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Supramolecular Dynamics

Cyclodextrin-Based Size-Complementary [3]Rotaxanes: Selective Synthesis and Specific Dissociation

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Abstract: α-Cyclodextrin (CD)-based size-complementary [3]rotaxanes with alkylene axles were prepared in one-pot by end-capping reactions with aryl isocyanates in water. The selective formation of [3]rotaxane with a head-to-head regularity was indicated by the X-ray structural analyses. Thermal degradation of the [3]rotaxanes bearing appropriate end groups proceeded by stepwise dissociation to yield not only the original components but also [2]rotaxanes. From the kinetic profiles of the deslippage, it turned out that the maximum yield of [2]rotaxane was estimated to be 94%. Thermodynamic studies and NOESY analyses of such rotaxanes revealed that [2]rotaxanes are specially stabilized, and that the dissociation capability of the [3]rotaxanes to the components can be adjusted by controlling the structure of the end groups, direction of the CD groups, and length of the alkylene axle.

Introduction

Size-complementary rotaxanes, a peculiar group of rotaxanes, have substituents that are size-complementary to the wheel cavity at the axle terminus.[1] These rotaxanes can be dissociated to their components using certain stimuli by deslippage of the wheel without destruction of any covalent bonds. Therefore, rotaxanes showing such unique dissociation behavior have been exploited as key materials for the construction of stimuli-responsive systems, for example, network polymers and topology-switchable polymers.[2–5] Cyclodextrin (CD), as a representative wheel in rotaxanes, is capable of incorporating a variety of linear axle components consisting of alkylene chains, aromatics, and polymers.[6,7] Although the synthesis and applications of CD-based rotaxanes have been extensively studied to date,[8] there are few reports on CD-based size-complementary rotaxanes[9] because of the challenges associated with the synthesis of CD-based rotaxanes with exact components. We previously reported a new method for the synthesis of α-CD-based size-complementary [3]rotaxanes by a one-pot process.[10] Recently, we achieved the selective synthesis of various α-CD-containing size-complementary [3]rotaxanes and evaluated their useful dissociation behavior, the results of which are presented herein. Thermal degradation of [3]rotaxanes bearing appropriate end groups proceeds by stepwise dissociation to yield not only the original components but also the corresponding [2]rotaxanes. Notably, the dissociation capability of [3]rotaxanes can be adjusted by controlling the structure of the end groups, direction of the CD groups, and length of the alkylene axle. Thermodynamic studies of the deslippage behavior clarify the effect of the size-complementary end-groups on the deslippage process. The transformation of these rotaxanes also provides a new method for regulating the structure of CD-based rotaxanes.

Results and Discussion

One-pot synthesis of α-CD-based rotaxanes

Syntheses of [3]rotaxanes were performed according to a one-pot method.[10] After considerable efforts, we found that the pseudorotaxanation reaction facilitates at temperature over the melting points of the axle components (around 70 °C), which is probably due to the insolubility of the axle components in water. The threading complexation of 1,12-diaminododecane or 1,10-diaminodecane with α-CD in refluxing water for 1 h gave a heterogeneous mixture consisting of pseudo[3]rotaxanes, to which various phenyl isocyanate derivatives were added at 0 °C. Standard workup afforded the corresponding [3]rotaxanes in good yields without the formation of [2]rotaxanes (Table 1, Scheme 1). It is worth mentioning that the present end-capping method includes several advantageous conditions to give high yields of CD-based rotaxanes such as the reaction in water to make hydrophobic interactions of intermediary pseudo[3]rotaxane strong and the low-temperature reaction to suppress entropy-driven decomposition of the pseudorotaxane. Three remarkable points should be also emphasized about these results as shown in Table 1: 1) Less bulky agents such as 2-methyl and 3-methoxy phenyl isocyanates

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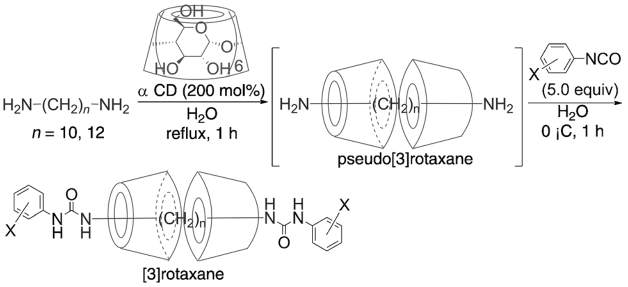
Table 1. Synthesis of [3]rotaxanes.

End-cap agent		2-BrC_6H_4NCO	2-$MeOC_6H_4NCO$	3,5-$Me_2C_6H_3NCO$	2,6-$Me_2C_6H_3NCO$
n[a] = 12	[3]rotaxane	**1**, 73 %	**4**, 64 %	**8**, 60 %	**10**, 13 %
	[2]rotaxane	**2**, –[b]	**5**, –[b]	–[b]	–[b]
n[a] = 10	[3]rotaxane	–[b]	**6**, 21 %	**9**, 28 %	–[b]
	[2]rotaxane	–[b]	**7**, –[b]	–[b]	–[b]

[a] n = number of alkylene carbon atoms in the axle (Scheme 1). [b] Not detected.



Scheme 1. One-pot synthesis of [3]rotaxanes from α,ω-diaminoalkanes and α-CD by the urea end-capping method.

yield only dumbbell-shaped products derived from the axle;[11] 2) phenyl isocyanates with a bulky substituent at the *ortho* position such as 2-isopropyl-, 2-iodo-, and 2-ethyl phenyl isocyanate suppress urea formation, and thus no reaction occurs[11] probably because of the steric hindrance around the isocyanate moieties; and 3) the use of 1,12-diaminododecane as a longer axle affords higher yields of [3]rotaxanes because the longer axle reduces the coverage of CD around the axle termini, thus increasing the nucleophilicity of the amine and the hydrophobic interactions between the components, which results in stabilization of the intermediary pseudo[3]rotaxanes. Furthermore, it should be noted that all [3]rotaxanes obtained have a head-to-head regularity, which was determined by ^{1}H NMR[11] and single crystal X-ray structural analyses (Figure 1). The selective formation of this head-to-head structure is a result of the effective formation of multipoint hydrogen bonds between the two head faces, which indirectly supports the preferential formation of [3]rotaxanes over [2]rotaxanes. The X-ray crystal structure clearly exhibits the structural characteristics of [3]rotaxane **1**: The distances between the mutual oxygen atoms of head faces were around 2.7–2.9 Å, indicating the presence of hydrogen bonding between the head faces (O–H···O), and the bromophenyl moieties as an end-capping group have no attractive interaction with CD components.

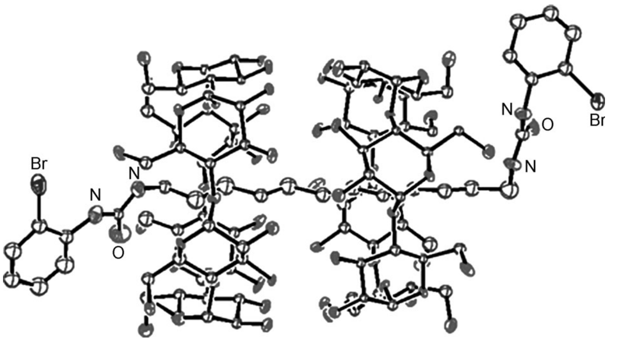


Figure 1. ORTEP diagram of [3]rotaxane **1**. Ellipsoids are set at 50 % probability; hydrogen atoms and solvating molecules are omitted for clarity.

Thermodynamic analyses of rotaxanes

These [3]rotaxanes were sufficiently stable in [D_6]DMSO for room temperature ^{1}H NMR analysis. To examine the size complementarity of the [3]rotaxanes, solutions of [3]rotaxanes in [D_6]DMSO were heated at arbitrary temperatures. Figure 2 shows the time-dependent NMR spectral changes during the deslippage reaction of **4**. A clear spectral change was observed after heating the solution at 80 °C that progressed as the heating time was prolonged, indicating the prompt thermal degradation of **4** in a manner similar to that previously reported for **1** (Figure 2).[10] Structural analyses of the products supported the formation of not only [2]rotaxane **5** but also dumbbell-shaped molecule **11**, both of which were easily purified by reverse-phase column chromatography (Scheme 2, Figure 3). This result indicates that the thermal deslippage of α-CD from both **4** and **5** occurs. Furthermore, the detection of intermediary [2]rotaxane **5** indicates that the deslippage from **5** to **11** is sufficiently slower than that from **4** to **5**. Kinetic profiles of the deslippage of both **4** and **5** were thus investigated to clarify the detailed deslippage process.

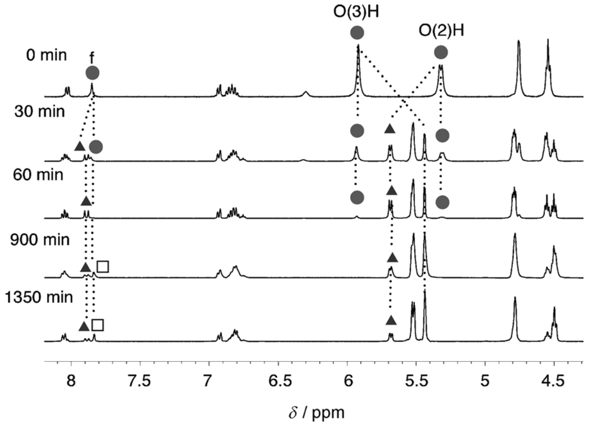
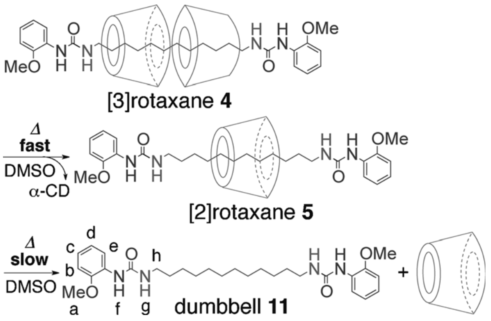


Figure 2. Time-dependent NMR spectral changes in the 4.5–8.0 ppm region (400 MHz, [D_6]DMSO, 298 K) during the degradation of **4** (8.5 mmol L^{-1} in [D_6]DMSO at 353 K). The diagnostic peaks are marked as **4** (●), **5** (▲), and **11** (□).

Solutions of **4** in [D_6]DMSO were heated at 40, 60, 80, and 100 °C and subjected to ^{1}H NMR analysis. Assuming that the deslippage reaction obeys first-order kinetics, the rate constants were determined from the time vs. ln([rotaxane]/[rotaxane]$_0$) plots using the integral ratios from the ^{1}H NMR spectra (Table 2). The resultant time–yield curves for **4**, **5**, and **11** are shown in Figure 4. The formation of [2]rotaxane **5** began soon after heating was initiated, while **11** appeared more gradually.



Scheme 2. Thermal degradation of [3]rotaxane **4** to [2]rotaxane **5** and dumbbell **11** by the deslippage of α-CD.

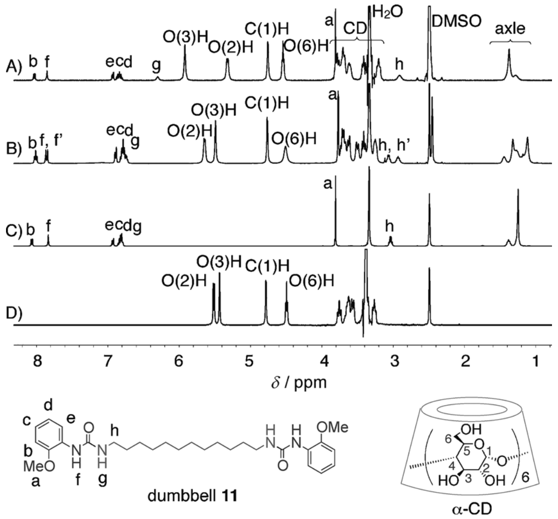


Figure 3. ^{1}H NMR spectra of A) **4**, B) **5**, C) **11**, and D) α-CD (400 MHz, [D$_6$]DMSO, 298 K).

The maximum yield of **5** was estimated to be 94% after 1.5 h. The deslippage half-lives of **4** at all temperatures were approximately 100 times greater than those of **5**. These results clearly suggest the stepwise deslippage of **4** by the fast formation of **5** and subsequent slow decomposition of **5** to **11**, thus facilitating the isolation of **5**.

The CD component of [2]rotaxane can deslip from not only the narrower rim (tail face), but also the wider rim (head face), being different from [3]rotaxane. Therefore, the deslippage of [2]rotaxanes was expected to be faster than that of [3]rotaxanes. However, contradictory results were observed. To evaluate such extraordinary stability of [2]rotaxanes, NOESY NMR study was carried out.[11] For **2**, the NOE correlations indicated the existence of an inclusion stabilization effect between the CD moiety and the end group. On the other hand, in the NOESY NMR spectrum of **5**, no correlation was observed between protons of the two moieties, although the correlations between the CD and alkylene chain protons were detected (Figure 5). This difference in localized position of the CD must depend on the electronic and/or steric properties of the end groups. The methoxy end group may be polar enough to positively interact with the solvent and/or bulky enough to disfavor the approach of CD.

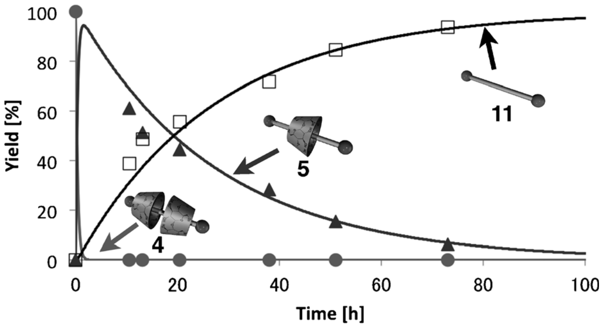


Figure 4. Time-yield curves for the degradation of **4** (●) to **5** (▲) and **11** (□) (8.5 mmol L^{-1} in [D$_6$]DMSO at 353 K). Theoretical curves were drawn by using the kinetic parameters of each compounds.[11]

Interestingly, [3]rotaxane **8** exhibited different deslippage behavior compared with those of other [3]rotaxanes. Unlike other [3]rotaxanes, for which deslippages occurred approximately at 60 °C, the deslippage of **8** required a temperature above 100 °C. Furthermore, no ^{1}H NMR signals of the corresponding [2]rotaxane were observed in the NMR spectrum of **8** under degradation conditions.[11] The result suggests that the

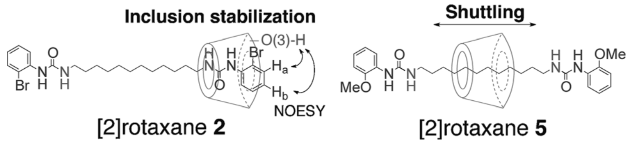


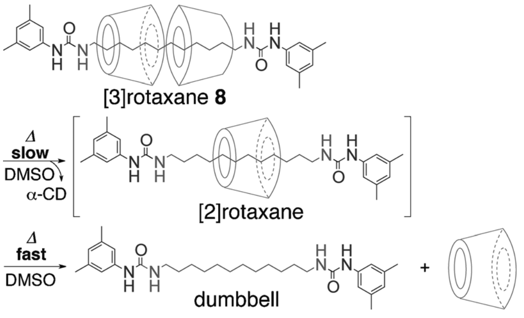
Figure 5. Difference of localization position of CD on [2]rotaxanes **2** and **5**.

Table 2. Thermodynamic parameters for the deslippage of [2] and [3]rotaxanes.[a]

Rotaxane	Half-life τ [h] 40 °C	50 °C	60 °C	70 °C	80 °C	100 °C	120 °C	Activation enthalpy $\Delta H^{\neq}$ [kJ mol^{-1}]	Activation entropy $\Delta S^{\neq}$ [J mol^{-1}·K^{-1}]
[3]rotaxane **1**	–[b]	–[b]	9.2	–[b]	3.0	0.39	–[b]	78	−100
[2]rotaxane **2**	–[b]	–[b]	80	–[b]	29	3.7	0.68	85	−99
[3]rotaxane **4**	18	–[b]	1.3	–[b]	0.25	–[b]	–[b]	96	−34
[2]rotaxane **5**	–[b]	–[b]	320	–[b]	19	2.3	–[b]	120	7.7
[3]rotaxane **6**	2.8	1.1	0.48	–[b]	–[b]	–[b]	–[b]	73	−91
[2]rotaxane **7**	–[b]	–[b]	100	28	8.8	–[b]	–[b]	120	−7.2
[3]rotaxane **8**	–[b]	–[b]	–[c]	–[b]	–[c]	31	–[b]	–[b]	–[b]

[a] Determined by ^{1}H NMR analyses. The details of experiments and calculations are given in the Supporting Information. The reaction was performed using a solution of each rotaxane (8.5 mmol L^{-1} in [D$_6$]DMSO). [b] Not measured. [c] No reaction.

deslippage from **8** to [2]rotaxane is much slower than the conversion of [2]rotaxane to the dumbbell-shaped molecule. This behavior is clearly different from that of [3]rotaxanes other than **8** (Scheme 3). Furthermore, the NMR analyses of compounds **9** and **10** suggested that the deslippage of two CDs of **9** and **10** may be competitive and occur by a mechanism similar to that of **8**. Although the precise thermodynamic analyses of **9** and **10** could not be achieved owing to much less solubility of **9** and **10** and its derivatives, it was found that two types of the decompositions were operated depending on the axle terminal structure.



Scheme 3. Thermal degradation of [3]rotaxane **8** to the dumbbell and α-CD.

The kinetic and thermodynamic parameters for the deslippage processes of several [2]- and [3]rotaxanes are summarized in Table 2. The activation enthalpy ($\Delta H^{\neq}$) and activation entropy ($\Delta S^{\neq}$) were obtained by the Eyring plots. A comparison of the half-lives of **1**, **2**, **4**, and **5** at 60 °C revealed that the deslippage of **4** was faster than that of **1**, whereas the deslippage of **5** was slower than that of **2**. Furthermore, the enthalpy term ($\Delta H^{\neq}$), rather than the entropy term ($T\Delta S^{\neq}$), was observed to be dominant in these systems. Moreover, the deslippage processes for two rotaxanes with methoxy groups (**4** and **5**) were found to have larger $\Delta H^{\neq}$ and smaller $\Delta S^{\neq}$ than those of the rotaxanes with bromo substituents (**1** and **2**). Figure 6a presents illustrations to explain these results. Based on the NOESY analyses mentioned above, the mobility of the two CDs in [3]rotaxane **1** is expected to be greater than that of **4**, probably because the methoxy substituents of **4** suppress the approach of the CDs to the end groups. Assuming that the flexibility of CD is restricted during the deslippage transition state, $\Delta S^{\neq}$ for the entire deslippage process in **1** is greater than that of **4**. Based on the enthalpy–entropy compensation rule,[12] the deslippage system in **4** is expected to have a larger $\Delta H^{\neq}$ than **1**. Meanwhile, the enthalpy gain by the inclusion complex formation of **2** results in a smaller $\Delta H^{\neq}$ for the deslippage process compared with that of **5**, leading to the faster deslippage of **2**. On the other hand, deslippage rates for the shorter axle-containing rotaxanes (**6** and **7**) were approximately three times faster than those of the longer-axle containing rotaxanes (**4** and **5**).

This difference may be attributed to the smaller $\Delta H^{\neq}$ values of **6** and **7** compared to those of **4** and **5**, which originates from the higher probability that the CDs in the shorter axle-containing rotaxanes exist near the bulky end groups. Because of the dynamic movement of the CD groups, it is possible that their original structures can somewhat resemble that of the transition-state structure. Furthermore, the deslippage of **8** was very slow even compared with those of deslippage for **2** and **5**, which have special stabilizing factors. This result suggests that steric effect of the narrower rim (tail face) on **8** during the deslippage is larger than such stabilization energy (Figure 6b). Because the CD in the corresponding [2]rotaxane of **8** can readily deslip from a wider rim after the first deslippage step,[9a] the first deslippage in **8** is energetically large enough to be the rate-determining step for the entire process (Figure 6c).

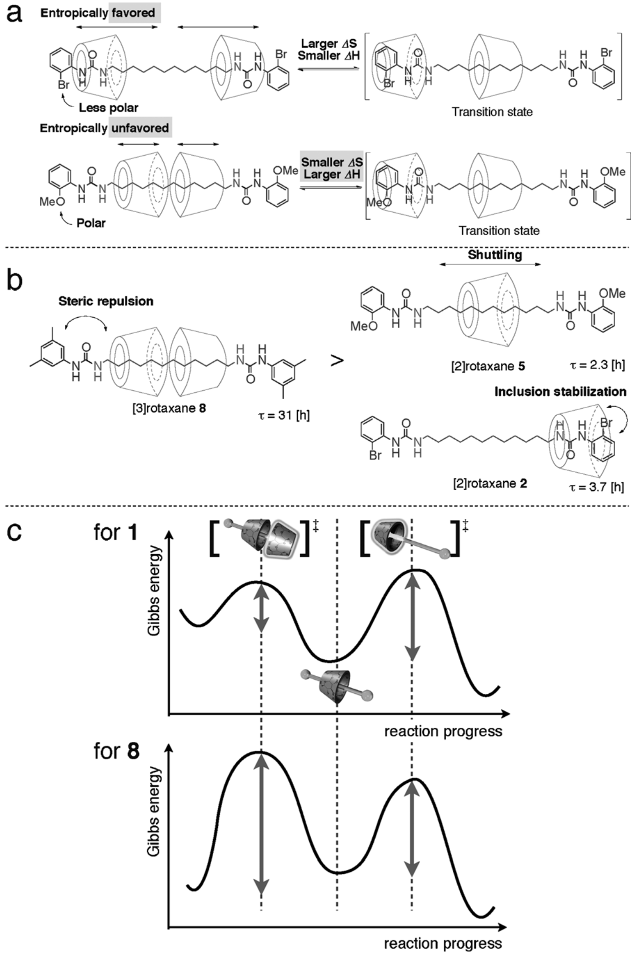


Figure 6. a) Illustration of the difference in $\Delta H^{\neq}$ according to the enthalpy–entropy compensation rule using [3]rotaxanes **1** and **4**; b) illustration of the inhibitory capacity of the deslippage depending on the end group structures using [3]rotaxane **8** and [2]rotaxanes **2** and **5**; c) energy profile difference of the stepwise degradation of **1** (top) and **8** (bottom).

Conclusion

In conclusion, a practical synthetic method for α-CD-based size-complementary [3]rotaxanes was developed. This method consists of quantitative formation of pseudo[3]rotaxanes followed by a rapid end-capping reaction between terminal amine and phenyl isocyanate in one pot, enabling the effective conversion to [3]rotaxanes. The deslippage rate of the components of these rotaxanes strongly depends on the structure of the end group, direction of the CD, length of the alkylene axle, and the reaction temperature from the detailed studies on the thermodynamic behaviors of the size-complementary rotaxanes. The results of this work might promote the development of sophisticated molecular devices based on new stimuli-responsive systems.

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Keywords: cyclodextrin · rotaxane · size-complementary groups · supramolecular chemistry · thermodynamics

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