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Electronic Supplementary Information

A Light-operated Pillar[6]arene-based Molecular Shuttle

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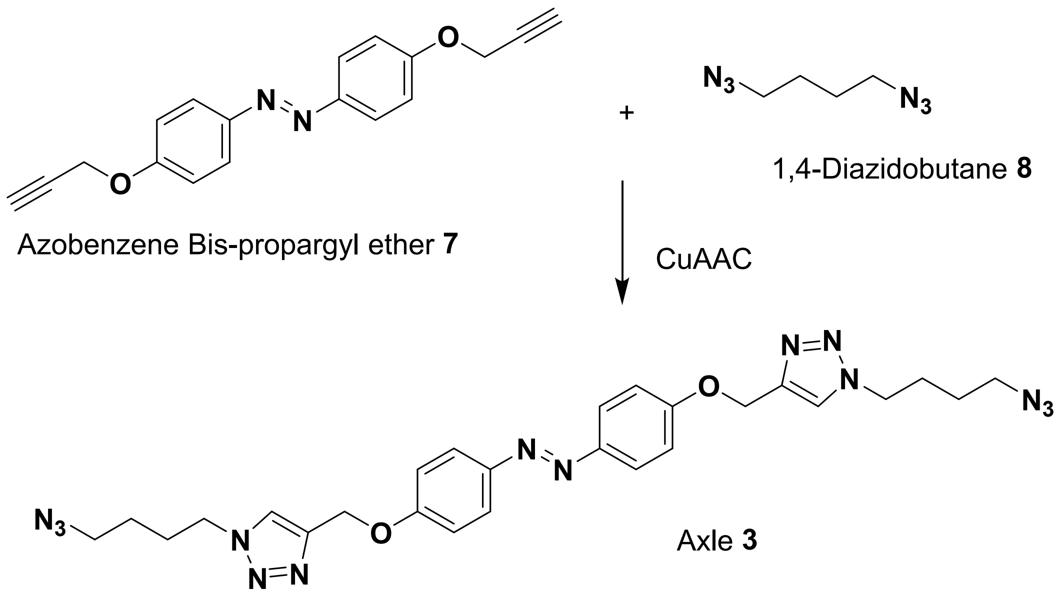
Experimental section

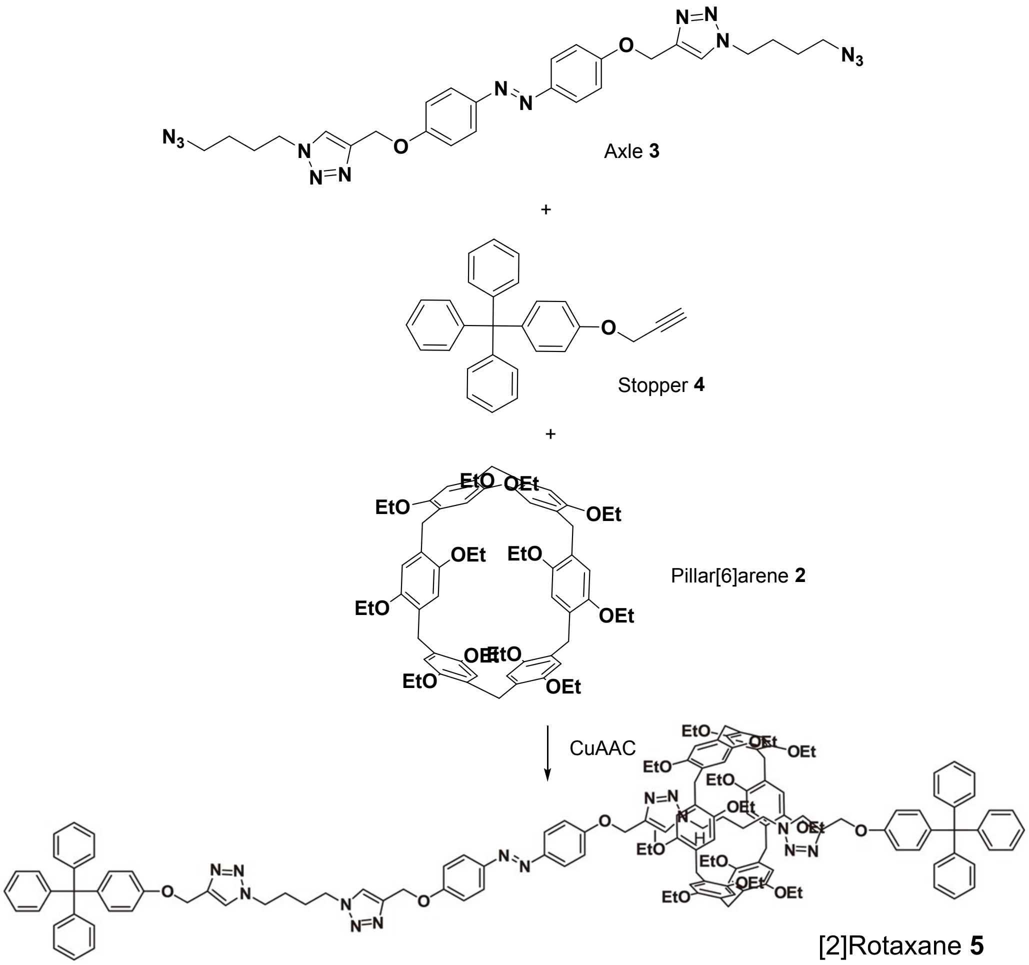
Materials. All solvents and reagents were used as supplied. Axle **1**, per-ethylated pillar[6]arene **2** and stopper **4** were synthesized according to the previous papers.[S1-S3]

Measurements. The ^1H NMR spectra were recorded at 500 MHz and ^{13}C NMR spectra were recorded at 125 MHz with a JEOL-ECA500 spectrometer. UV-Vis absorption spectra were recorded with a JASCO V-670. For UV-Vis absorption measurements, one centimeter quartz cuvets were used.

Axle 3. To a solution of azobenzene bis-propargyl ether **7**[S4] (100 mg, 0.345 mmol), 1,4-diazidobutane **8**[S3] (1.00 g, 7.14 mmol) in chloroform (15 mL), TBTA (9.50 mg, 0.0179 mmol) was added. The reaction mixture was stirred at 25 °C for 1 h. To the mixture, $Cu(CH_3CN)_4PF_6$ (5.16 mg, 0.0138 mmol) was added, and the mixture was stirred at 25 °C for 24 h. The solution was poured into *n*-hexane and the precipitate was collected by filtration. Column chromatography (silica gel; ethyl acetate) afforded a solid (axle **3**, 100 mg, 0.175 mmol, Yield: 51%). ^1H NMR ($CDCl_3$, 500 MHz, ppm) : δ = 7.88 (d, J = 9.2 Hz, 4H, azobenzene), 7.63 (s, 2H, triazole), 7.10 (d, J = 8.6 Hz, 4H, azobenzene), 5.30 (s, 4H, methylene), 4.42 (t, J = 6.9 Hz, 4H, methylene), 3.35 (t, J = 6.6 Hz, 4H, methylene), 2.03 (br, 4H, methylene), 1.61 (br, 4H, methylene) (Fig. S1a), ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) : δ = 160.2, 147.4, 144.0, 124.4, 122.6, 115.1, 62.3, 50.7, 49.8, 27.5, 26.0. (Fig S1b) ESI-HRMS: Calcd for $C_{26}H_{30}N_{14}NaO_2$ (*m*/*z*): $[M+Na]^+$, 593.2574, found 593.25686.



[2]Rotaxane 5. Axle **3** (80.0 mg, 0.140 mmol) and pillar[6]arene **2** (748 mg, 0.700 mmol) were dissolved in chloroform (5 mL). To the mixture, stopper **4** (157 mg, 0.420 mmol) and TBTA (3.70 mg, 6.97 μmol) was added. The reaction mixture was stirred at 25 °C for 24 h. To the mixture, $Cu(CH_3CN)_4PF_6$ (2.00 mg, 5.37 μmol) was added, and the mixture was stirred at 25 °C for 24 h. The solvent was removed by vacuum, to obtain the residue. Column chromatography (silica gel; dichloromethane : ethyl acetate = 3 : 1) afforded a solid ([2]rotaxane **5**, 130 mg, 0.0545 mmol, Yield: 39%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) : δ = 7.89 (d, J = 8.3 Hz, 4H, azobenzene), 7.25-7.10 (m, 38H, trityl and azobenzene), 6.90 (d, J = 8.6 Hz, 2H, trityl), 6.65 (br, 12H, phenyl of pillar[6]arene), 5.21 (s, 4H, methylene), 5.12 (s, 4H, methylene), 3.87-3.62 (br, 36H, methylene bridge and methylene of pillar[6]arene), 1.25 (br, 36H, methyl of pillar[6]arene) (Fig. S2a), ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) : δ = 160.4, 156.5, 156.2, 150.5, 147.2, 177.0, 147.9, 132.3, 132.1, 131.3, 131.1, 130.8, 123.0, 115.1, 115.0, 113.6, 113.5, 113.3, 64.4, 64.3, 64.2, 63.9, 61.9, 61.2, 48.7, 31.8, 26.8, 26.6, 26.5, 15.2 (Fig. S2a). ESI-HRMS: Calcd for $C_{148}H_{157}N_{14}NaO$ (*m*/*z*): $[M+Na]^+$, 2410.1878, found 2410.1874.



Dumbbell 6. Axle **3** (48.0 mg, 0.0842 mmol) was dissolved in chloroform (8 mL). To the mixture, stopper **4** (180 mg, 0.481 mmol) and TBTA (2.54 mg, 4.79 μmol) was added. The reaction mixture was stirred at 25 ^{o}C for 1 h. To the mixture, $Cu(CH_3CN)_4PF_6$ (1.80 mg, 4.83 μmol) was added, and the mixture was stirred at 25 ^{o}C for 24 h. The solvent was removed by vacuum, to obtain the residue. The residue was washed with *n*-hexane. Column chromatography (silica gel; dichloromethane : methanol = 9 : 1) afforded a solid (Dumbbell **6**, 103 mg, 0.0781 mmol, Yield: 93%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) : δ = 7.86 (d, J = 8.6 Hz, 4H, azobenzene), 7.58 (s, 2H, triazole), 7.56 (s, 2H, triazole), 7.24-7.16 (m, 30H, trityl), 7.12 (d, J = 9.2 Hz, 4H, azobenzene), 7.07 (d, J = 8.6 Hz, 4H, phenyl), 6.86 (d, J = 8.6 Hz, 4H, phenyl), 5.27 (s, 4H, methylene), 5.16 (s, 4H, methylene), 4.39 (br, 8H, methylene), 1.95 (br, 8H, methylene) (Fig. S3a), ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) : δ = 160.2, 156.3, 147.4, 147.0, 139.8, 132.4, 131.2, 127.5, 126.0, 124.5, 122.8, 115.1, 113.6, 64.4, 62.3, 62.1, 49.5, 27.1 (Fig S3b), APCI-HRMS. Calcd for $C_{82}H_{74}N_{14}O_4$ (*m/z*): $[M + H]^+$, 1319.6090, Found: 1319.6098.

NMR

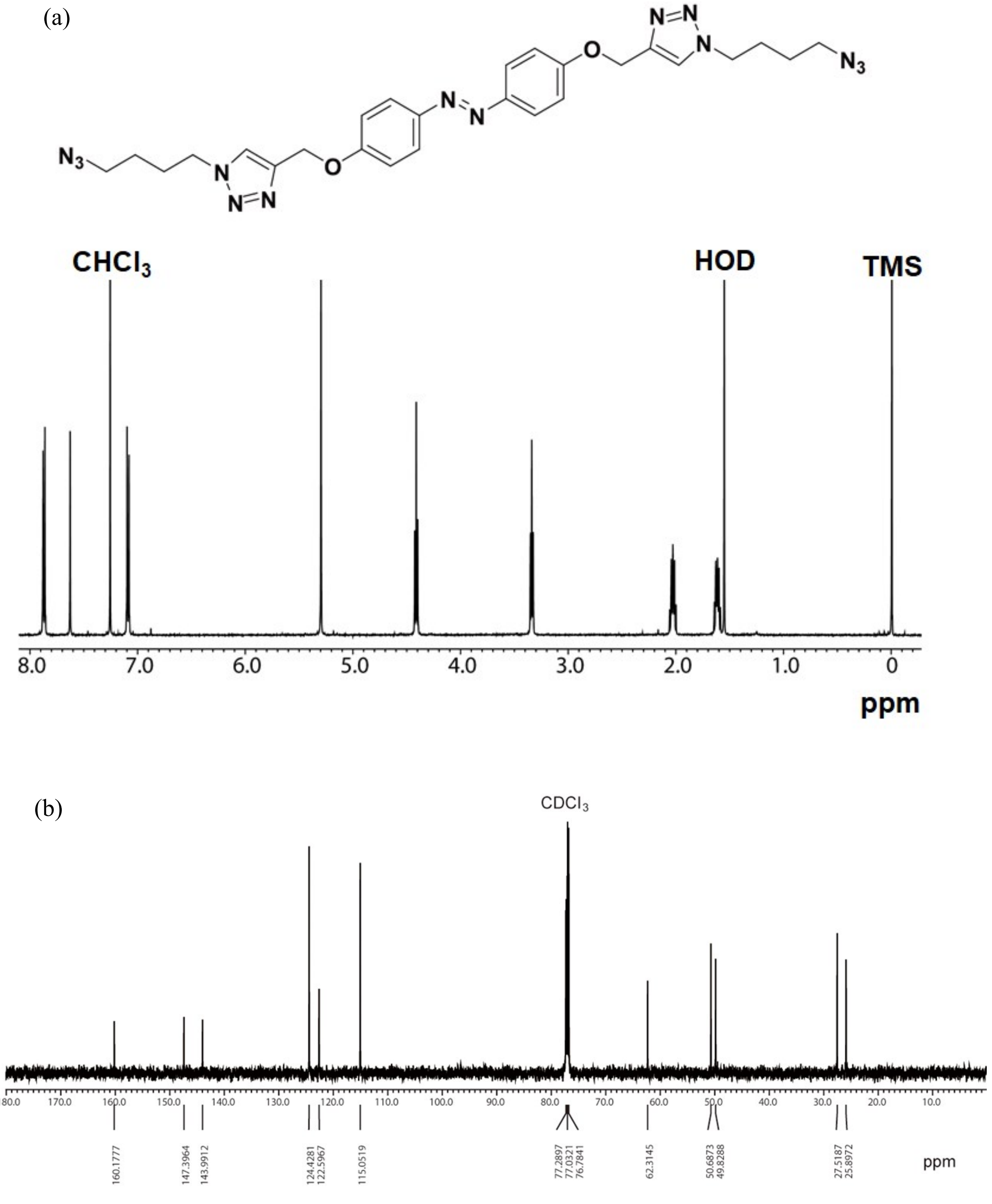


Fig. S1 (a) ^{1}H and (b) ^{13}C NMR spectra (298 K, $CDCl_3$) of axle **3**.

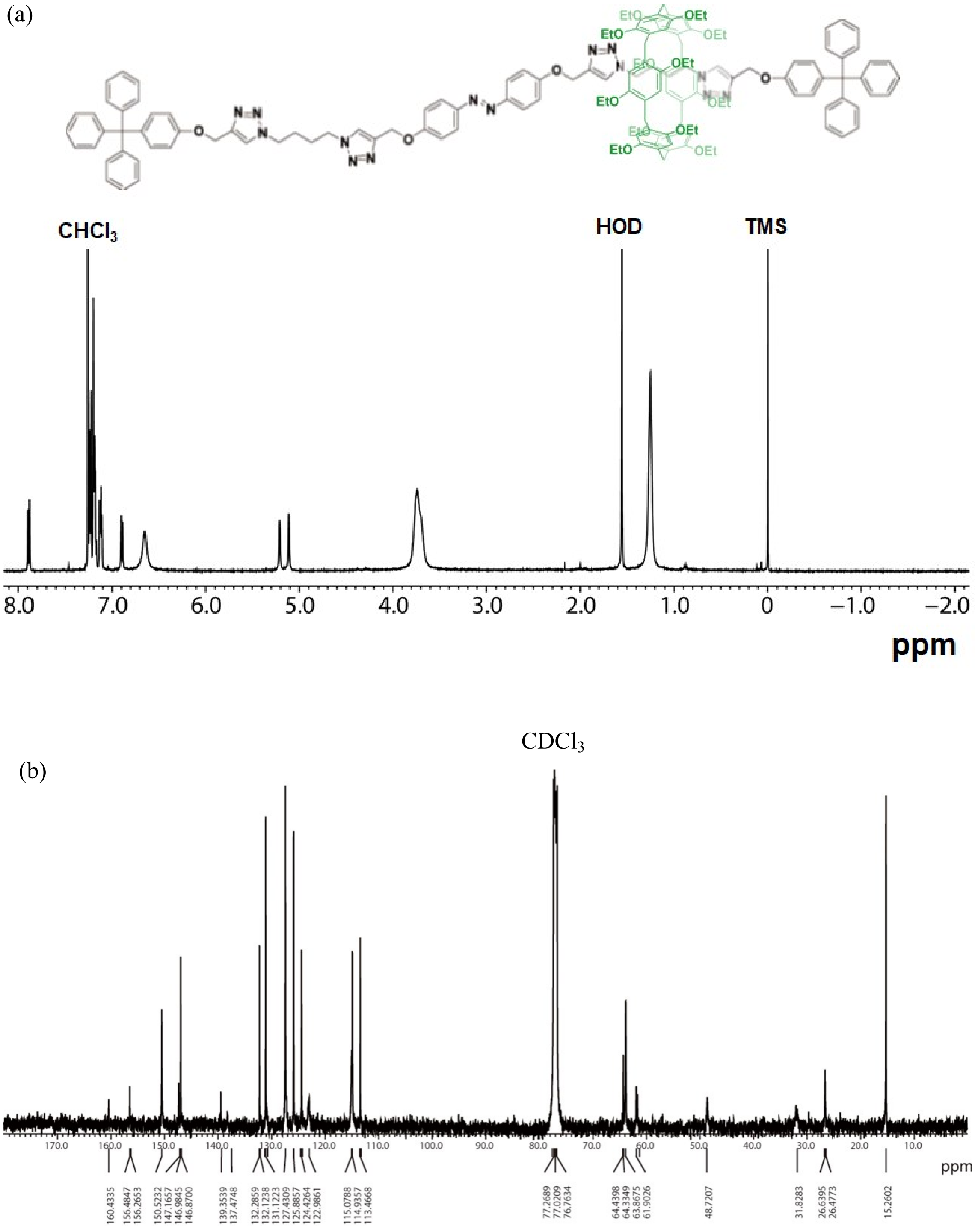


Fig. S2 (a) ^{1}H and (b) ^{13}C NMR spectra (298 K, CDCl$_3$) of *E*-[2]rotaxane **5**.

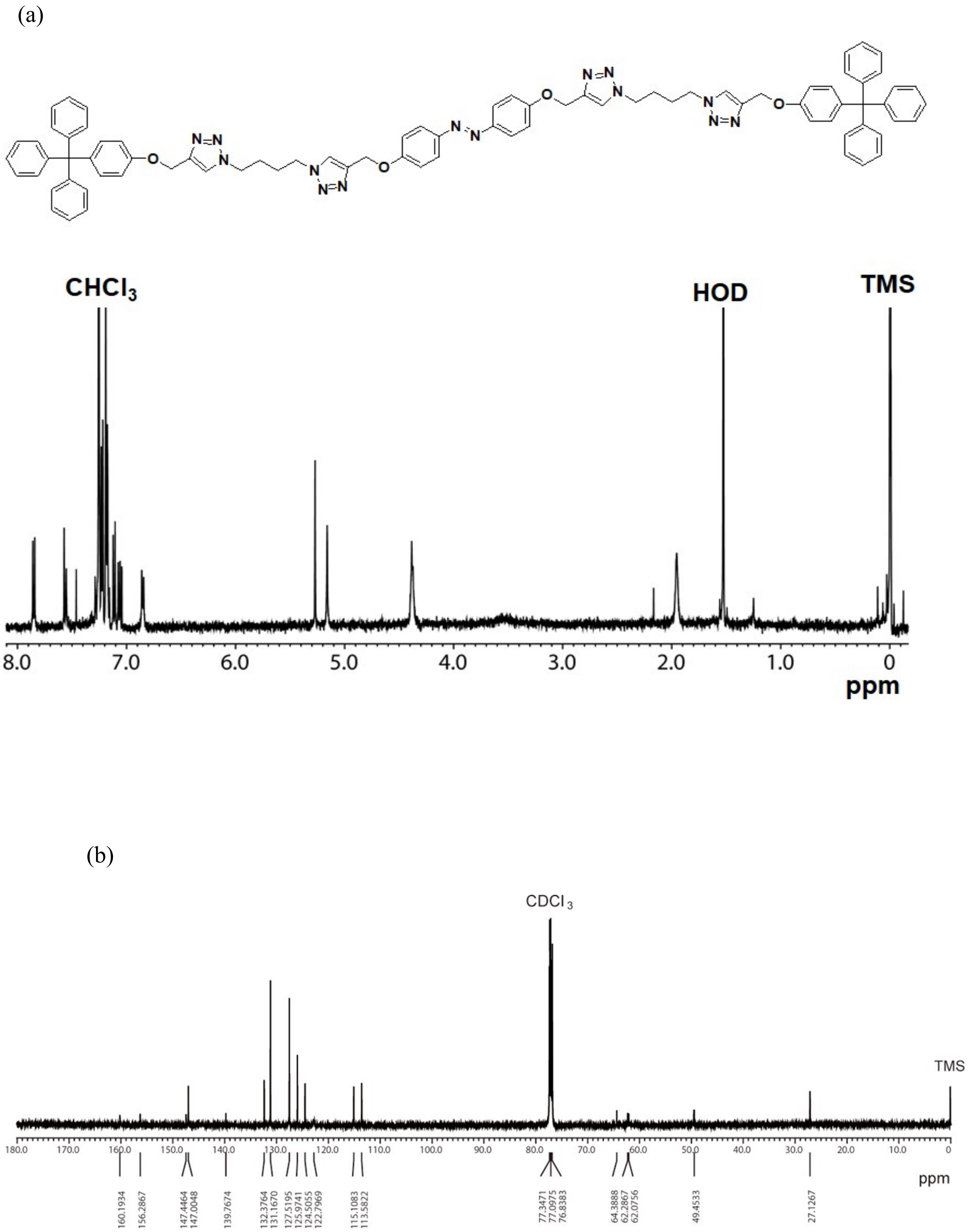


Fig. S3 (a) ^{1}H and (b) ^{13}C NMR spectra (298 K, CDCl$_3$) of Dumbbell **6**.

Job plot for a mixture of axle 1 and pillar[6]arene 2

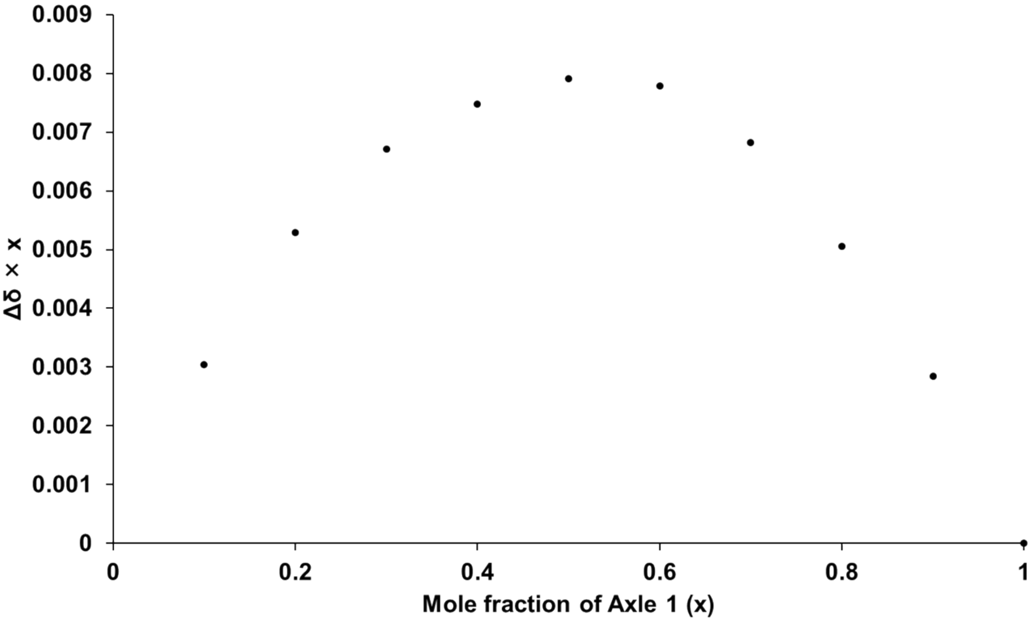


Fig. S4 Job plot between axle **1** (guest) and wheel **2** (host) was collected by plotting the Δδ in chemical shift of the proton signal of methylene moiety of axle **1** observed by ^{1}H NMR spectroscopy (298 K, $CDCl_3$) against the change in the mole fraction of the wheel **2**. Concentration: [axle **1**] + [wheel **2**] = 5 mM. The plot indicates a 1:1 binding between the host and guest.

Determination of association constants. In axle **1**-pillar[6]arene **2** 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 axle **1** (1 mM) and varying concentrations of pillar[6]arene **2**. By the non-linear curve-fitting method,[S4] the association constant K for the host-guest complex between pillar[6]arene **2** and axle **1** was calculated as $K = 1.6 \pm 0.1$ M^{-1}.

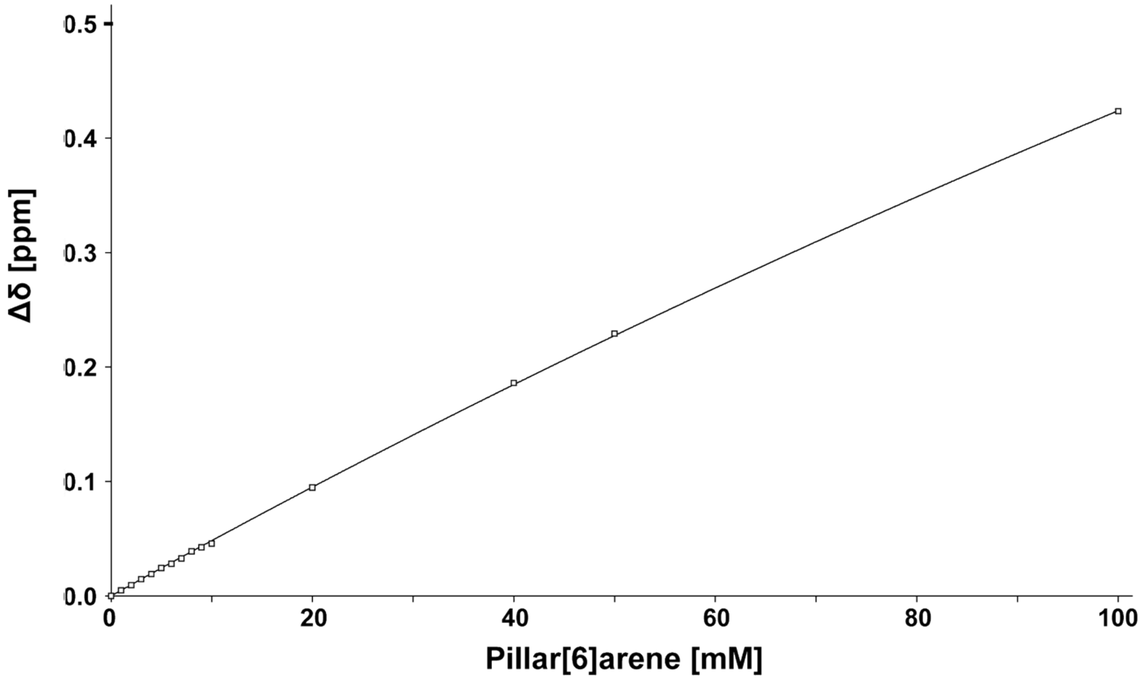
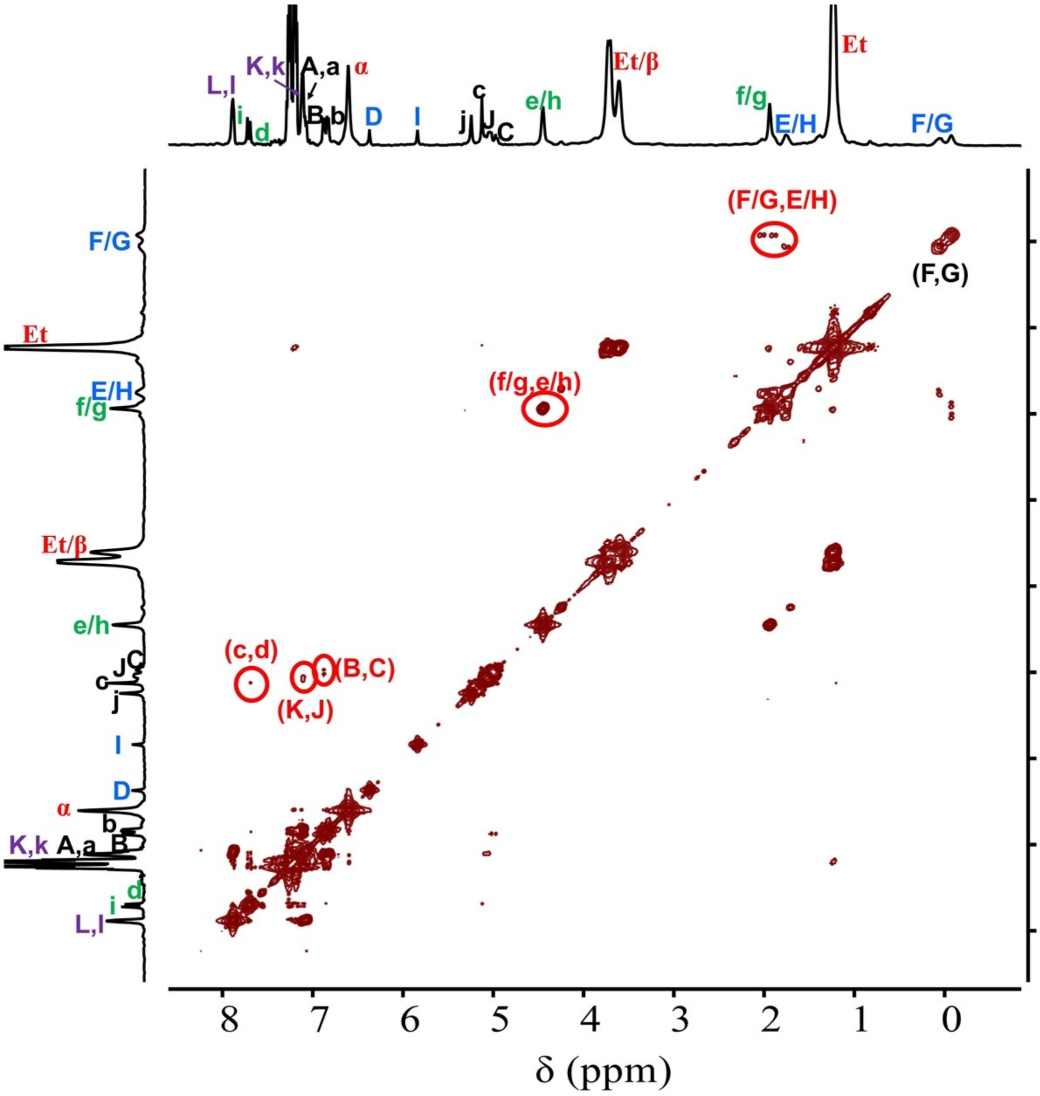


Fig. S5 ^1H NMR titration of Axle **1** (methylene protons) with pillar[6]arene **2** in $CDCl_3$ at 298 K.

^{1}H-^{1}H COSY and NOESY NMR of *E*-[2]Rotaxane 5

(a) ^{1}H-^{1}H COSY NMR



(b) 2D NOESY NMR

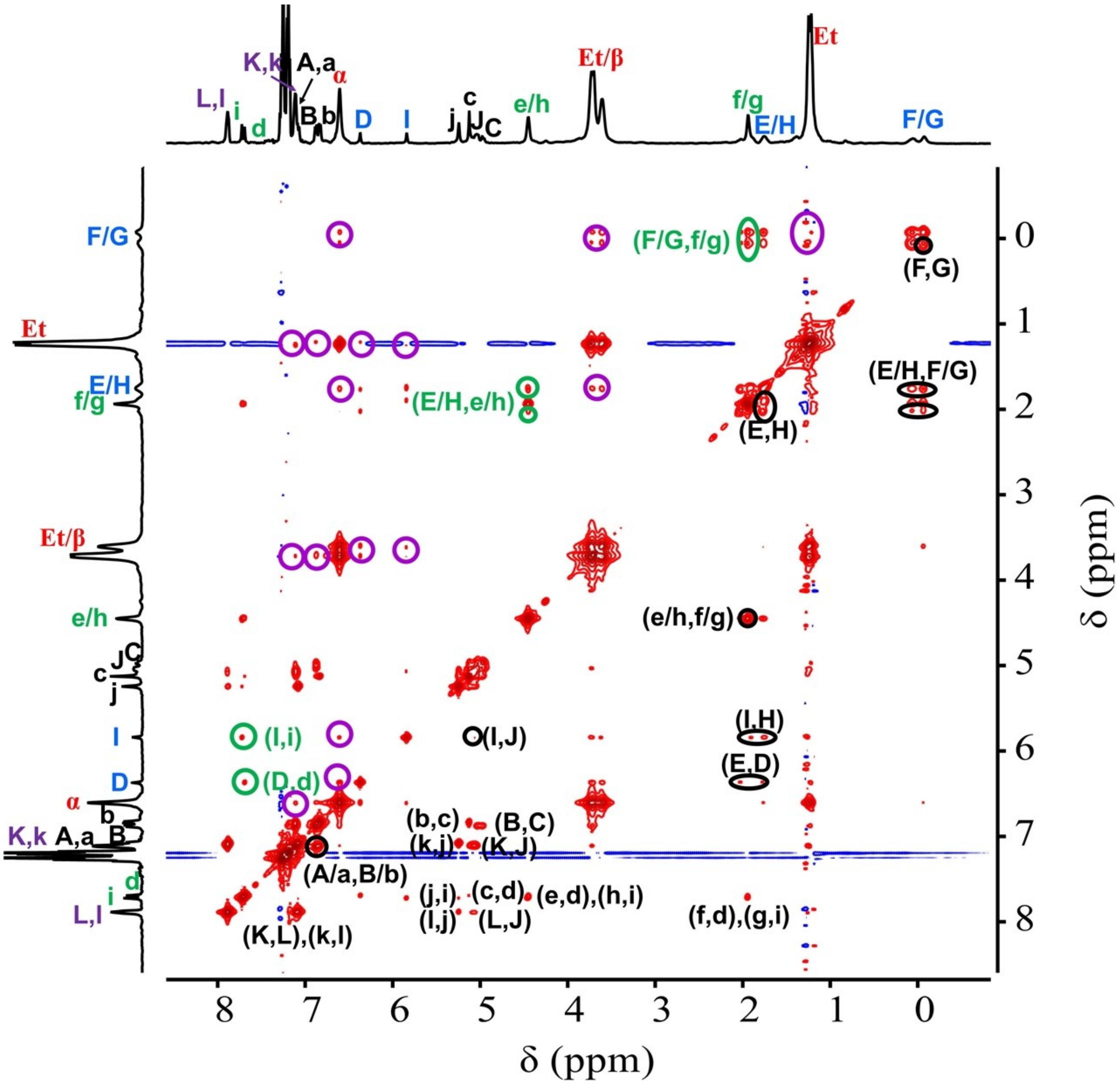


Fig. S6 (a) ^{1}H-^{1}H COSY and (b) NOESY NMR of *E*-[2]rotaxane **5** at 213 K in CDCl$_3$. In (b), cross peaks in green circles indicate EXSY between complex and un-complex stations. Cross peaks in purple circles indicate NOE between pillar[6]arene ring and axle in *E*-[2]rotaxane **5**.

Determination of the Rate of the Ring Shuttling of *E*-[2]Rotaxane 5

From Variable Temperature ^{1}H NMR Measurements

The free energy of activation for the exchange ΔG‡ was estimated by using the approximate expression[S5,6]:

$$\Delta G^{\ddagger} = 8.314T_c[22.96 + \log(T_c/\delta\nu)]$$

where δν is the chemical shift difference between the proton signals from complexed and un-complexed species. The coalescence temperature T_c was estimated on the coalescence signal.

The extrapolated value of k at 298 K was obtained from the Eyring equation:

$$\Delta G^{\ddagger} = -RT\ln(kh/k_BT)$$

where R is the gas constant, h is Plank's constant and k_B is Boltzmann's constant.

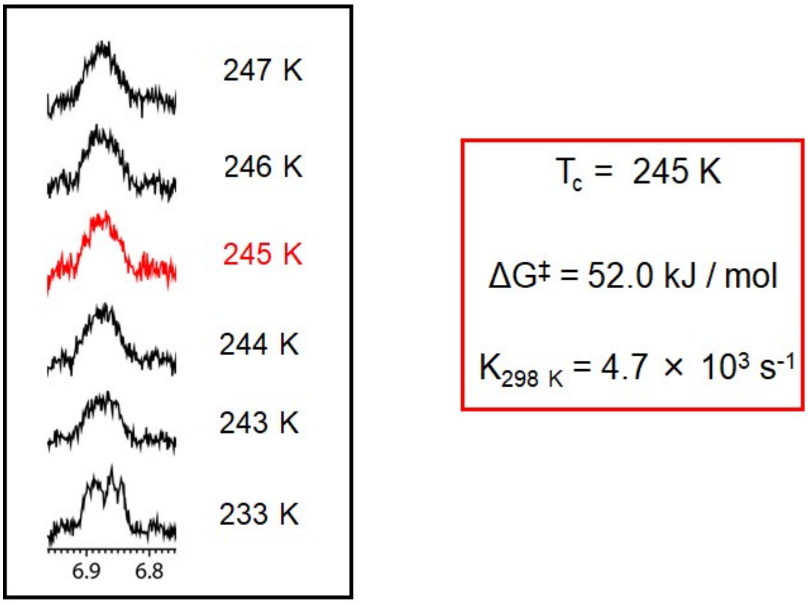


Fig. S7 Partial variable temperature ^{1}H NMR spectra of *E*-[2]rotaxane **5** around coalescence temperatures in $CDCl_3$. Proton signals of trityl stopper (signals b and B) of *E*-[2]rotaxane **5** were used.

From EXSY Measurements

The EXSY measurements were carried out with a phase-sensitive NOESY pulse sequence. The exchange rate constant k of the ring shuttling was determined by the following equations:[S7]

$$k = \frac{1}{I?_m} \ln \frac{I3 + 1}{I3 - 1}$$

where τ_m is mixing time and γ is defined by the following equation:

$$I3 = \frac{4X_A X_B (I_{AA} + I_{BB})}{I_{AB} + I_{BA} - (X_A - X_B)^2}$$

where X_A and X_B are integration of proton signals (H_i, H_I) of uncomplex and complex stations, respectively, I_{AA} and I_{BB} are the intensities of the diagonal peaks, I_{AB} and I_{BA} are the intensities of the cross peaks, respectively.

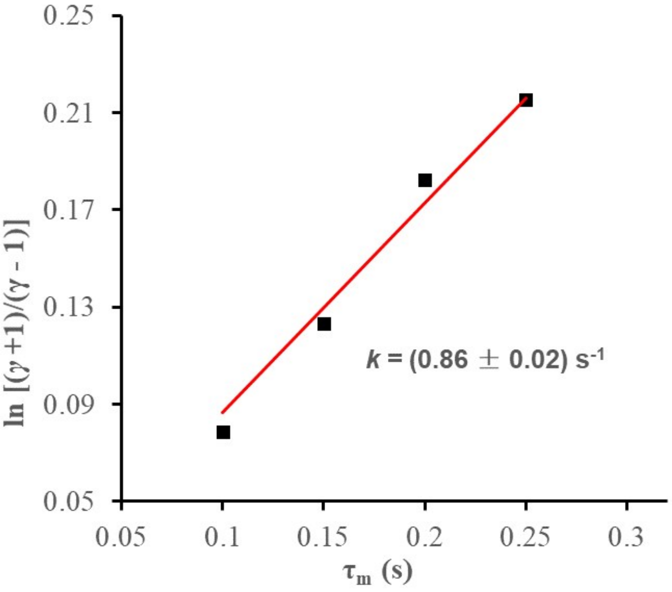


Fig. S8 Plots of ln [(γ + 1)/ (γ − 1)] as a function of mixing time τ_m.

^{1}H NMR Spectrum and ^{1}H-^{1}H COSY of *Z*-Dumbbell 6

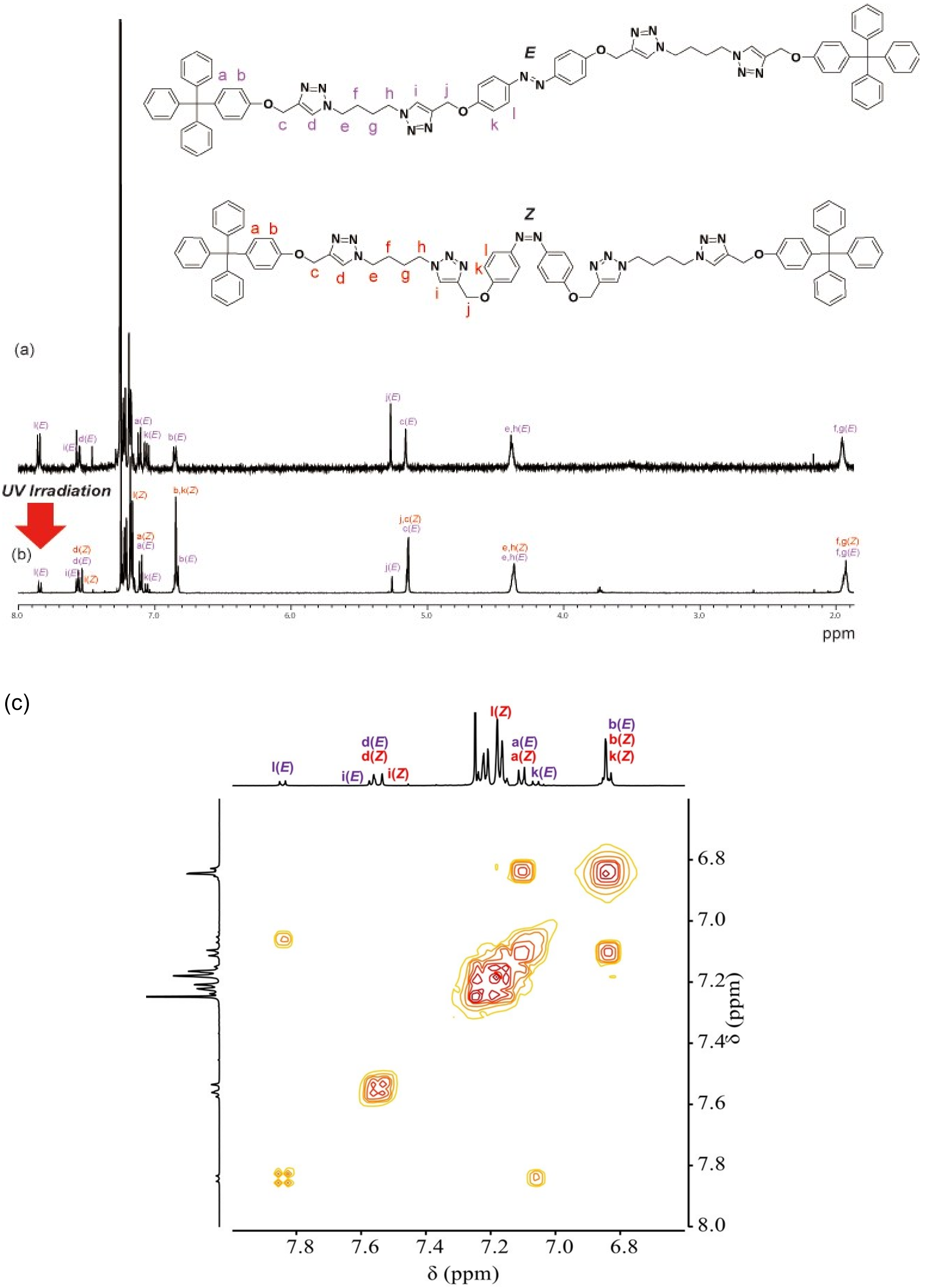


Fig. S9 ^{1}H NMR Spectra (293 K, $CDCl_3$) of (a) *E*-Dumbbell **6** and (b) Z-dumbbell **6** (*E*/*Z* = 14/86) and (c) ^{1}H-^{1}H COSY of *Z*-Dumbbell **6**.

VT ^{1}H NMR Spectra of [2]Rotaxane 5 in *Z* Isomer

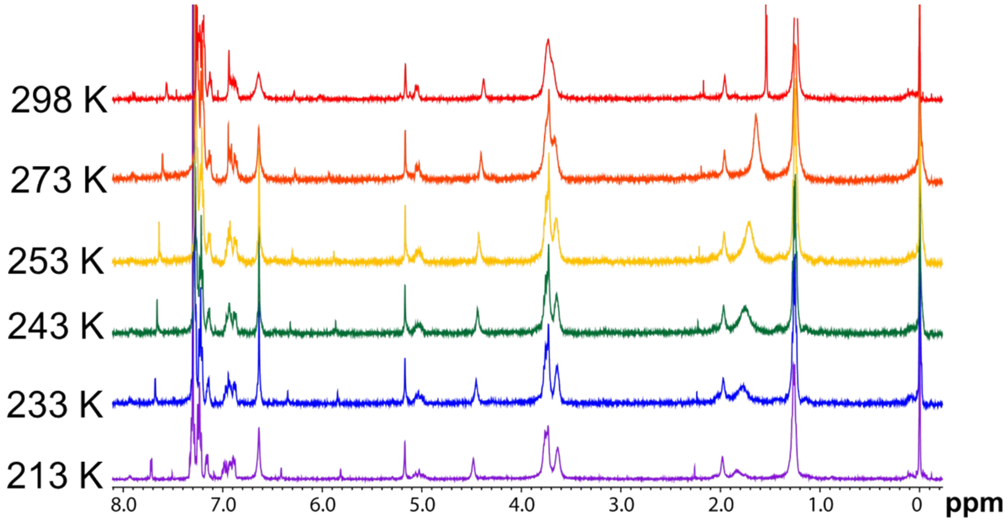


Fig. S10 Variable temperature ^{1}H NMR spectra of *Z*-[2]Rotaxane **5** (*E*/*Z* = 10/90) in $CDCl_3$.

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