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A New [3]Rotaxane Molecular Machine Based on a Dibenzylammonium Ion and a Triazolium Station

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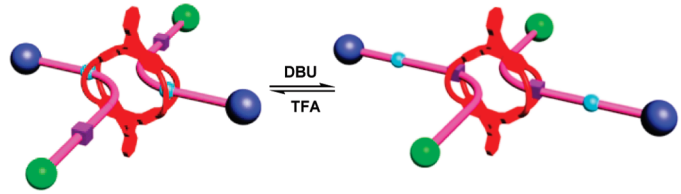
ABSTRACT



A novel two-station [3]rotaxane molecular machine based on triptycene-derived macrotricyclic host was conveniently synthesized by the click reaction and methylation of the subsequent 1,2,3-tiazole group. The shuttle process of the [3]rotaxane molecular machine can be reversibly achieved by acid−base control.

Mechanically interlocked molecules,[1] in particular rotaxanes and catenanes, have currently attracted great interest for not only their aesthetic structures but also their potential applications in nanoscale molecular machines.[2] Rotaxanes that can be switched between two or more states by different external stimuli have gained much more attention.[3] Various external stimuli, such as chemical,[4] electrical,[5] ion binding,[6] or light irradiation[7] stimuli, have been employed to induce such switching. During the past two decades, various rotaxanes have been synthesized in high efficiency approaches since the templates[8] were applied. However, the synthesis of high order [*n*]rotaxane molecular machines remains a considerable challenge for supramolecular chemists on account of the considerable challenges in synthesis.[9] Moreover, to the best of our knowledge, no [3]rotaxane

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molecular machines with two threads passing through one host have hitherto been reported.

During the past several years, we have proven that the triptycene with unique 3D rigid structure could be utilized as a useful building block for the synthesis of novel macrocyclic hosts with specific structures and properties.[10] As a result, we reported a triptycene-based macrotricyclic host **1** (Figure 1a), which could form [3]pseudorotaxanes,

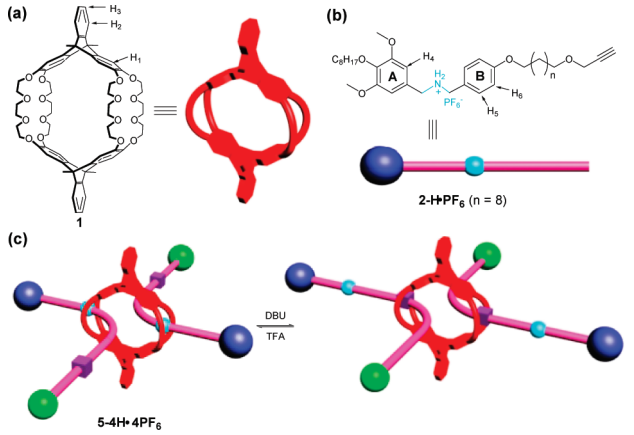
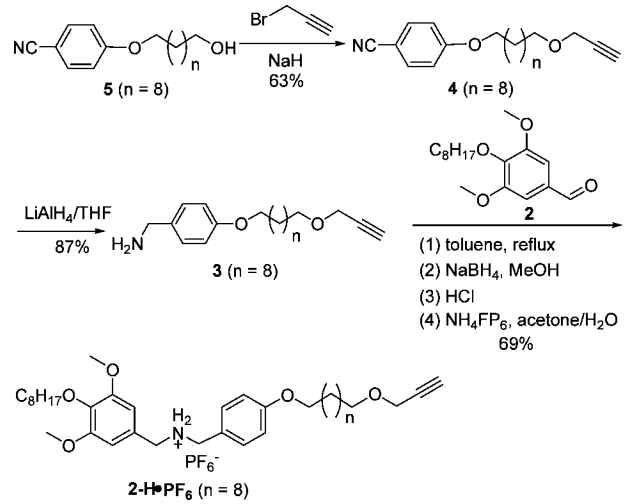


Figure 1. Graphical representation of (a) macrotricyclic host **1**, (b) dibenzylammonium ion **2-H·PF$_6$**, and (c) [3]rotaxane molecular machine by acid−base control.

[3]rotaxanes, and subsequent mechanically interlocked polymers.[11] On the basis of the previous work, we herein report a novel acid−base controllable [3]rotaxane molecular machine. The synthetic strategy is based on the copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of organic azide and terminal alkyne **2-H·PF$_6$** (Figure 1b),[12] and the subsequent alkylation of the 1,2,3-triazole, which has been described as a molecular station for dibenzo-24-crown-8 (DB24C8).[13] Consequently, the targeted [3]rotaxane containing a dibenzylammonium ion and a *N*-methyltriazolium station with different affinity for the DB24C8 subunits of host **1** can be easily synthesized, and the shuttle process between two different stations can be efficiently achieved by acid−base control (Figure 1c).

Synthesis of the unsymmetrical dibenzylammonium salt **2-H·PF$_6$** is outlined in Scheme 1. Reaction of compound **5**

Scheme 1. Synthesis of the Dibenzylammonium Salt **2-H·PF$_6$**



with propargyl bromide in THF in the presence of NaH, and then reduction of the cyano group by $LiAlH_4$ in THF gave the primary amine **3**. Condensation of the amine **3** with the aldehyde **2** gave the corresponding reversible dynamic imine, which was then reduced by $NaBH_4$ in MeOH to give the kinetically stable amine. Protonation of the free amine with an excess of HCl and subsequent counterion exchange with saturated NH_4PF_6 solution afforded the dibenzylammonium salt **2-H·PF$_6$** in 69% total yield for the four steps. The salt **2-H·PF$_6$** has good solubility in acetonitrile, chloroform, THF, and dichloromathane.

We first investigated the complexation between **1** and **2-H·PF$_6$** in solution. Consequently, it was found that the ^{1}H NMR spectrum of a 1:2 mixture of **1** and **2-H·PF$_6$** in $CDCl_3$ and CD_3CN (1:1, v/v) showed a great difference from those for **1** and **2-H·PF$_6$**. The aromatic signals of the complex were assigned by its ^{1}H−^{1}H COSY and NOESY 2D NMR spectra.[14] It was noted that a strong NOE effect between aromatic proton H_1 of **1** and H_6 of **2-H·PF$_6$** was observed. Especially, the signals for protons H_5 and H_6 of **2-H·PF$_6$** shifted upfield obviously, while a downfield shift of aromatic proton H_1 of host **1** was also observed. These results indicated that the complex **1·(2-H·PF$_6$)$_2$** formed, and the benzene ring **B** (Figure 1) positioned inside the cavity of host **1**. Moreover, the electrospray ionization mass spectrum (ESI-MS) provided more evidence for formation of the 1:2 complex **1·(2-H·PF$_6$)$_2$**. Consequently, the strong peak at *m*/*z* 1171.8 for $[\mathbf{1}\cdot(\mathbf{2\text{-}H})_2]^{2+}$ was observed.[14] Formation of **1·(2-H·PF$_6$)$_2$** provide a chance to further synthesize [3]rotaxane.

As we previously described,[11b] we tried to prepare [3]rotaxane **4**−**2H·2PF$_6$** using two 3,5-dimethylphenyl groups as the stoppers. As shown in Scheme 2, after the macrotricyclic host **1** and **2-H·PF$_6$** were mixed and stirred at room temperature in CH_2Cl_2 for 24 h, the mixture was treated with azide **7** in the presence of a catalytic amount of $[Cu(CH_3CN)_4]PF_6$ to afford **4-2H·2PF$_6$** in 41%

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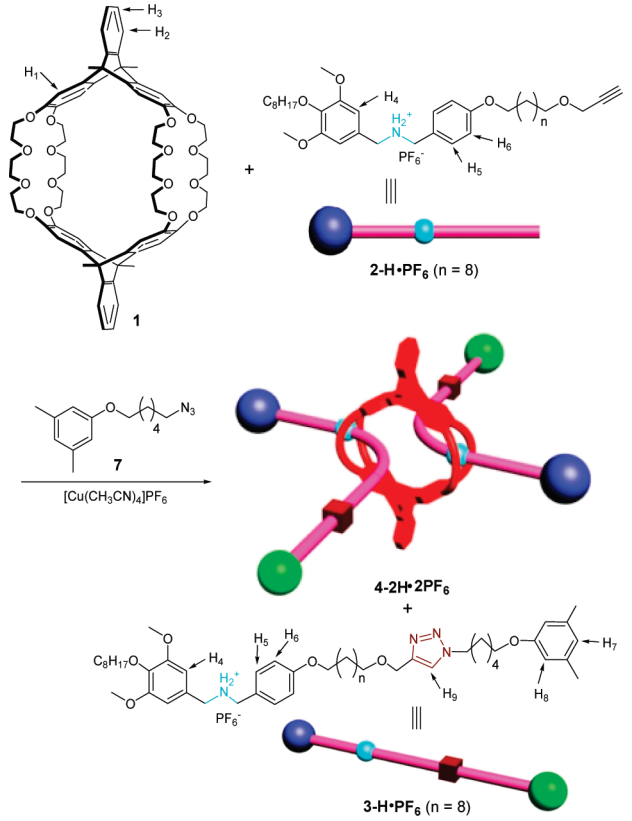
(14) See the Supporting Information for details.

Scheme 2. Synthesis of the [3]Rotaxane **4-2H·2PF$_6$**



yield. The partial proton NMR spectrum of [3]rotaxane **4-2H·2PF$_6$** in 1:1 (v/v) CD_3CN:$CDCl_3$ was shown in Figure 2b. The aromatic proton H_1 of **1** and proton H_4 of

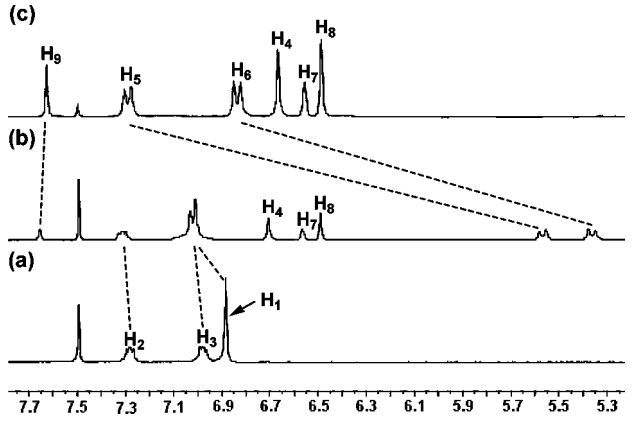
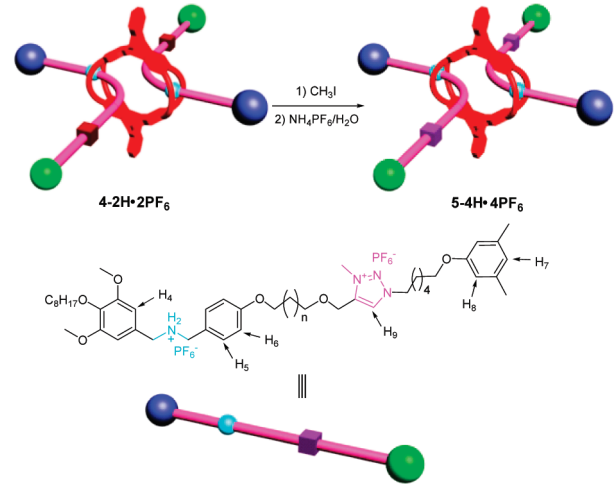


Figure 2. Partial ^{1}H NMR spectra (300 MHz, 298 K, 1:1 CD_3CN:$CDCl_3$) of (a) host **1**, (b) [3]rotaxane **4-2H·2PF$_6$**, and (c) **3-H·PF$_6$**. Resonance protons are labeled in Scheme 2.

3-H·PF$_6$ in the **4-2H·2PF$_6$** moved downfield, while the aromatic protons H_5 and H_6 shifted upfield greatly ($\Delta\delta$ = 1.72 and 1.47 ppm, respectively), which might be due to the strong shielding effect of the aromatic rings in host **1**. Especially, it was further evidenced that the signal for proton H_9 corresponding to 1,2,3-triazole emerged at 7.66 ppm. Moreover, the ESI-HRMS of **4-2H·2PF$_6$** also revealed a high-intensity signal at *m/z* 1417.8513 corresponding to the ion mass of $[M - 2PF_6^-]^{2+}$,[14] that is, the loss of $2PF_6^-$ from the [3]rotaxane.

As shown in Scheme 3, the subsequent regioselective methylation of the triazole group in [3]rotaxane **4-2H·2PF$_6$**

Scheme 3. Synthesis of the [3]Rotaxane **5-4H·4PF$_6$**



with iodomethane was carried out at room temperature for four days, and followed by anion exchange with saturated NH_4PF_6 solution to afford the two-station [3]rotaxane **5-4H·4PF$_6$** quantitatively, which was structurally confirmed by the ^{1}H NMR and ^{13}C NMR spectra.[14] The ESI-HRMS provided further evidence for formation of the [3]rotaxane **5-4H·4PF$_6$**. As a result, the strong peak at *m/z* 1003.5758 for $[M - 3PF_6^-]^{3+}$ was observed, which is consistent with the calculated value (*m/z* 1003.5743).[14]

Compared with **4-4H·4PF$_6$**, the ^{1}H NMR spectrum of **5-4H·4PF$_6$** did not show significant changes, in which the signals for protons H_5 and H_6 corresponding to the dibenzylammonium ions emerged at 5.59 and 5.37 ppm, respectively, and the signal for proton H_9 corresponding to the triazolium moiety emerged at 7.66 ppm. This indicated that macrotricyclic host **1** still complexed with the dibenzylammonium ions. To achieve the shuttle of the two threads in the [3]rotaxane, a series of ^{1}H NMR experiments were carried out with variation of the pH. As shown in Figure 3b, when 4 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added to a solution of [3]rotaxane **5-4H·4PF$_6$** in CD_3CN/$CHCl_3$ (1:1, v/v) solution, dramatic changes in the ^{1}H NMR spectrum were observed. Especially, it is found that the signals for protons H_5, H_6, and H_9 all shifted downfield significantly, indicating that the triazolium ions moved to the cavities of host **1**, whereas reformation of the $-NH_2^+-$ centers by the addition of 8 equiv of trifluoroacetic acid (TFA) into the above system resulted in the

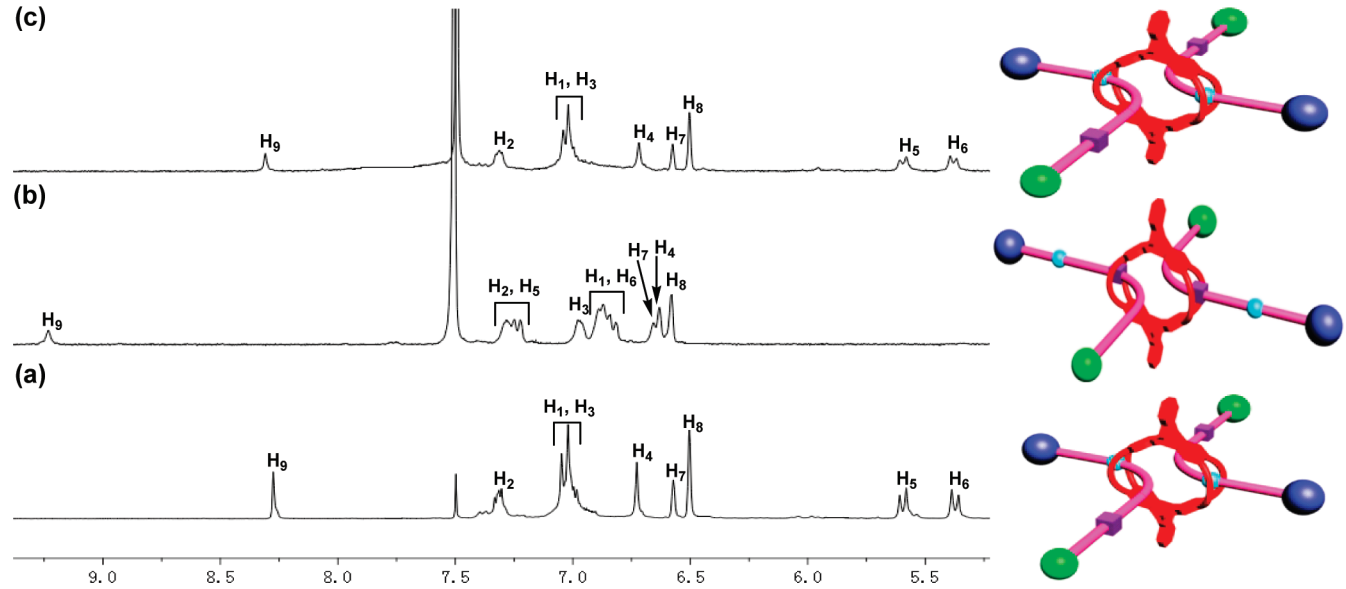


Figure 3. ^{1}H NMR spectra (300 MHz, 1:1 CD_3CN:$CHCl_3$, 298 K) recorded on **5-4H·4PF$_6$** before (a) and after (b) the addition of 4 equiv of DBU. (c) The original spectrum is regenerated by the addition of 8 equiv of TFA. The corresponding operation of the molecular machine is shown on the right-hand side. Resonance protons are labeled in Scheme 3.

recovery of the proton signals of rotaxane **5-4H·4PF$_6$**, indicating that the dibenzylammonium ions moved to the crown ether cavities of host **1** again (Figure 3c). Thus, the ^{1}H NMR spectroscopic measurements demonstrated that the two threads could reversibly shuttle with respect to host **1** in [3]rotaxane **5-4H·4PF$_6$** under the acid−base control.

In conclusion, we have synthesized a novel two-station [3]rotaxane molecular machine based on triptycene-derived macrotricyclic host by the click reaction and subsequent methylation of the 1,2,3-tiazole group, and further demonstrated that the shuttle process between the macrocyclic host and the two different stations could be efficiently and chemically controlled by acid and base. The results presented here will be helpful for constructing new supramolecular assemblies with specific structures and properties, such as the external stimulus responded poly[3]rotaxanes, which is underway in our laboratory.

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Supporting Information Available: Experimental procedures and characterization data for new compounds; partial ^{1}H NMR spectra of **1**, **2-H·PF$_6$**, and **1** and 2.0 equiv of **2-H·PF$_6$**; partial ^{1}H−^{1}H COSY and NOESY 2D NMR spectra of the [3]pseudorotaxane and [3]rotaxanes; and HRMS spectra of [3]rotaxanes **4-2H·2PF$_6$** and **5-4H·4PF$_6$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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