Pseudorotaxanes on Gold

A Pseudorotaxane on Gold: Formation of Self-Assembled Monolayers, Reversible Dethreading and Rethreading of the Ring, and Ion-Gating Behavior**

*Kyungpil Kim, Woo Sung Jeon, Jin-Koo Kang, Jae Wook Lee, Sang Yong Jon, Taisun Kim, and Kimoon Kim**

Artificial molecular machines,[1] assemblies of a distinct number of molecular components designed to perform machinelike motions in response to appropriate external stimuli, have received much attention in recent years because of their potential applications in nanotechnology.[2] Pseudorotaxanes, a class of supramolecular species in which a molecular thread is encircled by a molecular bead, have been employed in the construction of prototype molecular machines because dethreading and rethreading movements of a thread through the center of a ring are reminiscent of the action of a linear motor. Although a number of molecular machines based on pseudorotaxanes were reported, their behavior in solution was mostly studied.[3–5] To realize the full potential of these molecules, however, they need to be organized on surfaces so that they behave coherently. Nevertheless, few studies on self-assembled monolayers (SAMs) of pseudorotaxanes on solid surfaces and their behavior have been reported.[6] Herein we report a self-assembled monolayer of a pseudorotaxane on gold and its machinelike behavior—reversible dethreading and rethreading of the ring. Furthermore, unprecedented ion-gating behavior associated with threading and dethreading is also reported.

Cucurbituril (CB[6]),[7,8] a macrocyclic cage compound comprising six glycoluril units, forms host–guest complexes with diaminoalkanes such as diaminobutane, the stability of which strongly depends on pH. Taking advantage of the pH-dependent complexation–decomplexation behavior of CB[6]-diaminoalkanes, we and others synthesized (pseudo)rotaxane-based molecular machines or switches working in solution.[9,10] To realize a molecular machine working on a gold surface, we have now designed and synthesized novel pseudorotaxane **1**[11] containing CB[6] threaded on a molecular string that consists of a diaminobutane unit as a station for the molecular bead, and a 1,2-dithiolane group[12] as an anchoring point toward a gold surface (Scheme 1).

A self-assembled monolayer (SAM) of the pseudorotaxane on gold is easily prepared by immersing a gold substrate in deionized water containing 1 mM of **1** for 24 h.[13] Figure 1 a shows the reflectance FTIR spectrum of the SAM developed on the gold substrate. The peaks at 1755 cm^{-1} and 1474 cm^{-1} corresponding to CO and CN stretching motions of CB[6], respectively, confirm the attachment of the pseudorotaxane to the surface. The S(2p) peaks at 162.1 eV (S(2p$_{3/2}$)) and 163.3 eV (S(2p$_{1/2}$)) in X-ray photoelectron spectroscopy (XPS) are also consistent with the attachment of the 1,2-dithiolane group on the gold surface.[14]

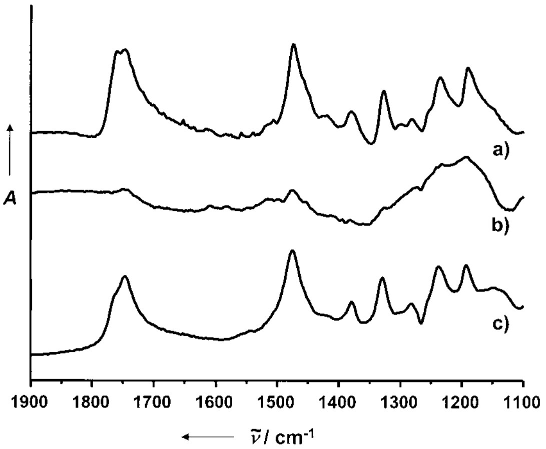

Figure 1. FTIR spectra of pseudorotaxane SAM: a) after preparation, b) after dethreading, and c) rethreading of CB[6].

The reversible dethreading and rethreading of CB[6] in the pseudorotaxane SAM has been studied. Dethreading of CB[6] from the pseudorotaxane SAM is achieved by exposing it to 0.1M NaOH solution for 1 h, and rethreading of CB[6] is performed by soaking the substrate into 1 mM CB[6] in 0.1M ammonium chloride solution (pH ~5) with stirring for 10 h.

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[*] Prof. Dr. K. Kim, K. Kim, W. S. Jeon, J.-K. Kang, Dr. J. W. Lee, Dr. S. Y. Jon
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. T. Kim
Department of Chemistry, Hallym University
1 Ockchon-Dong, Chunchon
Kangwon-Do 200-702 (Republic of Korea)

[**] We gratefully acknowledge the Creative Research Initiative 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 Kyungpil Kim, W. S. Jeon, and J.-K. Kang. We thank Tae Wan Kim for his contribution at the early stage of this work.

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

DOI: 10.1002/ange.200250692

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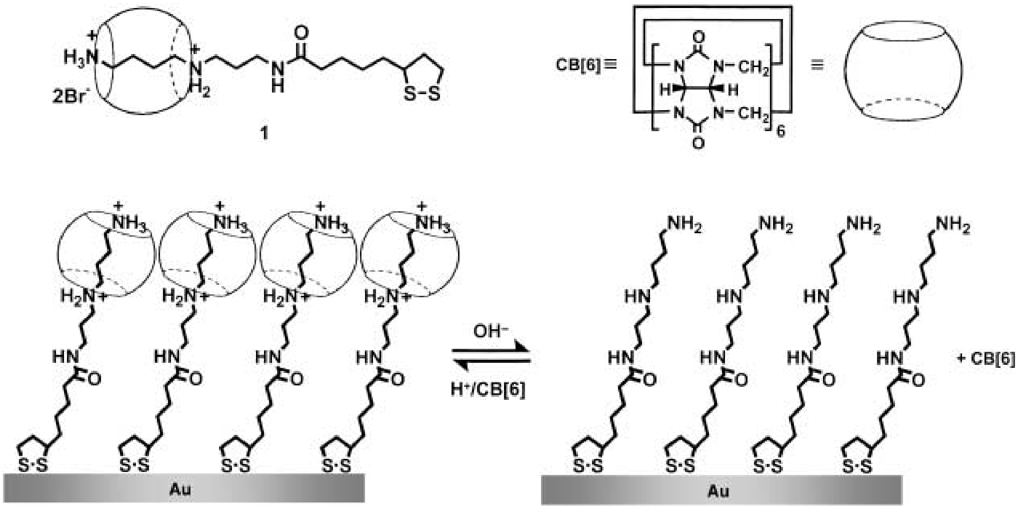

Scheme 1. Self-assembled monolayer of pseudorotaxane **1** on Au and dethreading and rethreading of molecular bead CB[6].

The dethreading and rethreading of CB[6] is confirmed by the disappearance and reappearance of the characteristic peaks of CB[6] in FTIR spectra (Figure 1 b and c). These processes are reversible and have been repeated up to three cycles with ~10–20 % decrease in the intensities of FTIR signals in each cycle.

The pseudorotaxane monolayer formation, and dethreading and rethreading processes are monitored in situ by surface plasmon resonance (SPR) spectroscopy.[15,16] The following solutions are flowed over a gold substrate in sequence and the surface is washed with a HBS buffer solution (pH 7.4) after each solution is passed: 1) HBS buffer solution (pH 7.4) containing 0.5 mM of **1** and thioctic acid (1:1), 2) 0.1 M NaOH solution, 3) 1 mM CB[6] in HBS solution, and 4) 0.1 M NaOH solution. The resulting SPR sensorgram is shown Figure 2. A large change in resonance angle, which corresponds to increase in density to 0.49 ng mm^{-2}, after step 1 (and subsequent washing) is consistent with the formation of a mixed SAM of **1** and thioctic acid on the gold surface. The subsequent changes in resonance angle are consistent with dethreading and rethreading of CB[6]: after step 2, the density decreases to 0.23 ng mm^{-2}, which corresponds to ~80 % dethreading of CB[6], and step 3 increases the density to 0.39 ng mm^{-2}, suggesting ~70 % of CB[6] are rethreaded. The density decrease to 0.26 ng mm^{-2} after step 4 suggests that ~80 % of CB[6] are dethreaded again.

The reversible threading and dethreading of the bulky CB[6] beads suggests that the pseudorotaxane SAM may behave as a gate. For example, it may block or allow the access of electroactive species to the electrode surface depending on the presence or absence of threaded CB[6]. To test this idea, the pseudorotaxane modified electrode was first treated with 1 mM thioctic acid in ethanol to fill up defect sites of the pseudorotaxane SAM.[17] The accessibility of the electrode surface to [Fe(CN)$_6$]$^{3-}$ was then examined by cyclic voltammetry. The defect-free pseudorotaxane SAM does not display any redox peaks in the cyclic voltammogram (Figure 3; ——). After dethreading CB[6], however, a quasireversible redox wave of [Fe(CN)$_6$]$^{3-}$ is observed (Figure 3, -----). This result suggests that dethreading of CB[6] opens up

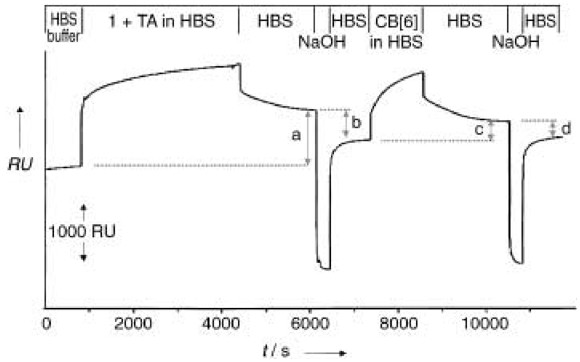

Figure 2. The SPR sensorgram showing reversible dethreading and rethreading of CB[6] in pseudorotaxane SAM: a) formation of mixed SAM of **1** and thioctic acid (TA), b) dethreading of CB[6], c) rethreading of CB[6] and d) dethreading of CB[6]. The top *x* axis represents the continuous flow of the indicated solutions.

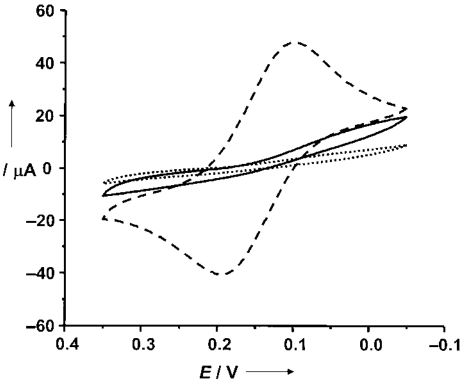

Figure 3. Cyclic voltammograms of [Fe(CN)$_6$]$^{3-}$ (0.5 mM) obtained with a) a gold electrode modified with SAM of **1** and thioctic acid (——), b) after dethreading of CB[6] (-----), and c) after treating with thioctic acid (•••••). Supporting electrolyte: 0.1 M KCl in universal buffer at pH 8.0; scan rate 0.1 V s^{-1}.

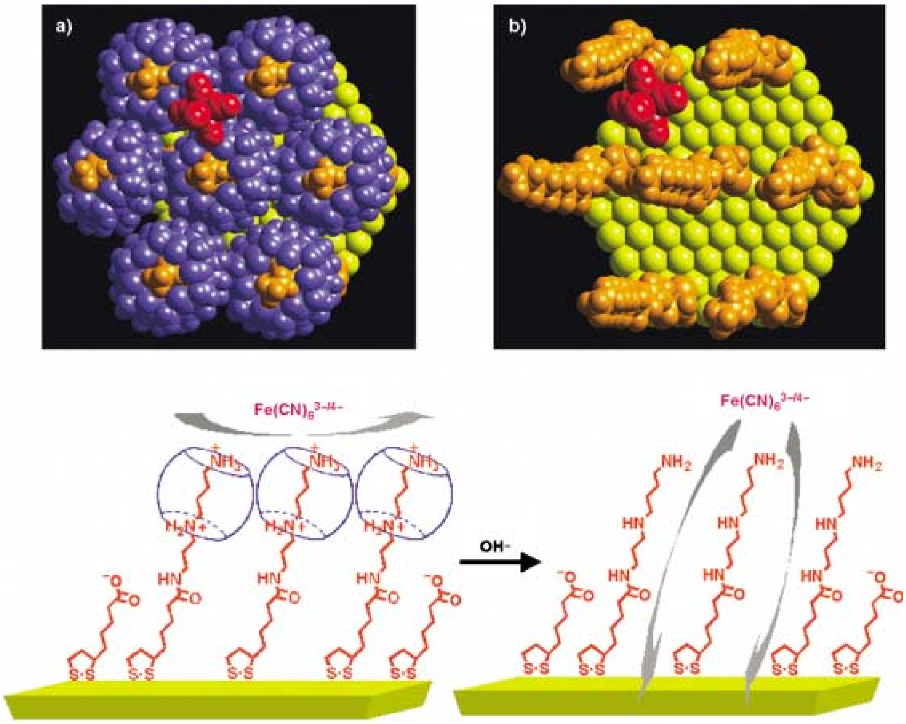

Figure 4. Space-filling (top) and chemical (bottom) representations of pseudorotaxane SAM of **1** on gold a) before and b) after dethreaded of CB[6] to illustrate that $[Fe(CN)_6]^{3-}$ can access the gold surface after dethreading. The string, CB[6] bead, $[Fe(CN)_6]^{3-}$ and gold surface are represented in orange, blue, red and yellow colors, respectively.

the "channels" through which the negatively charged $[Fe(CN)_6]^{3-}$ can now approach to the electrode surface and be reduced (Figure 4). Treatment of the CB[6]-dethreaded SAM with thioctic acid to fill up the exposed Au surface results in the disappearance of the redox wave of $[Fe(CN)_6]^{3-}$ (Figure 3, •••••).[18] Although further careful studies are needed, such an ion-gating phenomenon associated with threading and dethreading of pseudorotaxanes attached to electrode surfaces is unprecedented.

In summary, we have designed and constructed a pseudorotaxane SAM on a gold surface. The reversible dethreading and rethreading of CB[6] has been demonstrated by SPR and other experiments. Moreover, unprecedented ion-gating behavior associated with threading and dethreading of the molecular bead has been observed. This work may provide an insight in designing elaborate molecular machines on surface that may find useful applications in nanotechnology; we are currently working along this line.

Received: December 4, 2002 [Z50692]

Keywords: cyclic voltammetry · molecular devices · rotaxanes · self-assembly · supramolecular chemistry

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[16] BIACore 2000 and Pioneer Sensor Chip J1 Au surface were used for SPR studies. SPR measures the angle of light (θ) reflected from the backside of the gold substrate that has a minimum intensity. Changes in this angle ($\Delta\theta$) are linearly related to the index of refraction of the solution above the surface and therefore to the density of adsorbed molecules ($\Delta\theta$ of $0.10^\circ = 1\,\text{ng}\,\text{mm}^{-2} = 1000$ RU).

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[18] In principle, complete rethreading of CB[6] would block the access of $[Fe(CN)_6]^{3-}$ to the electrode surface resulting in no redox wave of the electroactive species in cyclic voltammetry. However, as described in the text, the rethreading of the molecular bead is achieved only up to ~80% and therefore, a quasireversible redox wave of $[Fe(CN)_6]^{3-}$ is still observed with substantially decreased but significantly high peak currents even after rethreading. For this reason, fully reversible and perfect ion-gating behavior by dethreading and rethreading of the bead (induced by pH change of the solution) is not achieved with this system. We are currently working on other systems with better ion-gating behavior.

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