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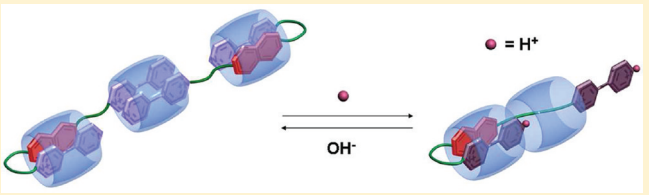
Interconversion between [5]Pseudorotaxane and [3]Pseudorotaxane by Pasting/Detaching Two Axle Molecules

Zhi-Jun Zhang, Heng-Yi Zhang, Ling Chen, and Yu Liu*

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China

Supporting Information

ABSTRACT: An acceptor−donor−acceptor-type linear molecule $\mathbf{1}^{2+}$ containing one electron-rich naphthoxy (**NP**) unit and two monocharged viologen (**MCV**) units was synthesized. Through the noncovalent interaction of cucurbit[8]uril (CB[8]) with one **NP** and one **MCV** in $\mathbf{1}^{2+}$, we first obtained a [2]pseudorotaxane ($[\mathbf{1}^{2+}]\subset$CB[8]), and the excess CB[8] included simultaneously the two bare **MCV** units of two [2]pseudorotaxanes to form a [5]pseudorotaxane ($[\mathbf{1}^{2+}]_2\subset[\mathrm{CB[8]}]_3$). Its transformation to [3]pseudorotaxane was achieved through detaching the two axle molecules in the presence of acid, and then the addition of base may result in a reversible switch between two different pseudorotaxanes. This novel methodology elongating reversibly linear molecules by noncovalent interactions will benefit the development of stimuli-responsive functional molecular devices.



INTRODUCTION

The linear axle molecule is an indispensable component for both pseudorotaxane and rotaxane.[1] Compared with the cyclic wheel components, chemists spent more effort on designing and synthesizing the various axle components.[2] In particular, the linear axle molecules for pseudopolyrotaxanes and polyrotaxanes must be longer and have more recognition sites,[3] which undoubtedly increases the difficulty of synthesis. On the other hand, through noncovalent interactions, such as hydrogen bonding,[4] metal−ligand interactions,[4a,5] and hydrophobic interactions,[6] chemists recently found they can interconnect different molecules to longer chains[7] or networks.[8] In this respect, cucurbit[8]uril (CB[8]) is a useful molecular connector.[9] Its 1:1:1 ternary complex with the positively charged viologen and electron-rich naphthoxy (**NP**) derivatives is a powerful and effective platform for elongating polymer chains,[10] immobilizing colloids onto the Au substrates,[11] and preparing networks,[12] protein−polymer conjugations,[13] and heterowheel [3]pseudorotaxanes.[14] However, these interconnected supramolecular systems are hardly reversible. Herein, we designed and synthesized a linear axle molecule $\mathbf{1}^{2+}$ (Scheme 1) in which two monocharged viologen (**MCV**) units are located at its two ends and one **NP** group is at the middle of $\mathbf{1}^{2+}$ and then prepared a [5]pseudorotaxane mediated by CB[8]. Furthermore, the [5]pseudorotaxane can turn into a [3]pseudorotaxane in the presence of acid. The addition of base may result in a reversible switch[15] between two different pseudorotaxanes.

RESULTS AND DISCUSSION

Synthesis of axle molecules. The axle molecule $\mathbf{1}^{2+}$ was synthesized by reaction of 2,6-bis(2-(2-(2-iodoethoxy)ethoxy)-ethoxy)naphthalene with 4,4′- bipyridine in 45% yield and characterized using ^{1}H and ^{13}C NMR and HRMS. As a control compound containing one **NP** and one **MCV** group, the axle molecule $\mathbf{5}^{+}$ was also synthesized through four steps (see the Supporting Information). All of the resonances were assigned on the basis of the analysis of ^{1}H NMR and COSY spectra. In the structure of $\mathbf{1}^{2+}$, each 4,4′-bipyridinium unit has only one side modified with the triethylene glycol linker to get one positive charge. Through comparison of the ^{1}H NMR spectra of $\mathbf{1}^{2+}$ and the mixture of the 1-methyl-4,4′-bipyridinium iodide (**MBipy**) molecule[10b] and 2,6-dihydroxynaphthalene, the upfield shifts of all the aromatic protons indicate the existence of an intramolecular CT interaction between the donor and acceptor units in the guest (Figure S10 in the Supporting Information).

Formation of [5]Pseudorotaxane $\mathbf{4}^{4+}$. Upon the addition of 1.0 equiv of CB[8] to the aqueous solution of $\mathbf{1}^{2+}$, the color of the solution turned to yellow with a characteristic charge transfer (CT) band centered around 425 nm in the UV/vis spectrum (Figure 1), indicating the formation of a CT complex between **NP** and **MCV** of $\mathbf{1}^{2+}$. ROESY experiment was carried out to support the structure of $\mathbf{2}^{2+}$ (see Figure 3). No NOE correlation is found between the proton H_d and H_a, which indicates that the head-to-tail stacking of two **MCV** units does not exist in the 1:1 complex. Furthermore, the NOE correlations (peaks A and B) between **MCV** (H_d and H_b) and **NP** units (H_k and H_l) suggest the close proximity of these two units. From the strong NOE correlations (peaks C, D, E, F, and G) between the protons on **NP** units (H_k, H_l, and H_m) and CB[8] (H_α, H_β, and H_γ), it can be confirmed that **NP** unit is located inside the cavity of CB[8].[16]

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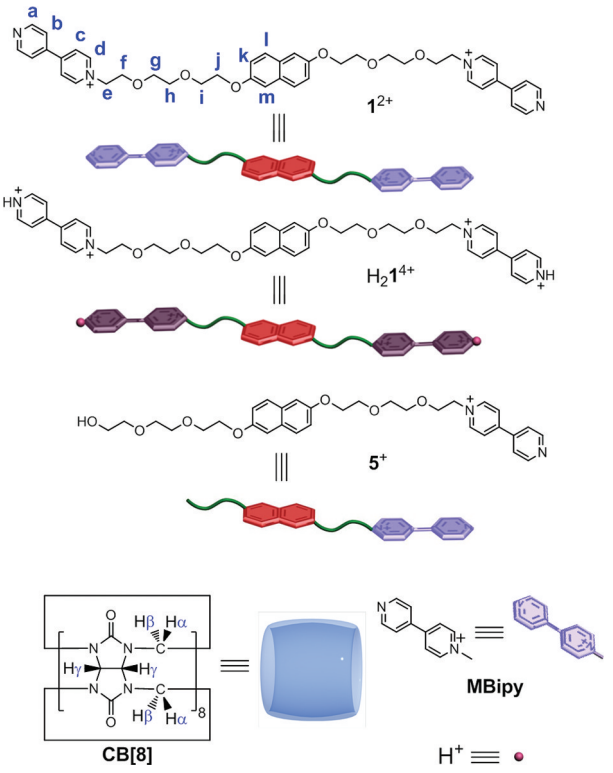
Scheme 1. Structures of CB[8] and Axle Molecules 1^{2+}, H_21^{4+}, 5^+, and MBipy



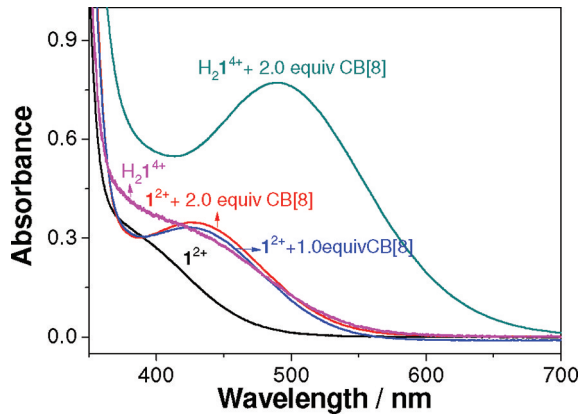


Figure 1. Absorption spectra of (a) 1^{2+}, (b) 1^{2+} + 1.0 equiv of CB[8] (1.0 mM), (c) 1^{2+} + 2.0 equiv of CB[8] (2.0 mM), (d) H_21^{4+}, (e) H_21^{4+} + 2.0 equiv of CB[8] (2.0 mM) ($[1^{2+}] = [H_21^{4+}] = 1.0$ mM).

In order to ascertain whether the **NP** and **MCV** units in the CT complex come from one axle molecule, we performed the NMR experiments of 1^{2+}·CB[8] in the absence and presence of methylviologen (**MV**) (Figure S11 in the Supporting Information). Because there are both donor and acceptor units in 1^{2+}, it has the possibility to form *n*:*n* polymeric species because of the strong stability of the CB[8]-induced heteroguest CT complex.[17] If there is such a ternary complex including CB[8] and the **NP** and **MCV** units from two axle molecules, addition of methylviologen as a stronger acceptor would compete and affect the complex. However, no such observation is found from the NMR spectra; thus, we can confirm that the **NP** and **MCV** from the same axle molecule form a stable intramolecular CT complex upon inclusion by CB[8]. A control compound 5^+ containing one **NP** and one **MCV** group, which formed a stable 1:1 CT complex with CB[8], was used to further confirm the structure of 2^{2+} (see the Supporting Information). Combining the results of 1D and 2D NMR, we can confirm that **NP** and **MCV** in the CT complex come from one axle molecule. That is, the CT complex 2^{2+} is an intramolecular heteroguest pair mediated by CB[8],[18] as illustrated in Figure 2.

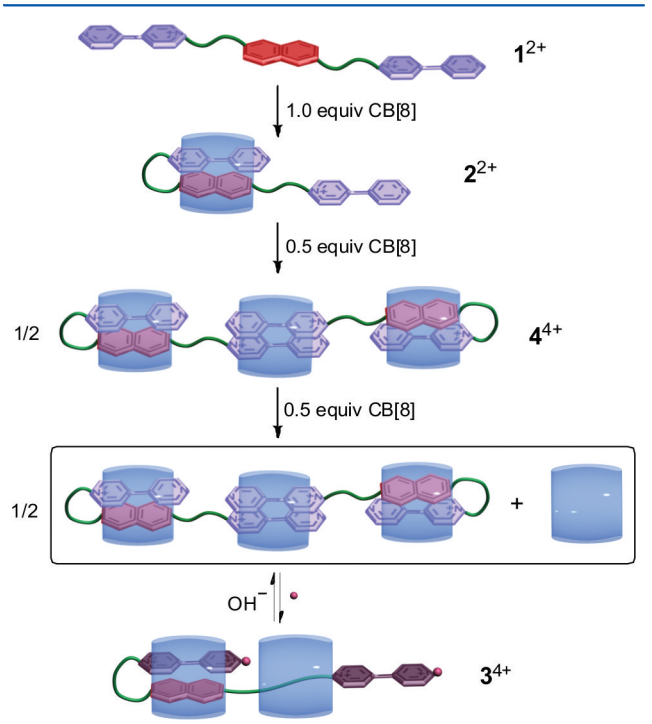


Figure 2. Schematic representation of the binding modes and the interconversion process.

^{1}H NMR was used to investigate the binding process of 1^{2+} with CB[8]. Upon the addition of 1.0 equiv of CB[8] to the solution of 1^{2+} (Figure 4c), the proton signals in **NP** are shifted upfield, which indicates that **NP** should be included in the cavity of CB[8]. When another 0.5 equiv of CB[8] was added (Figure 4e), the chemical shifts of the protons in **MCV** and H_α/H_γ in CB[8] significantly changed. Further addition of CB[8] hardly affected any peaks (Figure 4f). Through analysis of the COSY spectrum of 1^{2+} in the presence of 2.0 equiv of CB[8] (Figure S12 in the Supporting Information), we can assign these resonances of the **MCV** protons as two groups. One group belongs to the CT complex, and they are respectively labeled as H_d, H_a, H_c, and H_b. As can been seen from Figure 4f, the four **MCV** protons and the three **NP** protons (H_k, H_l, and H_m) are significantly shifted to higher field compared with those in Figure 4a, indicating that a host-stabilized intramolecular CT complex exists. The splitting of **NP** protons is attributed to the breaking of magnetically equivalent environments due to the significant conformational restriction inside CB[8][19] and lock of fast exchange by the addition of new CB[8]. H_e and H_f on the linker are shifted downfield, which indicates that the linker is outside CB[8]. From the UV/vis spectra of 1^{2+} in the presence of 2.0 equiv of CB[8] (Figure 1), we can confirm that the host-induced intramolecular CT complex still exists in solution.

For the other group protons (H_d', H_a', H_c' and H_b') in **MCV**, H_a' and H_d' exhibit a remarkable downfield shift, while H_c' and

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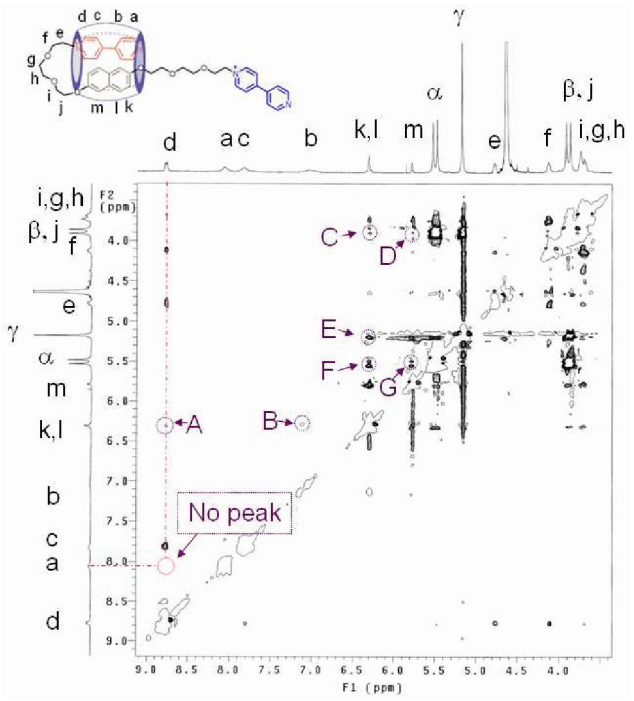

Figure 3. Partial ^{1}H−^{1}H ROESY NMR spectrum of $\mathbf{1}^{2+}$ with addition of 1.0 equiv of CB[8] ([$\mathbf{1}^{2+}$] = [CB[8]] = 1.0 mM, D_2O, 300 MHz, 298 K).

H_b' are shifted upfield. This observation should be attributed to the **MCV** unit existing inside CB[8]. In the NOESY spectrum of $\mathbf{1}^{2+}$ in the presence of 2.0 equiv of CB[8] (Figure 5), we can easily find a strong NOE cross-peak between H_a' and H_d' (peak H), indicating that the two protons must come from two head−tail-stacking **MCV** units. The NOE cross-peak between H_a and H_d may be attributed to the exchange of these two different **MCV** units. In the control experiment, we find that

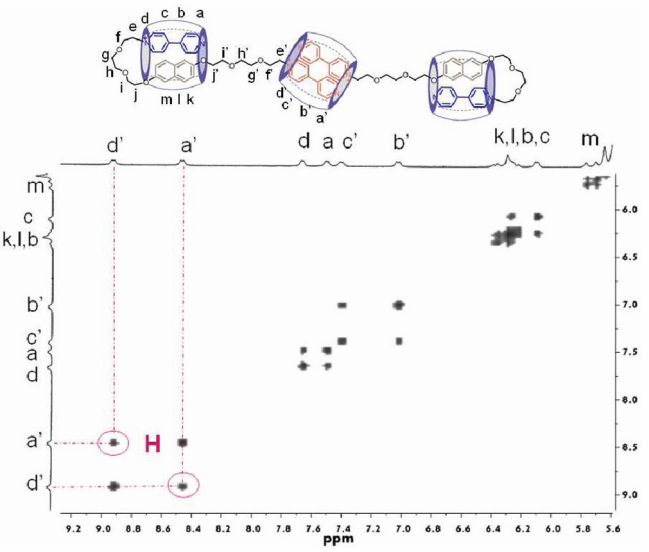

Figure 5. Partial ^{1}H−^{1}H NOESY NMR spectrum of $\mathbf{1}^{2+}$ (1.0 mM) with addition of 2.0 equiv of CB[8] (2.0 mM) (D_2O, 300 MHz, 298 K).

CB[8] dominantly includes two **MBipy** molecules to form a 1:2 complex (see the Supporting Information). In addition, two groups of distinctly different H_α/H_α' and H_γ/H_γ' peaks in Figure 4f suggest that CB[8] must include two different species. Combining the above observations, we may deduce reasonably that the present system is a [5]pseudorotaxane (Figure 2), in which there exist two 1:1:1 **MCV**·**NP**·CB[8] complex and one 2:1 **MCV**·CB[8] complex. The formation of the [5]-pseudorotaxane $\mathbf{4}^{4+}$ is further evidenced by ESI-MS. The peaks at 1016 and 1348 are assigned to [**1**·CB[8]]$^{2+}$ and [$\mathbf{1}_2$·CB[8]$_3$]$^{4+}$, respectively (Figure S13 in the Supporting Information). Moreover, a Job's plot also supports the formation of 3:2 host−guest complex in solution (Figure S14 in the Supporting Information).

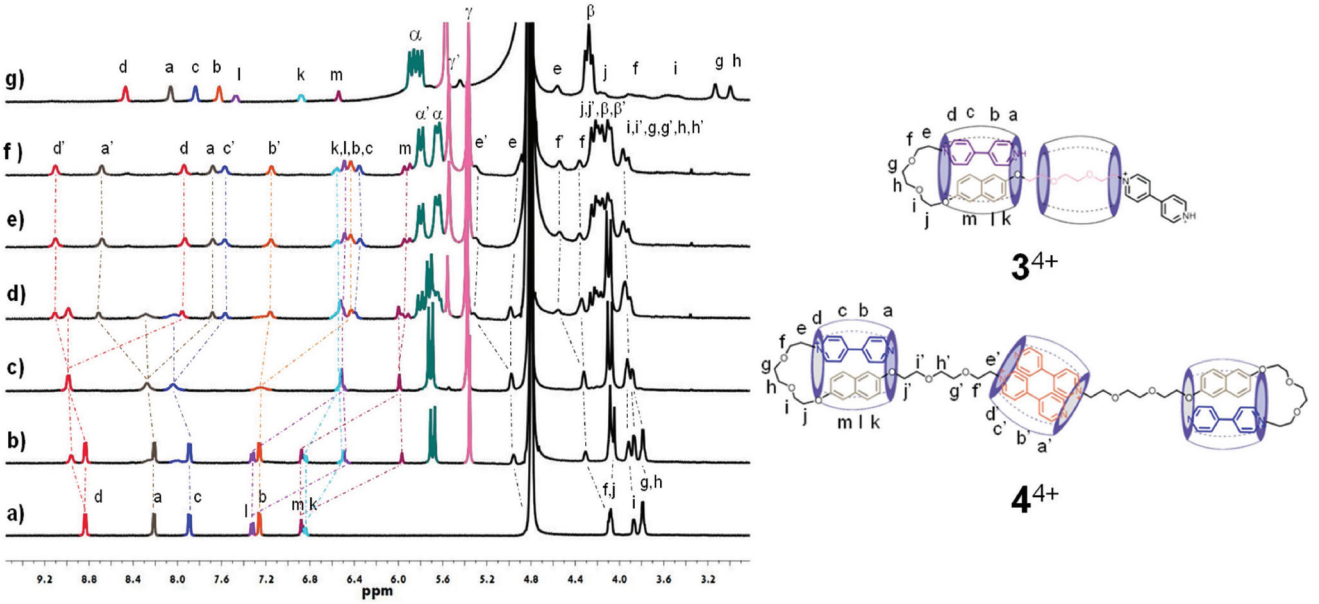

Figure 4. Partial ^{1}H NMR spectra (400 MHz, D_2O, 298 K) of (a) $\mathbf{1}^{2+}$, (b) $\mathbf{1}^{2+}$ + 0.4 equiv of CB[8] (0.4 mM), (c) $\mathbf{1}^{2+}$ + 1.0 equiv of CB[8] (1.0 mM), (d) $\mathbf{1}^{2+}$ + 1.2 equiv of CB[8] (1.2 mM), (e) $\mathbf{1}^{2+}$ + 1.5 equiv of CB[8] (1.5 mM), (f) $\mathbf{1}^{2+}$ + 2.0 equiv of CB[8] (2.0 mM), and (g) $H_2\mathbf{1}^{4+}$ + 2.0 equiv of CB[8] (2.0 mM). ([$\mathbf{1}^{2+}$] = [$H_2\mathbf{1}^{4+}$] = 1.0 mM, H_a', H_b', H_c', H_d', H_e', H_f', H_k', H_l', H_m', H_α' and H_γ' belong to the **MCV**·CB[8] 2:1 complex.)

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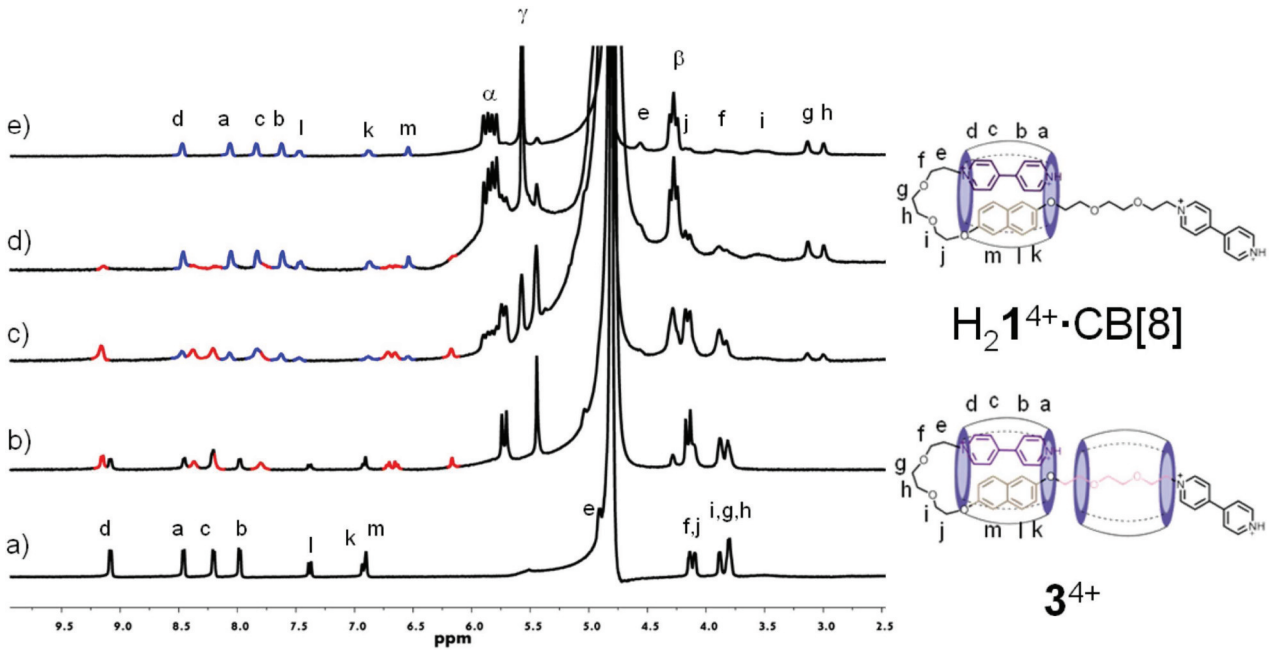

Figure 6. Partial ^{1}H NMR spectra: (a) $H_2\mathbf{1}^{4+}$, (b) $H_2\mathbf{1}^{4+}$ + 0.5 equiv of CB[8] (0.5 mM), (c) $H_2\mathbf{1}^{4+}$ + 1.2 equiv of CB[8] (1.2 mM), (d) $H_2\mathbf{1}^{4+}$ + 1.8 equiv of CB[8] (1.8 mM), (e) $H_2\mathbf{1}^{4+}$ + 2.2 equiv of CB[8] (2.2 mM). (D_2O, 400 MHz, 298 K, [$H_2\mathbf{1}^{4+}$] = 1.0 mM). The red peaks belong to the 1:1 host–guest complex $H_2\mathbf{1}^{4+}$·CB[8]; the blue peaks belong to the 2:1 host–guest complex $\mathbf{3}^{4+}$.

Switching Process of $\mathbf{4}^{4+}$ and [3]Pseudorotaxane $\mathbf{3}^{4+}$. Through acidification, the **MCV** unit is fully protonated to afford **MCVH**, and the axle molecule $\mathbf{1}^{2+}$ is accordingly transferred to $H_2\mathbf{1}^{4+}$. Upon the addition of 27.0 equiv of hydrochloric acid to the aqueous solution of $\mathbf{4}^{4+}$, the solution becomes red accompanied by a new CT band appeared around 490 nm in the UV/vis spectrum (Figure 1), which indicates the formation of the host-stabilized intramolecular heteroguest pair as 1:1:1 **MCVH**·**NP**·CB[8] complex.[18,20] Here, the 2:1 **MCVH**·CB[8] complex cannot exist because of the additional positive charge at the nitrogen terminal. Therefore, the disassembly of [5]pseudorotaxane $\mathbf{4}^{4+}$ is a spontaneous process.

To understand the condition of CB[8] after acidification, we performed NMR experiments to investigate the binding process of $H_2\mathbf{1}^{4+}$ with CB[8] (Figure 6). The ^{1}H NMR spectra suggest a complicated binding process. Initially, when 0.5 equiv of CB[8] was added, new proton signals (Figure 6b) appeared at 6.17 and 6.63–6.73 ppm which belong to the **NP** unit included by CB[8], and proton H_d is shifted downfield while proton H_a and H_b are shifted upfield. It is suggested that one of the bipyridinium units is also incorporated by CB[8], while the other one is "free". All of the observations indicate the formation of a host-stabilized CT complex $H_2\mathbf{1}^{4+}$·CB[8].

Upon the further addition of CB[8] to the solution, another group of resonances appears (Figure 6c) which belongs to a new complex, and after addition of 2.2 equiv of CB[8], further addition of CB[8] hardly affects any peaks (Figure 6e). The proton signals ascribed to 1:1 host–guest complex $H_2\mathbf{1}^{4+}$·CB[8] (see its structure in Figure 6) disappear, and only the new group of signals exists. From the analysis of the spectra of $H_2\mathbf{1}^{4+}$ with addition of 2.2 equiv of CB[8] (Figure 6e), it can be found that the resonances on the **NP** unit (H_m and H_k) were shifted upfield. Dramatic upfield shifts for the bipyridinium unit (proton H_a, H_b, H_c and H_d) are observed, suggesting that the free bipyridinium unit should be included in the cavity of CB[8]. It is noteworthy that the proton signals of triethylene glycol linker (H_e, H_f, H_g, H_i, and H_j) are also shifted upfield, indicating that the linker should also be included in the cavity of CB[8]. However, from the structure of $H_2\mathbf{1}^{4+}$, it is impossible that a CB[8] includes simultaneously both the linker and the free bipyridinium unit. In addition, it has been demonstrated that the triethylene glycol linker with one or two positive charged terminal can offer a stronger binding affinity than **MCVH** unit toward CB[8].[21] Thus, a second CB[8] could prefer the triethylene glycol linker. One reasonable explanation for the dramatic NMR change in the aromatic and the triethylene glycol regions is CB[8] shuttles between the bipyridinium unit and triethylene glycol linkers.

Combining above observations and analysis, a [3]-pseudorotaxane is suggested to exist in the solution as a dominant species. The formation of the [3]pseudorotaxane $\mathbf{3}^{4+}$ is further evidenced by ESI-MS. The peaks at 841 and 1120 were assigned to $[H_2\mathbf{1}\cdot CB[8]_2]^{4+}$ and $[H\mathbf{1}\cdot CB[8]_2]^{3+}$, respectively. The peaks at 678 was assigned to $[H\mathbf{1}\cdot CB[8]]^{3+}$ (Figure S21 in the Supporting Information). This [3]-pseudorotaxane should contain a 1:1:1 **MCVH**·**NP**·CB[8] complex and a 1:1 linker/CB[8] complex, as $\mathbf{3}^{4+}$ in Figure 2.

To switch $\mathbf{3}^{4+}$ back to $\mathbf{4}^{4+}$, NaOH was added to the solution of $\mathbf{3}^{4+}$ and the solution color changed back to yellow. Upon neutralization by NaOD, the ^{1}H NMR spectrum of $\mathbf{3}^{4+}$ (Figure S16 in the Supporting Information) is similar with that of $\mathbf{4}^{4+}$. These observations suggest that the [5]pseudorotaxane structure has been restored. Moreover, through monitoring the change of CT band in UV/vis spectra, we can confirm the acid/base controlled cycling process (Figure S17 in the Supporting Information).

We also performed a diffusion-ordered spectroscopy (DOSY) experiment to investigate the acid/base controlled interconversion process between the two pseudorotaxanes (Figures S19 and S20 in the Supporting Information). Only one species was found in each pseudorotaxane system. When acid was added to the solution of $\mathbf{4}^{4+}$, the measured diffusion

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coefficients increased considerably from 1.73×10^{-10} to 2.29×10^{-10} m^2 s^{-1}. From the Stokes–Einstein equation:[22]

$$D = \frac{k_b T}{6\pi\eta R} \quad (1)$$

$$\left(\frac{D_1}{D_2}\right)^3 = \left(\frac{R_2}{R_1}\right)^3 = \frac{V_2}{V_1} \quad (2)$$

Thus the complex size change can be estimated by the ratio of the diffusion coefficients:

$$\frac{V_2}{V_1} = \left(\frac{2.29 \times 10^{-10}}{1.73 \times 10^{-10}}\right)^3 = 2.3 \quad (3)$$

This result suggests that the average aggregation size decreases by 2.3 times upon acidification.[23,a] This result is consistent with the size change between the two supramolecular species.

CONCLUSIONS

We have prepared a [5]pseudorotaxane through "pasting" two axle molecules $\mathbf{1}^{2+}$ mediated by a cyclic wheel component CB[8], in which one **MCV** unit in $\mathbf{1}^{2+}$ constitutes heteroguest pair with the **NP** unit to form the host-induced intramolecular CT complex, while the other **MCV** does homoguest pair with one of **MCV** units in the other $\mathbf{1}^{2+}$ to form 2:1 complex with CB[8]. Furthermore, the [5]pseudorotaxane can transform to a [3]pseudorotaxane through the addition of acid. By controlling the assembly and disassembly of the CB[8]·**MCV** 1:2 ternary complex, we can achieve the interconversion between [5]-pseudorotaxane $\mathbf{4}^{4+}$ and [3]pseudorotaxane $\mathbf{3}^{4+}$. The result presented here not only provides an unexplored approach for elongating reversibly the linear molecules by noncovalent interactions, but also will benefit the application to dynamic, smart, self-healing functional materials and the development of the stimuli-responsive molecular devices.

EXPERIMENTAL SECTION

General Methods and Materials. All chemicals were commercially available unless noted otherwise. Compound **6**[24] was prepared according to the literature procedure. NMR data were recorded on 300 M, 400 and 600 M spectrometer, and chemical shifts were recorded in parts per million (ppm). All chemical shifts were referenced to the internal MeOH signal at 3.34 ppm or MeCN signal at 2.06 ppm.[25] Absorption spectra were recorded on a UV/vis spectrometer. Mass spectra were recorded using ESI or MALDI mode MS. The acidified guests were obtained through addition of 27.0 equiv of DCl or HCl to the solution directly, and it is an excess amount to ensure the full conversion of the complexes. The neutralization was realized through addition of equivalents of NaOD or NaOH to the acidified solution.

Preparation of Compound 7. 2,6-Dihydroxynaphthalene (2.00 g, 12.5 mmol) and triethylene glycol monotosylate **6** (7.52 g, 24.7 mmol) were dissolved in acetonitrile (150 mL), and then K_2CO_3 (6.86 g, 49.6 mmol) and LiBr (100 mg, 1.10 mmol) were added to this solution. The resulting mixture was heated under reflux in a N_2 atmosphere for 48 h. After being cooled, the reaction mixture was filtered and then concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL) and then washed twice with 100 mL of brine/10% NaOH aqueous solution (3:1). The organic phase was dried and evaporated. The crude product was purified by column chromatography over silica gel (eluent: $CHCl_3/CH_3OH$ = 40:1) to afford **7** as a white solid (3.77 g, 71.2%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 (s, 2H), 7.29 (s, 2H), 7.15 (s, 2H), 4.18 (s, 4H), 3.81 (s, 4H), 3.53 (m, 18H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.8, 129.4, 128.1, 118.9, 107.0, 72.4, 69.8, 69.0, 67.2, 60.2; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{22}H_{32}O_8Na^+$ 447.1989, found 447.1992. Anal. Calcd for $C_{22}H_{32}O_8{\cdot}H_2O$: C, 59.72; H, 7.74. Found: C, 59.43; H, 7.44.

Preparation of Compound 8. The diol **7** (3.00 g, 7.07 mmol), Et_3N (2.88 g, 28.5 mmol), and DMAP (20.0 mg, 0.160 mmol) were dissolved in $CHCl_3$ (100 mL). A solution of TsCl (2.69 g, 14.1 mmol) in $CHCl_3$ (50.0 mL) was added dropwise to this mixture during 1 h at room temperature. After the addition was complete, the reaction mixture was stirring for 8 h. It was then washed with saturated $NaHCO_3$ aqueous solution and brine. The organic phase was dried and evaporated off. The crude product was purified by column chromatography over silica gel (eluent: EtOAc/petroleum ether = 2:1) to afford **8** as a white solid (4.29 g, 86.6%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.6 Hz, 4H), 7.62 (d, J = 8.9 Hz, 2H), 7.31 (d, J = 7.9 Hz, 4H), 7.14 (d, J = 8.9 Hz, 2H), 7.09 (s, 2H), 4.20 (t, J = 4.6 Hz, 4H), 4.16 (t, J = 4.6 Hz, 4H), 3.88 (t, J = 4.5 Hz, 4H), 3.73–3.67 (m, 8H), 3.64 (m, 4H), 2.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 144.8, 133.0, 129.8, 128.2, 128.0, 119.3, 107.1, 70.81, 69.9, 69.3, 68.8, 67.5, 21.6; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{36}H_{44}O_{12}S_2Na^+$ 755.2166, found 755.2157. Anal. Calcd for $C_{36}H_{44}O_{12}S_2{\cdot}CH_3OH$: C, 58.10; H, 6.32. Found: C, 58.19; H, 6.18.

Preparation of Compound 9.[26] A solution of the ditosylate **8** (4.00 g, 5.71 mmol) and NaI (8.64 g, 57.7 mmol) in Me_2CO (100 mL) was heated under reflux in N_2 atmosphere for 24 h and filtered after cooling. The residue was washed with $CHCl_3$ (100 mL), and the solvent was removed under reduced pressure to afford **9** as a white solid (3.51 g, 95.5%), which was used in subsequent reactions without further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 9.0 Hz, 2H), 7.16 (d, J = 8.9 Hz, 2H), 7.10 (s, 2H), 4.24 (t, J = 4.3 Hz, 4H), 3.93 (t, J = 4.4 Hz, 4H), 3.77 (m, 8H), 3.71 (m, 4H), 3.26 (t, J = 6.9 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 129.8, 128.2, 119.3, 107.2, 72.0, 70.9, 70.3, 69.9, 67.5, 3.0; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{22}H_{30}I_2O_6Na^+$ 667.0024, found 667.0021.

Preparation of Compound 1·2Br. 2,6-Bis(2-(2-(2-iodoethoxy)-ethoxy)ethoxy)naphthalene **9** (840 mg, 1.30 mmol) was added portionwise during 3 days, seven times per day (40.0 mg per portion), to a refluxing solution of 4,4′-bipyridine (2.09 g, 13.4 mmol) in dry acetonitrile (50.0 mL) under N_2. The reaction mixture was maintained under reflux for a further 48 h, and then the solvent was removed under reduced pressure. The residue was purified by column chromatography over silica gel (eluent: 5:4:1 acetone/1.5 M NH_4Cl aqueous solution/methanol) to afford the product as a solid. To remove the NH_4Cl, the solid was dissolved in the minimum volume of H_2O and a concentrated aqueous solution of NH_4PF_6 was added until no further precipitation was observed. The precipitate was filtered off and washed with water to give pure hexafluorophosphate. The counterions were exchanged to Br^- using tetraethylammonium bromide to yield **1**·2Br as a grayish solid (510 mg, 45%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.18 (d, J = 6.5 Hz, 4H), 8.75 (d, J = 4.4 Hz, 4H), 8.56 (d, J = 6.4 Hz, 4H), 7.90 (d, J = 5.4 Hz, 4H), 7.63 (d, J = 8.9 Hz, 2H), 7.21 (s, 2H), 7.08 (d, J = 8.9 Hz, 2H), 4.85 (m, 4H), 4.11 (m, 4H), 3.99 (m, 4H), 3.74 (m, 4H), 3.62 (m, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.7, 152.4, 150.9, 145.8, 140.7, 129.3, 128.1, 124.9, 121.8, 118.8, 106.9, 69.6, 68.9, 68.5, 67.1, 59.8; HRMS (ESI) m/z M^{2+} calcd for $C_{42}H_{46}N_4O_6^{2+}$ 351.1703, found 351.1704; [M + Br]$^+$ calcd for $C_{42}H_{46}BrN_4O_6^+$ 781.2595, found 781.2603. Anal. Calcd for $C_{42}H_{46}Br_2N_4O_6{\cdot}4H_2O$: C, 53.97; H, 5.82; N, 5.99. Found: C, 54.17; H, 6.05; N, 6.21.

Preparation of Compound 10. The diol **7** (2.37 g, 5.59 mmol), Et_3N (1.16 g, 11.4 mmol), and DMAP (10.0 mg, 0.0820 mmol) were dissolved in $CHCl_3$ (100 mL). A solution of TsCl (1.07 g, 5.63 mmol) in $CHCl_3$ (40.0 mL) was added dropwise to this mixture during 12 h at room temperature. After the addition was complete, the reaction mixture was stirring for another 12 h. It was then washed with saturated $NaHCO_3$ aqueous solution and brine. The organic phase was dried and evaporated off. The crude product was purified by column chromatography over silica gel (eluent: $CHCl_3/CH_3OH$ = 100:1) to afford **10** as a white solid (1.46 g, 45%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 8.9 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.14 (dd, J = 11.5, 4.8 Hz, 2H), 7.09 (s, 2H), 4.19 (m, 6H),

3.95−3.84 (m, 4H), 3.78−3.66 (m, 10H), 3.65−3.60 (m, 4H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 144.8, 133.0, 129.8, 128.2, 128.0, 119.3, 107.1, 72.5, 70.8, 70.4, 69.8, 69.3, 68.8, 67.5, 61.8, 21.6; HRMS (FTMALDI) m/z $[M + Na]^+$ calcd for $C_{29}H_{38}O_{10}SNa^+$ 601.2078, found 601.2073. Anal. Calcd for $C_{29}H_{38}O_{10}S$: C, 60.19; H, 6.62. Found: C, 60.11; H, 6.52.

Preparation of Compound 11. *N*,*N*-Dimethylformamide (25.0 mL) was added to compound **10** (1.17 g, 2.02 mmol) and NH_4Br (400 mg, 4.10 mmol). After being stirred for 12 h at 80 °C under N_2, the reaction mixture was concentrated under reduced pressure. The residue was dissolved by $CHCl_3$ (80.0 mL) and then washed with 50.0 mL of distilled water. The organic phase was dried and evaporated off. The crude product was purified by column chromatography over silica gel (eluent: $CHCl_3/CH_3OH$ = 80:1) to afford **11** as a white solid (400 mg, 40.5%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.9 Hz, 2H), 7.16 (d, J = 8.9 Hz, 2H), 7.10 (d, J = 2.1 Hz, 2H), 4.27−4.20 (m, 4H), 3.96−3.89 (m, 4H), 3.83 (t, J = 6.3 Hz, 2H), 3.79−3.70 (m, 10H), 3.66−3.61 (m, 2H), 3.47 (t, J = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 129.8, 128.2, 119.3, 107.2, 72.5, 71.3, 70.9, 70.6, 70.4, 69.9, 69.8, 67.5, 67.4, 61.8, 30.4; HRMS (FTMALDI) m/z $[M + Na]^+$ calcd for $C_{22}H_{31}O_7Br^+$ 486.1248, found 486.1257. Anal. Calcd for $C_{22}H_{31}BrO_7{\cdot}H_2O$: C, 52.28; H, 6.58. Found: C, 52.32; H, 6.52.

Preparation of Compound 5·Br. The compound **11** (250 mg, 0.520 mmol) in 20.0 mL of CH_3CN was added dropwise during 6 h to a refluxing solution of 4,4′-bipyridine (160 mg, 1.00 mmol) in CH_3CN (20.0 mL) The reaction mixture was maintained under reflux for a further 24 h. The reaction mixture was concentrated under reduced pressure and then purified by column chromatography over silica gel (eluent: $CHCl_3/CH_3OH$ = 10:1) to afford **5**·Br as a yellow solid (1.48 g, 45.0%): ^{1}H NMR (400 MHz, D_2O) δ 8.55 (d, J = 6.6 Hz, 2H), 8.05 (d, J = 5.9 Hz, 2H), 7.66 (d, J = 6.3 Hz, 2H), 7.28−7.19 (m, 2H), 7.06 (d, J = 6.0 Hz, 2H), 6.82 (s, 2H), 6.75 (s, 1H), 6.64 (d, J = 8.8 Hz, 1H), 4.55 (m, 2H), 3.97 (m, 2H), 3.81 (m, 4H), 3.69 (m, 2H), 3.60−3.40 (m, 12H), 3.36 (m, 2H); ^{13}C NMR (100 MHz, D_2O) δ 154.4, 152.3, 149.3, 144.6, 140.5, 129.2, 128.5, 128.3, 124.5, 121.4, 118.8, 118.4, 107.2, 106.9, 71.7, 69.9, 69.7, 69.5, 69.0, 68.9, 68.2, 67.3, 67.1, 60.3; HRMS (FTMALDI) m/z M^+ calcd for $C_{32}H_{39}N_2O_7^+$ 563.2752, found 563.2758. Anal. Calcd for $C_{32}H_{39}BrN_2O_7{\cdot}2H_2O$: C, 56.56; H, 6.38; N, 4.12. Found: C, 56.60; H, 6.58; N, 4.14.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization data for new compounds. ^{1}H NMR, ^{1}H−^{1}H COSY, ^{1}H−^{1}H NOESY, DOSY experiment,s and ESI-MS spectra. These materials are available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yuliu@nankai.edu.cn.

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