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Rotaxanes | *Very Important Paper*

VIP

Insights into the Difference Between Rotaxane and Pseudorotaxane

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Abstract: Rotaxane and pseudorotaxane are two types of mechanically interlocked molecular architectures, and there is a clear topological difference and boundary between them. In this work, a "suggested [2]rotaxane **1**⊂α-CD" was constructed based on axle molecule **1** bearing two terminal ferrocene groups and a wheel component α-cyclodextrin (α-CD), but the result obtained indicated that the ferrocene group cannot prevent α-CD dethreading under UV irradiation. That is, **1**⊂α-CD is just a pseudo[2]rotaxane. Furthermore, the two ferrocene groups in **1**⊂α-CD were encapsulated by two cucurbit[7]uril (CB[7]) units to obtain a heteropseudo[4]rotaxane **1**⊂α-CD·2CB[7]. This heteropseudo[4]rotaxane displayed high stability towards harsh temperatures and the isomerization of azobenzene in **1**, so it can be regarded as a [2]rotaxane. In this [2]rotaxane, the stoppers are not the bulky groups covalently bonded to the axle, but the cyclic CB[7] units connected through noncovalent interactions.

Introduction

Pseudorotaxane is the supramolecular precursor of rotaxane, and both of them are challenging and interesting because of their potential applications in nanotechnology, molecular machines, and molecular electronics.[1] They are usually distinguished from each other by considering their structures, in particular, whether the two stoppers at the end of the axle component can prevent dethreading of the cyclic component. When the two stoppers are bulky enough to prevent dethreading of the cyclic component, we usually call it a rotaxane. In cases of the contrary, it is called as pseudorotaxane. Therefore, it seems that the only standard used to distinguish the rotaxane is whether the bulky groups at the end of the axle component can terminate dethreading of the ring component.[1a,2] In addition, it is also noted that the bulky groups as stoppers are normally linked to the axle component in the covalent bond. When some macrocycle molecules, such as cyclodextrin,[3] crown ether,[4] or cucurbituril,[5] are located at the recognition sites of the two ends of the axle by noncovalent interactions, we usually called them pseudo[*n*]rotaxanes, in which the two macrocycle molecules at the axle end were considered to be the ring components, not stoppers. However, if the affinity between these macrocycle molecules and the recognition sites of the axle is high enough to prevent their dethreading in the external stimulus, should we call this system a pseudo[*n*]rotaxane ($n \geq 4$) or a [$n-2$]rotaxane ($n \geq 4$)?

Cyclodextrins (CDs) and cucurbit[*n*]urils (CB[*n*]s) are the two best-established families of hosts and have been widely investigated owing to their fascinating characters.[6] The effective combination of these two host families has recently provided a feasible and convenient way to construct fascinating supramolecular nanostructures.[7] It is well known that CDs and CB[*n*]s bear similar cavity sizes (the cavity sizes of CB[6], CB[7], and CB[8] are similar to those of α-CD, β-CD, and γ-CD, respectively),[8] but they display clear differences in composition and binding properties. CB[*n*]s prefer to bind cationic molecules,[9] whereas CDs are apt to form inclusion complexes with anionic and neutral molecules.[10] CB[7] can form ultra-stable inclusion complexes with cationic ferrocenes, and the equilibrium association constants reach up to $10^{12}\,M^{-1}$ for mono-substituted and $10^{15}\,M^{-1}$ for bis-substituted cationic ferrocene.[11] In contrast, β-CD and γ-CD can form 1:1 inclusion complexes with ferrocene or its monosubstituted derivatives, but α-CD only forms 2:1 sandwich complexes owing to the larger size of ferrocene compared with the internal diameter of α-CD.[12] Therefore, the ferrocene group was normally chosen as the stopper for α-CD in the construction of rotaxane.[13] During the construction of rotaxane, when two or more macrocycle host molecules are used as cyclic components, the corresponding rotaxane is usually called a heterorotaxane, which represents a popular rotaxane system.[14] With the descriptions given above in mind, axle molecule **1** was designed and synthesized, in which two terminal ferrocene groups are bridged by azobenzene. Herein, we report that a "suggested [2]rotaxane" **1**⊂α-CD, in which α-CD is chosen as the cyclic component and ferrocene as stopper, is

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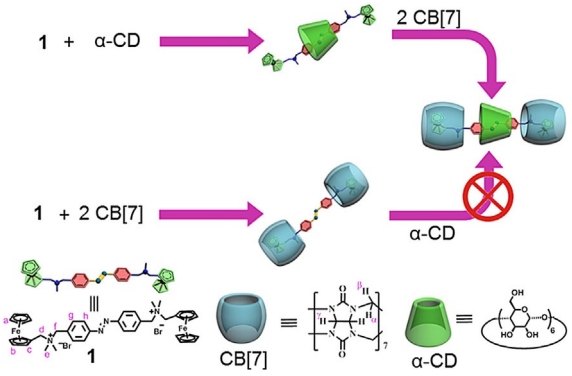
valid as a pseudo[2]rotaxane under UV irradiation, while the resultant pseudo[4]rotaxane capped by CB[7] units at the two ends of the above pseudo[2]rotaxane is very stable, so one could regard this pseudo[4]rotaxane as a [2]rotaxane terminated by CB[7] units (as shown in Scheme 1).



Scheme 1. Schematic illustration of the construction of the pseudorotaxane and rotaxane.

Results and Discussion

Axle molecule **1** was effectively synthesized and characterized by ^{1}H NMR, ^{13}C NMR, and ESI-MS spectroscopy. Firstly, the interaction between **1** and CB[7] was investigated by ^{1}H NMR spectroscopy. As shown in Figure 1, upon the addition of CB[7], all of the protons on ferrocene moieties, the methene protons d and f, and the methyl protons e experienced an upfield shift in various degrees, while the protons (g) on azobenzene shifted downfield. The corresponding CB[7]-induced shift pattern suggests that the two ferrocene residues in **1** are included deeply in the cavity of CB[7], and the positively charged nitrogen in **1** is just included slightly, whereas the azobenzene part interacts with the carbonyl oxygen atoms on the opening of CB[7]. The 2D rotating-frame Overhauser effect spectroscopy (ROESY)

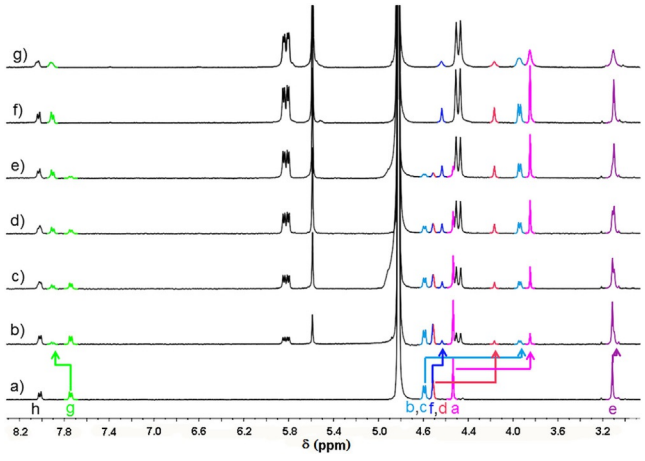


Figure 1. Partial ^{1}H NMR spectra (400 MHz, D_2O, 298 K) of a) **1**, b) **1** + 0.4 equiv of CB[7] (0.32 mM), c) **1** + 0.8 equiv of CB[7] (0.64 mM), d) **1** + 1.2 equiv of CB[7] (0.96 mM), e) **1** + 1.6 equiv of CB[7] (1.28 mM), f) **1** + 2.0 equiv of CB[7] (1.60 mM), and g) **1** + 2.4 equiv of CB[7] (1.92 mM).

experiment of compound **1** in the presence of CB[7] verified the above conformation (see Figure S5 in the Supporting Information). Thereafter, the interaction between **1** and CB[7] was also investigated by UV/Vis spectroscopy. As shown in Figure S6 in the Supporting Information, there is a hyperchromicity for the characteristic absorption of azobenzene with the gradual addition of CB[7], and the intensity of the absorbance increases gradually and is almost fixed at a constant value after two equivalents of CB[7] have been added. On taking the downfield shift of protons g with the addition of CB[7] into consideration, the hyperchromicity phenomenon is probably caused by the formation of hydrogen bonding between protons g and carbonyl oxygen atoms of CB[7]. The combined results of the ^{1}H NMR and UV/Vis spectroscopy experiments jointly demonstrate the formation of pseudo[3]rotaxane **1**⊂2CB[7], as illustrated in Scheme 1 and Figure S5.

As is well known, α-CD can form stable 1:1 inclusion complexes with azobenzene derivatives in its *trans* form owing to the high binding affinities,[15] but only forms 2:1 sandwich complexes with ferrocene and its mono-substituted derivatives.[12b] That is to say, the ferrocene group cannot pass through the cavity of α-CD. However, we found unexpectedly that α-CD cannot prevent the ferrocene groups in **1** from passing through its cavity. We firstly mixed **1** and α-CD with a molar ratio of 1:1 in aqueous solution; then the mixture was subjected to ultrasound at 313 K for half an hour. A small red-shift accompanied by a little hypochromicity was observed in its absorbance spectrum compared with free **1** (Figure 2a). For the circular dichroism (CD) spectrum of this mixture, the negative Cotton peak and the positive Cotton peak (Figure 2b) were assigned to the n–π* and π–π* characteristic absorptions of azobenzene, respectively, which indicates that the azobenzene moiety is located in the cavity of α-CD, that is, the product is a binary inclusion complex **1**⊂α-CD. In the ^{1}H NMR spectrum of **1** in the presence of α-CD (Figure S7 in the Supporting Information), the protons on azobenzene underwent considerable changes, which were mainly caused by the formation of the inclusion complex with α-CD. Furthermore, the 2D ROESY spectrum provided more detailed structural information about **1**⊂α-CD. As shown in Figure S8 in the Supporting Information, the obvious cross-peak is assignable to the nuclear Overhauser enhancement (NOE) correlation between the azobenzene protons and α-CD. The formation of the 1:1 **1**⊂α-CD complex is also evidenced by ESI-MS. The peak at *m/z* 910 was assigned to $[\mathbf{1}\subset\alpha\text{-CD}+\text{MeOH}+\text{K}-\text{Br}]^{2+}$ (see Figure S9 in the Supporting Information). By combining the above results together in this special azobenzene-bridged bis-ferrocene **1**, it might demonstrate that α-CD can slip over the ferrocene groups of **1** to its azobenzene part, thereby forming the 1:1 inclusion complex **1**⊂α-CD. This "unreasonable" process may be attributed to a tumbling or rotating of the glycosidic bonds in α-CD with an external energy input, thus being beneficial to ferrocene slipping over the cavity of α-CD.

When two equivalents of CB[7] are added to the solution of **1**⊂α-CD in D_2O, the proton signals on the ferrocene residues are significantly shifted to higher field, whereas those on the azobenzene hardly change relative to those of **1**⊂α-CD (see

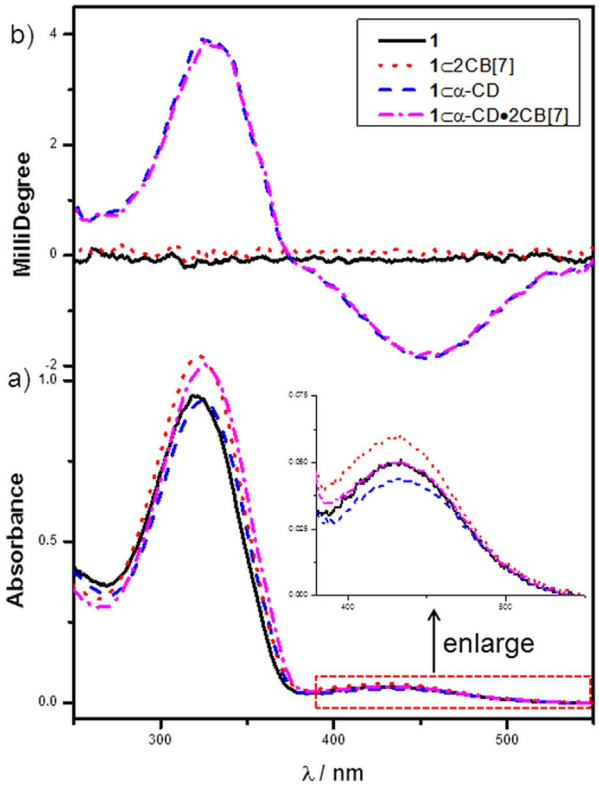


Figure 2. a) UV/Vis and b) CD spectra of **1**, **1**⊂α-CD, **1**⊂2CB[7], and **1**⊂α-CD·2CB[7]; the inset is the enlarged UV/Vis spectra from 380–550 nm (pH 7.2 phosphate buffer, 298 K; [**1**] = [α-CD] = 1/2[CB[7]] = 0.05 mM).

Figure S7 in the Supporting Information). The absorption intensity of **1**⊂α-CD is enhanced clearly by the addition of CB[7] (Figure 2a), whereas the intensity of the CD signal undergoes little change after the addition of CB[7] (Figure 2b). In the 2D ROESY spectrum of this quaternary mixture of **1**, α-CD, and 2CB[7]s (Figure 3), we can easily find NOE cross-peaks not only between the protons of azobenzene and H3 and H5 of α-CD (peaks A), but also between the protons of ferrocene and those of CB[7] (peaks B). These combined observations indicate that the azobenzene and ferrocene moieties of **1** are included in the cavities of α-CD and CB[7], respectively. That is, when two equivalents of CB[7] are added, the pseudo[2]rotaxane **1**⊂α-CD is transformed to the pseudo[4]rotaxane **1**⊂α-CD·2CB[7].

Unexpectedly, when an equivalent of α-CD was added to the solution of pseudo[3]rotaxane **1**⊂2CB[7] in D_2O and then the mixture was subjected to ultrasound at 313 K for half an hour, the proton signals on axle molecule **1** hardly changed (see Figure S10 in the Supporting Information). This observation suggests that α-CD cannot slip over the terminal group of pseudo[3]rotaxane **1**⊂2CB[7] to form pseudo[4]rotaxane **1**⊂α-CD·2CB[7]. That is to say, the inclusion interaction between CB[7] and the ferrocene residues in **1** should be stable enough, which leads to hardly any dissociated **1** for α-CD slipping over.

There is an azobenzene group in axle molecule **1**, so it could isomerize from the *trans* to *cis* form under UV irradiation. As expected, with irradiation at 365 nm, the π–π* characteristic absorption of azobenzene decreases clearly in **1**, **1**⊂α-CD, **1**⊂2CB[7], and **1**⊂α-CD·2CB[7], whereas that of n–π* increased (Figure 4). These results indicate that the azobenzene moiety can isomerize from the *trans* to *cis* form not only in **1** but also in its inclusion complexes. As shown in Table S1 in the Supporting Information, the photoisomer rates calculated by the first dynamic function are $k_1 < k_{1\subset\alpha\text{-CD}} \approx k_{1\subset 2CB[7]} < k_{1\subset\alpha\text{-CD}\cdot 2CB[7]}$. That is, the greater the number of components in the complexes, the faster the rate of photoisomerism. This observation could be attributed to the addition of α-CD and/or CB[7], which leads to the redshift and enhancement of the absorption intensity of **1**, and the resulting enhancement of the absorption efficiency at 365 nm.[16] However, the percentage of the *cis* form at the photostationary state (PSS) undergoes little change, which is mainly determined by the structure of azobenzene.[17]

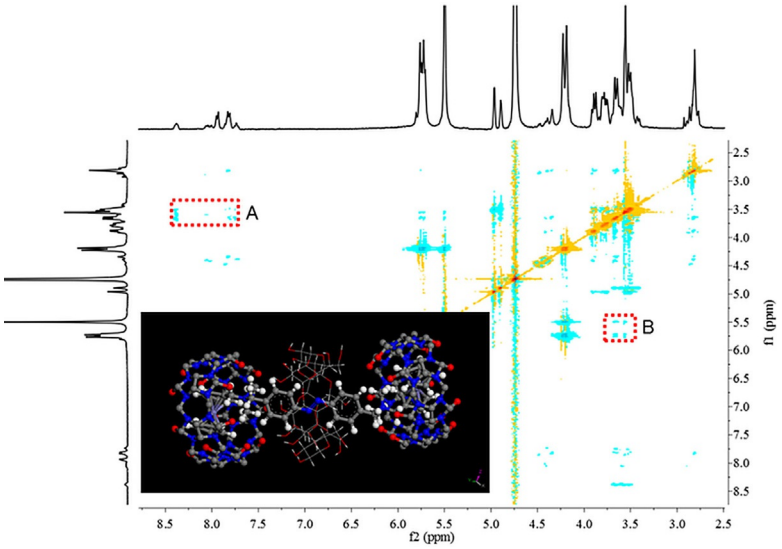


Figure 3. 2D ROESY spectrum of **1**⊂α-CD·2CB[7] (D_2O, 400 MHz, pD 7.2, 298 K; [**1**] = [α-CD] = 1/2[CB[7]] = 0.8 mM).

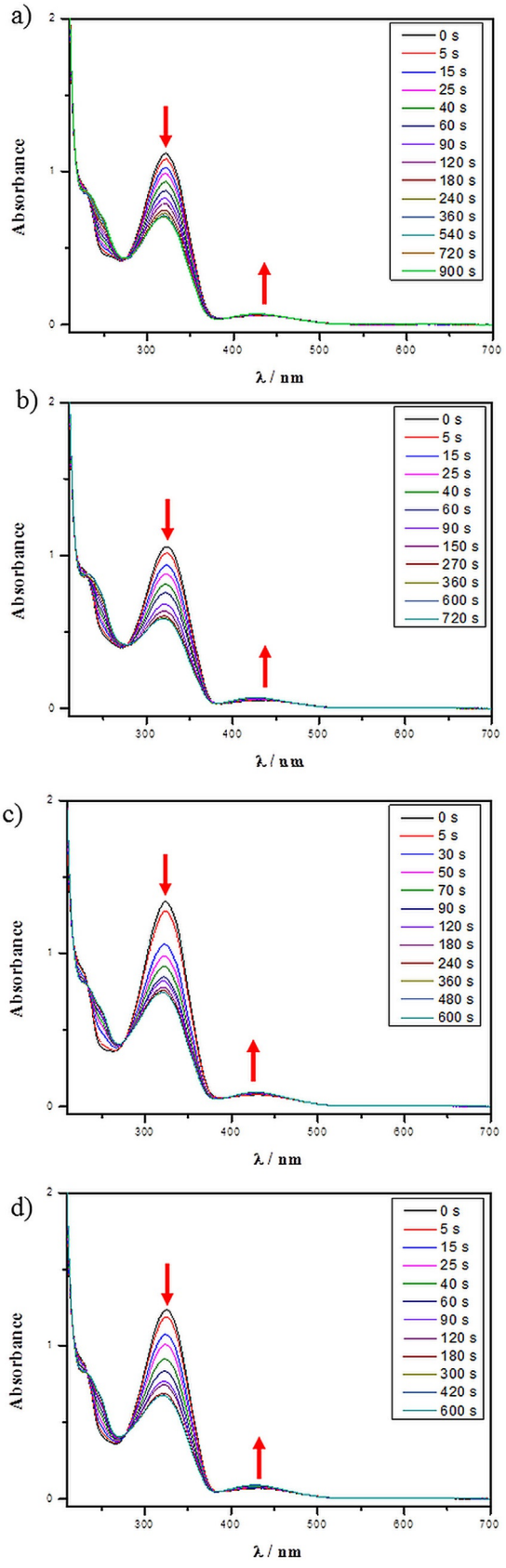


Figure 4. UV/Vis spectra of a) **1**, b) **1**⊂α-CD, c) **1**⊂2CB[7], and d) **1**⊂α-CD·2CB[7] under UV irradiation (365 nm) with different times in phosphate buffer (pH 7.2, 0.1 M) at 298 K ([**1**] = [α-CD] = 1/2[CB[7]] = 0.05 mM).

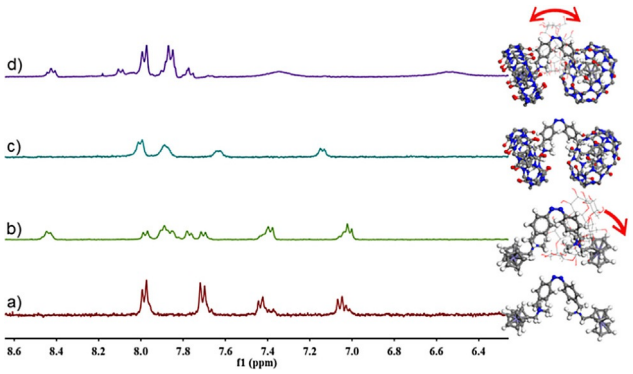


Figure 5. Partial ^{1}H NMR spectra (D_2O, 400 MHz, 298 K) of the photostationary state of a) **1**, b) **1**⊂α-CD, c) **1**⊂2CB[7], and d) **1**⊂α-CD·2CB[7] with UV irradiation for 20 min.

The photoisomer behavior was also investigated by NMR spectroscopy. As can be seen from Figure 5a, there are two groups of azobenzene protons in **1** that appear upfield after irradiation. They should be assigned to those of the *cis* form of azobenzene. A similar phenomenon also takes place for **1**⊂α-CD and **1**⊂2CB[7], which suggests that the *cis* form of the azobenzene moiety in **1** is not included by α-CD or CB[7]. That is to say, the photoisomerization of azobenzene leads α-CD to slip off ferrocene in the **1**⊂α-CD complex, thus we may define this binary inclusion complex as a pseudo[2]rotaxane. Regarding this special axle molecule **1**, α-CD can slip over the ferrocence group to form a binary inclusion complex and be dethreaded with UV irradiation. It is also easily noticed that the proton signals of the quarternary complex **1**⊂α-CD·2CB[7] exhibit a fast-exchange equilibrium on the ^{1}H NMR spectroscopic timescale after irradiation at 365 nm (Figure 5d), which indicates that α-CD should swing quickly at the *cis* form of the azobenzene moiety. The two ferrocene⊂CB[7] moieties in **1**⊂α-CD·2CB[7] play a role as stopper. Furthermore, the reversibility of the photoisomerization of the pseudo[4]rotaxane **1**⊂α-CD·2CB[7] was investigated by UV/Vis spectroscopy. As shown in Figure S11 in the Supporting Information, it displayed good reversibility towards UV (365 nm) and visible (450 nm) light.

To accompany the investigation of the photobehavior of **1** and its inclusion complexes, their thermostability was further investigated by UV/Vis spectroscopy with temperatures ranging from 298 to 343 K.[18] As shown in Figure 6 and in Figure S12 in the Supporting Information, the absorption intensities of **1** and **1**⊂α-CD at 323 nm undergo a slight decrease as the temperature is increased, whereas those of **1**⊂2CB[7] and **1**⊂α-CD·2CB[7] are almost fixed at a stable value. The first phenomenon is probably caused by the concentration being diluted from the heat-expansion effect, and the second might be attributed to CB[7] including the ferrocene part much deeper and drawing the azobenzene fraction closer to the carboxyl of CB[7] with the temperature increased, thereby offsetting the heat-expansion effect. Furthermore, the absorption intensity of the inclusion complexes containing α-CD remains smaller than that without α-CD during the increase of the temperature

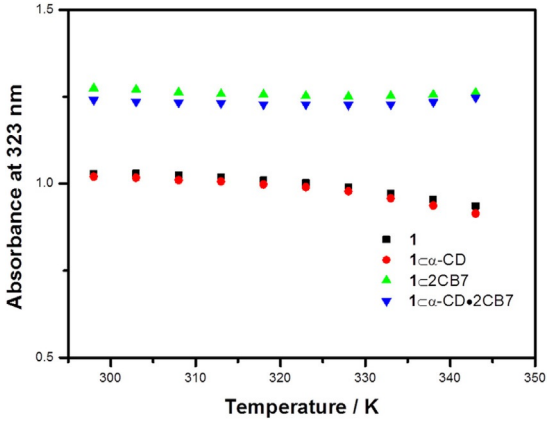


Figure 6. The stability of **1**, **1**⊂α-CD, **1**⊂2CB[7], and **1**⊂α-CD·2CB[7] towards temperature at 323 nm by UV/Vis spectroscopy (pH 7.2 phosphate buffer.)

from 298 to 343 K. As shown above in Figure 2, the absorption spectrum of **1** undergoes a redshift and hypochromicity when forming inclusion complexes with α-CD. On taking this as standard, the results jointly indicate that axle molecule **1** cannot be dethreaded from α-CD and CB[7]. That is to say, the inclusion complexes formed by **1** and α-CD and/or CB[7]s have a high stability toward harsh temperatures.

On combining the investigation of photobehaviors and thermostabilities together, the **1**⊂α-CD·2CB[7] complex constructed from the pseudo[2]rotaxane capped by CB[7] displays high stability towards UV irradiation and high temperature. Thus, this raises the question as to whether the CB[7] in these inclusion complexes should be considered a "ring" or a "stopper", and furthermore, whether this quaternary complex should be called a pseudo[4]rotaxane or [2]rotaxane. By definition, rotaxanes are compounds in which "bulky end groups prevent the extrusion of a threaded chain from a macrocycle".[2d] Therefore, the quaternary inclusion complex **1**⊂α-CD·2CB[7] can be called a [2]rotaxane, in which the two ferrocene⊂CB[7] moieties are considered to be a "stopper", and it was bulky enough and insurmountable for α-CD to be dethreaded from axle molecule **1**.

Conclusion

In conclusion, axle molecule **1** with azobenzene-bridged bisferrocene groups was synthesized, and pseudo[2]rotaxane **1**⊂α-CD was constructed with α-CD. Distinctly differing from the reported conclusion about the ferrocene group as the stopper of α-CD, the present ferrocene groups in **1** cannot prevent α-CD dethreading in the case of the isomerization of the azobenzene moiety from the *trans* to *cis* form under UV irradiation. However, after the two ferrocene groups in **1**⊂α-CD are encapsulated by CB[7]s, the resultant pseudo[4]rotaxane is very stable despite the isomerization of azobenzene and heating stimulus. Therefore, we would regard the stable pseudo[4]rotaxane as [2]rotaxane, in which the stoppers are not the covalently bonded bulky groups, but the cyclic CB[7] through noncovalent interaction. This new observation will open a door for the design of a wide range of rotaxanes, which may have use in specific applications like molecular cars and molecular bearings.

Experimental Section

Materials

All the reagents and solvents were commercially available and used as received unless stated otherwise. The phosphate buffer solution (pH 7.2) was prepared by dissolving disodium hydrogen phosphate ($Na_2HPO_4{\cdot}12H_2O$, 25.75 g) and sodium dihydrogen phosphate ($NaH_2PO_4{\cdot}2H_2O$, 4.34 g) in distilled deionized water (1 L) to make a 0.1 M solution. The pH value of the buffer solution was then verified on a pH meter calibrated with two standard buffer solutions.

Measurements

NMR spectra were recorded by using a Bruker AV400 instrument or a Varian Mercury VX-300 spectrometer in D_2O/[D_6]DMSO. Electrospray ionization mass spectra (ESI-MS) were measured by using an Agilent 6520 Q-TOF-MS mass spectrometer. UV/Vis spectra were recorded on a UV/Vis spectrometer (light path 10 mm). CD spectra were collected on a spectropolarimeter (light path 10 mm) using a quartz cell. The temperature was controlled by a TCU accessory with a temperature probe that was plunged into the cuvette to measure the sample temperature.

Synthesis of Bis(4-methylphenyl)diazene (A1)

Cuprous chloride (30 g) was added to anhydrous pyridine (170 mL), and the mixture was kept stirring at room temperature for more than 10 min; then the solid was filtered and washed with pyridine (30 mL). A portion of *p*-toluidine (43.2 g) was added slowly into the above filtrate and the mixture was stirred for at least 12 h with air blowing over the sample. The pyridine solution was dried directly under vacuum and the solid was washed with a large amount of dichloromethane. The orange solution was dried and further purified by flash column chromatography to give orange compound **A1** (32.4 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.81 (d, $J = 8.3$ Hz, 4H), 7.31 (d, $J = 8.1$ Hz, 4H), 2.43 ppm (s, 6H).

Synthesis of Bis(4-bromomethylphenyl)diazene (A2)

Compound **A2** was synthesized and purified according to a literature procedure.[19] A mixture of **A1** (8.0 g), *N*-bromosuccinimide (NBS; 17.2 g), and benzoyl peroxide (BPO; 0.26 g) was added to CCl_4 (360 mL), and the mixture was heated at reflux overnight under an argon gas atmosphere. The resulting solution was filtered while it was hot and the filter cake was washed with water. Then the orange product was dried under vacuum overnight (9.2 g, 65.6%). ^{1}H NMR (400 MHz,$CDCl_3$): $\delta = 7.90$ (d, $J = 8.4$ Hz, 4H), 7.54 (d, $J = 8.4$ Hz, 4H), 4.56 ppm (s, 4H).

Synthesis of Azobenzene-Bridged Bis-Ferrocenes (1)

A mixture of **A2** (368 mg, 1 mM) and ferrocenemethylamine (972 mg, 4 mM) was dissolved in *N*,*N*-dimethylformamide (DMF; 50 mL) and degassed. The mixture was stirred overnight under an argon atmosphere; thereafter the precipitate was filtered and washed with diethyl ether, and dried under vacuum to give pure orange compound **1** (673 mg, 78.5%). ^{1}H NMR (400 MHz, [D_6]DMSO): $\delta = 8.03$ (d, $J = 7.6$ Hz, 4H), 7.83 (d, $J = 7.6$ Hz, 4H), 4.62–4.52 (m, 12H), 4.43 (s, 4H), 4.28 (s, 10H), 2.83 ppm (s, 12H);

^{13}C NMR (101 MHz, [D$_6$]DMSO): δ = 152.58, 134.39, 131.66, 122.90, 72.77, 72.30, 70.16, 69.00, 65.50, 65.17, 48.05 ppm; ESI-MS: *m/z*: 772.9 $[M-Br]^+$, 805.0 $[M-Br+MeOH]^+$.

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Keywords: cyclodextrins · isomerization · pseudorotaxanes · rotaxanes · supramolecular chemistry

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