Electronic Supporting Information

Effect of metallosupramolecular polymer concentration on the synthesis of poly[*n*]catenanes

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Materials /Methods/ Experimentation

Materials

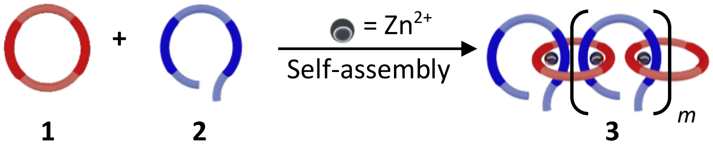
Dichloromethane (DCM) was purchased from Acros Organics and distilled over CaH_2 under argon atmosphere before using. Dimethylformamide (DMF, extra dry) was purchased from ACROS was used as received. Deuterated solvents, containing tetramethylsilane (TMS) as internal standard, were purchased from Acros Organics. All other solvents were purchased from Fisher Scientific and used without purification. 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

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 1H{19F,13C,31P} QNP probe, using Topspin 2.1. Chemical shifts were calibrated with TMS for all measurements. All Diffusion Pulsed-Gradient Spin-Echo (PGSE) measurements were performed on the 500 MHz spectrometer using the Stejskal-Tanner method.[1] Two identical pulsed field gradients with duration $\delta = 0.004$ s separated by a delay time of either $\Delta = 0.05413$ s (poly[*n*]catenane (**5**) samples, 1.0 mM MSP (**3**), and 2.5 mM MSP (**3**) samples) or $\Delta = 0.1201$ s (10.0 mM MSP (**3**) sample) were incorporated into a spin-echo sequence, one before and the other after the 180° pulse. 1H NMR spectra were recorded in $CDCl_3$ or 1:4 $CD_3CN:CDCl_3$ at 295.5 K without sample spinning. During each experiment, the gradient strength (G) was varied between 0 and 34 G/cm. The gradient was calibrated using a solution of 2% H2O in D2O. NMR spectra were processed by either MestReNova software or Bruker Topspin 4.0.6. GPC was performed on a Shimadzu Prominance LC system with PLgel Mixed-D columns using a mixture of 25% HPLC grade dimethylformamide (DMF) and 75% HPLC grade tetrahydrofuran (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 of poly[n]catenane **5** was 0.2125, measured by injecting a series of diluted samples of **5** in 25% DMF/THF solution (concentration: 0.1, 0.2, 0.4, and 0.8 mg/mL) subsequently into the RI detector until receiving a stable signal for each concentration and processed by Wyatt Astra software.

Experimental Procedures

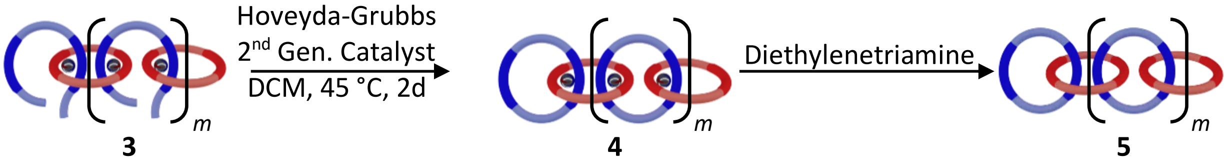
Metallosupramolecular Polymer (MSP) Assembly



Compounds **1** and **2** were synthesized using literature procedure.[2] Two separate vials for titration were prepared: the first vial contained **1** (300 mg, 0.20 mmol) in 3 mL $CDCl_3$ and the second vial **2** (317 mg, 0.20 mmol) dissolved in 1 mL $CDCl_3$. The solution of **2** was slowly titrated into the solution of **1**; each addition was monitored by NMR by monitoring the relative integrations of the most downfield shifted doublets for both **1** (8.30 ppm) and **2** (8.35 ppm) as well as the triplets at 4.56 ppm (for **1**) and 4.76 ppm (for **2**). The titration ceased when the two components were at a ratio of 1:1.

Zn(II) ions (Zinc di[bis(trifluoromethylsulfonyl)imide] ($Zn(NTf_2)_2$) in deuterated acetonitrile, 0.40 mM) were titrated into the 1:1 mixture and monitored by NMR. The complete disappearance of the doublets at 8.30 and 8.35 ppm (and the corresponding growth of the peak at 8.9 ppm) indicates that all of the Bip units are bound with metal in a 2:1 Bip:metal ratio. The completed MSP (**3**) was dried under vacuum and stored at -8 °C.

Poly[*n*]catenane synthesis



Example procedure for the 2.5 mM reaction: A 10 mL reaction vessel, stir bar, and water condenser were dried overnight at 130°C for use in the catenation reaction. MSP **3** (60 mg, 0.013 mmol) of was added to the dried vessel and dissolved in 5.2 mL of dried DCM (2.5 mM). The solution was stirred and heated to reflux (45°C) followed by bubbling argon for 30 minutes to remove dissolved oxygen. Then Hoveyda-Grubbs second generation catalyst in DCM (1.0 mg, 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 reaction mixture was obtained as a yellow or slightly brown solid. The solid material was washed with acetonitrile to remove residual Hoveyda-Grubbs second generation catalyst before GPC and NMR characterization.

The same procedure was repeated for the reactions carried out at different concentrations (0.25, 0.5, 1.0, 5.0, and 10.0 mM) in DCM. The Hoveyda-Grubbs second generation catalyst was added at a concentration of 0.32 mM for each addition (x2), with the exception of the 10.0 mM samples, which received catalyst at a concentration of 0.64 mM for both additions. The work up for all samples remained the same.

Partial purification of crude reaction mixture:

For the partially purified samples, (Figure 9 in the manuscript) the demetallated reaction mixture was partially re-metalated with $Zn(NTf_2)_2$ until ca. 50% of the poly[*n*]catenane was metalated as observed by NMR. The sample was fully dried under vacuum and washed 5 times with a solution of 2:1 chloroform:hexane to remove the non-metal-containing compounds. The remaining metallated compounds was 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.

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:

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

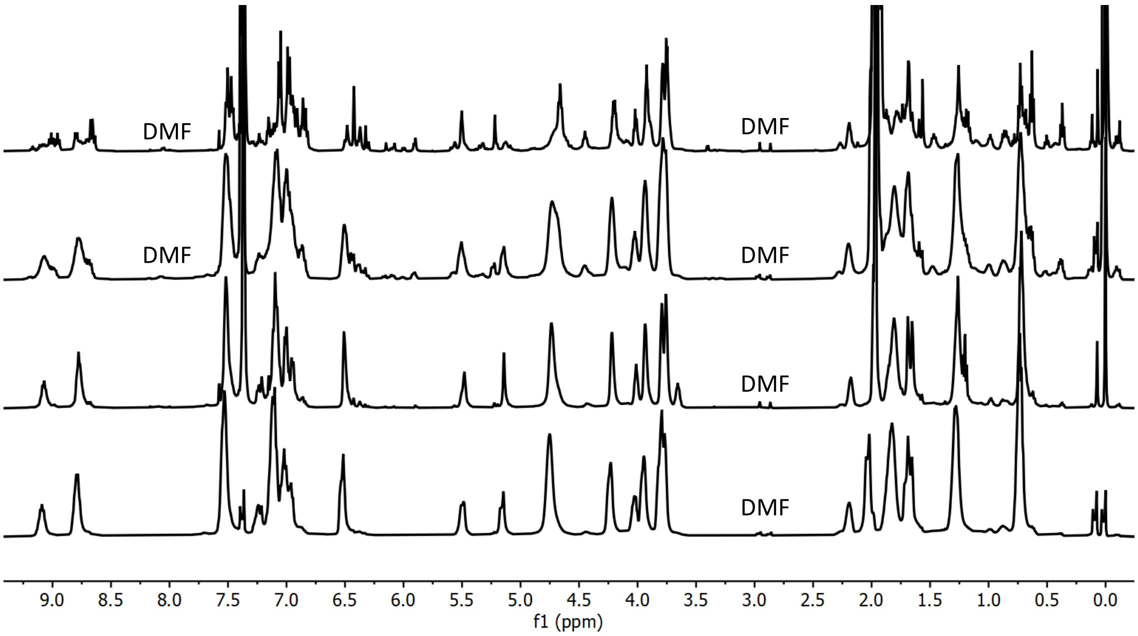


Figure S1: Full ^{1}H NMR spectra (500 MHz, 1:5 CD_3CN:$CDCl_3$, 25 °C) of Figure 5a for MSP samples at the indicated concentrations (From top to bottom: 0.25, 1.0, 2.5, and 10.0 mM).

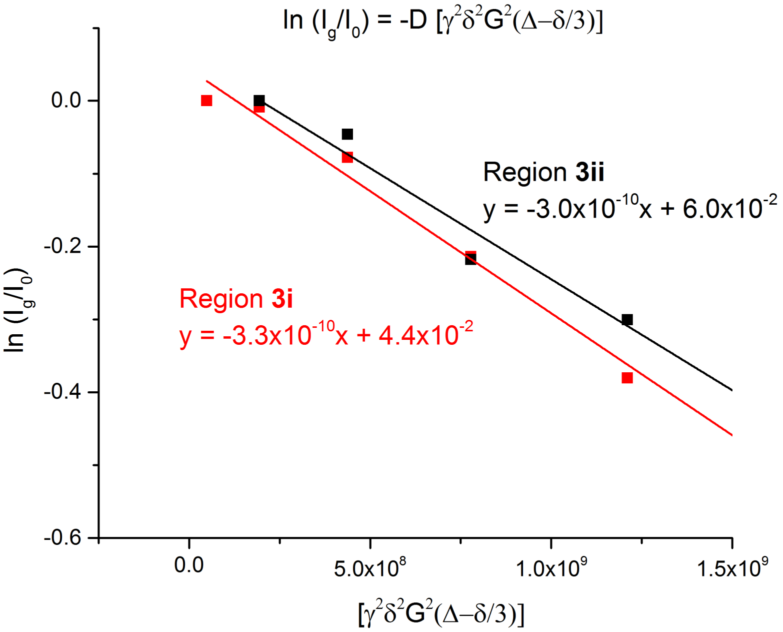


Figure S2: Calculation of diffusion coefficients (500 MHz, 1:4 CD_3CN:$CDCl_3$, 25 °C) for MSP **3** at 1.0 mM.

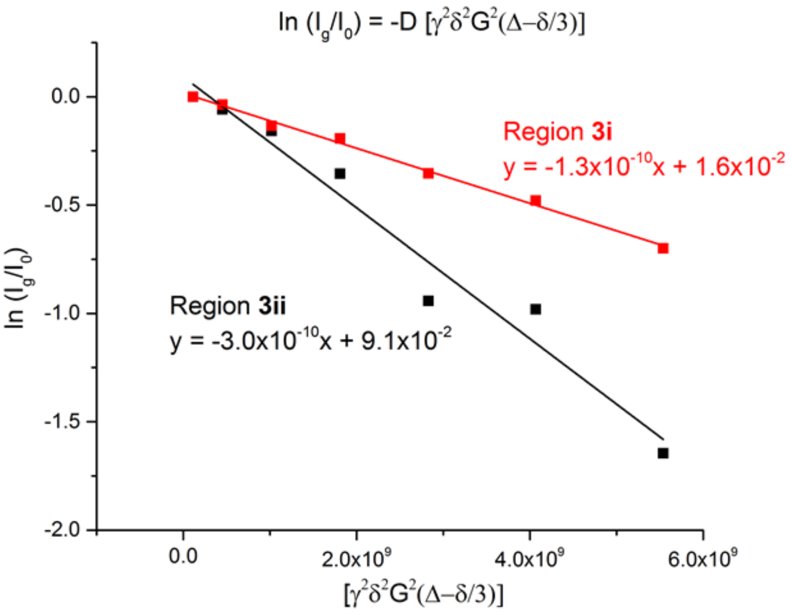


Figure S3: Calculation of diffusion coefficients (500 MHz, 1:4 CD_3CN:$CDCl_3$, 25 °C) for MSP **3** at 2.5 mM.

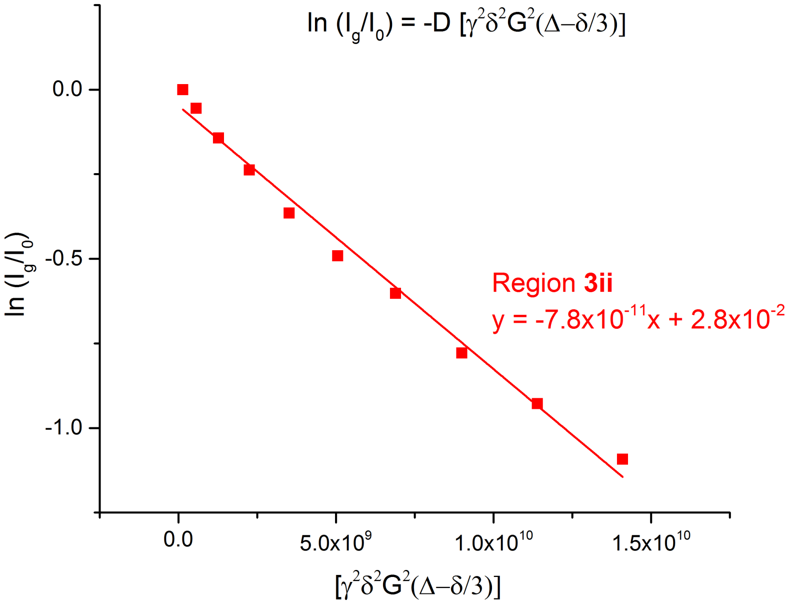


Figure S4: Calculation of diffusion coefficients (500 MHz, 1:4 CD_3CN:$CDCl_3$, 25 °C) for MSP **3** at 10.0 mM.

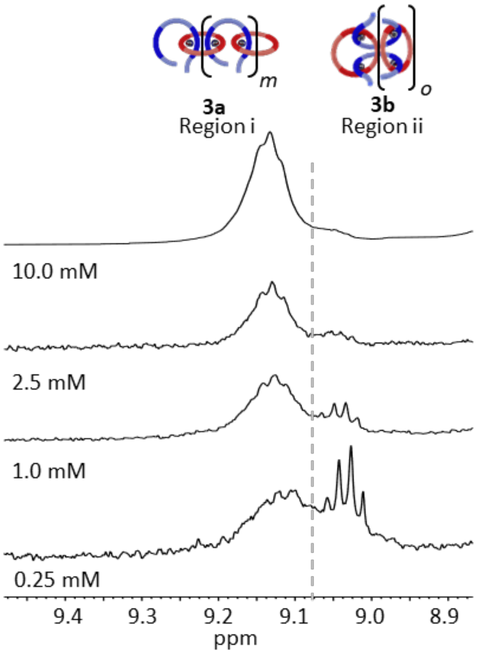


Figure S5: Distributions of the MSP protons for DCM^{1}H-NMR of the MSP **3** (500 MHz, CD_2Cl_2, 298 K).

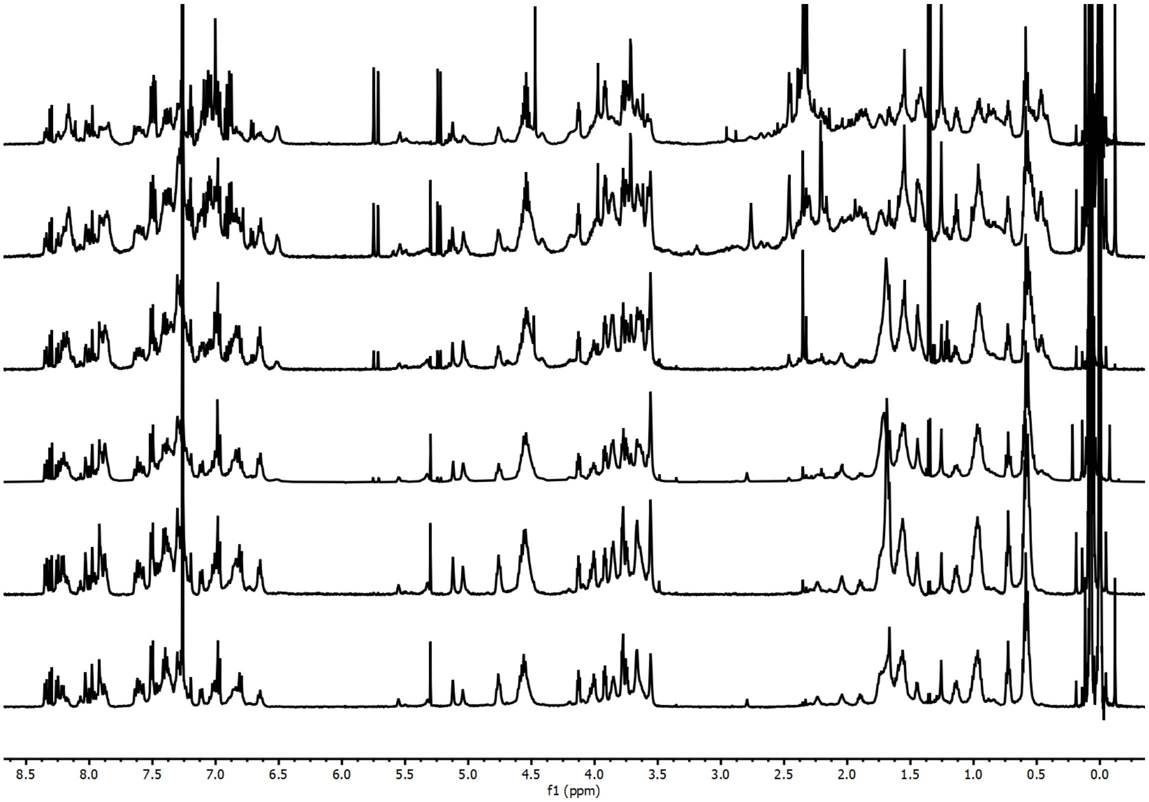


Figure S6: Full ^{1}H NMR spectra (500 MHz, $CDCl_3$, 25 °C) for representative samples at each concentration. Top to bottom: 0.25 mM, 0.5 mM, 1.0 mM, 2.5 mM, 5.0 mM, 10.0 mM.

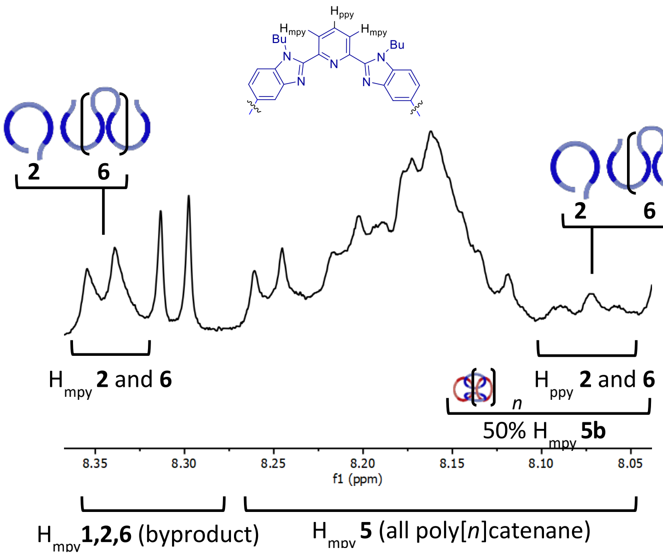


Figure S7: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C) for an example % poly[*n*]catenane yield and cyclic conversion calculation (0.5 mM sample). In order to determine the size of the triplet at 8.07 ppm the integration of the doublet at 8.35 ppm is used, which is in a 2:1 ratio with the triplet at 8.07 ppm. The contribution from this triplet, based on this integration, is removed from the final catenane conversion calculation and cyclic poly[*n*]catenane (**5b**) concentration.

Calculation of Cyclic Catenane

$$\%\,Cyclic\ Catenane = \frac{2\times Integration\ ((8.05\text{–}8.15\ ppm)-Triplet\ at\ 8.07\ ppm)}{Integration\ (((8.05\text{–}8.27\ ppm)-Triplet\ at\ 8.07\ ppm)} \qquad \text{Eq. S2}$$

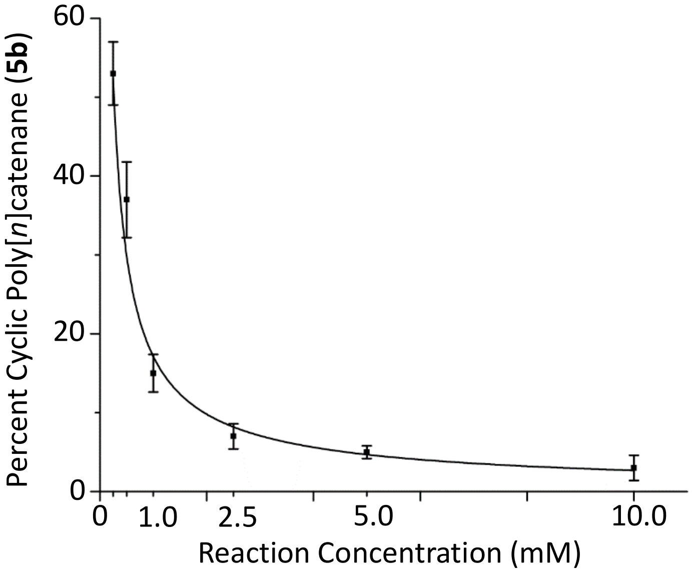


Figure S8: Percent yield of cyclic catenane (**5b**) calculated via ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) assuming that 50% of the cyclic catenane protons appear in the region 8.05-8.15 ppm.[2] Peaks from ADMET **6** and residual thread **2** were considered and removed from the final value (see Eq. S1).

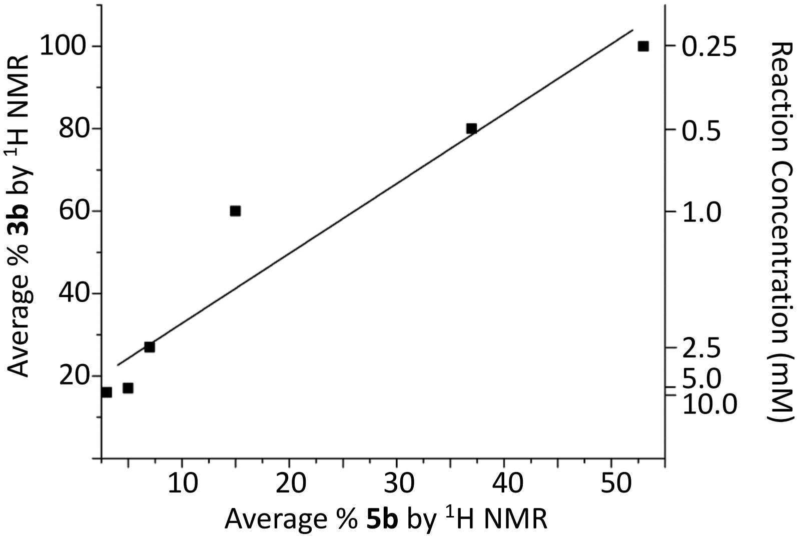


Figure S9: Comparison of the amount of cyclic MSP **3b** at each reaction concentration versus the yield of cyclic poly[*n*]catenane (**5b**) at the same concentration. % **3a** calculated based on the assumption that Region ii of Figure 5a corresponds to 50% of the total **3b** in each sample. % **5b** calculated via the assumption[2] that only 50% of the cyclic catenane appears in the region 8.05-8.15 ppm where no other catenane appears. Peaks from **6** were considered and removed from the final value when numbers were obtained.

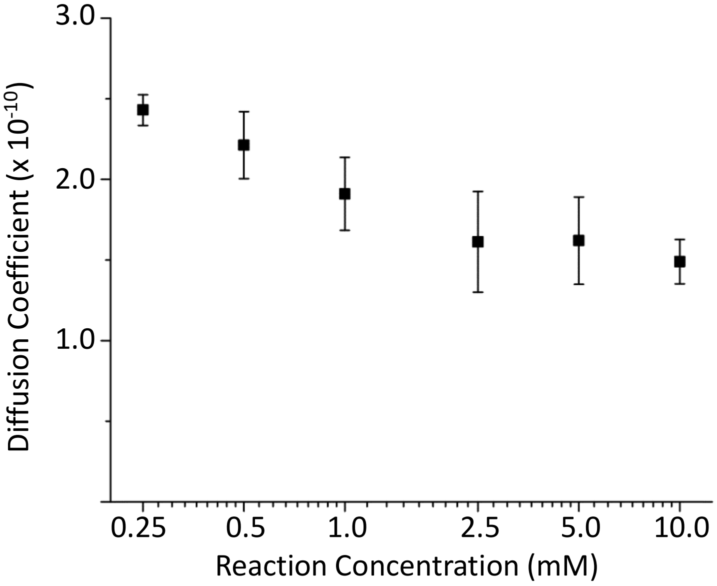


Figure S10: Average diffusion coefficients obtained from diffusion NMR studies of the H_{mpy} of the catenanes (500 MHz, $CDCl_3$, 25 °C). Error was calculated based on a 95% confidence (n = 4).

Gel Permeation Chromatography (GPC) Data

All GPC data was processed using OriginPro multiple peak fit Gaussian analysis software. Peak centers were chosen based on the apparent peaks seen within the trace (qualitative assessment) as well as maintaining the location consistency of peaks A-I throughout the various samples (elution time consistency of each proposed product). The peak areas and widths were found by optimizing the overall fit to the precise RI trace of the data.

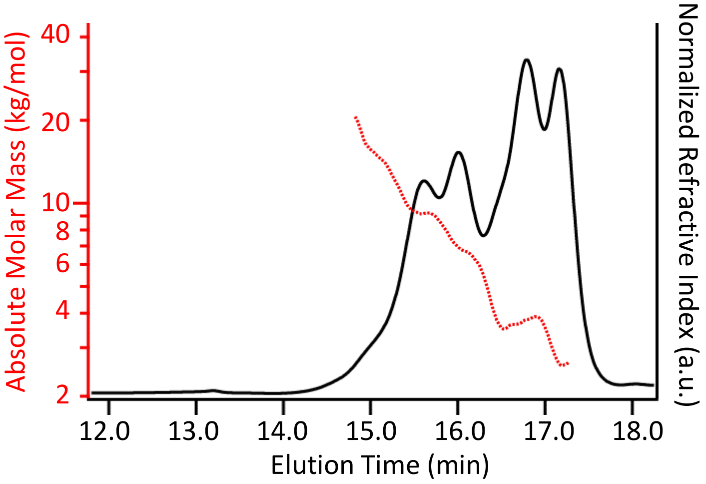


Figure S11: Absolute molar mass for the 0.25 mM sample given determined by MALS-GPC (25% HPLC grade dimethylformamide (DMF) and 75% HPLC grade tetrahydrofuran (THF) as the eluent (1mL/min) at 25 °C).

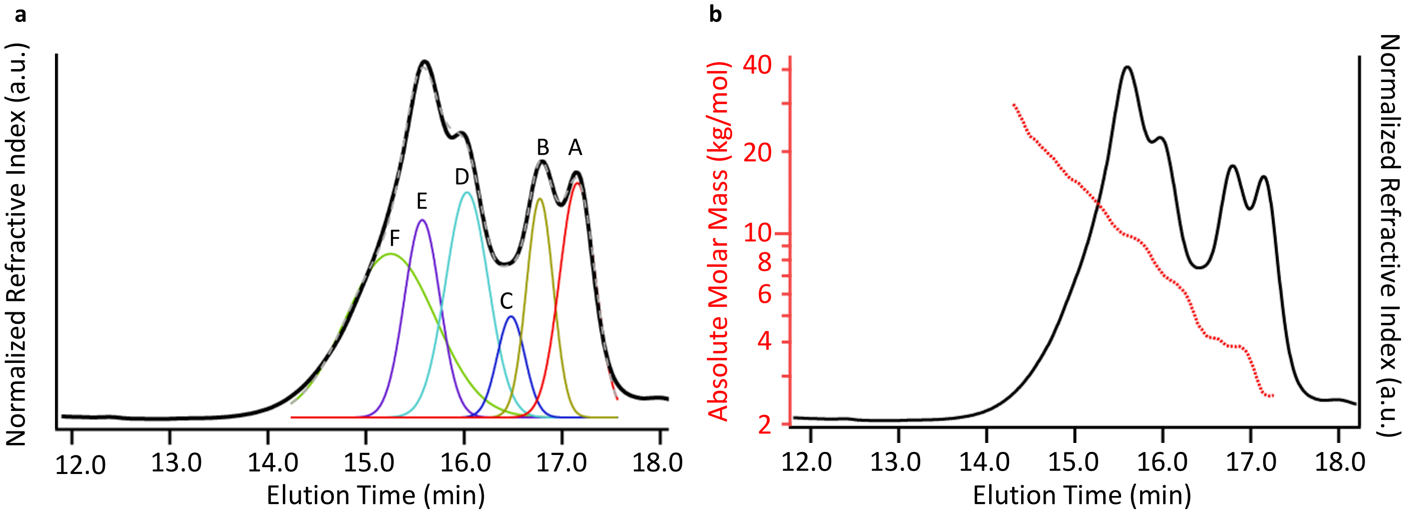


Figure S12: a) Deconvolution of GPC RI trace (black) for the ring closing reaction of the MSP at 0.5 mM (25% HPLC grade dimethylformamide (DMF) and 75% HPLC grade tetrahydrofuran (THF) as the eluent (1mL/min) at 25 °C). Deconvolution performed using a Gaussian fit (cumulative peak fit, grey dash). b) Absolute molar mass for the 0.5 mM sample given, determined by MALS.

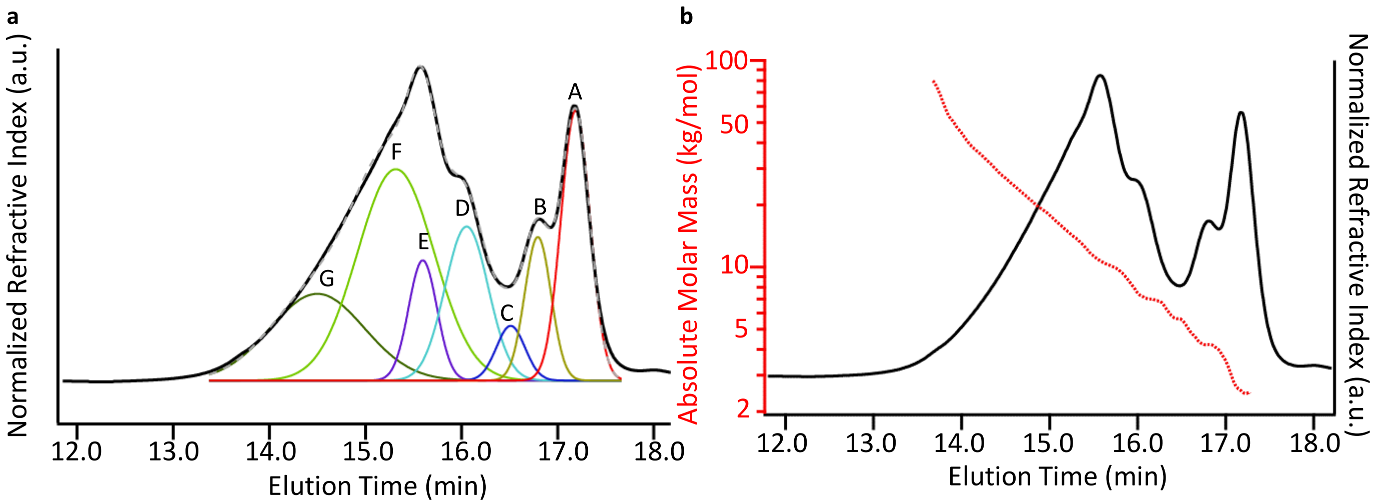


Figure S13: a) Deconvolution of GPC RI trace (black) for the ring closing reaction of the MSP at 1.0 mM (25% HPLC grade dimethylformamide (DMF) and 75% HPLC grade tetrahydrofuran (THF) as the eluent (1mL/min) at 25 °C). Deconvolution performed using a Gaussian fit (cumulative peak fit, grey dash). b) Absolute molar mass for the 1.0 mM sample given, determined by MALS.

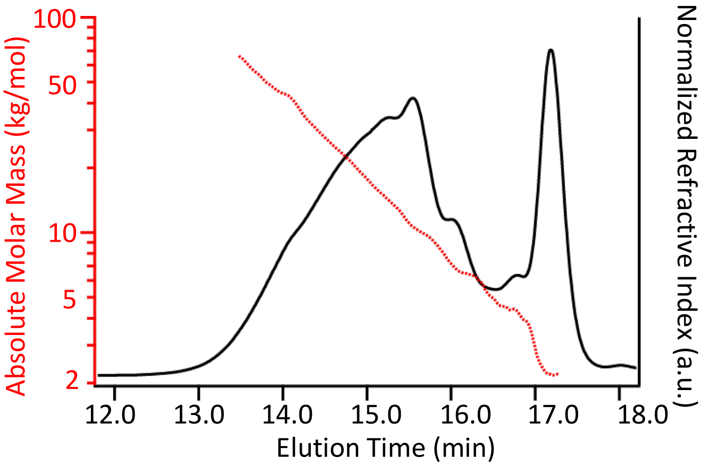


Figure S14: Absolute molar mass for the 2.5 mM sample given determined by MALS-GPC (25% HPLC grade dimethylformamide (DMF) and 75% HPLC grade tetrahydrofuran (THF) as the eluent (1mL/min) at 25 °C).

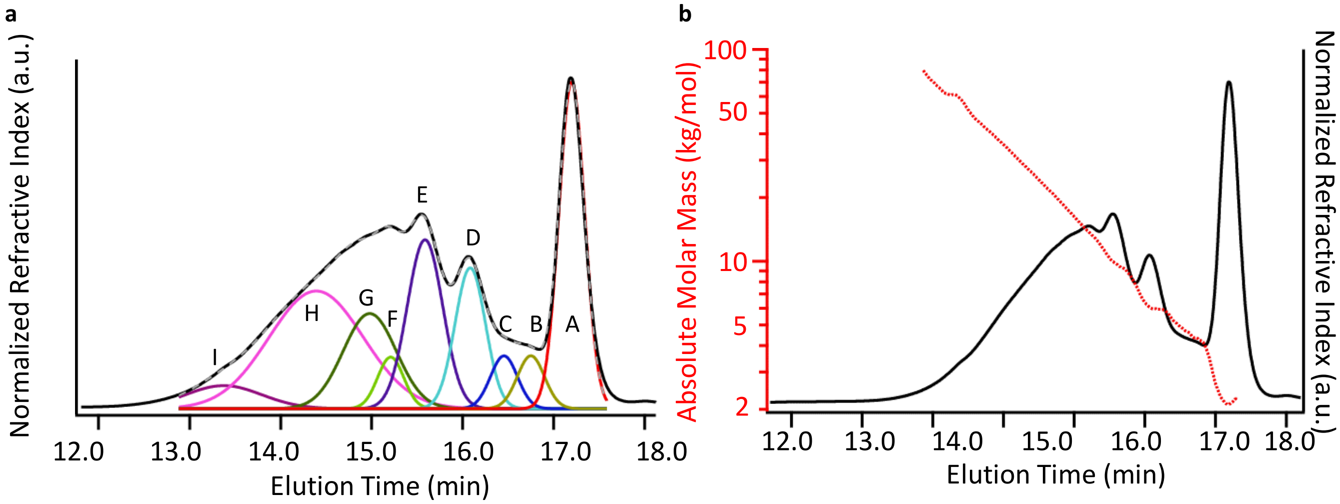


Figure S15: a) Deconvolution of GPC RI trace (black) for the ring closing reaction of the MSP at 5.0 mM (25% HPLC grade dimethylformamide (DMF) and 75% HPLC grade tetrahydrofuran (THF) as the eluent (1mL/min) at 25 °C). Deconvolution performed using a Gaussian fit (cumulative peak fit, grey dash). b) Absolute molar mass for the 5.0 mM sample given, determined by MALS.

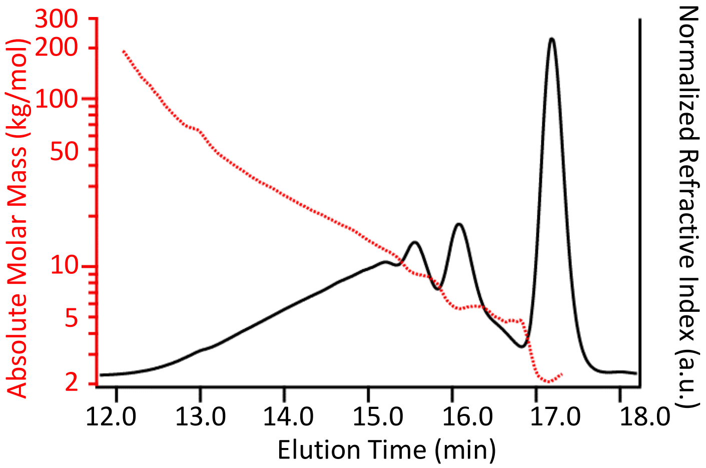


Figure S16: Absolute molar mass for the 10.0 mM sample given determined by MALS-GPC (25% HPLC grade dimethylformamide (DMF) and 75% HPLC grade tetrahydrofuran (THF) as the eluent (1mL/min) at 25 °C).

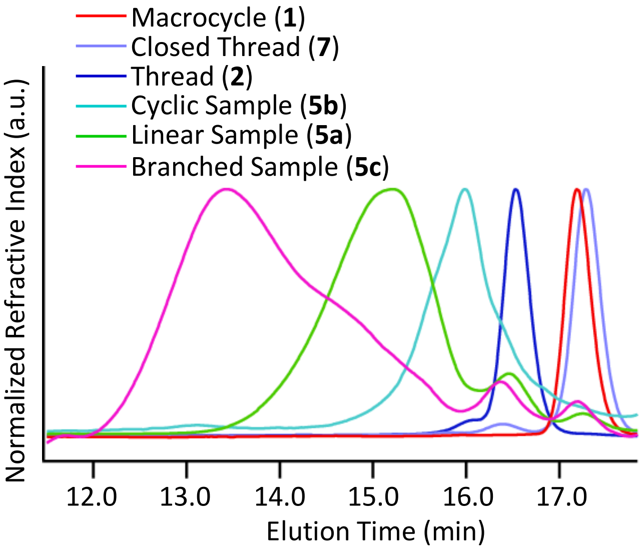


Figure S17: GPC traces taken for macrocycle (**1**), thread (**2**), ring closed thread (**7**), the sample made according to literature preparation[2] of cyclic catenane (**5b**), the purified primarily linear sample (**5a**), and the purified primarily branched sample ($N_c = 12$, **5c**).

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

$$N_C = \overline{DP} \times \frac{2 \times Integration(\,8.24\text{−}8.27\ ppm)}{Integration\ (8.05\text{−}8.27)} \qquad \text{Eq. S3}$$

Where $\overline{DP}$ is taken from Eq. S1.

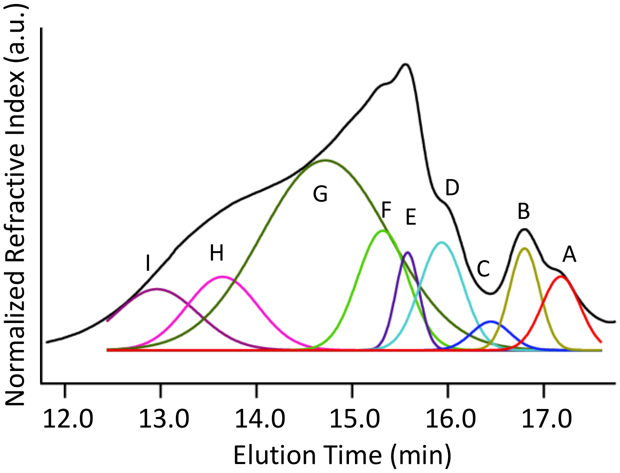


Figure S18: Deconvolution of RI trace (25% HPLC grade dimethylformamide (DMF) and 75% HPLC grade tetrahydrofuran (THF) as the eluent (1mL/min) at 25 °C) for a partially purified 2.5 mM concentration sample. Deconvolution performed using a Gaussian fit.

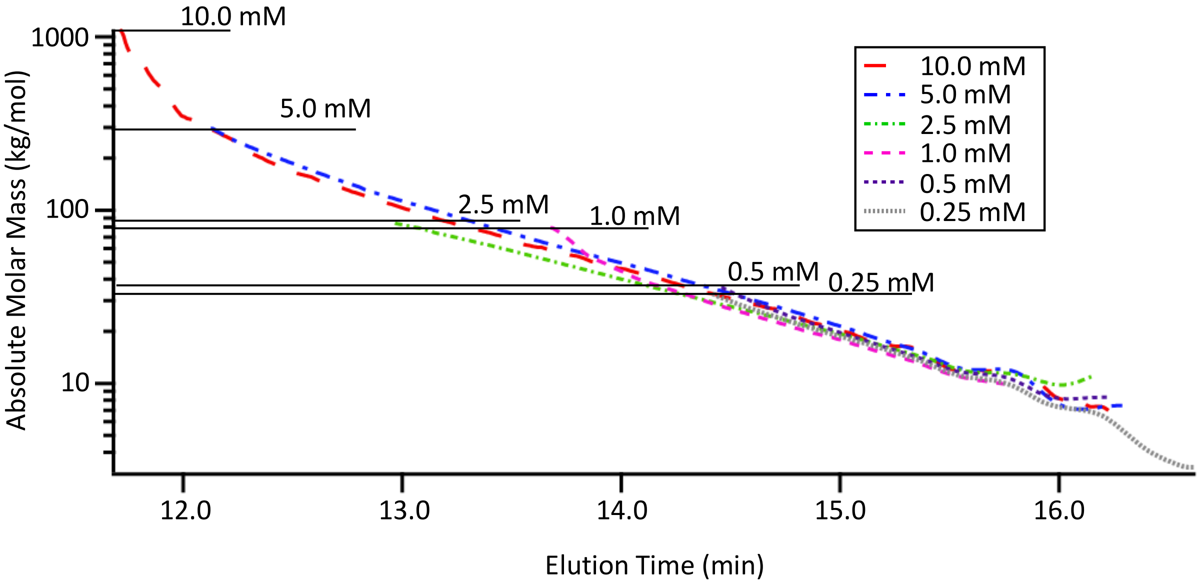


Figure S19: MALS data used in tandem with RI trace to determine molecular weight from partially purified samples (25% HPLC grade dimethylformamide (DMF) and 75% HPLC grade tetrahydrofuran (THF) as the eluent (1mL/min) at 25 °C).

Table S1. Summary of the poly[*n*]catenane synthesis reactions run at different concentrations

Conc. (mM)	Avg. % interlocked yield[a]	Avg. % byproduct **1** remaining	Avg. % byproducts **2** and **6**	% Cyclic ^{1}H NMR[b]	Avg. Diff. Coeff. (m/s^2)[c]	M_n[d]	DP[d]
0.25	69 ± 5	12	19	52 ± 4	2.25 x 10^{-10} ± 8.02 x 10^{-12}	6200	4
0.5	82 ± 6	9	9	38 ± 6	2.05 x 10^{-10} ± 1.88 x 10^{-11}	9300	6
1.0	80 ± 5	10	10	15 ± 3	1.77 x 10^{-10} ± 2.06 x 10^{-11}	13800	9
2.5	73 ± 5	12	15	7 ± 2	1.50 x 10^{-10} ±2.89 x 10^{-11}	15300	10
5.0	71 ± 7	14	15	5 ± 1	1.50 x 10^{-10} ± 2.52 x 10^{-11}	16700	11
10.0	65 ± 10	13	22	4 ± 2	1.37 x 10^{-10} ± 1.18 x 10^{-11}	15800	10

(a) Conversion to catenane calculated by integrating H$_{mpy}$ doublets corresponding to non-interlocked products **1** and **6** (8.36-8.28 ppm) against H$_{mpy}$ protons corresponding to **5** (8.28-8.10 ppm). (b) Cyclic conversion calculated via the assumption[2] that only 50% of the cyclic catenane appears in the region 8.05-8.15 ppm where no other catenane appears. Peaks from **6** were considered and removed from the final value when numbers were obtained (Eq. S1). (c) Diffusion coefficients were obtained on a 500 MHz spectrometer in CDCl$_3$ (d) MALS data was obtained from the crude catenane samples and values were determined assuming the calculated dn/dc of 0.2125.

Table S2. GPC Gaussian deconvolution peak analysis

Reaction conc. (mM)	Peak A (% total area) Macrocycle (**1**)	Peak B (% total area)	Peak C (% total area) Thread (**2**)	Peak D (% total area)	Peak E (% total area)	Peak F (% total area)	Peak G (% total area)	Peak H (% total area)	Peak I (% total area)
0.25	24	17	18	16	18	7	0	0	0
0.5	17	12	6	20	15	30	0	0	0
1.0	16	8	3	14	7	35	17	0	0
2.5	16	4	3	11	10	15	24	17	0
5.0	20	4	4	11	15	3	12	27	4
10.0	26	1	4	14	11	4	11	25	4

References

(1) Stejskal, E. O.; Tanner, J. E. Spin Diffusion Measurements: Spin Echoes in the Presence of a Time-Dependent Field Gradient. *J. Chem. Phys.* **1965**, *42* (1), 288–292. https://doi.org/10.1063/1.1695690.

(2) Wu, Q.; Rauscher, P. M.; Lang, X.; Wojtecki, R. J.; de Pablo, J. J.; Hore, M. J. A.; Rowan, S. J. Poly[n]Catenanes: Synthesis of Molecular Interlocked Chains. *Science (80-.).* **2017**, *358* (6369), 1434–1439. https://doi.org/10.1126/science.aap7675.