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A Novel Pentiptycene Bis(crown ether)-Based [2](2)Rotaxane Whose Two DB24C8 Rings Act as Flapping Wings of a Butterfly

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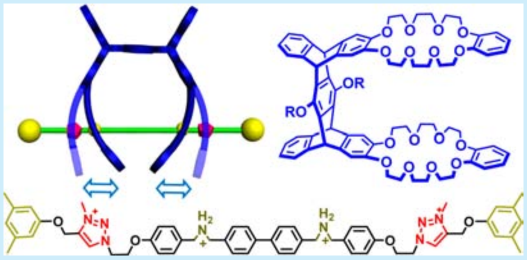
Supporting Information

ABSTRACT: A novel [2](2)rotaxane based on pentiptycene-derived bis(crown ether) can be efficiently synthesized via a "click chemistry" method and the subsequent *N*-methylation. Due to the different affinities of DB24C8 with the ammonium and triazolium stations, the wing-flapping movement of the DB24C8 "wings" in the [2](2)rotaxane can be easily achieved by acid/base stimulus.



With the aim of mimicking nature, artificial molecular machines (AMMs)[1] based on mechanically interlocked molecules (MIMs)[2] with special properties and functions have been representing a hot issue and major challenge in supramolecular chemistry. During the past decade, various highly complicated and well-defined MIMs, such as molecular shuttles,[3] molecular elevators,[4] molecular cable cars,[5] molecular information ratchets,[6] and so on,[7] have been designed and constructed. Among numerous building blocks for MIMs, the ammonium ion−crown ether recognition pair has been widely used in the construction of acid−base responsive MIMs.[7f,8] In 2008, Coutrot and Busseron[9] reported the first [2]rotaxane shuttle based on an anilinium and triazolium station through a two-step sequence templated approach, containing "click chemistry"[10] and subsequent *N*-methylation. Recently, Coutrot and his co-workers[11] also reported a pH-sensitive double-lasso molecular machine from an ends-activated [c2]daisy chain. So far, some [2]rotaxanes based on ammonium and triazolium stations have been obtained for a broadening range of applications, due to their clean and clear shuttle process between the two stations in response to the acid and base stimuli.[9,12]

Pentiptycene,[13] as a common member of the iptycene family, has specific applications in low dielectric constant materials,[14] fluorescent chemosensors,[15] molecular machines,[16] and so on, due to its unique rigid, aromatic, and H-shaped scaffold. Recently, we[17] reported a series of pentiptycene-derived hosts by the combination of a rigid pentiptycene moiety and flexible crown ether chains. Since pentiptycene-derived bis(crown ether) **H** contains two DB24C8 moieties in the *cis* position, we deduce that it can show strong interactions with two ammonium cations[18] and two triazolium salts simultaneously, which thus provides an opportunity to construct a novel interlocked molecule of [2](2)rotaxane[19] by the ammonium template moiety through alkyne−azide "click chemistry" and subsequent *N*-methylation. Herein, we report the synthesis of the [2](2)rotaxane based on host **H**. Especially, it is found that the shuttle process of two DB24C8 moieties of the host between the ammonium and *N*-methyltriazolium stations can be easily achieved by acid−base stimulus, which makes the opening−closing movement of the two DB24C8 moieties act as the flapping motions of a butterfly (Figure 1).[20]

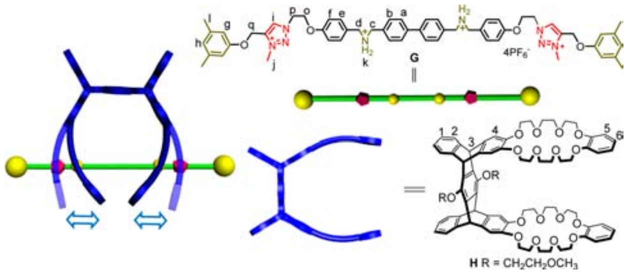


Figure 1. Cartoon representation of the flapping motions of the [2](2)rotaxane, and proton designations of the host and the guest.

First, we synthesized diammonium salt **1** containing two terminal azido groups. Starting from [1,1′-biphenyl]-4,4′-diyldimethanamine, the corresponding reversible dynamic imine could be obtained via the condensation with the 4-(2-azidoethoxy)benzaldehyde. Then reduction of the imine with $NaBH_4$ in CH_3OH could afford the kinetically stable amine. The target diammonium salt **1** could be obtained in an ideal total yield (73%) through further protonation with 10 equiv of HCl and the counterion exchange with saturated NH_4PF_6 solution, subsequently.

The complexation between host **H** and diammonium salt **1** in solution was then studied by the ^1H NMR spectroscopic method. We mixed the host **H** (3.0 mM) with 1.0 equiv of **1** in

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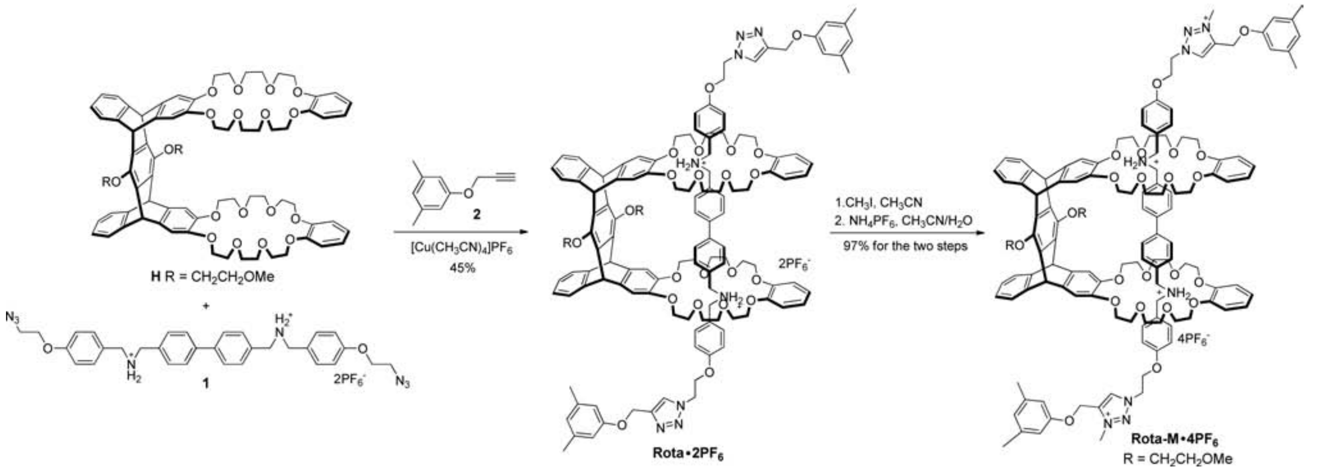
Scheme 1. Synthesis of the [2](2)Rotaxane Rota-M·4PF$_6$



1:1 (v/v) CD$_3$CN/CDCl$_3$, and the ^{1}H NMR spectrum[21] of the 1:1 mixture exhibited a great difference from those of free host **H** and diammonium salt **1** with only one set of peak signals, which suggested that the complexation of host **H** with diammonium salt **1** was a corresponding fast complexation process in solution. The signals for the benzylic methylene protons H$_c$ and H$_d$ adjacent to the NH$_2$ centers showed the large downfield shift of 0.71 and 0.20 ppm, respectively. Meanwhile, the signals of the protons in crown rings also exhibited significant changes, due to the effect of the diammonium axle. These observations suggested that diammonium salt **1** as an axle ran through two crown ether rings of **H**. In addition, all the protons H$_a$, H$_b$, H$_e$, and H$_f$ in diammonium salt **1** obviously shifted upfield to different degrees, which may be due to the shielding effect. It revealed that the diphenyl section of **1** was included in the shielding area between the DB24C8 moieties of **H**. All of the signal changes mentioned above confirmed that the novel pentiptycene-based [2]pseudorotaxane was formed, as we supposed.

With this [2]pseudorotaxane containing two terminal azido groups in hand, we further performed a copper(I)-catalyzed alkyne−azide 1,3-dipolar cycloaddition[22] with 1,3-dimethyl-5-(prop-2-yn-1-yloxy) benzene **2** in DCM. As shown in Scheme 1, the mixture of host **H** and 1.0 equiv of diammonium salt **1** was stirred for 2 h at room temperature to form a [2]pseudorotaxane, which was then reacted with alkyne **2** via the "CuAAC click chemistry" in the presence of a stoichiometric amount of [Cu(CH$_3$CN)$_4$]PF$_6$ to give the target [2]rotaxane **Rota·2PF$_6$** in 45% yield. **Rota·2PF$_6$** was subsequently treated with an excess of iodomethane in dry CH$_3$CN at 50 °C for 48 h, followed by anion exchange with NH$_4$PF$_6$ to afford our designed [2](2)rotaxane **Rota-M·4PF$_6$** containing two stations. We assigned most of the resonance protons of [2](2)rotaxane **Rota-M·4PF$_6$** with the help of ^{1}H−^{1}H COSY and ROESY 2D NMR spectroscopic experiments.[21] It was found that the characteristic signal for proton H$_i$ corresponding to the triazolium moiety emerged at 8.50 ppm. Compared to free axle **G**, we noted that the benzylic methylene protons H$_c$ and H$_d$ adjacent to the NH$_2$ centers showed great downfield shifts ($\Delta\delta$ = −0.69 for H$_c$ and $\Delta\delta$ = −0.19 ppm for H$_d$), which revealed that two NH$_2$ stations were located in the cavities of two crown ether rings, respectively. At the same time, the proton signals of DB24C8 moieties also exhibited the corresponding changes, due to the effect of the NH$_2$ station. Additionally, all of the aromatic protons (H$_a$, H$_b$, H$_e$, and H$_f$) of the axle section shifted toward upfield obviously; especially, for the protons H$_a$ and H$_b$ of the diphenyl moiety, the upfield shifts could reach up to 0.51 and 0.56 ppm, respectively (Figure 2). These observations suggested that the axle threads through the two DB24C8 moieties, and the diphenyl moiety was located in the stronger shielding zone between the two DB24C8 rings. Further evidence for the formation of the [2](2)rotaxane came from the ESI-HRMS, in which the three high-intensity signals at m/z 1262.0077, 793.0169, and 558.5218 corresponding to the ion masses of [M − 2PF$_6$]$^{2+}$, [M − 3PF$_6$]$^{3+}$, and [M − 4PF$_6$]$^{4+}$, respectively, were observed.[21]

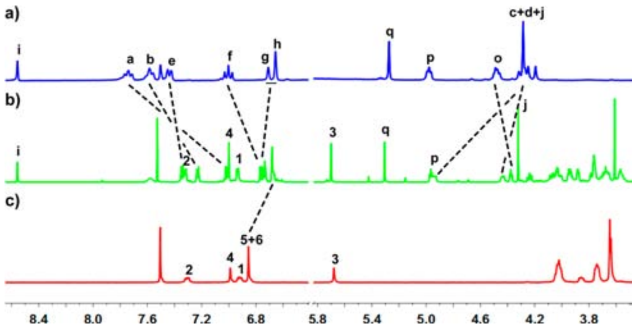
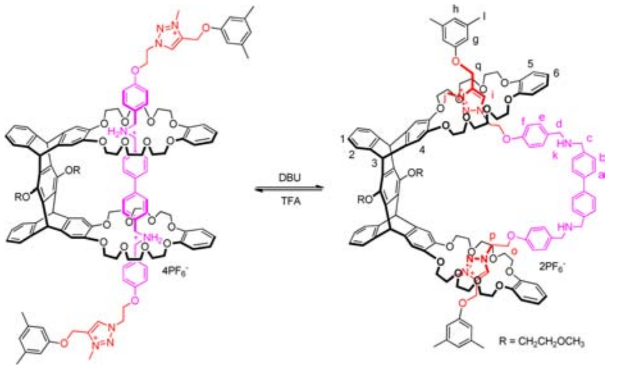


Figure 2. Partial ^{1}H NMR spectra (300 MHz, CDCl$_3$/CD$_3$CN = 1:1, v/v, 298 K) of (a) free **G**, (b) **Rota-M·4PF$_6$**, and (c) free **H**. Resonance protons are labeled in Figure 1

We also carried out a 2D ROESY spectral experiment for the [2](2)rotaxane **Rota-M·4PF$_6$**. The cross-peaks between H$_c$ (H$_d$) and the protons in crown ether units of **H** could be found. This observation revealed that the DB24C8 moieties in **Rota-M·4PF$_6$** still encircled the ammonium station.[21] Actually, there were ammonium and triazolium complexation stations in the axle for DB24C8 moieties, so we further tested the response of **Rota-M·4PF$_6$** to acid and base (Scheme 2). When we added 2.2 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to a solution of **Rota-M·4PF$_6$** in CD$_3$CN/CHCl$_3$ (1:1, v/v), the obvious changes could be observed in its ^{1}H NMR spectrum. As shown in Figure 3, proton H$_i$ of the triazolium moiety moved downfield with a shift of 0.31 ppm. Moreover, the signals of the methylene protons adjacent to the ammonium center (H$_c$ and H$_d$) also showed dramatic changes that included their multiple splitting pattern disappearing, along

Scheme 2. Representing the Wing-Flapping Motions



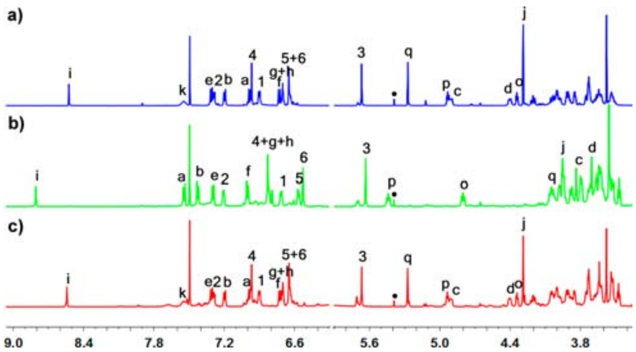


Figure 3. Partial ^{1}H NMR spectra (600 MHz, $CD_3CN/CDCl_3$ = 1:1, v/v, 298 K) of (a) free **Rota-M·4PF$_6$**, (b) to the solution of a were added 2.2 equiv of DBU, and (c) to the solution of b were added 4.0 equiv of TFA. [**Rota-M·4PF$_6$**]$_0$ = 3.0 mM. DCM peaks are marked with ●.

with the great upfield shifts ($\Delta\delta$ = 1.07 ppm for H_c and $\Delta\delta$ = 0.70 ppm for H_d). While the methylene protons (H_p and H_q) attached to the triazolium station moved upfield with great shifts. The H_a and H_b of the diphenyl moiety moved back downfield, which emerged at 7.53 and 7.42 ppm. These signal changes revealed that the successful deprotonation of the ammonium ion, and subsequently the movement of DB24C8 moieties to triazolium stations, occurred. The two triazolium stations of the encircled axle were too distant; the pure bending of the axle without any torsion of the host seems to be too difficult to achieve these signal changes. Thus, we suggested these changes might come from the opening of the DB24C8 moieties, just like a butterfly spreading its wings from the amine center to the triazolium station. The corresponding cross-peaks between the protons close to the triazolium station and the ones of crown ether rings could be observed in the 2D ROESY spectrum, which further revealed this "spread-wing" process.[21]

The introduction of 4.0 equiv of trifluoroacetic acid (TFA) to the above mixture solution resulted in a recovery of the proton signals compared to that of the [2](2)rotaxane **Rota-M·4PF$_6$** in the absence of any additive. Host **H** closed its DB24C8 "wings" back to the ammonium station with the reformation of the NH_2 centers. These ^{1}H NMR spectroscopic measurements demonstrated that the variation of pH could induce the motion of the two DB24C8 "wings" of [2](2)rotaxane **Rota-M·4PF$_6$**, which was reminiscent of the butterfly wing-flapping movement. In addition, we noted that only an approximate equivalent amount of DBU to ammonium ions could make the DB24C8 moieties spread to the triazolium station. This observation revealed that this [2](2)rotaxane **Rota-M·4PF$_6$** was relatively sensitive to pH stimulus. Moreover, the relational signals in ^{1}H NMR spectrum showed the cyclic shift by the successive addition of DBU-TFA-DBU-TFA (Figure S17) without any obvious difference. Thus, it demonstrated that the wing-flapping movement of the DB24C8 "wings" in **Rota-M·4PF$_6$** could cycle several times under acid/base control.

In conclusion, we have constructed a novel [2](2)rotaxane based on a pentiptycene-derived bis(crown ether) host, which is an extension of the Coutrot's system of molecular machinery via a "click chemistry" method and the subsequent *N*-methylation. Since the [2](2)rotaxane contained ammonium and triazolium stations with a different affinity for DB24C8, subsquently, the wing-flapping movement of the DB24C8 "wings" in the [2](2)rotaxane could be achieved efficiently and chemically controlled by the addition of acid and base. The results presented here represent the first example of a mechanically interlocked molecular switch based on the pentiptycene-derived synthetic host. We believe that this kind of mechanically interlocked molecules could be useful for further construction of more complicated and well-defined mechanically interlocked supramolecular systems based on the pentitycene scaffold and serve as inspiration for the development of smart bionic machines.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, compounds characterization, ^{1}H−^{1}H COSY and ROESY 2D NMR spectra, and other materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(19) **Rota-M·4PF$_6$** was named as [2](2)rotaxane, in which the number in brackets was used to indicate the number of molecular components, and after the brackets another number in parentheses could be designated as the number of threadings involved.

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