Molecular Machines

A [2]Pseudorotaxane-Based Molecular Machine: Reversible Formation of a Molecular Loop Driven by Electrochemical and Photochemical Stimuli**

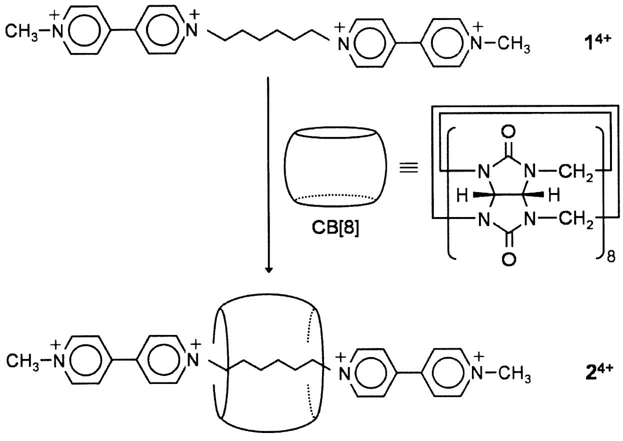
*Woo Sung Jeon, Albina Y. Ziganshina, Jae Wook Lee, Young Ho Ko, Jin-Koo Kang, Chongmok Lee, and Kimoon Kim**

Artificial molecular machines,[1] which can be defined as assemblies of a distinct number of molecular components designed to perform machinelike motions in response to appropriate external stimuli, such as light, electrons, or pH changes, are of great interest because of their potential applications in the creation of nanometer-scale molecular devices.[2] Mechanically interlocked molecules such as catenanes and rotaxanes have received a great deal of attention in the design of molecular machines because of their ability to switch between two or more states as a result of induced relative movement of their noncovalently interacting components on application of external stimuli. A number of prototype molecular machines based on rotaxanes,[3] pseudorotaxanes,[4] and catenanes,[5] which exploit shuttling, threading/dethreading, and circumrotational motions, respectively, have been reported over the past decade.

Cucurbituril (or cucurbit[6]uril),[6] a macrocycle comprised six glycoluril units, has been employed in the construction of a wide variety of interlocked molecules[7] and, more recently, rotaxane-based molecular machines and switches as well.[8] The recent discovery of cucurbituril homologues[9] containing a different number of glycoluril units has further widened the scope of cucurbituril chemistry.[10,11] In particular, cucurbit[8]uril (CB[8]) with a cavity comparable to that of γ-cyclodextrin can include two identical guest molecules to form a 1:2 complex,[9] or two different guest molecules to form a 1:1:1 complex.[10a] Furthermore, the guest-binding stoichiometry of CB[8] can be reversibly controlled by the redox chemistry of the guest.[10e] For example, CB[8] and methylviologen (MV^{2+}) form a 1:1 inclusion complex which can convert completely and reversibly into the 2:1 inclusion complex $(MV^{+\bullet})_2{\subset}CB[8]$ upon one-electron reduction of the guest. The formation of the stable methylviologen radical cation dimer ($(MV^{+\bullet})_2$) in the cavity of CB[8] appears to be the driving force for the redox-triggered transformation. This interesting observation prompted us to design a new type of electrochemically controllable molecular machine. Here we report a [2]pseudorotaxane-based molecular machine that can reversibly form a molecular loop in response to electrochemical as well as photochemical stimuli (Figure 1).

Figure 1. Novel [2]pseudorotaxane-based molecular machine that can reversibly form a molecular loop in response to external stimuli.

The hexamethylene-bridged bisviologen 1^{4+} and CB[8] readily form a stable 1:1 inclusion complex or [2]pseudorotaxane (2^{4+}; Scheme 1) in water which has been characterized by elemental analysis and various spectroscopic methods. The ^1H NMR spectrum and the parent ion peak at $m/z = 1754$ in the MALDI-TOF mass spectrum of 2^{4+} confirmed the formation of a stable 1:1 host–guest complex. The formation constant of 2^{4+} is estimated to be $2.3\times10^5\,M^{-1}$ from UV/Vis spectroscopic titration experiments. The large up-field shift of the aliphatic proton signals in the NMR spectrum of 2^{4+} indicates that CB[8] mainly resides on the hexamethylene unit (see Supporting Information). The major



Scheme 1. Synthesis of [2]pseudorotaxane 2^{4+}.

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[*] Prof. Dr. K. Kim, W. S. Jeon, Dr. A. Y. Ziganshina, Dr. J. W. Lee,[+] Dr. Y. H. Ko, J.-K. Kang
National Creative Research Initiative Center for
Smart Supramolecules and
Department of Chemistry
Division of Molecular and Life Sciences
Pohang University of Science and Technology
San 31 Hyojadong, Pohang 790-784 (Republic of Korea)
Fax: (+82) 54-279-8129
E-mail: kkim@postech.ac.kr
Prof. Dr. C. Lee
Department of Chemistry
Ewha Womans Univeristy
11-1 Daehyundong, Seoul 120-750 (Republic of Korea)

[+] Current address: Department of Chemistry
Dong-A University
840 Hadandong, Busan 604–714 (Republic of Korea)

[**] We gratefully acknowledge the Creative Research Initiative Program and the International R&D Cooperation Program of the Korean Ministry of Science and Technology for support of this work and the Brain Korea 21 Program of the Korean Ministry of Education for graduate studentships (to W.S.J. and J.-K.K.). C.L. also thanks the Korea Science and Engineering Foundation for support (grant no. R01-2000-00050). We thank Dr. S. Samal for his help in the preparation of the manuscript.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200351925

driving force for the stable [2]pseudorotaxane formation appears to be the charge–dipole interaction between the pyridinium nitrogen atoms of $\mathbf{1}^{4+}$ and the portal oxygen atoms of CB[8] as well as the hydrophobic interaction between the aliphatic chain of $\mathbf{1}^{4+}$ and the inner cavity of CB[8].

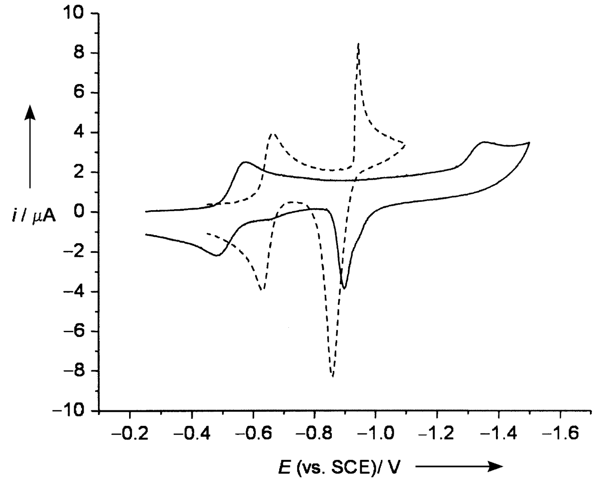
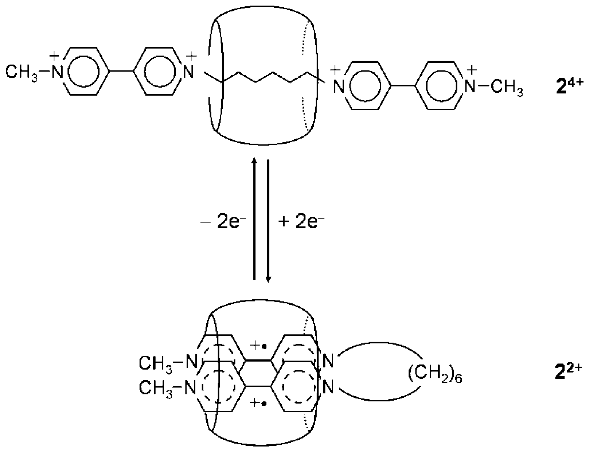


Figure 2. Cyclic voltammograms of $\mathbf{1}^{4+}$ (0.25 mM, dashed line) and $\mathbf{2}^{4+}$ (0.25 mM, solid line) in 0.1 M phosphate buffer solution (pH 7.0). Scan rate = 25 mV s^{-1}.

The machinelike behavior of $\mathbf{2}^{4+}$ has been investigated by cyclic voltammetry. Typical cyclic voltammograms of $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ are shown in Figure 2. As expected, the bisviologen thread $\mathbf{1}^{4+}$ undergoes two consecutive two-electron reduction processes, with a sharp second wave that indicates strong adsorption of the fully reduced species (**1**) on the electrode surface. Compared to $\mathbf{1}^{4+}$, however, $\mathbf{2}^{4+}$ exhibits a large positive shift of the first reduction peak and a very large negative shift of the second reduction peak. This cyclic voltammetric behavior is quite similar to that of the 1:1 inclusion complex formed between MV^{2+} and CB[8],[10e] where the similar potential shifts for the reduction process have been attributed to facile formation of the stable methylviologen radical cation dimer $(MV^{+\bullet})_2$ inside CB[8] after one-electron reduction of MV^{2+}. Thus, the cyclic voltammetric behavior of $\mathbf{2}^{4+}$ suggests that the two-electron reduction of $\mathbf{2}^{4+}$ results in the generation of a species containing two terminal viologen radical cation units, which then undergo a rapid intramolecular pairing process inside CB[8] to form the stable inclusion species $\mathbf{2}^{2+}$—a molecular loop (Scheme 2).[12] This conjecture has been supported by a spectroelectrochemical study: the absorption spectrum (Figure 3) of the species $\mathbf{2}^{2+}$ generated by the two electron reduction of $\mathbf{2}^{4+}$ (applied potential: −0.8 V versus the saturated calomel electrode (SCE)) is essentially identical to that of $(MV^{+\bullet})_2\subset$CB[8].[10e] A two-electron oxidation of the intramolecular viologen radical cation pair in CB[8] ($\mathbf{2}^{2+}$) regenerates the [2]pseudorotaxane $\mathbf{2}^{4+}$ with the initial linear structure. Taken together, these studies support a machinelike behavior of **2** in which an electrochemically triggered reversible folding/unfolding motion of the thread occurs. This operation mechanism is unprecedented in molecular machines based on mechanically interlocked systems.[13]



Scheme 2. Electrochemically triggered interconversion between $\mathbf{2}^{4+}$ with a linear structure and $\mathbf{2}^{2+}$ with a loop structure.

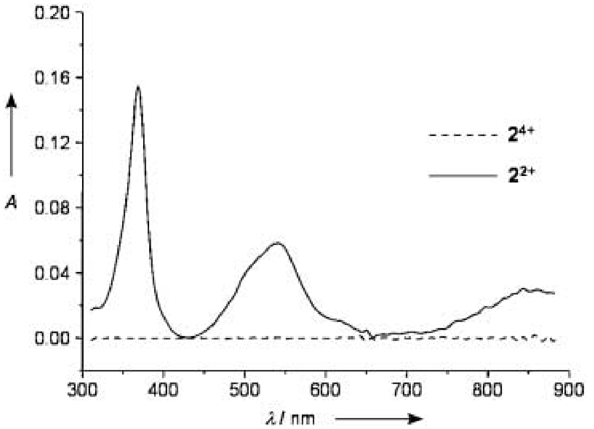


Figure 3. Absorption spectra of $\mathbf{2}^{4+}$ and $\mathbf{2}^{2+}$; the latter was generated by two-electron reduction of the former (applied potential, −0.8 V versus SCE).

Figure 4 shows the energy-minimized structures of $\mathbf{2}^{4+}$ and $\mathbf{2}^{2+}$ obtained by a semiempirical calculation,[14] which are in accord with the observation described above. Most importantly, the supermolecule undergoes a dramatic change not only in shape but also in size in response to electrochemical stimuli: the molecular dimension of $\mathbf{2}^{4+}$ with a linear structure is approximately 28 × 18 Å whereas that of $\mathbf{2}^{2+}$ with a loop

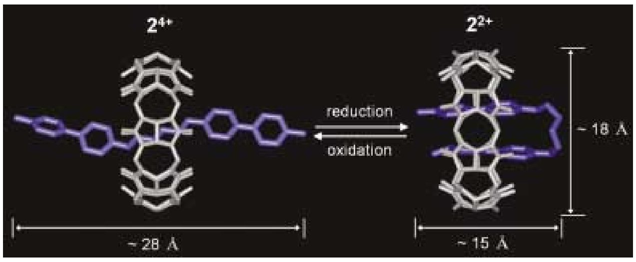
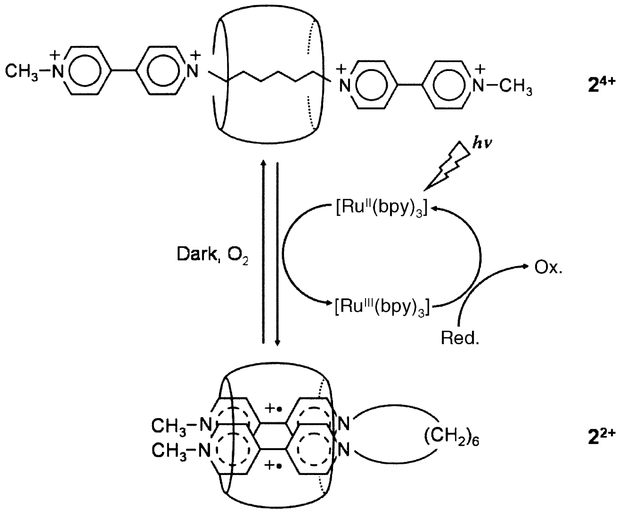


Figure 4. Energy-minimized structures of $\mathbf{2}^{4+}$ and $\mathbf{2}^{2+}$ obtained by a semiempirical calculation.

structure is only about 15 × 18 Å. The hydrodynamic volumes of $\mathbf{2}^{4+}$ and $\mathbf{2}^{2+}$ measured by diffusion NMR (DOSY) studies[15] (see Supporting Information) are 1.7 and 1.4 times, respectively, as large as that of CB[8],[16] and consistent with the computational results. Such a large, reversible structural change triggered by electrochemical stimuli is rare in supramolecular systems.[13]

The [2]pseudorotaxane $\mathbf{2}^{4+}$ also behaves as a light-driven molecular machine. Irradiation of an aqueous solution of $\mathbf{2}^{4+}$ with a visible light ($\lambda > 350$ nm) in the presence of $[\mathrm{Ru(bpy)_3}]^{2+}$ (bpy = 2,2′-bipyridine), which is capable of a photoinduced transfer of electrons to viologen,[17] and triethanolamine (sacrificial reductant) causes noticeable spectral changes which indicate that the terminal viologen units of $\mathbf{2}^{4+}$ are reduced. After 5 h, the absorption spectrum of the solution is almost the same as that observed in the spectroelectrochemical experiment described above: the characteristic absorption bands of the dimeric viologen radical cation are mainly observed (see Supporting Information). Furthermore, the absorbance at 368 nm increases linearly with increasing concentration of $\mathbf{2}^{4+}$ in the range from 7.5×10^{-6} to 1.0×10^{-3} M (see Supporting Information). This linear dependence of the absorbance on concentration, along with the above diffusion NMR results, suggests that the spectral change is predominantly a result of intramolecular pairing of the terminal viologen radical cation units inside CB[8] rather than intermolecular dimerization.[18] Thus, $\mathbf{2}^{4+}$ changes from a linear to a loop structure upon photochemical reduction (Scheme 3). When the irradiation is stopped and oxygen is allowed to enter the irradiated solution, the spectral changes are reversed and the initial absorption spectrum is restored, thus indicating the regeneration of $\mathbf{2}^{4+}$ with the linear structure.



Scheme 3. Photochemically driven interconversion between $\mathbf{2}^{4+}$ with a linear structure and $\mathbf{2}^{2+}$ with a loop structure.

In summary, we have designed and constructed a novel [2]pseudorotaxane-based molecular machine in which the folding and unfolding of the thread can be reversibly controlled by electrochemical and photochemical stimuli. The key feature of the machinelike behavior is the reversible formation of a molecular loop by intramolecular pairing of the terminal viologen radical cation units inside CB[8] upon reduction. The large, reversible change in its size as well as shape on application of external stimuli may provide an insight into the designing of molecular actuators with useful applications.

Experimental Section

2: The tetrabromide salt of N',N''-(hexylene)bis(1-methyl-4,4′-bipyridinium) ($\mathbf{1}^{4+}\cdot 4\,\mathrm{Br}^-$) was prepared by the literature procedure[19] with a minor modification. A mixture of $\mathrm{CB[8]\cdot H_2SO_4\cdot 16\,H_2O}$ (34 mg, 20 μmol) and $\mathbf{1}^{4+}\cdot 4\,\mathrm{Br}^-$ (15 mg, 18 μmol) in water (20 mL) was stirred at 50 °C overnight. After the undissolved solid had been filtered off, the volume of the filtrate was reduced to 2 mL under a reduced pressure. It was then allowed to stand in a refrigerator overnight to produce a yellow precipitate which was filtered, washed, and dried to afford $\mathbf{2}^{4+}\cdot 4\,\mathrm{Br}^-$ (38 mg, 80 %). ^{1}H NMR (500 MHz, $\mathrm{D_2O}$): $\delta = 0.87$ (m, 4H), 1.46 (m, 4H), 4.26 (d, $J = 15$ Hz, 16H), 4.53 (s, 6H), 5.56 (s, 16H), 5.80 (d, $J = 15$ Hz, 16H), 8.52 (m, 4H), 8.66 (m, 4H), 8.82 (d, $J = 6$ Hz, 4H), 9.09 ppm (d, $J = 6$ Hz, 4H); MALDI-MS: 1754 [M^+]; elemental analysis calcd (%) for $(\mathrm{C_{28}H_{34}N_4}^{4+})\cdot 4\,\mathrm{Br}^-\subset(\mathrm{C_{48}H_{48}N_{32}O_{16}})\cdot \mathrm{H_2SO_4}\cdot 25\,\mathrm{H_2O}$: C 34.79, H 5.15, N 19.22; found: C 34.74, H 5.42, N 19.45.

Received: May 19, 2003
Revised: June 30, 2003 [Z51925]

Keywords: electrochemistry · molecular devices · photochemistry · rotaxanes · supramolecular chemistry

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