Synthesis of an Organic-soluble π-Conjugated [1]Rotaxane

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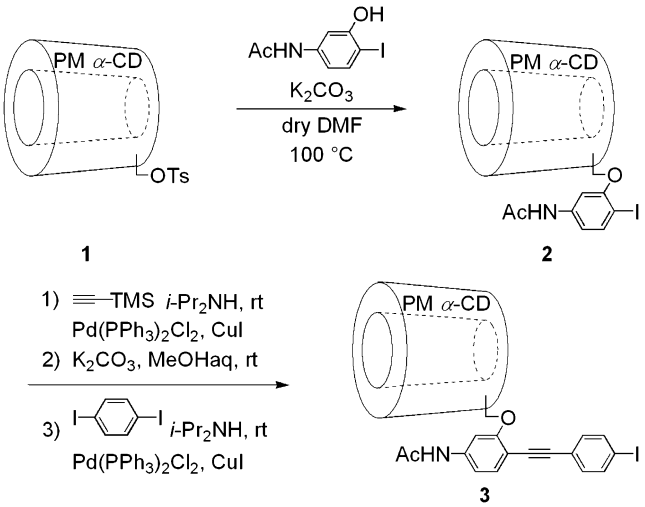
An organic-soluble π-conjugated [1]rotaxane has been synthesized by intramolecular self-inclusion of a lipophilic permethylated α-cyclodextrin bearing a rigid π-conjugated system as a guest moiety. End-capping has been achieved successfully by connecting an aniline moiety without using bulky stoppers. The structure of the [1]rotaxane was determined by 2D NMR spectroscopy.

π-Conjugated systems constitute a core technology for next-generation electronic materials such as organic light-emitting diodes (OLEDs), organic thin-film field-effect transistors, and fluorescent probes. Recently, particular attention has been paid to insulated π-conjugated systems with high stability, high solubility, and high fluorescence quantum yield arising from the decreased π–π interaction among the π-conjugated systems and/or their separation from the external environment.[1] Various water-soluble rotaxanes[2] having insulated π-conjugated systems have been prepared using cyclodextrins (CDs) as a protective cylindrical sheaths.[3] For example, [2]rotaxanes have been synthesized by the inclusion of a π-conjugated system into a CD in aqueous medium followed by the end-capping of the complex with two water-soluble bulky stoppers. Tian et al. synthesized a [1]rotaxane[4,5] by forming an intramolecular self-inclusion complex of an azobenzene-linked β-CD and subsequent end-capping with a water-soluble bulky stopper for a light-driven molecular machine. We report herein a new synthetic method of rotaxanes having high organic solubility and high coverage of a π-conjugated system (axial guest) with a macrocyclic host.

Our strategy to fabricate a [1]rotaxane is based on intramolecular self-inclusion of lipophilic permethylated α-cyclodextrin (PM α-CD) bearing a diphenylacetylene derivative as a rigid π-conjugated system and on a subsequent end-capping with a nonbulky π-conjugated unit.

The substitution reaction of 6-*O*-monotosyl PM α-CD **1**[6] with 2-iodo-5-acetamidophenol[7] gave a modified PM α-CD iodide **2** in 98% yield. The desired modified PM α-CD **3** was prepared using a sequential Sonogashira coupling reaction of **2** with trimethylsilylacetylene and 1,4-diiodobenzene in 67% yield (Scheme 1). Detailed procedures and the spectral data of these compounds are described in Supporting Information.[8]

The intramolecular self-inclusion phenomenon of **3** has been confirmed by CPK model and been examined by ^{1}H NMR employing different solvents and concentrations. As shown in Figure 1, the NMR spectrum of **3** in $CDCl_3$ at room temperature reveals the exclusion of the diphenylacetylene moiety from the cavity of the PM α-CD. The spectrum in CD_3OD at room temperature indicates the presence of a mixture of **3** and its supramolecular complex (pseudo[1]rotaxane) **3′**. The intensity of new



Scheme 1. Synthesis of a modified PM α-CD **3**.

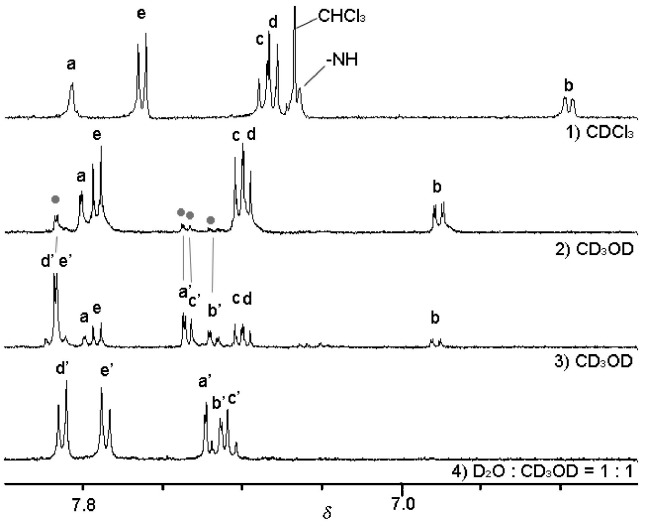
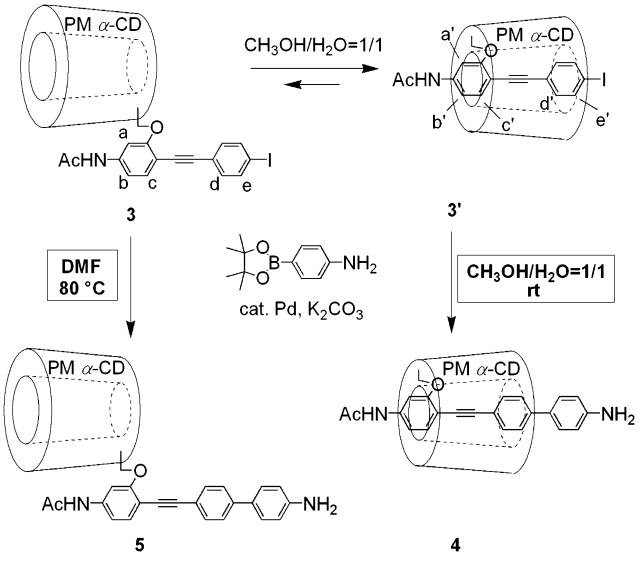


Figure 1. The aromatic region of 400 MHz ^{1}H NMR spectra of **3** in several solvents at rt. 1) $CDCl_3$; 2) CD_3OD (soon after dissolved); 3) CD_3OD after heating at 60 °C for 60 min and cooling to rt; 4) D_2O:CD_3OD = 1:1 after heating at 60 °C for 60 min and cooling to rt.

peaks (**a′**–**e′**) increased on standing at room temperature overnight or by warming up to 60 °C and then cooling to room temperature indicating the slow equilibrium process at room temperature. **3** was converted to the supramolecular complex **3′** in D_2O:CD_3OD = 1:1 and disappeared completely. The evidence that



Scheme 2. Synthesis of [1]rotaxane **4** and uninsulated compound **5** by cross-coupling reaction in different solvents.

the NMR spectra of **3′** at different concentrations in D_2O:CD_3OD = 1:1 showed no new peaks ascribable to oligomeric and/or polymeric supramolecular complexes may support intramolecular self-inclusion complex (pseudo[1]rotaxane) **3′**.

The formation of **3′** resulted in the following up- or downfield shifts of aromatic protons in **3′**, $H_{a-a'}$ (−0.25), $H_{b-b'}$ (+0.56), $H_{c-c'}$ (+0.13), $H_{d-d'}$ (+0.49), and $H_{e-e'}$ (+0.09 ppm). The remarkably large downfield shift of $H_{d-d'}$ suggests that the protons are located very close to the α-1,4-glucosidic oxygen atoms of PM α-CD.[9]

In order to fix pseudo[1]rotaxane **3′** by capping the end of the guest moiety with a π-conjugated unit, **3′** was treated with aniline boronic ester under Suzuki–Miyaura coupling conditions in H_2O:CH_3OH = 1:1 solution (Scheme 2). The desired [1]rotaxane **4** was purified by silica gel column chromatography and was obtained in pure form in high yield (80%).[8] This [1]rotaxane is soluble in various organic solvents such as methanol, ethyl acetate, chloroform, toluene, and DMF. It is known that the decomplexation of [1]rotaxane through "flipping" mechanism is often observed owing to large flexibility of PM α-CD in comparison to that of native α-CD.[10] However, [1]rotaxane **4** was stable in $CDCl_3$ for more than seven days without decomplexation. The corresponding uninsulated compound **5** was intentionally synthesized by the reaction of **3** with aniline boronic ester in DMF instead of 1:1 solution of H_2O and CH_3OH.

Kaneda et al. succeeded in synthesizing dimeric cyclic [2]rotaxane via end capping of dimeric cyclic inclusion compound of a para substituted azophenol-linked PM α-CD by azo coupling using sterically hindered naphthol derivative.[9] In our [1]rotaxane synthesis, however, MALDI-TOF mass spectrum exhibited only the peak at m/z 1558 corresponding to $[\mathbf{4} + Na]^+$. No evidence for the formation of dimeric cyclic [2]rotaxane was detected by MALDI-TOFMS and GPC analysis. It is quite interesting that a pseudo[1]rotaxane was selectively generated from ortho substituted diphenylacetylene-linked PM α-CD via intramolecular self-inclusion. The structure of this [1]rotaxane was confirmed by 2D TOCSY, COSY, and ROESY NMR. The NOEs between protons on the diphenylacetylene moiety and the internal protons of the PM α-CD were observed. The details are described in Supporting Information.[8]

Table 1. Electronic spectra and fluorescence quantum yields[a]

Sample	Absorption (λ_{max}/nm)	Emission (λ_{max}/nm)	$\Phi_{solution}$	Φ_{solid}
4	328	398	0.89	0.68
5	338	396	0.71	0.06

[a]Spectra were recorded in $CHCl_3$. Absolute quantum yields were determined by a calibrated integrating sphere system.

In order to examine the shielding effect of PM α-CD, we compared the fluorescence quantum yield of **4** with that of the corresponding uninsulated compound **5** (Table 1). As expected, there is a significant fluorescence enhancement in **4** especially in solid state suggesting that encapsulation of the chromophore by PM α-CD is essential to attain efficient fluorescence properties.

In conclusion, an organic-soluble [1]rotaxane was prepared via intramolecular self-inclusion of PM α-CD bearing a diphenylacetylene moiety and subsequent end-capping with an aniline unit by the Suzuki–Miyaura coupling. The present study revealed that bulky stoppers are not necessary when [1]rotaxane consist of PM α-CD as a macrocyclic host and a rigid conjugated system as the guest unit are linked each other.

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