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

Susumu Tsuda,[1] Jun Terao,*[2] 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*

(Received October 16, 2008; CL-080993; E-mail: terao@scl.kyoto-u.ac.jp)

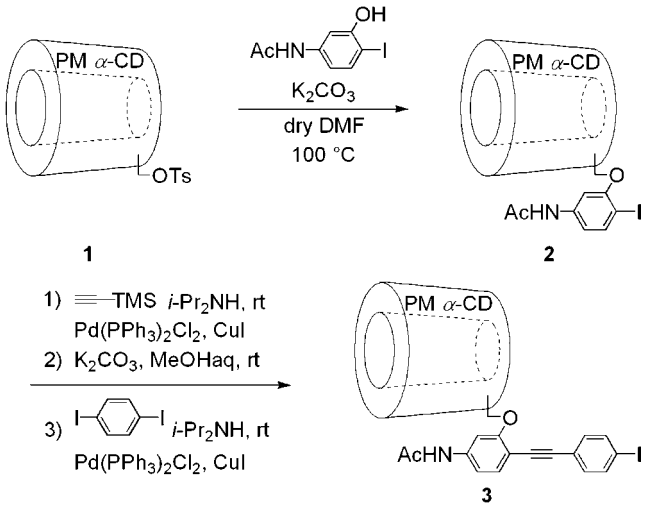
An organic-soluble π-conjugated [1]rotaxane has been synthesized by intramolecular self-inclusion of a lipophilic permethylated α-cyclodextrin bearing a rigid π-conjugated system as a guest moiety. End-capping has been achieved successfully by connecting an aniline moiety without using bulky stoppers.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

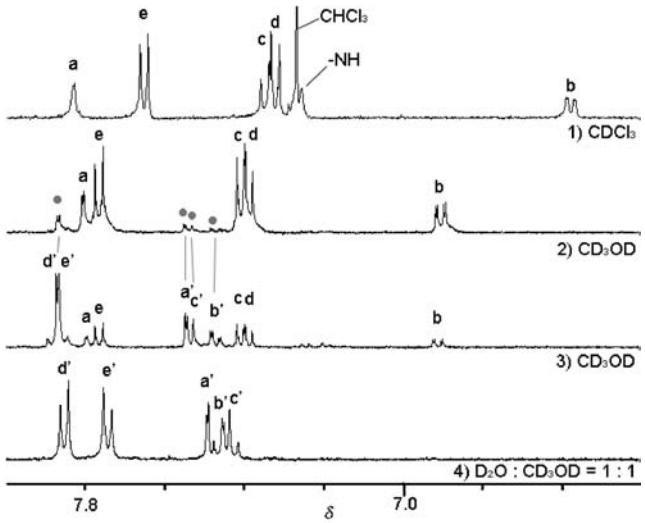
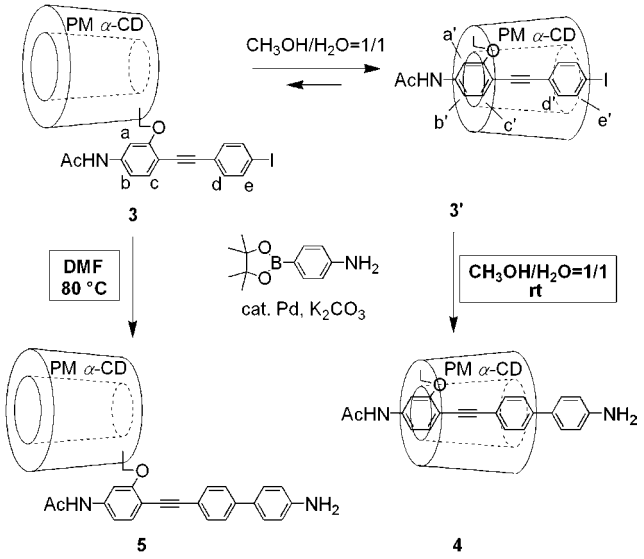



**Figure 1.** The aromatic region of 400 MHz $^1$H NMR spectra of **3** in several solvents at rt. 1) $CDCl_3$; 2) $CD_3OD$ (soon after dissolved); 3) $CD_3OD$ after heating at 60 °C for 60 min and cooling to rt; 4) $D_2O$:$CD_3OD$ = 1:1 after heating at 60 °C for 60 min and cooling to rt.

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 $\alpha$-1,4-glucosidic oxygen atoms of PM $\alpha$-CD.[9]

In order to fix pseudo[1]rotaxane **3′** by capping the end of the guest moiety with a $\pi$-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 $\alpha$-CD in comparison to that of native $\alpha$-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 $\alpha$-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 $\alpha$-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 $\alpha$-CD were observed. The details are described in Supporting Information.[8]

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

| Sample | Absorption ($\lambda_{max}$/nm) | Emission ($\lambda_{max}$/nm) | $\Phi_{solution}$ | $\Phi_{solid}$ |
|---|---|---|---|---|
| **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 $\alpha$-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 $\alpha$-CD is essential to attain efficient fluorescence properties.

In conclusion, an organic-soluble [1]rotaxane was prepared via intramolecular self-inclusion of PM $\alpha$-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 $\alpha$-CD as a macrocyclic host and a rigid conjugated system as the guest unit are linked each other.

**References and Notes**

1 M. J. Frampton, H. L. Anderson, *Angew. Chem., Int. Ed.* **2007**, *46*, 1028.
2 For nomenclature of rotaxanes, see: A. Yerin, E. S. Wilks, G. P. Moss, A. Harada, *Pure Appl. Chem.* **2008**, *80*, 2041.
3 a) S. Anderson, R. T. Aplin, T. D. W. Claridge, T. Goodson, III, A. C. Maciel, G. Rumbles, J. F. Ryan, H. L. Anderson, *J. Chem. Soc., Perkin Trans. 1* **1998**, 2383. b) C. A. Stanier, M. J. O'Connell, H. L. Anderson, W. Clegg, *Chem. Commun.* **2001**, 493. c) J. S. Park, J. N. Wilson, K. I. Hardcastle, U. H. F. Bunz, M. Srinivasarao, *J. Am. Chem. Soc.* **2006**, *128*, 7714. d) M. T. Stone, H. L. Anderson, *Chem. Commun.* **2007**, 2387. e) R. Eelkema, K. Maeda, B. Odell, H. L. Anderson, *J. Am. Chem. Soc.* **2007**, *129*, 12384. f) K. Sakamoto, Y. Takashima, H. Yamaguchi, A. Harada, *J. Org. Chem.* **2007**, *72*, 459. g) J. Sugiyama, I. Tomita, *Eur. J. Org. Chem.* **2007**, 4651. h) L. Zhu, X. Ma, F. Ji, Q. Wang, H. Tian, *Chem.—Eur. J.* **2007**, *13*, 9216.
4 a) X. Ma, D. Qu, F. Ji, Q. Wang, L. Zhu, Y. Xu, H. Tian, *Chem. Commun.* **2007**, 1409. b) X. Ma, Q. Wang, H. Tian, *Tetrahedron Lett.* **2007**, *48*, 7112.
5 a) S. Kanamathareddy, C. D. Gutsche, *J. Am. Chem. Soc.* **1993**, *115*, 6572. b) C. Reuter, A. Mohry, A. Sobanski, F. Vögtle, *Chem.—Eur. J.* **2000**, *6*, 1674. c) C. Reuter, W. Wienand, C. Schmuck, F. Vögtle, *Chem.—Eur. J.* **2001**, *7*, 1728. d) H. Onagi, C. J. Blake, C. J. Easton, S. F. Lincoln, *Chem.—Eur. J.* **2003**, *9*, 5978. e) G. Fukuhara, T. Fujimoto, T. Kaneda, *Chem. Lett.* **2003**, *32*, 536. f) K. Hiratani, M. Kaneyama, Y. Nagawa, E. Koyama, M. Kanesato, *J. Am. Chem. Soc.* **2004**, *126*, 13568.
6 For synthetic details, see: T. Kaneda, T. Fujimoto, J. Goto, K. Asano, Y. Yasufuku, J. H. Jung, C. Hosono, Y. Sakata, *Chem. Lett.* **2002**, 514.
7 For synthetic details, see: H. Wunderer, *Arch. Pharm.* **1973**, *306*, 371.
8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp./journals/chem-lett/index.html.
9 T. Fujimoto, Y. Sakata, T. Kaneda, *Chem. Commun.* **2000**, 2143.
10 a) T. Yamada, G. Fukuhara, T. Kaneda, *Chem. Lett.* **2003**, 534. b) R. Nishiyabu, K. Kano, *Eur. J. Org. Chem.* **2004**, 4988.

Published on the web (Advance View) December 13, 2008; doi:10.1246/cl.2009.76