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New Insights into the Difference between Rotaxane and Pseudorotaxane

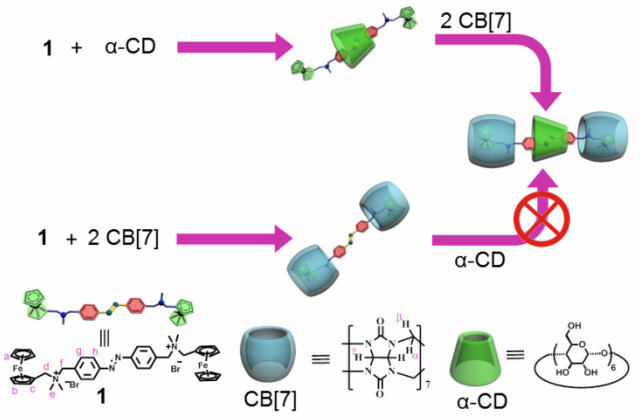
He-Lue Sun,[a] Heng-Yi Zhang,[a,b] Zhen Dai,[a] Xu Han,[a] and Yu Liu*[a,b]

Abstract: Rotaxane and pseudorotaxane are two sorts of different mechanically interlocked molecular architectures, and there is obvious topological difference and boundary between them. In this work, a "suggested [2]rotaxane **1**⊂α-CD" was constructed based on an 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]urils (CB[7]s) to obtain a heteropseudo[4]rotaxane **1**⊂α-CD·2CB[7]. This heteropseudo[4]rotaxane displayed high stability towards tough temperature 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 connected to the axle in covalent bond, but the cyclic CB[7]s by non-covalent interaction.

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] From their topology structures, one usually distinguishes them from 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 as rotaxane. On the contrary, it is called as pseudorotaxane. Therefore, it seems to be the only standard to distinguish the rotaxane 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 covalent bond. When some macrocycle molecules, such as cyclodextrin,[3] crown ether,[4] cucurbituril,[5] locate at the recognition sites of the two end of the axle by non-covalent interaction, we usually called them as pseudo[n]rotaxanes, in which the two macrocycle molecules at the axle end were considered as the ring components, not stoppers. However, if the affinity between these macrocycle molecules and the recognition sites of the axle is enough high to prevent their dethreading in the external stimulus, should we call this system as pseudo[n]rotaxane ($n \geq 4$) or [$n - 2$]rotaxane ($n \geq 4$)?

Cyclodextrins (CDs) and cucurbit[n]urils (CB[n]s) are the two best-established families of hosts and widely investigated due to their fascinating characters.[6] The effective combination of these two host families has provided a feasible and convenient way to construct fascinating supramolecular nanostructures recently.[7] It is well known that CDs and CB[n]s bear similar cavity sizes (the cavity sizes of CB[6], CB[7], CB[8] are similar to these of α-CD, β-CD, γ-CD respectively),[8] but they display obvious differences in composition and binding properties. CB[n]s prefer to bind cationic molecules,[9] while CDs are apt to form inclusion complex with anionic and neutral molecules.[10] For ferrocene derivatives, CB[7] can form ultra-high stable inclusion complex towards 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] On the other hand, β-CD and γ-CD can form 1:1 inclusion complexes with ferrocene or its monosubstituted derivatives, but α-CD only does 2:1 sandwich complexes due to the larger size of ferrocene comparing 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 as heterorotaxane, which stands as a popular system of rotaxane.[14] With these descriptions above in mind, the axle molecule **1** was designed



Scheme 1. Schematic Illustration of the Construction of Pseudorotaxane and Rotaxanes.

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and synthesized, in which two terminal ferrocene groups were bridged by azobenzene. Herein, we want to report that a "suggested [2]rotaxane" **1**⊂α-CD, in which α-CD is chosen as the cyclic component and ferrocene as stopper, is validated to be a pseudo[2]rotaxane under UV irradiation, while the resultant pseudo[4]rotaxane capped by CB[7]s at the two end 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]s (as shown in Scheme 1).

Results and Discussion

The axle molecule **1** was effectively synthesized and characterized by ^{1}H NMR, ^{13}C NMR and ESI-MS spectra. 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 the protons on ferrocene moieties, the methene protons d,f and the methyl protons e experienced an upfield shift in various degree, while the protons g on azobenzene fraction shift 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, while the azobenzene part interacts with the carbonyl oxygens on the portal of CB[7]. The 2D Rotating Frame Overhauser Effect Spectroscopy (ROESY) experiment of compound **1** in the presence of CB[7] certificated the above conformation (Figure S5). Thereafter, the interaction between **1** and CB[7] was also investigated by UV-vis spectra.

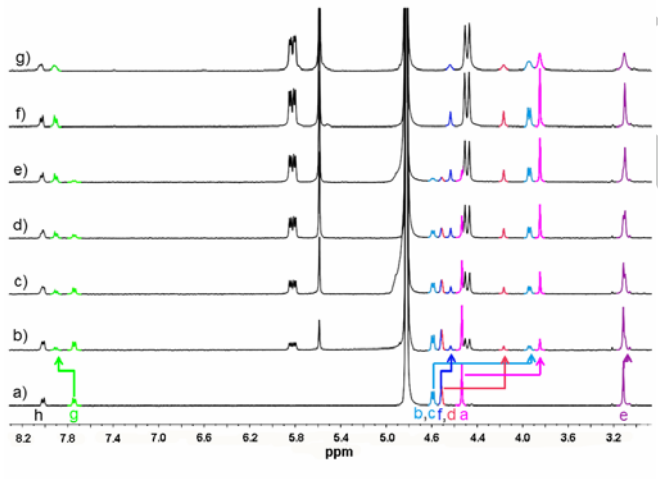

Figure 1. Partial ^{1}H NMR spectra (400 MHz, D_2O, 298 K) of (a) **1**, (b) **1** + 0.4 equiv. of CB[7] (0.32 mM), (c) **1**+ 0.8 equiv. of CB[7] (0.64 mM), (d) **1** + 1.2 equiv. of CB[7] (0.96 mM), (e) **1** + 1.6 equiv. of CB[7] (1.28 mM), (f) **1** + 2.0 equiv. of CB[7] (1.60 mM), (g) **1** + 2.4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

As shown in Figure S6, there is a hyperchromicity for 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 2 equ. CB[7]s added. 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 oxygens of CB[7]. The combined results of ^{1}H NMR and UV-vis experiments jointly demonstrate the formation of pseudo[3]rotaxane **1**⊂2CB[7], as illustrated in Scheme 1 and Figure S5.

As well known, α-CD can form the stable 1:1 inclusion complexes with azobenzene derivatives in its *trans*- form due to the high binding affinities,[15] but only do 2:1 sandwich complex 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** pass through its cavity. We mixed firstly **1** and α-CD with molar ratio 1:1 in aqueous solution, and then the mixture solution was under ultrasound at 313 K for half an hour. A small red-shift accompanying with a little hypochromicity was observed in its absorbance spectrum comparing with free **1** (Figure 2a). The circular dichroism (CD) spectrum of this mixture gives the negative cotton peak and the positive cotton peak (Figure 2b) assigning to the n-π* and π-π* characteristic

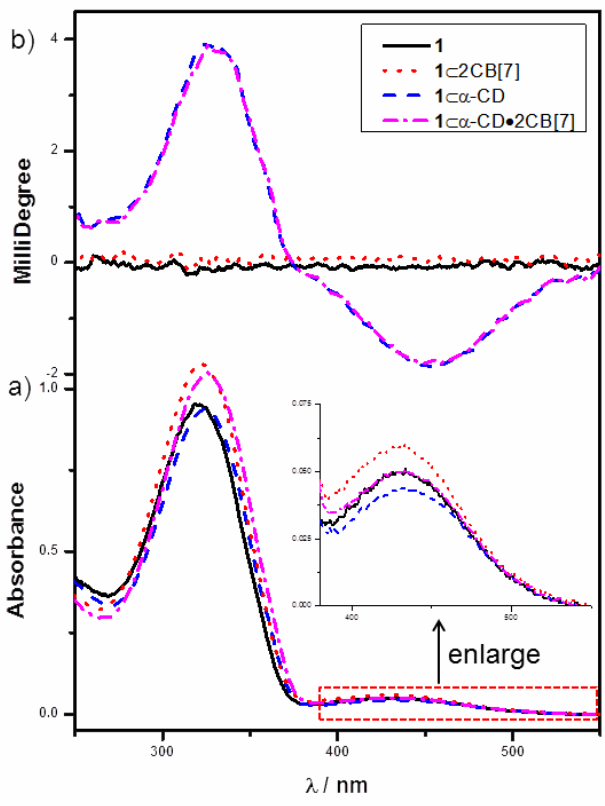

Figure 2. a) UV-vis and b) CD spectra of **1**, **1**⊂α-CD, **1**⊂2CB[7], and **1**⊂α-CD·2CB[7]; the insert is the enlarged UV-vis spectra from 380-550nm. (pH 7.2 phosphate buffer, 298 K; [**1**] = [α-CD] = 1/2[CB[7]] = 0.05 mM)

absorption 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 present of α-CD (Figure S7), the protons on azobenzene underwent considerable changes, which were mainly caused by the formation of inclusion complex with α-CD. Furthermore, the 2D ROESY spectrum provided more detailed structural information about **1**⊂α-CD. As shown in Figure S8, the obvious cross-peak is assignable to the nuclear overhause enhancement (NOE) correlation between protons azobenzene and α-CD. The formation of the 1:1 **1**⊂α-CD complex is also evidenced by ESI-MS. The peak at 910 is assigned to [**1**⊂α-CD + MeOH + K - Br]$^{2+}$ (Figure S9). Combinating the above results together to this special azobenzene-bridged bis-ferrocenes **1**, it might demonstrate that α-CD can slip over the ferrocene groups of **1** to its azobenzene fraction, forming the 1:1 inclusion complex **1**⊂α-CD. The "unreasonable" process may be attributed to a tumbling or rotating of the glycosidic bonds in α-CD with external energy input, thus being beneficial to ferrocene slipping over the cavity of α-CD.

When 2 equiv. of CB[7] were added to the D_2O solution of **1**⊂α-CD, the proton signals on ferrocene residues are significantly shifted to higher field, and those on azobenzene fractions hardly change comparing with those of **1**⊂α-CD (Figure S7). The absorption intensity of **1**⊂α-CD is enhanced obviously with the addition of CB[7] (Figure 2a), while the intensity of CD signal undergoes little change after addition of CB[7] (Figure 2b). In the 2D ROESY spectrum of this quaternary mixture **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 combining observations indicate that the azobenzene and ferrocene moieties of **1** are included in the cavities of α-CD and CB[7], respectively. That is, with two equivalent CB[7]s added, the pseudo[2]rotaxane **1**⊂α-CD is transferred to the pseudo[4]rotaxane **1**⊂α-CD·2CB[7].

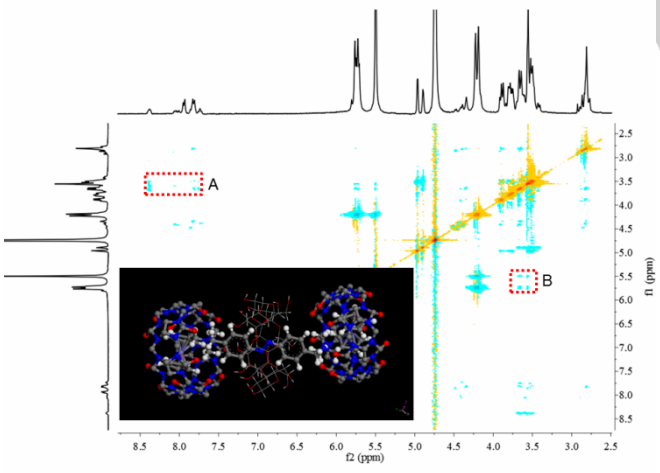

Figure 3. 2D ROESY spectrum of **1**⊂α-CD·2CB[7]. (D2O, 400MHz, pD 7.2, 298K; [**1**] = [α-CD] = 1/2[CB[7]] = 0.8 mM).

Unexpectedly, when equivalent α-CD was added to the D_2O solution of pseudo[3]rotaxane **1**⊂2CB[7] and then the mixture solution was under ultrasound at 313 K for half an hour, all proton signals on axle molecule **1** hardly changed (Figure S10). This observation suggests that α-CD cannot slip over the terminal group of the pseudo[3]rotaxane **1**⊂2CB[7] to form the 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 leading to hardly the dissociated **1** for α-CD slipping over.

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

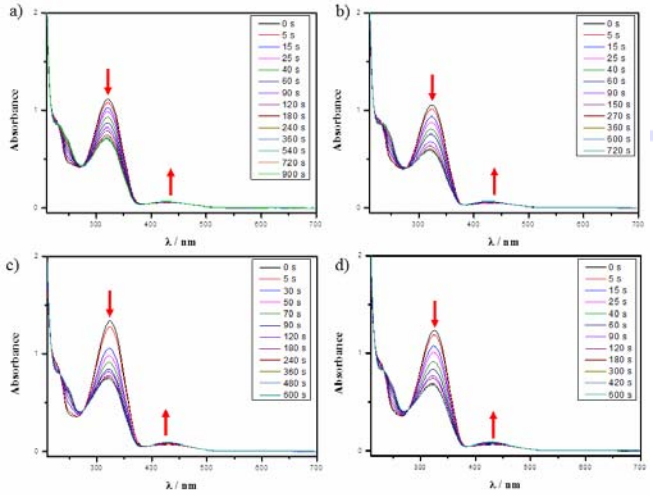

Figure 4. UV-vis spectra of **1** (a), **1**⊂α-CD (b), **1**⊂2CB[7] (c), and **1**⊂α-CD·2CB[7] (d) under UV irradiation (365 nm) with different time in phosphate buffer (pH 7.2, 0.1 M) at 298 K. ([**1**] = [α-CD] = 1/2[CB[7]] = 0.05 mM)

Furthermore, the photoisomer behaviors were investigated by NMR experiments. As can be seen from Figure 5a, there are two groups of azobenzene protons in **1** appeared at up-field after irradiation. They should be assigned to those of the *cis*-form azobenzene. The similar phenomena also take place for **1**⊂α-CD and **1**⊂2CB[7], suggesting that the *cis*-form azobenzene

moiety in **1** is not included by α-CD or CB[7]. That is to say, the photoisomerization of azobenzene leads to α-CD slip off from ferrocene in the **1**⊂α-CD complex, thus we may define this binary inclusion complex as a [2]pseudorotaxane. Towars this special axle molecule **1**, α-CD can slip over the ferrocence group forming binary inclusion complex and dethread off with UV irradition. It is also noticed easily that the proton signals of the quarternary complex **1**⊂α-CD·2CB[7] exhibit the fast-exchange equilibrium during ^{1}H NMR time scale after irradiation under 365 nm (Figure 5d), indicating that α-CD should swing quickly at the cis-form azobenzene moiety. The two ferrocene⊂CB[7] moieties in **1**⊂α-CD·2CB[7] play a role as stopper. Furtherly, the reversiblity of photoisomerization of the pseudo[4]rotaxane **1**⊂α-CD·2CB[7] was investigated by UV-vis experiment. As shown in Figure S11, it displayed good reversibility towards UV (365 nm) and visible (450 nm) light.

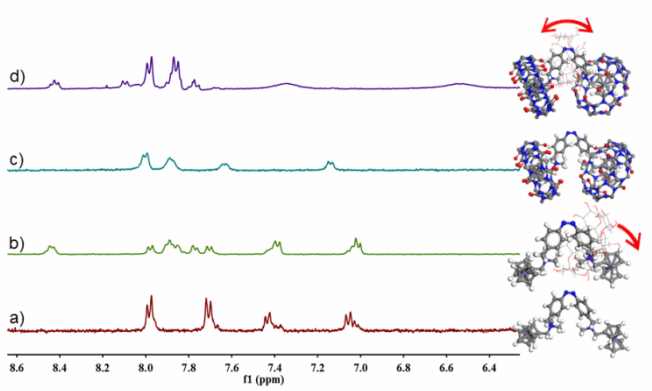

Figure 5. The 1H NMR spectra (D2O, 400 MHz, 298 K) of the photostationary state of (a) **1**, (b) **1**⊂α-CD, (c) **1**⊂2CB[7], and (d) **1**⊂α-CD·2CB[7] with UV irradiation for 20 min.

Accompanied with the investigation of photo behaviors of **1** and its inclusion complexes, their thermostability was further investigated by UV-vis spectrum ranging from 298 K to 343 K.[18] As shown in Figure 6 and Figure S12, the absorption intensities at 323 nm of the axle molecule **1** and **1**⊂α-CD undergo a bit decrease with the temperature increased, while 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 concentration diluted from heat-expansion effect, and the second might be attributed to CB[7] including the ferrocene portion much deeper and drawing the azobenzene fraction closer to the carboxyl of CB[7] with the temperature increased, offsetting the heat-expansion effect. Furthermore, the absorption intensity of the inclusion complexes containing α-CD keep smaller than that without α-CD during rising the temperature from 298 K to 343 K. As mentioned in Figure 2, the absorption spectra of **1** undergo red-shift and hypochromicity when forming inclusion complexes with α-CD. Taking this as a standard, the results jointly indicate that the alxe molecule **1** cannot dethread off from α-CD and CB[7]. That is to say, these inclusion complexes formed by **1** and α-CD or/and CB[7]s bear high stability toward tough temperature.

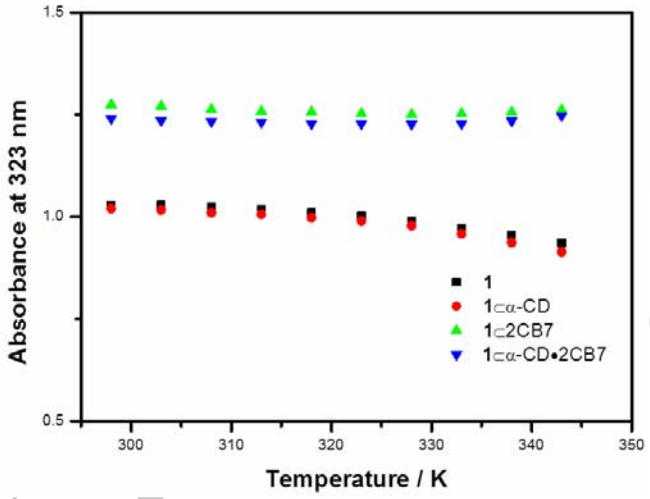

Figure 6. The stability of **1**, **1**⊂α-CD, **1**⊂2CB[7] and **1**⊂α-CD·2CB[7] towards temperature recording at 323 nm by UV-vis experiment. (pH 7.2 phosphate buffer)

Combining the investigation of photo-behaviors 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, there is a rising question confused us whether the CB[7] in these inclusion complexes should be considered as “ring” or “stopper”, furtherly, whether this quaternary complex should be called as 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, this quaternary inclusion complex **1**⊂α-CD·2CB[7] can be called a [2]rotaxane, in which the two ferrocene⊂CB[7] moieties are considered as a “stopper”, and it was bulk enough and insurmountable for α-CD dethreading off the axle molecule **1**.

Conclusions

In conclusion, the axle molecule **1** with azobenzene bridged bis-ferrocene groups was synthesized, and the 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 *trans*- to *cis*- form under UV irradiation. However, after the two ferrocene groups in **1**⊂α-CD were 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 is not the bulky groups in covalent bond, but the cyclic CB[7] by non-covalent interaction. This new observation will open a door for designing a wide range of rotaxane, which maybe possess a lot of specific applications like molecular cars, molecular bearings.

Experimental Section

Materials. All the reagents and solvents were commercially available and used as received unless otherwise specified purification. The phosphate buffer solution of pH 7.2 was prepared by dissolving disodium hydrogen phosphate (Na2HPO4·12H2O, 25.75 g) and sodium dihydrogen phosphate (NaH2PO4·2H2O, 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 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 Agilent 6520 Q-TOF-MS. UV-vis spectra were recorded on a UV-vis spectrometer (light path 10 mm). CD spectra were collected on a spectropolarimeter in a light path 10 mm quartz cell. The temperature was controlled by a TCU accessory with temperature probe which was plunged into the cuvette to measure the sample temperature.

Synthesis of bis-(4-methyl-phenyl)-diazene (A1).

Cuprous chloride (30 g) was added into 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 30 ml pyridine. P-toluidine (43.2 g) was added slowly into the above filtrate and the mixture was stirred at least for 12 h with air blowing. The pyridine solution was dried directly under vacuum. and the solid was washed with large amount of dichloromethane. The orange solution was dried and further purified by flash column chromatography to give out orange compound **A1** (32.4 g, 75%). ^{1}H NMR (400 MHz,$CDCl_3$, ppm): δ = 7.81 (d, J=8.3, 4H), 7.31 (d, J=8.1, 4H), 2.43 (s, 6H).

Synthesis of bis-(4-bromomethyl-phenyl)-diazene (A2).

A2 was synthesized and purified according a literature procedure.[19] A mixture of **A1** (8.0 g), NBS (17.2 g) and BPO (0.26 g) was added into 360 ml CCl_4, the mixture solution was refluxed overnight under Ar 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. (9.2g, 65.6%). ^{1}H NMR (400 MHz,$CDCl_3$, ppm): δ = 7.90 (d, J=8.4, 4H), 7.54 (d, J=8.4, 4H), 4.56 (s, 4H).

Synthesis of azobenzene-bridged bis-ferrocenes (1).

A mixture of **A2** (368 mg, 1 mM) and ferrocenemethylamine (972 mg, 4 mM) were dissolved in DMF (50 ml) and degassed. The mixture was stirred overnight under argon atmosphere, thereafter the precipitation was filtered and washed with mount of ether, dried in vacuo, and then gave out pure orange compound 1 (673 mg, 78.5 %). ^{1}H NMR (400 MHz, DMSO-d6, ppm): δ = 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 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d6): δ = 152.58, 134.39, 131.66, 122.90, 72.77, 72.30, 70.16, 69.00, 65.50, 65.17, 48.05. ESI-MS: 772.9 $[M - Br]^+$, 805.0 $[M - Br + MeOH]^+$.

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Keywords: Supramolecular Chemistry • Pseudorotaxane • Rotaxane

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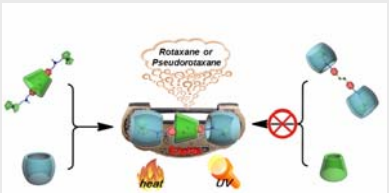
Layout 1:

FULL PAPER

Pseudo[2]rotaxane **1**⊂α-CD and pseudo[3]rotaxane **1**⊂2CB[7] were constructed by axle molecule 1 with α-CD and CB[7] respectively. With CB[7]s capped at the ternimal of **1**⊂α-CD, the heteropseudo[4]rotaxane **1**⊂α-CD·2CB[7] was successfully obtained. Significantly, it displayed high stability towards UV irradiation and tough temperature, hence, it can be regarded as a [2]rotaxane.



*H.-L. Sun, Prof. Dr. H.-Y. Zhang, Z. Dai, X. Han, and Prof. Dr. Y. Liu**

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