Electronic Supplementary Information (ESI)

Thermally Responsive Shuttling Behavior of Pillar[6]arene-based [2]Rotaxane

Tomoki Ogoshi, Daiki Yamafuji, Takamichi Aoki and Tada-aki Yamagishi*

Table of Contents

Experimental section S2-S6
Figs. S1-S5 ^{1}H and ^{13}C NMR spectra S7-S11
Fig. S6 Job plot for a mixture of axle **1** and **C2[5]** S12
Fig. S7 Job plot for a mixture of axle **1** and **C2[6]** S13
Fig. S8 ^{1}H NMR titration of axle **1** with **C2[6]** in $CDCl_3$ S14
Fig. S9 HRESIMS spectra of [2]rotaxane **3** S15
Fig. S10 HRESIMS spectra of [2]rotaxane **4** S16
Fig. S11 Variable-temperature ^{1}H NMR spectra of [2]rotaxane **3** S17
Fig. S12 Variable-temperature ^{1}H NMR spectra of [2]rotaxane **4** S18
Fig. S13 2D ^{1}H-^{1}H COSY NMR of [2]rotaxane **4** at – 20 °C S19
Fig. S14 2D EXSY NMR of [2]rotaxane **4** at – 20 °C S20
References S21

Experimental section

Materials. All solvents and reagents were used as supplied. Per-ethylated pillar[5]arene (**C2[5]**) and pillar[6]arene (**C2[6]**) were synthesized according to the previous papers.[1,2]

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

Determination of association constants. In axle **1-C2[5]** complex in $CDCl_3$, chemical exchange between free and complexed species is slow on an NMR timescale. Thus, ^{1}H NMR spectra of mixtures of **C2[5]** and axle **1** in different ratio showed two sets of resonances for complexed and free axle **1**. The association constant for axle **1-C2[5]** complex was calculated from integrations of complexed (**Fig. 2**, blue peak g') and free signals (**Fig. 2**, blue peak g) of the pyridinium moiety of axle **1**.

In axle **1-C2[6]** complex in $CDCl_3$ and axle **1-C2[6]** complex in $CDCl_3$, chemical exchange between free and complexed species was fast on an NMR timescale. Thus, NMR titrations were done with solutions which had a constant concentration of axles (1 mM) and varying concentrations of **C2[6]**. By the non-linear curve-fitting methods, the association constant for axle **1-C2[6]** complex in $CDCl_3$ was estimated to be 19.1 ± 2.2 M^{-1} for 1:1 stoichiometry. The non-linear curve-fitting was based on the equation:[3]

$$\Delta\delta_{obs} = \frac{\Delta\delta_{11}}{2K[G]_0}\left[1 + K[H]_0 + K[G]_0 - \{(1 + K[H]_0 + K[G]_0)^2 - 4K^2[H]_0[G]_0\}^{1/2}\right]$$

Where $\Delta\delta_{obs}$ is the chemical shift change of proton signal of pyridinium moiety of the axle (**Fig. 3**, blue peak g) at $[H]_0$, $\Delta\delta_{11}$ is the chemical shift change of the axle proton resonance when the axle is completely complexed, $[G]_0$ is the fixed initial concentration of the axle, and $[H]_0$ is the initial concentration of the host **C2[6]**.

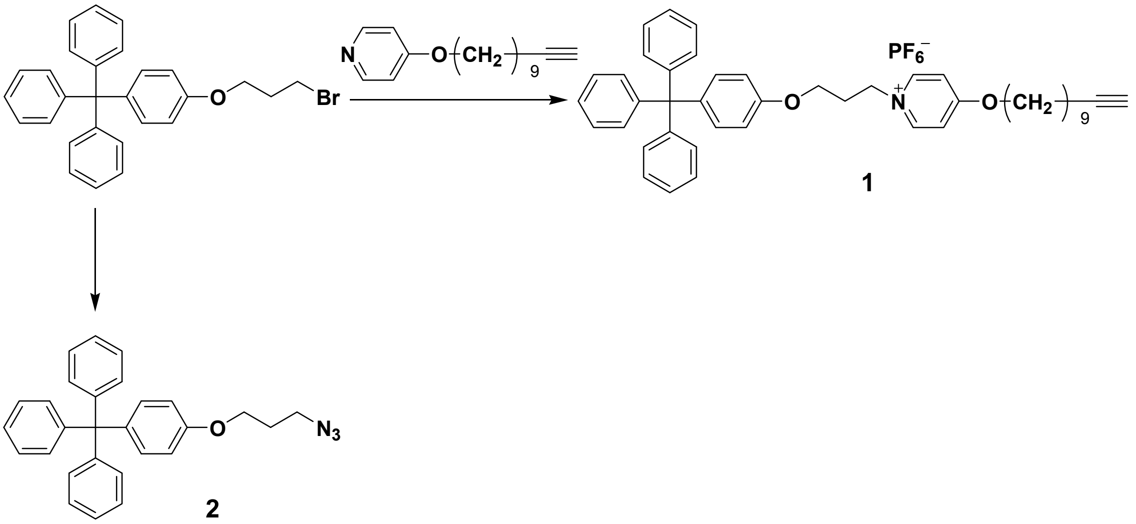
Study of thermodynamic parameters by variable-temperature ^{1}H NMR measurements. The thermodynamic parameters such as ΔH, ΔS, ΔG, and equilibrium constant K were determined from the temperature dependence of K by the use of the linear van't Hoff plots:

$$\ln K = -\Delta H / RT + \Delta S/R$$

The ΔH and ΔS for the shuttling from station I to II were calculated from the slope and intercept by plotting ln K vs $1/T$. ΔG was obtained according to the equation:

$$\Delta G = \Delta H - T\Delta S$$

Compounds for synthesis of C2[5]- and C2[6]-based [2]rotaxanes



Axle 1. To a solution of 1-(3-bromopropoxy)-4-(triphenylmethyl)benzene[4] (1.25 g, 3.28 mmol) in *N*,*N*-dimethylformamide (10 mL), 4-(undec-10-yn-1-yloxy)pyridine[5] (0.670 g, 2.74 mmol) was added. The mixture was heated at 100 °C for 72 h under nitrogen. The resulting solution was concentrated under *vacuo*. The obtained product was dissolved in the mixture of acetone (20 mL) and water (20 mL). To the mixture, $NaPF_6$ (2.30 g, 13.7 mmol) was added. The reaction mixture was stirred at 25 °C for 1 h. The resulting solution was concentrated under *vacuo*. The residue was poured into water and the precipitate was collected by filtration. Column chromatography (silica gel; dichloromethane : methanol = 8 : 1) afforded an white solid (axle **1**, 630 mg, 0.821 mmol, Yield: 30%). ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.40 (d, J = 6.3 Hz, 2H, pyridyl), 7.34 (d, J = 6.3 Hz, 2H, pyridyl), 7.16-7.25 (m, 15 H, phenyl), 7.12 (d, J = 7.4 Hz, 2H, phenyl), 6.76 (d, J = 7.4 Hz, 2H, phenyl), 4.49 (t, J = 5.6 Hz, 2H, methylene), 4.37 (t, J = 6.7 Hz, 2H, methylene), 4.11 (t, J = 5.6 Hz, 2H, methylene), 2.37 (q, J = 5.6 Hz, 2H, methylene), 2.17 (m, 2H, methylene), 1.92 (s, 1H, terminal alkyne), 1.91 (m, 2H, methylene), 1.50 (q, J = 7.5 Hz, 2H, methylene), 1.37 (m, 2H, methylene), 1.27-1.32 (m, 8H, methylene). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 170.4, 156.3, 147.0, 145.3, 139.5, 132.3, 131.1, 127.5, 125.9, 114.1, 113.2 (C of phenyl and pyridyl),

84.7 (C of alkyne), 68.2 (C of methylene), 68.0 (C of alkyne), 64.3 (C of methylene), 63.1 (sp3 carbon of triryl), 60.6, 31.1, 29.1, 28.8, 28.6, 28.4, 18.3 (C of methylene). HRFABMS: *m*/*z* Calcd for $C_{44}H_{48}NO_2$ $[M-PF_6]^+$: 622.3680, found 622.3689.

Stopper 2. To a solution of 1-(3-bromopropoxy)-4-(triphenylmethyl)benzene (400 mg, 0.876 mmol) in *N*,*N*-dimethylformamide (10 mL), sodium azide (68.4 mg, 1.05 mmol) was added. The reaction mixture was heated at 50 °C for 5 h, cooled to room temperature and added to ethyl acetate. The solution was washed with water, and dried (Na_2SO_4). After evaporation of the solvent, the residue was purified by column chromatography (silica gel; hexane : ethyl acetate = 9 : 1) to give a white solid (stopper **2**, 340 mg, 0.810 mmol, Yield: 92%).^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.16-7.25 (m, 15H, phenyl), 7.10 (d, J = 7.4 Hz, 2H, phenyl), 6.77 (d, J = 7.4 Hz, 2H, phenyl), 4.01 (t, J = 5.8 Hz, 2H, methylene), 3.50 (t, J = 6.9 Hz, 2H, methylene), 2.03 (q, J = 6.3 Hz, 2H, methylene). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 156.6, 147.0, 139.3, 132.2, 131.1, 127.4, 125.4, 113.2 (C of phenyl), 64.3 (sp3 carbon of triryl), 48.3, 28.8 (C of methylene). HRFABMS: *m*/*z* Calcd for $C_{28}H_{26}N_3O$ $[M+H]^+$: 420.2076, found 420.2068.

Pillar[5]arene-based [2]rotaxane 3. To a solution of axle **1** (76.3 mg, 0.100 mmol), **C2[5]** (445 mg, 0.500 mmol) and stopper **2** (41.2 mg, 0.120 mmol) in chloroform (1 mL), tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA, 53.0 mg, 0.100 mmol) was added. The reaction mixture was stirred at 25 °C for 1 h. To the mixture, $Cu(CH_3CN)_4PF_6$ (37.2 mg, 0.100 mmol) was added, and the mixture was stirred at 25 °C for 24 h. The resulting solution was concentrated under *vacuo*. Column chromatography (silica gel; ethyl acetate : dichloromethane = 1 : 10 to 1 : 1) afforded a white solid (pillar[5]arene-based [2]rotaxane **3,** 120 mg, 0.0601 mmol, Yield: 60%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.42 (s, 1H, triazole), 7.16-7.26 (m, 30H, phenyl), 7.11-7.14 (m, 4H, phenyl), 6.95 (m, 2H, pyridinium), 6.93 (s, 5H, phenyl of **C2[5]** moiety), 6.82 (d, J = 7.5 Hz, 2H, phenyl), 6.77 (d, J = 7.5 Hz, 2H, phenyl), 6.68 (s, 5H, phenyl of **C2[5]** moiety), 5.98 (d, J = 5.8 Hz, 2H, pyridinium), 4.57 (m, 2H, methylene), 4.46 (m, 2H, methylene), 4.18 (m, 2H, methylene), 3.99 (m, 2H, methylene), 3.95-4.00 (m, 30H, methylene and methylene bridge of **C2[5]**), 2.76 (t, J = 6.9 Hz, 2H, methylene), 2.40 (m, 2H, methylene), 1.76 (m, 2H, methylene), 1.47 (t, J = 6.3 Hz ,15H, methyl of **C2[5]**), 1.44 (m, 2H, methylene), 1.34 (t, J = 6.3 Hz ,15H, methyl of **C2[5]**), 1.31 (m, 2H, methylene), 1.15 (m, 2H, methylene), 0.73 (m, 2H, methylene), 0.64 (m, 2H, methylene), -0.06 (m, 2H, methylene), -1.16 (m, 2H, methylene). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 169.1, 156.6, 156.4, 150.3, 149.4, 147.0, 144.0, 139.5, 139.3, 132.3, 131.1, 129.9, 129.2, 127.4, 125.9, 121.3, 116.2, 115.0, 113.2, 112.3 (C of phenyl, pyridinium and triazole), 68.2, 65.4 (C of methylene), 64.3 (sp3 carbon of triryl), 64.1, 63.5, 57.3, 47.1, 30.9, 30.1, 30.0, 29.8, 29.2, 29.0, 28.4, 27.7, 26.5, 25.8 (C of methylene), 15.5, 15.3 (C of methyl of **C2[5]**). HRESIMS: *m*/*z* Calcd for $C_{127}H_{143}N_4O_{13}$ $[M-PF_6]^+$: 1932.0652, found 1932.06502.

Pillar[6]arene-based [2]rotaxane 4. To a solution of axle **1** (76.3 mg, 0.100 mmol), **C2[6]** (534 mg, 0.500 mmol) and stopper **2** (41.2 mg, 0.120 mmol) in chloroform (1 mL), TBTA (53.0 mg, 0.100 mmol) was added. The reaction mixture was stirred at 25 ^{o}C for 1 h. To the mixture, $Cu(CH_3CN)_4PF_6$ (37.2 mg, 0.100 mmol) was added, and the mixture was stirred at 25 ^{o}C for 24 h. The resulting solution was concentrated under *vacuo*. Column chromatography (silica gel; ethyl acetate : dichloromethane = 1 : 10 to 1 : 1) afforded a orange solid (Pillar[5]arene-based [2]rotaxane **4,** 30.0 mg, 0.00138 mmol, Yield: 14%).^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.48 (s, 1H, triazole), 7.17-7.23 (m, 30H, phenyl), 7.14 (m, 2H, phenyl), 7.09 (m, 2H, phenyl), 6.76 (m, 2H, phenyl), 6.71 (br, 12H, phenyl of **C2[6]**), 6.69 (m, 2H, phenyl), 6.12 (br, 2H, pyridinium), 5.12 (d, J = 6.3 Hz, 2H, pyridinium), 4.54 (m, 2H, methylene), 3.97 (m, 2H, methylene), 3.93 (m, 2H, methylene), 3.89 (br, 36H, methylene and methylene bridge of **C2[6]**), 3.46 (br, 2H, methylene), 2.72 (m, 2H, methylene), 2.37 (m, 2H, methylene), 2.24 (br, 2H, methylene), 1.96 (br, 2H, methylene), 1.70 (m, 2H, methylene), 1.38 (br, 36H, methyl of **C2[6]**), 1.06-1.31 (m, 10H, methylene). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 168.4, 167.7, 156.6, 156.4, 150.7, 148.2, 147.0, 146.9, 143.1, 139.8, 139.2, 132.4, 132.2, 131.1, 129.4, 129.0, 127.5, 127.4, 125.9, 125.8, 121.5, 115.8, 113.3, 112.7, 111.5 (C of phenyl, pyridinium and triazole), 66.6, 65.7 (C of methylene), 64.3 (sp3 carbon of triryl), 62.8, 57.8, 47.1, 32.5, 31.9, 30.8, 30.2, 29.6, 29.4, 29.2, 29.1, 29.0, 28.6, 28.1, 27.3, 26.4, 25.7, 25.6 (C of methylene), 15.4 (C of methyl of **C2[6]**). HRESIMS: *m*/*z* Calcd for $C_{138}H_{157}N_4O_{15}$ $[M-PF_6]^+$: 2110.1645, found 2110.1645.

Dumbbell 5. This compound was prepared using the same conditions as those used for the preparation of pillar[5]arene-based [2]rotaxane **3** in the absence of **C2[5]**. Column chromatography (silica gel; ethyl acetate) afforded an white solid (94.9 mg, 0.0802 mmol, Yield: 80%.). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.41 (d, J = 6.9 Hz, 2H, pyridinium), 7.33 (s, 1H, triazole), 7.31 (d, J = 6.9 Hz, 2H, pyridinium), 7.16-7.23 (m, 30H, phenyl), 7.01-7.11 (m, 4H, phenyl), 6.72-6.76 (m, 4H, phenyl), 4.51 (t, J = 6.6 Hz, 2H, methylene), 4.46 (t, J = 6.0 Hz, 2H, methylene), 4.37 (t, J = 7.5 Hz, 2H, methylene), 4.08 (t, J = 5.7 Hz, 2H, methylene), 3.92 (t, J = 5.5 Hz, 2H, methylene), 2.66 (t, J = 7.5 Hz, 2H, methylene), 2.29-2.38 (m, 4H, methylene), 1.88 (br, 2H, methylene), 1.60 (m, 2H, methylene), 1.18-1.38 (m, 10H, methylene). ^{13}C NMR (acetone-d_6, 125 MHz, ppm): δ171.5, 157.8, 157.7, 148.0, 147.0, 140.0, 132.9, 131.8, 128.4, 126.8, 121.4, 114.9, 114.2 (C of phenyl, pyridinium and triazole), 68.9, 65.3, 65.1 (C of methylene), 64.5 (sp3 carbon of triryl), 60.8, 47.4, 31.7, 30.8, 26.5, 26.2 (C of methylene). HRESIMS: *m*/*z* Calcd for $C_{72}H_{73}N_4O_3$ $[M-PF_6]^+$: 1041.5683, found 1041.5729.

^{1}H and ^{13}C NMR spectra of axle 1

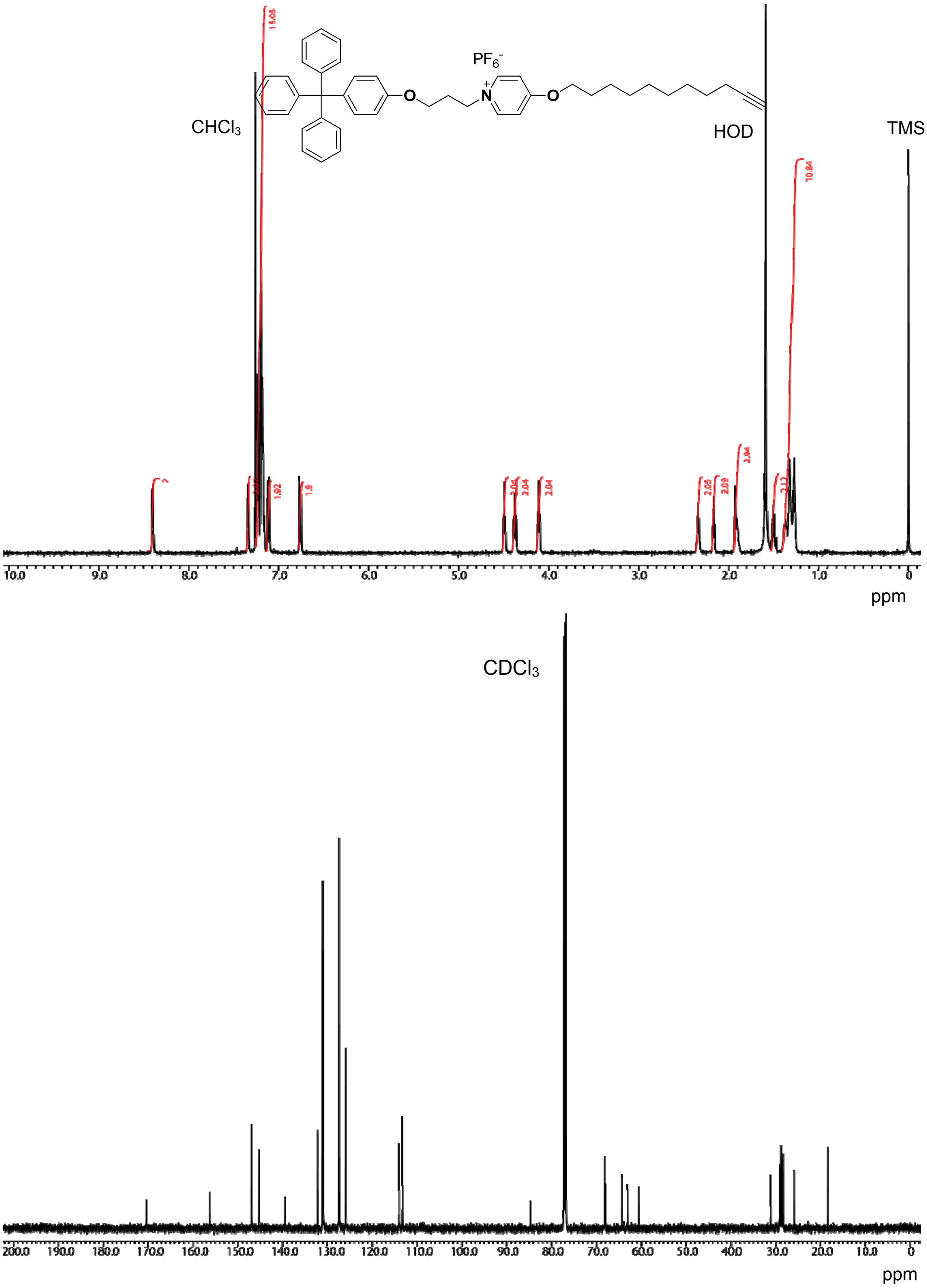


Fig. S1 ^{1}H and ^{13}C NMR spectra of axle **1** in $CDCl_3$ at 25 °C.

^{1}H and ^{13}C NMR spectra of stopper 2

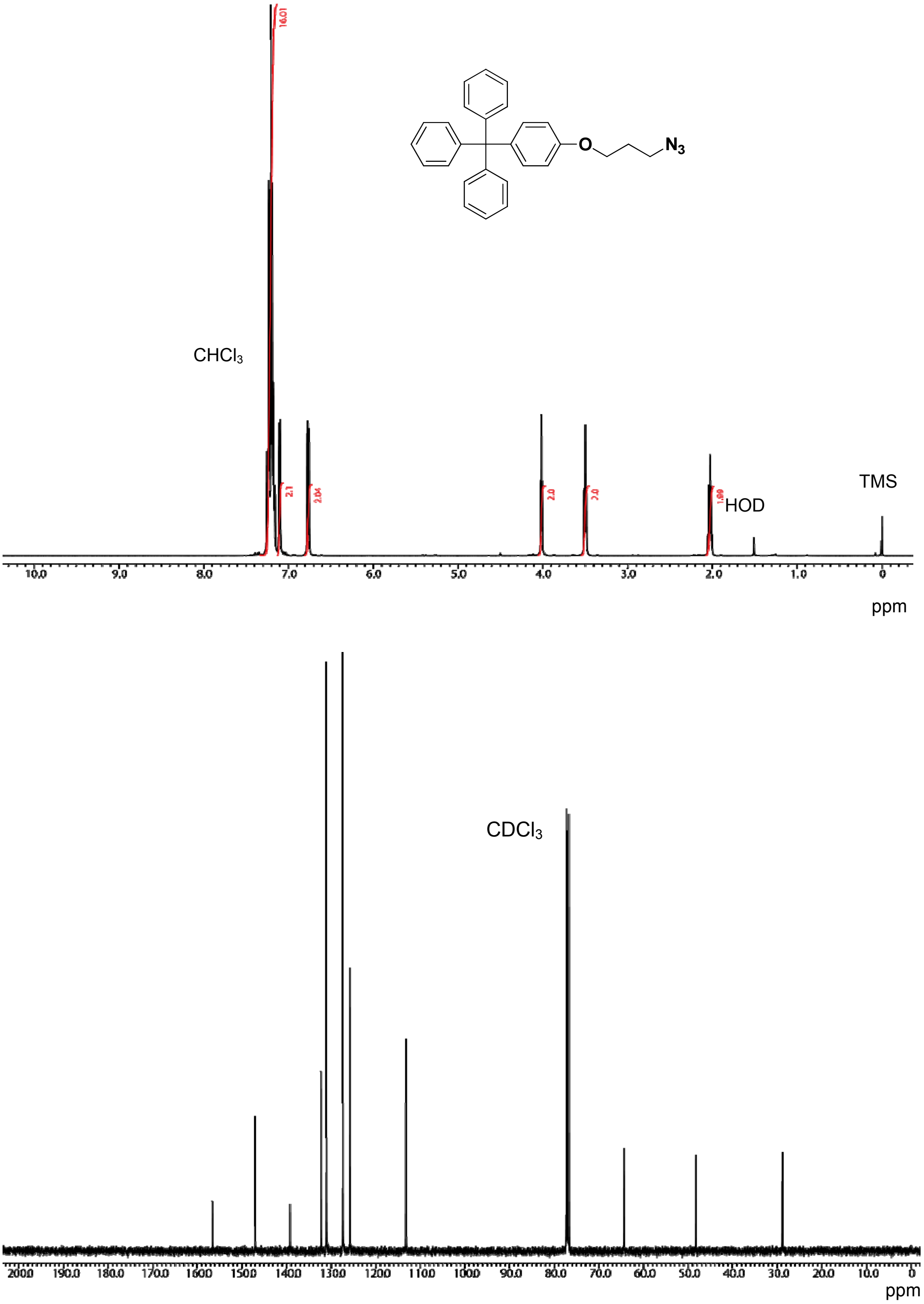
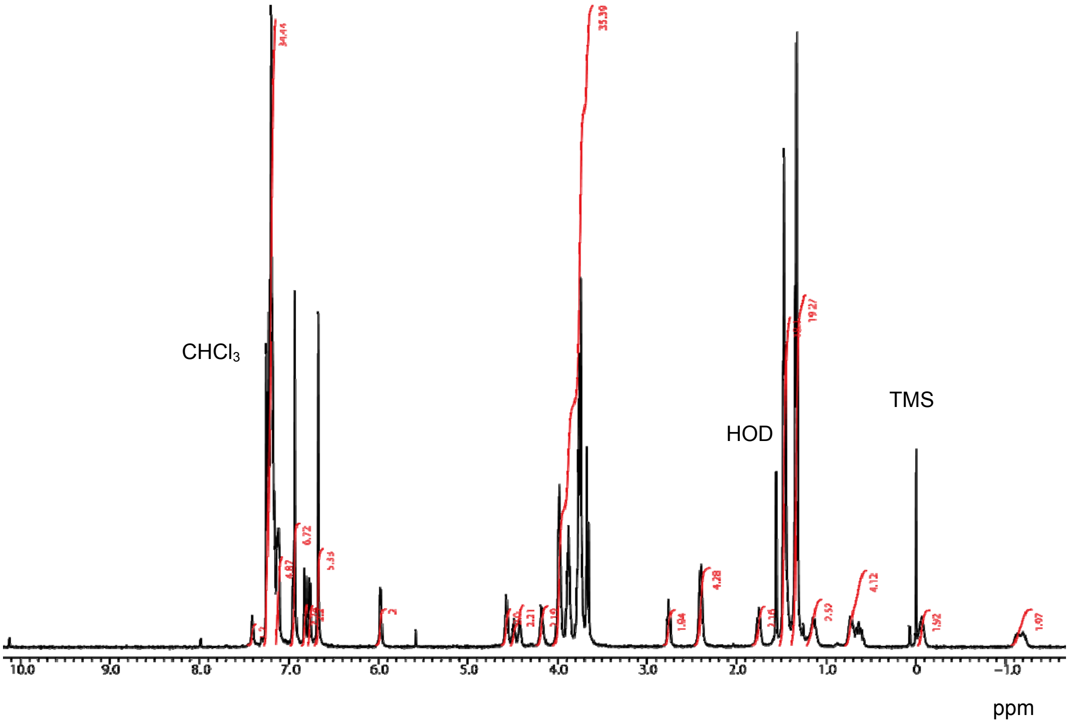


Fig. S2 ^{1}H and ^{13}C NMR spectra of stopper **2** in $CDCl_3$ at 25 °C.

^{1}H and ^{13}C NMR spectra of pillar[5]arene-based [2]rotaxane 3



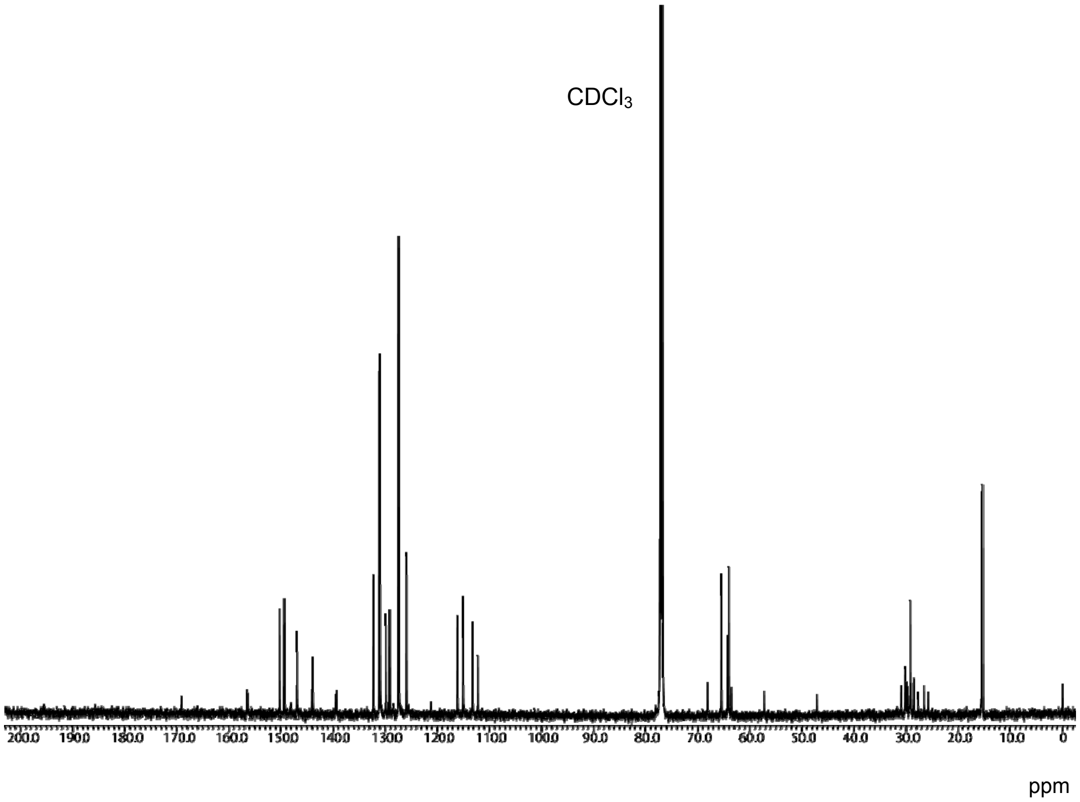


Fig. S3 ^{1}H and ^{13}C NMR spectra of pillar[5]arene-based [2]rotaxane **3** in $CDCl_3$ at 25 °C.

^{1}H and ^{13}C NMR spectra of pillar[6]arene-based [2]rotaxane 4

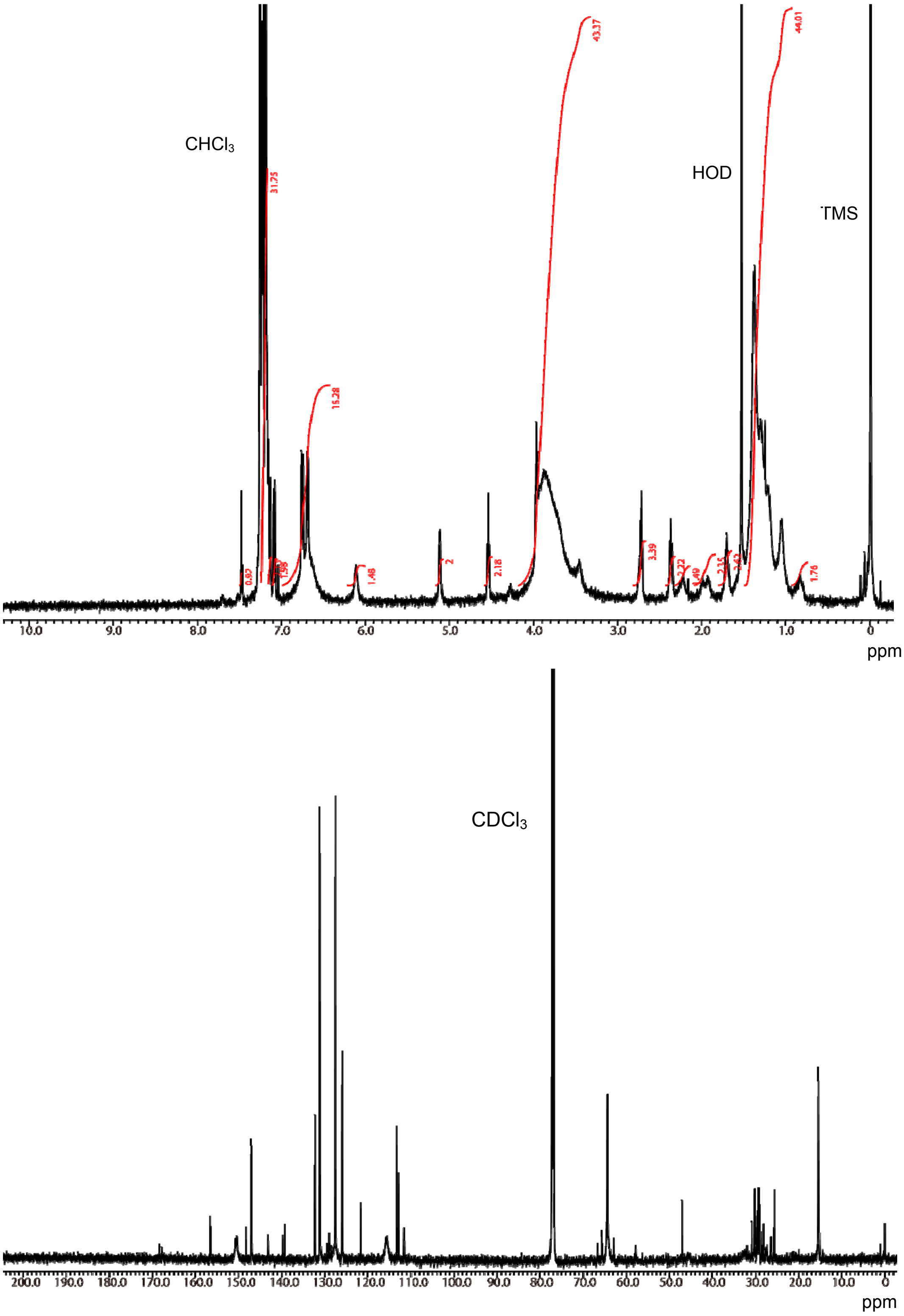


Fig. S4 ^{1}H and ^{13}C NMR spectra of pillar[6]arene-based [2]rotaxane **4** in CDCl$_3$ at 25 °C.

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

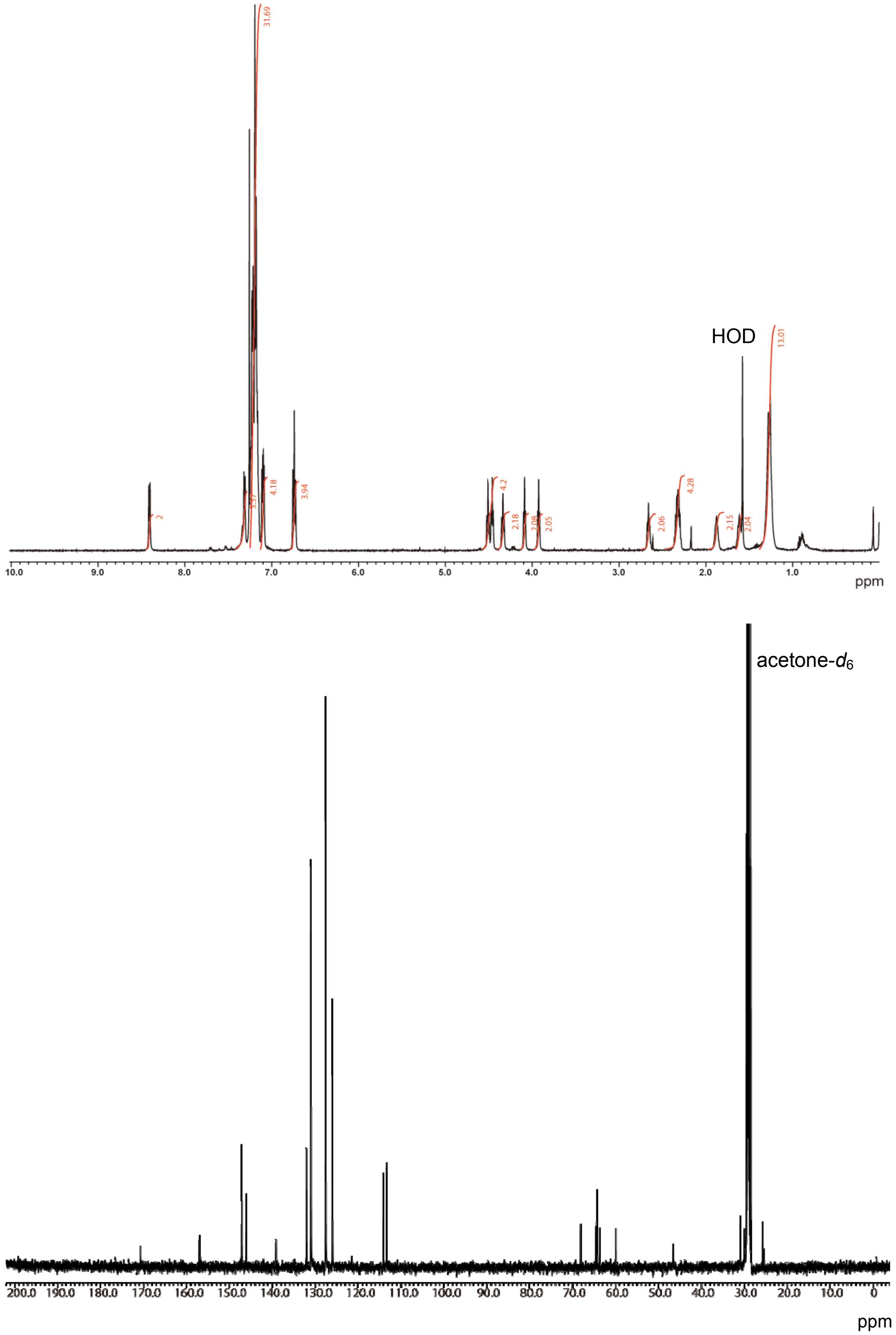


Fig. S5 ^{1}H NMR spectrum of dumbbell **5** in $CDCl_3$ and ^{13}C NMR spectrum of dumbbell **5** in acetone-d_6 at 25 °C.

Job plot for a mixture of axle 1 and C2[5]

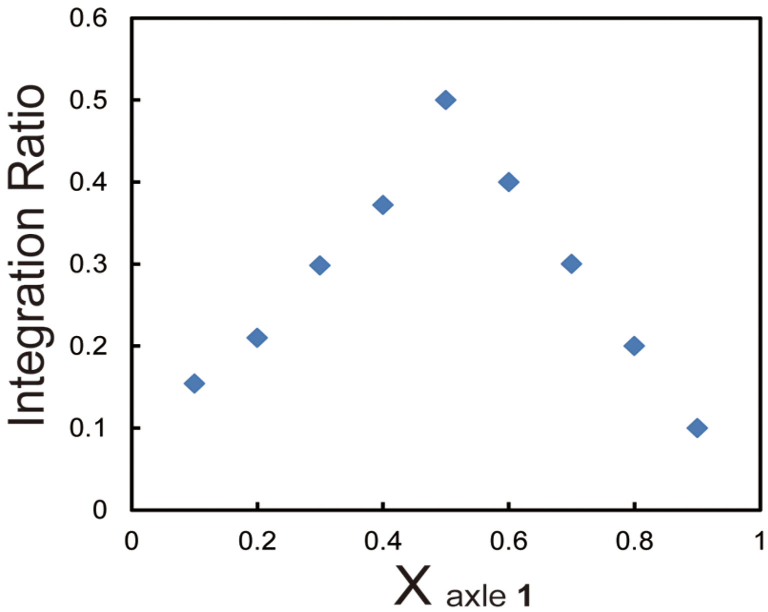


Fig. S6 Job plot between axle **1** (guest) and **C2[5]** (host). The job plot was conducted by varying the mole fractions of the guest and host. Integration ratios between free and complexed pyridinium proton signals (**Fig. 2**, blue peaks g and g') were utilized. Concentration: [axle **1**] + [**C2[5]**] = 10 mM. The plot indicates a 1:1 binding between the host and guest.

Job plot for a mixture of axle 1 and C2[6]

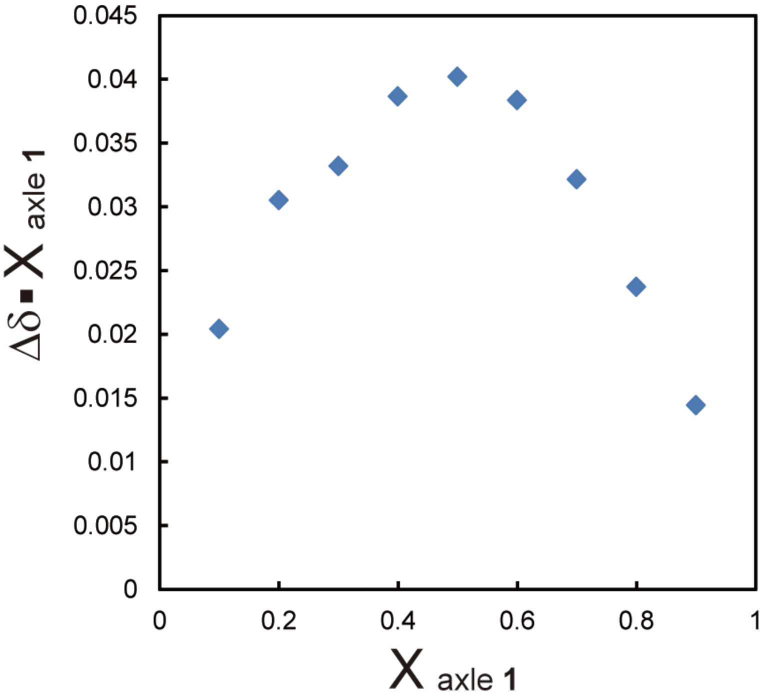


Fig. S7 Job plot between axle **1** (guest) and **C2[6]** (host) was collected by plotting the Δδ in chemical shift of the proton signal of pyridinium moiety (**Fig. 3**, blue peak g) of axle **1** observed by ^{1}H NMR spectroscopy against the change in the mole fraction of the guest ($X_{\text{axle }\mathbf{1}}$). Concentration: [axle **1**] + [**C2[6]**] = 10 mM. The plot indicates a 1:1 binding between the host and guest.

^{1}H NMR titration of axle 1 with C2[6] in $CDCl_3$

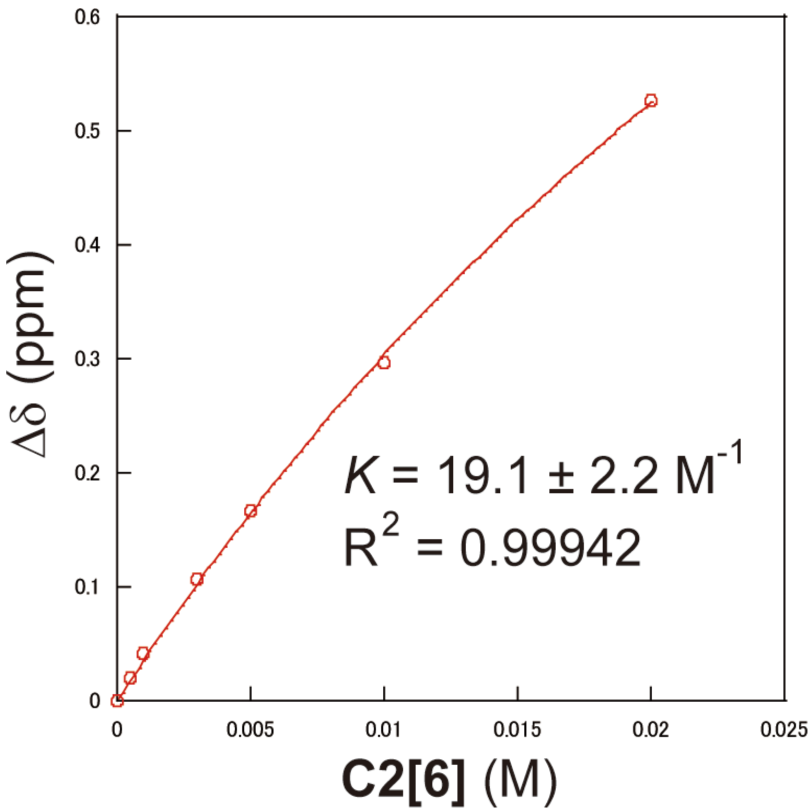


Fig. S8 ^{1}H NMR titration of axle **1** (**Fig. 3**, pyridinium proton peak g) with **C2[6]** in $CDCl_3$ at 25 °C.

HRESIMS spectra of [2]rotaxane 3

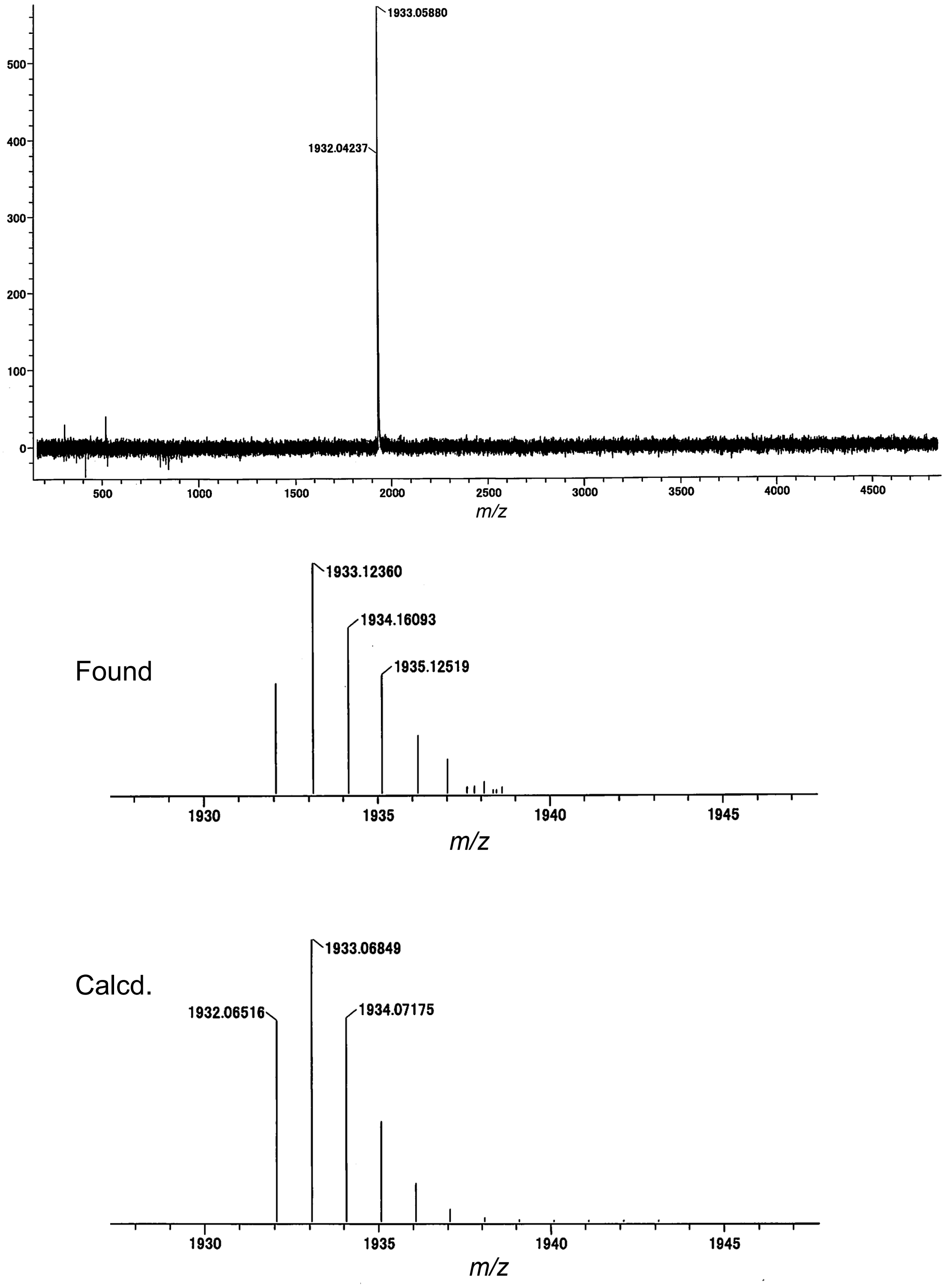


Fig. S9 HRESIMS spectra ($CHCl_3$) of [2]rotaxane **3**.

HRESIMS spectra of [2]rotaxane 4

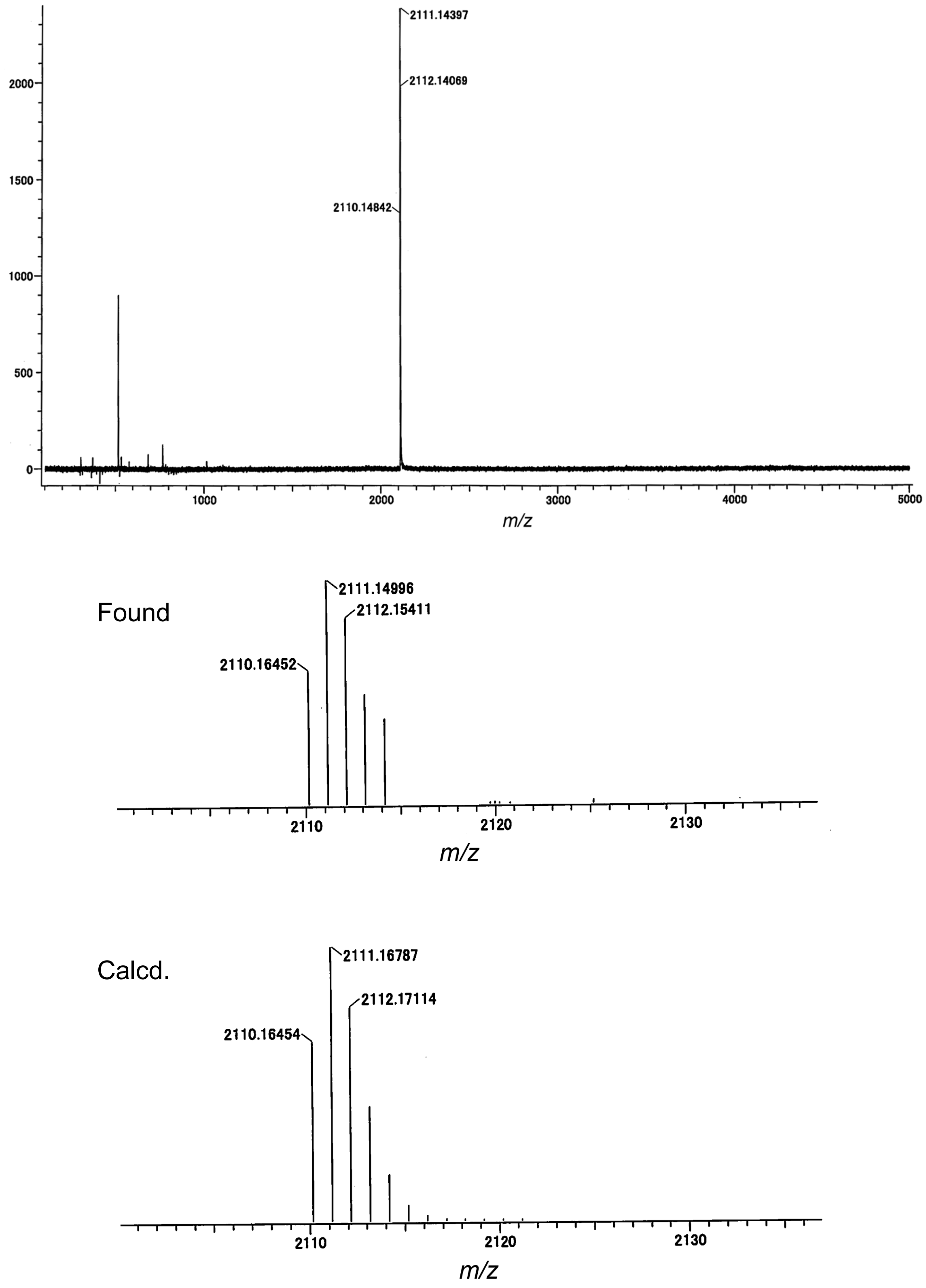


Fig. S10 HRESIMS spectra ($CHCl_3$) of [2]rotaxane **4**.

Variable-temperature ^{1}H NMR spectra of [2]rotaxane 3

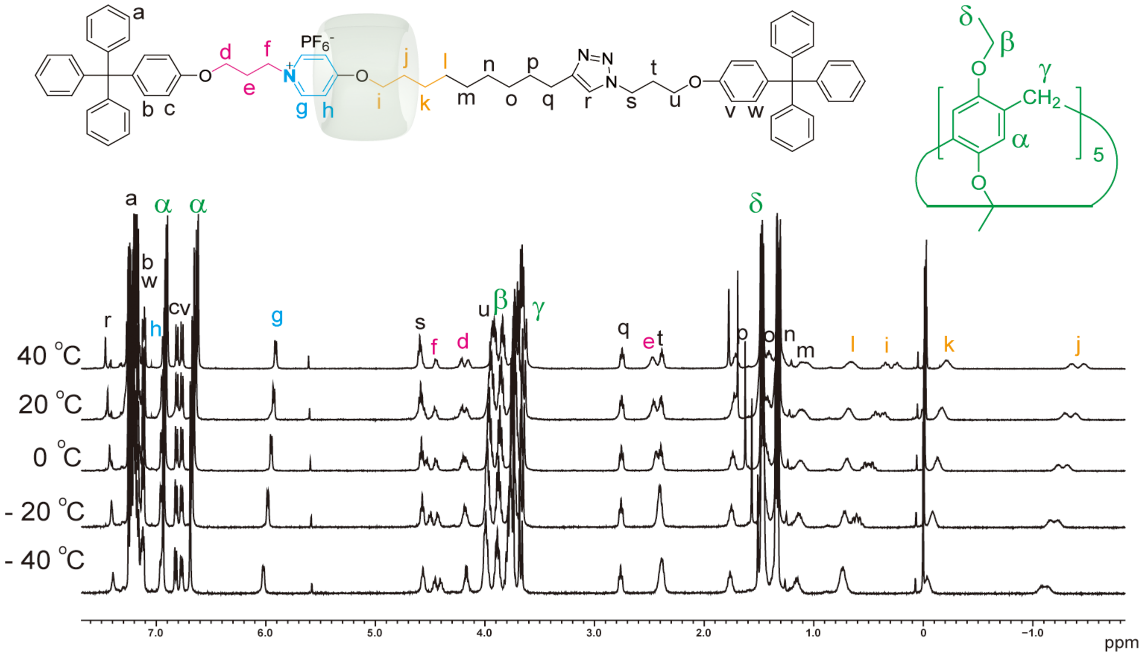


Fig. S11 Variable-temperature ^{1}H NMR spectra of [2]rotaxane **3** (5 mM in $CDCl_3$). The signals of [2]rotaxane **3** hardly changed when the sample was cooled and heated, indicating that the shuttling of the **C2[5]** wheel along the axle did not take place in the temperature investigated.

Variable-temperature ^{1}H NMR spectra of [2]rotaxane 4

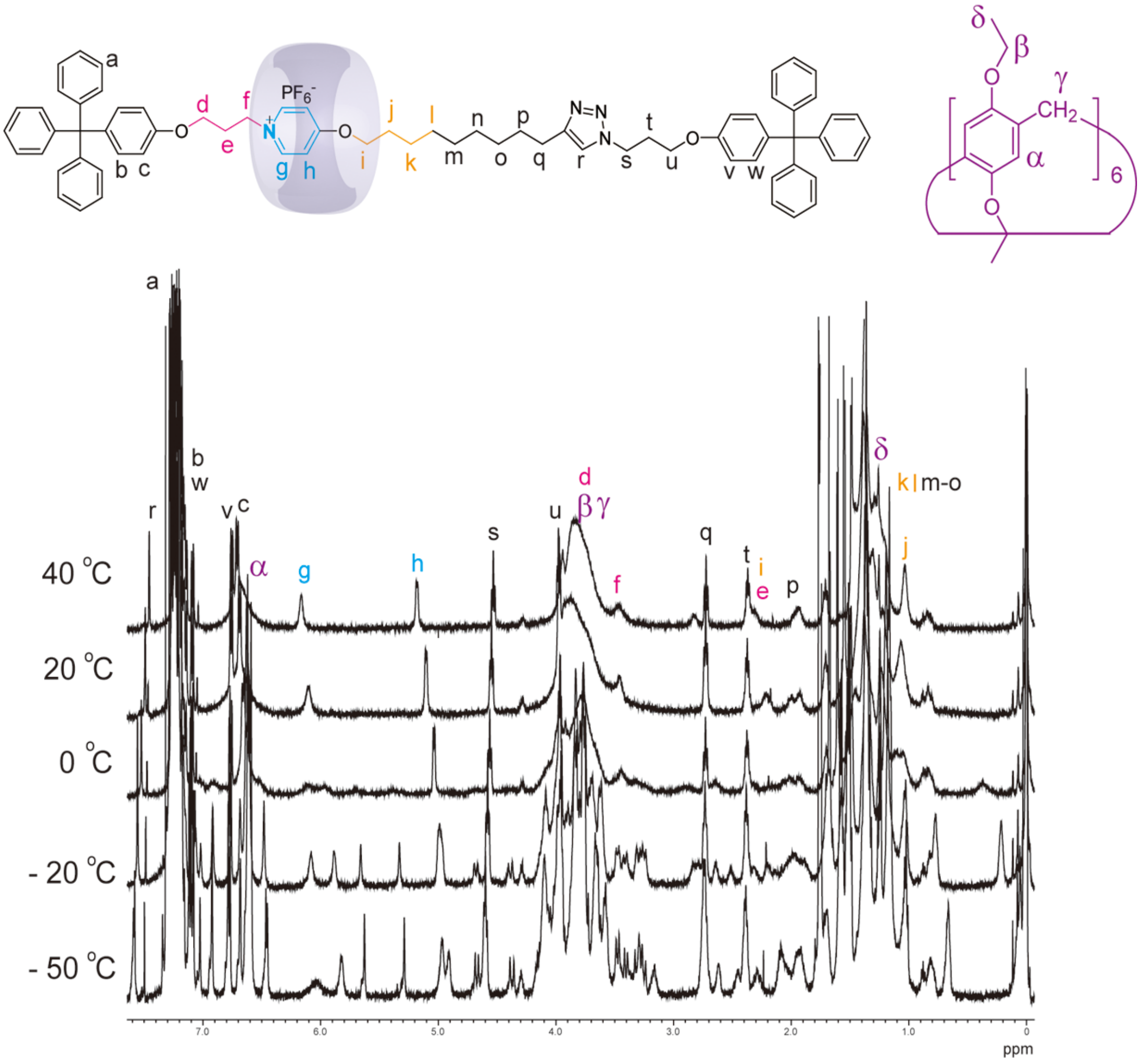


Fig. S12 Variable-temperature ^{1}H NMR spectra of [2]rotaxane **4** (5 mM in $CDCl_3$). The signals of [2]rotaxane **4** became sharp and split when the sample was cooled and heated, indicating shuttling of the **C2[6]** wheel along the axle.

2D ^{1}H-^{1}H COSY NMR of [2]rotaxane 4 at – 20 °C

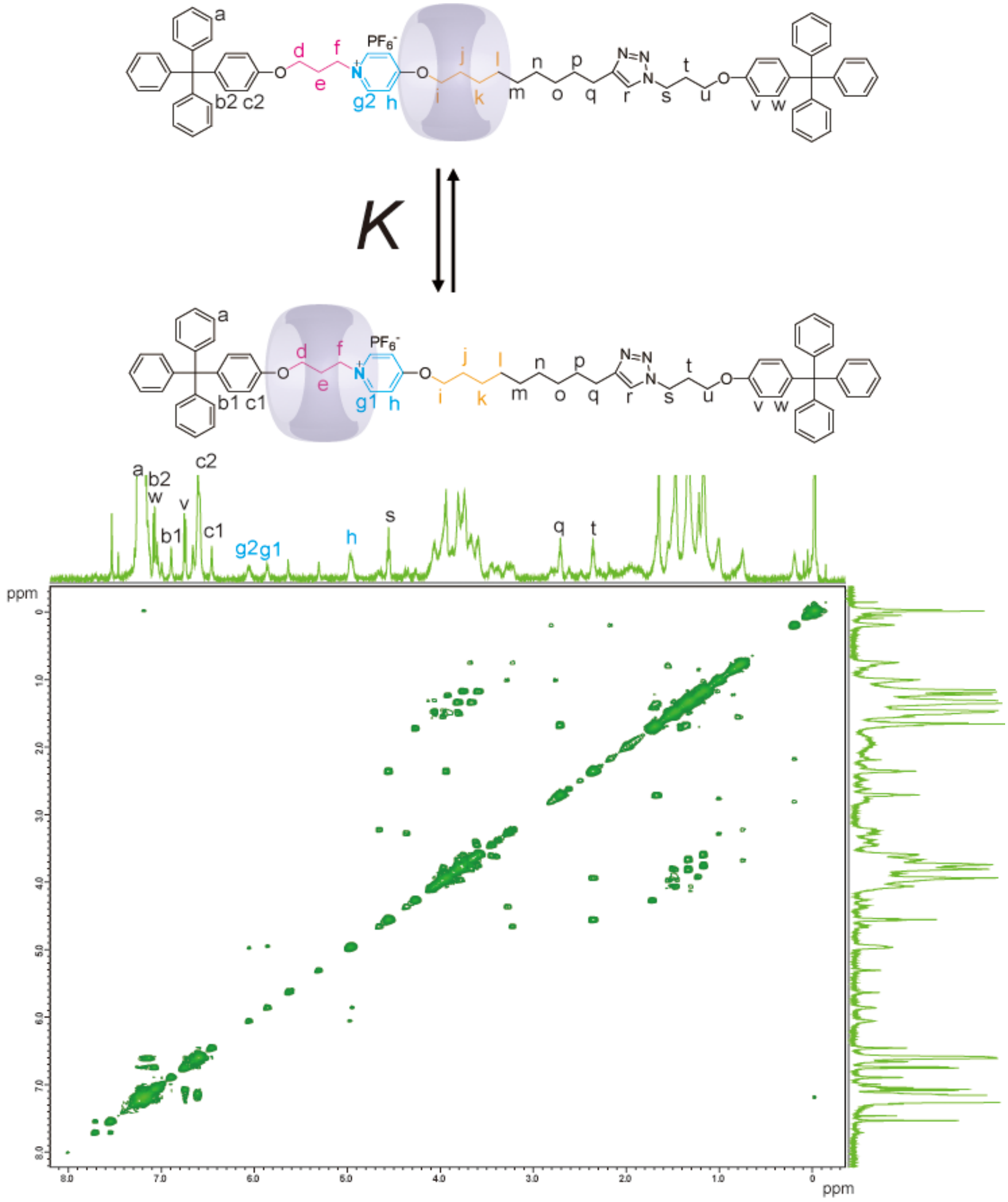


Fig. S13 2D ^{1}H-^{1}H COSY NMR of [2]rotaxane **4** at – 20 °C in CDCl$_3$.

2D EXSY NMR of [2]rotaxane 4 at – 20 °C

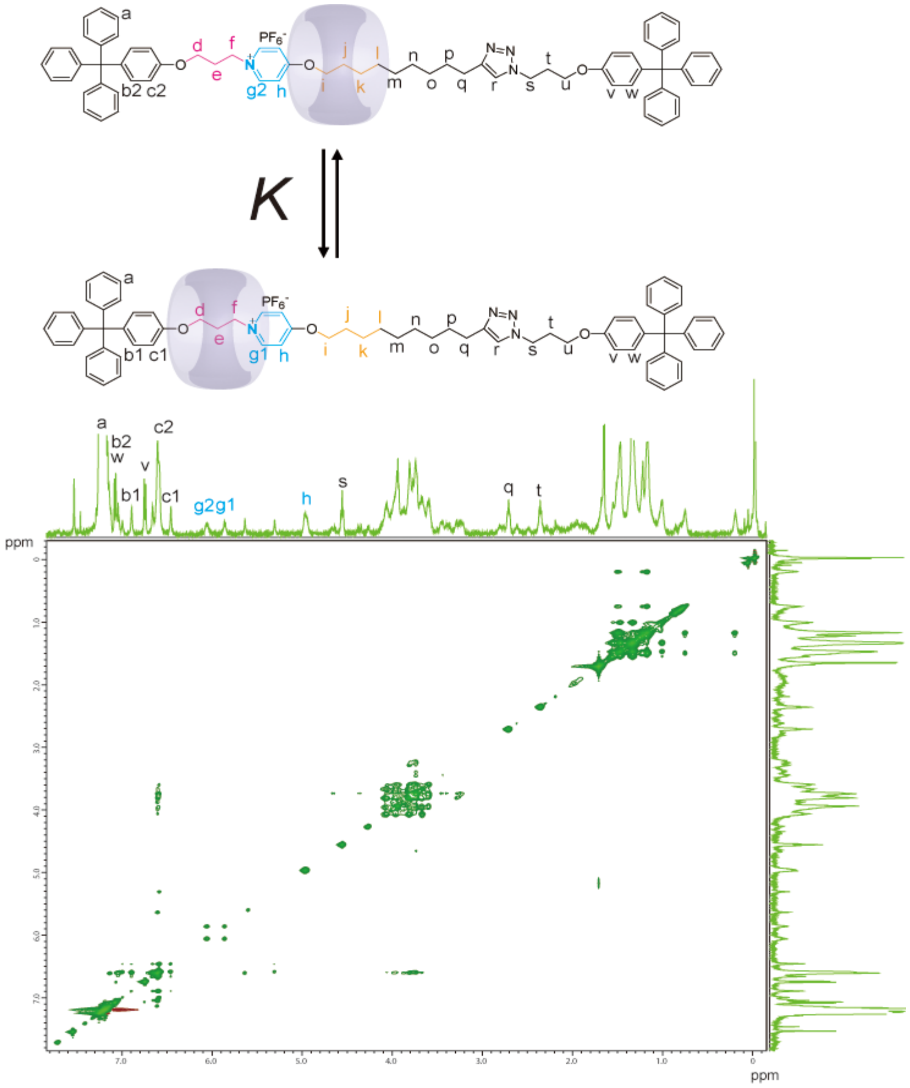


Fig. S14 2D EXSY NMR of [2]rotaxane **4** at – 20 °C in $CDCl_3$.

References

(1) T. Ogoshi, K. Kitajima, T. Aoki, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Org. Chem.,* 2010, **75**, 3268.
(2) D. Cao, Y. Kou, J. Liang, Z. Chen, L. Wang and H. Meier, *Angew. Chem. Int. Ed.*, 2009, **48**, 9721.
(3) P. R. Ashton, R. Ballardini, V. Balzani, M. Bělohradský, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi and D. J. Williams, *J. Am. Chem. Soc.,* 1996, **118**, 4931.
(4) Y. Leydeta, F. J. Romero-Salguerob, C. Jiménez-Sanchidriánb, D. M. Bassania, N. D. McClenaghan, *Inorg. Chim. Acta*, 2007, **360**, 987.
(5) T. Ogoshi, D. Yamafuji, T. Aoki, K. Kitajima, T. Yamagishi, Y. Hayashi and S. Kawauchi, *Chem. Eur. J.*, 2012, DOI: 101.1002/chem.201200122.