

Electronic Supplementary Information (ESI)

Pillar[5]arene-based Nonionic Polyrotaxanes and a Topological Gel Prepared from Cyclic Host Liquids

Tomoki Ogoshi*, Takamichi Aoki, Seita Ueda, Yuko Tamura and Tada-aki Yamagishi

*Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-
machi, Kanazawa, 920-1192, Japan*

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Experimental section

Materials. All solvents and reagents were used as supplied. Pillar[5]arene-based CHL **2**, and stopper **4** were synthesized according to the previous papers.^{S1,S2}

Measurements. The ¹H NMR spectra were recorded at 500 MHz and ¹³C NMR spectra were recorded at 125 MHz with a JEOL-ECA500 spectrometer.

CHL 3. *per*-Hydroxylated pillar[5]arene **1**^{S3} (0.32 g, 0.52 mmol) was dissolved in DMF (8 mL). Sodium hydride (0.40 g, 10 mmol) was added and the reaction mixture was stirred. Then, excess of 2-allylethyl *p*-toluenesulfonate^{S4} (3.4 g, 10 mmol) was added and the reaction mixture was heated at 80 °C for 48 h. The solvent was evaporated to give a liquid. Column chromatography (silica gel; ethyl acetate : methanol = 1 : 2) afforded a yellow liquid (0.10 g, 0.044 mmol, Yield: 8%). ¹H NMR (CDCl₃, 500 MHz, ppm): δ 6.83 (s, 10H, phenyl), 5.82 (m, 10H, allyl), 5.19 (d, 10H, allyl), 5.11 (d, 10H, allyl), 4.01 (t, 20H, methylene), 3.91 (t, 20H, methylene), 3.82 (t, 20H, methylene), 3.74 (s, 10H, methylene bridge), 3.72 (t, 20H, methylene), 3.63 (t, 20H, methylene), 3.56 (t, 20H, methylene), 3.47 (t, 20H, methylene). ¹³C NMR (CDCl₃, 500 MHz, ppm): δ 149.9, 134.9, 128.7, 117.1, 115.3, 72.2, 70.8, 69.4, 68.1, 29.4. HRESIMS: *m/z* Calcd for C₁₂₅H₂₀₀Na₁₀O₄₀ [M+Na]⁺: 2354.2731, found 2354.2747.

Polyrotaxane 5. PTHF^{S5} (7.2 mg, 0.10 mmol) and stopper **4** (1.4 mg, 6.5 μmol) were dissolved CHL **2** (2.1 g, 1.0 mmol) with Cu(CH₃CN)₄PF₆ (2.4 mg, 6.5 μmol) and tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA, 3.4 mg, 6.5 μmol). The mixture was stirred for 12 h at 25 °C. The excess CHL **2** was removed by washing with water. To remove the excess stopper **3** and PTHF containing no and small amount of pillar[5]arene wheels, the residue was washed with hexane to give polyrotaxane **5** (14.2 mg, yield 44%). ¹H NMR (CDCl₃, 500 MHz, ppm): 7.47 (br, 2H, triazole), 7.18 (br, 4H, stopper), 7.11 (br, 2H, stopper), 6.89 (s, phenyl proton of pillar[5]arene wheel), 4.80-4.90 (br, 4H, methylene), 3.28-4.20 (m, protons from methylene and methoxy of pillar[5]arene wheel), 2.9-3.2 (br, methylene protons of PTHF), 1.33 (br, 24H, stopper), 0.90-1.40 (br, methylene protons of PTHF). ¹³C NMR (CDCl₃, 500 MHz, ppm): δ 149.7, 128.7, 114.9, 72.0, 70.8, 70.7, 70.6, 70.3, 67.9, 59.0, 29.4, 26.1.

Polyrotaxane 6. PTHF (3.9 mg, 0.054 mmol) and stopper **4** (1.2 mg, 5.3 μmol) were dissolved in CHL **3** (0.10 g, 0.044 mmol) with Cu(CH₃CN)₄PF₆ (2.0 mg, 5.3 μmol) and

TBTA (2.8 mg, 5.3 μ mol). The mixture was stirred for 12 h at 25 °C. The excess CHL **3** was removed by washing with a mixture of water and methanol (water : methanol = 1 : 1). To remove the excess stopper **3** and PTHF containing no and small amount of pillar[5]arene wheels, the residue was washed with hexane to give polyrotaxane **6** (8.2 mg, yield 35%). ^1H NMR (CDCl_3 , 500 MHz, ppm): 7.47 (br, 2H, triazole), 7.17 (br, 4H, stopper), 7.10-7.13 (br, 2H, stopper), 6.88 (s, phenyl protons of pillar[5]arene wheel), 5.85-5.93 (m, allyl protons of pillar[5]arene wheel), 5.13-5.30 (m, allyl protons of pillar[5]arene wheel), 4.80-4.90 (br, 4H, methylene), 3.30-3.75 (m, protons from methylene of pillar[5]arene wheel), 2.90-3.30 (br, methylene protons of PTHF), 0.90-1.52 (br, stopper and methylene protons of PTHF). ^{13}C NMR (CDCl_3 , 500 MHz, ppm): δ 149.6, 134.8, 128.6, 117.1, 114.7, 72.2, 70.7, 69.4, 67.8, 29.0, 26.5, 26.2.

Synthesis of Topological Gel. Polyrotaxane **6** (8.2 mg) was dissolved in chloroform (0.3 mL). To the mixture, Grubbs first generation catalyst (benzylidene-bis(tricyclohexylphosphine)-dichlororuthenium, 0.80 mg, 0.097 μ mol) was added. The solution was stirred at 25 °C. After 10 h, gelation took place. To remove Grubbs first generation catalyst, the gel was washed with chloroform and methanol (6.1 mg, yield 75%).

Measurement of Swelling Degrees. The topological gel was placed in the following organic solvents including hexane (dielectric constant: $\epsilon = 1.9$), chloroform ($\epsilon = 4.9$), THF ($\epsilon = 7.6$), dichloromethane ($\epsilon = 9.0$), acetone ($\epsilon = 21$) and methanol ($\epsilon = 32$). After immersion for 24 h, we measured Q of the gels, which is defined by as the following equation:

$$Q = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}} \text{ (wt/wt)}$$

where W_{dry} and W_{wet} are the weights of the dried gel and the wet gel, respectively.

^1H and ^{13}C NMR spectra of CHL **3**

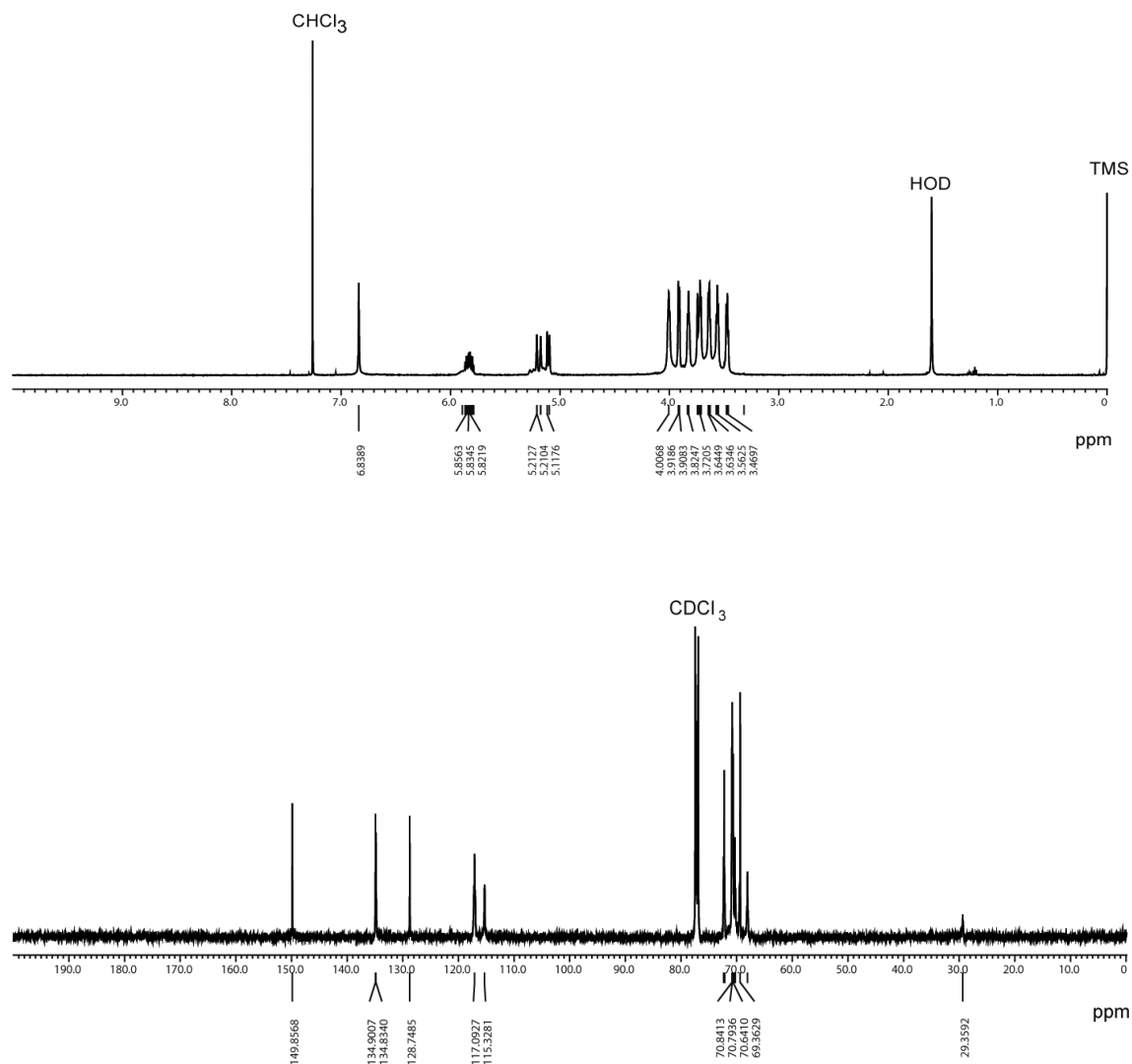


Fig. S1 ^1H and ^{13}C NMR spectra of CHL **3** in CDCl_3 at 25 °C.

^1H and ^{13}C NMR spectra of polyrotaxane **5**

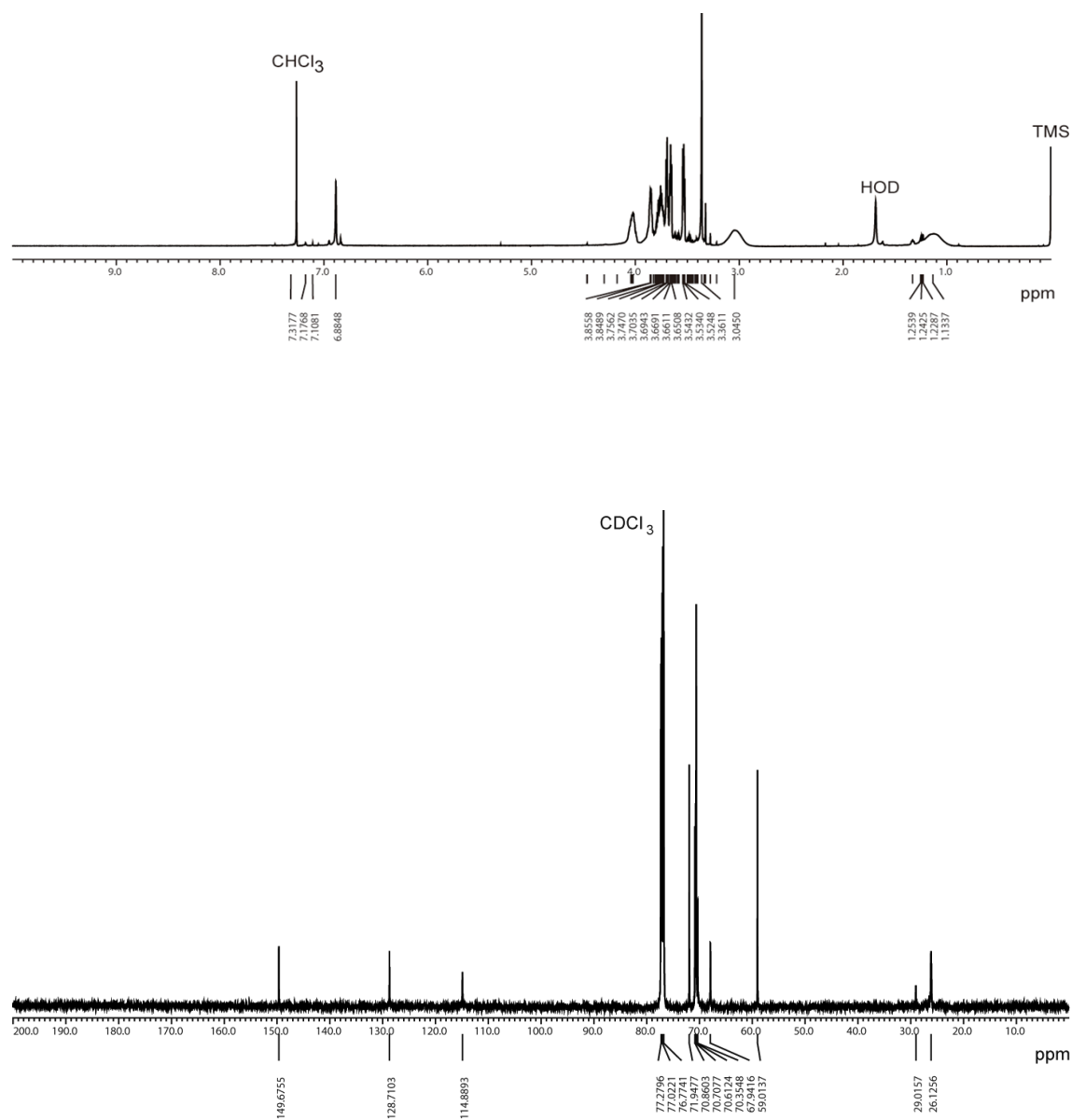


Fig. S2 ^1H and ^{13}C NMR spectra of polyrotaxane **5** in CDCl_3 at 25 °C.

^1H and ^{13}C NMR spectra of polyrotaxane 6

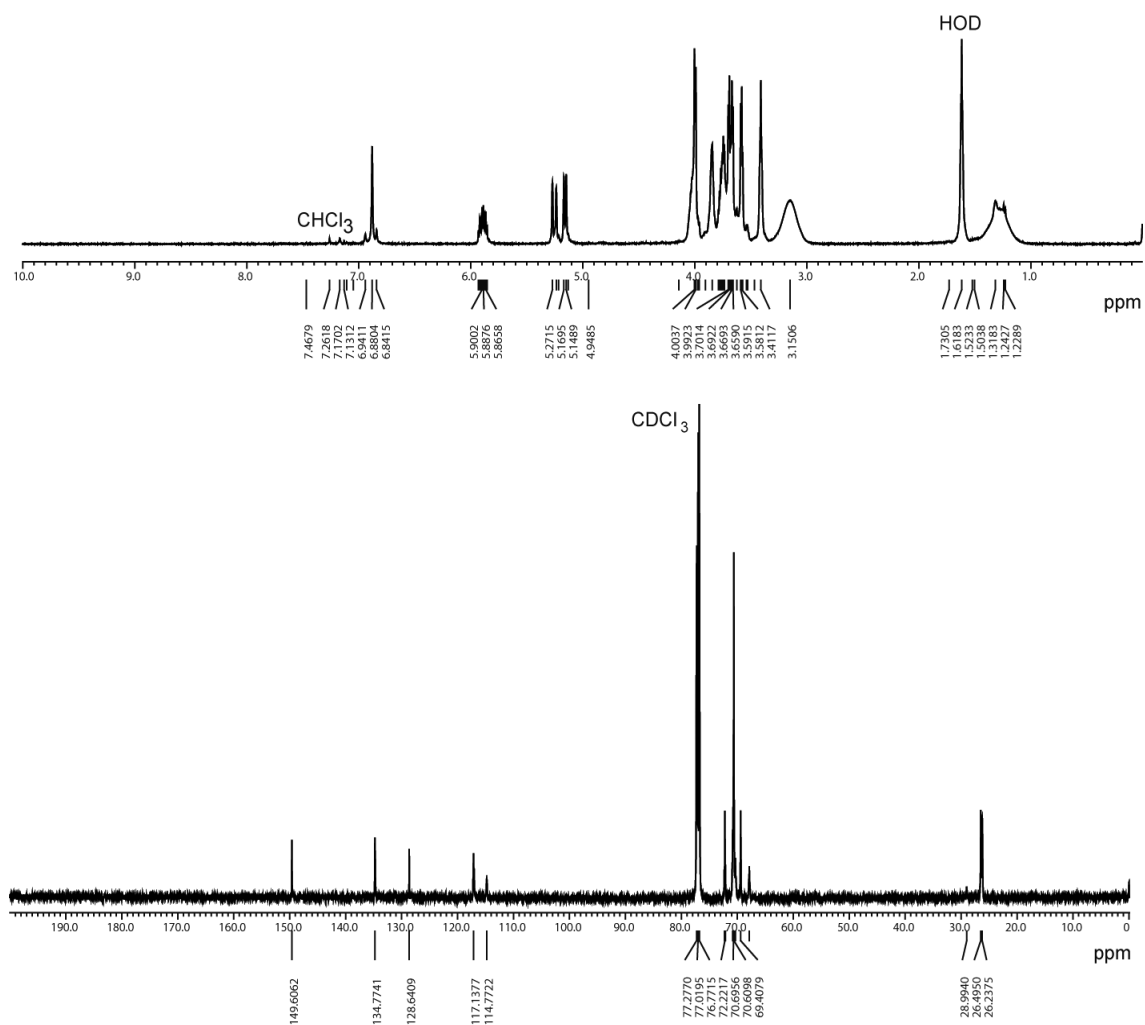


Fig. S3 ^1H and ^{13}C NMR spectra of polyrotaxane 6 in CDCl_3 at 25 °C.

^1H NMR spectrum of a mixture of PTHF and **2 in CDCl_3**

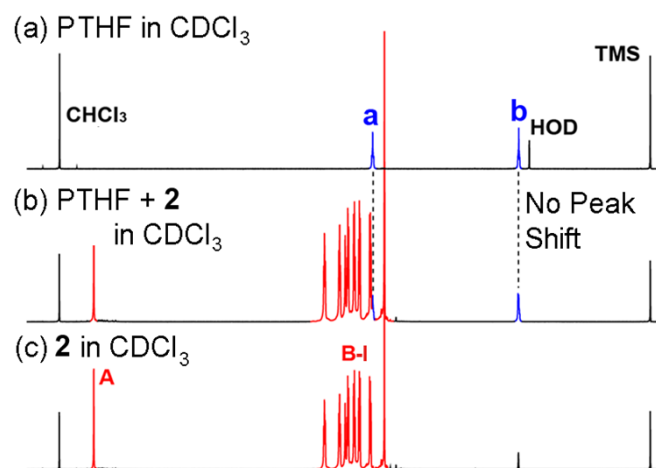


Fig. S4 ^1H NMR spectra of (a) PTHF, (b) a mixture of PTHF and **2**, and (c) **2** in 10 mM in CDCl_3 at 42 $^\circ\text{C}$.

Determination of conversions to polyrotaxanes **5**

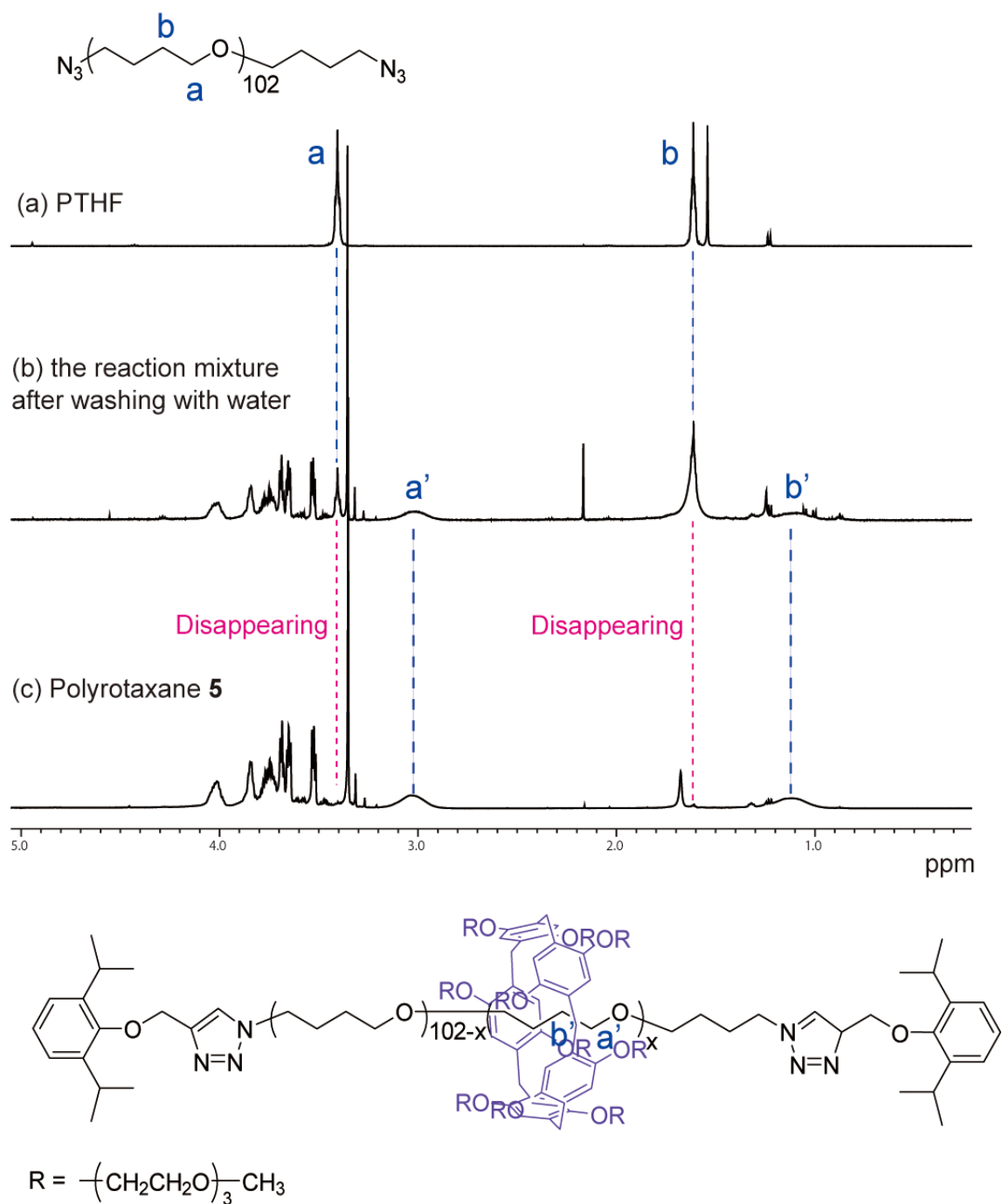


Fig. S5 Partial ^1H NMR spectra (25 $^\circ\text{C}$, CDCl_3) of (a) PTHF, (b) the reaction mixture for the synthesis of polyrotaxane **5** after washing with water, and (c) polyrotaxane **5**, which was isolated by washing with water and hexane. In Figure S5(b), The new peaks were observed at 1.1 and 3.0 ppm (a' and b'). The new peaks were caused by shielding of the methylene moiety of polyrotaxane **5** by pillar[5]arene wheels. Thus, these peaks are assigned as methylene moiety of PTHF in the polyrotaxane **5**. The proton peaks of the methylene moiety of PTHF containing no wheel pillar[5]arenes **1** were also observed at 1.6 and 3.4 ppm (a and b). Conversions to polyrotaxanes **5** were determined by the integration ratios between these peaks (a and a').

2D NOESY NMR of polyrotaxane **5**

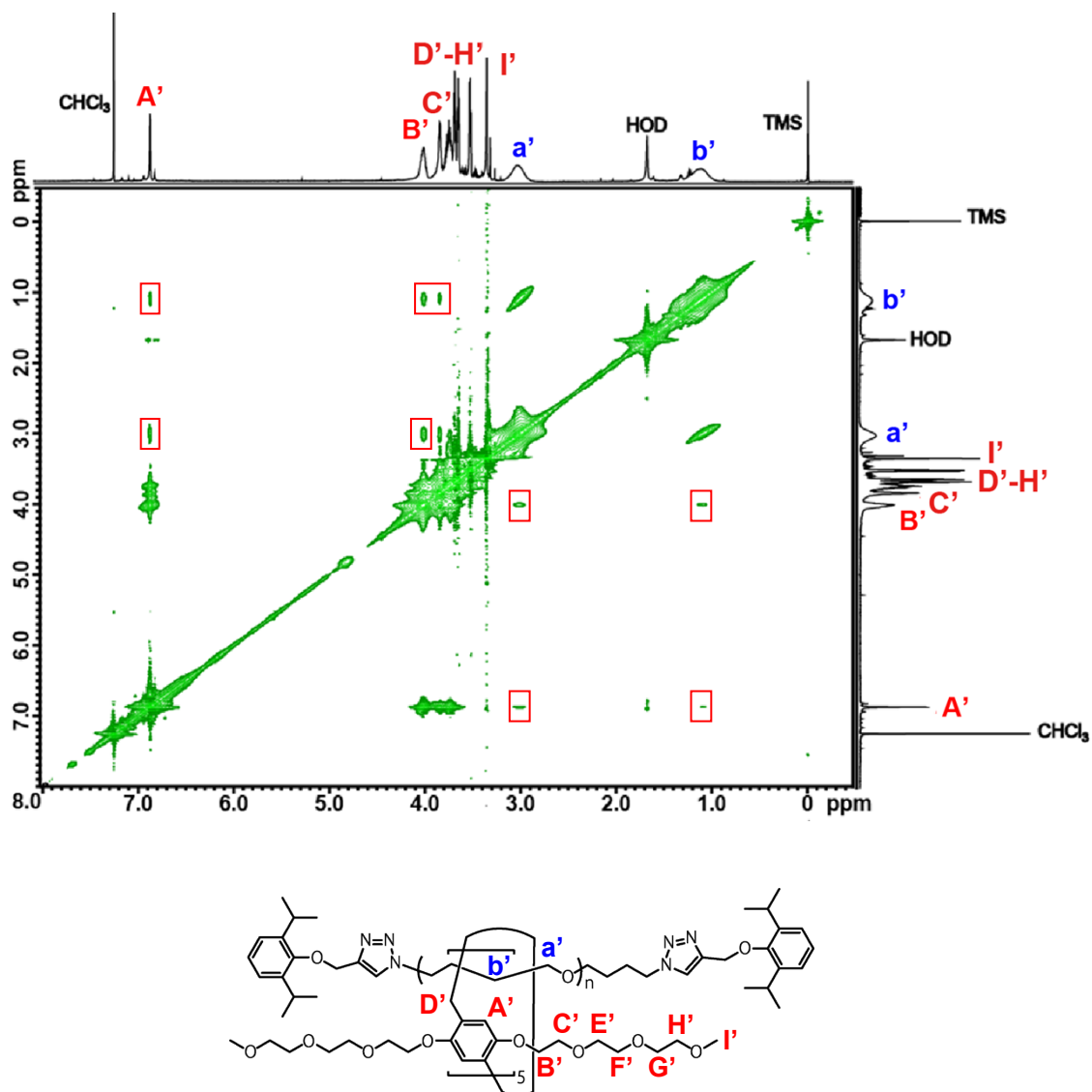


Fig. S6 2D NOESY study of polyrotaxane **5** in CDCl₃.

2D NOESY NMR of polyrotaxane 6

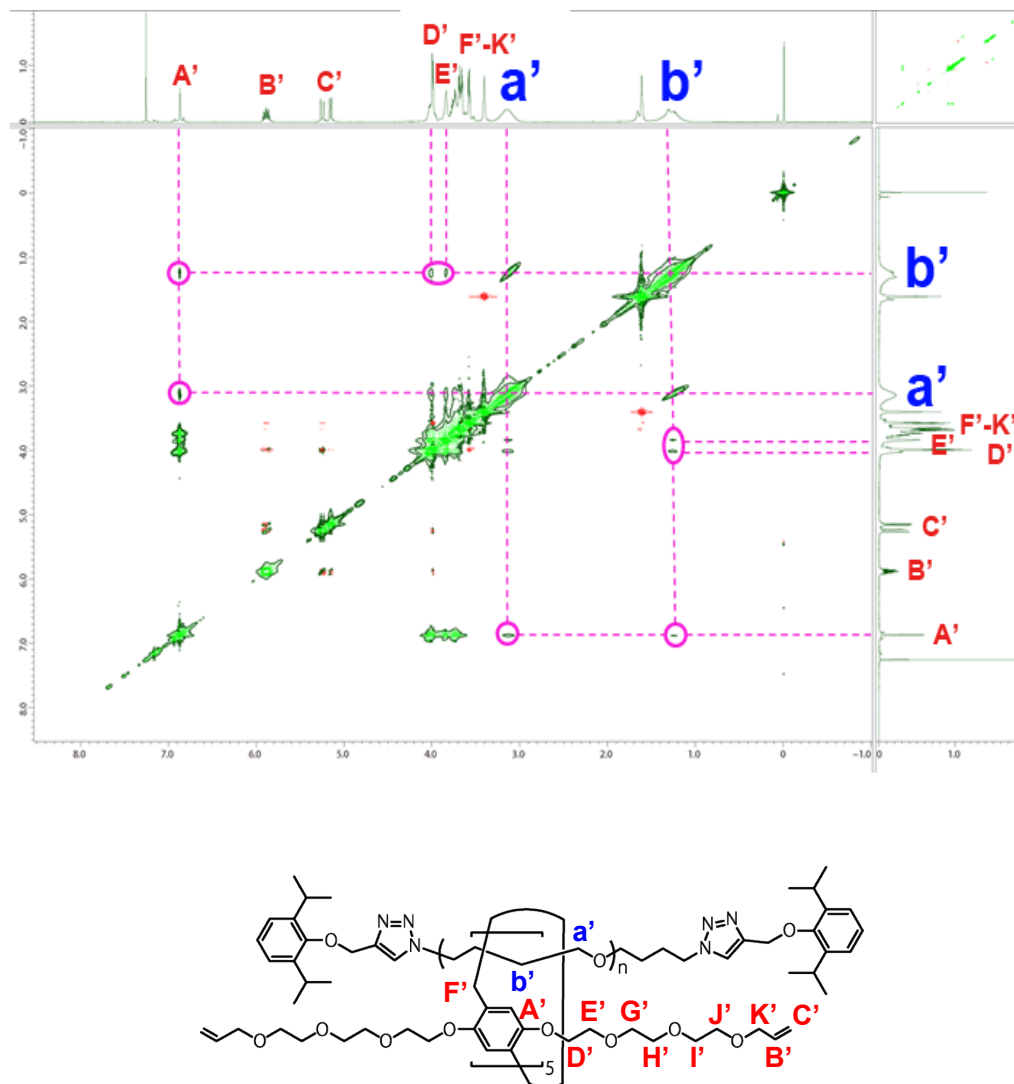


Fig. S7 2D NOESY study of polyrotaxane 6 in CDCl₃.

DSC trace of CHL 3

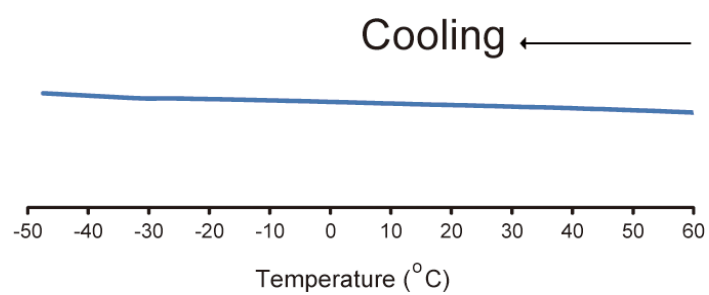


Fig. S8 DSC trace of CHL 3.

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