Electronic Supplementary Information

Facile and Efficient Formation and Dissociation of Pseudo[2]rotaxane by Slippage Approach Using Pillar[5]arene-Based Cyclic Host Liquid and Solvent

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Experimental Section

Materials. All solvents and reagents were used as supplied. Pillar[5]arene-based CHL **1** and (*R*)-2-azido-3-methylbutanoic acid and stopper **4** were synthesized according to the previous papers.[S1-S3]

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.

Axle 2. (*R*)-2-azido-3-methylbutanoic acid (450 mg, 3.10 mmol) was dissolved in THF (5 mL). *N*-methylmethylmorphiline (0.40 mL, 3.70 mmol) and isobutylchloroformate (0.50 mL, 3.70 mmol) was added at 0 ^{o}C and the reaction mixture was stirred at 0 ^{o}C for 1 h. Then, 1,12-diaminododecane (240 mg, 1.2 mmol) in THF (5 mL) was added to the mixture, and the reaction mixture was stirred at 25 ^{o}C for 24 h. The residue obtained after evaporation of solvents was dissolved in ethyl acetate and washed twice with water. Solution in organic solvent was dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was washed with *n*-hexane. (Axle **2**, 272 mg, 0.604 mmol, yield 50%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 6.32 (s, 2H), 3.83 (d, 2H), 3.27 (m, 4H), 1.51 (m, 4H), 1.21-1.36 (m, 18H), 1.08 (d, 6H), 0.90 (d, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 168.8, 71.0, 39.4, 31.9, 29.5, 29.2, 26.9, 19.7, 16.6. HRESIMS: *m*/*z* Calcd for $C_{22}H_{42}N_8NaO_2$ $[M+Na]^+$: 473.3328, found 473.3325.

[2]Rotaxane 3. Axle **2** (22.5 mg, 0.0500 mmol) was dissolved in CHL **1** (103 mg, 0.500 mmol). The reaction mixture was heated at 100 ^{o}C for 1 h. Column chromatography (silica gel; ethyl acetate : methanol = 10 : 1) afforded a transparent slight yellow liquid. ([2]rotaxane **3**, 35 mg, 0.0139 mmol, yield 28%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 6.87 (s, 10H), 6.09 (s, 2H), 4.01 (m, 20H), 3.84 (m, 20H), 3.71-3.79 (m, 30H), 3.68 (m, 20H), 3.64 (m, 20H), 3.52 (m, 20H), 3.35 (s, 30H), 2.51 (m, 4H), 2.31 (m, 2H), 1.07, 0.98 (m, 12H), 0.53 (m, 4H), 0.32 (m, 4H), 0.24 (m, 4H), -0.06 (m, 4H), -0.31 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 168.5, 149.7, 129.0, 115.0, 71.9, 70.8, 70.7, 70.5, 70.3, 70.2, 69.9, 69.7, 68.2, 68.1, 59.0, 39.6, 31.4, 31.3, 30.7, 30.2, 29.3, 29.0, 28.8, 28.7, 26.0, 19.7, 17.7, 17.6. HRESIMS: *m*/*z* Calcd for $C_{127}H_{212}N_8NaO_{42}$ $[M+Na]^+$: 2544.4597, found 2544.4592.

[2]Rotaxane 5. Axle **2** (22.5 mg, 0.0500 mmol), stopper **4** (13.0 mg, 0.0600 mmol) and

tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA, 3.4 mg, 6.5 μmol) were dissolved CHL **1** (103 mg, 0.500 mmol). The mixture was heated at 100 °C for 24 h. To the mixture, $Cu(CH_3CN)_4PF_6$ (18.5 mg, 0.0500 mmol) was added, and the mixture was heated at 100 °C for 24 h. Column chromatography (silica gel; ethyl acetate : methanol = 10 : 1) afforded a transparent slight yellow liquid. ([2]rotaxane **5**, 32 mg, 0.0108 mmol, yield 22%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): 8.15 (s, 2H), 7.12-7.14 (m 6H) 6.86 (s, 10H), 4.94 (m, 4H), 4.87 (m, 2H), 3.99 (m, 20H), 3.82 (m, 20H), 3.72-3.78 (m, 30H), 3.67 (m, 20H), 3.64 (m, 20H), 3.50 (m, 20H), 3.45 (m, 4H), 3.30 (s, 30H), 2.55-2.75 (m, 4H), 2.51 (m, 2H), 1.23-1.27 (m, 24H), 1.10 (m, 6H), 0.82 (m, 6H), 0.40-0.62 (m, 4H), 0.07-0.20 (m, 8H), -0.04 (m, 4H), -0.12 (m, 4H). ^{13}C NMR ($CDCl_3$, 500 MHz, ppm): δ 167.5, 167.4, 153.0, 149.8, 144.4, 141.9, 129.0, 128.9, 125.0, 124.2, 122.6, 115.2, 115.0, 71.8, 70.7, 70.6, 70.5, 70.4, 70.2, 68.2, 68.1, 59.0, 40.1, 40.0, 32.6, 30.9, 30.3, 29.9, 29.3, 29.2, 29.1, 29.0, 28.8, 28.6, 26.6, 26.3, 24.1, 19.4, 18.7. HRESIMS: *m*/*z* Calcd for $C_{157}H_{252}N_8Na_2O_{44}$ $[M+2Na]^{2+}$: 1500.3778, found 1500.3778.

Thermodynamic parameters by van't Hoff plots. The thermodynamic parameters such as ΔH and ΔS were determined from the temperature dependence of K by the use of the linear van't Hoff plots:

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

where T is the temperature and R is the gas constant. The ΔH and ΔS for pseudorotaxanation were calculated from the slope and intercept by plotting ln K vs. $1/T$.

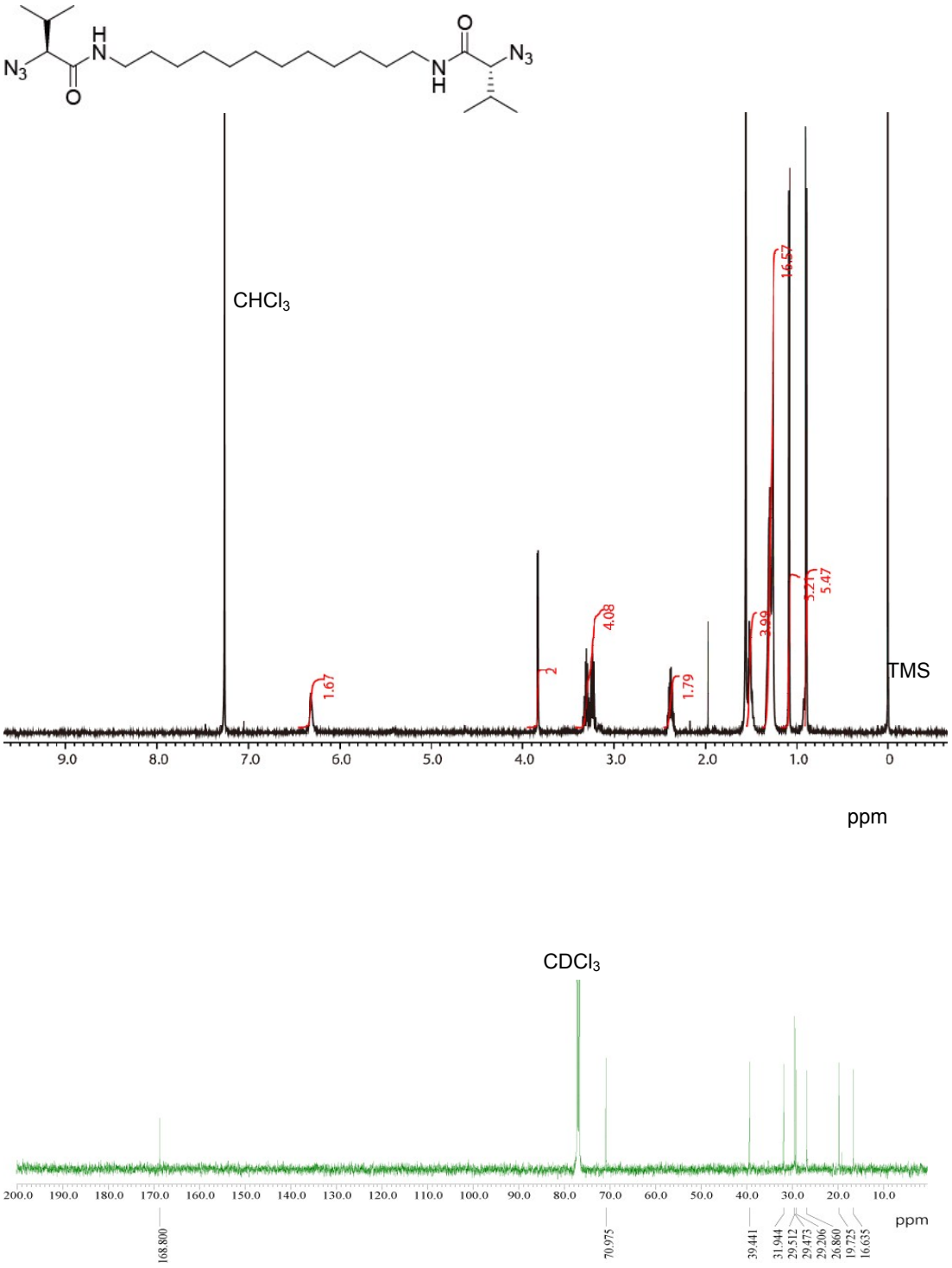


Fig. S1 ^{1}H and ^{13}C NMR spectra of axle **2** in $CDCl_3$ at 25 ^{o}C.

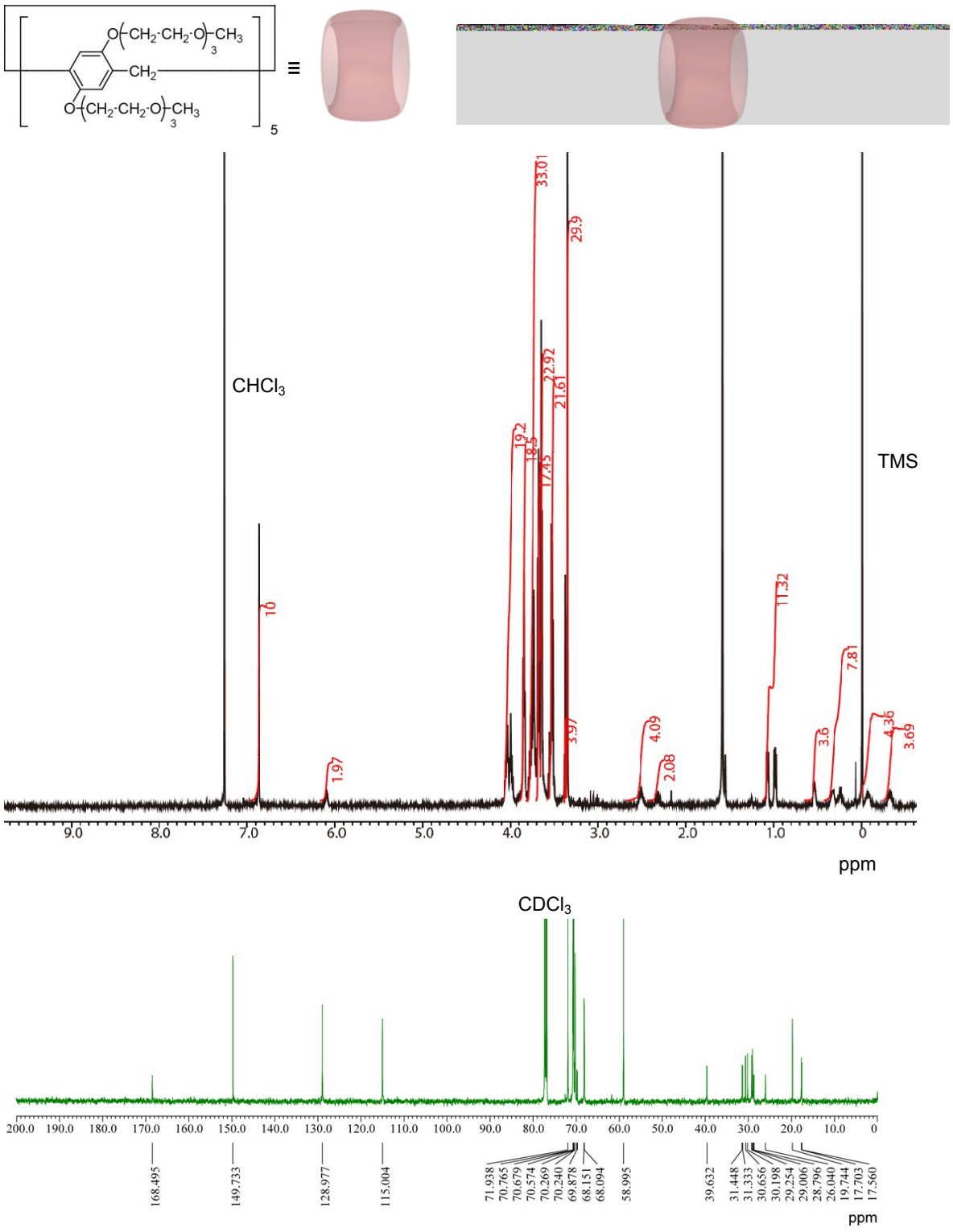
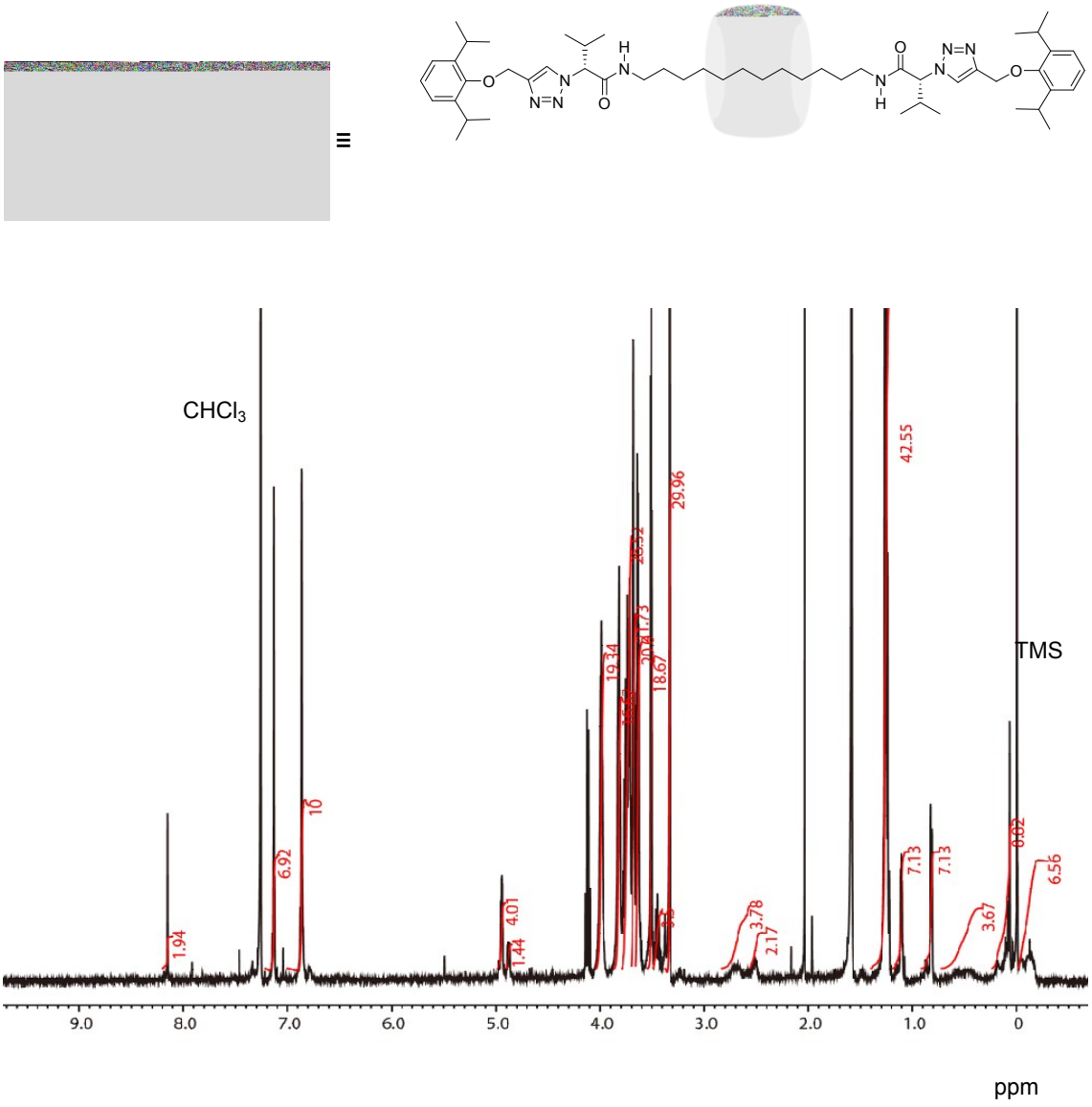


Fig. S2 ^{1}H and ^{13}C NMR spectra of [2]rotaxane **3** in $CDCl_3$ at 25 °C.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1.94
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3.67
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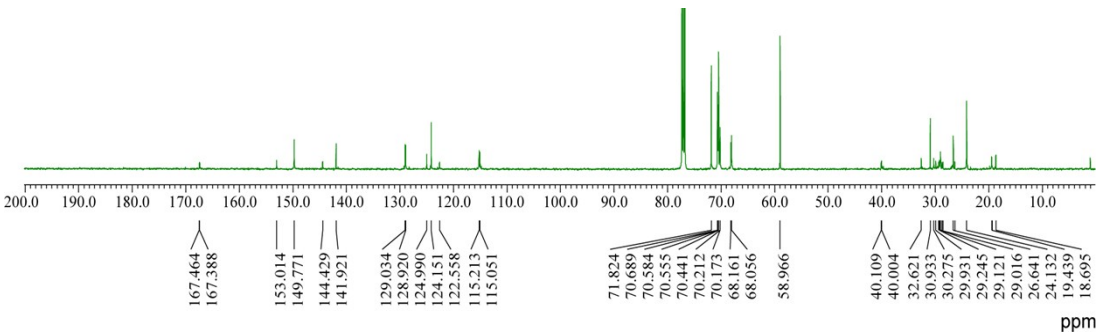
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26.641
24.132
19.439
18.695
ppm

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

Temperature (°C)	70	80	90	100	110
K	2.3	1.9	1.6	1.15	1.1
ΔG ($\times 10^2$) (J/mol)	-24.2	-19.2	-14.2	-9.15	-4.14

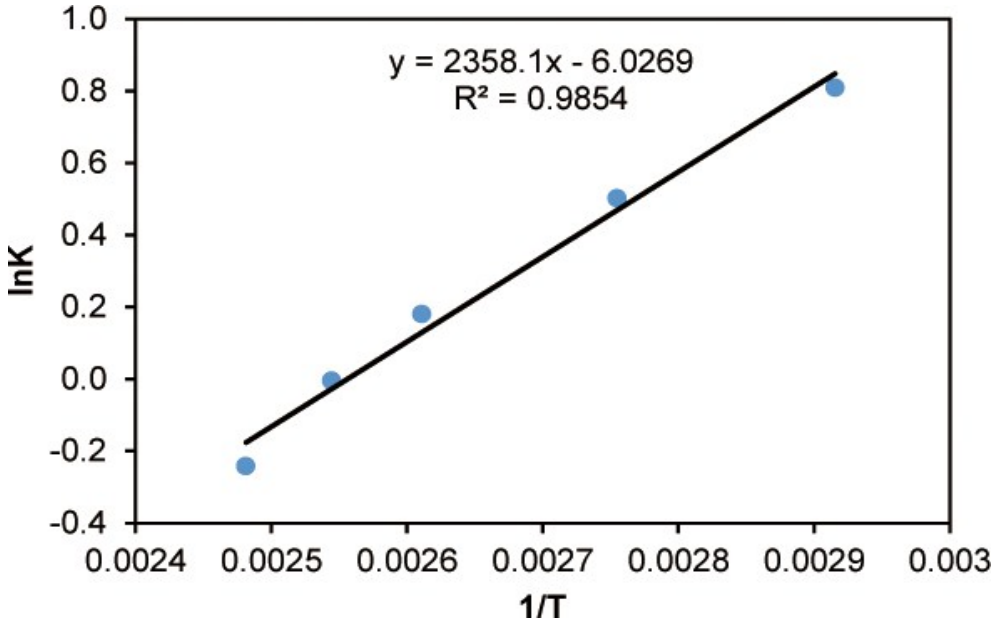

Fig. S4 van't Hoff plots for (a) formation of [2]rotaxane **3**. From the van't Hoff plots, *ΔH* and *ΔS* were calculated to be -21.9 $kJmol^{-1}$ and -56.1 $JK^{-1}mol^{-1}$, respectively.

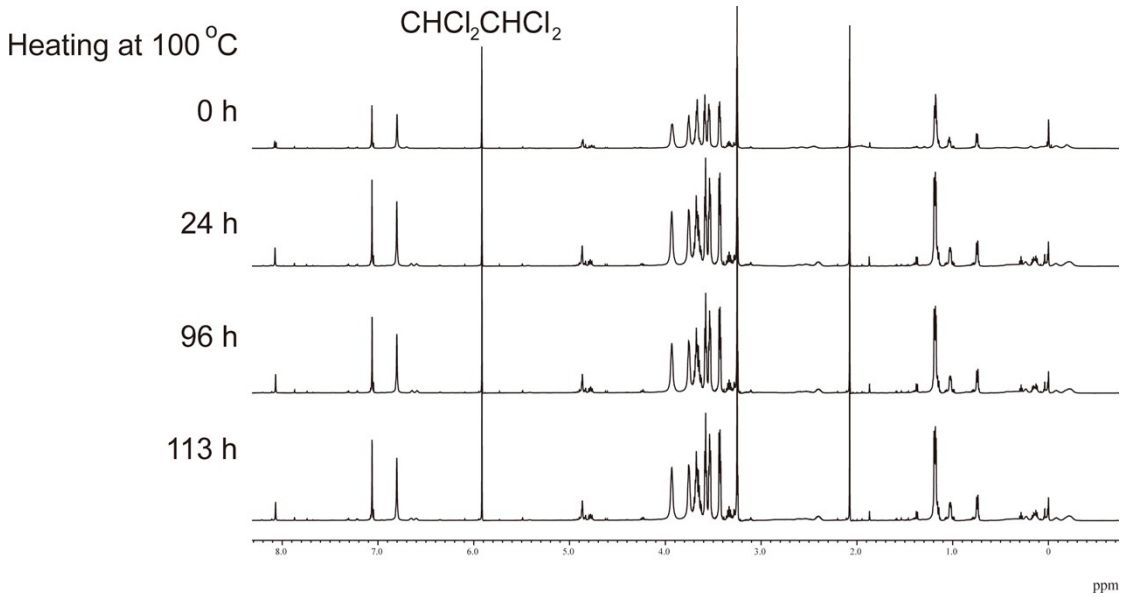

Fig. S5 ^{1}H NMR spectra (25 °C, $CDCl_2CDCl_2$) of [2]rotaxane **5** after heating 100 °C. No spectral change indicates no dissociation of [2]rotaxane **5** even after heating at 100 °C.

References

S1. T. Ogoshi, R. Shiga and T. Yamagishi, *J. Am. Chem. Soc.,* 2012, **134**, 4577.
S2. M. R. Davis, E. K. Singh, H. Wahyudi, L. D. Alexander, J. B. Kunicki, L. A. Nazarova, K. A. Fairweather, A. M. Giltrap, K. A. Jolliffe and S. R. McAlpine. *Tetrahedron.*, 2012, **68**, 1029.
S3. W. Zhang, W. R. Dichtel, A. Z. Stieg, D. Benítez, J. K. Gimzewski, J. R. Heath and J. F. Stoddart, *Proc. Natl Acad. Sci. USA,* 2008, **105**, 6514.