CHEMISTRY
AN ASIAN JOURNAL

DOI: 10.1002/asia.200800054

Synthetic Molecular Machine Based on Reversible End-to-Interior and End-to-End Loop Formation Triggered by Electrochemical Stimuli

Jae Wook Lee,[a] Ilha Hwang,[a] Woo Sung Jeon,[a] Young Ho Ko,[a] Shigeru Sakamoto,[b] Kentaro Yamaguchi,[b] and Kimoon Kim*[a]

Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: We have designed and synthesized a novel [2]pseudorotaxane-based molecular machine in which the interconversion between end-to-interior and end-to-end loop structures is reversibly controlled by electrochemical stimuli. Cucurbit[8]uril (CB[8]) and the thread molecule $\mathbf{3}^{4+}$ with an electron-rich hydroxynaphthalene unit and two electron-deficient viologen units form the 1:1 complex $\mathbf{4}^{4+}$ with an end-to-interior loop structure, which is reversibly converted into an end-to-end structure upon reduction. Large changes in shape and size of the molecule accompany the reversible redox process. The key feature of the machine-like behavior is the reversible interconversion between an intramolecular charge-transfer complex and viologen cation radical dimer inside CB[8] triggered by electrochemical stimuli.

Keywords: charge transfer · electrochemistry · molecular machines · pseudorotaxanes · supramolecular chemistry

Introduction

Artificial molecular machines have received much attention in recent years because of their potential applications in the creation of molecular devices.[1,2] A wide variety of molecular machines such as shuttles,[3] rotors,[4] muscles,[5] scissors,[6] and elevators[7] have been reported. Nevertheless, design and synthesis of new molecular machines reminiscent of macroscopic machines or biological machines would further widen the scope of this chemistry.

Loop formation plays an important role in regulation of biological processes. For example, DNA looping is a fundamental mechanism for the regulation of gene expression. Intrachain loop formation is also a fundamental step of protein folding.[8,9] Three different types of intramolecular loops are known. End-to-end loops are formed between the chain ends. However, loop formation between an end and the interior of the chain (end-to-interior loops) or between two internal residues (interior-to-interior loops) is more commonly observed.[9d] Despite the importance of loop formation in biological processes, synthetic molecular machines mimicking the reversible formation of loops are rare.[10,11]

Cucurbit[*n*]uril (CB[*n*], $n=5$–10),[12] a family of macrocycles comprising *n* glycoluril units, have been employed not only in molecular recognition but also in construction of a wide variety of supramolecular assemblies including mechanically interlocked molecules[13] and molecular machines and switches.[11,14,18] In particular, CB[8] with a cavity comparable to that of γ-cyclodextrin can include two identical guest molecules to form a 1:2 complex,[12b] or two different guest molecules to form a 1:1:1 complex.[15] The formation of the ternary complex is driven by the markedly enhanced charge-transfer (CT) interaction between an electron-rich

[a] Dr. J. W. Lee,[+] Dr. I. Hwang, Dr. W. S. Jeon, Dr. Y. H. Ko, Prof. Dr. K. Kim
National Creative Research Initiative Center for Smart Supramolecules and
Department of Chemistry
Pohang University of Science and Technology
San 31 Hyojadong, Pohang 790-784 (Korea)
Fax: (+82) 54-279-8129
E-mail: kkim@postech.ac.kr

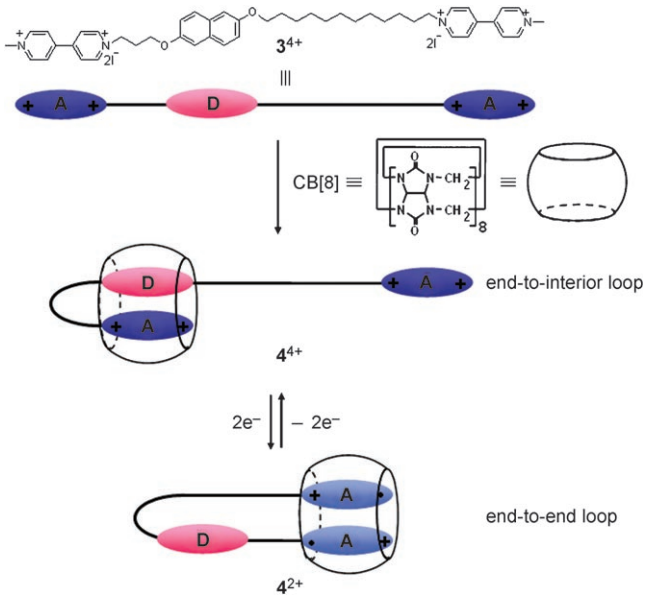
[b] Dr. S. Sakamoto, Prof. Dr. K. Yamaguchi
Laboratory of Analytical Chemistry and
Department of Pharmaceutical Technology
Faculty of Pharmaceutical Sciences at Kawaga Campus
Tokushima Bunri University
Shido, Sanuki-city, Kagawa 769-2193 (Japan)

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

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.200800054.

and electron-deficient guest pair inside the hydrophobic cavity of CB[8]. The discovery of the host-stabilized CT complex formation inside of CB[8] offered a new opportunity to construct novel supramolecular assemblies.[16] For the last several years, we and others have reported a wide variety of supramolecular assemblies and their applications[17] including molecular necklaces,[17a] redox-controllable vesicles,[17b] and dendrimers,[17c–e] based on this chemistry.

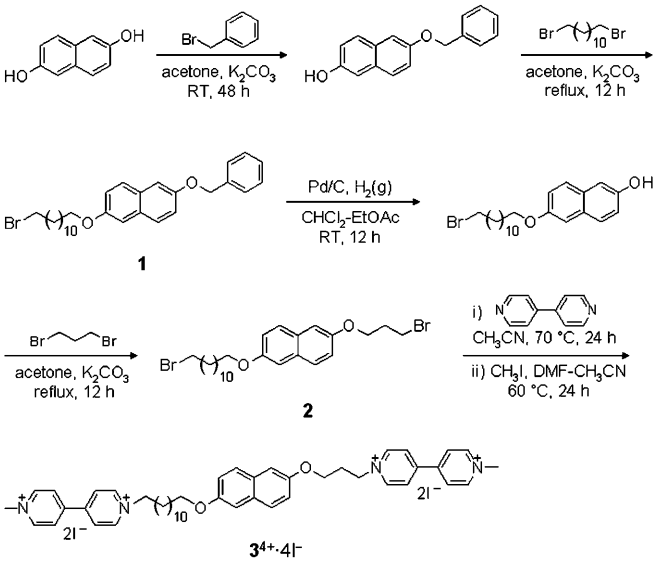
Furthermore, the ternary complex undergoes a redox-coupled guest-exchange process.[18] For example, treating a 1:1 mixture of $\mathbf{MV}^{2+}$ and the ternary complex ($\mathbf{MV}^{2+}$·**HN**)⊂CB[8] ($\mathbf{MV}^{2+}$ = methyl viologen; **HN** = 2,6-dihydroxynaphthalene) with a reducing agent such as sodium dithionite ($Na_2S_2O_4$) resulted in near-quantitative formation of 2:1 inclusion complex ($\mathbf{MV}^{+\cdot}$)$_2$⊂CB[8] and free **HN**. This guest exchange is completely reversible since oxidation reinstates the hetero-guest pair inclusion complex and $\mathbf{MV}^{2+}$. This redox-coupled guest-exchange process has been exploited in designing a molecular machine reminiscent of a loop lock.[18] In expanding this work, we have now designed a new electrochemically driven molecular machine, the behavior of which is reminiscent of the intrachain loop formation in biological processes (Scheme 1). Herein we report the synthesis and machine-like behavior of a novel [2]pseudorotaxane-based molecular machine that undergoes reversible conversion between end-to-interior and end-to-end loop structures triggered by electrochemical stimuli.



Scheme 1. Novel [2]pseudorotaxane-based molecular machine.

Results and Discussion

To construct a new electrochemically controllable molecular machine by exploiting the unique redox-coupled guest-exchange behavior of the host-stabilized CT complex described above, we designed and synthesized a guest molecule $\mathbf{3}^{4+}$ containing a 2,6-dihydroxynaphthalene derivative as an electron-rich group and two viologen units as an electron-deficient group connected by the three- and twelve-carbon chains (Scheme 2).



Scheme 2. Synthesis of $\mathbf{3}^{4+}$.

In water CB[8] and $\mathbf{3}^{4+}$ readily form the 1:1 complex $\mathbf{4}^{4+}$ in which $\mathbf{3}^{4+}$ forms an intramolecular CT complex inside CB[8], as confirmed by UV/Vis and ^{1}H NMR spectroscopy and mass spectrometry. First of all, upon addition of one equivalent of CB[8] to a solution of $\mathbf{3}^{4+}$ in H_2O, the color of the solution turned from pale yellow to violet with a characteristic CT band at around 570 nm in the UV/Vis spectrum (Figure 1), which indicated the formation of a CT complex.[15]

Abstract in Korean:

전기화학적 자극을 이용하여 '끝과 안이 연결된 (end-to-interior)' 고리구조에서 '끝과 끝이 연결된 (end-to-end)' 고리구조로의 상호변환을 가역적으로 조절할 수 있는 [2]유사로택산 형태의 새로운 분자기계를 고안, 합성하였다. 이러한 분자 운동을 보이기 위해 전자주개인 히드록시나프탈렌 하나와 전자받개인 바이올로젠 두 개를 가진 실 분자 $\mathbf{3}^{4+}$를 합성하였으며, 이 분자는 쿠커비투[8]릴과 1:1 로 결합하여 '끝과 안이 연결된' 고리형태의 $\mathbf{4}^{4+}$를 형성한다는 것을 흡광분석법, 핵자기공명법, 질량분석법 등의 분석방법을 이용하여 확인하였다. 이 복합체를 전기화학적 방법을 이용하여 환원하면 '끝과 끝이 연결된' 고리형태로 분자구조가 변한다는 것을 분광전기화학 방법을 이용하여 확인하였다. 이와 같이 전기화학적 산화·환원을 이용하여 분자 구조에 큰 변화를 가역적으로 일으킬 수 있었다. 이러한 기계와 같은 움직임은 전기화학적 자극에 의해 분자 내 전하-이동 복합체와 바이올로젠 양이온 라디칼 이합체 간의 상호 변환에 의해 일어난다.

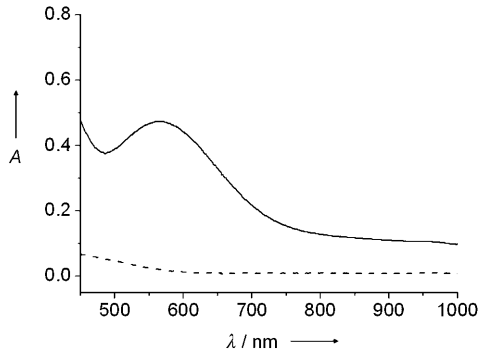


Figure 1. Absorption spectra of $\mathbf{3}^{4+}$ (dashed line) and $\mathbf{4}^{4+}$ (solid line) in H_2O (1.0 mM in both cases).

The ^{1}H NMR spectrum of $\mathbf{4}^{4+}$, the assignments of which were aided by 2D NMR techniques including ROESY and COSY (see the Supporting Information), not only supports the formation of the 1:1 complex, but also provides the structural information. All the signals for $\mathbf{4}^{4+}$ are divided into two groups, indicating that there are two different conformers, **A** and **B** (Figure 2). In the case of conformer **A**, the proton signals for the naphthalene and the viologen unit close to naphthalene are upfield shifted up to $\delta \approx 1.8$ ppm. In the case of conformer **B**, the proton signals for the viologen unit adjacent to long alkyl chain are upfield shifted up to $\delta \approx 1.7$ ppm, while the three-carbon chain and the viologen unit close to naphthalene show a downfield shift by about 0.1 to 0.3 ppm compared with the signals of free $\mathbf{3}^{4+}$. These observations are consistent with the structures of the host-stabilized intramolecular CT complexes, **A** and **B** both with an end-to-interior loop structure. The complex with a short-chain loop (conformer **A**) is dominant over that with a long-chain loop (conformer **B**) in a 3:1 ratio, which was estimated from the integration of the well-resolved signals (k, x, and x′) for the two conformers of $\mathbf{3}^{4+}$. The conversion rates between conformers **A** and **B** in D_2O were estimated to be $k_{AB} = 13 \pm 4\ s^{-1}$ and $k_{BA} = 41 \pm 4\ s^{-1}$ at 298 K by 2D EXSY.

Further evidence for the formation of a 1:1 complex comes from the size of the supramolecular species estimated from the diffusion coefficient measured by pulsed field gradient NMR techniques. The estimated size of both conformers is only about 1.8 times that of CB[8] itself, thus supporting the 1:1 complex formation. Most convincingly, however, strong peaks at 680 and 510 corresponding to $\mathbf{4}^{3+}$ and $\mathbf{4}^{4+}$ ions, respectively, in the ESI mass spectrum provides unequivocal evidence for the 1:1 complex formation.

The machine-like behavior of $\mathbf{4}^{4+}$ was investigated by cyclic voltammetry. To understand the electrochemical behavior of the inclusion complex, we compared the cyclic voltammogram of $\mathbf{4}^{4+}$ with that of the "free" guest, $\mathbf{3}^{4+}$. Typical cyclic voltammograms of $\mathbf{3}^{4+}$ and $\mathbf{4}^{4+}$ are shown in Figure 3. As expected, $\mathbf{3}^{4+}$ undergoes two consecutive two-electron reduction processes, with sharp peaks that indicate strong adsorption of the reduced species ($\mathbf{3}^{2+}$ and $\mathbf{3}^{0}$) on the electrode surface (see the Supporting Information). Compared to $\mathbf{3}^{4+}$, however, $\mathbf{4}^{4+}$ exhibits a moderate negative shift of

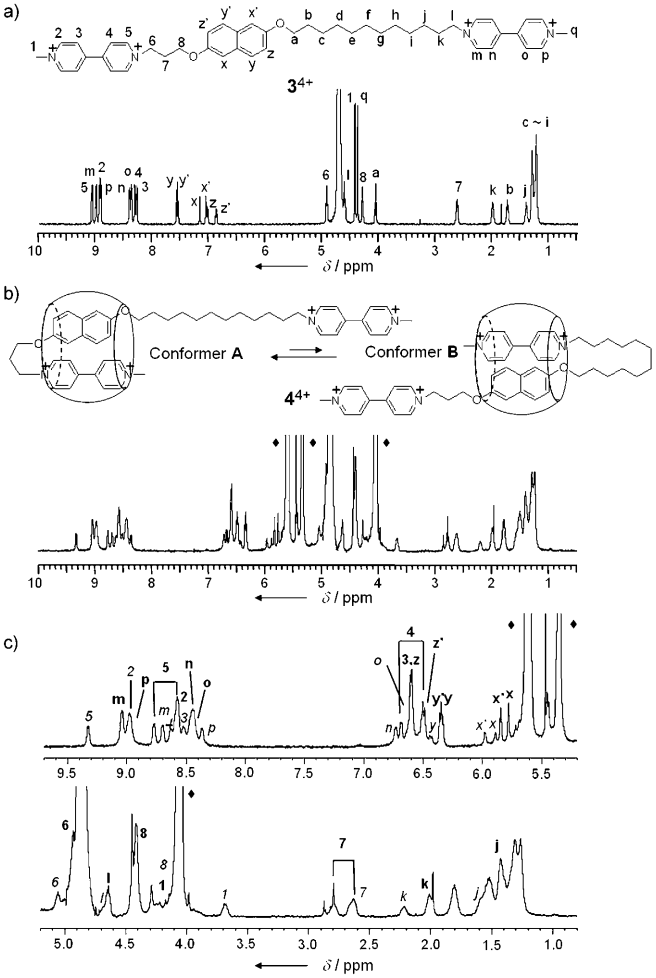


Figure 2. Comparison of ^{1}H NMR spectra in D_2O and their assignments: a) $\mathbf{3}^{4+}$, b) $\mathbf{4}^{4+}$ (at 298 K), c) $\mathbf{4}^{4+}$ (at 283 K). The assignments of the conformers **A** and **B** are indicated in (c) by letters in bold and italics, respectively. The signals for CB[8] (♦) are also shown.

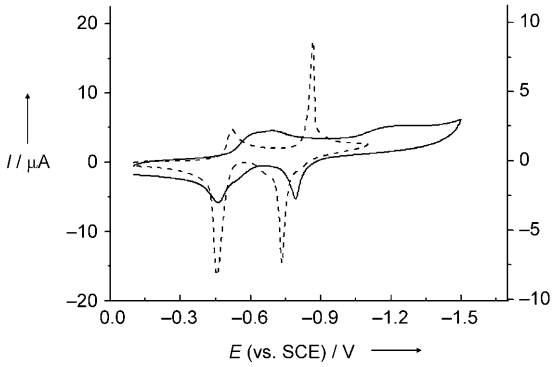


Figure 3. Cyclic voltammograms of 0.25 mM of $\mathbf{3}^{4+}$ (dashed line, left ordinate) and $\mathbf{4}^{4+}$ (solid line, right ordinate). Supporting electrolyte: 0.1 M phosphate buffer (pH 7.0). Scan rate: 25 mV s^{-1}.

the first reduction peak and a very large negative shift of the second reduction peak. This cyclic voltammetric behavior is similar to that of the CT complex formed between

$\mathbf{MV}^{2+}$ and **HN** inside CB[8], where a similar potential shift for the reduction process has been attributed to facile formation of the stable methyl viologen radical cation dimer inside CB[8] after one-electron reduction of $\mathbf{MV}^{2+}$.[18,19] In addition, the first reduction peak of $\mathbf{4}^{4+}$ consists of two closely overlapping peaks corresponding to two electrochemically different viologen units. One is involved in the CT complex formation with the naphthalene moiety of the thread ($\mathbf{3}^{4+}$) inside CB[8] while the other is free. The former viologen unit shows a more negative-shifted reduction wave than the latter.[18] Thus, the cyclic voltammetric behavior of $\mathbf{4}^{4+}$ suggests that the two-electron reduction of $\mathbf{4}^{4+}$ with an end-to-interior loop structure results in generation of a species containing two terminal viologen radical cation units, which then undergo a rapid intramolecular paring process inside CB[8] to form the stable complex $\mathbf{4}^{2+}$ with an end-to-end loop structure (Scheme 1).[11,18,20]

This conjecture was supported by a spectro-electrochemical study (Figure 4). The absorption spectrum of $\mathbf{4}^{2+}$ generated by two-electron reduction of $\mathbf{4}^{4+}$ (applied potential: −0.75 V vs. SCE) is essentially identical to that of $(\mathbf{MV}^{+})_2\subset$CB[8].[11,19] In addition, when −0.30 V was applied to a solution of $\mathbf{4}^{2+}$ or the solution is exposed to the air, the absorption spectrum $\mathbf{4}^{4+}$ was completely restored. Taken together, these studies support a machine-like behavior of $\mathbf{4}^{4+}$ in which an electrochemically triggered reversible change in the conformation of the thread occurs.[21]

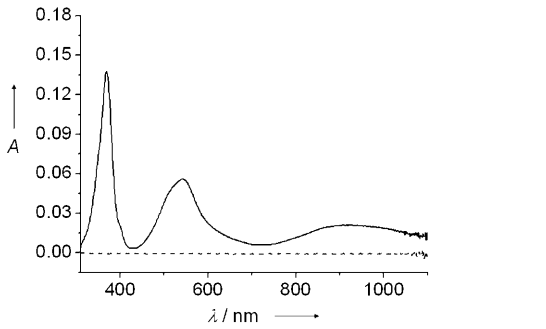


Figure 4. Absorption spectra of $\mathbf{4}^{4+}$ (dashed line) and $\mathbf{4}^{2+}$ (solid line); the latter was generated by two-electron reduction of the former (applied potential: −0.75 V vs. SCE).

Figure 5 shows the energy-minimized structures of $\mathbf{4}^{4+}$ (conformer **A**) and $\mathbf{4}^{2+}$ obtained by a molecular-modeling study in the gas phase. It should be noted that the structure of $\mathbf{4}^{4+}$ is rather flexible because of the long alkyl linker, and its conformation in aqueous solution can be different from the one depicted in Figure 5. Nevertheless, $\mathbf{4}^{4+}$ undergoes a dramatic change not only in shape but also in size in response to electrochemical stimuli. Such a large, reversible structural change triggered by electrochemical stimuli may provide insight into the designing of molecular actuators with useful applications.

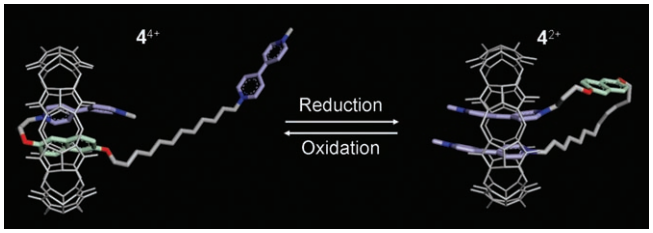


Figure 5. Energy-minimized structures of $\mathbf{4}^{4+}$ and $\mathbf{4}^{2+}$ obtained by a molecular-modeling study in the gas phase.

Conclusions

We have designed and synthesized a novel [2]pseudorotaxane-based molecular machine in which the interconversion between end-to-interior and end-to-end loop structures is reversibly controlled by electrochemical stimuli. CB[8] and the thread molecule $\mathbf{3}^{4+}$ containing an electron-rich hydroxynaphthalene unit and two electron-deficient viologen units form the 1:1 complex $\mathbf{4}^{4+}$ with an end-to-interior loop structure, which is reversibly converted into an end-to-end structure upon reduction. Large changes in shape and size of the molecule are accompanied by the reversible redox process. The key feature of the machine-like behavior is the reversible conversion between an intramolecular CT complex and viologen cation radical dimer formed inside CB[8] triggered by electrochemical stimuli. This novel electrochemically driven molecular machine not only mimics the loop formation in biological processes but also may provide useful insights in designing novel molecular devices such as molecular actuators.

Experimental Section

General

All reagents and solvents employed were commercially available and used as supplied without further purification. NMR data were recorded on a Bruker DRX500 spectrometer. UV/Vis absorption spectra were recorded on a Hewlett–Packard 8453 diode array spectrophotometer. Molecular-modeling studies were carried out using the Discover module of the Materials Studio 4.1 package (Accelrys Inc.).

NMR Experiments

^{1}H–^{1}H correlation spectroscopy (COSY) and rotating-frame Overhauser effect spectroscopy (ROESY) experiments were performed on a Bruker DRX500 NMR spectrometer operating at the proton Larmor frequency of 500.23 MHz at 25 °C. ROESY spectra were recorded using the time proportional phase increment method with a mixing time of 0.3 s and a recycle delay of 4 s. 2D EXSY spectra were recorded at 298 K at 500 MHz with a phase-sensitive NOESY pulse sequence supplied with the Bruker software. Rate constants were calculated from measurements of the cross-peak to diagonal-peak intensities and the molar fractions of the different compounds undergoing exchange.

Diffusion coefficient measurements were carried out using a 5 mm Bruker QNP probe with an actively shielded *z* gradient coil. Diffusion coefficients were extracted from a series of ^{1}H NMR spectra measured by the bipolar pulse longitudinal encode–decode pulse sequence as a function of gradient amplitude. The hydrodynamic volume of a complex was estimated by the ratio $V_{complex}/V_{CB[8]}$, where $V_{complex}$ and $V_{CB[8]}$ represent the volumes of the complex and CB[8], respectively, which was cal-

culated from the diffusion coefficient ratio ($V_{complex}/V_{CB[8]}=(D_{complex}/D_{CB[8]})^{-3}$).

Electrochemical and Spectro-Electrochemical Experiments

Electrochemical experiments were performed with a Princeton Applied Research Model 273 multipurpose instrument interfaced to a personal computer. A glassy carbon working electrode (0.07 cm^2), a Pt counter electrode, and a saturated calomel electrode (SCE) as a reference electrode separated with a fine glass frit were utilized in a single-compartment cell. The surface of the working electrode was polished with a 0.05 μm alumina/water slurry on a felt surface and rinsed with purified water prior to electrochemical experiments. All solutions were deoxygenated by purging with argon gas and maintained under an inert atmosphere during the electrochemical experiments.

A spectro-electrochemical cell was assembled with a piece of glass sheet and a piece of indium tin oxide (ITO) coated glass and a spacer film (thickness 200 μm). Electrolysis was achieved by applying a potential to the ITO working electrode. UV/Vis absorption spectra were recorded on a Hewlett–Packard 8453 diode array spectrophotometer. The solution prior to electrolysis was used as a blank reference.

Syntheses and Characterization

1: 2-Benzyloxy-6-hydroxynaphthalene was synthesized according to the literature.[17d] A solution of 2-benzyloxy-6-hydroxynaphthalene (0.46 g, 1.9 mmol) and excess dibromododecane (1.6 g, 4.9 mmol) in acetone (15 mL) in the presence of K_2CO_3 (0.70 g, 5.1 mmol) was refluxed for 12 h. Usual aqueous workup followed by purification using column chromatography yielded **1** (0.38 g, 1.5 mmol, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.65 (d, J=4.9 Hz, 1H), 7.62 (d, J=5.1 Hz, 1H), 7.50–7.32 (m, 5H), 7.19 (s, 1H), 7.17 (dd, J=2.5, 23 Hz, 1H), 7.14 (dd, J=2.5, 23 Hz, 1H), 7.10 (s, 1H), 5.16 (s, 2H), 4.05 (t, J=6.6 Hz, 2H), 3.41 (t, J=6.9 Hz, 2H), 1.85 (q, J=6.8 Hz, 2H), 1.83 (q, J=6.1 Hz, 2H), 1.45–1.37 (m, 4H), 1.30 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=156.1, 155.6, 137.5, 130.4, 130.0, 129.0, 128.5, 128.4, 128.0, 119.7, 119.6, 108.0, 107.3, 70.5, 68.5, 34.5, 33.3, 29.9, 29.8, 29.7, 29.2, 28.6, 26.5 ppm; MS (EI): m/z: 159, 160, 405, 407, 416, 496, 498 [M^+]; HRMS (EI) calcd for $C_{29}H_{37}BrO_2$: 496.1977; found: 496.1979.

2: Stirring a solution of **1** (0.26 g, 0.52 mmol) in CH_2Cl_2-EtOA (1:1, 30 mL) in the presence of Pd/C under H_2 atmosphere for 12 h at room temperature, followed by filtration and concentration, afforded 2-hydroxy-6-bromododecanyloxynaphthalene, which was directly used in the next step without further purification. To a solution of 2-hydroxy-6-bromododecanyloxynaphthalene in acetone (10 mL) was added excess dibromopropane (1.3 g, 6.4 mmol) and K_2CO_3 (0.68 g, 4.9 mmol). Heating the solution at reflux for 12 h, followed by aqueous workup and purification using column chromatography yielded **2** (0.27 g, 0.50 mmol, 97%). ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.64 (s, 1H), 7.61 (s, 1H), 7.15–7.09 (m, 4H), 4.20 (t, J=5.7 Hz, 2H), 4.05 (t, J=6.5 Hz, 2H), 3.65 (t, J=6.4 Hz, 2H), 3.41 (t, J=6.8 Hz, 2H), 1.86 (q, J=6.9 Hz, 2H), 1.83 (q, J=6.6 Hz, 2H), 1.45–1.37 (m, 4H), 1.39 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=156.1, 155.5, 130.3, 130.0, 128.6, 128.5, 119.7, 119.3, 107.6, 107.4, 68.5, 65.8, 34.5, 33.3, 32.8, 30.5, 29.9, 29.8, 29.7, 29.2, 28.6, 26.5 ppm; MS (EI): m/z: 159, 160, 200, 280, 366, 446, 448, 526, 528 [M^+]; HRMS (EI) calcd for $C_{25}H_{36}Br_2O_2$: 526.1082; found: 526.1083.

3^{4+}·4I$^-$: A solution of **2** (0.90 mg, 0.18 mmol) and 4,4′-bipyridine (0.55 g, 3.5 mmol) in CH_3CN was stirred for 24 h at 70°C. After cooling to room temperature, the resulting pyridinium salt was filtered and washed with acetonitrile. The resulting pyridinium salt was directly used in the next step without further purification. A solution of the pyridinium salt and excess amount of iodomethane (0.50 g, 3.5 mmol) in DMF-CH_3CN was stirred for 24 h at 60°C and the resulting precipitate was filtered and washed with acetonitrile and diethyl ether and dried to give an orange-colored solid (0.19 g, 0.17 mmol, 95%). ^{1}H NMR (300 MHz, [D$_6$]DMSO) δ=9.57 (d, J=6.3 Hz, 2H), 9.50 (d, J=6.3 Hz, 2H), 9.40 (d, J=6.1 Hz, 2H), 9.39 (d, J=6.0 Hz, 2H), 8.92–8.86 (m, 8H), 7.80 (d, J=8.2 Hz, 1H), 7.77 (d, J=7.7 Hz, 1H), 7.34 (s, 2H), 7.22 (d, J=9.0 Hz, 1H), 7.03 (d, J=9.1 Hz, 1H), 5.05 (t, J=6.6 Hz, 2H), 4.79 (t, J=7.2 Hz, 2H), 4.55 (s, 6H), 4.33 (t, J=5.6 Hz, 2H), 4.12 (t, J=6.3 Hz, 2H), 2.67 (t, J=6.0 Hz, 2H), 2.08 (m, 2H), 1.86 (m, 2H), 1.54 (m, 2H), 1.42–1.38 ppm (m, 14H); ^{13}C NMR (125 MHz, [D$_6$]DMSO) δ=156.0, 155.1, 149.6, 149.4, 149.1, 149.0, 147.5, 147.0, 146.6, 130.5, 130.1, 129.0, 128.9, 127.4, 127.3, 127.0, 119.9, 119.4, 108.0, 107.8, 68.4, 65.7, 61.8, 60.0, 49.0, 31.7, 30.0, 29.94, 29.88, 29.80, 29.75, 29.3, 26.6, 26.4 ppm; MS (ESI): m/z (%): 177 (100) [M^{4+}], 236 [M^{3+}], 355 [M^{2+}], 482 [$M^{4+}+2I^-]^{2+}$. Elemental analysis (%) calcd for ($C_{47}H_{58}N_4O_2^{4+}$)·4I$^-$·3H$_2$O: C 44.36, H 5.07, N 4.40; found: C 44.05, H 4.95, N 4.85.

4^{4+}: To a solution of **3**$^{4+}$·4I$^-$·3H$_2$O (3.7 mg, 2.9 μmol) in water (4 mL) was added CB[8]·2H$_2$SO$_4$·16H$_2$O (6.2 mg, 3.4 μmol) and the resulting mixture was sonicated with occasional heating until all solid materials were dissolved. Undissolved solid was filtered off, and the filtrate (**4**$^{4+}$·4I$^-$) was used for the next experiments including characterization by ESI mass spectrometry. MS (ESI): m/z: 510 [M^{4+}], 680 [M^{3+}], 722 [$M^{4+}+I^-]^{3+}$.

Acknowledgements

We gratefully acknowledge the Creative Research Initiative and the Brain Korea 21 Program of the Korean Ministry of Education, Science and Technology for support of this work.

[1] For reviews, see: a) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem.* **2000**, *112*, 3484–3530; *Angew. Chem. Int. Ed.* **2000**, *39*, 3348–3391; b) E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem.* **2007**, *119*, 72–196; *Angew. Chem. Int. Ed.* **2007**, *46*, 72–191; c) W. R. Browne, B. L. Ferringa, *Nat. Nanotechnol.* **2006**, *1*, 25–35.

[2] Molecular machines special issues: a) *Acc. Chem. Res.* **2001**, *34*, 409–522; b) *Adv. Funct. Mater.* **2007**, *17*, 671–840.

[3] For representative examples, see: a) P. L. Anelli, N. Spencer, J. F. Stoddart, *J. Am. Chem. Soc.* **1991**, *113*, 5131–5133; b) R. A. Bissell, E. Córdova, A. E. Kaifer, J. F. Stoddart, *Nature* **1994**, *369*, 133–137; c) A. S. Lane, D. A. Leigh; A. Murphy, *J. Am. Chem. Soc.* **1997**, *119*, 11092–11093; A. Murphy, *J. Am. Chem. Soc.* **1997**, *119*, 11092–11093; d) P. R. Ashton, R. Ballardini, V. Balzani, I. Baxter, A. Credi, M. C. T. Fyfe, M. T. Gandolfi; M. Gómez-López, M.-V. Martínez-Díaz, A. Piersanti, N. Spencer, J. F. Stoddart, M. Venturi, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1998**, *120*, 11932–11942; M. Gómez-López, M.-V. Martínez-Díaz, A. Piersanti, N. Spencer, J. F. Stoddart, M. Venturi, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1998**, *120*, 11932–11942; e) A. M. Brouwer, C. Frochot, F. G. Gatti, D. A. Leigh, L. Mottier, F. Paolucci, S. Roffia, G. W. H. Wurpel, *Science* **2001**, *291*, 2124–2128; f) H.-R. Tseng, S. A. Vignon, J. F. Stoddart, *Angew. Chem.* **2003**, *115*, 1529–1533; *Angew. Chem. Int. Ed.* **2003**, *42*, 1491–1495; g) G. Bottari, F. Dehez, D. A. Leigh, P. J. Nash, E. M. Pérez, J. K. Y. Wong, F. Zerbetto, *Angew. Chem.* **2003**, *115*, 6066–6069; *Angew. Chem. Int. Ed.* **2003**, *42*, 5886–5889; h) C. M. Keaveney, D. A. Leigh, *Angew. Chem.* **2004**, *116*, 1242–1244; *Angew. Chem. Int. Ed.* **2004**, *43*, 1222–1224; i) J. Berná, D. A. Leigh, M. Lubomska, S. M. Mendoza, E. M. Pérez, P. Rudolf, G. Teobaldi, F. Zerbetto, *Nat. Mater.* **2005**, *4*, 704–710; j) V. Balzani, M. Clemente-León, A. Credi, B. Ferrer, M. Venturi, A. H. Flood, J. F. Stoddart, *Proc. Natl. Acad. Sci. USA* **2006**, *103*,1178–1183.

[4] For representative examples, see: a) T. R. Kelly, H. De Silva, R. A. Silva, *Nature* **1999**, *401*, 150–152; b) N. Koumura, R. W. J. Zijlstra, R. A. van Delden, N. Harada, B. L. Feringa, *Nature* **1999**, *401*,152–155; c) H. Jian, J. M. Tour, *J. Org. Chem.* **2003**, *68*, 5091–5103; d) D. A. Leigh, J. K. Y. Wong, F. Dehez, F. Zerbetto, *Nature* **2003**, *424*, 174–179; e) J. V. Hernández, E. R. Kay, D. A. Leigh, *Science* **2004**, *306*, 1532–1537; f) X. Zheng, M. E. Mulcahy, D. Horinek, F. Galeotti, T. F. Magnera, J. Michl, *J. Am. Chem. Soc.* **2004**, *126*, 4540–4542; g) S. P. Fletcher, F. Dumur, M. M. Pollard, B. L. Feringa, *Science* **2005**, *310*, 80–82; h) D. Pijper, R. A. van Delden, A. Meetsma, B. L. Feringa, *J. Am. Chem. Soc.* **2005**, *127*, 17612–17613.

[5] a) M. C. Jiménez, C. Dietrich-Buchecker, J.-P. Sauvage, *Angew. Chem.* **2000**, *112*, 3422–3425; *Angew. Chem. Int. Ed.* **2000**, *39*, 3284–3287; b) M. C. Jiménez-Molero, C. Dietrich-Buchecker, J.-P. Sauvage, *Chem. Eur. J.* **2002**, *8*, 1456–1466; c) M. C. Jiménez-Molero, C. Dietrich-Buchecker, J.-P. Sauvage, *Chem. Commun.* **2003**, 1613–1616; d) Y. Liu, A. H. Flood, P. A. Bonvallet, S. A. Vignon, B. H. Northrop, H.-R. Tseng, J. O. Jeppesen, T. J. Huang, B. Brough, M. Baller, S. Magonov, S. D. Solares, W. A. Goddard, C.-M. Ho, J. F. Stoddart, *J. Am. Chem. Soc.* **2005**, *127*, 9745–9759.

[6] a) T. Muraoka, K. Kinbara, Y. Kobayashi, T. Aida, *J. Am. Chem. Soc.* **2003**, *125*, 5612–5613; b) T. Muraoka, K. Kinbara, T. Aida, *Nature* **2006**, *440*, 512–515.

[7] a) J. D. Badjić, V. Balzani, A. Credi, S. Silvi, J. F. Stoddart, *Science* **2004**, *303*, 1845–1849; b) J. D. Badjic, C. M. Ronconi, J. F. Stoddart, V. Balzani, S. Silvi, A. Credi, *J. Am. Chem. Soc.* **2006**, *128*, 1489–1499.

[8] a) L. Finzi, J. Gelles, *Science* **1995**, *267*, 378–380; b) S. H. Yoshimura, H. Maruyama, F. Ishikawa, R. Ohki, K. Takeyasu, *Genes Cells* **2004**, *9*, 205–218; c) Y. Zhang, C. L. Smith, A. Saha, S. W. Grill, S. Mihardja, S. B. Smith, B. R. Cairns, C. L. Peterson, C. Bustamante, *Mol. Cell* **2006**, *24*, 559–568.

[9] a) F. Krieger, B. Fierz, O. Bieri, M. Drewello, T. Kiefhaber, *J. Mol. Biol.* **2003**, *332*, 265–274; b) R. R. Hudgins, F. Huang, G. Gramlich, W. M. Nau, *J. Am. Chem. Soc.* **2002**, *124*, 556–564; c) L. J. Lapidus, W. A. Eaton, J. Hofrichter, *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 7220–7225; d) B. Fierz, T. Kiefhabar, *J. Am. Chem. Soc.* **2007**, *129*, 672–679.

[10] a) S. Shinkai, M. Ishihara, K. Ueda, O. Manabe, *J. Chem. Soc. Perkin Trans. 2* **1985**, 511–518; b) P. R. Ashton, R. Ballardini, V. Balzani, S. E. Boyd, A. Credi, M. T. Gandolfi, M. Gómez-López, S. Iqbal, D. Philp, J. A. Preece, L. Prodi, H. G. Ricketts, J. F. Stoddart, M. S. Tolley, M. Venturi, M. Venturi, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1997**, *3*, 152–170; c) Y. Liu, A. H. Flood, J. F. Stoddart, *J. Am. Chem. Soc.* **2004**, *126*, 9150–9151.

[11] W. S. Jeon, A. Y. Ziganshina, J. W. Lee, Y. H. Ko, J.-K. Kang, C. Lee, K. Kim, *Angew. Chem.* **2003**, *115*, 4231–4234; *Angew. Chem. Int. Ed.* **2003**, *42*, 4097–4100.

[12] a) W. A. Freeman, W. L. Mock, N.-Y. Shih, *J. Am. Chem. Soc.* **1981**, *103*, 7367–7368; b) J. Kim, I.-S. Jung, S.-Y. Kim, E. Lee, J.-K. Kang, S. Sakamoto, K. Yamaguchi, K. Kim, *J. Am. Chem. Soc.* **2000**, *122*, 540–541; c) A. Day, A. P. Arnold, R. J. Blanch, B. Snushall, *J. Org. Chem.* **2001**, *66*, 8094–8100; d) S. Liu, P. Y. Zavalij, L. Isaacs, *J. Am. Chem. Soc.* **2005**, *127*, 16798–16799.

[13] a) D. Whang, Y.-M. Jeon, J. Heo, K. Kim, *J. Am. Chem. Soc.* **1996**, *118*, 11333–11334; b) D. Whang, K. Kim, *J. Am. Chem. Soc.* **1997**, *119*, 451–452; c) D. Whang, K.-M. Park, J. Heo, K. Kim, *J. Am. Chem. Soc.* **1998**, *120*, 4899–4900; d) S.-G. Roh, K.-M. Park, G.-J. Park, S. Sakamoto, K. Yamaguchi, K. Kim, *Angew. Chem.* **1999**, *111*, 671–675; *Angew. Chem. Int. Ed.* **1999**, *38*, 637–641; e) E. Lee, J. Heo, K. Kim, *Angew. Chem.* **2000**, *112*, 2811–2813; *Angew. Chem. Int. Ed.* **2000**, *39*, 2699–2701; f) E. Lee, J. Kim, J. Heo, D. Whang, K. Kim, *Angew. Chem.* **2001**, *113*, 413–416; *Angew. Chem. Int. Ed.* **2001**, *40*, 399–402; g) J. W. Lee, Y. H. Ko, S.-H. Park, K. Yamaguchi, K. Kim, *Angew. Chem.* **2001**, *113*, 769–771; *Angew. Chem. Int. Ed.* **2001**, *40*, 746–749; h) D. Tuncel, J. H. G. Steinke, *Chem. Commun.* **2001**, 253–254; i) K.-M. Park, D. Whang, E. Lee, J. Heo, K. Kim, *Chem. Eur. J.* **2002**, *8*, 498–508; j) K.-M. Park, S.-Y. Kim, J. Heo, D. Whang, S. Sakamoto, K. Yamaguchi, K. Kim, *J. Am. Chem. Soc.* **2002**, *124*, 2140–2147; k) K. Kim, *Chem. Soc. Rev.* **2002**, *31*, 96–107; l) S. Choi, J. W. Lee, Y. H. Ko, K. Kim, *Macromolecules* **2002**, *35*, 3526–3531; m) Y. Tan, S. Choi, J. W. Lee, Y. H. Ko, K. Kim, *Macromolecules* **2002**, *35*, 7161–7165; n) K.-M. Park, E. Lee, S.-G. Roh, J. Kim, K. Kim, *Bull. Korean Chem. Soc.* **2004**, *25*, 1711–1713; o) S.-Y. Kim, J. W. Lee, S. C. Han, K. Kim, *Bull. Korean Chem. Soc.* **2005**, *26*, 1265–1268; p) V. Sindelar, K. Moon, A. E. Kaifer, *Org. Lett.* **2004**, *6*, 2665–2668; q) H.-J. Buschmann, L. Mutihac, E. Schollmeyer, *J. Inclusion Phenom. Macrocyclic Chem.* **2005**, *53*, 85–88; r) J. W. Lee, G. T. Lim, *J. Korean Chem. Soc.* **2005**, *49*, 112–116; s) M. V. Rekharsky, H. Yamamura, M. Kawai, I. Osaka, R. Arakawa, A. Sato, Y. H. Ko, N. Selvapalam, K. Kim, Y. Inoue, *Org. Lett.* **2006**, *8*, 815–818; t) Z.-B. Wang, H.-F. Zhu, M. Zhao, Y.-Z. Li, T. Okamura, W.-Y. Sun, H.-L. Chen, N. Ueyama, *Cryst. Growth Des.* **2006**, *6*, 1420–1427; u) D. Tuncel, N. Cindir, Ü. Koldemir, *J. Inclusion Phenom. Macrocyclic Chem.* **2006**, *55*, 373–380; v) F.-J. Huo, C.-X. Yin, P. Yang, *J. Inclusion Phenom. Macrocyclic Chem.* **2006**, *56*, 193–196; w) Z.-S. Hou, Y.-B. Tan, K. Kim, Q.-F. Zhou, *Polymer* **2006**, *47*, 742–750; x) Y. Liu, C.-F. Ke, H.-Y. Zhang, W.-J. Wu, J. Shi, *J. Org. Chem.* **2007**, *72*, 280–283; y) R. Eelkema, K. Maeda, B. Odell, H. L. Anderson, *J. Am. Chem. Soc.* **2007**, *129*, 12384–12385; z) M. Zhao, Z.-B. Wang, Y.-Z. Li, H.-L. Chen, *Inorg. Chem. Commun.* **2007**, *10*, 101–104.

[14] a) S. I. Jun, J. W. Lee, S. Sakamoto, K. Yamaguchi, K. Kim, *Tetrahedron Lett.* **2000**, *41*, 471–475; b) J. W. Lee, K. Kim, K. Kim, *Chem. Commun.* **2001**, 1042–1043; c) K. Kim, W. S. Jeon, J.-K. Kang, J. W. Lee, S. Y. Jeon, T. Kim, K. Kim, *Angew. Chem.* **2003**, *115*, 2395–2398; *Angew. Chem. Int. Ed.* **2003**, *42*, 2293–2296; d) V. Sindelar, S. Silvi, A. E. Kaifer, *Chem. Commun.* **2006**, 2185–2187; e) T. Ooya, D. Inoue, H. S. Choi, Y. Kobayashi, S. Loethen, D. H. Thompson, Y. H. Ko, K. Kim, N. Yui, *Org. Lett.* **2006**, *8*, 3159–3162; f) D. Sobransingh, A. E. Kaifer, *Org. Lett.* **2006**, *8*, 3247–3250; g) D. Tuncel, H. B. Tiftik, B. Salih, *J. Mater. Chem.* **2006**, *16*, 3291–3296; h) V. Sindelar, S. Silvi, S. E. Parker, D. Sobransingh, A. E. Kaifer, *Adv. Funct. Mater.* **2007**, *17*, 694–701; i) D. Tuncel, Ö. Özsar, H. B. Tiftik, B. Salih, *Chem. Commun.* **2007**, 1369–1371; j) S. Chakrabarti, P. Mukhopadhyay, S. Lin, L. Isaacs, *Org. Lett.* **2007**, *9*, 2349–2352; k) Y. Liu, X.-Y. Li, H.-Y. Zhang, C.-J. Li, F. Ding, *J. Org. Chem.* **2007**, *72*, 3640–3645.

[15] H.-J. Kim, J. Heo, W. S. Jeon, E. Lee, J. Kim, S. Sakamoto, K. Yamaguchi, K. Kim, *Angew. Chem.* **2001**, *113*, 1574–1577; *Angew. Chem. Int. Ed.* **2001**, *40*, 1526–1529.

[16] a) J. W. Lee, S. Samal, N. Selvapalam, H.-J. Kim, K. Kim, *Acc. Chem. Res.* **2003**, *36*, 621–630; b) J. Lagona, P. Mukhopadhyay, S. Chakrabarti, L. Isaacs, *Angew. Chem.* **2005**, *117*, 4922–4949; *Angew. Chem. Int. Ed.* **2005**, *44*, 4844–4870; c) Y. H. Ko, E. Kim, I. Hwang, K. Kim, *Chem. Commun.* **2007**, 1305–1315.

[17] a) Y. H. Ko, K. Kim, J.-K. Kang, H. Chun, J. W. Lee, S. Sakamoto, K. Yamaguchi, J. C. Fettinger, K. Kim, *J. Am. Chem. Soc.* **2004**, *126*, 1932–1933; b) Y. J. Jeon, P. K. Bharadwaj, S. W. Choi, J. W. Lee, K. Kim, *Angew. Chem.* **2002**, *114*, 4654–4656; *Angew. Chem. Int. Ed.* **2002**, *41*, 4474–4476; c) W. Wang, A. E. Kaifer, *Angew. Chem.* **2006**, *118*, 7200–7204; *Angew. Chem. Int. Ed.* **2006**, *45*, 7042–7046; d) S.-Y. Kim, Y. H. Ko, J. W. Lee, S. Sakamoto, K. Yamaguchi, K. Kim, *Chem. Asian J.* **2007**, *2*, 747–754; e) J. W. Lee, S. C. Han, J. H. Kim, Y. H. Ko, K. Kim, *Bull. Korean Chem. Soc.* **2007**, *28*, 1837–1840; f) J. W. Lee, K. Kim, S. Choi, Y. H. Ko, S. Sakamoto, K. Yamaguchi, K. Kim, *Chem. Commun.* **2002**, 2692–2693; g) K. Kim, D. Kim, J. W. Lee, Y. H. Ko, K. Kim, *Chem. Commun.* **2004**, 848–849; h) M. E. Bush, N. D. Bouley, A. R. Urbach, *J. Am. Chem. Soc.* **2005**, *127*, 14511–14517; i) V. Sindelar, M. A. Cejas, F. M. Raymo, W. Chen, S. E. Parker, A. E. Kaifer, *Chem. Eur. J.* **2005**, *11*, 7054–7059; j) Y. H. Ko, K. Kim, E. Kim, K. Kim, *Supramol. Chem.* **2007**, *19*, 287–293; k) J.-K. Kang, I. Hwang, Y. H. Ko, W. S. Jeon, H.-J. Kim, K. Kim, *Supramol. Chem.* **2008**, *20*, 149–155.

[18] W. S. Jeon, E. Kim, Y. H. Ko, I. Hwang, J. W. Lee, S.-Y. Kim, H.-J. Kim, K. Kim, *Angew. Chem.* **2005**, *117*, 89–93; *Angew. Chem. Int. Ed.* **2005**, *44*, 87–91.

[19] W. S. Jeon, H.-J. Kim, C. Lee, K. Kim, *Chem. Commun.* **2002**, 1828–1829.

[20] One of the reviewers suspected that decomplexation of **4** seems to occur upon full reduction. Although the nature of the fully reduced species ($\mathbf{4}^{0}$) has not been established, decomplexation of **4** does not seem to occur at least on the cyclic voltammetric time scale for the following reasons: a) Essentially the same cyclic voltammograms are obtained for **4** and no growth of the peaks corresponding to **3** is observed in the successive full scans, b) The anodic peak for **4** at −0.8 V is sharp, presumably owing to adsorption of the fully reduced species, but clearly different from the corresponding anodic peak for **3** in terms of both potential and current (Figure 3),

CHEMISTRY
AN ASIAN JOURNAL

c) When the scan potential is reversed at −1.0 V, the reoxidation peak occurs at the same potential (−0.45 V) as before (Figure S4 in the Supporting Information).

[21] The formation of intermolecular viologen radical cation dimers such as a 2:2 complex with a face-to-face dimer structure cannot be ruled out. However, the intermolecular dimerization should be entropically much more unfavorable; therefore it is less likely to happen at the concentration of the ligand (0.25 mM) employed in this study.

Received: February 22, 2008
Published online: June 23, 2008

