

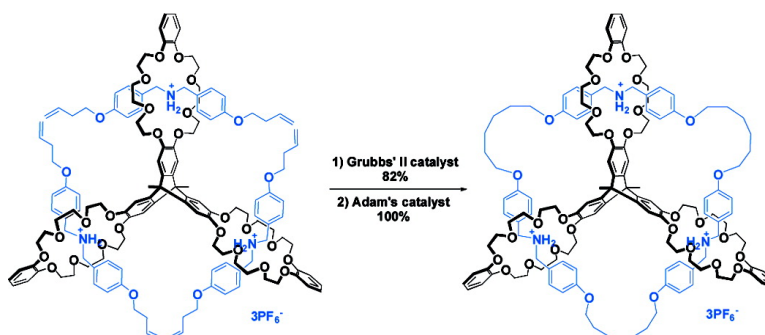
Communication

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A Highly Efficient Approach to [4]Pseudocatenanes by Threefold Metathesis Reactions of a Triptycene-Based Tris[2]pseudorotaxane

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Interlocked molecules, such as catenanes, pseudorotaxanes, and rotaxanes, have currently attracted great interest,^{1,2} not only for their aesthetic appeal but also for their potential applications in nanotechnology and molecular machines. Following the development of various template strategies in the last two decades, some classes of such topologically intriguing supermolecules are now becoming much more easily available than before.³ However, the synthesis of high order interlocked assemblies still remains a considerable challenge for supramolecular chemists.

Triptycene, for its three-dimensional rigid structure, was found to be a useful building block for the construction of supramolecular systems with unique structures and properties.⁴ Inspired by the fact that dibenzo-24-crown-8 (DB24C8) can be threaded by a secondary dialkylammonium ion to form [2]pseudorotaxane,⁵ we deduced that a triptycene-based homotripodal host **1** could assemble with proper dialkylammonium ions into a tris[2]pseudorotaxane. If there are two connectable groups at the ends of the ammonium ion, the tris[2]pseudorotaxane could further be transferred into [4]pseudocatenanes.⁶ Although pseudocatenanes with specific structures could show interesting properties and functions similar to other interlocked molecules, little is so far known about them. Here, we report the facile preparation of a triptycene tris(crown ether) **1** and subsequently the highly efficient synthesis of a [4]pseudocatenane **3-3H-3PF₆** by threefold metathesis reactions⁷ of a triptycene-based tris[2]pseudorotaxane, followed by hydrogenation (Figure 1).

Synthesis of the host **1** is depicted in Scheme 1. Compound **6** was obtained in 65% yield by the reaction of 2,3,6,7-tetramethoxy-9,10-dimethylantracene **4**⁸ and 4,5-dimethoxybenzenediazonium-2-carboxylate **5**. Demethylation of **6** with boron bromide gave triptycene tri(catechol) **7** in 98% yield, which was then reacted with the bistosylate **8**⁹ in DMF in the presence of Cs₂CO₃ under a high dilution condition to afford **1** in 35% yield. ¹H and ¹³C NMR spectra of **1** are consistent with its D_{3h} symmetry. The preparation of bisbenzylammonium salt **2-H•PF₆** involves the condensation of *p*-(but-3-enyloxy)benzylamine with *p*-(but-3-enyloxy)benzaldehyde, then reduction, protonation, and anion-exchange steps. Both host **1** and guest **2-H•PF₆** have good solubility in chloroform.

The ¹H NMR spectrum of a 1:3 mixture (8 mM) of **1** and **2-H•PF₆**, recorded in CDCl₃, revealed a dispersed array of well-defined resonances¹⁰ (Figure 2c) and great difference with those for host **1** (Figure 2a) and guest **2-H•PF₆** (Figure 2b). The large downfield shift (0.4 ppm) of the signal for the benzylic methylene protons H_h adjacent to the NH₂⁺ centers and significant changes in the chemical shifts of the protons H_{c/c'}, H_{d/d'}, and H_{e/e'} in crown rings were observed, which suggested that a novel triptycene-based tris[2]pseudorotaxane **[1•(2-H)]₃•3PF₆**¹¹ was formed. Moreover, the upfield shift of the signals for protons of H_i (−0.16 ppm) and H_j (−0.23 ppm) in **2-H•PF₆**, which may be due to a π–π stacking interaction between the phenyl groups in the salt and the catechol rings in the crown subunits,⁵ is also in keeping with the self-assembly superstructure. Moreover, by vapor diffusion of ether into

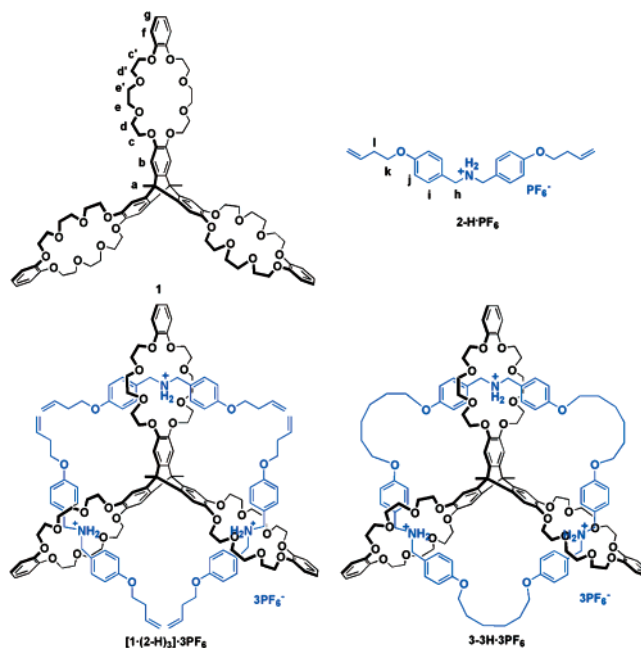
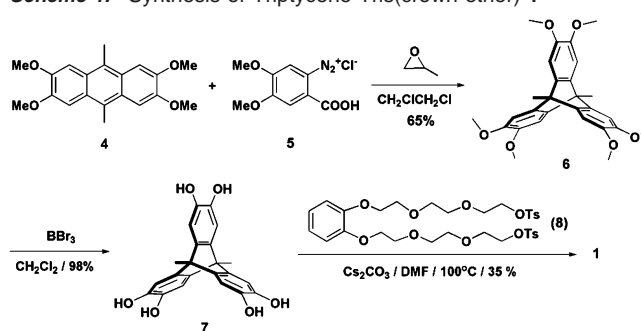


Figure 1. Structure and proton designations of host **1**, guest **2-H•PF₆**, tris[2]pseudorotaxane **[1•(2-H)]₃•3PF₆**, and [4]pseudocatenane **3-3H•3PF₆**.

Scheme 1. Synthesis of Triptycene Tris(crown ether) **1**



a 1:3 mixture of **1** and **2-H•PF₆** in CH₂Cl₂, the complex **[1•(2-H)]₃•3PF₆** could be easily isolated in 90% yield.¹² Its ESI mass spectrum revealed peaks, encountered at *m/z* = 1035.9 and 803.0, corresponding to **[1•(2-H)]₂²⁺** and **[1•(2-H)]₃³⁺**, respectively. It was also found that the tris[2]pseudorotaxane was partly decomposed in CD₃CN and completely decomposed in DMSO-*d*₆ (Supporting Information).

With the tris[2]pseudorotaxane in hand, we further performed the olefin metathesis reaction. When a solution of **[1•(2-H)]₃•3PF₆** in dichloromethane (1 mM) was treated with the second-generation Grubbs' catalyst¹³ (5 mol %), it was found that the reaction went along smoothly and exclusively gave the threefold metathesis product **3'-3H•3PF₆** in 82% yield. This high efficiency may be due to the combination of high stability of the complex in dichloro-

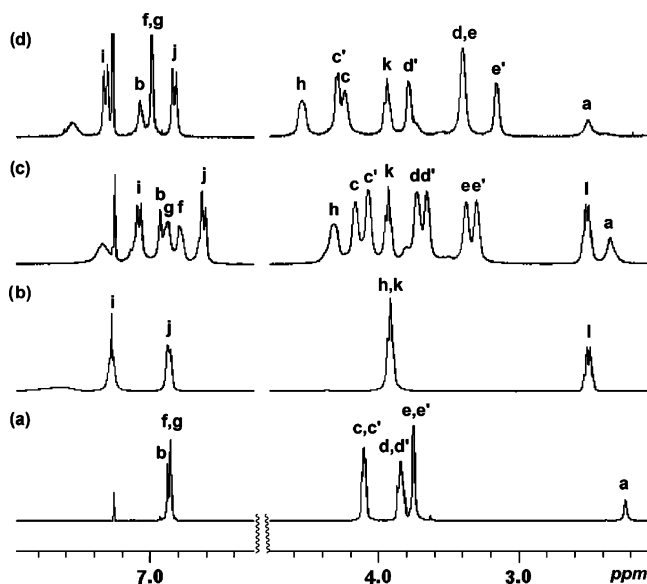


Figure 2. Partial ^1H NMR spectra (CDCl_3) of (a) **1**, (b) **2-H-PF₆**, (c) a 1:3 mixture of **1** and **2-H-PF₆**, and (d) **3-3H-3PF₆**.

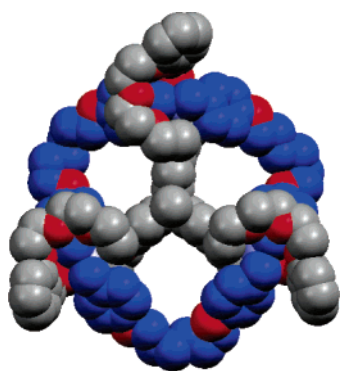


Figure 3. Space-filling representation of the molecular structure of [4]-pseudocatenane in the crystalline state. Solvent molecules and anions are omitted for clarity.

methane and high activity of the catalyst.¹⁴ The ^1H NMR spectrum showed that signals of terminal vinyl protons in the tris[2]-pseudorotaxane disappeared instead of new ones at 5.63–5.67 ppm for $-\text{CH}=\text{CH}-$ protons in **3'-3H-3PF₆** as a *cis/trans* isomeric mixture. The MALDI-TOF mass spectrum of **3'-3H-3PF₆** displayed a strong peak at m/z 2321.5 for the $[\mathbf{3}'\text{-2H}]^+$ ion. Furthermore, hydrogenation of **3'-3H-3PF₆** with Adam's catalyst afforded [4]-pseudocatenane **3-3H-3PF₆** quantitatively. Although **3-3H-3PF₆** has 72 aromatic carbons and 58 aliphatic carbons, it showed only 10 signals for aromatic carbons and 10 signals for the aliphatic carbons, which is in accord with its D_{3h} symmetry. With the aid of $^1\text{H}-^1\text{H}$ COSY and NOESY 2D NMR spectroscopic experiments (Supporting Information), all resonances of the [4]pseudocatenane were assigned. It was noted that the signals for the protons H_i and H_j moved back to downfield (Figure 2d), and it suggested the disappearance of the $\pi-\pi$ interaction between the two interlocked components after the formation of the [4]pseudocatenane, which was proved by the single-crystal analysis of **3-3H-3PF₆** (Figure 3).

Colorless crystals were grown by slow diffusion of diisopropyl ether into a chloroform solution of **3-3H-3PF₆** and analyzed by single-crystal X-ray diffraction. The crystal structure (Figure 3) confirms that the macrocycle containing three ammonium ions threads through the three cavities in the triptycene tri(crown ether)

to form a novel topological superstructure in the solid state. In the structure, there exist three new large cavities formed between the two interlocked components, which will be potential bound sites for guests.

In conclusion, we have presented a highly efficient approach to a novel [4]pseudocatenane by threefold metathesis reactions of a triptycene-based tris[2]pseudorotaxane, which may be conveniently used to synthesize more elegant [4]pseudocatenanes with well-defined structures and functions. Further study of supramolecular systems derived from the [4]pseudocatenane is in progress in our laboratory.

Acknowledgment. We thank the National Natural Science Foundation of China and the Chinese Academy of Sciences for financial support.

Supporting Information Available: Synthesis of **1**, **2-H-PF₆**, **[1-(2-H)₃]-3PF₆**, and **3-3H-3PF₆**; ^1H NMR spectra, $^1\text{H}-^1\text{H}$ COSY spectra, NOESY 2D NMR of **[1-(2-H)₃]-3PF₆** and **3-3H-3PF₆**; an X-ray crystallographic file (CIF) for **3-3H-3PF₆**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) The average association constant (K_a) between host **1** and dibenzylammonium hexafluorophosphate in CD_3CN was calculated to be $236(\pm 7) \text{ M}^{-1}$, which suggests that **1** binds to dialkylammonium ions with a similar strength as does DB24C8 (Supporting Information).
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