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A [2]Rotaxane Capped by a Cyclodextrin and a Guest: Formation of Supramolecular [2]Rotaxane Polymer

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Recently, much attention has been focused on interlocked molecules, such as rotaxanes, catenanes, and knots,[1] because of their unique structures and properties. Cyclodextrins (CDs) have been extensively used as a *rotor* of rotaxanes and catenanes.[2] However, [2]rotaxanes using CD as a *stopper* have not been reported. If a [2]rotaxane containing a CD at one end of the axle and a guest at the other end is available, intermolecular complexes will be formed to give supramolecular polymers because a rotaxane structure is rigid enough to prevent intramolecular complexation (Chart 1). Now, we have prepared a [2]rotaxane containing α-CD as a rotor, *β*-CD as a stopper, and a trinitrophenyl group as an another stopper (Scheme 1). We found that a *β*-CD stopper forms intermolecular complexes with a guest stopper of another [2]-rotaxane to give supramolecular [2]rotaxane polymers in which α-CD and *β*-CD line up in an alternating manner.

Previously, we reported that 6-aminocinnamoyl-α-CD (6-aminoCiO-α-CD) formed supramolecular oligomers in aqueous solutions.[3] When the supramolecular polymers were stabilized by attaching a bulky substituent (a trinitrophenyl group), "a cyclic tri-[2]rotaxane" was obtained. In contrast, 6-aminoCiO-*β*-CD was found to form intermolecular complexes with tail-to-tail fashion in the solid state (Figure 1).[4] 6-aminoCiO-*β*-CD is sparingly soluble in water because the dimer units tightly stacked by intermolecular hydrogen bonding form a head-to-head channel-type structure.

We also reported that 6-*p*-*tert*-Boc-aminocinnamoylamino-*β*-CD (6-*p*-^{t}BocCiNH-*β*-CD) formed intramolecular complexes in aqueous solutions.[5] With an addition of α-CD having the adamantane group as a competitive guest to 6-4-^{t}BocCiNH-*β*-CD, supramolecular polymers with alternating α- and *β*-CD units were formed using conformational change in aqueous solutions.

When 1-adamantane carboxylic acid (AdCx) was added to the suspension of 6-aminoCiO-*β*-CD, 6-aminoCiO-*β*-CD was solubilized in water to give a clear solution, indicating that *β*-CD binds AdCx in the cavity in place of the cinnamoyl group to give soluble complexes, and that the cinnamoyl group was exposed to water (Figure S1 in the Supporting Information). AdCx is bound to *β*-CD strongly with the association constant of 10^5 M^{-1}.[6] α-CD has no solubilizing effects on 6-aminoCiO-*β*-CD. However, when α-CD was added to the aqueous solution of the complex of 6-aminoCiO-*β*-CD with AdCx, the cinnamoyl group was included in an α-CD cavity, as proven by the ^{1}H NMR spectroscopic analysis. α-CD does not bind AdCx strongly, but binds an aminoCiO group with the association constant of 10^3 M^{-1}.

When the complex was treated with trinitrobenzene sulfonic acid sodium salt, *β*-CD-capped [2]rotaxane bearing complexed AdCx was obtained. When AdCx was removed by extraction with organic solvents, free nonincluded *β*-CD-capped [2]rotaxane was obtained.[7]

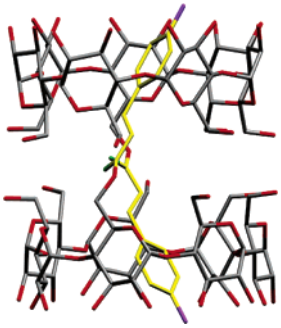
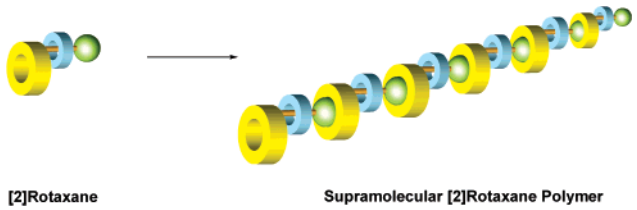
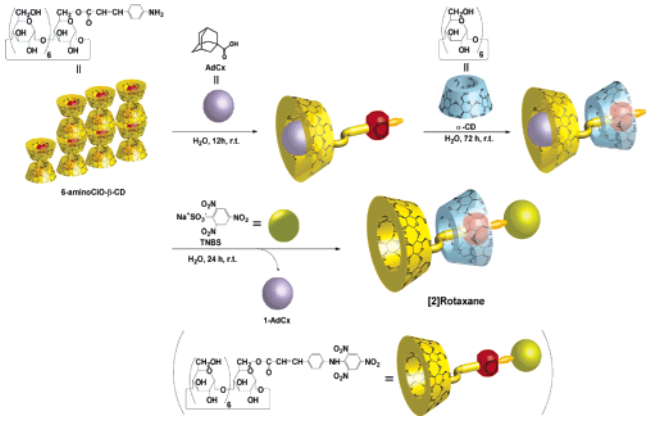


Figure 1. Crystal structure of 6-aminoCiO-*β*-CD. Carbon and oxygen of *β*-CD ring are shown in gray and red, respectively. Carbon, oxygen, and nitrogen of substitution part are shown in yellow, green, and purple, respectively.

Chart 1



Scheme 1. Synthesis of [2]Rotaxane



The MALDI-TOF mass spectra of the product showed a peak at the molecular weight of the [2]rotaxane (2487.1, Na adducts of [2]rotaxane). The ^{1}H NMR spectrum of the product showed the existence of both α-CD and *β*-CD together with a cinnamoyl group and a trinitrophenyl group (Figure S3 in the Supporting Information). The 2D ROESY NMR spectra of the [2]rotaxane in DMSO-d_6 showed a correlation between a resonance of the proton (b) and that of the proton of C(2)−OH of α-CD, indicating that α-CD is

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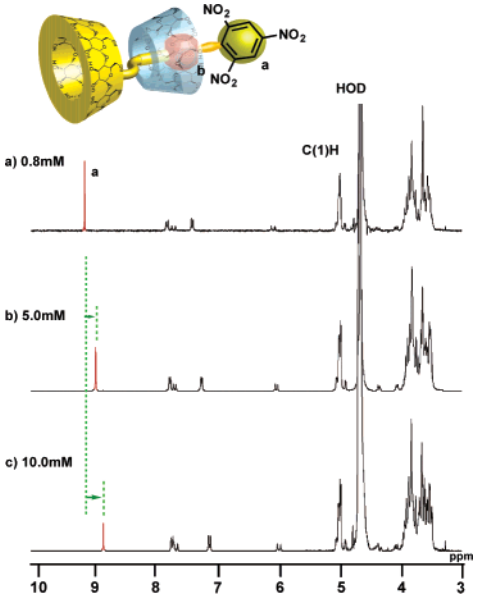

Figure 2. ^{1}H NMR (400 MHz) spectra of the [2]rotaxane containing a β-CD and a 2,4,6-trinitrophenyl group in D_2O at 30 °C: (a) 0.8 , (b) 5.0 , and (c) 10 mM.

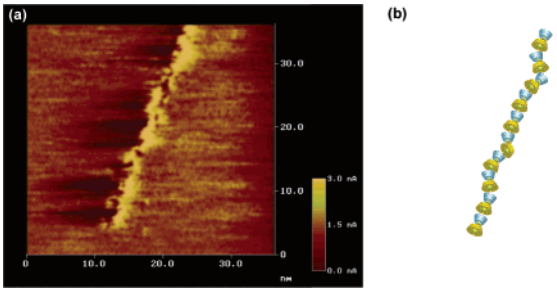

Figure 3. STM image of the [2]rotaxane from concentrated aqueous solution on a HOPG substrate (a) and its schematic structure (b).

placed in the [2]rotaxane with a tail-to-tail fashion with the β-CD stopper group (Figure S4 in the Supporting Information).

Figure 2 shows the ^{1}H NMR spectra of [2]rotaxane at various concentrations in D_2O solutions. The signal of the stopper group (a) of the ^{1}H NMR spectroscopy shifted to an upper field as the concentration increased, indicating that β-CD binds the trinitrophenyl group to give supramolecular polymers, although the peaks did not change in DMSO-d_6. When the phenyl proton of the stopper was irradiated, inner protons of cyclodextrins (C3−H and C5−H) showed a correlation with the phenyl proton, indicating that the stopper group is included in the cavity of β-CD (Figure S6 in the Supporting Information). The VPO (vapor pressure osmometry) measurements of the [2]rotaxane in water showed that the molecular weight increased with increasing concentration and reached 20 000 at 10 mM. The pulsed field gradient NMR measurements confirm the formation of supramolecular polymers.[8,9] Figure 3 shows the scanning tunneling microscopic (STM) image of the [2]rotaxane and its schematic structure.[10] The image shows a long chain of the [2]rotaxanes (>20 nm). The width and heights of the observed chain correspond to those of CD in the [2]rotaxane. Figure 4 shows the schematic representation of a possible supramolecular structure formed by [2]rotaxane in aqueous solution.

In conclusion, a [2]rotaxane capped by β-CD and a trinitrophenyl group has been prepared. A β-CD at the end binds a trinitrophenyl group stopper of another [2]rotaxanes to give supramolecular [2]-rotaxane polymers. The detailed structure and properties of the [2]-rotaxane are now under investigation.

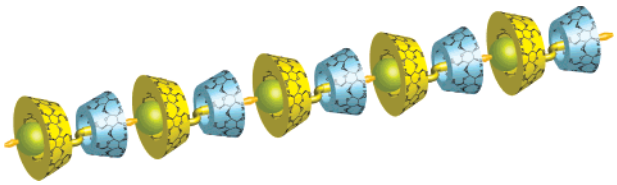

Figure 4. A proposed structure of a supramolecular [2]rotaxane polymer.

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Supporting Information Available: ^{1}H NMR spectra, MALDI-TOF mass spectra of [2]rotaxane. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Synthesis and characterization of [2]rotaxane: To a suspension of 6-aminoCiO-β-CD (83.2 mg, 6.48×10^{-5} mol) in 30 mL of H_2O was added AdCx (35.2 mg, 1.95×10^{-4} mol). After the mixture was stirred for 12 h at room temperature, the suspension gradually became clear, and the precipitate was removed by filtration. α-CD (1.21 g, 1.25×10^{-3} mol) was added to the solution. After the mixture was stirred for 3 days, TNBS (39.0 mg, 1.11×10^{-4} mol) was added successively, and it was stirred for 1 more day. The obtained orange transparent solution was injected into a semipreparative Sephadex G-25 column (eluent: water). The frontal band was collected, concentrated, and poured into acetone. The precipitate was filtered, washed with acetone, and dried under vacuum to give a [2]rotaxane. Yield 14.2 mg (8.89%). Positive ion MALDI-TOF mass *m*/*z* 2487.1 ($M + Na^+$). ^{1}H NMR (400 MHz, DMSO-d_6, 30 °C): δ = 10.26 (s, 1H, −NH−), 8.95 (s, 2H, 3-H of trinitrophenyl), 7.74 (s, 2H, 2-H of phenyl), 7.66 (d, 3H, Ph−C*H*═ and 3-H of phenyl), 7.20 (s, 1H, ═C*H*−CO), 5.78−5.66 (m, 14H, C(2)−OH and C(3)−OH of β-CD), 5.78−5.66 (m, 12H, C(2)−OH and C(3)−OH of α-CD), 4.82−4.73 (m, 13H, C(1)H of α-CD and β-CD), 4.34 (m, 6H, C(6)−OH of α-CD), 4.54−4.47 (m, 6H, C(6)−OH of β-CD), 3.80−3.21 (m, overlaps with HOD). IR (KBr, cm^{-1}): 1707 (vs, νC═O), 1597 (s, νN−H), 1333 (s, νC−O). Anal. Calcd for $C_{93}H_{138}N_4O_{72}\cdot 5H_2O$: C, 43.73; H, 5.84; N, 2.19. Found: C, 43.74; H, 6.33; N, 2.00.

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(9) Diffusion constant of β-CD measured by the field gradient NMR spectroscopy is 3.28×10^{-6} $cm^2\cdot s^{-1}$, and those of the [2]rotaxane are 2.58×10^{-6} $cm^2\cdot s^{-1}$ at 0.5 mM and 2.18×10^{-6} $cm^2\cdot s^{-1}$ at 5.0 mM.

(10) As the sample preparation of STM measurements, an aqueous solution of the [2]rotaxane (5.0×10^{-9} M) was dropped onto a graphite (HOPG) substrate, followed by slow evaporation at room temperature overnight. The STM image was obtained under the condition of the sample bias voltage (+194.4 mV) and tunneling current (1.778 nA).

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