Synthesis of a Linked [1]–[1]Rotaxane

Susumu Tsuda,[1] Jun Terao,*[2] Keisuke Tsurui,[1] and Nobuaki Kambe*[1]
[1]*Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871*
[2]*Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510*

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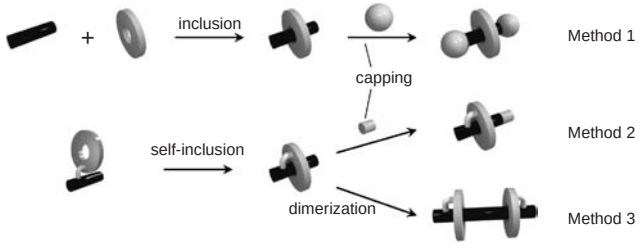
Highly organic soluble [1]–[1]rotaxane also known as linked [3]rotaxane was synthesized by intramolecular self-inclusion of a modified permethylated α-cyclodextrin (PM α-CD) to form a pseudo[1]rotaxane followed by dimerization. The NMR spectroscopy of thus formed rotaxane suggests that the diphenylacetylene units are fully encapsulated by the PM α-CDs. The Stern–Volmer analysis of fluorescence quenching using a viologen analogue shows that the PM α-CDs inhibits electron transfer efficiently suggesting a high coverage ratio of the π-conjugated axle with the PM α-CDs.

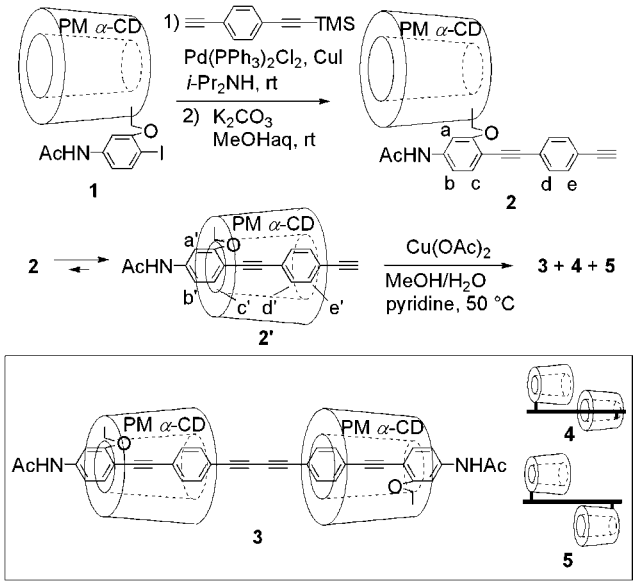
Rotaxanes have attracted considerable attention because of their unique physical properties and potential applications in molecular devices.[1] It is known that the encapsulation of π-conjugated systems can lead to an enhancement in their chemical stability and fluorescence efficiency.[2] Rotaxanes have usually been synthesized by threading an axle molecule through a macrocycle followed by capping with two bulky stoppers (Scheme 1, Method 1).[3] We have revealed in a previous paper that an organic soluble [1]rotaxane also known as linked [2]rotaxane[4] can be synthesized in a good yield by the intramolecular self-inclusion of a lipophilic PM α-CD carrying a rigid π-conjugated axle moiety followed by capping with a small aniline unit as a stopper (Scheme 1, Method 2).[4] Herein, we report the synthesis of a [1]–[1]rotaxane[5] without using any bulky stopper molecules via intramolecular self-inclusion and dimerization of thus-formed pseudo[1]rotaxanes (Scheme 1, Method 3).

Scheme 2 shows our strategy for the synthesis of [1]–[1]rotaxane. The reaction of 6-*O*-monotosyl PM α-CD with 2-iodo-5-acetamidophenol results in a modified PM α-CD iodide **1**[4] in 98% yield. The Sonogashira coupling of **1** with (4-ethynylphenylethynyl)trimethylsilane[6] followed by deprotection of the trimethylsilyl group gave an ethynyldiphenylacetylene-linked PM α-CD **2** in 71% yield.[7]

The intramolecular self-inclusion phenomenon of **2** has been confirmed by using solvent- and concentration-dependent ^{1}H NMR methods.[4] As shown in Figure 1, the NMR spectrum



Scheme 1. Synthetic strategies for rotaxanes.



Scheme 2. Synthesis of a linked [1]–[1]rotaxane **3**.

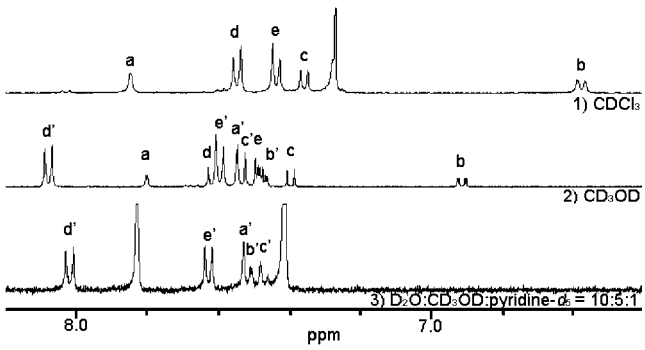


Figure 1. The aromatic region of 400 MHz ^{1}H NMR spectra of **2** in several solvents. 1) $CDCl_3$ at rt; 2) CD_3OD at rt; 3) D_2O:CD_3OD:pyridine = 10:5:1 at 50 °C.

of **2** in $CDCl_3$ reveals the exclusion of the diphenylacetylene moiety from the cavity of the PM α-CD. A spectrum in CD_3OD showed an equilibrium mixture of two species, **2** and its supramolecular complex (pseudo[1]rotaxane) **2′**. When a more hydrophilic medium, D_2O/CD_3OD/pyridine-d_5 (10/5/1) was used at 50 °C, this complex **2′** formed quantitatively. The fact that there was no change in the ^{1}H NMR spectra at different concentrations in the hydrophilic medium (Eglinton coupling conditions) indicated that the intramolecular self-inclusion complex (pseudo-[1]rotaxane) **2′** was selectively generated from **2**.

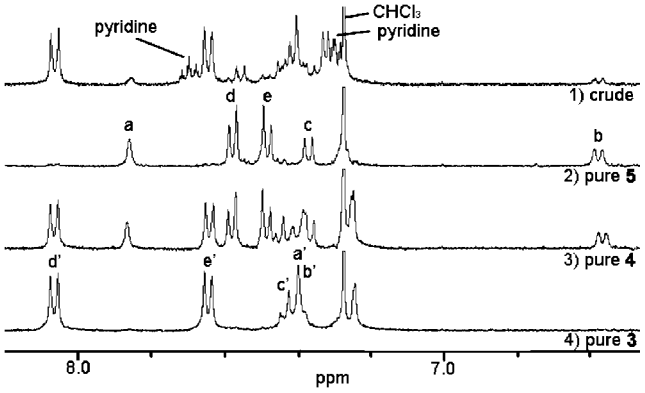


Figure 2. The aromatic region of 400 MHz ^{1}H NMR spectra in $CDCl_3$ at rt. 1) Eglinton reaction mixture; 2) unencapsulated dimer **5**; 3) [1]rotaxane **4**; 4) [1]–[1]rotaxane **3**.

We then carried out the dimerization of **2′** by using the Eglinton coupling in D_2O/CD_3OD/pyridine-d_5 (10/5/1) at 50 °C for 10 days. The formation of the desired dimer **3** was inferred from the MALDI-TOF mass spectrum, which displayed a strong signal at m/z 2959 for the corresponding $[\mathbf{3} + \mathrm{Na}]^+$ ion. The NMR analysis of the crude product indicated the formation of the desired [1]–[1]rotaxane **3** along with [1]rotaxane **4** and unencapsulated dimer **5** as by-products. **3**, **4**, and **5** were successfully separated in pure form by using silica gel column chromatography in 52%, 18%, and 2% yield, respectively. This result suggests that the reactivity of psuedo[1]rotaxane **2′** is lower than that of unencapsulated compound **2** due to steric hindrance. Compounds **3**, **4**, and **5** had the same sodiated molecule peak (m/z) in the MALDI-TOF mass spectrum but exhibited considerably different ^{1}H NMR spectra (Figure 2).

The inclusion structure of [1]–[1]rotaxane **3** was characterized by 2D TOCSY, COSY, and ROESY NMR. The NOEs between the axial diphenylacetylene proton H_D and CD protons (H_3 and H_5) and between H_E and H_3 indicated that the axial π-conjugated system was embedded in the PM α-CD cavity to form [1]–[1]rotaxane (Figure 3).

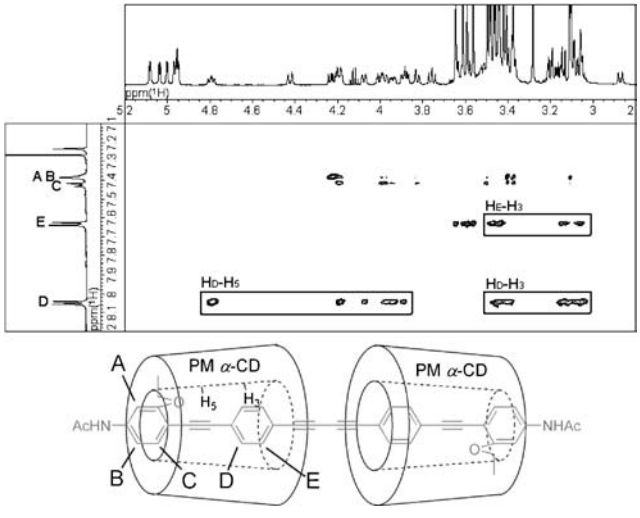


Figure 3. The section of the 600 MHz ROESY NMR spectrum of [1]–[1]rotaxane **3** in $CDCl_3$ at 25 °C with a mixing time of 300 ms and the proposed conformation.

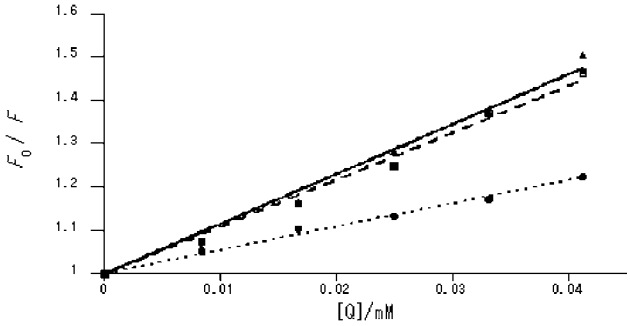


Figure 4. Stern–Volmer plots for titration of **3** (dotted line, circle), **4** (dashed line, square) and **5** (solid line, triangle) with 1,1′-di-*n*-heptyl-4,4′-bipyridinium dibromide in $CHCl_3$. The concentration of **3**, **4**, and **5** was 5.3×10^{-8} M.

In order to examine the shielding effect of PM α-CD, we investigated the fluorescence quenching of **3**, **4**, and **5** with an electron acceptor. As shown by the Stern–Volmer plots in Figure 4, the viologen analog (1,1′-di-*n*-heptyl-4,4′-bipyridinium dibromide) quenched the fluorescence of the [1]–[1]rotaxane **3** considerably less than those of [1]rotaxane **4** and unencapsulated π-conjugated molecule **5**. It is noteworthy that fluorescence of partially encapsulated [1]rotaxane **4** was quenched at the same level as **5** suggesting that high coverage ratio of the whole conjugated axle is essential to attain efficient fluorescence properties. Further experiments will be required to determine the fluorescence quenching mechanisms in these systems.[8]

In conclusion, a highly organic soluble and highly encapsulated π-conjugated system was synthesized without using any another bulky stopper molecules. This supramolecular structure of symmetric [1]–[1]rotaxane was determined by 2D NMR measurement. The Stern–Volmer plots of titration experiments indicated that the present [1]–[1]rotaxane exhibits strong insulation effect in prohibiting the approach of a quencher to the π-conjugated system.

This paper is dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday.

References and Notes

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