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Unidirectional Threading Synthesis of Isomer-Free [2]Rotaxanes

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Abstract: The threading of an α-cyclodextrin (α-CyD) by an unsymmetrical dumbbell generally results in two isomeric [2]rotaxanes differing in the orientation of the α-CyD. In this work, two methods have been developed for the unidirectionally threading an α-CyD to obtain isomer-free [2]rotaxanes. These methods use the Suzuki coupling of a boronic acid derivative and a halide in aqueous alkaline solution. The conformations of the two unidirectional [2]rotaxanes-**R3** and **R4** were determined by 2D ^{1}H ROESY NMR spectra. The optical spectral studies revealed that each of the two [2]rotaxanes can proceed with *E*/*Z* photoisomerization and shuttling motions of the α-CyD ring on the thread under alternating irradiation at 330 and 275 nm, accompanied by fluorescence intensity changes at 530 nm. The induced circular dichroism (ICD) spectra of another two analogous [2]rotaxanes **R1** and **R2** were also studied. Distinctive ICD signal changes resulting from the photoisomerization with respect to the movements of α-CyD were detected. This demonstrates that, besides the fluorescence, ICD signal is another way to identify the shuttling motions of α-CyD in these [2]rotaxanes.

Keywords: cyclodextrins · molecular shuttles · photoisomerization rotaxanes · supramolecular chemistry

Introduction

Cyclodextrins (CyDs) continue to be attractive wheel components in constructing supramolecular assemblies, such as pseudorotaxanes,[1] rotaxanes[2] and catenanes.[3] A rotaxane is described as a molecular system in which a macrocycle (wheel) threads a linear subunit (dumbbell) with two bulky stoppers. Rotaxanes have attracted more and more attention because of their challenging constructions and potential applications in areas such as nanostructured functional materials,[4] molecular switches,[5] molecular logic gates,[6] molecular wires,[7] and memory devices.[8]

The foundation for the construction of a CyD-based rotaxane is the interactions between the hydrophobic cavity of the CyD and the special hydrophobic unit in the linear component. Since the early 1980s, CyD-based [2]rotaxanes have been prepared by encapsulation of a symmetrical linear molecule with CyD and subsequent "locking" by coordination.[2a,9] Symmetry and the lack of stability are the two major issues in these [2]rotaxanes. To improve the stability, many CyD-based [2]rotaxanes, in which the bulky stoppers were linked covalently to the linear part instead of coordination, were developed.[10] At the same time, many unsymmetrical [2]rotaxanes, in which a CyD ring encircles an unsymmetrical dumbbell, were also set up.[11] However, when an asymmetric CyD was threaded by a nonsymmetrical dumbbell, it would give two isomers which differ in orientation of CyD with respect to the different ends of the dumbbell. As a result, isomeric [2]rotaxanes were always obtained in these systems.

It was expected that unidirectional threading of a CyD ring by a linear subunit during the formation of a [2]rotaxane could be achieved in order to construct more complicated rotaxanes. So far, there are few reports concerning unidirectional threading,[12] and the reports concerning CyD-based unidirectional [2]rotaxanes are rare.[13] Recently, we have set up two [2]rotaxane systems for molecular shuttles.[14,15] The two [2]rotaxanes, **R1** and **R2** shown in Figure 1, were obtained as unidirectional [2]rotaxanes. From this point of view, we would like to widen the scope of these work to develop new methods for controlling the orientation of an α-CyD when synthesizing [2]rotaxanes for molecular shuttles. Here we report the unidirectional threading an α-CyD by the Suzuki coupling reaction between a boronic acid and a halide in an aqueous α-CyD solution.

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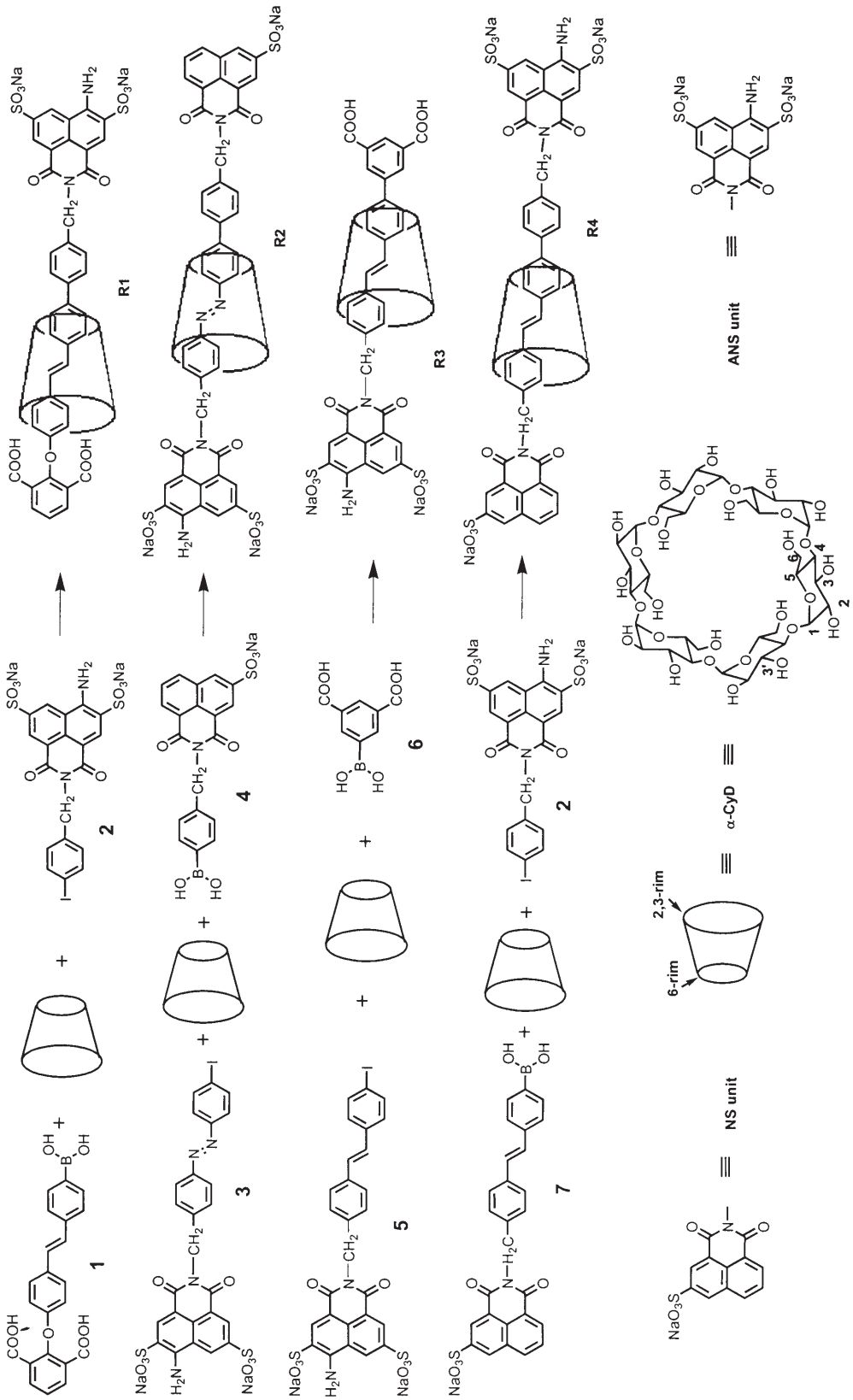

Figure 1. Synthesis and chemical structures of rotaxanes **R1**, **R2**, **R3** and **R4**.

Results and Discussion

Synthesis and co-conformational identification of R3: The synthesis of the shuttle **R3** is similar to that of **R2** (shown in Figure 1), which was obtained from the combination of compound **5** with α-CyD and the subsequent coupling with compound **6**.[15] Thus, after **5** was stirred with α-CyD in H_2O for 50 h, it was coupled with **6** under the catalysis of $Pd(OAc)_2$, and the molar ratios of **5**/α-CyD/**6**/$Pd(OAc)_2$ were 1:1.2:1:0.15. **R3** was obtained with a yield of 6.4% by chromatography.

It has been confirmed that only one isomer was present in **R2**, where the 2,3-rim of the α-CyD faces the **ANS** stopper, as shown in Figure 1.[15] The same fact was also found in **R3**, whose co-conformation was confirmed by 2D ^{1}H ROESY NMR (500 MHz) spectrum in D_2O at 298 K, as shown in Figure 2. The observed NOEs from the aromatic protons Hm, Hn, Ho, Hp of the dumbbell to the internal proton H3 of the α-CyD, and from Hn, Ho, Hp, Hq to H5, as well as from the Hq, Hr to H6, indicate that the 6-OH rim of the α-CyD faces the isophthalic acid stopper, and that the α-CyD ring encircles the stilbene unit.

We now consider the unidirectionality of the two [2]rotaxane. For the synthesis of **R3**, α-CyD was first stirred with **5** to form inclusion complexes, which might contain two isomers, that is, [2]pseudorotaxanes **5-CD-a** and **5-CD-b** as shown in Figure 3. This is confirmed by the ^{1}H NMR spectrum. After mixing **5** with α-CyD in D_2O for 50 min (Figure 3b), the presence of two isomeric [2]pseudorotaxanes can be clearly observed. However, as time elapses, the isomer **5-CD-b** disappears almost completely after 36 h (Figure 3c). These facts indicate that the threading rates of stil-

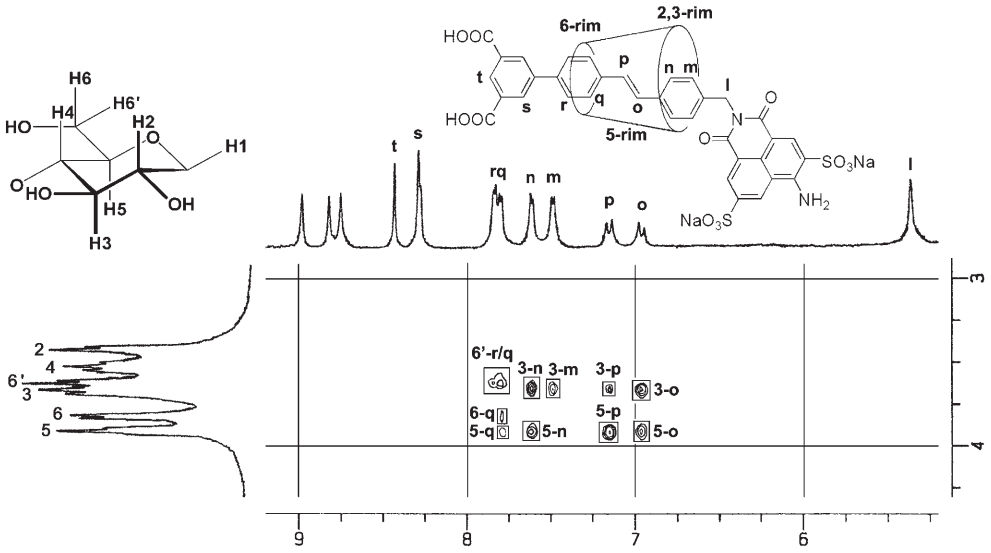

Figure 2. Selected 2D ^{1}H ROESY NMR (500 MHz) spectrum of **R3** in D_2O recorded at 298 K.

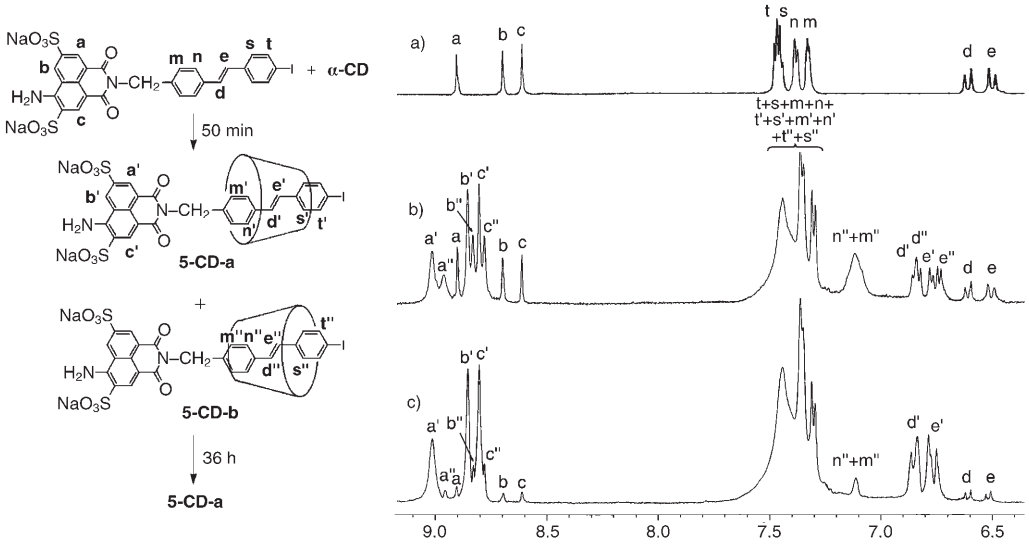

Figure 3. ^{1}H NMR spectra of a) **5** and the mixture of **5** and α-CyD at b) 50 min, and c) 36 h after the addition of α-CyD to **5**.

bene unit through the narrow 6-rim and through the wide 2,3-rim are not much different, but the dethreading rate of the former [2]pseudorotaxane is much faster than that of the latter, giving mostly the thermodynamically stable isomer, where the 2,3-rim of the α-CyD faces the **ANS** stopper. Finally, the resulting [2]pseudorotaxane **5-CD-a** underwent Suzuki coupling with the boronic acid **6** which was added to the solution subsequently, and as a result, the [2]rotaxane **R3** formed, where the 2,3-rim of the α-CyD faces the **ANS** stopper, as shown in Figure 1.

From this point of view, it is not surprising that the [2]rotaxane **R2** was obtained as the sole isomer. Analogous to **R3**, it was synthesized from the reaction of a short-chain phenylboronic acid derivative with a long-chain phenylhalide one, which can also form an inclusion compound with α-CyD. The pure [2]pseudorotaxane was also obtained after mixing **3** with α-CyD for 48 h in H_2O. 2D ^{1}H ROESY NMR spectrum of the pseudo-rotaxane revealed that the direction of the CyD coincides with its analogue **3-CD-a**, in which the 2,3-rim of the CyD faces the **ANS** unit.[16] The subsequent coupling with **4** would no doubt result in the formation of the co-conformational-pure [2]rotaxane **R2**, as shown in Figure 1.

Synthesis and co-conformational identification of R4: The [2]rotaxane **R1** was synthesized from the Pd-catalyzed Suzuki coupling of **1** with **2** in an alkaline aqueous α-CyD solution, and it was confirmed that only one isomer, where the 2,3-rim of the α-CyD faces the isophthalic acid stopper, was obtained in the synthesis of **R1**, as shown in Figure 1.[14] The other possible isomer where the 2,3-rim of the α-CyD faces the **ANS** stopper was not present.

One might reasonably think that, as for **3** and **5**, the interaction of **1** with α-CyD would result in the formation of a thermodynamically more stable [2]pseudorotaxane isomer, which account for the co-conformation of **R1**. However, the 2D ^{1}H ROESY NMR revealed that no [2]peudorotaxane formed at the beginning of the mixing of **1** with α-CyD. Unlike the thermodynamic threading of **R2** and **R3**, it seems that the boronic acid **1** formed a diol complex with α-CyD on the 2,3-rim, and the unidirectional [2]rotaxane **R1** is more like a result of a kinetic threading.[16] The synthesis of **R4** is quite similar to that of **R1**, the difference between them is only that the isophthalic acid stopper in **1** is changed to **NS** unit in **7** (Figure 1). It has been confirmed that **R4** also have unique co-conformation, where the 2,3-rim of the CyD faces the **NS** stopper. This co-conformation was confirmed by the 2D ^{1}H ROESY NMR (500 MHz) spectrum of **R4** in D_2O, as shown in Figure 4. The two methylene protons Ha and Hj were separated into two singlets at δ 5.25 and 5.37, compared with one overlapping singlet at δ 5.26 in the dumbbell **PR4**.[16] The downfield shift of proton Ha in **R4** was believed to be due to threading through the α-CyD ring. Furthermore, the NOEs shown in Figure 4 observed from the aromatic protons Hc, Hd, He of the dumbbell to the internal proton H5 of the α-CyD, and from Hb, Hc, Ha (no Hj) to H3, as well as from the He, Hf to H6, indicate that the 2,3-OH rim of the α-CyD is close to the **NS** stopper, and that the α-CyD ring sits over the stilbene unit.

It should be noted that the CyD-free dumbbells **PR3** and **PR4**, resulting from the direct coupling of the boronic acids and the halides, were also isolated from the reaction mixtures of **R3** and **R4**, respectively (see Supporting Information).[16]

Detection of the shuttling motion

ICD spectra: The circular dichroism spectra have been widely used to interpret the absolute conformation of chiral compounds.[17] When an achiral guest chromophore is locat-

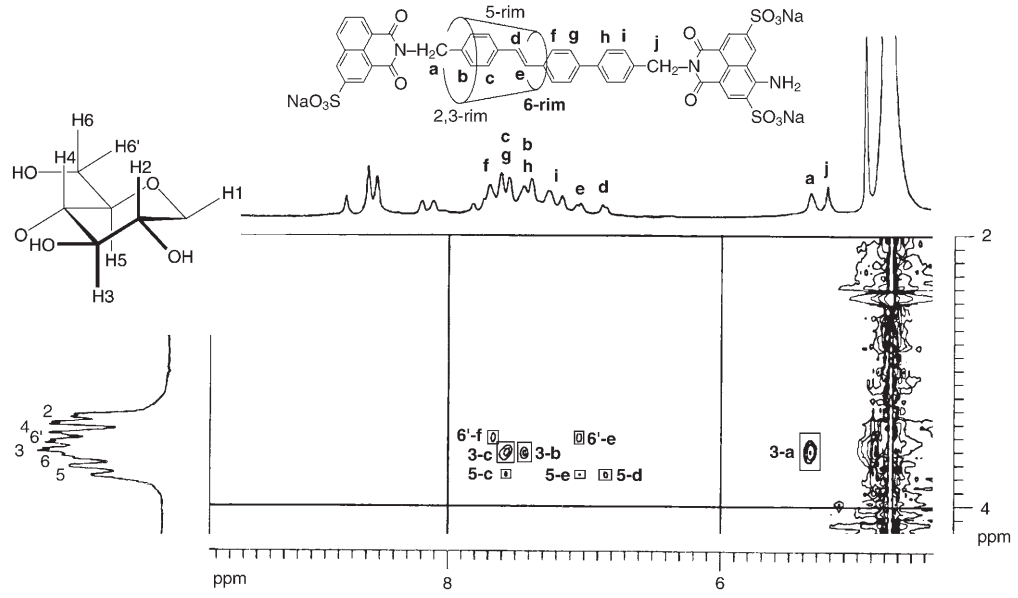

Figure 4. Selected 2D ^{1}H ROESY NMR (500 MHz) spectrum of **R4** in D_2O recorded at 298 K.

ed in a chiral host, the guest becomes optically active and induced circular dichroism (ICD) signals originates. Harata, Kajtár, and Shimizu et al. have developed a rule for the inclusion complexes of cone-shaped chiral hosts such as cyclodextrins. According to the rule, a positive ICD signal arises when the electric transition dipole moment is aligned parallel to the axis of the chiral host, but the signal is negative and half as strong when it is oriented in a perpendicular manner (Figure 5).[18–21] Recently, a similar rule has also been developed by Kodaka for ICD effects outside the chiral host cavity, where the sign of the ICD signal is opposite to that arising inside the host cavity (Figure 5).[22]

The prolonged irradiation of aqueous **R1-alk** solution (10 mol solid Na_2CO_3 were added to the **R1** and the isophthalic acid unit was changed to the anionic form) at 335 nm would result in the photoisomerization of the *E* to *Z* form and the shuttling of the α-CyD ring from the stilbene unit to the biphenyl unit, which was previously confirmed by 2D ROESY NMR spectrum.[14] In this work, the ICD spectra with respect to the photoisomerization of aqueous **R1-alk** (2.0×10^{-5} M) solution are shown in Figure 6.

Before the irradiation, the ICD spectrum shows a weak negative Cotton effect ($\Delta\varepsilon=-0.21\,L\,mol^{-1}\,cm^{-1}$) at 431 nm (Figure 6A, curve a). This is because the **ANS** unit is far from the α-CyD and the α-CyD affects little the naphthalimide group. Aqueous **R1-alk** solution is then irradiated at 335 nm for 100 min to reach the photostationary state. The $E\rightarrow Z$ photoisomerization leads to the decrease in the ICD signal at around 434 nm ($\Delta\varepsilon=-1.64\,L\,mol^{-1}\,cm^{-1}$) and the presence of an isobestic points at 288 nm as shown in Figure 6A (curve d). The result coincides with the Kodaka's rule as the **ANS** unit in the *Z* form is closed to the α-CyD ring due to the shuttling of the α-CyD ring. This co-conformation results in a more negative ICD signal (Figures 5 and 6) at around 430 nm, which is the λ_{abs}^{max} of the **ANS** unit. Parallel to the Harata's rule, the strong positive ICD signal at around 300 nm ($\Delta\varepsilon=1.06\,L\,mol^{-1}\,cm^{-1}$) before irradiation should be attributed to the stilbene π system in the cavity of

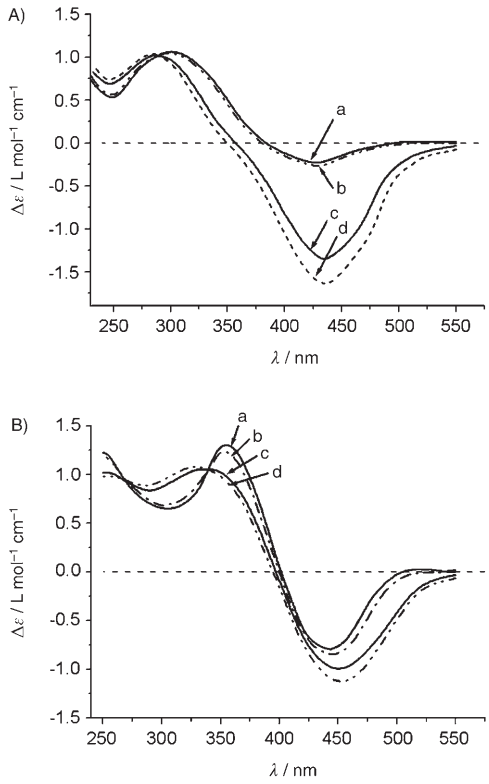

Figure 6. A) ICD spectra of **R1** (2.0×10^{-5} M) aqueous solution (a) and after the irradiation at 335 nm for 75 min (c), 100 min (d). The spectral change can be shifted back by the irradiation at 280 nm (40 min, curve b). B) ICD spectra of **R2** (2.0×10^{-5} M) aqueous solution (a) and after the irradiation at 360 nm for 15 min (c), 25 min (d). The spectral change can be shifted back by the irradiation at 430 nm (10 min, curve b).

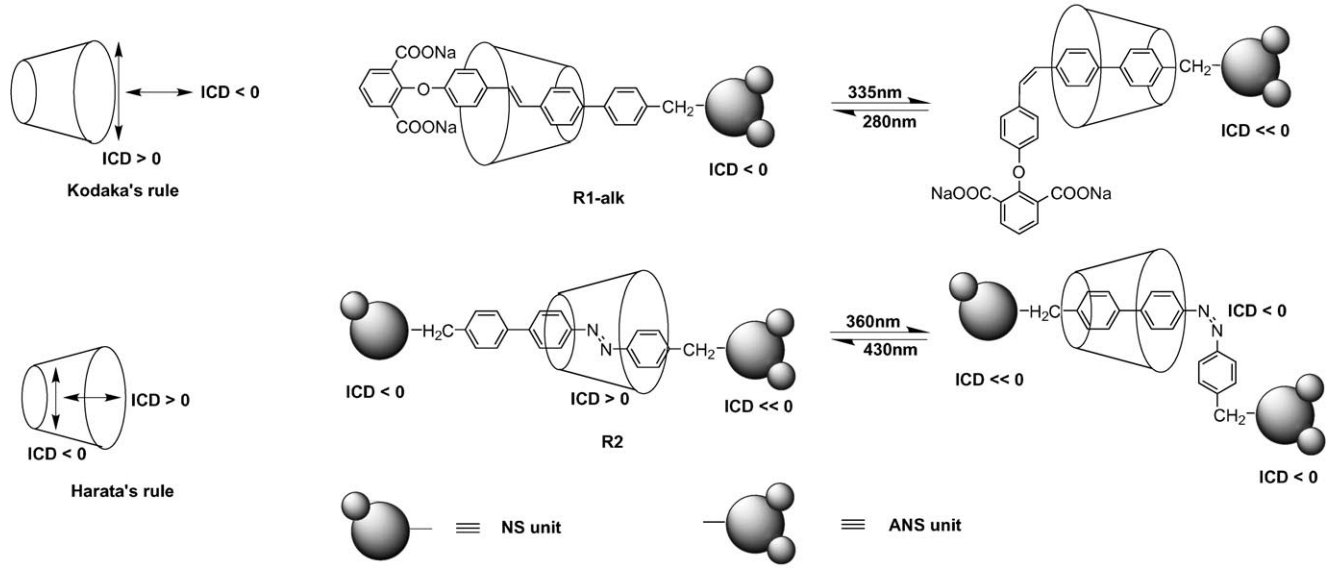

Figure 5. Harata's rule and the Kodaka's rule, and the ICD signals of *E*/*Z* **R1** and *E*/*Z* **R2** according to the rules. The arrows on the left represent the electric transition dipole moments of the guests.

the α-CyD ring. However, the signal blue shifts to 284 nm after the photoisomerization for the sake that the π system becomes weaken in the *Z* form. Nevertheless, the intensity of the ICD signal change little because the π system still locates in the cavity of the α-CyD ring, as shown in Figure 6.

The ICD spectra for **R2** are more complex because all of the **NS** unit, **ANS** unit and the azo group generate ICD signals. According to the Kodaka's rule, in the *E* form of **R2**, because the **ANS** unit is closed to the α-CyD ring, a negative Cotton effect should appear at around 430 nm, which is the λ_{abs}^{max} of the **ANS** unit; and the **NS** unit is far away from the α-CyD ring, thus a weak negative ICD signal would be induced at around 340 nm. Simultaneously, the azo group is included in the cavity of the α-CyD, and according to the Harata's rule, a characteristic strong positive Cotton effect would have to appear at around 360 nm. As a consequence, the aqueous solution of **R2** (2.0×10^{-5} M) shows a positive Cotton effect ($\Delta\varepsilon = 1.31\ L\,mol^{-1}\,cm^{-1}$) at 355 nm, as well as a negative Cotton effect ($\Delta\varepsilon = -0.78\ L\,mol^{-1}\,cm^{-1}$) at 442 nm (Figure 6B, curve a).

It has also been confirmed that the irradiation of aqueous **R2** solution at 360 nm would induce the $E\rightarrow Z$ photoisomerization, and the α-CyD ring would move from the azo unit to the biphenyl unit.[15] As a consequence, the azo group would be located outside the α-CyD ring and the **ANS** unit would become far away from the CyD ring. (Figure S3 in the Supporting Information shows the absorption changes of **R2** upon the $E\rightarrow Z$ isomerization.[16]) Besides the absorption decrease at 360 nm, an additional absorption at around 430 nm would appear during the course of $E\rightarrow Z$ photoisomerization ($\Delta A = 0.02$). As a result, an ICD signal would originate at 430 nm. According to Kodaka's rule, the ICD signals are negative for both the **ANS** unit and the *Z* form of the azo unit (Figure 5). Although the increase of the absorption at 430 nm is relatively small compared with the absorption of the **ANS** unit ($A = 0.13$), it is likely that the azo unit is very closed to the α-CyD rim, which results in a more strong negative ICD, and that the **ANS** unit is far away from the α-CyD ring, which results in a small less negative ICD. As a result, after 25 min irradiation at 360 nm, the aqueous **R2** solution (2.0×10^{-5} M) gives a more negative ICD signal ($\Delta\varepsilon = -1.11\ L\,mol^{-1}\,cm^{-1}$) at 451 nm (Figure 6B, curve d) compared with the original one. Meanwhile, a decrease in $\Delta\varepsilon$ ($\Delta(\Delta\varepsilon) = -0.37\ L\,mol^{-1}\,cm^{-1}$) at 355 nm is also observed after the irradiation. This spectral change should be due to the more negative ICD signal at around 340 nm of **NS** unit when its position is close to the α-CyD ring (Figure 5).

It should be noted that the photoisomerized solutions of both **R1-alk** and **R2** can be induced reversible $Z\rightarrow E$ photoisomerization by irradiation at 280 and 430 nm, respectively.[14,15] These processes can also be addressed by the ICD spectra, as shown in Figure 6. The ICD spectra of the two isomerized solutions of **R1-alk** and **R2** after the irradiation (at 280 nm for **R1-alk** and 430 nm for **R2**) can be shifted back to their photostationary states (curve b in Figure 6A and B), which are almost the same as the original *E* ones.

It can be seen that the process of the α-CyD shuttling from the stilbene unit to the biphenyl unit ($E\rightarrow Z$ photoisomerization) in **R1-alk** is accompanied by an obvious increase (6.8 times) in the ICD value at around 440 nm. The shifted ICD spectra can be shifted reversibly back when the α-CyD shuttles back ($Z\rightarrow E$ photoisomerization). These facts reveal that ICD spectrum can identify distinctively the shuttling motions of CyD ring in a molecular shuttle. The different ICD signals before and after the shuttling can also represent the "0" and "1" states of these CyD-based [2]rotaxanes. Furthermore, the ICD spectrum provides possibilities to identify the movements of these CyD-based [2]rotaxanes in solid state, in which the ICD signals would become more intensive.[23]

Absorption spectra: The UV/Vis absorption spectra of [2]rotaxanes **R3** and **R4**, as well as the corresponding spectra of dumbbells **PR3** and **PR4** in H_2O are shown in Supporting Information.[16] The absorption maxima at around 427 nm for **R3** (curve a in Figure S4A)[16] and **PR3** attributes to **ANS** unit, and the maxima at around 330 nm ascribes the stilbene unit. For **R4** (curve a in Figure S4B)[16] and the corresponding dumbbell **PR4**, there is an obvious increase in absorption at the band around 330 nm with the **NS** unit. It can be observed that the two absorption spectra of **R3** and **PR3**, as well as the two of **R4** and **PR4**, are very similar, which means that the encircling of α-CyD on the dumbbells does not influence the absorption spectra.

It has been found that the irradiation on a stilbene based [2]rotaxane would induce $E\rightarrow Z$ photoisomerization, which results in absorption spectral changes.[2f,14] For [2]rotaxanes **R3** and **R4**, the same characteristic spectral changes in aqueous solution (9.1×10^{-6} M) were also found, as also shown in Figure S4A.[16] The irradiation on the **R3** solution at 330 nm for 40 min results in photoisomerization to give a *E*/*Z* mixture, characterized by a rise of the absorption at around 275 nm ($\Delta A = 0.016$) and a decrease in absorption at 330 nm ($\Delta A = 0.013$), as well as the presence of two isobestic points at 294 and 379 nm. The maximum absorption of **ANS** unit at around 427 nm changes little, as this stopper is separated from the residues by the methylene group. Similar results were obtained for **R4** solution after irradiation at 330 nm for 50 min, inducing an increase in absorption at around 275 nm ($\Delta A = 0.020$) and decrease in absorption at 330 nm ($\Delta A = 0.017$), as well as the appearance of two isobestic points at 296 and 361 nm (as illustrated in Figure S4B).[16]

Compared with **R3** and **R4** solutions, the corresponding aqueous solution of dumbbell **PR3** and **PR4** also undergo $E\rightarrow Z$ photoisomerization after the irradiation at 330 nm (Figures S5 and S6 in Supporting Information),[16] but reaches to the photostationary state within shorter time (21 and 29 min for **PR3** and **PR4**, respectively). There is a relative larger increase in the absorption at around 275 nm ($\Delta A = 0.027$ and $\Delta A = 0.045$ for **PR3** and **PR4**, respectively) and a relative large decrease at 330 nm ($\Delta A = 0.025$ and $\Delta A = 0.042$ for **PR3** and **PR4**, respectively). These results were

also found in **R1**[14] indicating that the dumbbells undergo easier $E \rightarrow Z$ photoisomerization than the corresponding [2]rotaxanes do. This again demonstrates the fact that $E \rightarrow Z$ isomerization becomes more difficult in the presence of the α-CyD ring.[2f]

Fluorescence spectra: Figure 7 shows the emission spectra of **R4** (curve a) and model compound **NS** (1,8-naphthalimide-3-sulfonic acid sodium salt, curve b) in aqueous solution

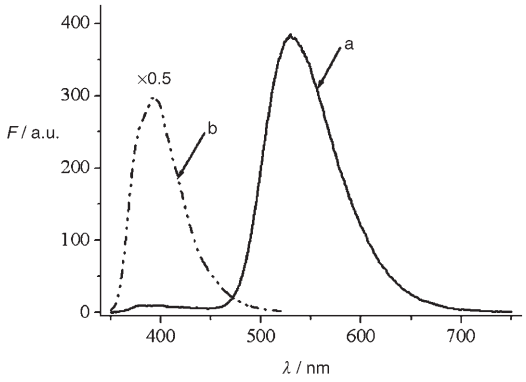

Figure 7. The fluorescence emission spectra of **R4** (curve a) and the model compound NS (1,8-naphthalimide-3-sulfonic acid sodium salt, curve b, half reduced) in aqueous solution (both 9.1×10^{-6} M) excited at 330 nm. The shoulder around 395 nm in the spectrum of **R4** is due to a very small contribution from the emission of NS unit.

(both 9.1×10^{-6} M) with excitation at 330 nm, the maximum absorption wavelength of the **NS** unit. Compared with the strong emission maximum at 395 nm of compound **NS**, the fluorescent intensity of **NS** unit in **R4** at around 395 nm is reduced to $^{1}/_{50}$ of that of compound **NS**. At the same time, a distinct emission maximum at 530 nm, which is the characteristic emission maximum of the **ANS** unit, is obtained. The quenching of the **NS** unit should be attributed to the singlet–singlet energy transfer from the **NS** unit to the **ANS** unit;[4a] the first excited singlet state of which lies at a lower energy state. Energy transfer in **R4** was confirmed by the fluorescence excitation spectra of **R4** for **ANS** emission measured at 530 nm (Figure S7).[16] The spectrum at around 330 nm region is parallel to the absorption of **R4** in the region.

As energy transfer from the **NS** unit to the **ANS** unit quenches the fluorescence of the **NS** unit, only the emission of the **ANS** unit was taken into account in **R4** and **PR4**. Compound **R4** has an emission maximum at 530 nm in aqueous solution (9.1×10^{-6} M) with the excitation at 427 nm, which is the maximum absorption wavelength of the **ANS** unit, as shown in Figure 8A. However, the fluorescent intensity of **R4** (216 a.u.) is higher than that of **PR4** (175 a.u.)[16] by about 23%. This is consistent with an 86% increase in the intensity of **R3** (151 a.u., curve a in Figure 8B) over that of **PR3** (81 a.u.)[16] at the same fluorescence band, and also a decrease in fluorescent intensity of dumbbell **PR1-alk** over that of **R1-alk** as observed in our previous work.[14] These

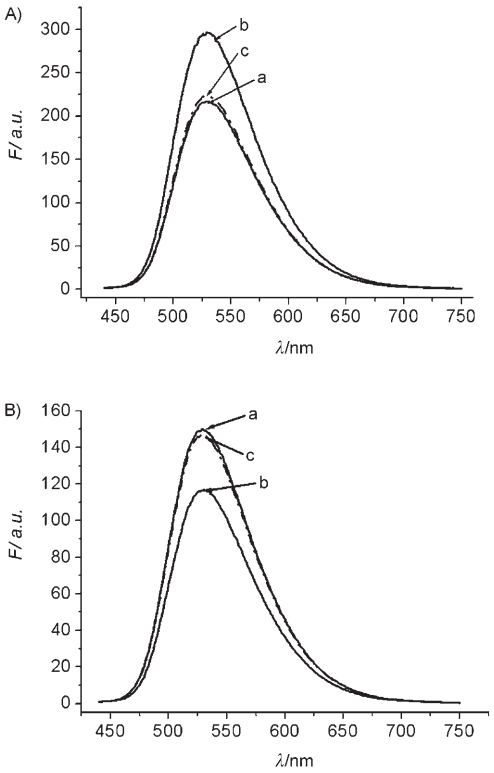

Figure 8. A) The fluorescence emission spectra of **R3** (9.1×10^{-6} M) aqueous solution (a), and after UV light (330 nm) irradiation for 40 min (b), the spectra change can be shifted back by the irradiation at 275 nm for 23 min (c); B) The fluorescence emission spectra of **R4** (9.1×10^{-6} M) aqueous solution (a), and after UV light (330 nm) irradiation for 50 min (b), the spectra change can be shitted back by the irradiation at 275 nm for 28 min (c); all of the spectra were recorded with the excitation at 427 nm.

facts should be ascribed to the rigidity of the α-CyD ring to the encircled stilbene unit, in which the vibration and the rotation of the bonds are hindered. It might also be considered that the stoppers increase fluorescence when the CD approaches due to displacement of solvent and due to shielding from molecular oxygen quenching. As a result, non-radiative excited energy loss from the excited singlet state of these [2]rotaxane is reduced.

It is known that the photoisomerization of encircled stilbene or azobenzene unit would result in the shuttling motion of the α-CyD ring.[2f,14,15] Moreover, shifting the α-CyD macrocycle away from a luminescent stopper would cause a decrease of the fluorescence intensity of the stopper. Shuttling of the α-CyD ring to another stopper would cause an increase in the intensity of the emission.[14,15] The same were found in **R3** and **R4**, as shown in Figure 8. On the one hand, once the shuttling of α-CyD ring to the biphenyl unit performed, the macrocycle becomes closer to the **ANS** unit in **R4**. Such movement of α-CyD results in an increasing by about 36% in the intensity of the fluorescence band at $\lambda_{max} = 530$ nm. On the other hand, as α-CyD ring moves away from the **ANS** unit in **R3**, a decreasing by about 29% in the intensity at the same fluorescence band is observed.

The fact that there is little change in the fluorescent intensity of the corresponding dumbbell **PR3** and **PR4** after the photoisomerization,[16] again confirms that only the movement of the α-CyD ring is responsible for the obvious spectral changes.

Reversibility: After the photoisomerization of **R3** and **R4** from the *E* to *Z* form, the equilibrium can be reversed by irradiation at 275 nm. This process is accompanied by decrease in the absorption at around 275 nm and increase in absorption at 330 nm (curve c in Figure S4A and S4B in the Supporting Information[16]), as along with an increase in the fluorescence intensity at $\lambda_{max}=530$ nm for **R3** (curve c in Figure 8A) and a decrease for **R4** (curve c in Figure 8B). Owing to the reversibility of the photoisomerization process, the photoinduced shuttling motion of the α-CyD ring can be carried out repeatedly with reversible fluorescent signal changes.

Conclusion

In summary, an unidirectional [2]pseudorotaxane can be thermodynamically prepared from interaction of a naphthalimide–stilbene compound with α-CyD, and an unidirectional [2]rotaxane can be obtained from the consequent Suzuki coupling of the [2]pseudorotaxane with a boronic acid. The [2]rotaxane **R3** was synthesized by this thermodynamic means. On the other hand, the Suzuki coupling of a "long chain" boronic acid and a halide stopper in aqueous α-CyD solution also results in the formation of an unidirectional [2]rotaxane **R4**. Unlike the thermodynamic threading, the threading of α-CyD in **R4** is likely a kinetic one, in which the "long" boronic acid might act as an orientation auxiliary group. The alternating irradiation with two different frequencies of UV light on the two [2]rotaxanes in aqueous solutions results in reversible *E*/*Z* photoisomerization and the shuttling motions of α-CyD, accompanied by obvious changes in the fluorescent intensity at 530 nm. The ICD spectra study of two previous prepared [2]rotaxanes, **R1** and **R2**, reveals that the reversible shuttling motions of the α-CyD ring can also induce distinctive ICD signal changes, which can in term identify the movements of the α-CyD resulting from the photoisomerization.

Experimental Section

Instruments: ^{1}H NMR spectra were measured on a Bruker AM 500 spectrometer. UV/Vis spectra were done on a Varian Cary 100 spectrophotometer (1 cm quartz cell used). Fluorescent spectra were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer (1 cm quartz cell used). The photoirradiation was carried on a CHF-XM 500-W high-pressure mercury lamp with suitable filters in a sealed Ar-saturated 1 cm quartz cell. ICD spectra were recorded on a Jasco J-720 spectropolarimeter in a 1 cm quartz cell.

UV-visible absorption and fluorescence emission spectral measurements: The absorption and emission spectra of the samples (all 9.1×10^{-6} M) were measured at 298 K in aqueous solution. The UV light irradiation at 330 nm on these solutions was carried out to induce *E*/*Z* photoisomerization. After prolonged irradiation for 40 min on **R3** (50 min for **R4**, 21 min for **PR3** and 29 min for **PR4**) solution, no additional change in the absorption was observed, which meant that the solution reached the photostationary state. The fluorescence emission spectra were recorded without delay. The wavelength of the irradiating UV light was then changed to 275 nm in order to induce *Z*/*E* photoisomerization. After the prolonged irradiation of the solution for 23 min (28 min for **R4**, 12 min for **PR3** and 16 min for **PR4**), the spectral change in absorption and emission was recorded.

Synthetic routes to R3 and R4: The synthetic schemes for the two [2]rotaxanes are shown in Scheme S1 and S2.[16] Boronic acid **7**, which was obtained from the reaction of 1,8-naphthalimide-3-sulfonic acid sodium salt with a benzyl bromide **A3**, was coupled with the halide **2** in the α-CyD aqueous solution catalyzed by $Pd(OAc)_2$ resulted in the formation of **R4**. Similarly, **R3** was prepared from the coupling of the halide **5** with the boronic acid **6**.

Compound R3: A mixture of **5** (0.35 g, 0.47 mmol), α-CyD (0.55 g, 0.56 mmol) in distilled water (15 mL) was stirred at 60 °C for 48 h, then Na_2CO_3 (0.7 g, 6.6 mmol), boronic acid **6** (0.15 g, 0.71 mmol) and $Pd(OAc)_2$ (15 mg) were added to the suspension, the resulting mixture was stirred under Ar at 80 °C for 24 h, acidified with acetic acid, evaporated to dryness, the resulting dark solid was purified by column chromatography to give pure **R3** (52 mg, 6.4 %) as yellow powder. No obvious m.p. was found, which might due to the decomposing of the α-cyclodextrin. ^{1}H NMR (500 MHz, D_2O, 25 °C, TMS): $\delta=8.98$ (s, 1H), 8.82 (s, 1H), 8.76 (s, 1H), 8.42 (s, 1H), 8.28 (s, 2H), 7.83 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.78 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.60 (d, ^3J(H,H) = 8.6 Hz, 2H), 7.46 (d, ^3J(H,H) = 8.6 Hz, 2H), 7.14 (d, ^3J(H,H) = 16.5 Hz, 1H), 6.95 (d, ^3J(H,H) = 16.5 Hz, 1H), 5.38 (s, 2H), 4.95 (s, 6H), 3.94 (dd, ^3J(H,H) = 9.0, 9.2 Hz, 6H), 3.83 (d, ^3J(H,H) = 8.7 Hz, 6H), 3.73 (dd, ^3J(H,H) = 10.2, 10.6 Hz, 6H), 3.68 (d, ^3J(H,H) = 9.0 Hz, 6H), 3.54 (dd, ^3J(H,H) = 9.2, 10.6 Hz, 6H), 3.48 ppm (d, ^3J(H,H) = 10.2 Hz, 6H); elemental analysis calcd (%) for $C_{71}H_{82}N_2Na_2O_{42}S_2\cdot11.5H_2O$ (1952.7): C 43.66, H 5.42, N 1.43; found: C 43.47, H 5.31, N 1.57.

Compound R4: A mixture of boronic acid **7** (0.5 g, 0.93 mmol), α-CyD (1.2 g, 1.2 mmol) and Na_2CO_3 (0.2 g, 1.9 mmol) in distilled water (25 mL) was stirred at 60 °C for 50 h, then Na_2CO_3 (0.35 g, 3.3 mmol), **2** (0.6 g, 0.95 mmol) and $Pd(OAc)_2$ (15 mg) were added to the suspension, the resulting mixture was stirred under Ar at 80 °C for 20 h, acidified with acetic acid, evaporated to dryness, the resulting dark solid was purified by column chromatography to give pure **R4** (88 mg, 4.9 %) as yellow powder. No obvious m.p. was found, which might due to the decomposing of the α-cyclodextrin. ^{1}H NMR (500 MHz, D_2O, 25 °C, TMS): $\delta=8.93$ (s, 1H), ~8.70 (m, 4H), 8.39 (s, 1H), 8.30 (s, 1H), 7.78 (dd, ^3J(H,H) = 8.2, 7.8 Hz, 1H), ~7.66 (m, 6H), 7.45 (m, 6H), 7.10 (d, ^3J(H,H) = 16.2 Hz, 1H), 6.93 (d, ^3J(H,H) = 16.2 Hz, 1H), 5.37 (s, 2H), 5.25 (s, 2H), 4.94 (d, ^3J(H,H) = 2.4 Hz, 6H), 4.13 (t, ^3J(H,H) = 9.4 Hz, 6H), 3.69 (m, 12H), 3.63 (m, 12H), 3.57 (d, ^3J(H,H) = 10.7 Hz, 6H), 3.53 (dd, 6H), 3.47 (dd, ^3J(H,H) = 2.4, 9.6 Hz, 6H); elemental analysis calcd (%) for $C_{82}H_{88}N_3Na_3O_{43}S_3\cdot13H_2O$ (2203.0): C 44.71, H 5.18, N 1.91; found: C 44.47, H 5.34, N 1.77.

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[23] The intensity of the ICD signals is relatively weak in solutions because the concentration of these rotaxanes is low. It should be noted that the E form of **R1-alk** or **R2** is not completely transferred to the Z form (for **R1-alk**, the ratio of *E*/*Z* at the photostationary is about 63/37, and for **R2** is about 59:41),[14,15] and this fact should also be responsible for the relative small change in the intensity of ICD signal.

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