Electronic Supplementary Information


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**References**

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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.\textsuperscript{S1-S3}

**Measurements.** The \textsuperscript{1}H NMR spectra were recorded at 500 MHz and \textsuperscript{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\textsuperscript{S4} (100 mg, 0.345 mmol), 1,4-diazidobutane 8\textsuperscript{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\textsubscript{3}CN)\textsubscript{4}PF\textsubscript{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%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz, ppm) : \(\delta = 7.88\) (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), \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 125 MHz, ppm) : \(\delta = 160.2, 147.4, 144.0, 124.4, 122.6, 115.1, 62.3, 50.7, 49.8, 27.5, 26.0\). (Fig S1b) ESI-HRMS: Calcd for C\textsubscript{26}H\textsubscript{30}N\textsubscript{14}NaO\textsubscript{2} (m/z): [M+Na]\textsuperscript{+}, 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$_3$CN)$_4$PF$_6$ (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) : $\delta$ = 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) : $\delta$ = 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$_{159}$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 °C for 1 h. To the mixture, Cu(CH₃CN)₄PF₆ (1.80 mg, 4.83 μmol) was added, and the mixture was stirred at 25 °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%). ¹H NMR (CDCl₃, 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), 4.39 (br, 8H, methylene) (Fig. S3a), ¹³C NMR (CDCl₃, 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 C₈₂H₇₄N₁₄O₄ (m/z): [M + H]⁺, 1319.6090, Found: 1319.6098.
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.
**Fig. S4** Job plot between axle 1 (guest) and wheel 2 (host) was collected by plotting the $\Delta\delta$ 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$^{-1}$.

![Graph showing NMR titration](image)

**Fig. S5** $^1$H 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

![COSY NMR spectrum](image)
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 $\Delta G^\ddagger$ was estimated by using the approximate expression\textsuperscript{85,6}:

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

where $\delta\nu$ 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:

$$\Delta G^\ddagger = -RT\ln(kh/k_B T)$$

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

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure}
\caption{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.}
\end{figure}
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:\textsuperscript{S7}

$$k = \frac{1}{\tau_m} \ln \frac{I_3 + 1}{I_3 - 1}$$

where $\tau_m$ is mixing time and $\gamma$ is defined by the following equation:

$$I_3 = \frac{4X_A X_B (I_{AA} + I_{BB})}{I_{AB} + I_{BA} - (X_A - X_B)^2}$$

where $X_A$ and $X_B$ are integration of proton signals ($H_i, H_j$) 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 $\ln [(\gamma + 1)/(\gamma - 1)]$ as a function of mixing time $\tau_m$. 

$k = (0.86 \pm 0.02) \text{ s}^{-1}$
$^1$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**

![ VT $^1$H NMR Spectra of [2]Rotaxane 5 in Z Isomer ](image)

**Fig. S10** Variable temperature $^1$H NMR spectra of Z-[2]Rotaxane 5 ($E/Z = 10/90$) in CDCl$_3$. 
References


