to 99/1 (v/v) as the mobile phase (one hour at 100/0, 45 minutes at 99.5/0.5, one hour at 99/1) and repeated precipitation with a mixture of chloroform and methanol. Crude ^{1}H NMR Yield: 46% Isolated yield: 4% as white waxy solid which is a mixture of *cis* and *trans* isomers. ^{1}H NMR (400 MHz, $CDCl_3$, *cis/trans* isomers are partially overlapped) δ_H (ppm) 8.33 – 8.23 (m, 4H), 8.06 – 7.96 (m, 4H), 7.94 – 7.89

(m, 2H), 7.88 – 7.77 (m, 4H), 7.58 – 7.36 (m, 16H), 7.32 (d, J = 8.3 Hz, 2H), 7.02 (d, J = 8.6 Hz, 4H), 6.94 (d, J = 8.7 Hz, 4H), 5.59 – 5.48 (m, 2H), 5.43 (s, 4H), 4.63 (dt, J = 19.2, 7.3 Hz, 8H), 4.00 (t, J = 6.5 Hz, 4H), 2.31 – 2.19 (m, 4H), 1.90 (p, J = 6.7 Hz, 4H), 1.76 – 1.60 (m, 8H), 1.03 (hept, J = 15.1, 7.5 Hz, 8H), 0.68 – 0.56 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$, *cis/trans* isomers are partially overlapped) δ_C (ppm) 158.50, 157.68, 150.73, 150.60, 150.15, 143.50, 143.46, 138.22, 136.29, 136.16, 135.90, 135.54, 135.51, 134.62, 134.13, 133.42, 132.64, 130.60, 128.63, 128.52, 128.48, 128.43, 125.62, 125.58, 125.56, 124.65, 123.33, 118.08, 116.02, 115.99, 115.05, 110.60, 110.52, 70.15, 66.86, 44.84, 44.76, 32.27, 32.24, 29.86, 28.76, 28.62, 19.94, 13.62, 13.61. MALDI-TOF MS: m/z 1476 ($[M]H^+$).

Synthesis of the acyclic diene metathesis (ADMET) Polymers (5)

In a 5 mL conical vial equipped with stir bar and water condenser, 50 mg (0.033 mmol) of **2(nap-5)** was dissolved in 0.66 mL of DCM. The solution was stirred and heated to reflux followed by bubbling argon for 5 minutes. Then 0.26 mg of catalyst (dissolved in 0.2 mL of DCM) was injected, and the solution was bubbled with argon for additional 10 mins. After 24 hours, 0.26 mg of catalyst (dissolved in 0.2mL of DCM) was injected, and the solution was bubbled with argon for additional 10 mins. During each argon purging step ~0.2 mL of DCM was lost due to evaporation, which is offset by the addition of the catalyst in 0.2 mL of DCM. When purging is stopped, the evaporation of DCM was negligible, and the concentration remains approximately constant (ca. 50 mM with respect to **2(nap-5)** and repeat units derived from **2(nap-5)**) through the entire reaction. The reaction solution was kept at reflux for another 24 hours for a total of 48 hours reacting. At which point the solution was cooled to room temperature followed by the addition of excess ethyl vinyl ether (~0.2 mL) to deactivate the catalyst. Then, the reaction mixture was precipitated into 20 mL cold MeCN under stirring. The suspension was cooled in a freezer (–18 °C) overnight to allow further precipitation. The product was collected by filtration and washed three times with cold MeCN. Yield is quantitative and the product (**5(nap-5)**) is obtained as a brown solid (color is due to the trace amount of residue deactivated catalyst.)

The procedure was repeated with both **2(nap-6)** and **2(xan-5)**.

5(xan-5) ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.35 (d, J = 7.9 Hz, 4H), 8.07 (t, J = 7.8 Hz, 2H), 8.03 (s, 4H), 7.66 – 7.55 (m, 12H), 7.48 (dd, J = 16.4, 8.5 Hz, 6H), 7.23 – 7.15 (m, 6H), 7.11 (d, J = 8.5 Hz, 4H), 7.03 (d, J = 8.4 Hz, 4H), 5.81-5.65 (m, 2H), 5.12 (s, 4H), 4.76 (t, J = 7.3 Hz, 8H), 4.08 (t, J = 6.3 Hz, 4H), 2.70-2.59 (m, 4H), 1.74 (q, J = 7.5 Hz, 8H), 1.60 (s, 6H), 1.14 (h, J = 7.3 Hz, 8H), 0.73 (t, J = 7.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C (ppm) 158.4, 158.3, 150.9, 150.6, 150.2, 149.6, 143.6, 138.3, 136.8, 136.4, 136.3, 135.7, 135.6, 134.8, 134.5, 129.8, 128.7, 128.6, 128.5, 126.7, 125.7, 123.3, 122.3, 118.3, 115.6, 115.4, 115.1, 110.6, 69.7, 67.9, 44.9, 34.1, 32.7, 32.3, 20.0, 13.7.

5(nap-5) ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.35 (d, J = 7.9 Hz, 4H), 8.07 (t, J = 7.8 Hz, 2H), 8.04 – 8.02 (m, 4H), 7.96 (s, 2H), 7.91 (d, J = 8.5 Hz, 2H), 7.66 – 7.55 (m, 14H), 7.50 (d, J = 8.6 Hz, 4H), 7.14 (d, J = 8.5 Hz, 4H), 7.03 (d, J = 8.4 Hz, 4H), 5.78 – 5.67 (m, 2H), 5.31 (s, 4H), 4.76 (t, J = 7.3 Hz, 8H), 4.08 (t, J = 6.5 Hz, 4H), 2.61 – 2.55 (m, 2H), 1.75 (p, J = 7.4 Hz, 8H), 1.14 (h, J = 7.4 Hz, 8H), 0.73 (t, J = 7.3 Hz, 12H) ^{13}C NMR (101 MHz, $CDCl_3$) δ_C (ppm) 158.4, 158.3, 150.9, 150.8, 150.2, 143.6, 138.3, 136.4, 136.3, 135.7, 135.6, 135.2, 134.8, 134.4, 133.4, 132.9,

128.7, 128.6, 128.5, 127.9, 126.5, 125.7, 123.3, 118.3, 118.2, 115.5, 115.1, 110.6, 70.4, 67.9, 44.9, 32.8, 32.3, 30.1, 20.0, 13.7.

5(nap-6) ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.35 (d, J = 7.9 Hz, 4H), 8.08 (t, J = 8.2 Hz, 2H) 8.04 (s, 4H), 7.96 (s, 2H), 7.91 (d, J = 8.5 Hz, 2H)7.67 – 7.55 (m, 14H), 7.50 (d, J = 7.3 Hz, 4H), 7.13 (d, J = 8.4 Hz, 4H), 7.02 (d, J = 8.6 Hz, 4H), 5.60 – 5.46 (m, 2H), 5.31 (s, 4H), 4.76 (t, J = 7.0 Hz, 8H), 4.03 (q, J = 9.8, 8.0 Hz, 4H), 2.36 – 2.17 (m, 4H), 1.89 (q, J = 6.7 Hz, 4H), 1.79 – 1.70 (m, 8H), 1.15 (h, J = 14.9, 7.4 Hz, 8H), 0.73 (t, J = 7.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C (ppm) 158.6, 158.3, 150.8, 150.1, 143.6, 138.3, 136.4, 136.2, 135.7, 135.2, 134.8, 134.3, 133.4, 132.9, 130.3, 128.6, 128.5, 126.5, 125.7, 123.3, 118.3, 115.5, 115.0, 110.6, 70.4, 67.5, 44.9, 32.3, 29.3, 29.1, 20.0, 13.7.

[1]H NMR analysis of new threads (2)

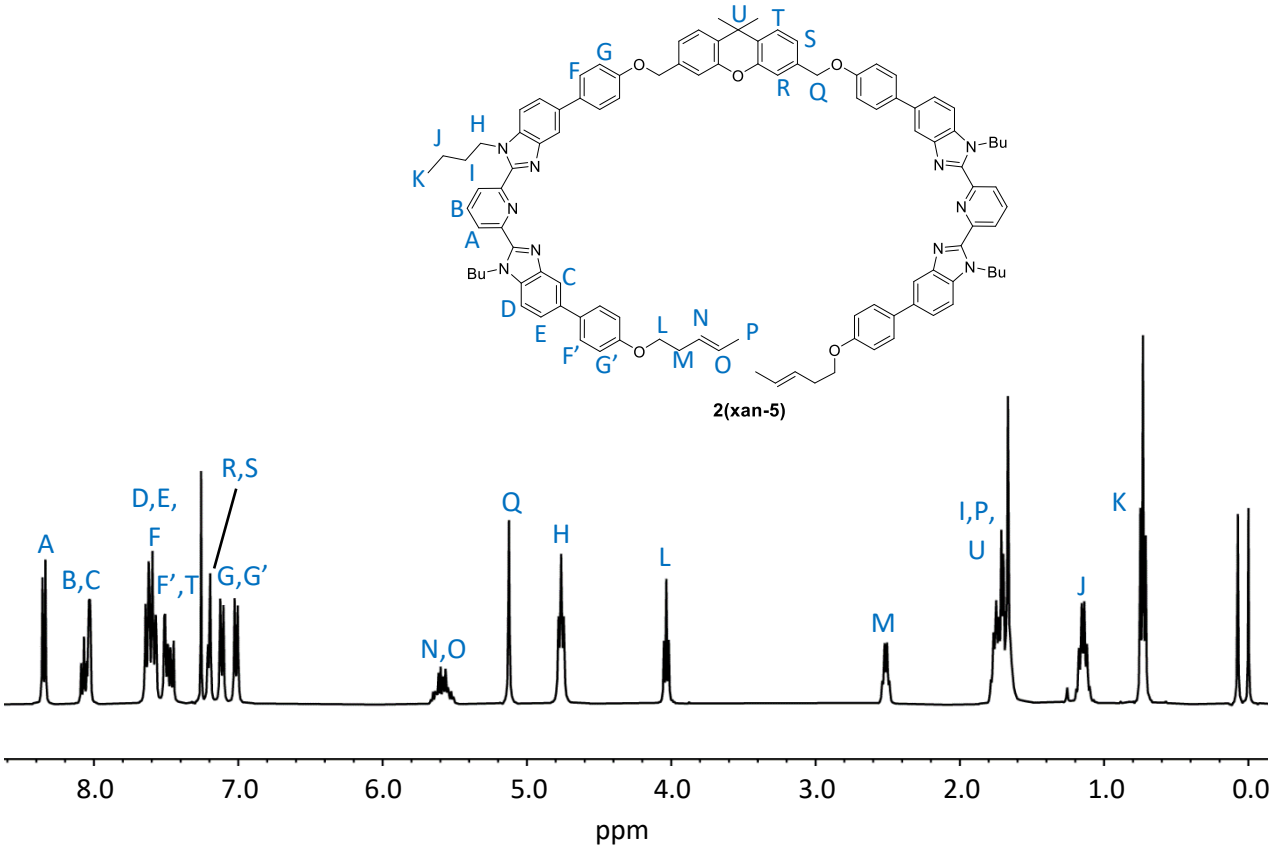


Figure S1: [1]H NMR ($CDCl_3$, 500 MHz) of **2(xan-5)**.

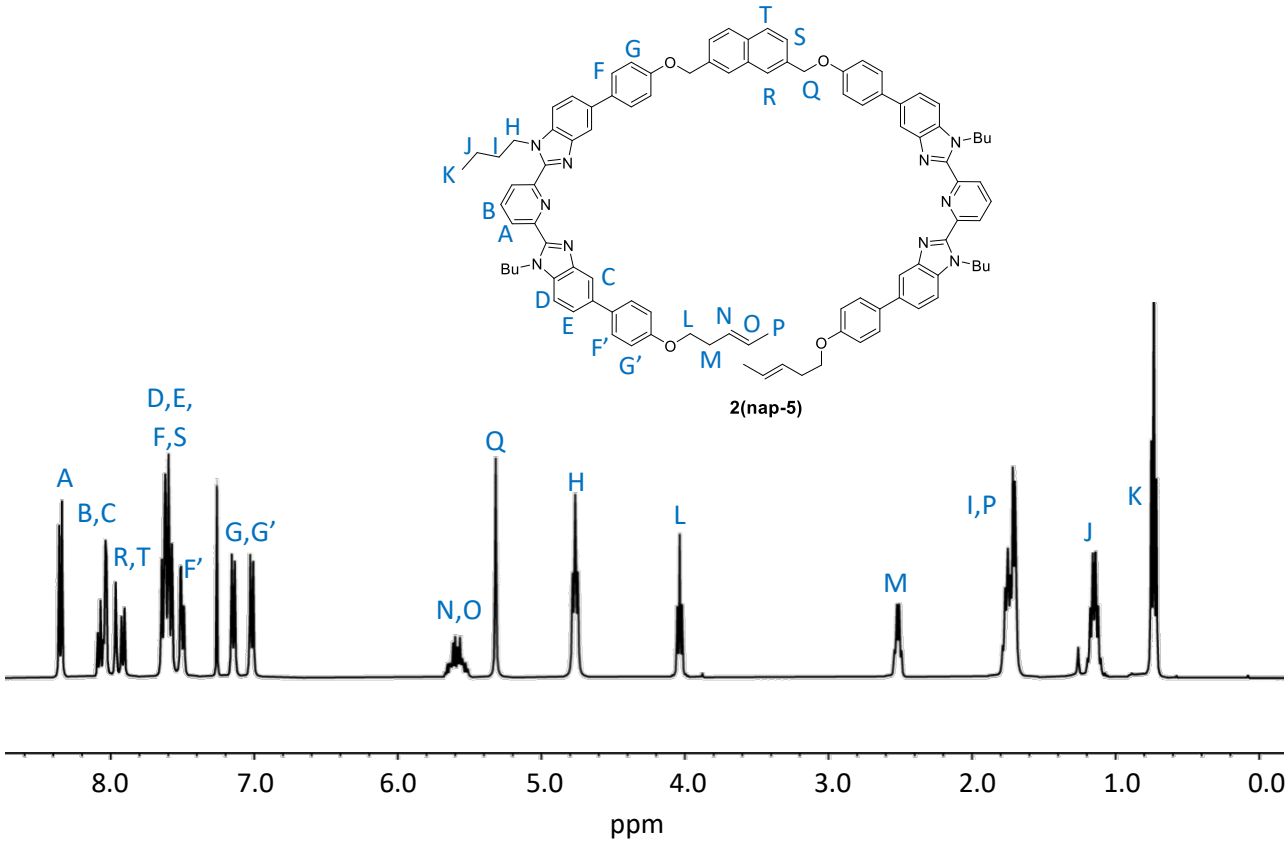


Figure S2: ^{1}H NMR ($CDCl_3$, 500 MHz) of **2(nap-5).**

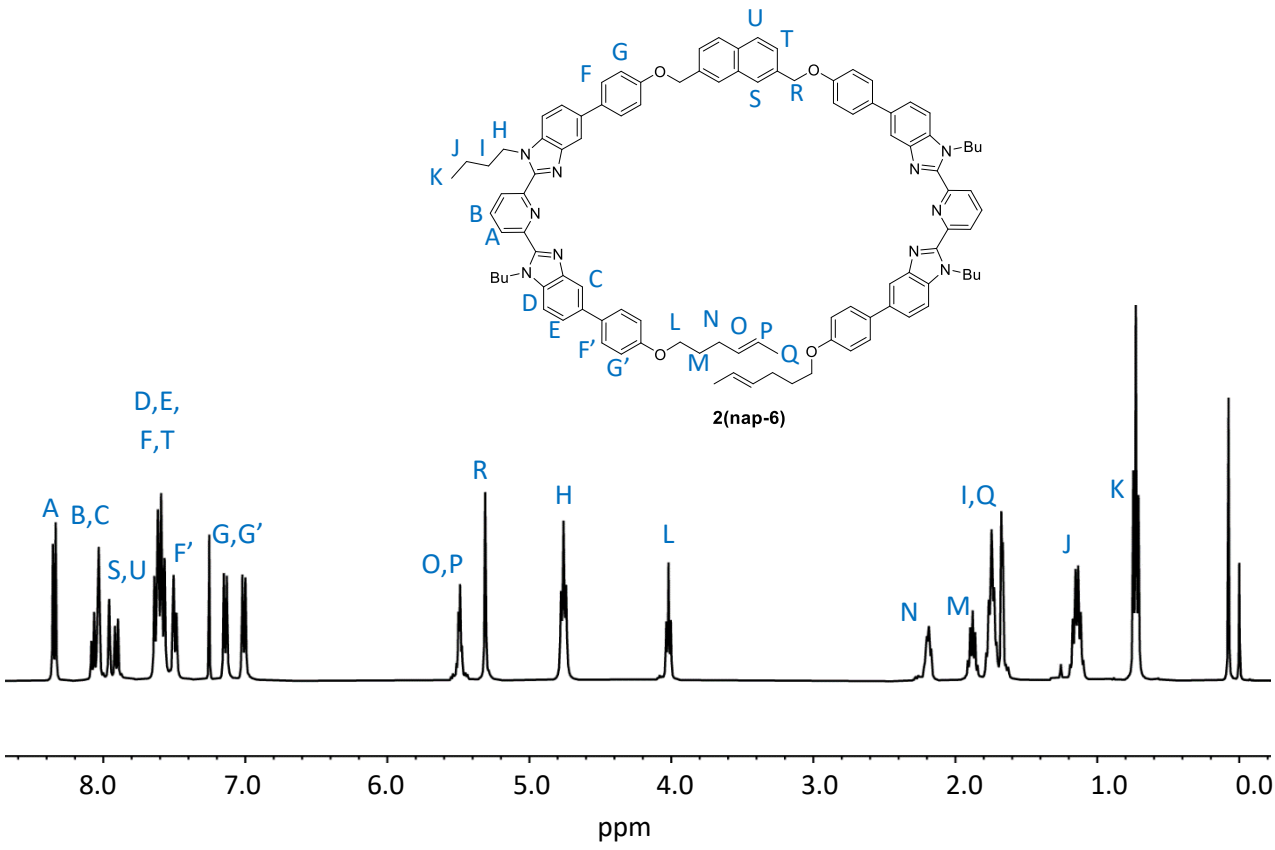
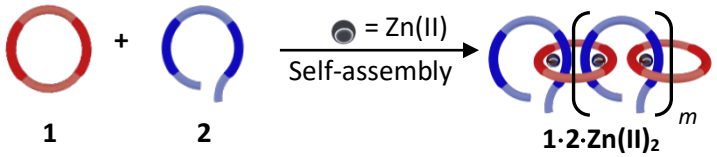


Figure S3: ^{1}H NMR ($CDCl_3$, 500 MHz) of **2(nap-6).**

Metallosupramolecular Polymer (MSP) Assembly (1·2(xan-5)·Zn(II)$_2$, 1·2(nap-5)·Zn(II)$_2$, 1·2(nap-6)·Zn(II)$_2$)



MSP assembly was performed following literature procedure.[2] A solution of **2** (in $CDCl_3$, concentration is dependent on experiment) was slowly titrated into **1** (in $CDCl_3$) until a precise 1:1 mixture of **1**:**2** was reached (as monitored by ^{1}H NMR integration). Once the 1:1 mixture had been achieved, zinc di[bis(trifluoromethylsulfonyl)imide] ($Zn(NTf_2)_2$) in d-acetonitrile was titrated until the peaks corresponding to the free ligand disappeared (at a ratio of 1:1:2 of **1**:**2**:Zn(II)).
Example procedure: 50 mg of **1** (0.033 mmol, 1 eq.) in 0.5 mL of $CDCl_3$ was placed in an NMR tube. A sample of **2** (63 mg, 0.039 mmol, 1.2 eq.) was prepared in a stock solution of 0.6 mL of $CDCl_3$. A second stock solution of $Zn(NTf_2)_2$ was prepared (49 mg, 0.078 mmol, 2.4 eq.) in 0.5 mL of d_3-MeCN. The titration proceeded as described above, with the titration stopping at a 1:1:2 ratio of **1**:**2**:Zn(II) (the entirety of the stock solutions was not utilized).

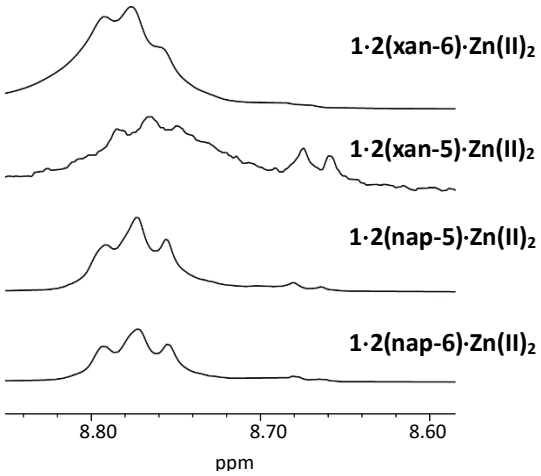


Figure S4: Region of the ^{1}H NMR spectra (500 MHz, 1:5 CD_3CN:$CDCl_3$, 298 K) corresponding to the H_{mpy} protons for the MSP at 10.0 mM for **1·2(xan-6)·Zn(II)$_2$**, **1·2(xan-5)·Zn(II)$_2$**, **1·2(nap-5)·Zn(II)$_2$**, **1·2(nap-6)·Zn(II)$_2$** (top to bottom).

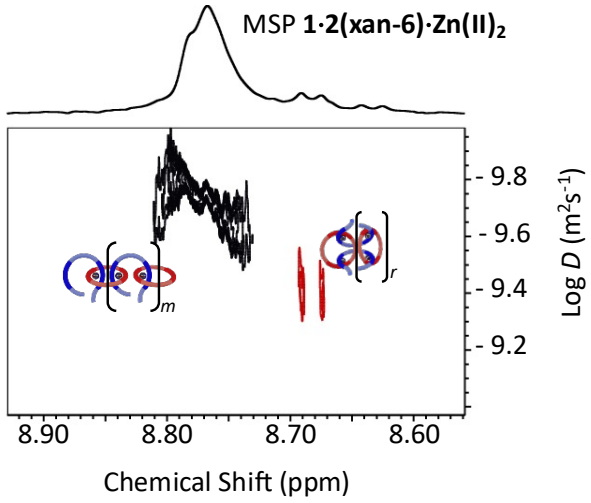


Figure S5: Processed DOSY NMR spectrum (500 MHz, CD_2Cl_2, 298 K) for the MSP **1·2(xan-6)·Zn(II)$_2$** at a concentration of 2.5 mM. Two distinctive regions assigned to the linear (black, diffusion coefficient of 2.4 x 10^{-10} m^2s^{-1}) and cyclic (red, 5.5 x 10^{-10} m^2s^{-1}) MSP can be observed.

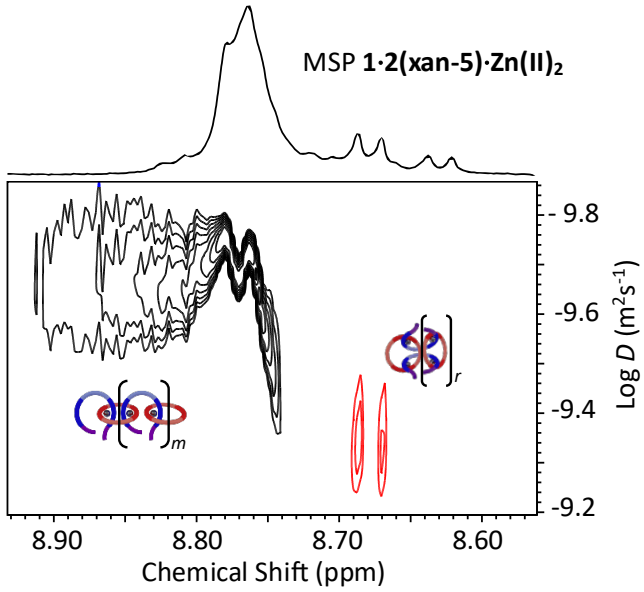


Figure S6: Processed DOSY NMR spectrum (500 MHz, CD_2Cl_2, 298 K) for the MSP **1·2(xan-5)·Zn(II)$_2$** at a concentration of 2.5 mM. Two distinctive regions assigned to the linear (black, diffusion coefficient of 1.9 x 10^{-10} m^2s^{-1}) and cyclic (red, 4.3 x 10^{-10} m^2s^{-1}) MSP can be observed.

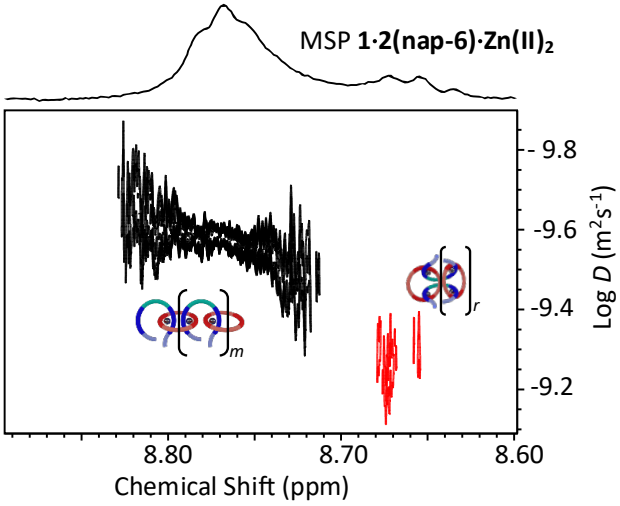
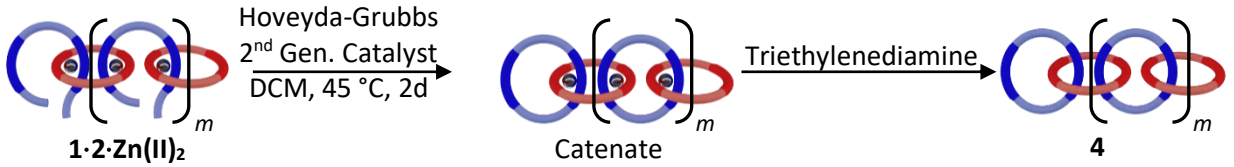


Figure S7: Processed DOSY NMR spectrum (500 MHz, CD_2Cl_2, 298 K) for the MSP **1·2(nap-6)·Zn(II)$_2$** at a concentration of 2.5 mM. Two distinctive regions assigned to the linear (black, diffusion coefficient of 2.2 x 10^{-10} m^2s^{-1}) and cyclic (red, 3.8 x 10^{-10} m^2s^{-1}) MSP can be observed.

Poly[*n*]catenane synthesis (4(xan-5), 4(nap-5), 4(nap-6))



All poly[*n*]catenane synthesis followed literature procedures.[2] Briefly, MSP **1·2·Zn(II)$_2$** (40 mg) was added to the dried vessel and dissolved in DCM (at a concentration of 2.5 mM w.r.t. **2**). The solution was stirred and heated to reflux followed by bubbling argon for 30 minutes to remove dissolved oxygen and equilibrate the MSP. Then Hoveyda-Grubbs second generation catalyst in DCM (0.32 mM) was added to the solution. To account for any solvent evaporation during the bubbling steps, additional DCM was added as required to maintain the original concentration (2.5 mM). While still under reflex, the solution was bubbled with argon for additional 30 mins. The Argon purge and catalyst addition was repeated 24 hours after the first addition. The reaction was carried out for a further 24 hours before the solution was cooled to room temperature and ethyl vinyl ether (~1mL) was added to deactivate the catalyst.

To demetallate the reaction products, 50 μL of diethylenetriamine was added to the reaction and allowed to stir. The resulting mixture was washed with 5 aliquots of water or until the aqueous wash was no longer basic. The organic layer was passed through a 0.45 μm PTFE syringe filter and the solvent was removed under vacuum. The resulting demetallated crude reaction mixture was obtained as a yellow or slightly brown solid.

Crude poly[*n*]catenane yields (by ^{1}H NMR) obtained (each reaction carried out three times): **4(xan-5)** (72%, 69%, 64%), **4(nap-5)** (78%, 78%, 69%), **4(nap-6)** (66%, 61%, 57%).

For the purposes of characterization, each of the samples of poly[*n*]catenane **4** were partially purified. For each material, the crude sample of **4** was fractionated via preparative size exclusion chromatography (SEC) using a mobile phase of 25% HPLC grade dimethylformamide (DMF) and 75% HPLC grade tetrahydrofuran (THF). Fractions were collected based on elution time. After this step, the individual fractions were characterized fully via ^{1}H NMR and SEC-MALS.

For 2D NMR characterization (COSY, NOESY), the fractionated material **4** was further purified via one of the following methods (*note- both methods were tried on each new poly[*n*]catenane materials and selection was based on the method that optimized purity and yield of **4**).

Method 1 (**4(nap-6)**, **4(xan-5)**): After SEC, a portion of fractions 1-3 (which contain the bulk of the larger poly[*n*]catenane materials) were recombined and partially re-metalated with $Zn(NTf_2)_2$ until ca. 30% of the poly[*n*]catenane was metalated as observed by NMR. The sample was fully dried under vacuum and washed 8 times with a solution of 2:1 chloroform:hexanes to remove the non-metal-containing compounds. The remaining metalated compounds were dissolved in DCM and demetallated using 50 μL of diethylenetriamine. The resulting mixture was washed with 5 aliquots of water or until the sample was no longer basic. After removal of residual water, the final material was collected. **4(xan-5)** was isolated in 85% purity with the residual byproduct identified as **5(xan-5)**. **4(nap-6)** was isolated in 76% purity with the residual byproduct identified as the ADMET polymer **5(nap-6)**.

Method 2 (**4(nap-5)**): After SEC, a portion of fraction 2 was purified via silica-preparative plates (pretreated with triethylamine (TEA)) using 5% MeOH in $CHCl_3$ as an eluant. The bottom fraction was collected and washed three times in 30% MeOH in $CHCl_3$. The solvent was removed under reduced pressure and the material was redissolved in pure chloroform. The solution was passed through a 0.2 μm PTFE syringe filter to remove residual silica. The chloroform was removed under pressure and the material was washed with pure hexanes to remove grease and other residual byproducts from the prep-TLC plate. The final material was collected to yield a sample of **4(nap-5)** in 96% purity with the residual byproduct identified as **5(nap-5)**.

4(xan-5) Polycatenane (84% of sample) ^{1}H NMR (500 MHz, $CDCl_3$) δ_H (ppm) 8.28 – 8.10 (m, 8H), 7.98 – 7.81 (m, 12H), 7.46 – 7.29 (m, 36H, overlapped with $CDCl_3$), 7.11 (d, J = 8.7 Hz, 2H), 6.98 (s, 2H), 6.89 – 6.75 (m, 8H), 6.71 – 6.54 (m, 8H), 5.58 – 5.27 (m, 2H), 5.07 – 4.93 (m, 4H), 4.63 – 4.42 (m, 16H), 4.04 – 3.95 (m, 4H), 3.92 – 3.47 (m, 32H), 1.68 – 1.61 (m, 16H, overlapped), 1.46 – 1.38 (m, 6H), 0.92 – 0.78 (m, 16H), 0.64 – 0.46 (m, 24H).
5(xan-5) Byproduct (16% of sample) 8.35 (d), 8.07 (t), 8.03 (s), 7.66 – 7.55 (m), 7.48 (dd), 7.23 – 7.08 (m), 7.03 (d), 5.81-5.65 (m), 5.12 (s), 4.76 (t), 4.08 (t), 2.70-2.59 (m), 1.74 (q), 1.60 (s), 1.14 (h), 0.73 (t). For full ^{1}H NMR and ^{13}C NMR information on **5(xan-5)**, see page S8.

4(nap-5) Polycatenane (96% pure) ^{1}H NMR (500 MHz, $CDCl_3$) δ_H (ppm) 8.27 – 8.08 (m, 8H), 7.93 – 7.82 (m, 12H), 7.72 – 7.56 (m, 4H), 7.45 – 7.30 (m, 16H), 7.30 – 7.27 (m, 10H), 7.23 – 7.14 (m, 8H), 6.86 (d, J = 7.8 Hz, 4H), 6.79 (dd, J = 25.9, 8.1 Hz, 8H), 6.58 (t, J = 8.3 Hz, 4H), 5.56 – 5.50 (m, 2H), 5.24 – 5.10 (m, 4H), 4.61 – 4.41 (m, 16H), 3.99 – 3.83 (m, 4H), 3.81 – 3.45 (m, 32H), 2.40 – 2.30 (m, 4H), 1.65 – 1.46 (m, 16H), 1.03 – 0.91 (m, 16H), 0.63 – 0.50 (m, 24H).

4(nap-6) Polycatenane (76%) ^{1}H NMR (500 MHz, $CDCl_3$) δ_H (ppm) 8.29 – 8.13 (m, 8H), 7.95 – 7.83 (m, 12H, overlapped with **6**), 7.76 – 7.66 (m, 4H), 7.46 – 7.31 (m, 26H, overlapped with $CDCl_3$), 7.24 – 7.17 (m, 8, overlapped with $CDCl_3$), 6.88 (d, J = 8.6 Hz, 4H), 6.81 (dd, J = 21.1, 8.1 Hz, 8H), 6.62 (d, J = 8.8 Hz, 4H), 5.50 – 5.36 (m, 2H, overlapped with **6**), 5.26 – 5.16 (m, 4H), 4.64 – 4.43 (m, 16H), 4.00 – 3.95 (m, 4H), 3.81 – 3.45 (m, 32H), 2.48 – 2.37 (m, 4H), 2.10 – 1.99 (m, 4H), 1.64 – 1.51 (m, 16H), 1.05 – 0.92 (m, 16H), 0.63 – 0.52 (m, 24H).
5(nap-6) Byproduct (23%) 8.35 (d), 8.08 (t), 8.04 (s), 7.96 (s), 7.67 – 7.55 (m), 7.50 (d), 7.15 (d), 7.02 (d), 5.60 – 5.46 (m), 5.31 (s), 4.76 (t), 4.03 (q), 2.36 – 2.17 (m), 1.89 (q), 1.79 – 1.70 (m), 1.15 (h), 0.73 (t). For full ^{1}H NMR and ^{13}C NMR information on **5(nap-5)**, see page S9.

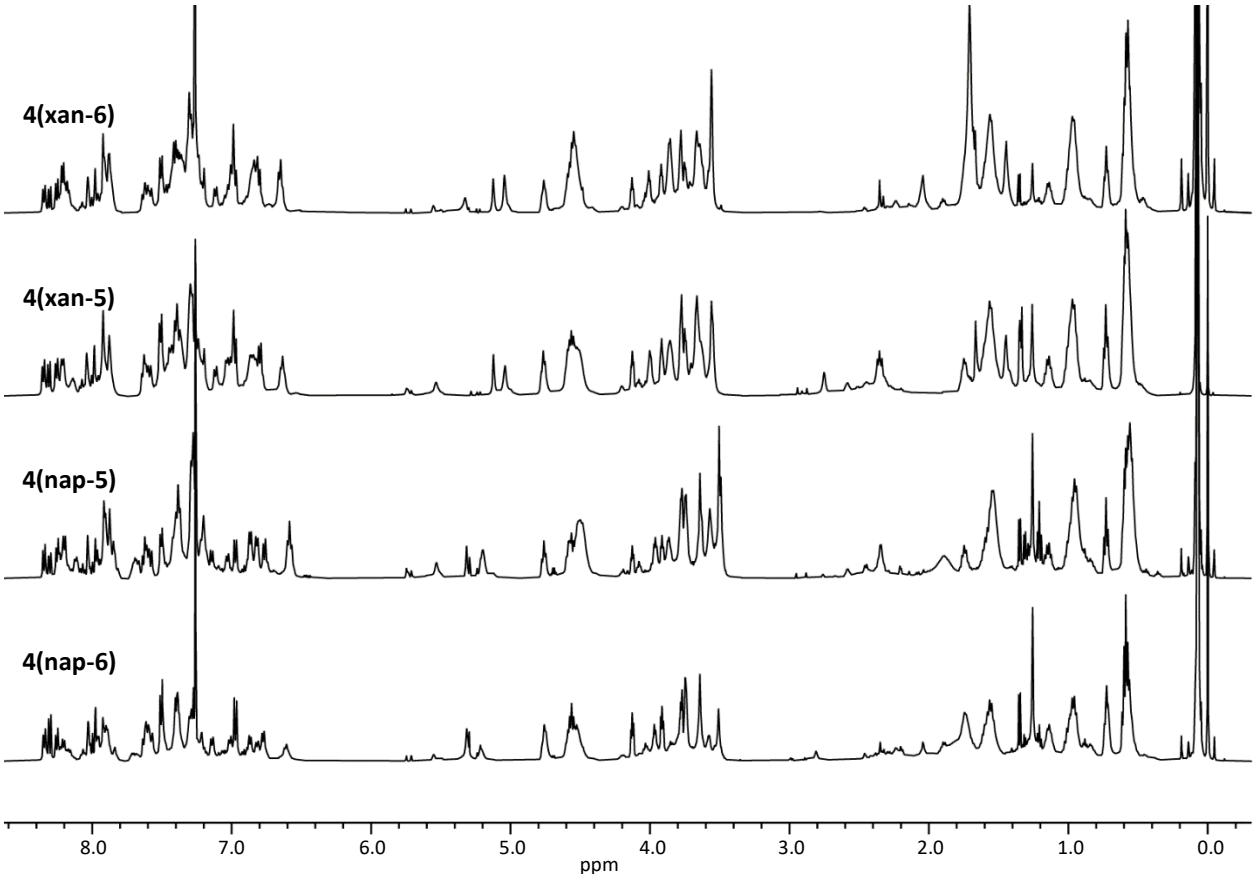


Figure S8: Full ^{1}H NMR spectra (500 MHz, 1:5 CD_3CN:$CDCl_3$, 25 °C) of Figure 3 for all crude poly[*n*]catenane materials.

[1]H NMR analysis of thread derivatives (3, 5)

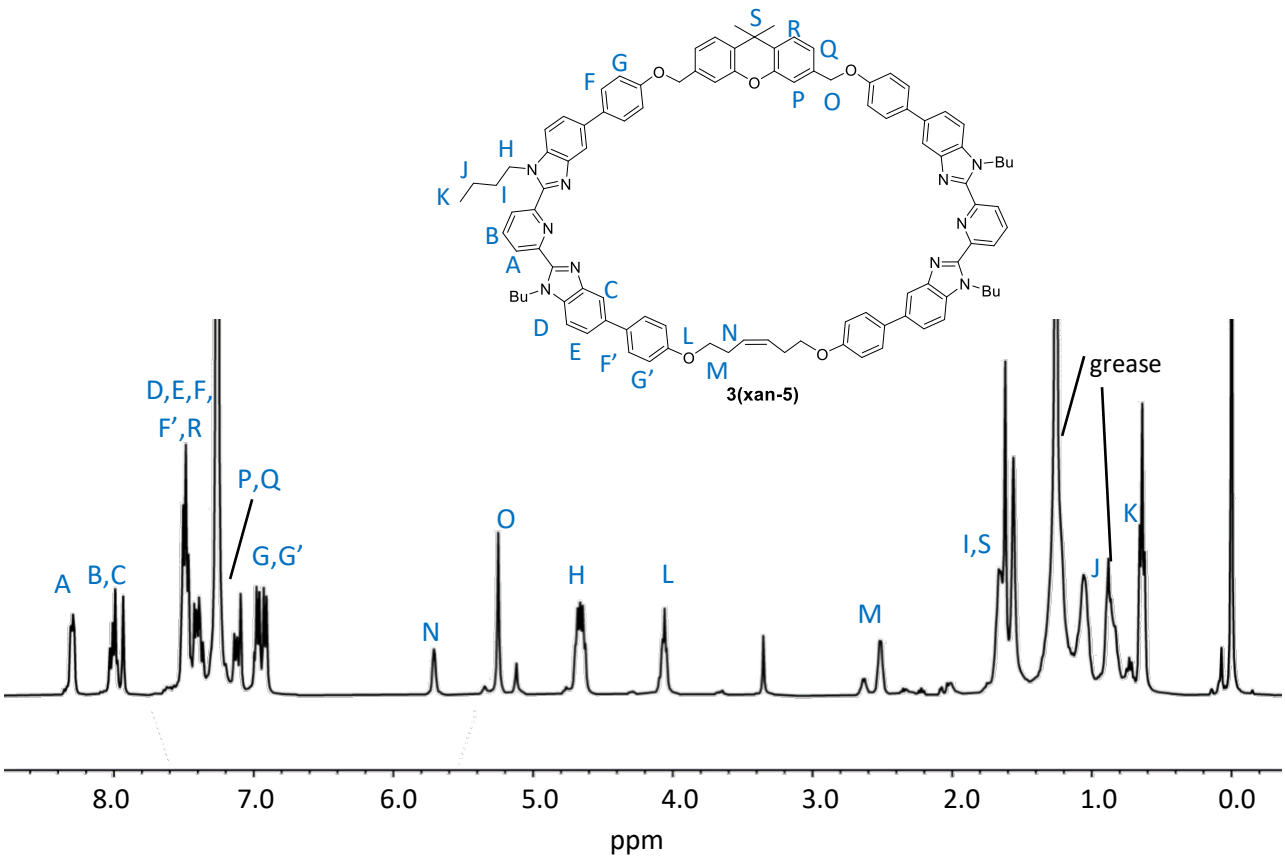


Figure S9: [1]H NMR ($CDCl_3$, 500 MHz) of **3(xan-5).**

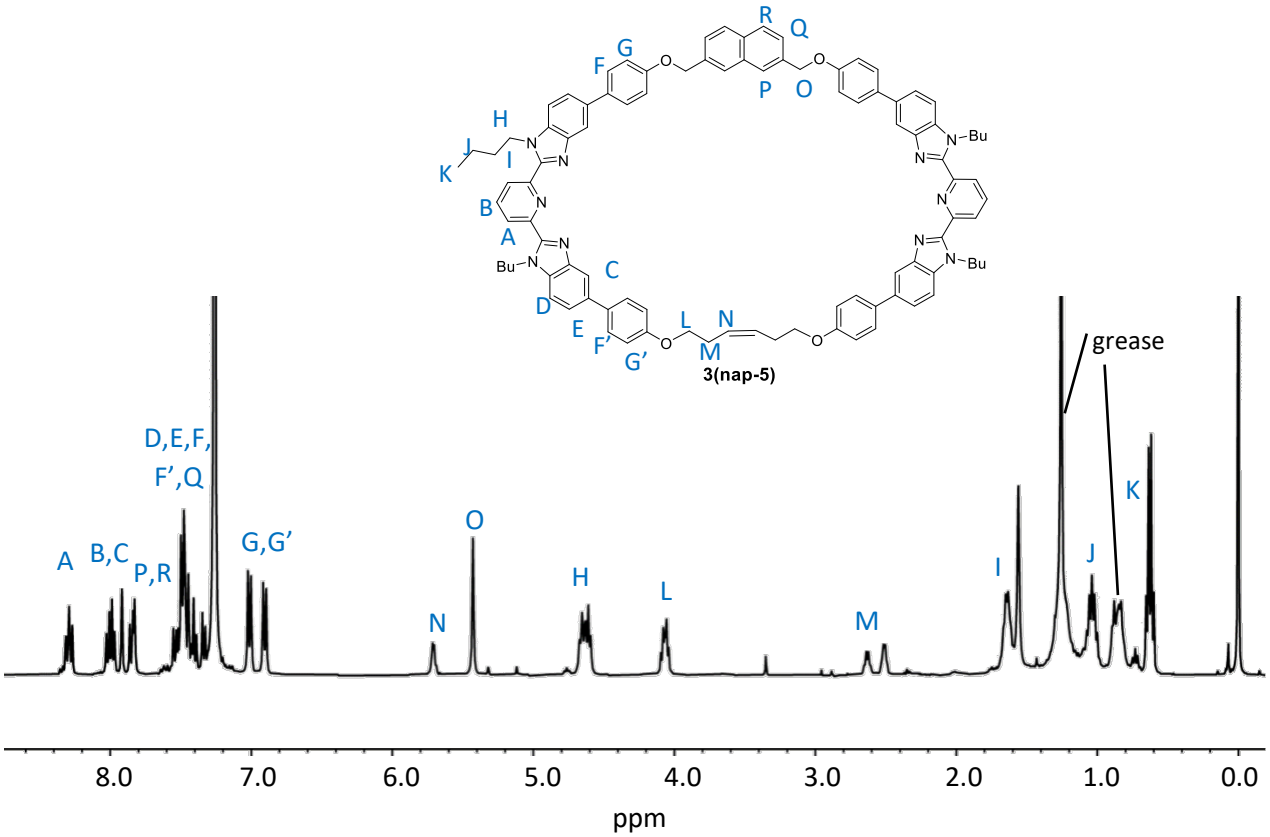


Figure S10: ^{1}H NMR ($CDCl_3$, 500 MHz) of **3(nap-5).**

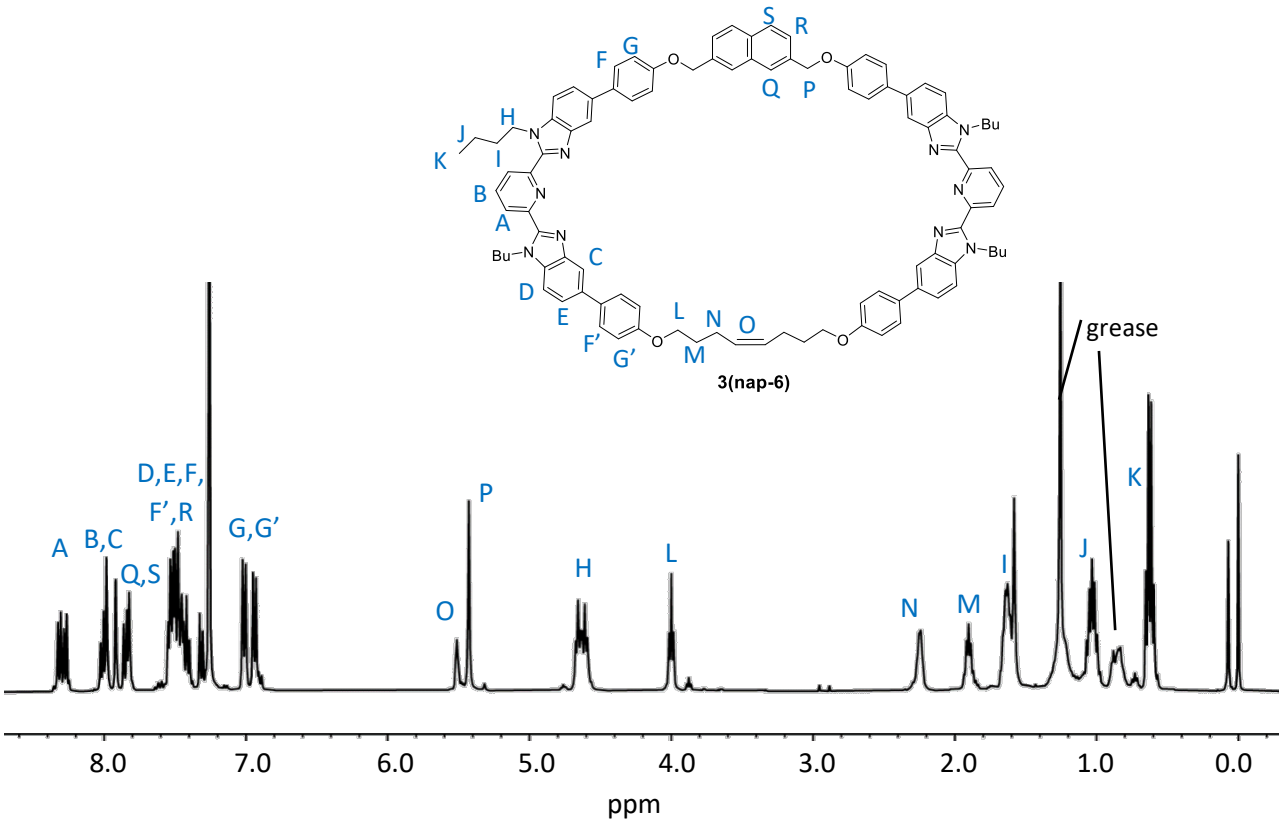


Figure S11: ^{1}H NMR ($CDCl_3$, 500 MHz) of **3(nap-6).**

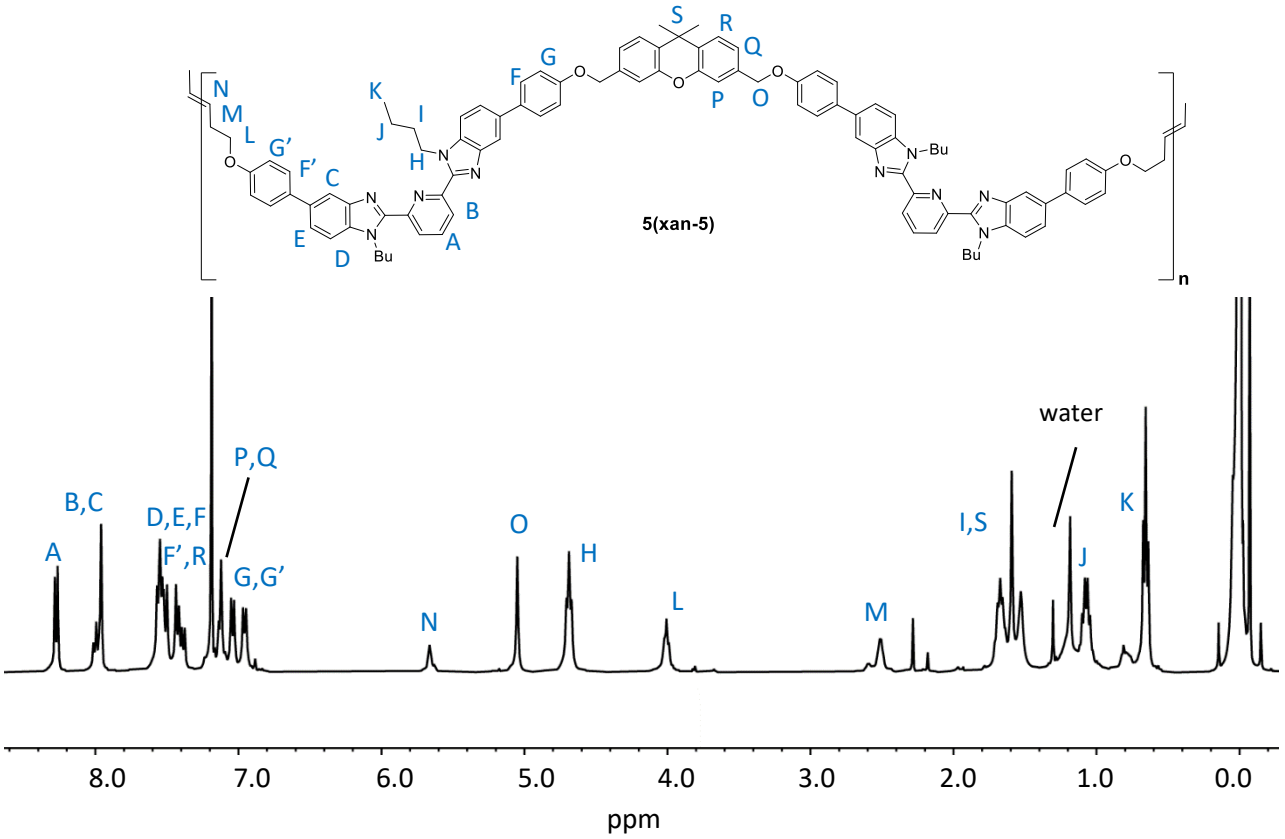


Figure S12: ^{1}H NMR ($CDCl_3$, 500 MHz) of **5(xan-5).**

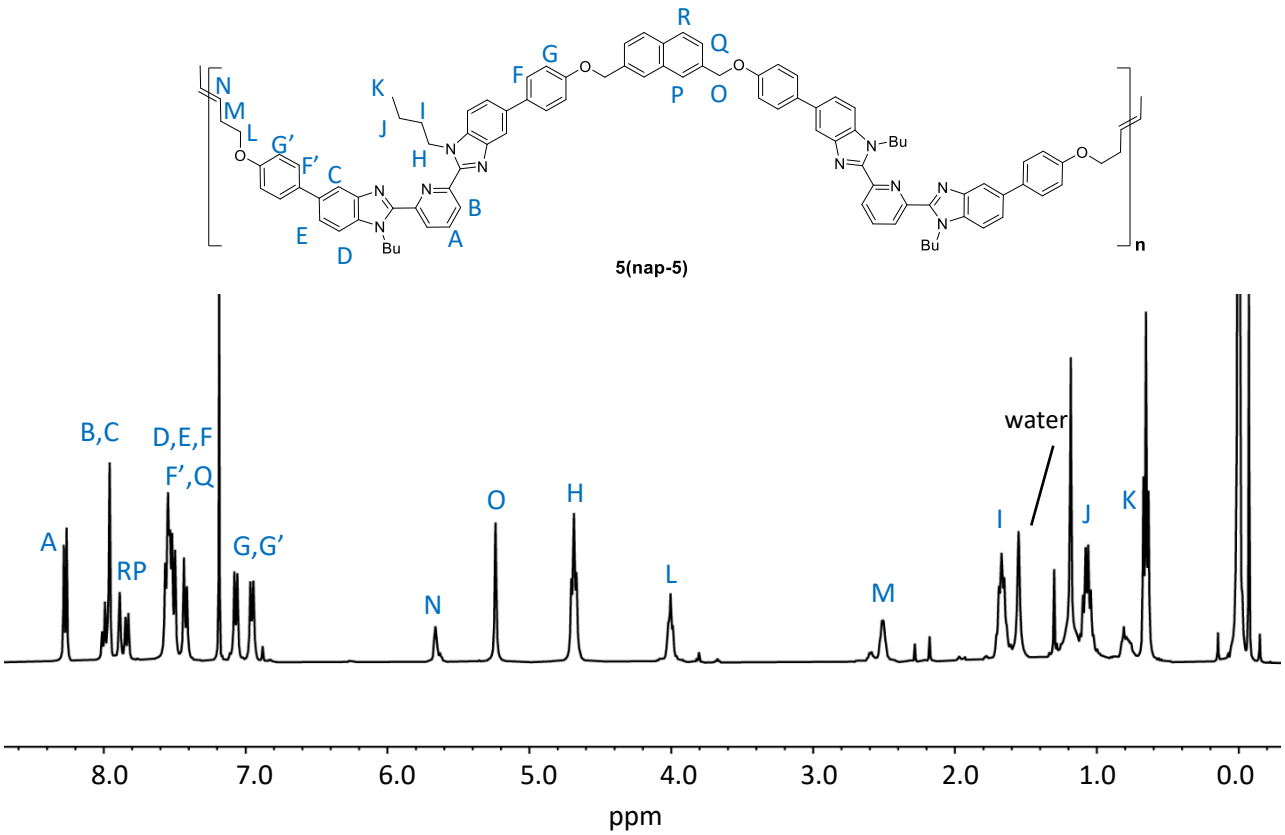


Figure S13: ^{1}H NMR ($CDCl_3$, 500 MHz) of **5(nap-5).**

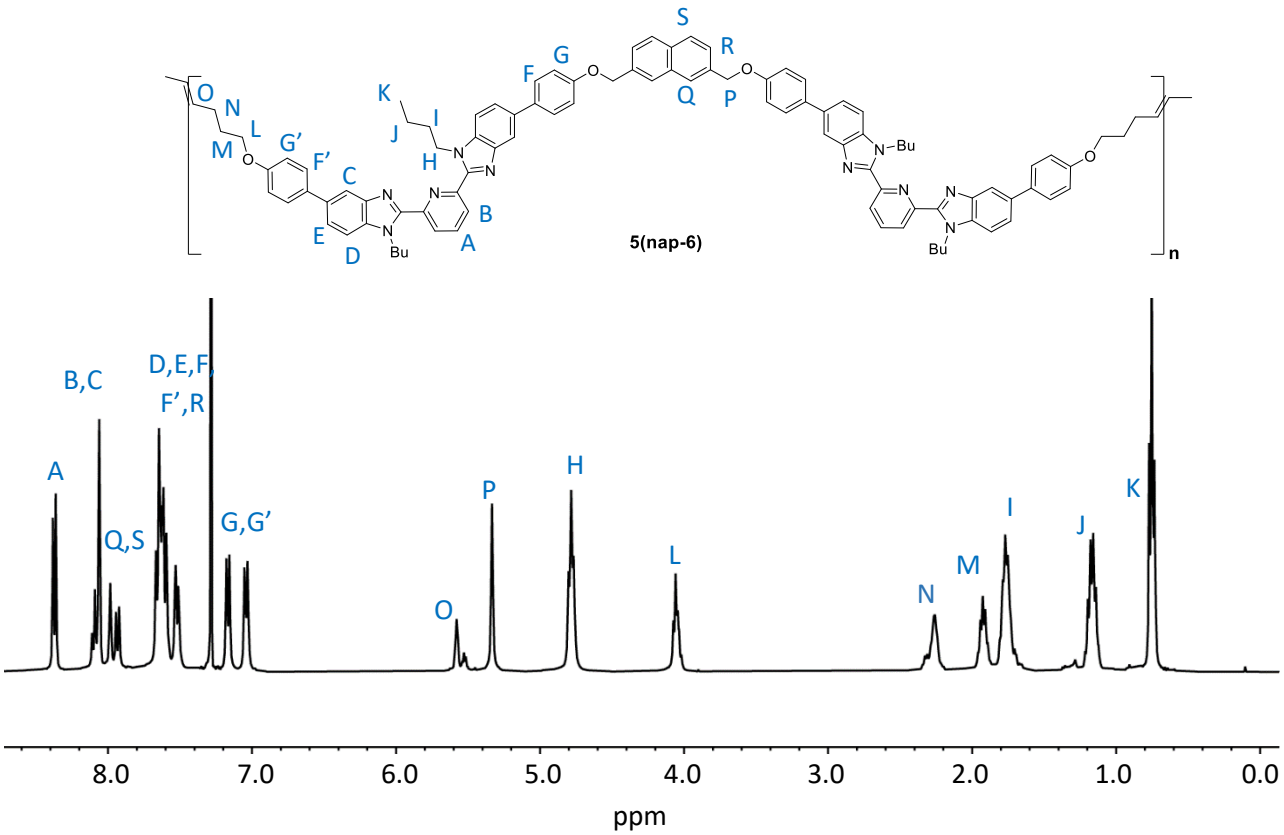


Figure S14: ^{1}H NMR ($CDCl_3$, 500 MHz) of **5(nap-6).**

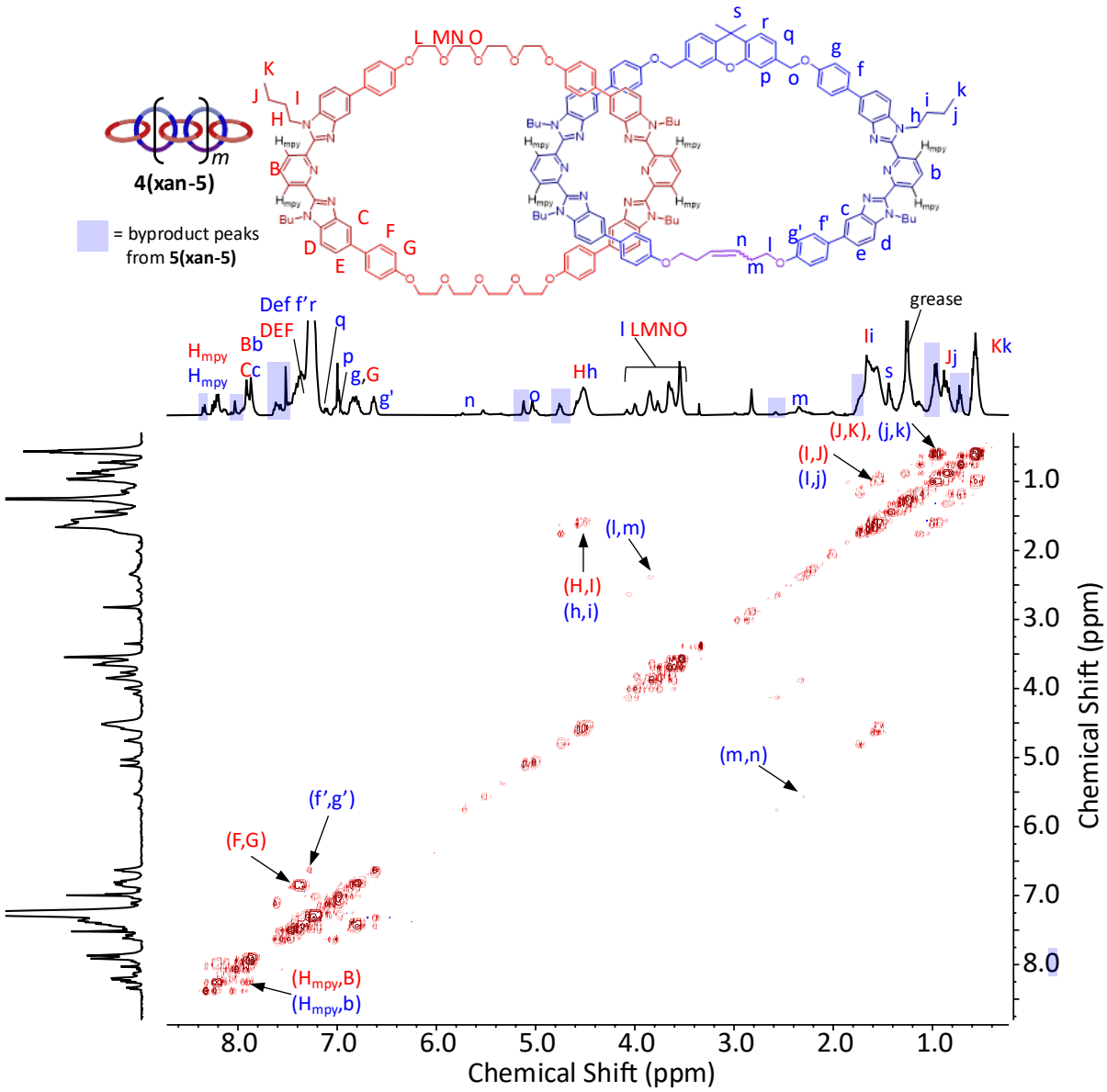


Figure S15: ^{1}H-^{1}H homonuclear correlation spectroscopy (COSY) (500 MHz, $CDCl_3$, 25 °C) of **4(xan-5)** (85% purified, 10 mg/mL). Peaks corresponding to the residual byproduct (**5(xan-5)**) are indicated via blue highlight.

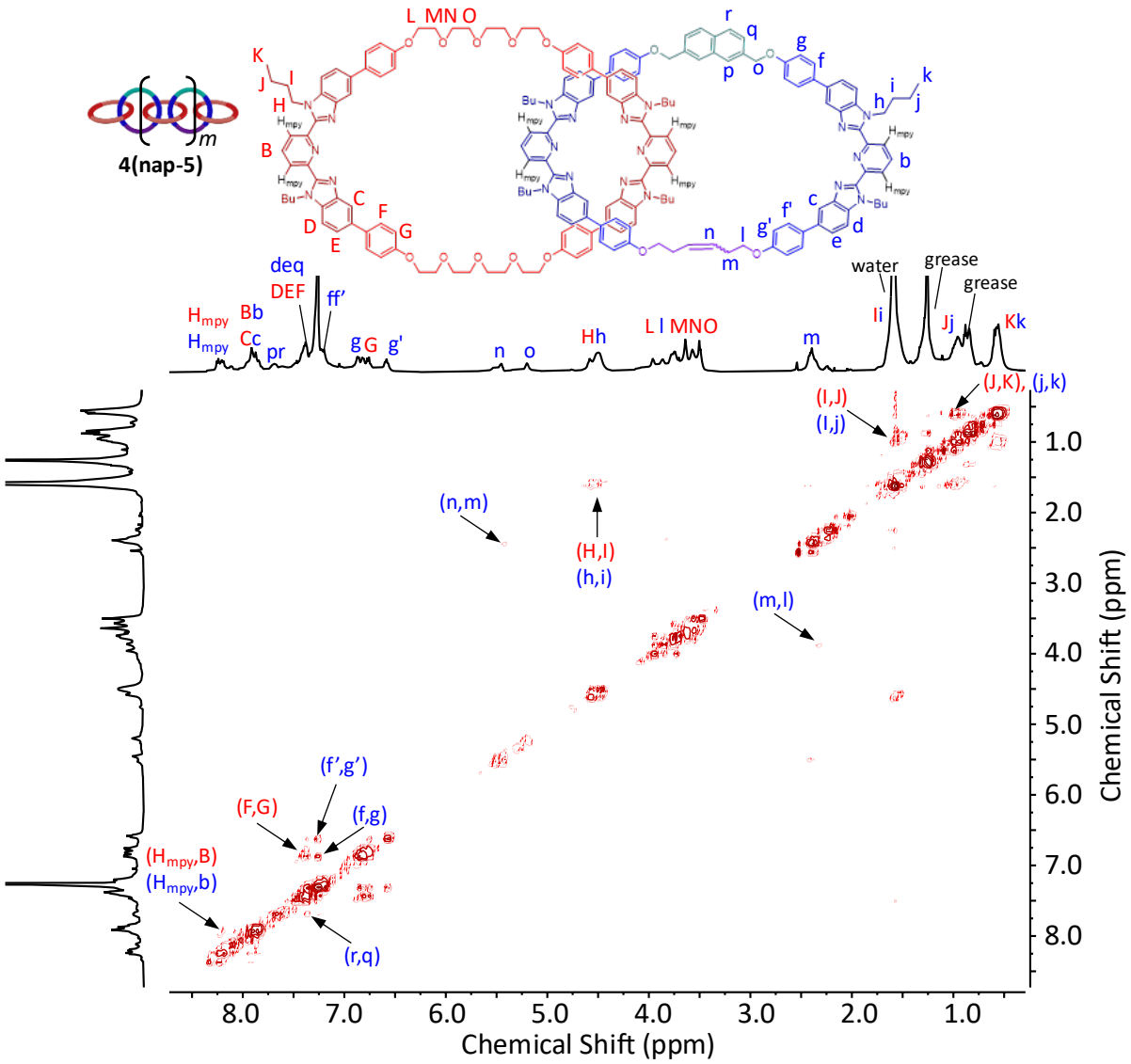


Figure S16: ^{1}H-^{1}H homonuclear correlation spectroscopy (COSY) (500 MHz, $CDCl_3$, 25 °C) of **4(nap-5)** (95% purified, 10 mg/mL).

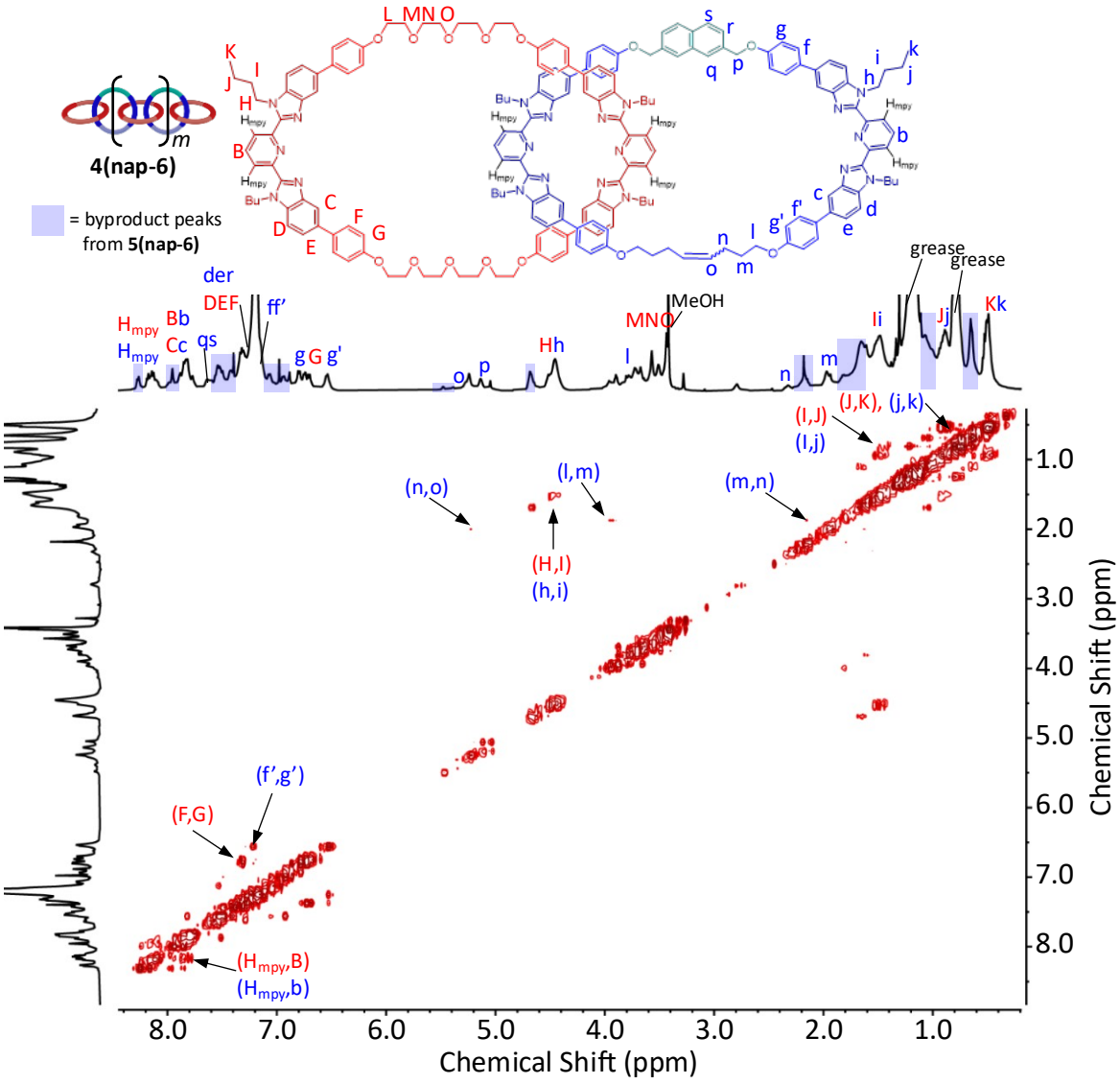


Figure S17: ^{1}H-^{1}H homonuclear correlation spectroscopy (COSY) (500 MHz, $CDCl_3$, 25 °C) of **4(nap-6)** (76% purified, 20 mg/mL). Peaks corresponding to the residual byproduct (**5(nap-6)**) are indicated via blue highlight.

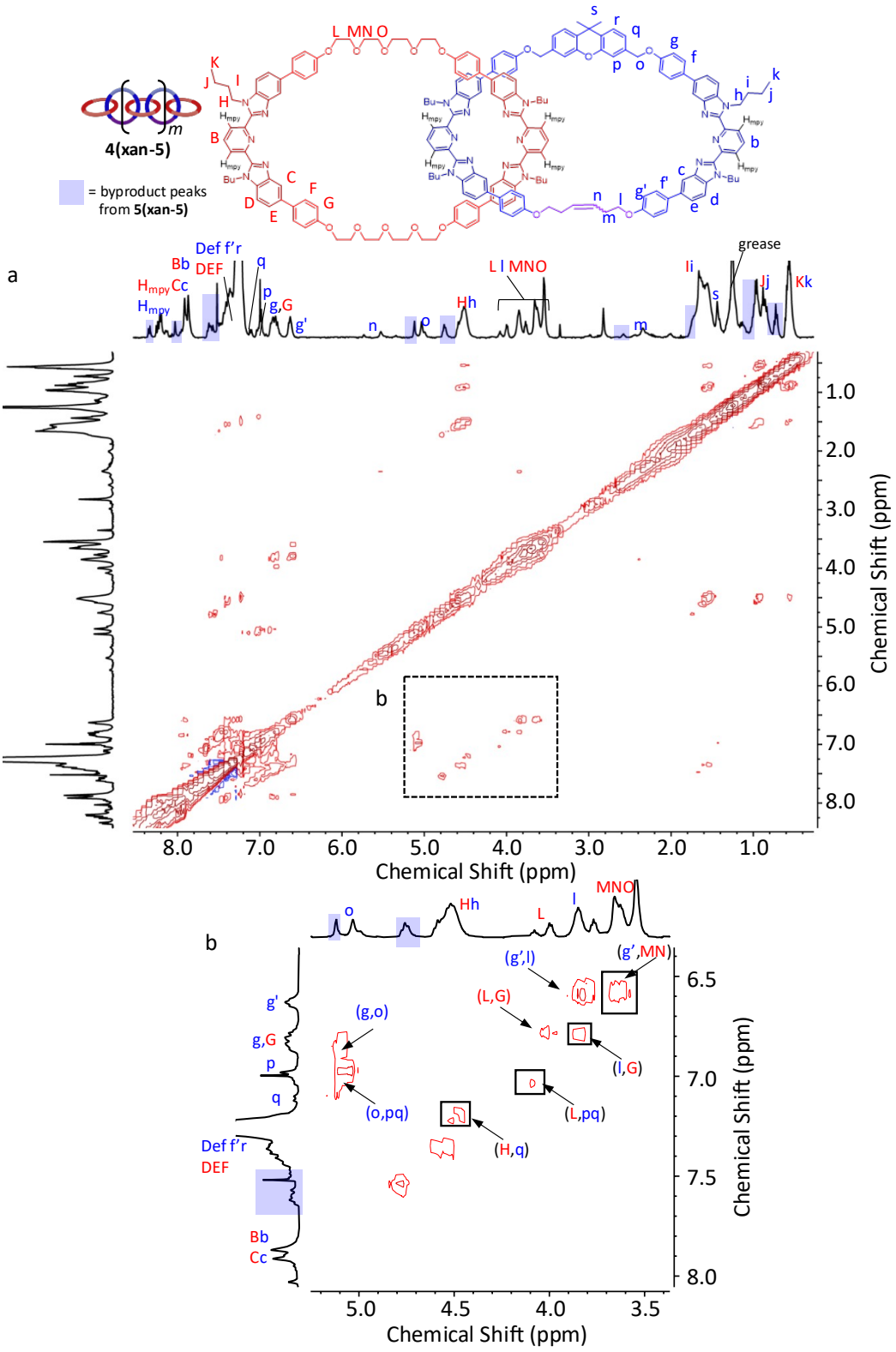


Figure S18: Nuclear Overhauser Effect Spectroscopy (NOESY) (500 MHz, $CDCl_3$, -25 °C) of (a) **4(nap-5)** (84% purified, 10 mg/mL), (b) zoomed in region corresponding to the dashed box in (a) with interlocked cross-peaks indicated by a solid black box in the zoomed region.

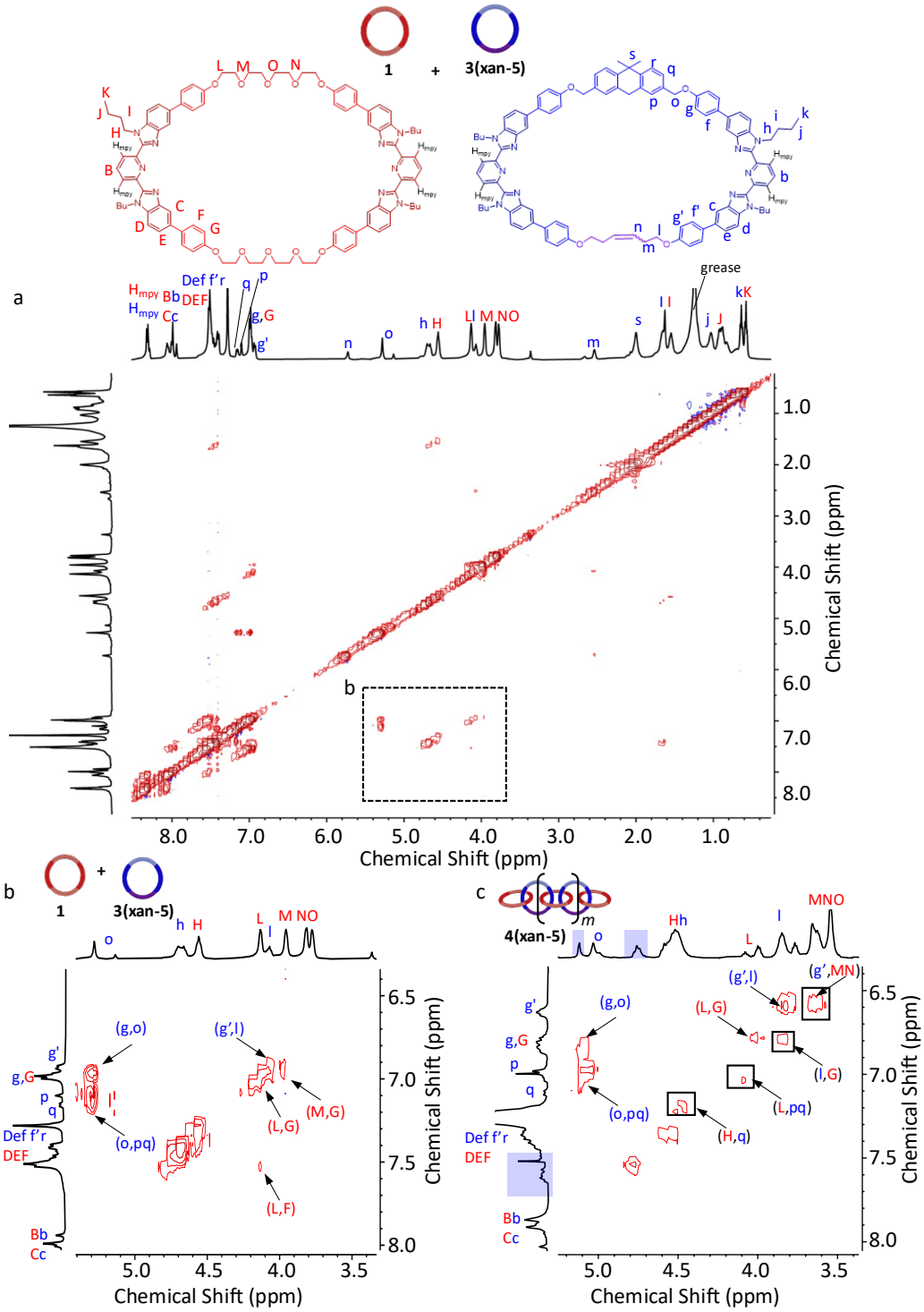


Figure S19: Nuclear Overhauser Effect Spectroscopy (NOESY) (500 MHz, $CDCl_3$, -25 °C) of (a) a mixture of **1** and **3(xan-5)** (10 mg/mL) for comparison with the interlocked **4(xan-5)**. (b) zoomed in region (indicated by the dashed box in (a)) of the **1** and **3(xan-5)** mixture to compare with (c) the analyzed region of the interlocked material (**4(xan-5)**) seen in Figure S18. The intercomponent cross-peaks (highlighted by the solid black boxes) observed in **4(xan-5)** (c) are not present in the 1:1 mixture, consistent with the fact that **4(xan-5)** has an interlocked structure.

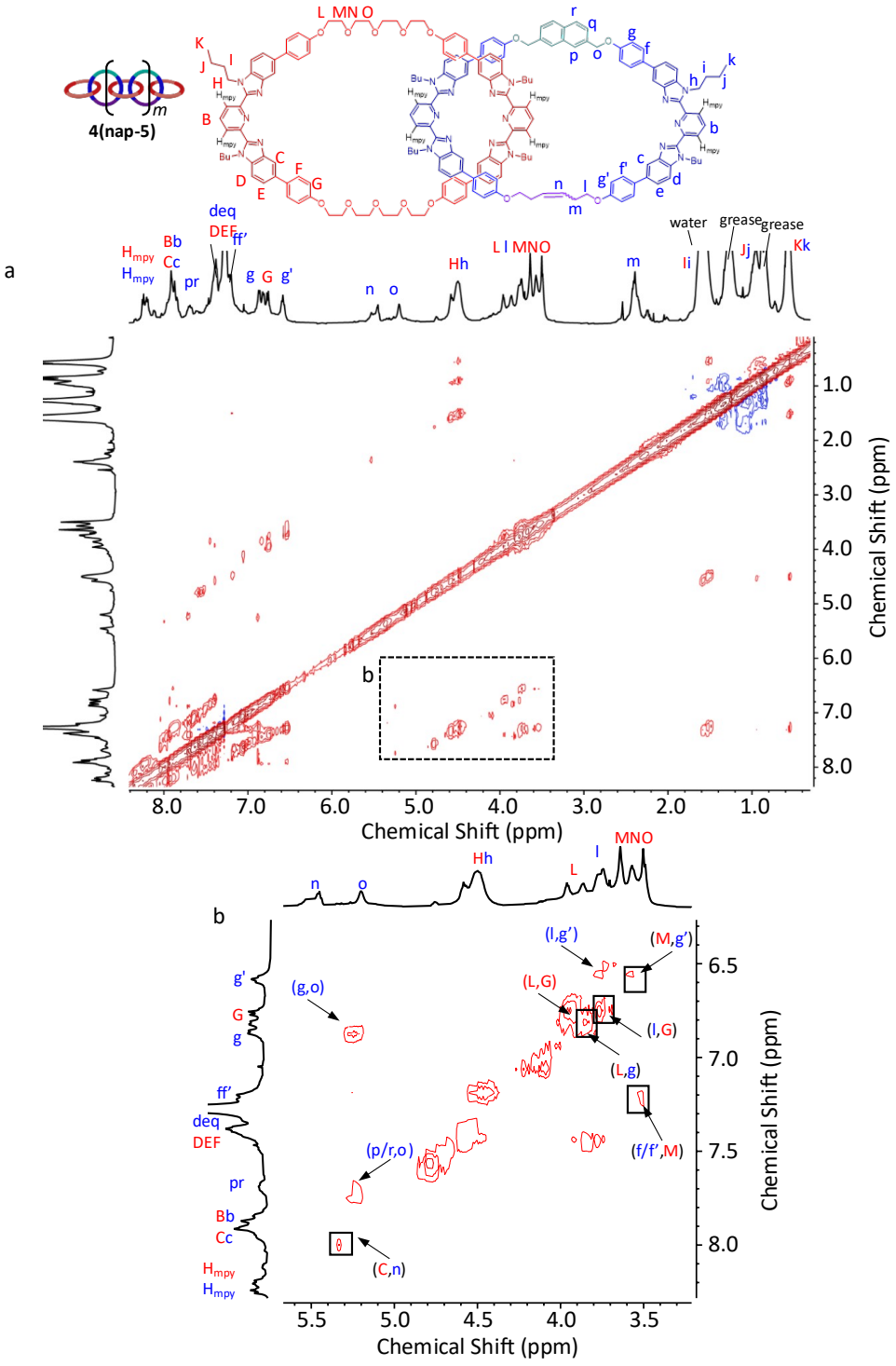


Figure S20: Nuclear Overhauser Effect Spectroscopy (NOESY) (500 MHz, $CDCl_3$, -25 °C) of (a) **4(nap-5)** (90% purified, 10 mg/mL), (b) zoomed in region corresponding to the dashed box in (a) with interlocked cross-peaks indicated by a solid black box in the zoomed region.

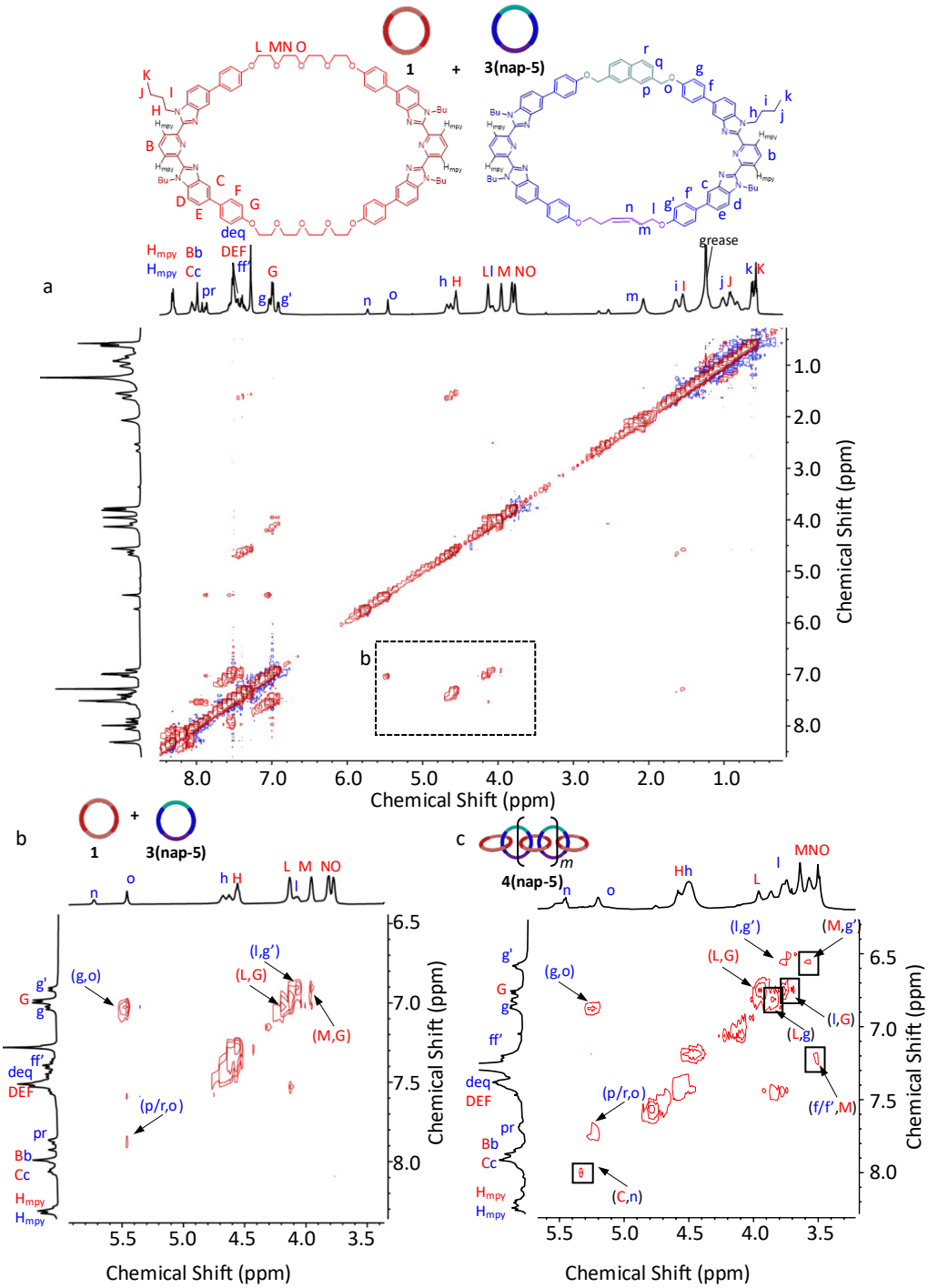


Figure S21: Nuclear Overhauser Effect Spectroscopy (NOESY) (500 MHz, $CDCl_3$, -25 °C) of (a) a mixture of **1** and **3(nap-5)** (10 mg/mL) for comparison with the interlocked **4(nap-5)**. (b) zoomed region (indicated by the dashed box in (a)) of the **1** and **3(nap-5)** mixture to compare with (c) the analyzed region of the interlocked material (**4(nap-5)**) seen in Figure S20. The intercomponent cross-peaks (highlighted by the solid black boxes) observed in **4(nap-5)** (c) are not present in the 1:1 mixture, consistent with the fact that **4(nap-5)** has an interlocked structure.

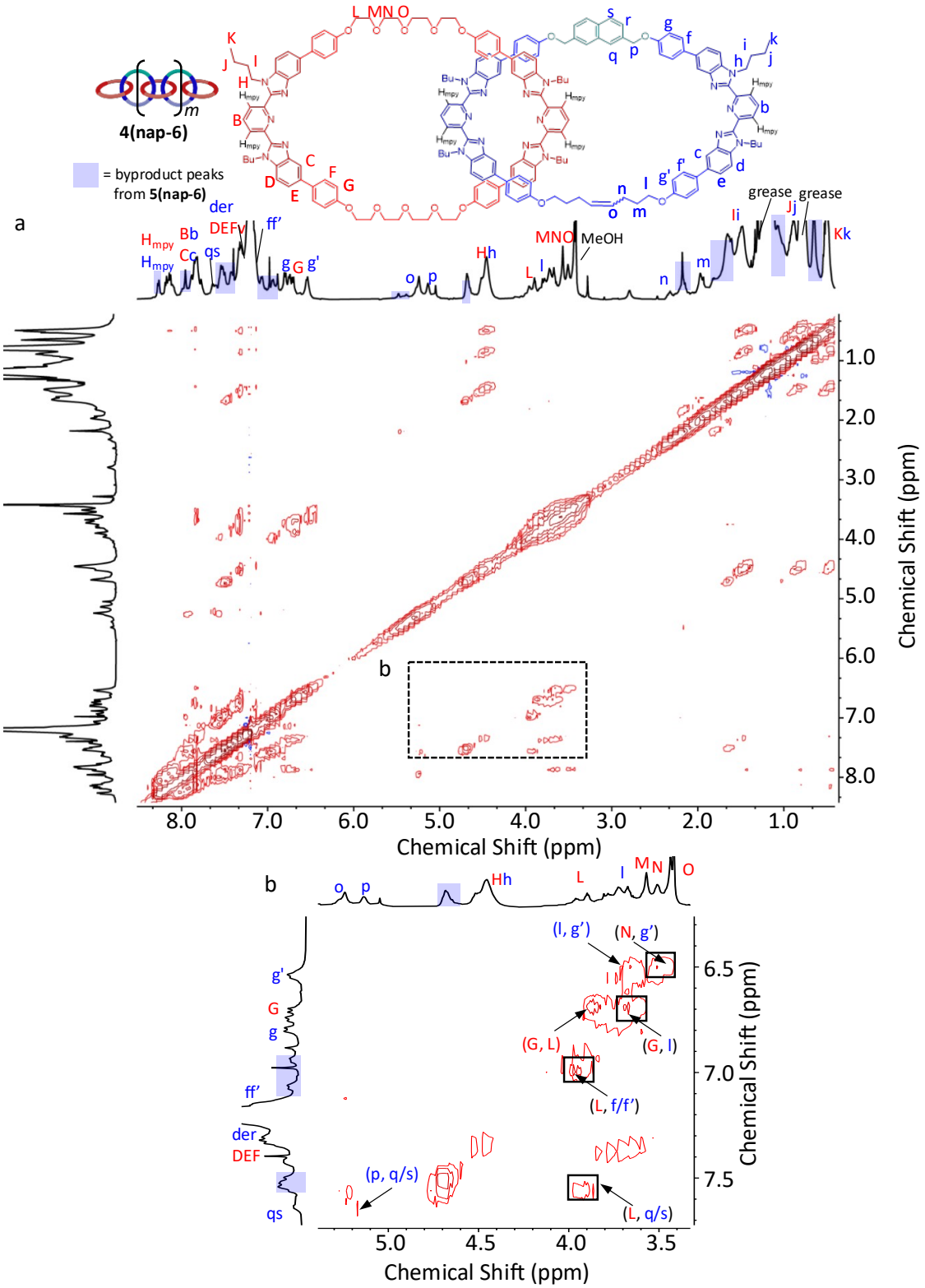


Figure S22: Nuclear Overhauser Effect Spectroscopy (NOESY) (500 MHz, $CDCl_3$, -25 °C) of (a) **4(nap-6)** (76% purified, 10 mg/mL), (b) zoomed in region corresponding to the dashed box in (a) with interlocked cross-peaks indicated by a solid black box in the zoomed region.

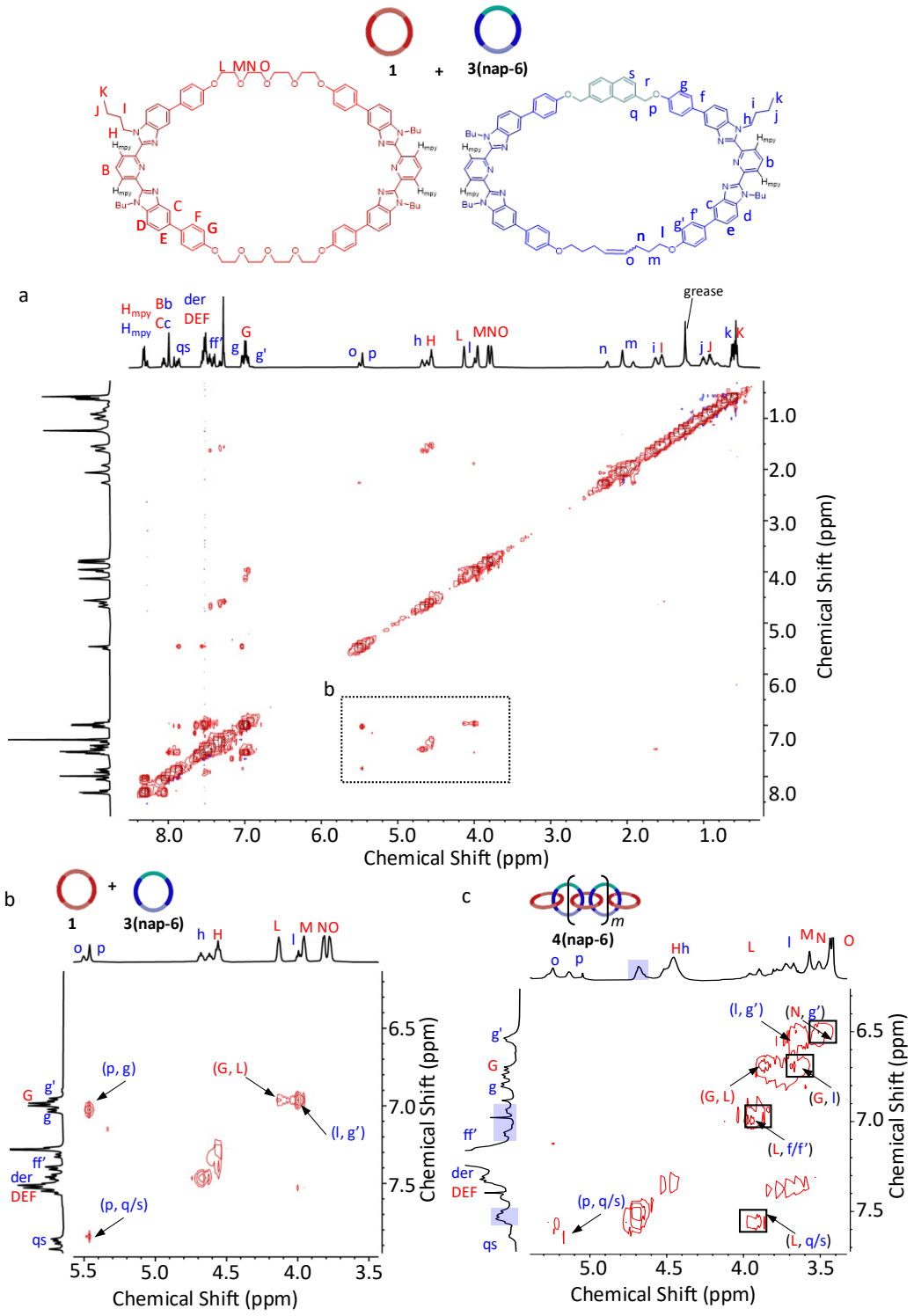


Figure S23: Nuclear Overhauser Effect Spectroscopy (NOESY) (500 MHz, $CDCl_3$, -25 °C) of (a) a mixture of **1** and **3(nap-6)** (10 mg/mL) for comparison with the interlocked **4(nap-6)**. (b) Zoomed region (indicated by the dashed box in (a)) of the **1** and **3(nap-6)** mixture to compare with (c) the analyzed region of the interlocked material (**4(nap-6)**) seen in Figure S22. The intercomponent cross-peaks (highlighted by the solid black boxes) observed in **4(nap-6)** (c) are not present in the 1:1 mixture, consistent with the fact that **4(nap-6)** has an interlocked structure.

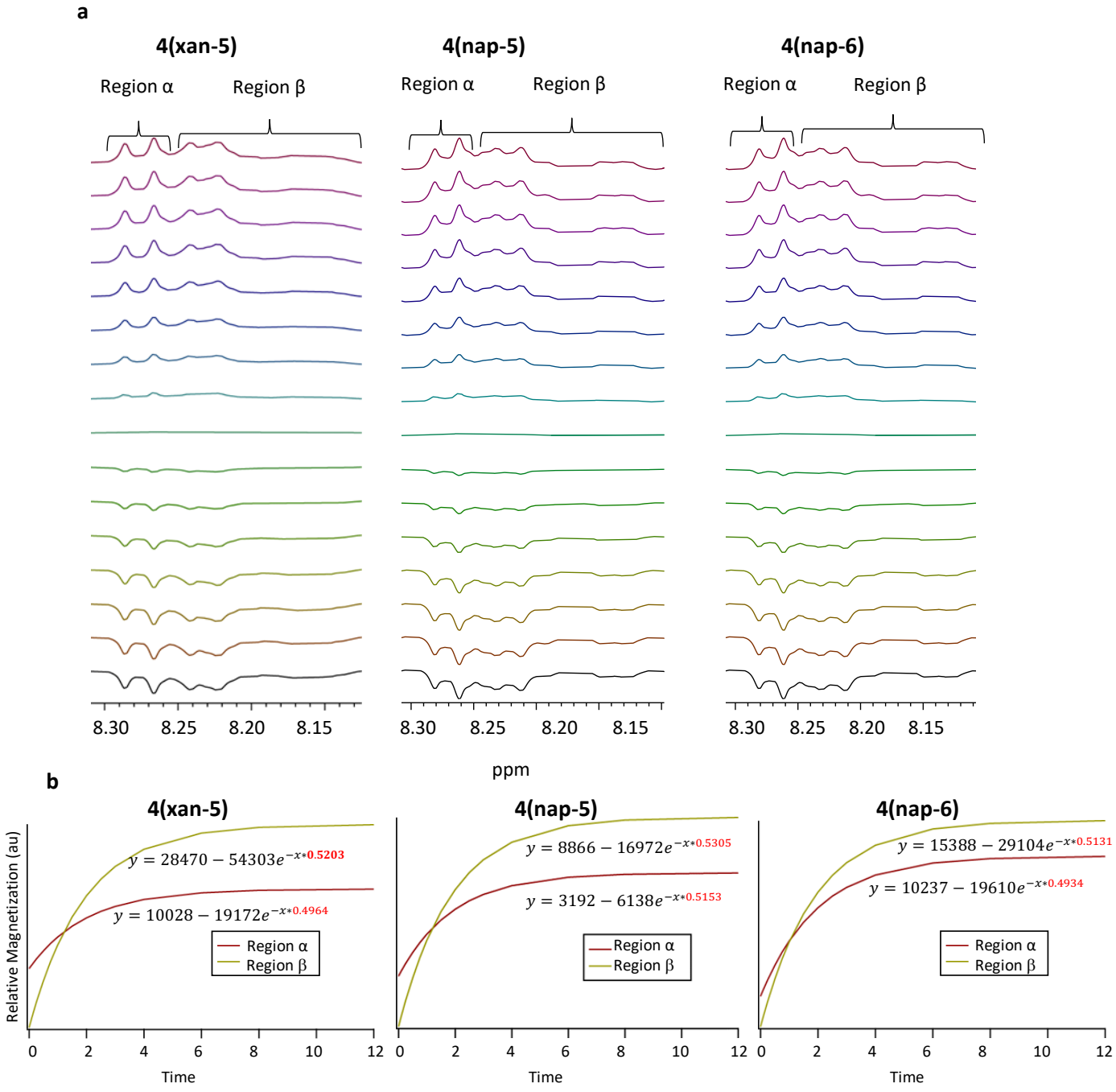


Figure S24: ^{1}H NMR relaxation studies on H_{mpy} for all new polycatenane materials. (a) depicts the individual ^{1}H NMR scans taken during the experiment while (b) shows the relative magnetization vs. time calculated from three parameter exponential fit (B+F*exp(-x*G)) via the Mestrenova software for each region (α and β). T_1 values taken from 1/G (G highlighted in red), displayed in Table S2.

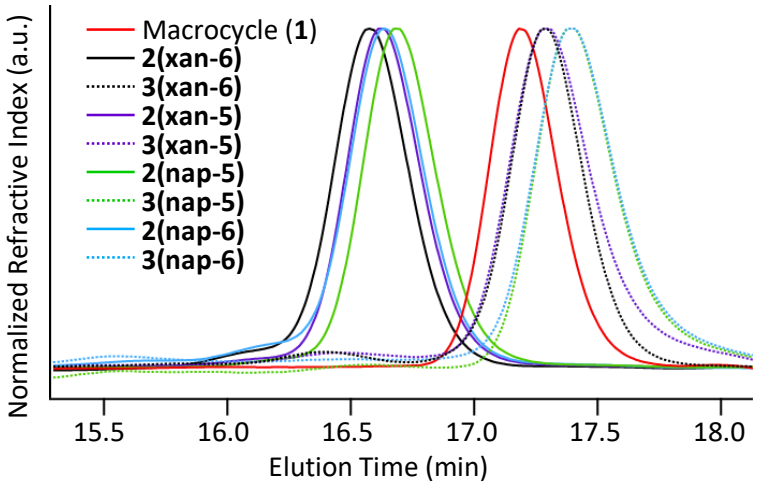


Figure S25: SEC traces (25% HPLC grade dimethylformamide (DMF) and 75% HPLC grade tetrahydrofuran (THF) as the eluent (1mL/min) at 25 °C) of the starting materials: the macrocycle (**1**), all four thread types: the original system[2,3] (**2(xan-6)**), **2(xan-5)**, **2(nap-6)** and **2(nap-5)**), and the ring closed versions of all three (**3(xan-6)**), **3(xan-5)**, **3(nap-6)** and **3(nap-5)**).

Calculation of Degree of Polymerization of Poly[*n*]catenane

Degree of polymerization for these materials will be reported as number of interlocked rings rather than number of repeat units:

$$\overline{DP_n} = \frac{M_n(obtained\ from\ GPC\ MALS\ analysis)}{(MW(\mathbf{1})+MW(\mathbf{2}))/2} \qquad \text{Eq. S1}$$

Calculation of Poly[*n*]catenane Chain Ends (N_c)

$$N_C = \overline{DP} \times \frac{2 \times Integration(\,8.24-8.27\ ppm)}{Integration\ (8.05-8.27)} \qquad \text{Eq. S2}$$

Where $\overline{DP_n}$ is obtained from Eq. S1.

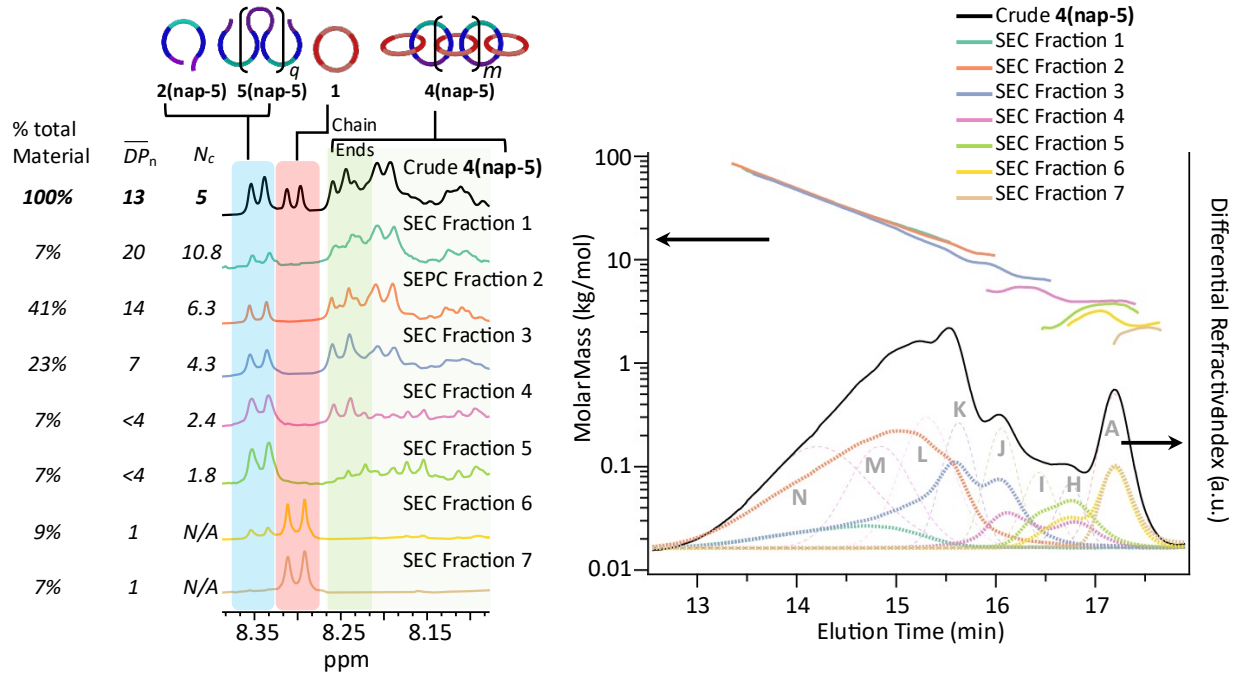


Figure S26: ^{1}H NMR and SEC-MALS traces for all fractionated **4(nap-5)** samples. The number average degree of polymerization (DP_n, Eqn. S1) and chain end calculations (N_c, Eqn. S2) for each fraction were used to assign the poly[*n*]catenane architectures in the crude SEC trace (assigned in Figure 7c, analysis below).

Peak A is assigned based on the SEC trace of pure macrocycle **1** (Figure S17).

Peak H is assigned based on the SEC trace of pure thread **2(nap-5)** (Figure S17).

Peak I is tentatively assigned to [2]catenane (and/or low molecular weight catenanes). Fraction 5 contains Peak I and unreacted thread **2(nap-5)** (Peak H) and has an N_c ~2 and $\overline{DP} < 4$. NMR shows the presence of different chain end peaks (at least two sets of doublets in the region 8.21-8.27 consistent with chain ends from both **1** and **3(nap-5)**) suggesting the presence of low molecular weight catenanes with both red and blue chain ends.

Peak J is tentatively assigned to [3]catenane. Fraction 4 is mainly a combination of Peak J and unreacted thread **2(nap-5)**, (Peak H) with an N_c ~2 and $\overline{DP} < 4$. NMR (region 8.21-8.27) suggests that the catenanes' chain-ends are primarily from macrocycle **1**, consistent with a [3]catenane.

Peak K is tentatively assigned to the ADMET byproduct **5(nap-5).** It present in Fractions 2 and 3 and to a lesser extent in Fraction 1. Based on the previously published work[2] and the prevalence of ADMET **5(nap-5)** in the ^{1}H NMR each of these fractions, Peak K has been tentatively assigned to the ADMET byproduct **5(nap-5)**.

Peak L is assigned to ***b*-4(nap-5)**. It is present in Fractions 2 and 3, which both have N_c values >4.

Peak M is assigned to ***b*-4(nap-5)**. It is a main component of Fraction 2 which has an N_c of ca. 6.

Peak N is assigned to a more highly branched ***b*-4(nap-5)**. It is main component of Fraction 1 and is also in Fraction 2 both have $N_c > 6$.

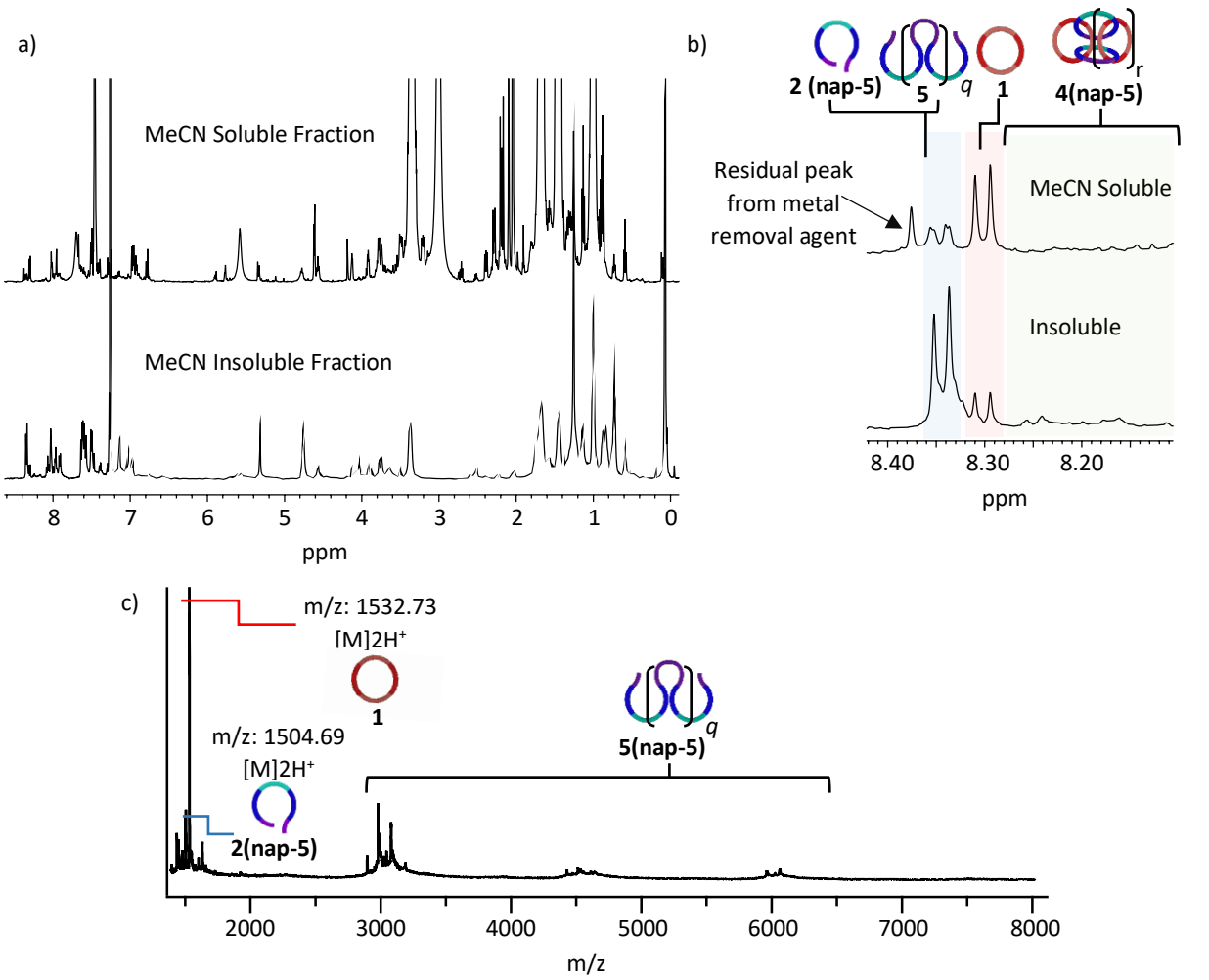


Figure S27: (a) Full ^{1}H NMR Spectrum for crude reaction mixture of the attempted synthesis of **c-4(nap-5)** after the work-up procedure which involved demetallation followed by washed with acetonitrile (MeCN).[3] The majority of **1**, the Hoveyda-Grubbs catalyst, and residual demetallating agent are soluble in the MeCN and the ADMET byproduct (**5(nap-5)**) and catenated material (**4(nap-5)**) crash out from the solution. The two fractions (soluble and insoluble) were collected and fully dried. Both fractions are soluble in $CDCl_3$ and analyzed via ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C). (b) ^{1}H NMR analysis of the H_{mpy} region (zoom). (c) Matrix-assisted laser desorption/ionization (MALDI) spectroscopy of the insoluble material to determine the ADMET (**5(nap-5)**) formation.

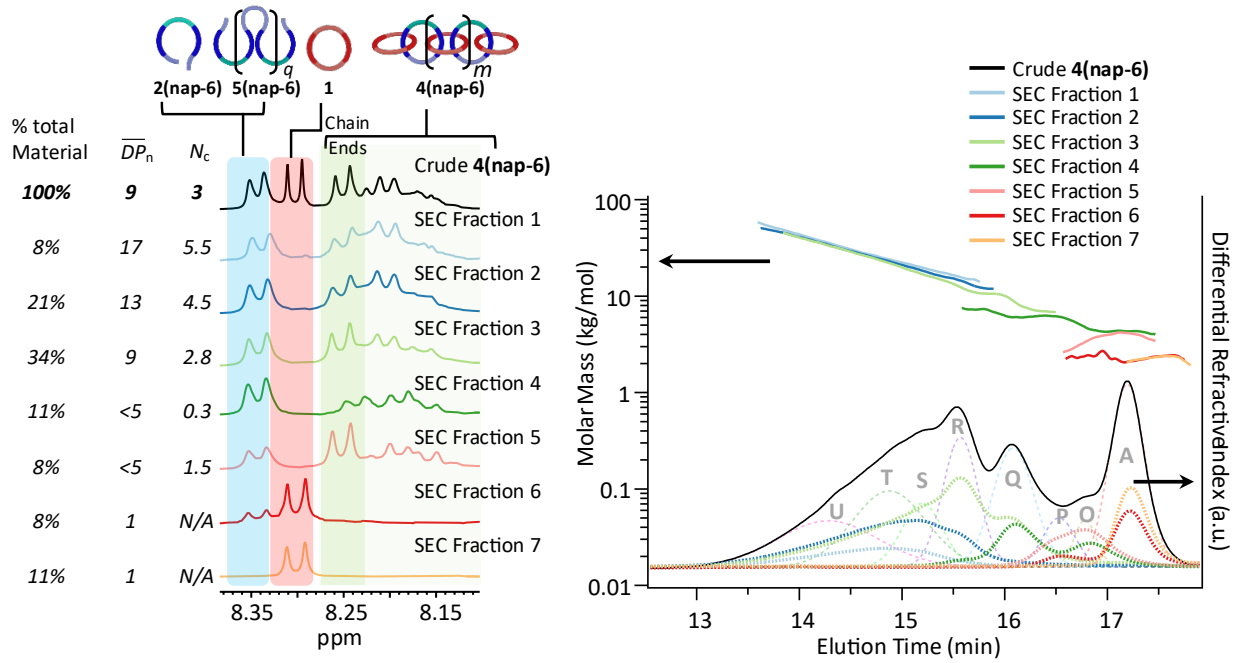


Figure S28: ^{1}H NMR and SEC-MALS traces for all fractionated **4(nap-6)** samples. The number average degree of polymerization (DP_n, Eqn. S1), chain end calculations (N_c, Eqn. S2) for each fraction were used to assign the poly[*n*]catenane architectures in the crude SEC trace (assigned in Figure 7d, analysis below).

Peak A is assigned based on the SEC trace of pure macrocycle **1** (Figure S17).

Peak O is tentatively assigned to the [2]catenane (and/or low molecular weight catenanes). Fraction 5 consists mostly of this peak (along with some peak P). Fraction 5 has an N_c of 1.5 and a $\overline{DP}$ <5 (MALS), which combined with the previously published analysis of **4(xan-6)**[2] and the above analysis of **4(nap-5)** is consistent with this assignment

Peak P is assigned based on the SEC trace of pure thread **2(nap-6)** (Figure S17).

Peak Q is assigned to ***c*-4(nap-6)**. Faction 4 contains primarily Peak Q, with contributions from Peaks O (assigned to [2]catenane), P (**2(nap-6)**), and R (tentatively assigned to ADMET **5(nap-6)**). Fraction 4 N_c = 0.3, suggesting that majority of the catenanted product in this sample is cyclic.

Peak R has been tentatively assigned to the ADMET byproduct **5(nap-6)**. Peak R is present in fractions 1-4 and the assignment is based on a combination of the prevalence of ADMET **5(nap-6)** in the ^{1}H NMR each of these fractions and comparison to the previously published work.[2]

Peak S is tentatively assigned to oligomeric ***l*-4(nap-6)**. Peak S is present mainly in fractions 2 and 3. Fraction 3 consists of primarily Peaks S and T, along with contributions from peaks U, R, and Q. The N_c of fraction 3 is 2.8, suggesting that the primary architecture present is the ***l*-4(nap-6)**, with contributions from the ***b*-(nap-6)**, this combined with previously published data,[2] is consistent with this tentative assignment.

Peak T is tentatively assigned to the polymeric ***l*-4(nap-6)**. With Peak T being present mainly in Fractions 2 and 3 the analysis for Peak T is similar to that of Peak S. The increased molecular

weight of this sample (as determined by MALS) is consistent with this peak corresponding to the higher molecular weight polymeric ***l*-4(nap-6)**.

Peak U is assigned to ***b*-4(nap-6)**. This peak is present mainly in Fractions 1 and 2 and these fractions have N_c >4.

Table S1. Diffusion coefficients for the peak two regions between 8.6-8.80ppm of the different MSPs

MSP	Region 8.80-8.72 ppm Diffusion Coefficient (x 10^{-10} m^2s^{-1})	Region 8.62-8.72 ppm Diffusion Coefficient (x 10^{-10} m^2s^{-1})
1·2(xan-6)·Zn(II)$_2$	2.4	5.5
1·2(xan-5)·Zn(II)$_2$	1.9	4.3
1·2(nap-5)·Zn(II)$_2$	2.3	5.8
1·2(nap-6)·Zn(II)$_2$	2.2	3.8

All values obtained using the Bruker Topspin 4.0.6 direct exponential curve resolution algorithm (DECRA) plotting method.

Table S2. T_1 relaxation values for the new poly[*n*]catenanes

Poly[*n*]catenane Sample	T_1 Value	
	Region α (Chain End)	Region β
4(xan-5)	2.01	1.92
4(nap-5)	1.94	1.88
4(nap-6)	2.03	1.95

Table S3. Quantitative SEC deconvolution data for each new sample

Sample	(**1**) + (**3**) (% total area)	Thread (**2**) (% total area)	ADMET (**5**) (% total area)	[2]Cat (% total area)	Cyclic (% total area)	[3]Cat (% total area)	Oligo (% total area)	Linear (% total area)	Branched (% total area)
4(xan-6)	11	4	11	6	9	0	14	23	21
4(xan-5)	23 (A)	5 (B)	12 (E)	*5*[a] (C)	*5*[a] (C)	17 (D)	0	0	38 (F,G)
4(nap-5)	13 (A)	3 (H)	10 (K)	6 (I)	0	10 (J)	0	0	58 (L,M,N)
4(nap-6)	21 (A)	5 (P)	16 (R)	3 (O)	13 (Q)	0	8 (S)	18 (T)	16 (U)

Peak name from Figure 5 indicated in parentheses.
(a) peak assigned as a combination of [2]catenane and cyclic catenane.

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(1) *1D and 2D Experiments Step-by-Step Tutorial; Advanced Experiments User Guide, Vers. 002*; Bruker Biospin, 2006.

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