

Supporting Information

Dynamic Combinatorial Libraries of a Dimercapto-Pillar[5]arene

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S1 Materials and Methods

Materials: All reagents were purchased from commercial suppliers: Innochem, Aladdin, Adamas, TCI, KESHI and used as received. Analytical grade solvents were purchased from commercial suppliers: KESHI and used as received. HPLC grade solvents were purchased from commercial suppliers: Energy Chemical.

Solution ^1H NMR, ^{13}C NMR Spectroscopy: ^1H NMR, ^{13}C NMR spectra were recorded on 400 MHz Agilent ProPulse (^1H 400 MHz, ^{13}C 100 MHz), Bruker BioSpin GmbH (^1H 400 MHz, ^{13}C 100 MHz) or 500 MHz Bruker AVANCE NEO equipped with Bruker 5 mm direct broadband BBFO RT Probe (^1H 500 MHz) instruments. Chemical shifts (δ) are reported in parts per million (ppm). Coupling constants are reported in Hertz (Hz), and signal multiplicity is denoted as singlet (s), doublet (d), multiplet (m) and broad (br). All spectra were acquired at 20 °C (293 K) unless otherwise noted. The common solvent impurities in ^1H and ^{13}C NMR in small amounts were water, dichloromethane and petroleum ether.

High-resolution mass spectra: The high-resolution mass spectra (HR-MS) data was acquired on a Bruker MaXis HD ESI-TOF mass spectrometer for high mass accuracy, coupled to a Thermo Scientific Dionex Ultra-High Performance Liquid Chromatography (UPLC) unit.

HPLC separation: The HPLC separation was performed on an SPD-20A liquid chromatography system with a CHIRALPAK IC column (10 mm \times 250 mm, 5 μm), by using the mobile phase of chloroform: methanol: n-hexane = 20:2:78 (v/v/v). Detection for HPLC analysis was conducted at 290 nm.

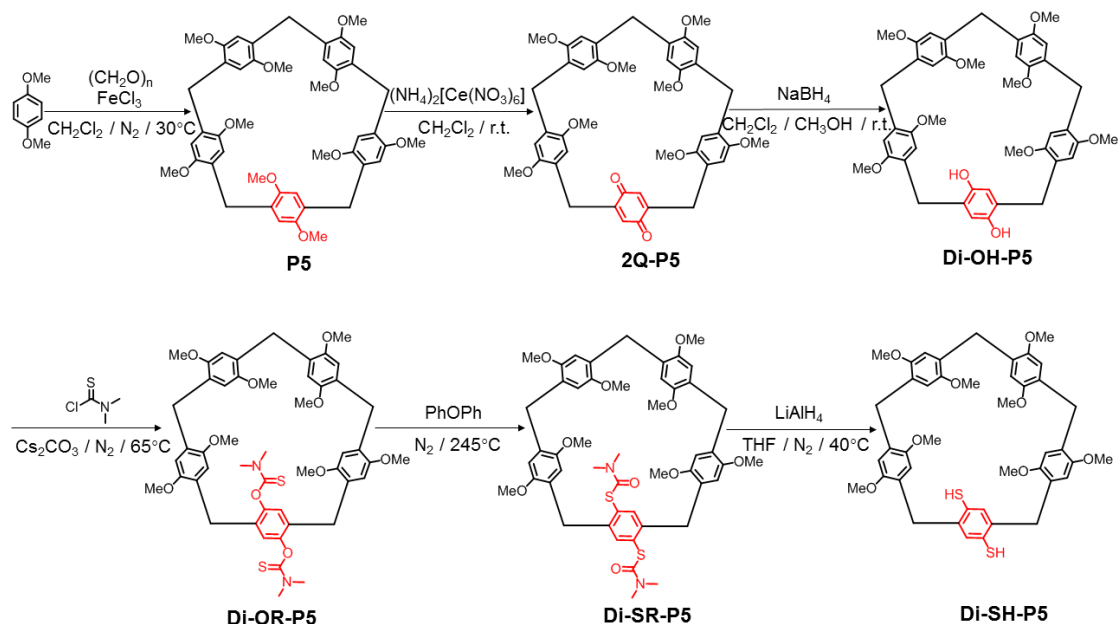
Electronic circular dichroism (ECD) spectroscopic: The circular dichroism (CD) spectra were recorded on a Jasco J-810 spectrophotometer. Samples were dissolved in dichloromethane at 20°C (293 K).

Single-crystal X-ray diffraction: Single crystal X-ray diffraction data were collected on an Agilent Technologies gemini plus X-Ray single crystal diffractometer using Mo

K α ($\lambda = 0.71073$ Å) micro-focus X-ray sources. The crystals cracks easily in air due to solvent molecular escape, therefore they were mounted on X-ray diffractometer immediately and kept in 180 K with liquid nitrogen stream during the unit cell determination and full data collection.

Compound P5, Compound 2Q-P5, Compound Di-OH-P5 have been reported and were synthesized according to reference¹⁻².

S2 Synthesis of Di-SH-P5



Scheme S1. The preparation of **Di-SH-P5**.

The synthesis of **Di-OR-P5**³⁻⁴: Dimethylcarbamothioic chloride (1.50 g, 12.14 mmol), **Di-OH-P5** (3.50 g, 4.84 mmol), Cs₂CO₃ (18.88 g, 57.95 mmol) was dissolved in acetone (400 mL) and heated at 65 °C for 12 h under N₂. The reaction was cooled down to room temperature and Cs₂CO₃ was removed by filtration. Filtrate was concentrated under reduced pressure, purified by column chromatography on silica-gel using ethyl acetate/petroleum ether as eluents (from 1:1 to 1:3) to afford a light-yellow solid. The light-yellow solid was washed with methanol to obtain the product **Di-OR-P5** as a white solid (2.50 g, 58 %). ¹H NMR (400 MHz, CDCl₃): δ (ppm): 6.75 (s, 4H), 6.72 (s, 2H), 6.54 (s, 2H), 6.46 (s, 2H), 3.76-3.75 (br d, 10H), 3.68 (s, 6H), 3.66 (s, 6H), 3.42 (s, 6H), 3.38 (s, 6H), 3.18 (s, 6H), 3.03 (s, 6H). ¹³C (100 MHz, CDCl₃): 187.24, 151.30, 151.24, 151.09, 150.57, 149.01, 133.19, 129.00, 128.64, 128.53, 127.43, 125.23, 115.21, 114.26, 114.23, 114.21, 56.39, 56.25, 55.99, 55.98, 43.27, 38.33, 32.17, 30.59, 29.15. ESI-HR MS: Calcd for C₄₃H₄₆O₈S₂ (m/z): [M + NH₄]⁺: 914.3720. Found: 914.3717.

The synthesis of **Di-SR-P5**⁵: **Di-OR-P5** (1.00 g, 1.11 mmol) was dissolved in diphenyl ether (28.00 g) and heated at 245 °C in the heating-mantle for 180 min under N₂. The

mixture was then cooled to room temperature, purified by column chromatography on silica-gel using ethyl acetate/petroleum ether as eluents (from 1:1 to 1:2) to obtain the product **Di-SR-P5** as a white solid (0.86 g, 86 %). ^1H NMR (400 MHz, CDCl_3): δ (ppm): 7.35 (s, 2H), 6.75 (s, 2H), 6.68 (s, 2H), 6.54 (s, 2H), 6.53 (s, 2H), 4.18 (d, $J=14.26$ Hz, 2H), 3.80-3.75 (m, 8H), 3.65 (s, 6H), 3.57 (s, 6H), 3.39-3.37 (br, 12H), 2.90 (s, 18H). ^{13}C (100 MHz, CDCl_3): 166.26, 151.24, 151.13, 151.02, 150.79, 143.60, 139.20, 129.38, 128.75, 128.67, 128.48, 128.00, 114.64, 114.43, 114.40, 114.38, 56.16, 56.14, 56.08, 55.84, 36.87, 33.08, 31.45, 30.51. ESI-HR MS: Calcd for $\text{C}_{43}\text{H}_{46}\text{O}_8\text{S}_2$ (m/z): $[\text{M} + \text{NH}_4]^+$: 914.3720. Found: 914.3715.

The synthesis of **Di-SH-P5**¹: Anhydrous THF (50 mL) was added to the mixture of **Di-SR-P5** (0.20 g, 0.22 mmol) and LiAlH_4 (1.12 g, 29.53 mmol, 134 eq) under N_2 . The mixture was stirred at 40 °C in the oil bath for 5.0 h before cooling to room temperature. The reaction was quenched by deoxygenated dilute hydrochloric acid and extracted with CH_2Cl_2 (50 mL \times 3). The combined organic phase was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure to afford a residue, which was purified by column chromatography on silica-gel using ethyl acetate/petroleum ether as eluents (1:10) to obtain the product **Di-SH-P5** as a white solid (135 mg, 80 %). ^1H NMR (400 MHz, CDCl_3): δ (ppm): 7.17 (s, 2H), 6.77 (s, 2H), 6.73 (s, 2H), 6.68 (s, 2H), 6.65 (s, 2H), 3.85 (s, 4H), 3.79 (s, 6H), 3.65 (s, 6H), 3.60 (s, 6H), 3.55 (s, 12H), 3.34 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm): 151.12, 150.96, 150.92, 150.80, 138.86, 133.79, 129.15, 128.61, 128.12, 127.17, 126.86, 114.47, 114.23, 114.21, 114.01, 56.01, 55.96, 55.87, 53.19, 33.67, 30.25, 30.04. ESI-HR MS. Calcd for $\text{C}_{43}\text{H}_{46}\text{O}_8\text{S}_2$ (m/z): $[\text{M} + \text{NH}_4]^+$: 772.2978. Found: 772.2981.

S3 Characterization of Di-SH-P5

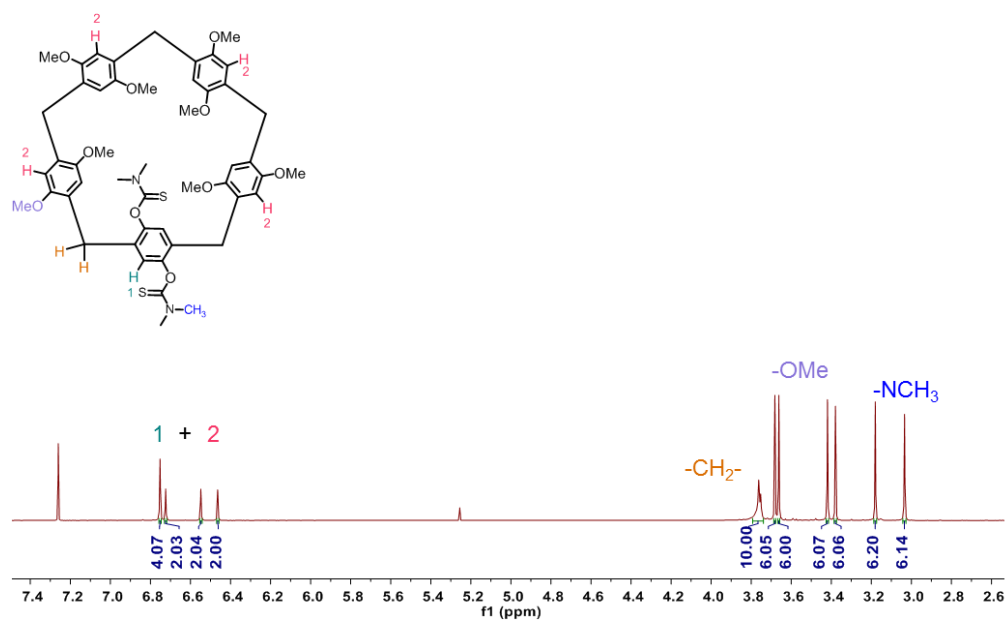


Figure S1 ¹H NMR of Di-OR-P5 (400 MHz, 293 K, CDCl₃)

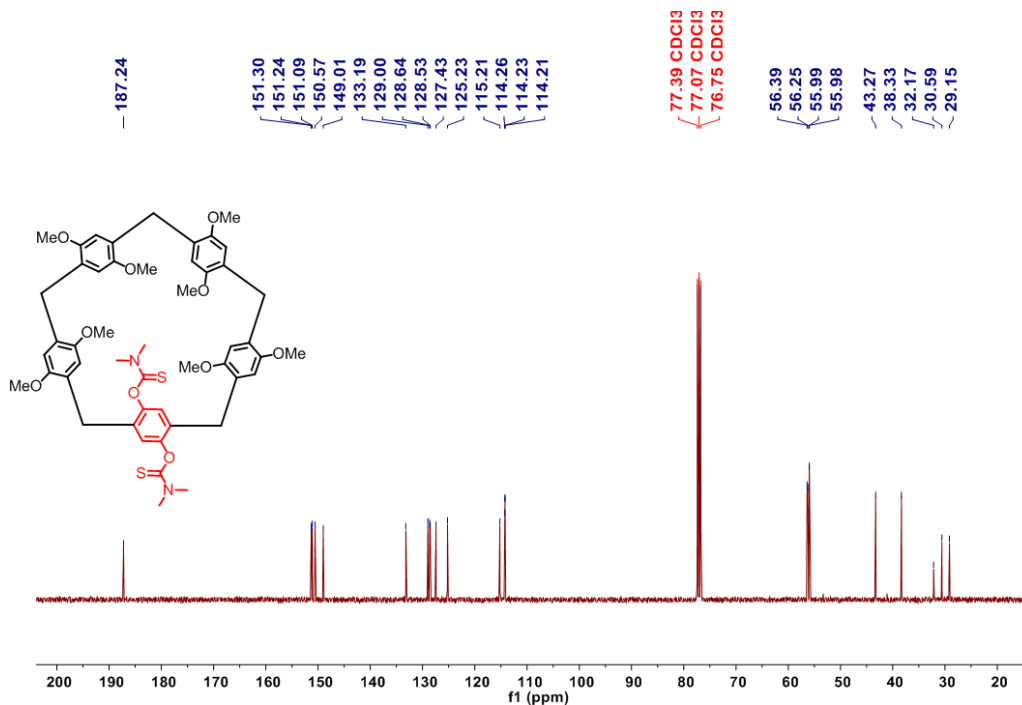


Figure S2 ¹³C NMR of Di-OR-P5 (100 MHz, 293 K, CDCl₃)

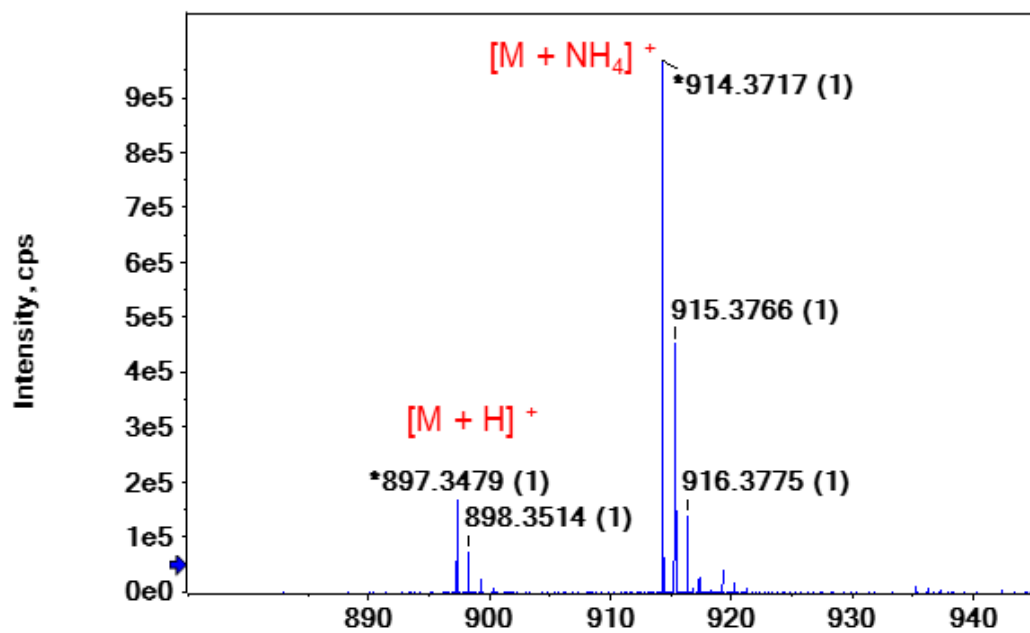


Figure S3 ESI-HR MS of Di-OR-P5

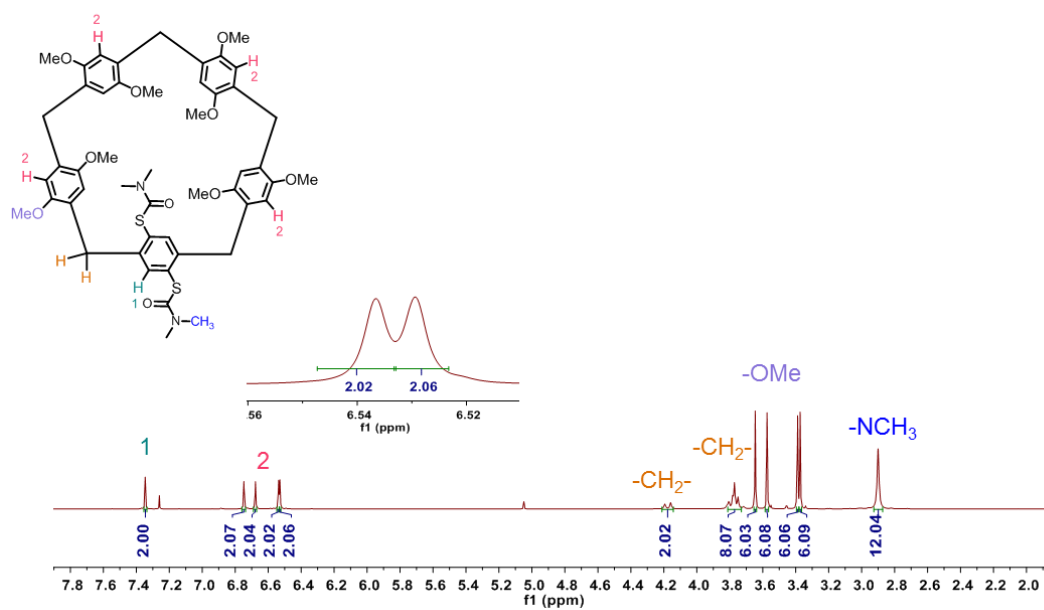
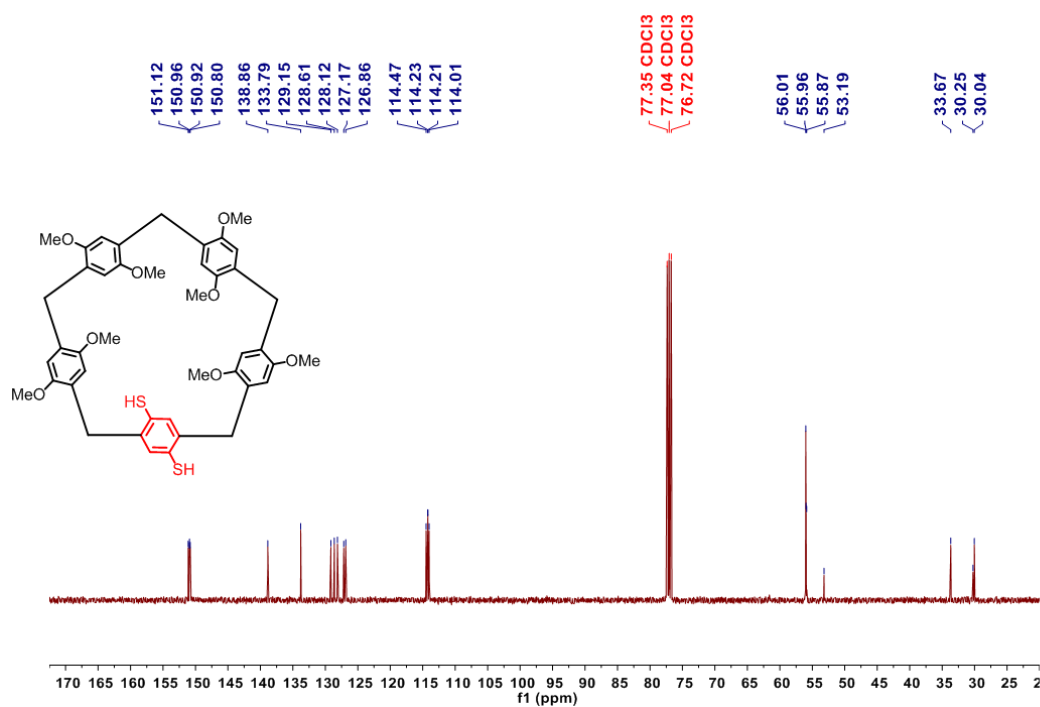
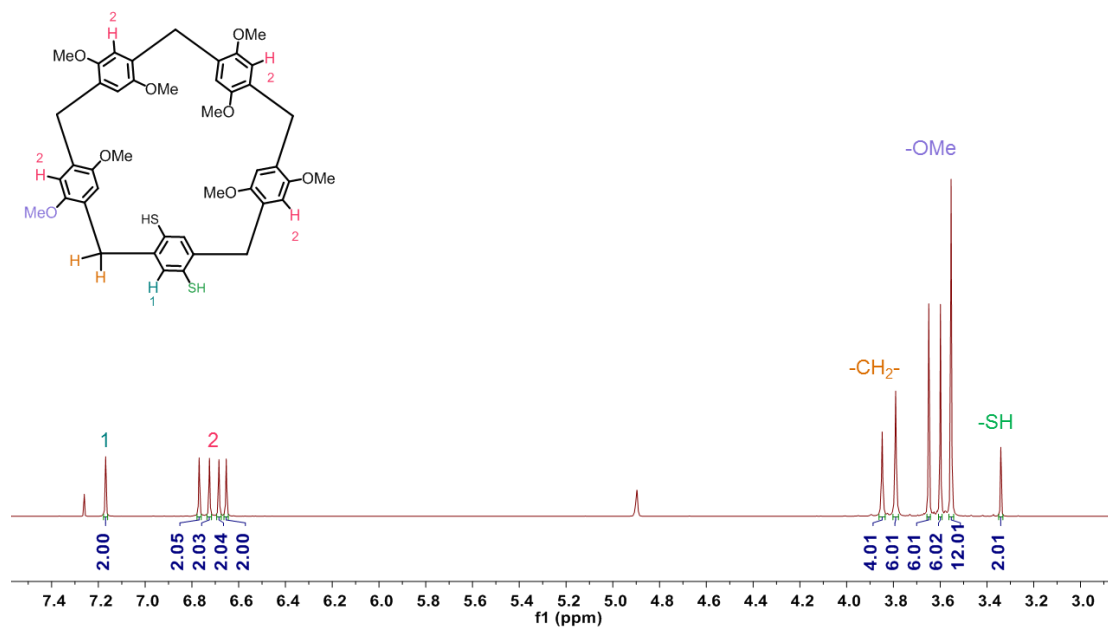


Figure S4 1H NMR of Di-SR-P5 (400 MHz, 293 K, $CDCl_3$)



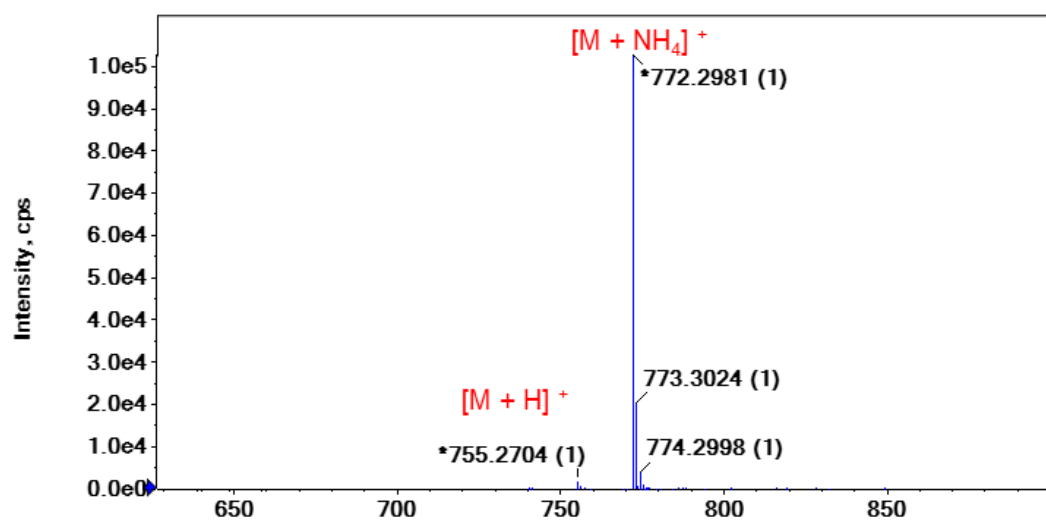
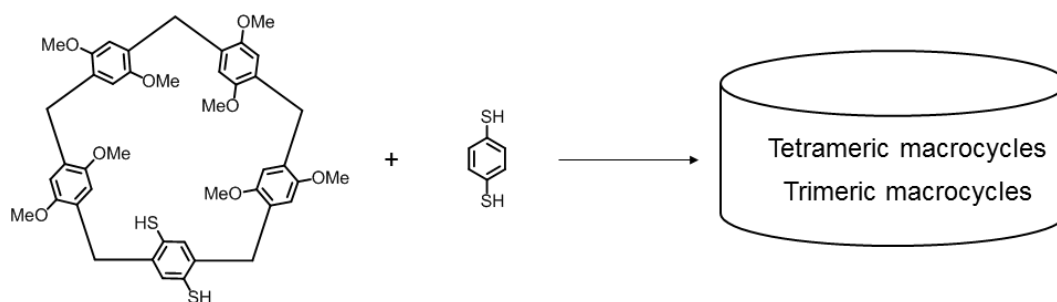


Figure S9 ESI-HR MS of Di-SH-P5

S4 Oxidation of Di-SH-P5



Scheme S2: Oxidation of **Di-SH-P5** and 1,4-Benzenedithiol.

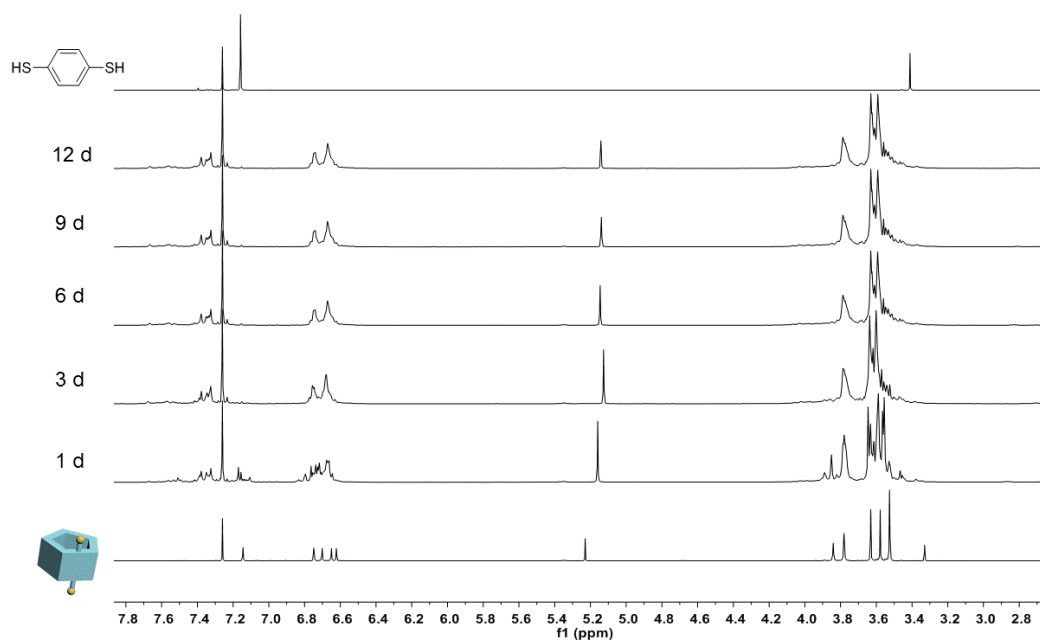


Figure S10 ¹H NMR monitoring of the oxidation of **Di-SH-P5** and 1,4-Benzenedithiol. **Di-SH-P5** (5 mg, 0.007 mmol) and 1,4-Benzenedithiol (1 mg, 1 eq) was dissolved in CDCl₃ (0.54 mL). Et₃N (0.5 μL) was added to the solution. The reaction was exposed to air and kept at room temperature with ¹H NMR monitoring.

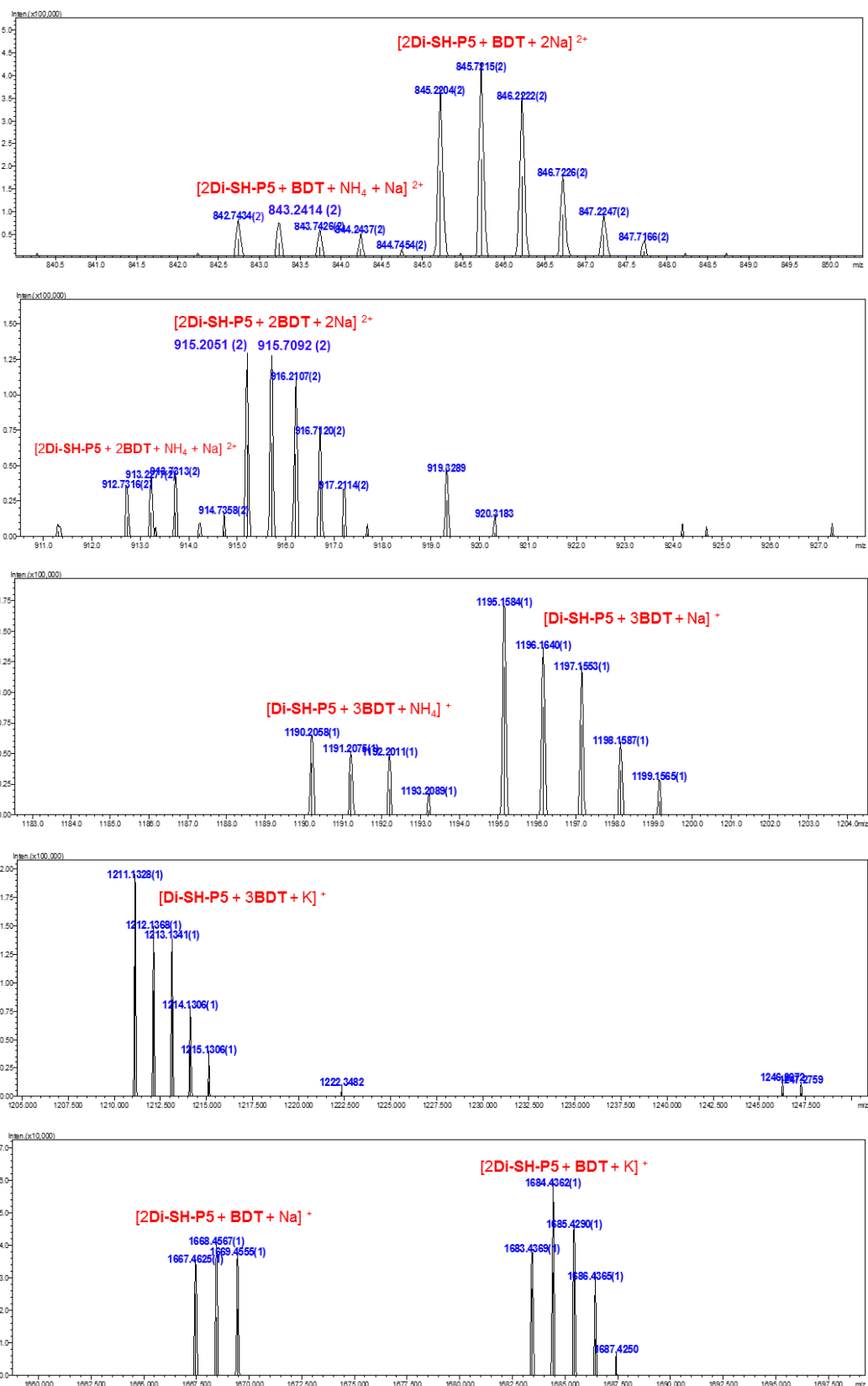


Figure S11 ESI-HR MS of the oxidation of **Di-SH-P5** and 1,4-Benzenedithiol. **Di-SH-P5** (54 mg, 0.07 mmol) and 1,4-Benzenedithiol (11 mg, 1.1 eq) was dissolved in CH_2Cl_2 (20 mL). Et_3N (100 μL), I_2 (65 mg, 0.26 mmol) was added to the solution. The reaction was stirred at room temperature

for 30 min. The peaks m/z : 843.2424, 845.7215 ($z=2$) and 1168.4567, 1684.4362 ($z=1$) may belong to trimeric macrocycles composed of two **Di-SH-P5** and one 1,4-benzenedithiol, calculated m/z : 843.2486 $[M + \text{NH}_4 + \text{Na}]^{2+}$, 845.7263 $[M + 2\text{Na}]^{2+}$, 1668.4634 $[M + \text{Na}]^+$, 1684.4373 $[M + \text{K}]^+$; the peaks m/z : 913.2277, 915.7092 ($z=2$) may belong to tetrameric macrocycles composed of two **Di-SH-P5** and two 1,4-Benzenedithiol, Calculated m/z : 913.2373 $[M + \text{NH}_4 + \text{Na}]^{2+}$, 915.7140 $[M + 2\text{Na}]^{2+}$; the peaks m/z : 1190.2058, 1195.1584, 1211.1329 ($z=1$) may belong to tetrameric macrocycles composed of one **Di-SH-P5** and three 1,4-Benzenedithiol, Calculated m/z : 1190.2085 $[M + \text{NH}_4]^+$, 1195.1639 $[M + \text{Na}]^+$, 1211.1378 $[M + \text{K}]^+$.

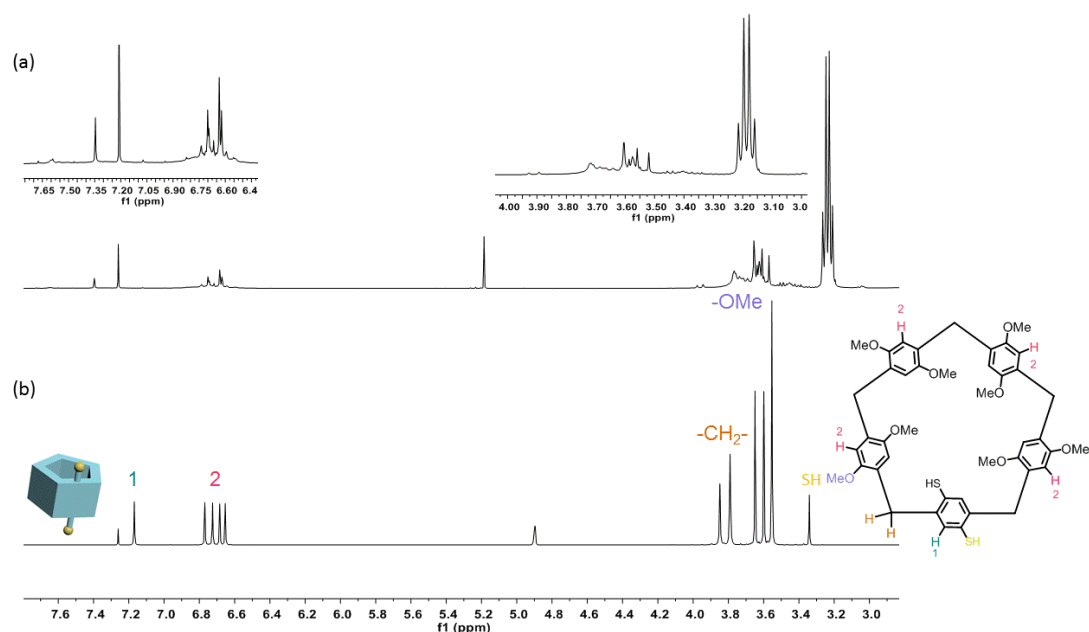


Figure S12 Partial ^1H NMR (400 MHz, 293 K, CDCl_3) spectra of (a) **Di-SH-P5** (5 mg, 0.007 mmol) was dissolved in CDCl_3 (0.5 mL). Et_3N (20 μL), I_2 (4 mg, 0.016 mmol) was added and the reaction was stood at room temperature for weeks. (b) **Di-SH-P5**.

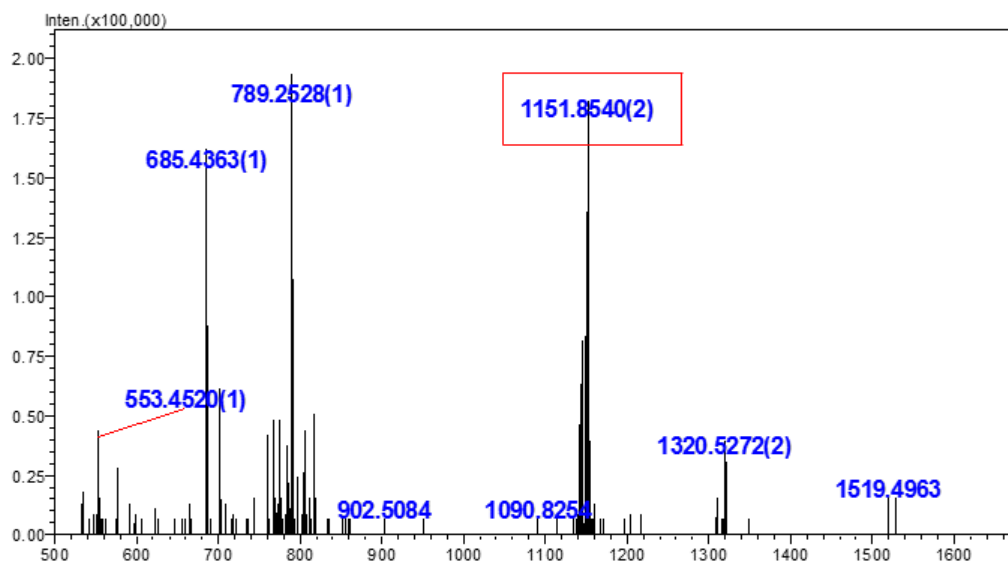


Figure S13 ESI-HR MS Spectrum of the crude sample in Figure S12a.

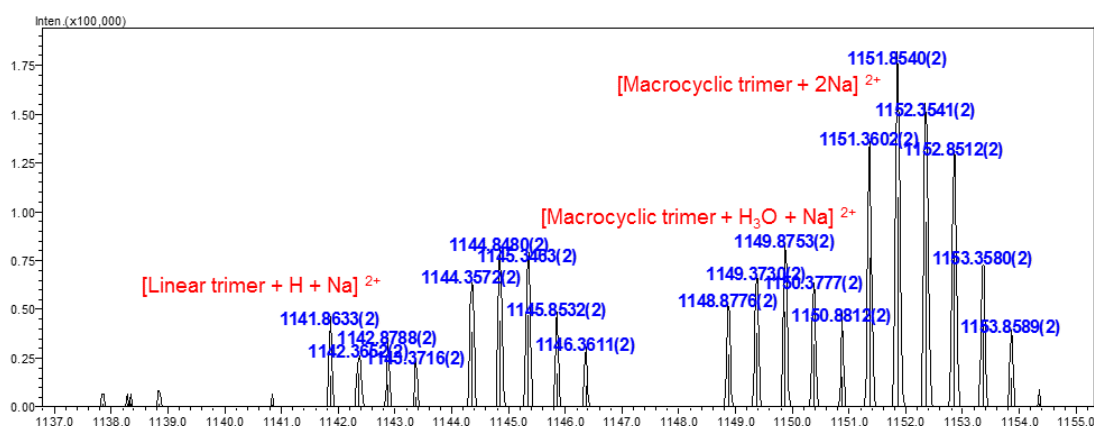


Figure S14 ESI-HR MS Spectrum around the peak m/z : 1151.8540 (with two positive charges) in Figure S13, the peak m/z ($z = 2$): 1141.8633 may belong to linear trimers (Calculated m/z : 1141.8794 $[M + H + Na]^{2+}$). The peaks m/z : 1149.8753, 1151.8540 may belong to trimeric macrocycles (Calculated m/z : 1149.8768 $[M + H_3O + Na]^{2+}$ and 1151.8625 $[M + 2Na]^{2+}$).

The preparation procedure of **Mixture-1: Di-SH-P5** (110 mg, 0.14 mmol) was dissolved in $CHCl_3$ (10 mL). Et_3N (200 μ L), I_2 (0.23 g, 0.91 mmol, 6.5 eq) was added to the solution. The reaction was stood at room temperature for 5 days. Then, the reaction was quenched by $Na_2S_2O_3$ aqueous solution and extracted with CH_2Cl_2 (10 mL \times 3). The combined organic phase was dried with anhydrous Na_2SO_4 and concentrated

under reduced pressure to afford a residue. Purified by column chromatography on silica-gel using ethyl acetate/petroleum ether as eluents (1:3) to obtain a mixture (**Mixture-1**) as a yellow solid (72 mg, 66%).

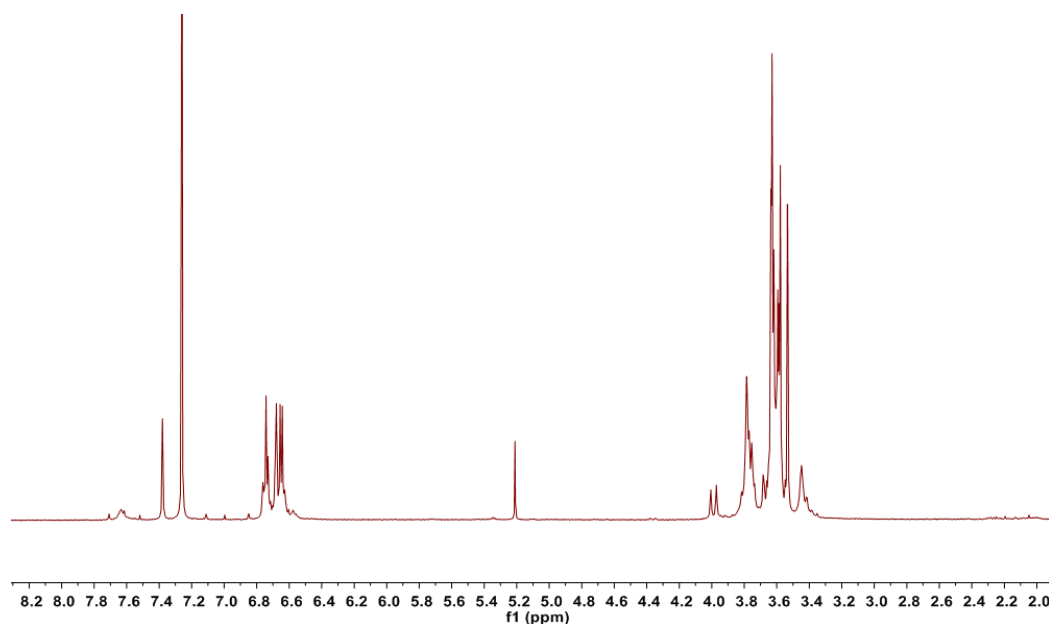


Figure S15 ¹H NMR Spectrum (400 MHz, 293 K, CDCl₃) of **Mixture-1**.

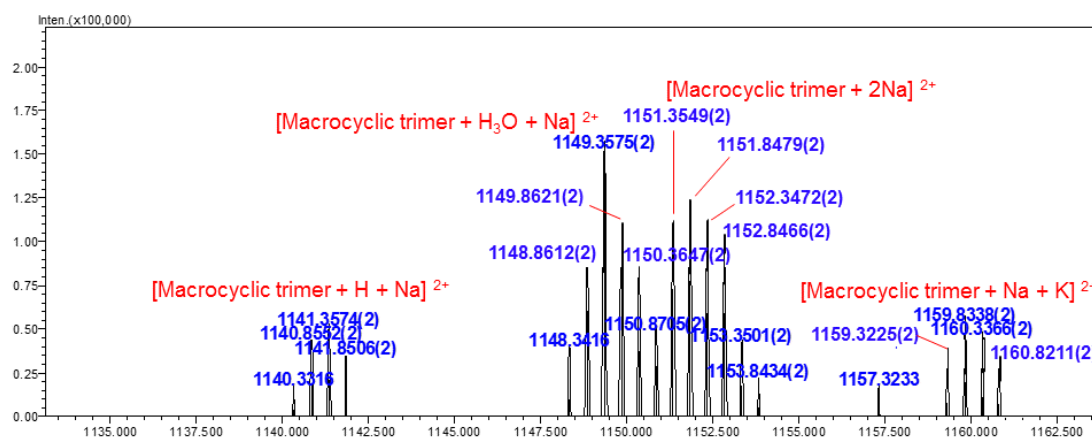


Figure S16 The ESI-HR MS of **Mixture-1** around the peak m/z: 1149.3575 (with two positive charges). The peaks m/z: 1149.3575, 1151.8479, 1159.8338 (with two positive charges) belong to trimeric macrocycles (Calculated m/z: 1149.3848 [M + NH₄ + Na]²⁺, 1151.8625 [M + 2Na]²⁺, 1159.8495 [M + K + Na]²⁺).

Mixture-1 was further purified by column chromatography on silica-gel using ethyl acetate/petroleum ether as eluents (1:8) to obtain racemic (*PPP*)-/(*MMM*)-**T** (yellow precipitate, 42 mg, 38%) as well as racemic (*PPM*)-/(*MMP*)-**T** (yellow precipitate, 19 mg, 18%). Another mixture (**Mixture-2**) composed of racemic (*PPP*)-/(*MMM*)-**T** and linear trimers were also obtained. Chiral HPLC was used to further purify **Mixture-2**.

(*PPP*)-/(*MMM*)-**T**: ^1H NMR (400 MHz, CDCl_3): δ (ppm): 7.38 (s, 6H), 6.73 (s, 6H), 6.67-6.73 (m, 18H), 4.00 (d, $J=13.59$ Hz, 6H), 3.82-3.74 (m, 18H), 3.66 (d, $J=13.67$ Hz, 6H), 3.63 (s, 18H), 3.62 (s, 18H), 3.57 (s, 18H), 3.53 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm): 151.07, 150.98, 150.93, 150.90, 140.64, 131.81, 131.39, 129.01, 128.63, 128.05, 127.26, 114.42, 114.22, 114.12, 113.71, 56.16, 55.94, 55.74, 33.47, 30.01, 29.74. ESI-HR MS. Calcd for $\text{C}_{129}\text{H}_{132}\text{O}_{24}\text{S}_6$ (m/z): 1146.9071 $[\text{M} + 2\text{NH}_4]^{2+}$, 1149.8768 $[\text{M} + \text{H}_3\text{O} + \text{Na}]^{2+}$, 1151.8625 $[\text{M} + 2\text{Na}]^{2+}$. Found: 1146.8998, 1149.8800, 1151.8604.

(*PPM*)-/(*MMP*)-**T**: ^1H NMR (400 MHz, CDCl_3): δ (ppm): 7.64 (s, 6H), 6.76 (s, 6H), 6.73 (s, 6H), 6.68 (s, 6H), 6.63 (s, 6H), 3.78-3.76 (br d, 30H), 3.62-3.59 (br m, 54H), 3.45 (br s, 18H).

Linear trimer: ^1H NMR (400 MHz, CDCl_3): δ (ppm): 7.72 (s, 2H), 7.64 (s, 2H), 7.13 (s, 2H), 6.87 (s, 2H), 6.76-6.70 (m, 18H), 6.65 (s, 2H), 6.61 (s, 2H), 4.36 (d, $J=13.59$ Hz, 2H), 3.97-3.91 (m, 4H), 3.86-3.82 (m, 4H), 3.79 (s, 16H), 3.75-3.71 (m, 4H), 3.69 (s, 6H), 3.67 (s, 6H), 3.65-3.61 (br m, 48H), 3.58 (s, 6H), 3.56 (s, 6H), 3.37 (d, $J=13.68$ Hz, 2H).

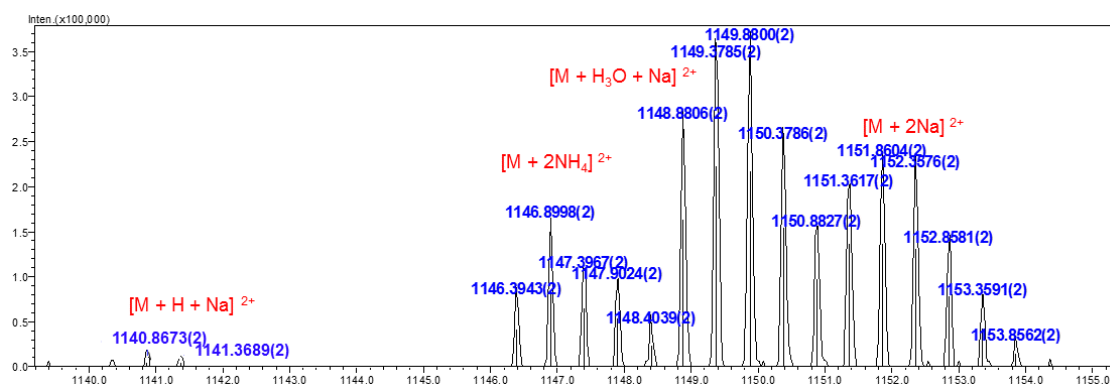


Figure S19 ESI-HR MS of the racemic compounds of *(PPP)-/(MMM)-T*. The peaks 1146.8998, 1149.8800, 1151.8604 belong to $[M + 2NH_4]^{2+}$, $[M + H_2O + Na]^{2+}$, $[M + 2Na]^{2+}$. (Calculated m/z : 1146.9071 $[M + 2NH_4]^{2+}$, 1149.8768 $[M + H_2O + Na]^{2+}$, 1151.8625 $[M + 2Na]^{2+}$)

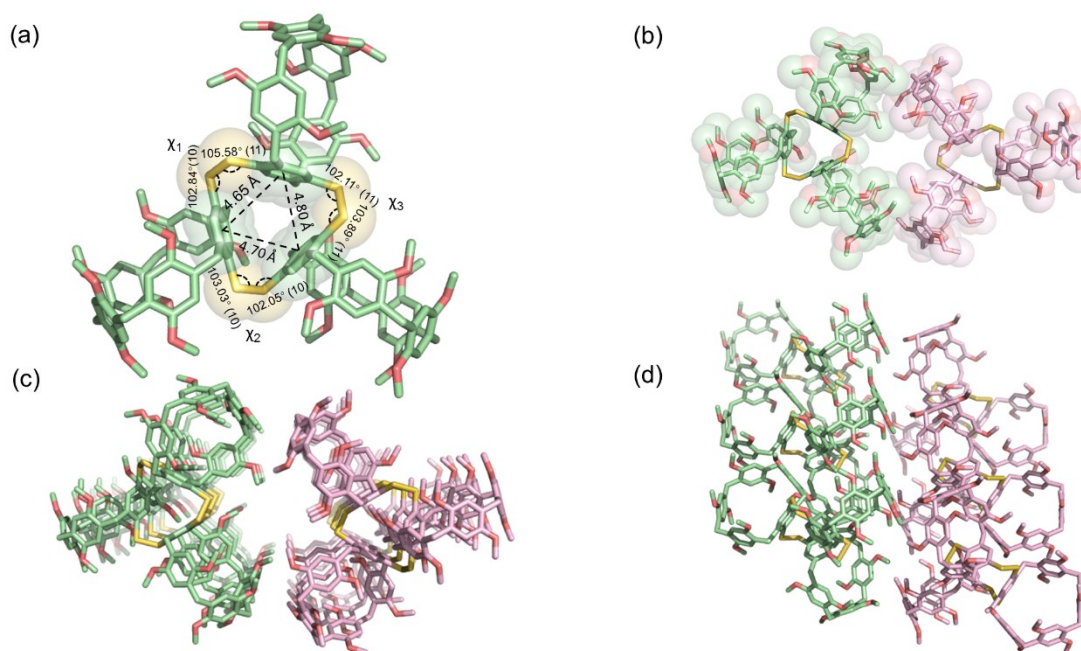


Figure S20 X-ray crystallography characterization shows (a) the cavity of the macrocycle forming by three disulfide bonds, the dihedral angles χ_1 , χ_2 and χ_3 are -65.0° (2), -65.3° (2) and -62.7° (1), respectively; (b) the enantiomeric configurations in solid state structure; and stacked solid state structures from (c) top view and (d) side view. Solvent molecules and all hydrogens are omitted for the sake of clarity. Color code: green and pink, carbon; red, oxygen; yellow, sulfur.

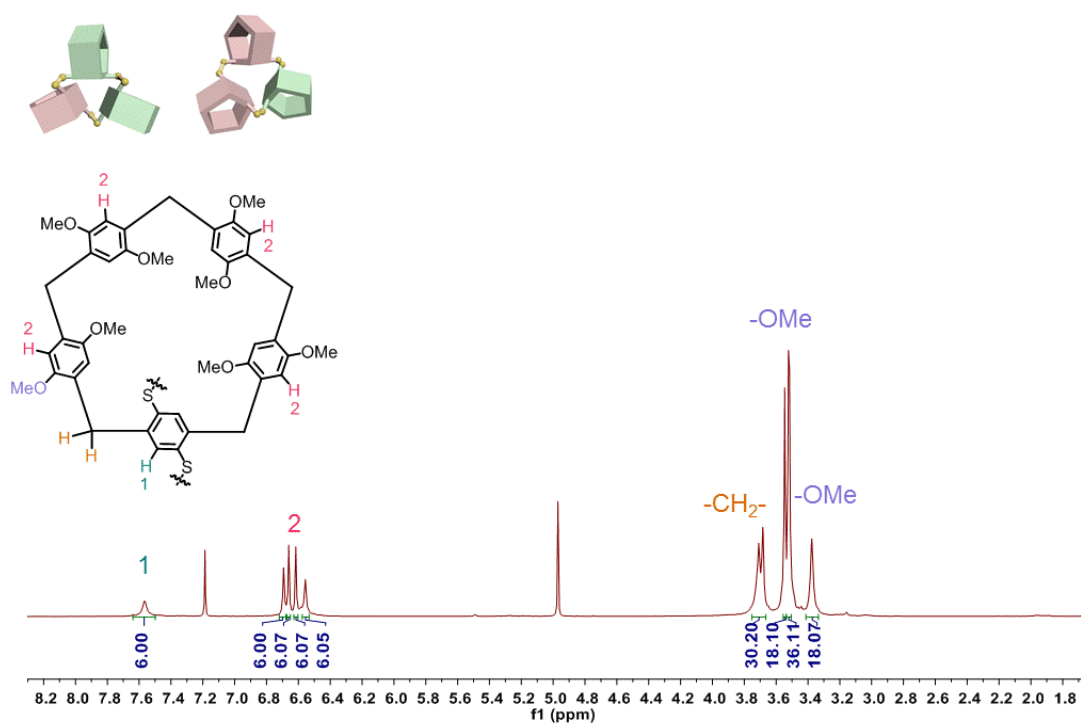


Figure S21 ^1H NMR of racemic compounds of the $(PPM)-(MMP)-T$ (400 MHz, 293 K, CDCl_3)

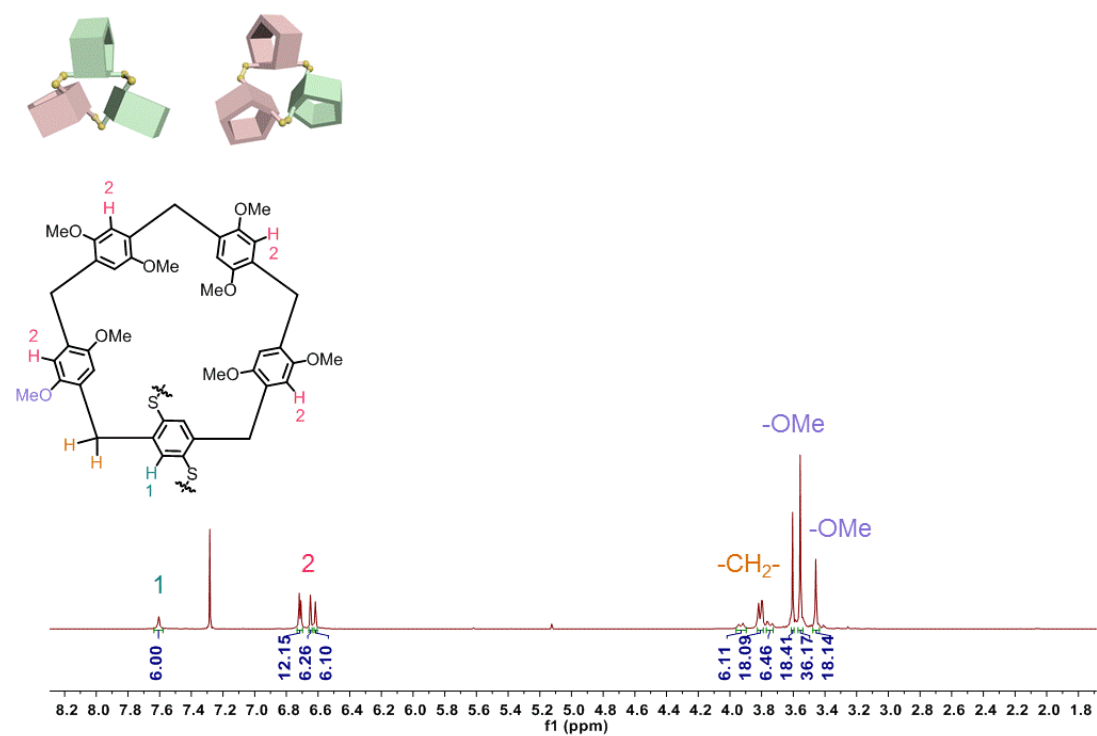


Figure S22 ^1H NMR of the racemic compounds of the $(PPM)-(MMP)-T$ (500 MHz, 328 K, CDCl_3)

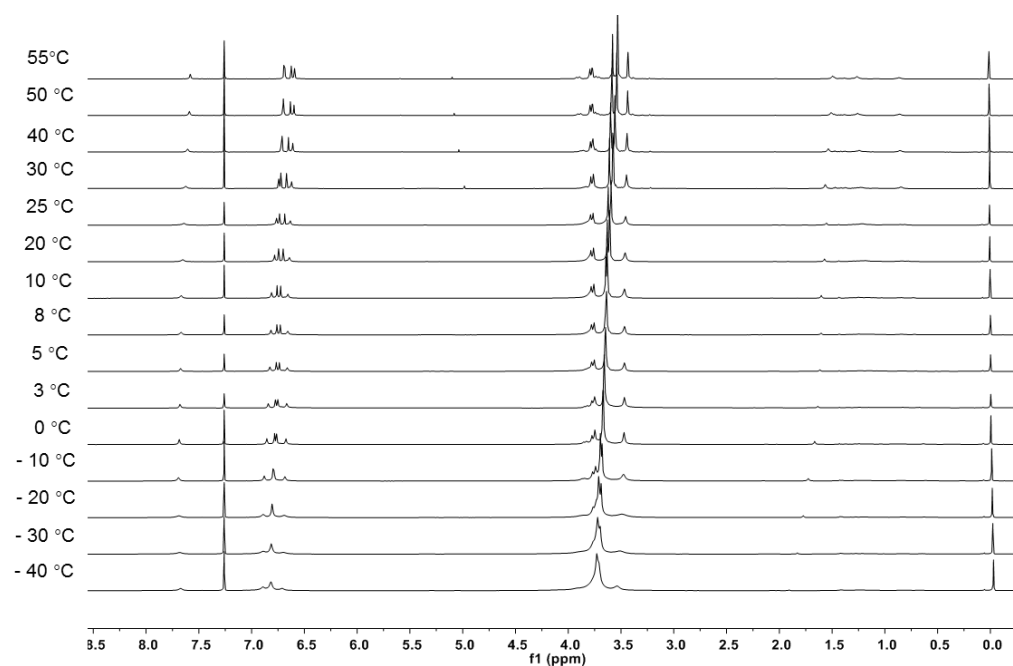


Figure S23 ^1H NMR (500 MHz, CDCl_3) of the racemic compounds of $(PPM)/(MMP)\text{-T}$ recorded at various temperatures. The temperatures from bottom to top are: -40°C , -30°C , -20°C , -10°C , 0°C , 3°C , 5°C , 8°C , 10°C , 20°C , 25°C , 30°C , 40°C , 50°C , 55°C .

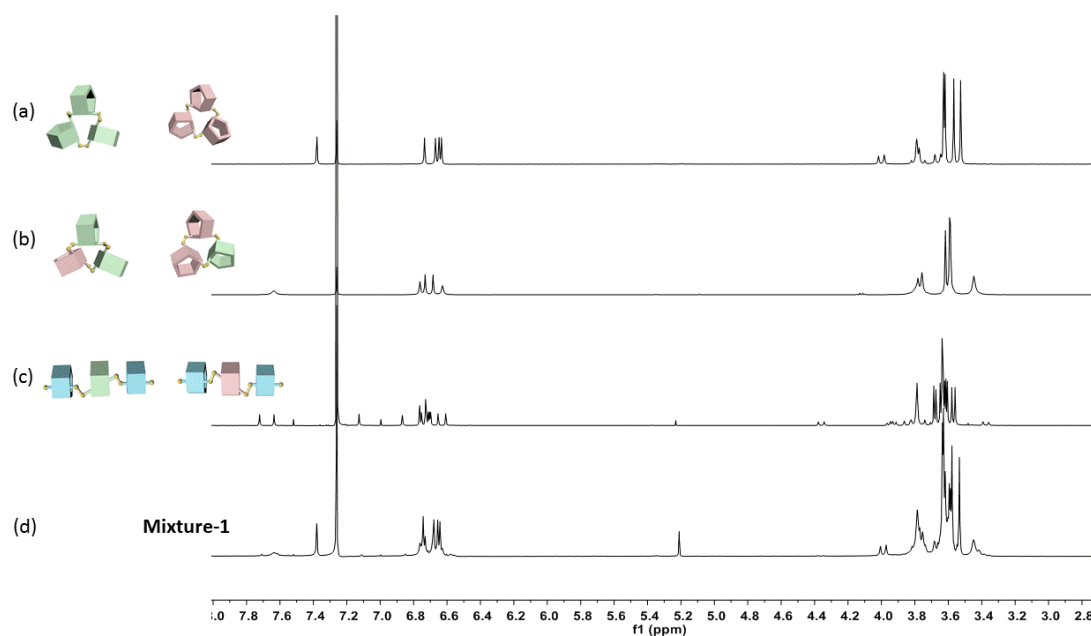


Figure S24 ^1H NMR (400 MHz, 293 K, CDCl_3) of (a) the racemic $(PPP)/(MMM)\text{-T}$; (b) racemic $(PPM)/(MMP)\text{-T}$; (c) linear trimers (400 MHz, 298 K, CDCl_3); (d) **Mixture-1**.

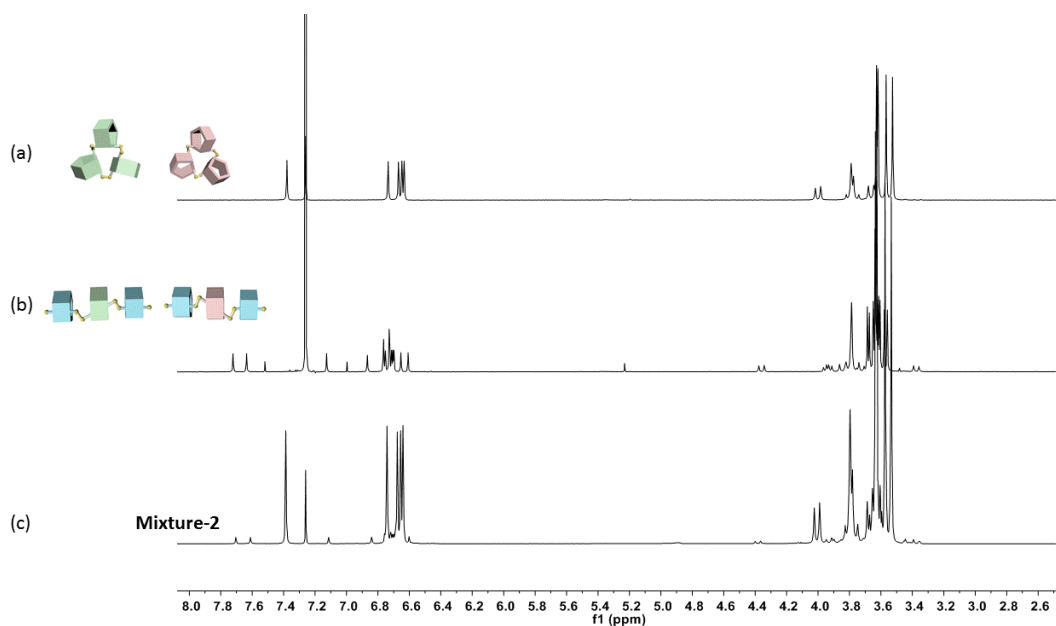


Figure S25 ^1H NMR (400 MHz, 293 K, CDCl_3) of (a) the racemic compounds of $(PPP)\text{-}/(MMM)\text{-T}$; (b) linear trimers; (c) **Mixture-2**.

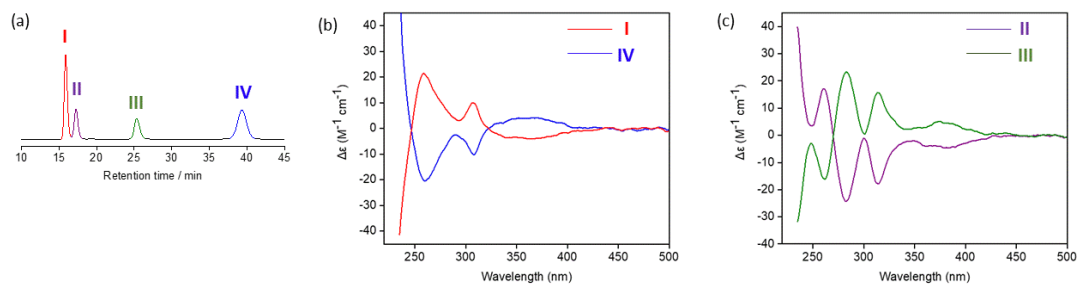


Figure S26 (a) Chiral HPLC spectrum. Recorded by the UV-vis detector. Four distinctive peaks in 35:15:15:35 integral ratio were observed. The mixture was subjected to prep-HPLC and three fractions corresponding to **I**, **III**, **IV** were isolated. The fraction corresponding to **II** was mixed with part of **I**; (b) ECD spectra of **I**, **IV**; (c) ECD spectra of **II**, **III**.

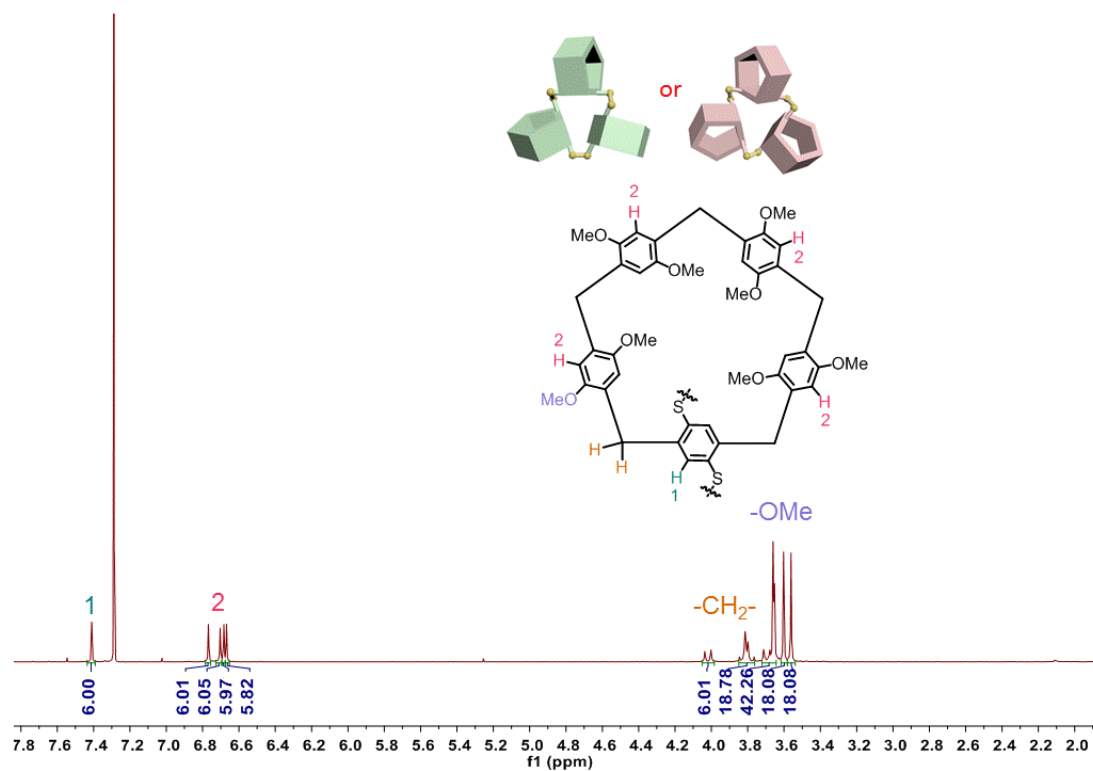


Figure S27 ^1H NMR (400 MHz, 298 K, CDCl_3) of **I** in Figure S26.

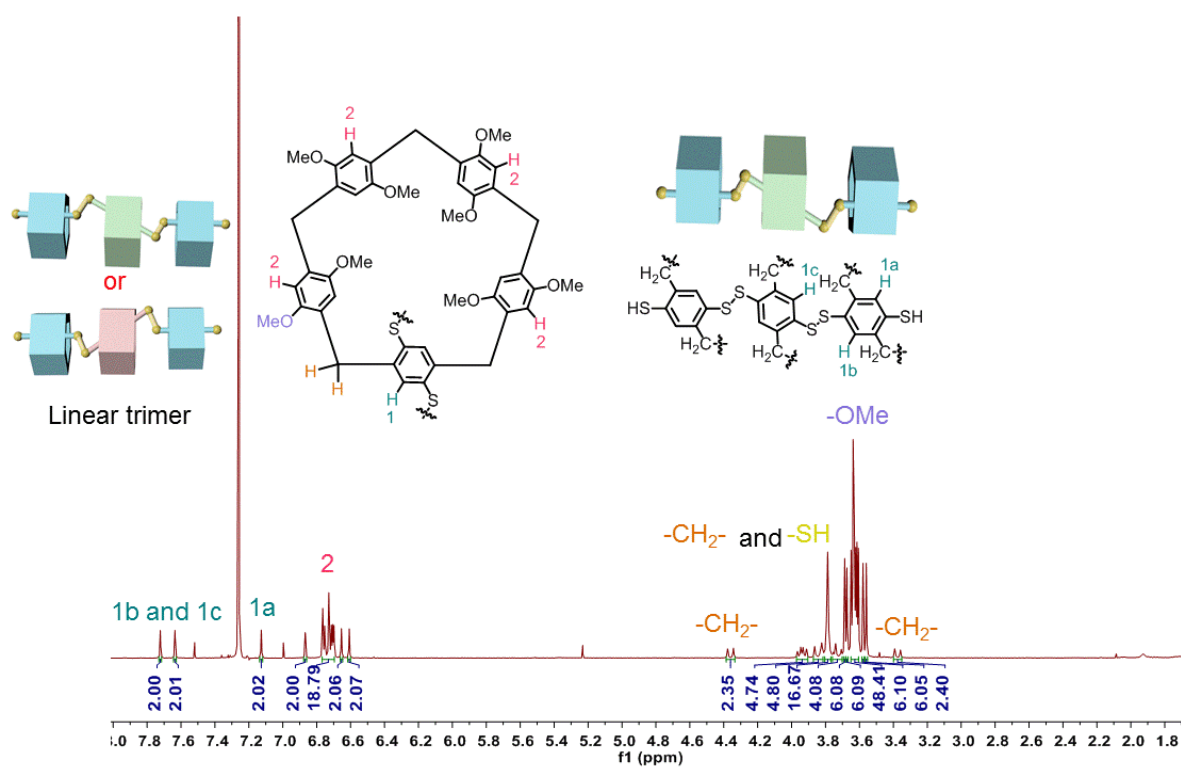


Figure S28 ^1H NMR (400 MHz, 298 K, CDCl_3) of **II** (Linear trimers) in Figure S26.

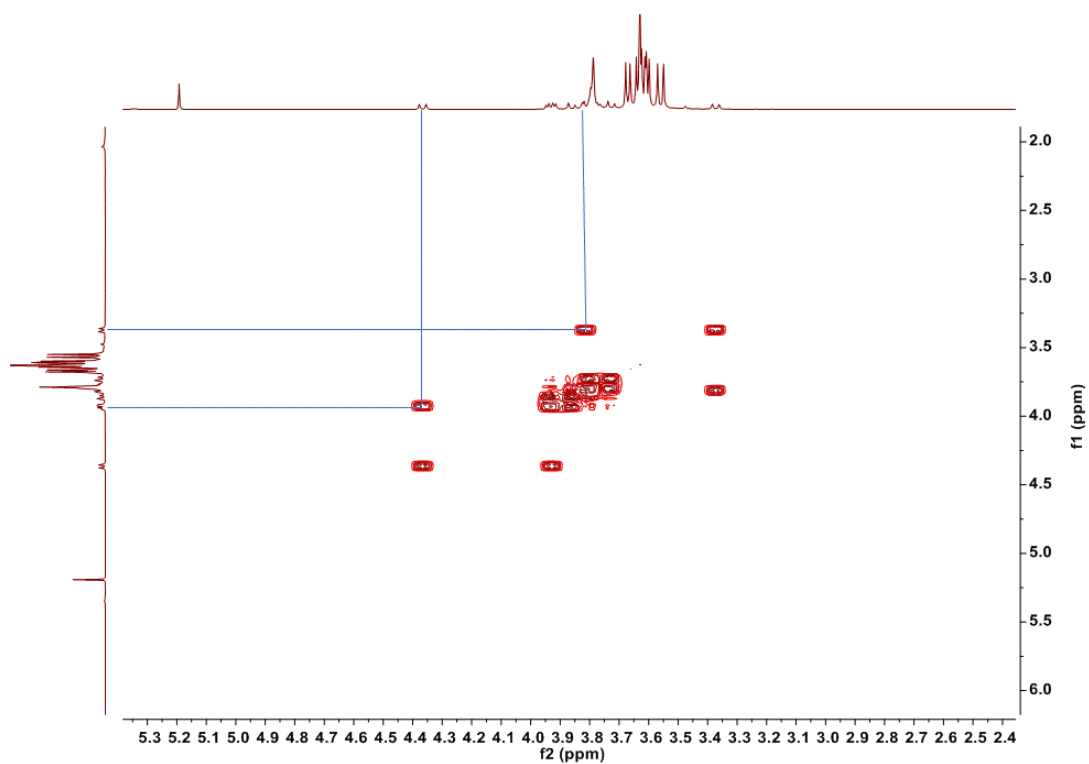


Figure S29 ^1H - ^1H COSY (400 MHz, 298 K, CDCl_3) of **II** (Linear trimers) in Figure S26.

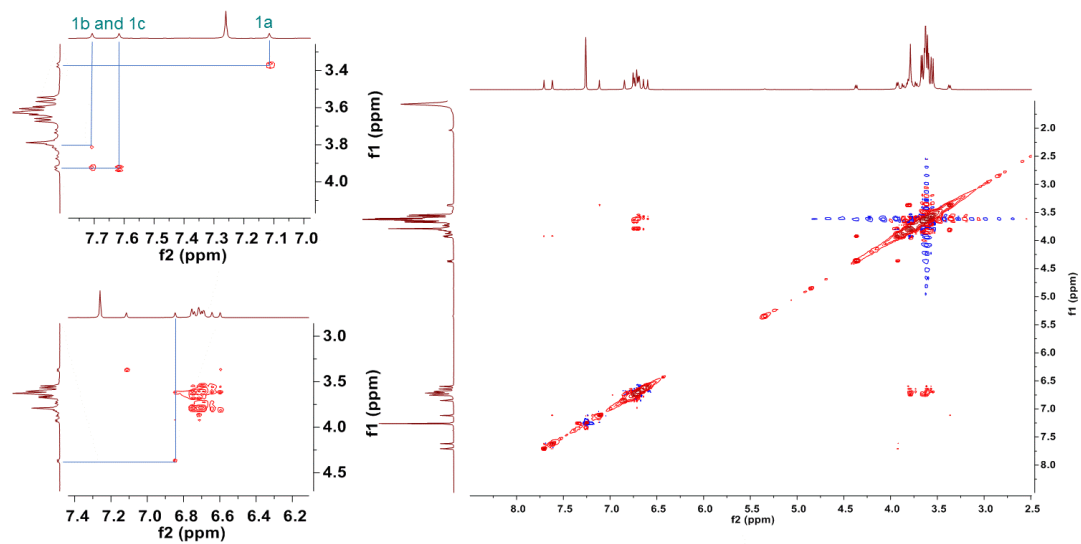


Figure S30 ^1H - ^1H NOESY (400 MHz, 298 K, CDCl_3) of **II** (Linear trimers) in Figure S26.

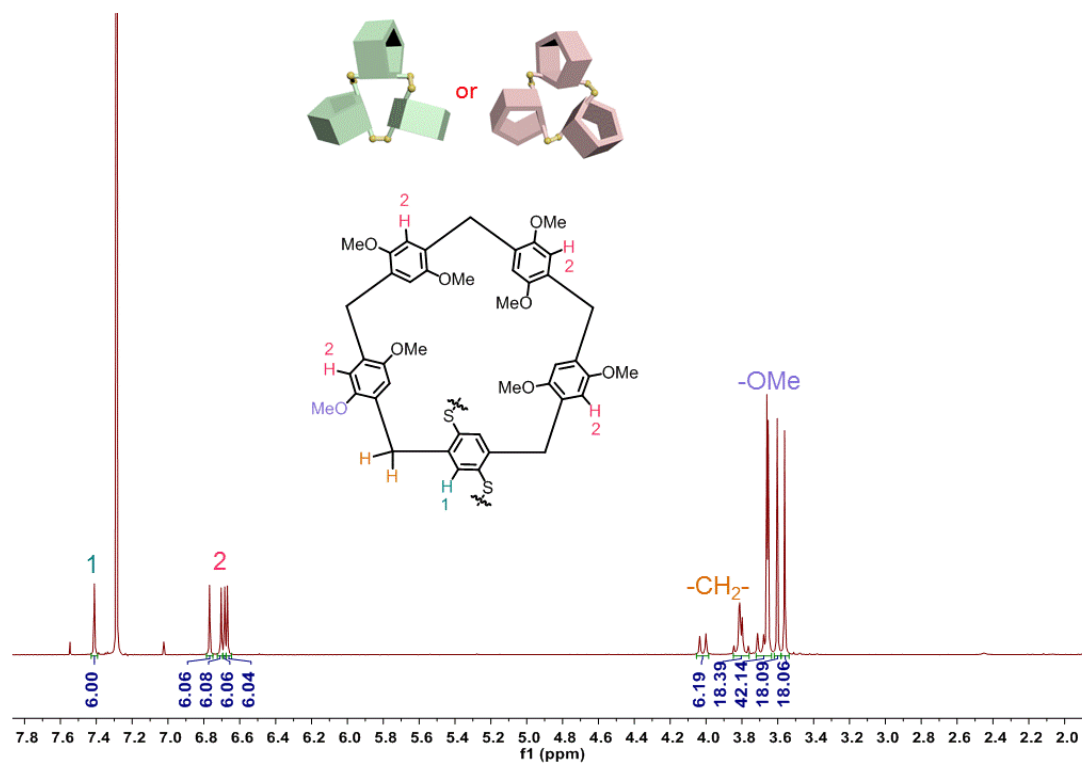


Figure S31 ^1H NMR (400 MHz, 298 K, CDCl_3) of **IV** in Figure S26.

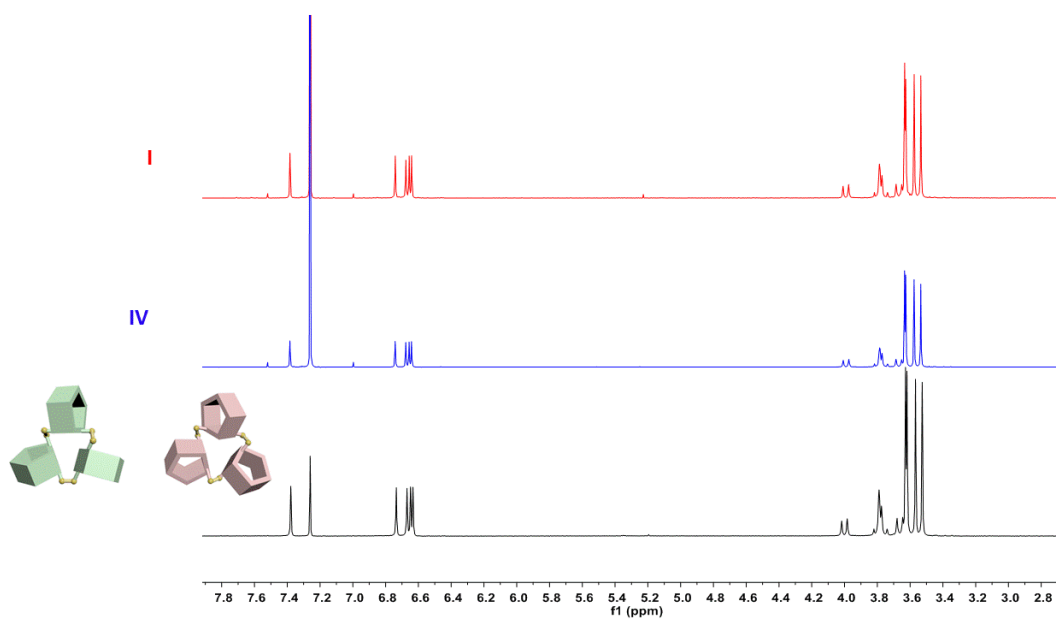


Figure S32 Comparison of ^1H NMR (400 MHz, 293 K, CDCl_3) of **I** (red), **IV** (blue) in Figure S26 and racemate of them (black). The chemical shifts after separation are identical as mixture.

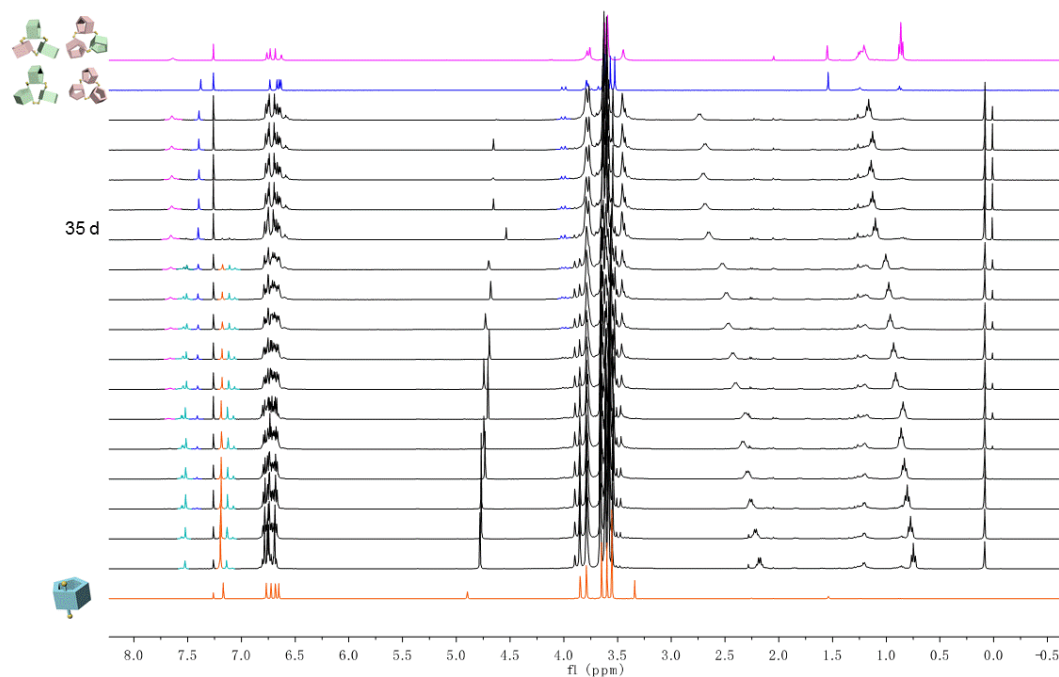


Figure S33 ^1H NMR (400 MHz, 293 K, CDCl_3) of oxidation process. It was after 35 days that the mixture was mainly the trimeric macrocycles. (In an NMR tube, **Di-SH-P5** (30 mg) was dissolved in CDCl_3 (0.52 mL), then Et_3N (0.4 μL) was added. The reaction was exposed to air and stood at room temperature.)

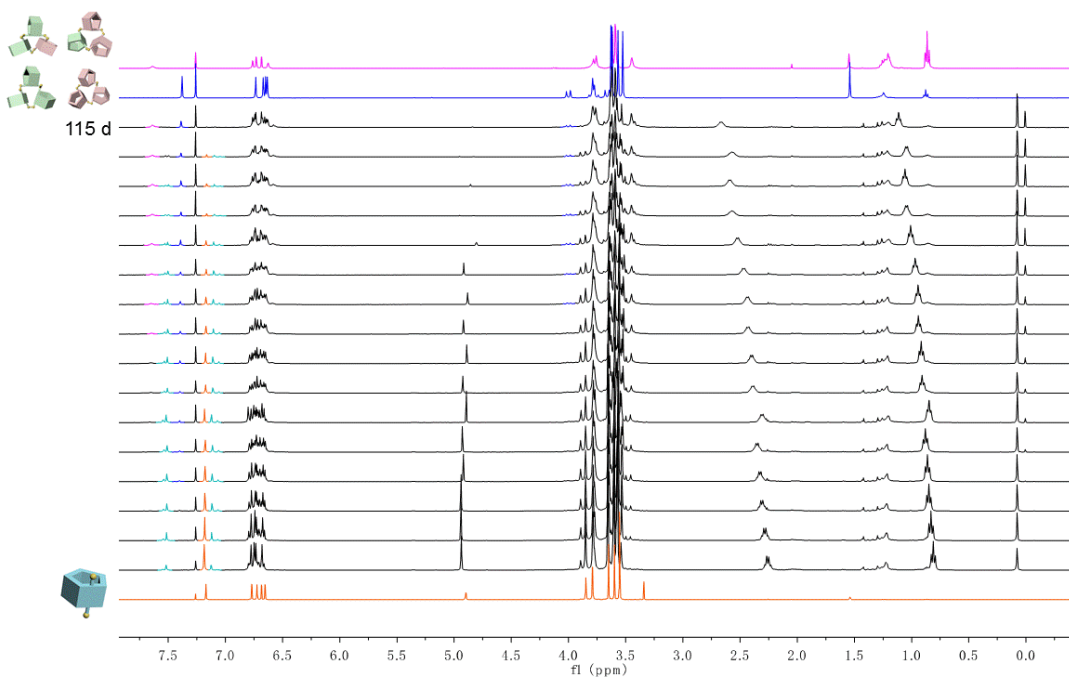


Figure S34 ^1H NMR (400 MHz, 293 K, CDCl_3) of oxidation process. **Di-SH-P5**: 20 mg. It was after 115 days that the mixture was mainly the trimeric macrocycles. (In an NMR tube, **Di-SH-P5**

(20 mg) was dissolved in CDCl_3 (0.52 mL), then Et_3N (0.4 μL) was added. The reaction was exposed to air and stood at room temperature.)

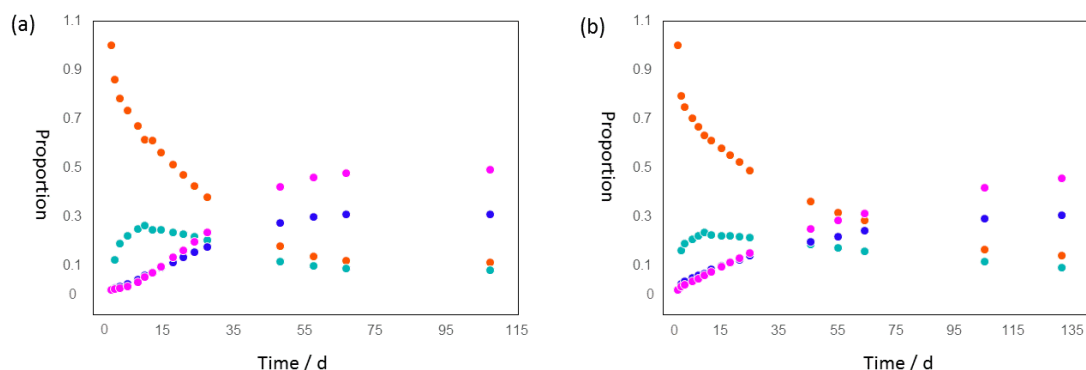


Figure S35: The molar fraction of the four major species (orange: **Di-SH-P5**, blue: racemate of (PPP)-/(MMM)-T, magenta: racemate of (PPM)-/(MMP)-T, Green: Linear dimer). (a) 30 mg; (b) 20 mg.

In an NMR tube, **Di-SH-P5** (30 mg) was dissolved in CDCl_3 (0.52 mL), then Et_3N (0.4 μL) was added. The reaction was exposed to air and stood at room temperature for four days before quenching. The mixture was purified by column chromatography on silica-gel using ethyl acetate/petroleum ether as eluents (1:5) to obtain the intermediate as a white solid.

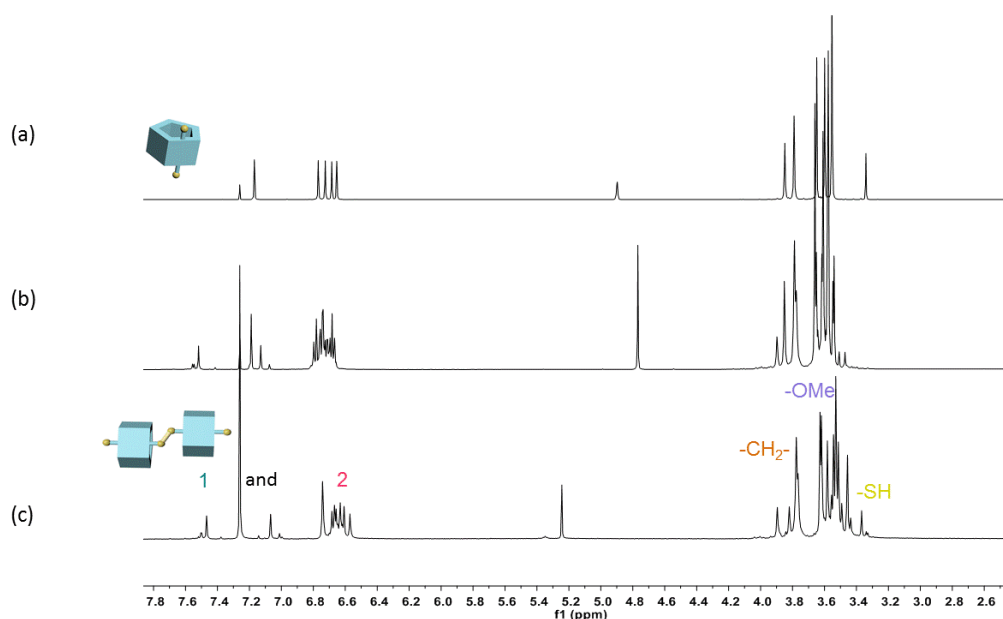


Figure S36 ^1H NMR (400 MHz, 293 K, CDCl_3). (a) **Di-SH-P5**; (b) before purification; (c) Purified by column chromatography on silica-gel.

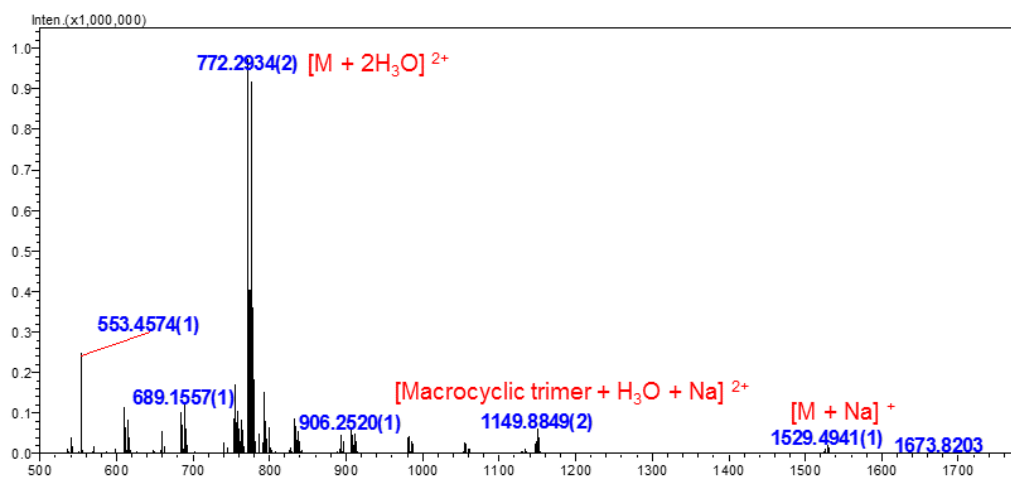


Figure S37 ESI-HR MS of (b) in Figure S34, the peak 772.2934 (with two positive charges) belongs to linear dimers $[M + 2H_3O]^{2+}$: 772.2734. The intermediate products were proved to be linear dimers.

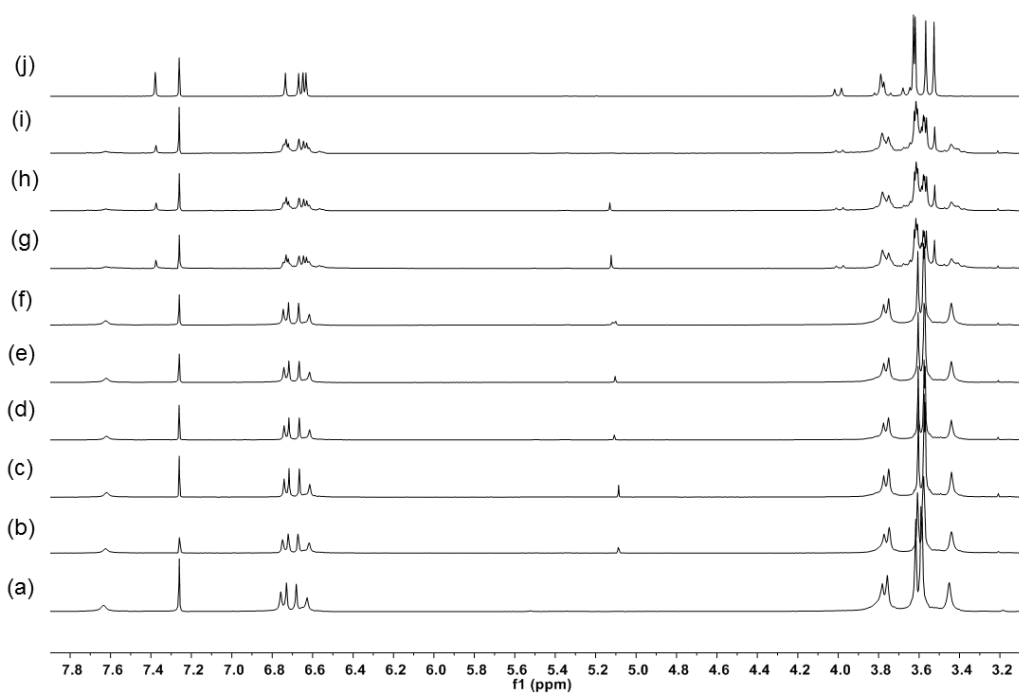


Figure S38 ^1H NMR (400 MHz, 293 K, CDCl_3). (a) *(PPM)*-(*MMP*)-**T** (5 mg) was dissolved in CDCl_3 (0.5 mL) and (b) 9 μL Et_3N was added, kept at room temperature for one day; (c) for four days; (d) **Di-SH-P5** (0.01 eq) was added, kept at room temperature for one day; (e) for three days; (f) for four days; (g) **Di-SH-P5** (0.1 eq) was added, kept at 60°C for 8h; (h) for 16h; (i) for 40h; (j) *(PPP)*-(*MMM*)-**T**.

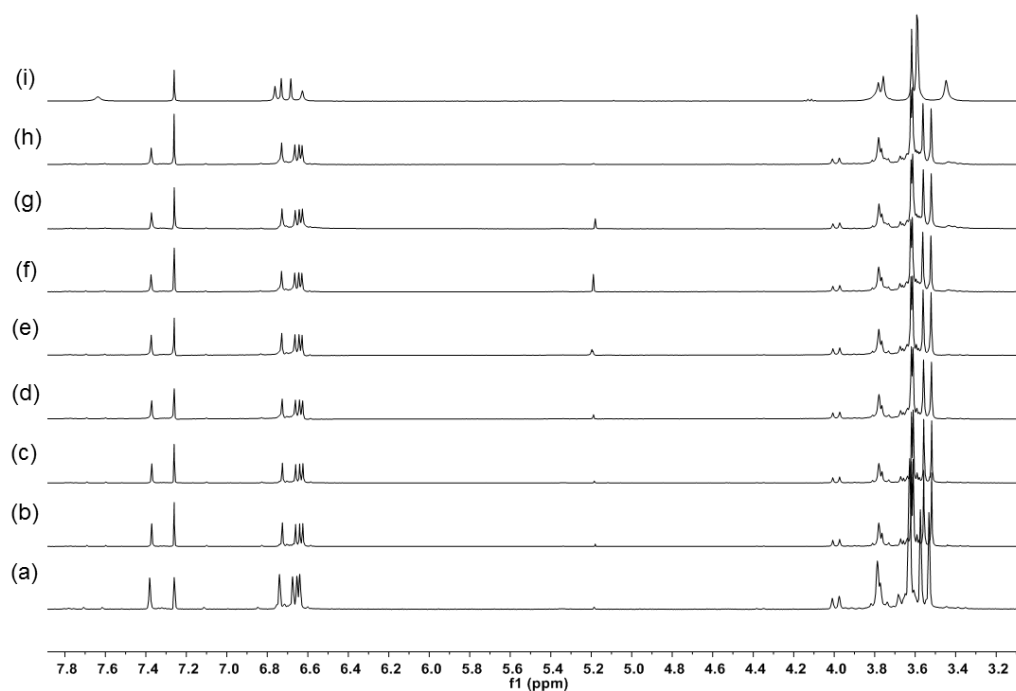


Figure S39 ^1H NMR (400 MHz, 293 K, CDCl_3). (a) $(PPP)\text{-}/(MMM)\text{-T}$ (5 mg, accompanied by few linear-trimers) was dissolved in CDCl_3 (0.5 mL) and (b) 9 μL Et_3N was added, kept at room temperature for one day; (c) for three days; (d) for five days; (e) for seven days; (f) **Di-SH-P5** (0.1 eq) was added, kept at 60°C for 8h; (g) for 16h; (h) for 40h; (i) $(PPP)\text{-}/(MMM)\text{-T}$.

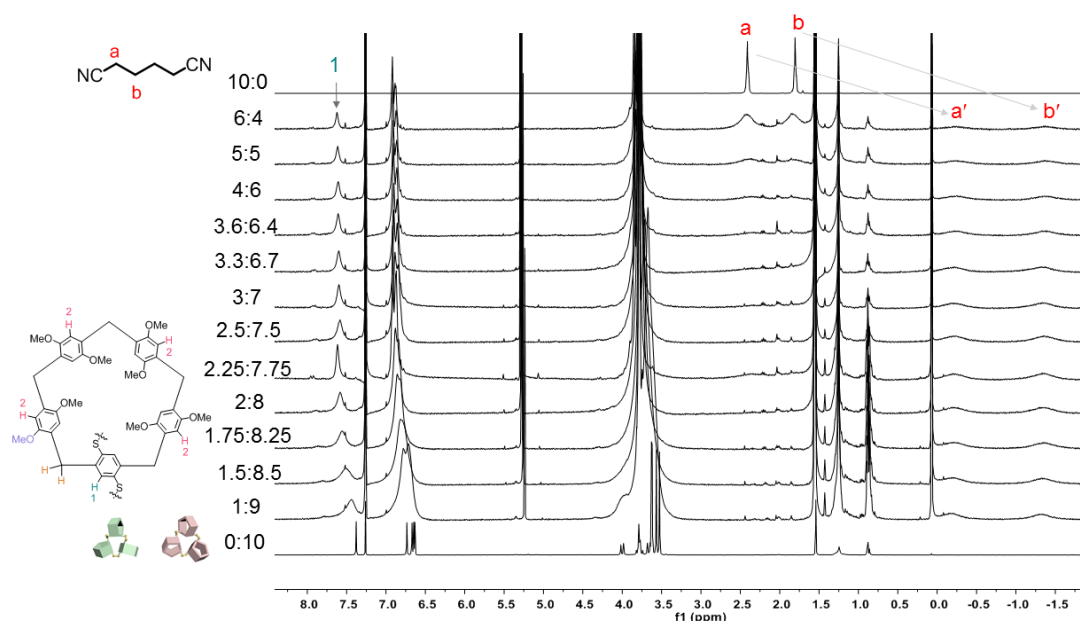


Figure S40 ^1H NMR (400 MHz, 293 K, CDCl_3) of $(PPP)\text{-}/(MMM)\text{-T}$ in the presence of 1,4-dicyanobutane. The samples were prepared so that the total molar concentration of compounds was 4.4 mM in each sample: only the ratios of host to guest were altered. From bottom to top, the ratios

between *(PPP)*-/*(MMM)*-T and 1,4-dicyanobutane are 10:0; 6:4; 5:5; 4:6; 3.6:6.4; 3.3:6.7; 3:7; 2.5:7.5; 2.25:7.75; 2:8; 1.75:8.25; 1.5:8.5; 1:9; 0:10.

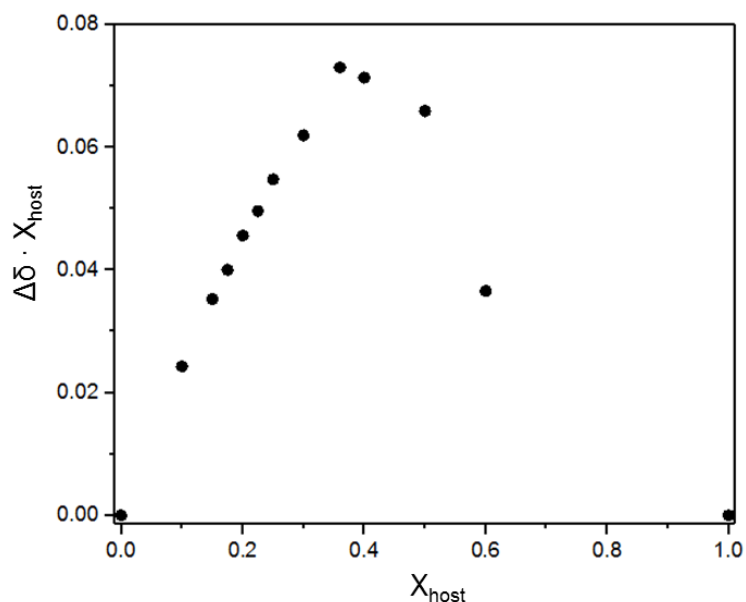


Figure S41 Job plot showing the 1 : 2 stoichiometry of the complex between *(PPP)*-/*(MMM)*-T and 1,4-dicyanobutane in CDCl_3 by plotting the $\Delta\delta$ in chemical shift of the host's proton H_1 (for proton designations, see Figure S40) observed by ^1H NMR spectroscopy against the mole fraction of guest. ($[\text{host}] + [\text{guest}] = 4.4 \text{ mM}$).

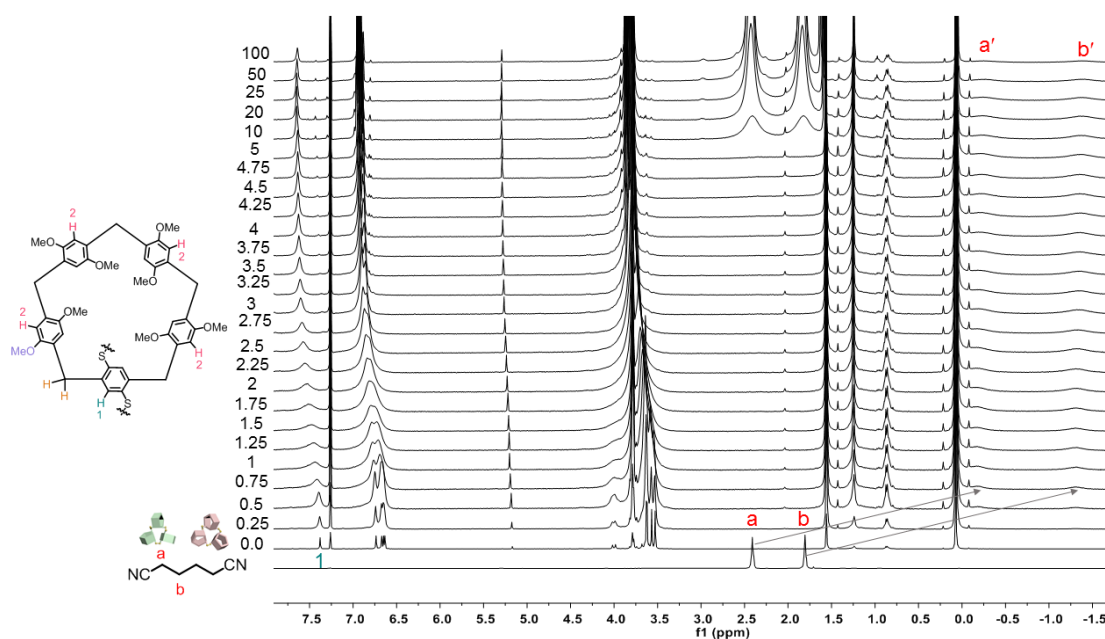


Figure S42 ^1H NMR (CDCl_3 , 400 MHz, 298 K) titration of 1,4-dicyanobutane (0.55 M) into a

solution of *(PPP)*–/*(MMM)*–**T** (4.4 mM). From bottom to top: 0.0, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2, 2.25, 2.5, 2.75, 3, 3.25, 3.5, 3.75, 4, 4.25, 4.5, 4.75, 5, 10, 20, 25, 50, 100 equivalents.

Determination of association constants by ¹H NMR titration

The association constant between the host *(PPP)*–/*(MMM)*–**T** and the guest 1,4-dicyanobutane was determined by ¹H NMR titration. A nonlinear curve-fitting method (Fitter: NMR 1:2; Method: Nelder-Mead; Flavour: None (Full))⁶ was applied to calculate the association constant for complexation between host and guest, which was based on the online tools for supramolecular chemistry research and analysis (<http://supramolecular.org>).

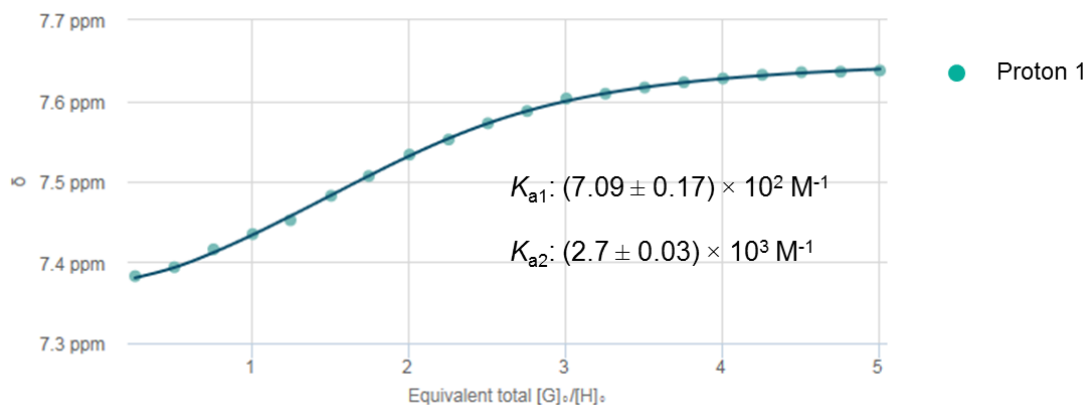


Figure S43 The nonlinear-fitting curves of H¹ by BindFit v0.5 based on Figure S42

S5 X-Ray Crystallography

Single Crystal Growth: Single crystals of 1.5(C₄H₈O), 2(C₃H₆O), 0.5(C₄H₈O), 2(C₄H₈O), 3(C₃H₆O)-loaded racemic compounds of (*PPP*)-/(*MMM*)-**T** were grown by evaporating acetone into a tetrahydrofuran solution of the racemic (*PPP*)-/(*MMM*)-**T** (3 mg in 400 μ L) for 7 days.

Table S1 Experimental single crystal X-ray data for 1.5(C₄H₈O), 2(C₃H₆O), 0.5(C₄H₈O), 2(C₄H₈O), 3(C₃H₆O)-loaded racemic compounds of (*PPP*)-/(*MMM*)-**T**

Empirical formula	C ₁₆₀ H ₁₉₄ O ₃₃ S ₆
Formula weight / g mol ⁻¹	2837.50
Temperature / K	180 K
Crystal system	Triclinic
Space group	P-1
a / Å	12.3614(6)
b / Å	23.4929(13)
c / Å	27.5134(14)
α / °	98.883(2)
β / °	93.032(2)
γ / °	103.195(2)
Volume/ Å ³	7653.4(7)
Z	2
ρ_{calc} / g cm ⁻³	1.231
μ / mm ⁻¹	0.163
F / 000	3028.0
Crystal size / mm ³	0.23 \times 0.11 \times 0.09
2 θ range for data collection / °	3.84 to 50
Index ranges	-14 \leq h \leq 13, -27 \leq k \leq 27, -32 \leq l \leq 32
Reflections collected	72729
Independent reflections	26605 [R _{int} = 0.0644, R _{sigma} = 0.0774]
Data/restraints/parameters	36605/0/1671
Goodness-of-fit on F ²	1.014
Final R indices [I > 2 σ (I)]	R ₁ = 0.0610, wR ₂ = 0.1347
Final R indices [all data]	R ₁ = 0.1007, wR ₂ = 0.1562
Largest diff. peak / hole / e Å ⁻³	1.01/-0.74

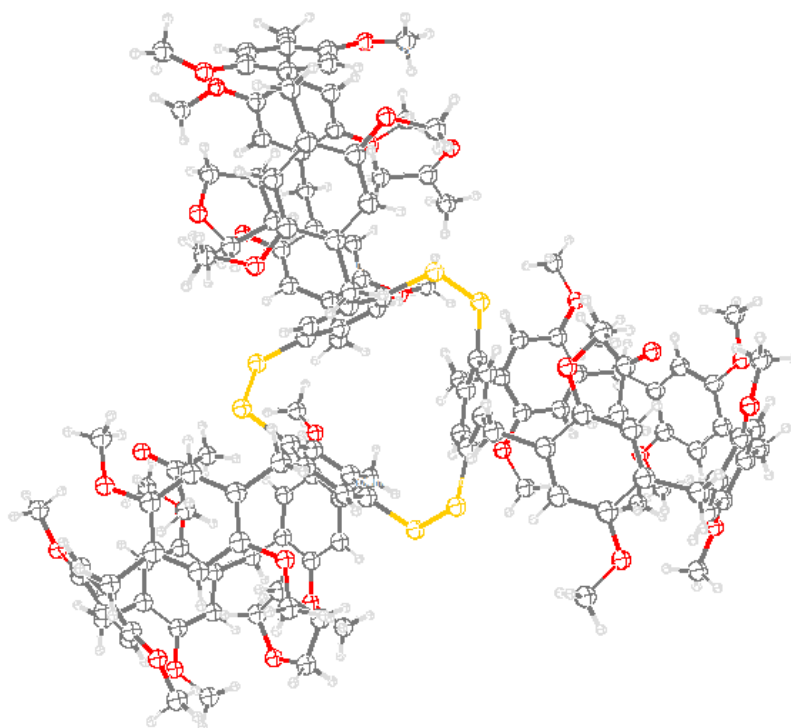


Figure S44 Thermal ellipsoid plot (50% probability level) for crystal structure. Color code: dark grey, carbon; red, oxygen; yellow, sulfur; light grey, hydrogen.

S6 References

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