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Synthesis of Linked Symmetric [3]Rotaxane Having an Oligomeric Phenylene–Ethynylene Unit as a π Guest via Double Sonogashira Cross-coupling

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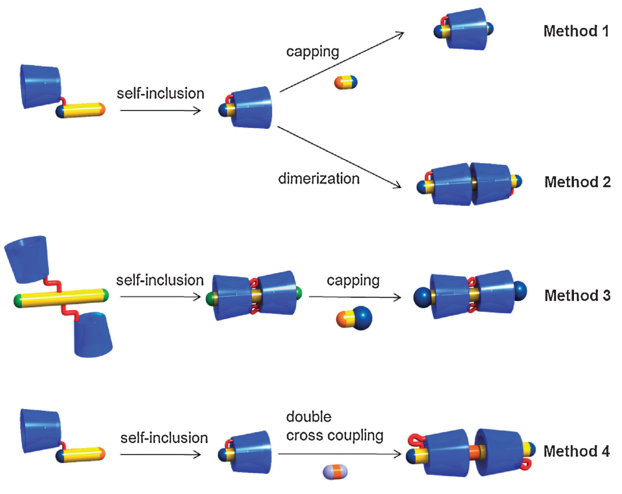
Linked symmetric [3]rotaxanes consisting of an oligomeric phenylene–ethynylene (OPE) unit as a π-conjugated guest and two molecules of organic soluble permethylated α-cyclodextrins (PM α-CDs) as macrocyclic hosts have been synthesized by intramolecular self-inclusion of an OPE guest moiety carrying PM α-CDs followed by double cross-coupling reaction with 1,4-diiodobenzene under the Sonogashira coupling conditions. The structure of thus formed rotaxane was determined by MALDI-TOF mass spectrum and two-dimensional NMR spectroscopy.

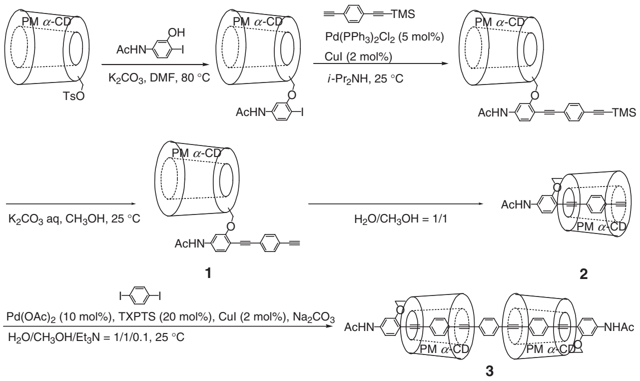
π-Conjugated molecules have attracted considerable attention because of their potential applicability as next-generation electronic materials such as organic light-emitting diodes (OLEDs), organic thin-film field-effect transistors, and fluorescent probes. Recently, particular attention has been paid to insulated π-conjugated compounds in which the conjugated units are covered by a protective sheath, limiting the π–π interaction and enhancing the fluorescence, solubility, and chemical stability as compared to those of the corresponding π-conjugated compounds.[1] In terms of commercial availability and the efficacy of inclusion via hydrophilic–hydrophobic interaction, methods for insulating organic molecules through cyclodextrin have been widely researched.[2] Oligomeric phenylene–ethynylenes (OPEs) are among the most extensively studied families of molecular electronics compounds due to their interesting photo- and electrophysical properties including nonlinear optical response and luminescence.[3]

We are interested in developing new methods for encapsulation of π-conjugated compounds having OPE units in order to realize higher solubility, fluorescence quantum yields, electroluminescence efficiencies, and chemical stabilities of the π-conjugated systems. Recently we have reported three new synthetic routes to linked rotaxanes bearing π-conjugated units as a guest and permethylated α-cyclodextrin (PM α-CD) as a macrocyclic host (Scheme 1).[4,5] Our strategies employed for the syntheses of these linked rotaxanes were based on intramolecular self-inclusion of a π-conjugated rigid guest unit through lipophilic PM α-CD linking to the guest moiety in a hydrophilic medium to form a pseudo[1]rotaxane which then gave rise to a [1]rotaxane (linked [2]rotaxane) by end-capping (Method 1),[5a] a linked [3]rotaxane ([1]–[1]rotaxane) by dimerization (Method 2),[5b] or sequential intramolecular self-inclusion and capping with two end-groups (Method 3).[5c]

Herein, we report a new synthetic method of an OPE-based linked symmetric [3]rotaxane via the double Sonogashira cross-coupling of two molecules of pseudo[1]rotaxane with 1,4-diiodobenzene (Method 4).



Scheme 1. Our synthetic routes to linked rotaxanes.



Scheme 2. Synthesis of a symmetric [3]rotaxane.

Scheme 2 shows our strategy for the synthesis of OPE-based linked [3]rotaxane. The reaction of 6-*O*-monotosyl PM α-CD[6] with 5-acetamido-2-iodophenol results in a modified PM α-CD iodide in 98% yield. The Sonogashira coupling of thus formed iodide with [(4-ethynylphenyl)ethynyl]trimethylsilane followed by deprotection of the trimethylsilyl group gave an ethynyltolan-linked PM α-CD **1** in 74% yield via two steps. The unique intramolecular self-inclusion phenomenon of **1** has been confirmed by using solvent- and concentration-dependent ^{1}H NMR methods. As shown in Figure 1, the NMR spectrum of **1** in $CDCl_3$ revealed the exclusion of the tolan moiety from the cavity of the PM α-CD. A spectrum in CD_3OD showed an equilibrium mixture of two species, **1** and its supramolecular complex (pseudo[1]rotaxane) **2**. When a more hydrophilic medium, D_2O/CD_3OD (1/1) was used at 25 °C, the exclusion complex converted completely into the inclusion complex **2**.

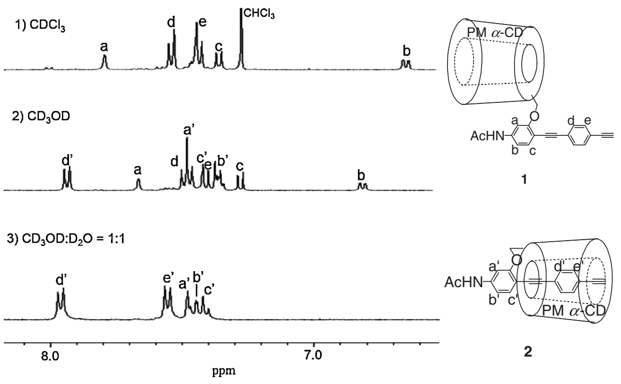


Figure 1. The aromatic region of 400 MHz ^{1}H NMR spectra of **1** in different solvents. 1) CDCl$_3$ at 25 °C, 2) CD$_3$OD at 25 °C, and 3) D$_2$O:CD$_3$OD = 1:1 at 25 °C.

The formation of **2** resulted in the following up- or downfield shifts of aromatic protons in **2**, $H_{a\text{–}a'}$ (−0.25), $H_{b\text{–}b'}$ (+0.56), $H_{c\text{–}c'}$ (+0.13), $H_{d\text{–}d'}$ (+0.49), and $H_{e\text{–}e'}$ (+0.09 ppm). The remarkably large downfield shift of $H_{d\text{–}d'}$ suggests that the protons are located very close to the α-1,4-glucosidic oxygen atoms of PM α-CD.[7] The fact that there was no change in the ^{1}H NMR spectra at different concentrations in the hydrophilic medium indicated that the intramolecular self-inclusion complex **2** was selectively generated from **1**. Recently, we have synthesized a linked [3]rotaxane having diyne unit by dimerization of **2** under the Glaser coupling conditions.[5b] To increase the effective conjugation length in the π-conjugated parts, a linked [3]rotaxane **3** having only a phenylene–ethynylene unit was synthesized by three component coupling of two molecules of **2** with 1,4-diiodobenzene using the sequential Sonogashira coupling in H$_2$O/CH$_3$OH (1/1). The formation of **3**[8] was inferred from the MALDI-TOF mass spectrum, which displayed a strong signal at m/z 3033 for the corresponding $[\mathbf{3} + \mathrm{Na}]^+$ ion. It should be noted that no evidence for the formation of uninsulated compounds was detected by the NMR analysis of the crude product. The three component coupling **3** was successfully separated in pure form by using silica gel column chromatography in 80% yield. The structure of thus formed [3]rotaxane was characterized by CD spectrum and 2D ^{1}H ROESY NMR.[9] According to 2D ^{1}H ROESY NMR, there are obvious NOEs between protons on the tolan moiety and the H$_3$ and H$_5$ protons on the interior of the permethylated cyclodextrin. High solubility of these PM α-CD derivatives **1**–**3** in various organic solvents such as ethyl acetate, chloroform, THF, and pyridine is advantageous for their isolation compared with the corresponding water-soluble CD derivatives. In order to examine the insulating effect of permethylated cyclodextrin, the uninsulated compound **4** was intentionally synthesized as a reference compound by three component coupling of two molecules of **2** with 1,4-diiodobenzene in Et$_3$N, instead of H$_2$O/CH$_3$OH (1/1) (eq 1).

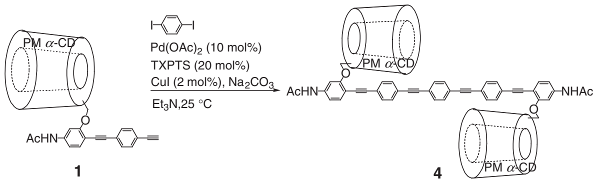
 (1)

Table 1. Fluorescence quantum yields of **3** and **4**[a]

	Absorption $\lambda_{\max}$/nm	Emission $\lambda_{\max}$/nm	Φ_{solution}	Φ_{solid}
3	355	400	0.97	0.38
4	366	408	0.95	0.22

[a] Absolute quantum yields were determined by a calibrated integrating sphere system (Hamamatsu C9920-02).

We then compared the fluorescence quantum yields of **3** with that of the corresponding uninsulated compounds **4** by a calibrated integrating sphere system. According to the absorption and emission spectra of **3** and **4**,[9] there is a slight blue-shift in both the absorption and the emission of the linked [3]rotaxane **3**. These shifts suggest that the structure of π-conjugated guest was changed by insulation. The indisputably clear vibration band around 420 nm in the emission spectrum of **3** indicates that the rigidity of π-conjugated back bone increased by insulation. The photoluminescence quantum yields of **3** and **4** are summarized in Table 1. As expected, there is a significant fluorescence enhancement in **3**, especially in the solid state, suggesting that encapsulation of OPE units by PM α-CD leads to efficient fluorescence properties.

In conclusion, a highly organic soluble and highly insulated OPE compound was synthesized by the double Sonogashira cross-coupling of two molecules of pseudo[1]rotaxane with 1,4-diiodobenzene. This unique supramolecular structure of symmetric [3]rotaxane was determined by 2D NMR measurement. The absolute quantum yield indicated that the present [3]rotaxane exhibits insulation in prohibiting the approach of any quencher to the oligomeric phenylene–ethynylene unit.

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