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Taco Complex Templated Syntheses of a Cryptand/Paraquat [2]Rotaxane and a [2]Catenane by Olefin Metathesis

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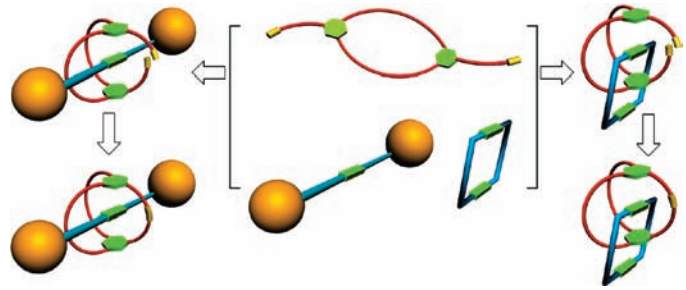
ABSTRACT



Taco complex templation based on the bis(*m*-phenylene)-32-crown-10/paraquat recognition motif is used to develop a general method for preparing mechanically interlocked molecules. A [2]rotaxane and a [2]catenane were synthesized in high yields by a ring-closing metathesis reaction, which was owed to the impactful template effect. Due to the high symmetry of (5,5′)-difunctional bis(*m*-phenylene)-32-crown-10 derivatives, this taco complex templated synthesis has potential to be a tempting method to solve a symmetry-based problem in the fabrication of complicated mechanically interlocked structures.

The efficient preparation of mechanically interlocked structures, such as rotaxanes and catenanes, is vital for their successful applications in fabricating molecular machines, sensors, and nano materials.[1] Based on molecular recognition, some imaginative template-directed protocols, including hydrogen bonding, $\pi-\pi$ donor−acceptor interactions, metal−ligand coordination, and anion templation, have shown great success in the fabrication of these interlocked structures.[2] Compared with kinetically controlled covalent bond formation, dynamic covalent approach leads to the formation of the most thermally stable product and always

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results in high yields of interlocked molecules.[3] Olefin metathesis, one of the most powerful dynamic covalent approaches, as well as imine bond formation,[4] has been proved to be an efficient method in the template-directed synthesis of mechanically interlocked compounds. It has been previously shown that olefin metathesis can be used to synthesize ammonium,[5] metallic ion,[6] anion,[7] hydrogen bond,[8] and $\pi-\pi$ donor−acceptor templated catenanes and rotaxanes.[9]

It has been reported that bis(*m*-phenylene)-32-crown-10 (BMP32C10) derivatives can bind paraquat derivatives efficiently and form taco complexes not only in the solid state as shown by single-crystal X-ray analysis[10] but also in solution since BMP32C10-based supramolecular cryptands form complexes with paraquat derivatives.[11] Therefore, the taco complex-type complexation between BMP32C10 and paraquat derivatives should be able to be used in the efficient templated synthesis of mechanically interlocked structures. Although bis(*p*-phenylene) and bis(*o*-phenylene) crown ethers, such as bis(*p*-phenylene)-34-crown-10 (BPP34C10) and dibenzo-24-crown-8 (DB24C8), are also good hosts for paraquat derivatives, the use of mono- and difunctionalized bis(*p*-phenylene) and bis(*o*-phenylene) crown ether hosts leads inevitably to complications as a result of the formation of stereoisomeric complexes when two or more hosts participate.[12] The symmetry-based problem can be solved when BMP32C10 derivatives instead of bis(*p*-phenylene) and bis(*o*-phenylene) crown ether derivatives are used in the preparation of complicated mechanically interlocked molecules containing two or more hosts.[12] Herein, we report the first examples of taco complex templated syntheses of a [2]rotaxane and a [2]catenane based on the BMP32C10/paraquat recognition motif using ring-closing metathesis (RCM) in high yields.

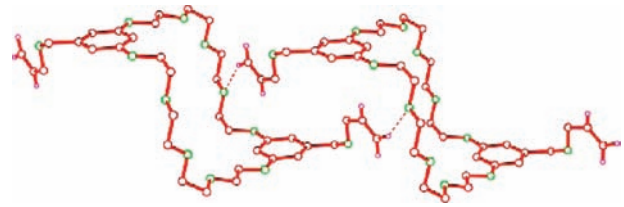

Figure 1. Crystal structure of BMP32C10 derivative **1**. Hydrogens except the ones involved in hydrogen bonding have been omitted for clarity. Carbons are red and oxygens are green. Hydrogen-bond parameters: H···O distance (Å), C−H···O angle (deg), C···O distance (Å), 2.522, 151, 3.452.

The bis-vinyl appended BMP32C10 derivative **1** was prepared in high yield via the diallylation of BMP32C10 diol.[13] As shown by single-crystal X-ray analysis (Figure 1), **1** molecules fold to a chair conformation via intermolecular hydrogen bonding in the solid state when no guests are involved. When **1** and the dumbbell-shaped paraquat derivative **2** were mixed and dissolved in acetone, the intermediate taco complex **1·2** was formed as indicated by the yellow color of the solution.[11,12b] Previously, it was demonstrated that tris(4-methoxyphenyl)phosphine groups are big enough to act as stoppers to form rotaxanes from BMP32C10-based pseudorotaxanes,[12b] so **2** could not thread into the cavity of **1** to form a threaded-type complex; only the taco complex formed in solution here. The association constant of taco complex BMP32C10·**2** has been measured to be 220 ($\pm$10) M^{-1} in acetone.[12b] Due to the similarity in structure of BMP32C10 and **1**, the binding interaction between **1** and **2** would not be very strong either, but it should be strong enough to be used in the preparation of mechanically interlocked molecules with dynamic covalent chemistry. After a Grubbs' II catalyst solution in dichloromethane was added into a mixture of **1** and **2** in acetone, the RCM reaction[14] of taco complex **1·2** afforded [2]rotaxane **5** in 90% yield (Scheme 1). Similarly, [2]catenane **6** was synthesized

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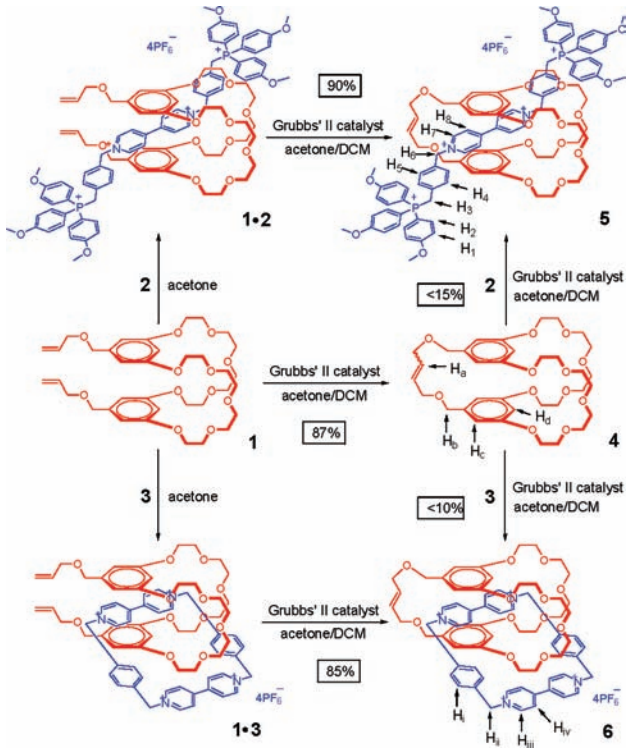
Scheme 1. Syntheses of [2]Rotaxane **5** and [2]Catenane **6**



via mixing **1** and cyclophane **3** in acetone to form taco complex **1·3** (more solvent was needed to dissolve **1** and **3** than for **1** and **2**) followed by the RCM reaction with Grubbs' II catalyst in 85% yield (Scheme 1); this yield is much higher than the 37% yield of a cryptand/paraquat catenane made by the traditional cyclophane-closing method.[15]

Cryptand **4** was prepared by the RCM reaction of **1** with Grubbs' II catalyst in 87% yield. Its alkene units exist in either *cis* or *trans* configuration. The *cis*/*trans* ratio was calculated from the integrations of the isomeric olefinic protons in the ^{1}H NMR spectrum of **4** (*cis* = 5.60 ppm, *trans* = 5.66 ppm) to be 3:1, which is different from the commonly reported *trans*-favored ratio for this kind of macrocycle.[16] However, the ^{1}H NMR spectra of **5** and **6** showed that only the energetically favored *trans* configuration was observed, which was further unambiguously confirmed by the single-crystal X-ray analysis (Figure 3). This presumably is due to the thermodynamic character of the metathesis reaction, the *trans* configuration being more stable in the mechanically interlocked structures **5** and **6**.

Furthermore, to demonstrate the inherent reversibility of interlocked structure formation by olefin metathesis, cryptand **4** was directly utilized to assemble rotaxane **5** and catenane **6**, respectively, with the dumbbell-shaped component **2** and cyclophane **3** (Scheme 1). However, the dynamic covalent processes were rather inefficient for rotaxane **5** and catenane **6** in CH_2Cl_2/CH_3COCH_3 (1:5); this is probably due to the high steric hindrance induced by the short link of alkene and the three-dimensional structure of cryptand **4**.[15,17] If longer chain alkene derivatives are used, the efficiency of the reversed dynamic covalent processes may increase.

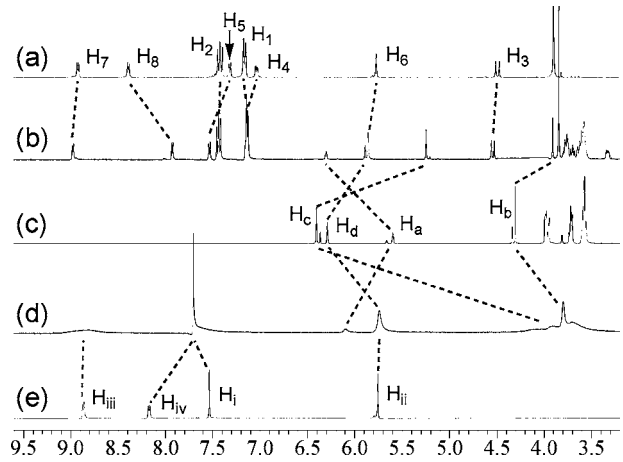


Figure 2. Partial proton NMR spectra (500 MHz, CD_3CN, 22 °C) of dumbbell-shaped component **2** (a), rotaxane **5** (b), cryptand **4** (c), catenane **6** (d), and cyclophane **3** (e).

Partial proton NMR spectra of dumbbell-shaped component **2**, rotaxane **5**, cryptand **4**, catenane **6**, and cyclophane **3** in CD_3CN are shown in Figure 2. After the formation of rotaxane **5**, dramatic upfield shifts were observed for the signals of the aromatic protons H_c and H_d, methylene protons H_b of cryptand **4** (Figure 2b versus Figure 2c), and β-pyridinium protons H_8 on **2** (Figure 2b versus Figure 2a), while the signals of olefinic protons H_a on cryptand **4** moved downfield (Figure 2b versus Figure 2c). Similarly, after the formation of catenane **6**, the signals of H_c, H_d, and H_b on cryptand **4** (Figure 2d versus Figure 2c) and β-pyridinium protons H_{iv} on **3** moved upfield (Figure 2d versus Figure 2e), while the signals of H_a on **4** moved downfield (Figure 2d versus Figure 2c). The formations of mechanically interlocked [2]rotaxane **5** and [2]catenane **6** were also confirmed by their electrospray ionization mass spectra (ESI-MS).[18]

The ^{1}H NMR spectrum of the [2]catenane **6** is very broad at room temperature as a consequence of fast dynamic-exchange processes on the NMR time scale (Figure 2d).[19] To demonstrate the temperature-dependent behavior of the

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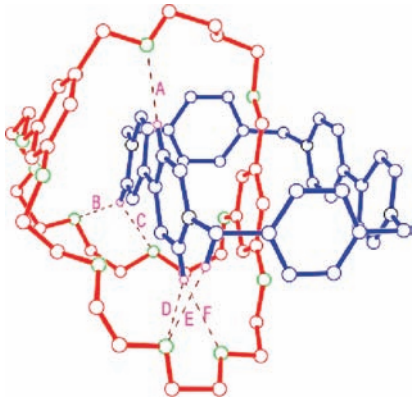

Figure 3. Ball-and-stick view of the X-ray structure of [2]catenane **6**. PF_6 counterions, solvent molecules, and hydrogen atoms except the ones involved in hydrogen bonding have been omitted for clarity. Cryptand **4** is red, cyclophane **3** is blue, hydrogens are magenta, oxygens are green, and nitrogen is black. Hydrogen-bond parameters: H···O distance (Å), C−H···O angle (deg), C···O distance (Å) **A**, 2.50, 153, 3.411; **B**, 2.61, 137, 3.366; **C**, 2.48, 154, 3.360; **D**, 2.41, 147, 3.252; **E**, 2.55, 138, 3.311; **F**, 2.36, 168, 3.30.

dynamic processes, variable-temperature NMR spectra were studied.[19] On cooling a CD_3CN solution of the [2]catenane to 0, −20, and −40 °C, respectively, the ^1H NMR spectrum became considerably more complicated and the signals became sharper since the dynamic processes were much slower at low temperatures (Figure S12, Supporting Information).[18]

The generation of [2]catenane **6** was further unambiguously confirmed by X-ray analysis (Figure 3) of an orange single crystal grown by vapor diffusion of pentane into an acetone solution of **6**. In the solid state, catenane **6** is stabilized by six hydrogen bonds and $\pi-\pi$ stacking interactions between the phenyl rings of the cryptand and the bipyridinium units on the cyclophane. The interplanar distances between the phenyl rings on the cryptand and their accompanying bipyridinium units are 3.94 Å (Ph_{out}/$BIPY_{in}$), 3.45 Å ($BIPY_{in}$/Ph_{in}), and 3.55 Å (Ph_{in}/$BIPY_{out}$), where Ph_{out}, $BIPY_{in}$, Ph_{in}, and $BIPY_{out}$ stand for the alongside phenyl ring on the cryptand, inside bipyridinium unit, inside phenyl ring on the cryptand, and alongside bipyridinium unit, respectively. The UV−vis absorptions of rotaxane **5** and catenane **6** at 400−450 nm are attributed to the charge transfer between the electron-rich phenyl rings of **4** and the electron-poor bipyridinium units.[18]

In summary, we have described the first taco complex templated syntheses of a [2]rotaxane and a [2]catenane based on the BMP32C10/paraquat recognition motif, from which the taco complexes have been shown to be effective templates for the preparation of mechanically interlocked structures. Considering the high symmetry of (5,5′)-difunctional BMP32C10 derivatives, this taco complex templated synthesis is a tempting method to solve the symmetry-based problem in the fabrication of more complicated mechanically interlocked structures when bis(*p*-phenylene) or/and bis(*o*-phenylene) crown ethers are used.[12]

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Supporting Information Available: Synthetic procedures and characterizations of **5** and **6**, crystal data for catenane **6**, and other materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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