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Isomeric [2]Rotaxanes and Unidirectional [2]Pseudorotaxane Composed of α-Cyclodextrin and Aliphatic Chain-Linked Carbazole-viologen Compounds

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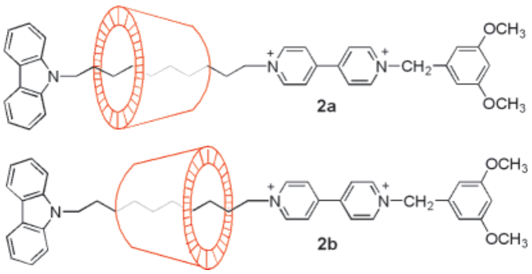
ABSTRACT



Capping the α-cyclodextrin (α-CD) complex of 1-(*N*-carbazole)-10-[4-(4-pyridinio)-1-pyridinio]decane with 3,5-dimethoxybenzyl bromide in DMF gives two isomeric [2]rotaxanes, 2a and 2b, while α-CD and 1-(*N*-carbazole)-10-[4-(1-methyl-4-pyridnino)-1-pyridinio]decane 3 in water form mostly a unidirectional [2]pseudorotaxane having the same α-CD orientation as 2b. Structures were elucidated from ^{1}H NMR and circular dichroism spectra. The orientational specificity of α-CD in the 3/α-CD [2]pseudorotaxane is due to the slow dethreading rate of the 2b-type isomer.

Rotaxanes and pseudorotaxanes are of great interest because of their interesting structures and potential application for supramolecular machines.[1−10] Cyclodextrins (CDs) have been widely used as wheels for supramolecular assemblies.[1,2,4−10] 4,4′-Bipyridinium dication, commonly known as viologen, has been extensively utilized as a component of macrorings

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or axles due to its unique redox characters and ability as an electron acceptor.[1−3,6,7] As CDs are nonsymmetric macrocycles, the [2]rotaxanes[8] and [2]pseudorotaxanes[7,9,10] composed of CDs and nonsymmetric rods can give two isomers that differ in the orientation of CDs with respect to the rod's ends. Two isomeric α-CD-based [2]rotaxanes were prepared and shown to exhibit quite contrasting physicochemical behaviors.[8] Yonemura and co-workers reported that aliphatic chain-linked carbazole-viologen compounds and α-CD form unidirectional [2]pseudorotaxanes.[7] Here we report the syntheses of two novel isomeric [2]rotaxanes, **2a** and **2b**, composed of α-CD and an aliphatic chain-linked carbazole-viologen and the conformations of the isomeric [2]rotaxanes studied by ^{1}H NMR and circular dichroism spectroscopic methods. We also show that α-CD and nonstoppered carbazole-viologen **3** form a unidirectional [2]pseudorotaxane of **2b** type and deduce the origin of the unidirectionality.

We prepared the isomeric [2]rotaxanes **2a** and **2b** by reacting an equilibrated solution of **1** and α-CD with 3,5-dimethoxybenzyl bromide in DMF (27% yield of a mixture of **2a** and **2b**) and isolated the isomers by fractional precipitation (4.5 and 8.7% yields of **2a** and **2b**, respectively).[11] Compound **3** was obtained from reaction between 9-(10-bromodecyl) carbazole with 1-methyl-4,4′-bipyridinium iodide.[7]

^{1}H NMR spectra of **2a**, **2b**, and [2]pseudorotaxane composed of **3** with α-CD are shown in Figure 2. ^{1}H NMR spectrum of **2a** shows no hint of contamination from **2b**, but that of **2b** indicates that the isolated **2b** is contaminated with **2a** by about 10%. Assignments of NMR peaks were made by ^{1}H−^{1}H COSY and two-dimensional ROESY spectra (see Supporting Information). The orientations of the α-CD ring in the [2]rotaxanes (Figure 1) were deduced from the spectra and NOE cross-peaks. In **2a**, H-3 protons of α-CD showed cross-peaks with i(j) protons of carbazole and α- to ζ-methylene protons, but not with ι- and κ-methylene protons. On the other hand, **2b** showed cross-peaks between H-5 protons of α-CD and γ- to θ-methylene protons and between H-3 protons of α-CD and ζ- to ι-methylene protons: the intensities of the cross-peaks of η- and θ-methylene protons with H-3 protons were much stronger than those with H-5 protons. The cross-peaks between H-6$_B$ and H-6$_A$ (or H-5) protons of α-CD and i and j carbazole protons were also observed. The ^{1}H NMR and two-dimensional ROESY spectra of **3**/α-CD [2]pseudorotaxane in the aliphatic chain and α-CD regions are remarkably similar to those of **2b**, indicating that **3**/α-CD [2]pseudorotaxane and **2b** have the same α-CD orientation.

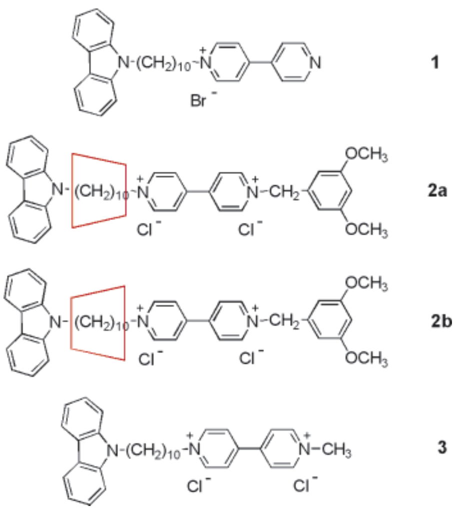

Figure 1. Structures of compounds and [2]rotaxanes studied.

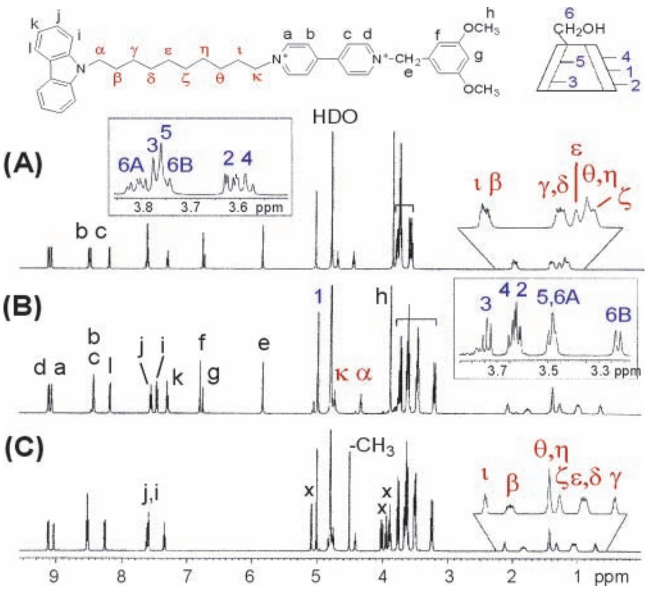

Figure 2. ^{1}H NMR (600 MHz) spectra in D$_2$O (δ_{HDO} = 4.800 ppm). (A) **2a**; (B) **2b**; (C) 4.5 mM **3** + 5.0 mM α-CD (equilibrated for 1 day). Peaks from the free α-CD in (C) are marked "x".

^{1}H NMR peaks of α- to ϵ-methylene protons of **2b** and **3**/α-CD [2]pseudorotaxane appear more upfield than the corresponding protons of **2a**, whereas their ζ- to ι-methylene protons appear more downfield than those of **2a**. Also protons of α-CD of **2b** and **3**/α-CD [2]pseudorotaxane, except H-2 protons, appear more upfield than the corresponding protons of **2a**. This might be due to ring current effects from aromatic groups and reflects the different location and orientation of the groups in the isomers.

Figure 3 shows the induced circular dichroism (ICD) spectra of the [2]rotaxanes and **3**/α-CD [2]pseudorotaxane. In the carbazole absorption region of 310−360 nm, **2a** exhibits a negative Cotton effect, whereas **2b** and **3**/α-CD [2]pseudorotaxane display a positive Cotton effect with similar ellipticity.

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[11] Experimental procedures and spectral data can be found in Supporting Information. **2a**: mp 222−224 °C (dec). Anal. Calcd for $C_{77}H_{107}Cl_2N_3O_{32}$: C, 55.57; H, 6.51; N, 2.54. Found: C, 55.79; H, 6.73; N, 2.47. **2b**: mp 210−212 °C (dec). Anal. Calcd for $C_{77}H_{107}Cl_2N_3O_{32}\cdot5H_2O$: C, 52.92; H, 6.64; N, 2.23. Found: C, 52.68; H, 6.75; N, 2.40.

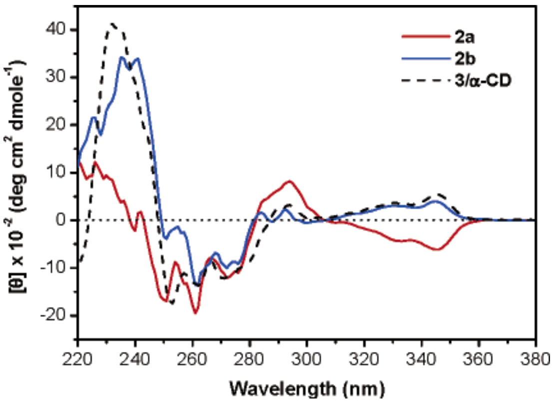

Figure 3. Circular dichroism spectra of [2]rotaxanes and **3**/α-CD [2]pseudorotaxane in water. The [2]pseudorotaxane spectrum was taken with a mixture of **3** (0.39 mM) and α-CD (0.65 mM) equilibrated for 1 day in water. [**2a**] = [**2b**] = 0.35 mM.

Applying the theoretically derived ICD rules of CD complexes[12] to the spectra in Figure 3, the transition dipole moment of the carbazole group responsible for the ICD band for **2a** is along the α-CD axis, but for **2b** it is at an angle greater than 54.7°. The large upfield shifts of β- to ϵ-protons and H-6 protons in **2b**, compared to those in **2a**, indicate that these protons are virtually beneath the carbazole ring. On the basis of these and two-dimensional ROESY spectra, we propose the structures of the [2]rotaxanes as shown in Figure 4. Both the NMR and ICD spectra suggest that the conformation of the **3**/α-CD pseudorotaxane is similar to that of **2b**: Yonemura et al. proposed a similar conformation for an α-CD complex of dodecamethylene chain-linked carbazole-viologen compound.[7] The bent structure of **2b** may be due to an energetically favorable interaction between the carbazole group and hydrated surface of α-CD. The possibility of such an interaction was suggested in β-CD complexes of alkyl sulfates.[13]

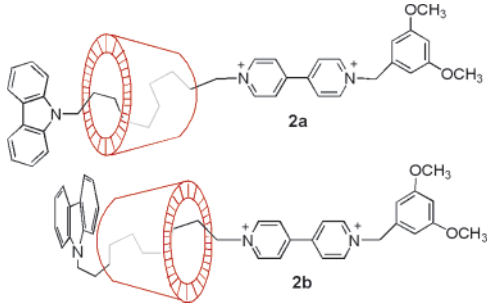

Figure 4. Proposed conformations of two isomeric [2]rotaxanes. The carbazole fused-ring is perpendicular to the secondary face of α-CD in **2a**, but it is parallel to the primary face in **2b**.

Now we consider the origin of the observed unidirectionality of the **3**/α-CD [2]pseudorotaxane. This can arise from the unidirectional threading of the rod molecule through the α-CD ring as suggested in the formation of calix[6]arene-based pseudorotaxanes threaded from a rod's end having a viologen moiety[3] or from the thermodynamic stability of the oriented [2]pseudorotaxane. To test these possibilities, we took ^{1}H NMR spectra at various time intervals after addition of α-CD to **3** in D$_2$O (Figure 5).

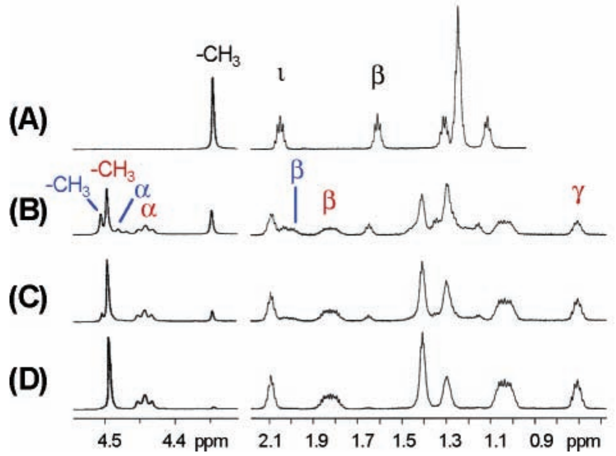

Figure 5. ^{1}H NMR spectra of **3** (A) and the mixture of **3** and α-CD at 18 min (B), 55 min (C), and 1 day (D) after addition of α-CD to **3**. [**3**] = 2 mM; [α-CD] = 3 mM. Notations of protons are the same as in Figure 2: black, free **3**; blue, **2a**-type isomer; red, **2b**-type isomer.

In the early stages, the presence of two isomeric **3**/α-CD [2]pseudorotaxanes is clearly seen and the integral ratio of **2b**-type to **2a**-type isomers becomes greater as time elapses. The ratio is about 2 at 18 min, and the peaks of the **2a**-type isomer disappear almost completely after a day. This indicates that the threading rates of viologen group through the narrow primary side of α-CD (to form the **2b**-type isomer) and through the wide secondary side (to form the **2a**-type isomer) are not much different, but the dethreading rate of the **2a**-type isomer is much faster than that of the **2b**-type isomer, giving mostly the thermodynamically stable **2b**-type isomer after a long time.

Complementary evidence of the dynamic equilibrium of **3**/α-CD [2]pseudorotaxanes was obtained by comparison of UV/vis and circular dichroism change during the formation of the [2]pseudorotaxanes (Figure 6). Aliphatic chain-linked aromatic-viologen compounds such as **3** exhibit diffused absorption bands in the visible region due to the intramolecular charge-transfer interaction between aromatic and viologen moieties, and the interaction is disrupted by

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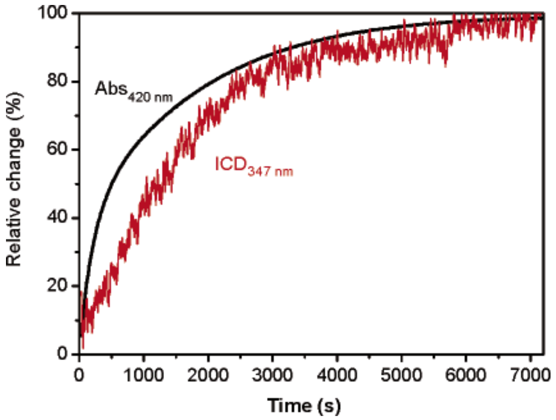

Figure 6. Variation of the charge-transfer absorption at 420 nm and ICD at 347 nm with elapsed time after addition of α-CD to **3**. The total concentrations after the addition are [**3**] = 0.78 mM and [α-CD] = 1.29 mM.

pseudorotaxane formation.[7,14,15] The trace of charge-transfer absorption change with elapsed time after mixing **3** and α-CD showed a typical pseudo-first-order kinetics as it follows the disappearance of free **3**. The relative change of ICD at the early stages was much less than the absorbance change. This reflects that the two [2]pseudorotaxane isomers show different ellipticities and the ratio of the species exhibiting large (actually positive) ellipticity to that of small (actually negative) ellipticity increases with elapsed time. This is consistent with the observations of the opposite sign of the ICD bands of the two isomers and thermodynamic stability of the isomer having positive ICD.

In a recent paper, we reported that the viologen dication moiety prefers the secondary face of β-CD 14 times more than the primary face.[16] The thermodynamic stability of the unidirectional **3**/α-CD [2]pseudorotaxane in which the secondary side of α-CD faces the viologen moiety as observed in this work agrees well with the report. The preference of a face of CDs for a specific group over the other was also revealed in the unidirectional photoinduced shuttling of α-CD ring in a rotaxane with a symmetric stilbene dumbbell.[5] However, such face selectivity of α-CD appears to be small for **1**/α-CD [2]pseudorotaxane in DMF:[17] we observed a ratio of [2]rotaxane isomers **2a** to **2b** of about 7:9 by stoppering the pseudorotaxane.

Finally, we discuss briefly the kinetics of threading/dethreading of viologen through α-CD[7,14] and possible applications of the present study. For the analysis of threading/dethreading kinetics, it is necessary to consider assembling and disassembling of both [2]pseudorotaxane isomers. However, previous studies were made without considering the difference in the rates of threading/dethreading through different sides of α-CD or under the preassumption of unidirectional threading/dethreading.[7,14] As we now have the microscopic spectral characteristics of the two [2]pseudorotaxane isomers and can get mixtures of the isomers with different isomeric ratios by adjusting the elapsed time after addition of α-CD to the rod solution, we may be able to obtain the directional threading/dethreading rates. Also on the basis of the large difference in dethreading rates depending on the orientation of the α-CD ring, it could be possible to achieve virtually unidirectional movement of the CD ring along rods having a viologen group. The formation of a unidirectional [2]pseudorotaxane consisting of α-CD and **3** in water could be utilized to prepare unidirectional rotaxanes by stoppering the pseudorotaxane.

In conclusion, we have prepared two isomeric [2]rotaxanes **2a** and **2b** by stoppering the **1**/α-CD [2]pseudorotaxane with 3,5-dimethoxybenzyl bromide in DMF. The isomers show quite contrasting NMR spectra and opposite Cotton effects. In contrast to this, **3**/α-CD [2]pseudorotaxane formed in water is unidirectional with the viologen moiety facing toward the secondary side of α-CD. This originates from the thermodynamic preference of a viologen group for the secondary face of α-CD, which results in a slow dethreading rate for the isomer. Extension of this work to study the directional threading/dethreading kinetics for passing viologens through CDs, synthesize unidirectional interlocked molecules incorporating CDs and viologens, and achieve one-way movement of CDs along rod components is underway.

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Supporting Information Available: Detailed synthetic procedures (for **1**, **2a**, **2b**, and **3**), ^{1}H NMR (for **2a**, **2b**, **3**, and **3**/α-CD), ^{1}H−^{1}H COSY (for **2a** and **2b**), and two-dimensional ROESY (for **2a**, **2b**, and **3**/α-CD) spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Because of the low solubility of **1** in water, we were not able to study the pseudorotaxane formation of **1** with α-CD and could not prepare rotaxanes from **1** in water.