

Formation of Pseudorotaxane Induced by Electrochemical Oxidation of Ferrocene-Containing Axis Molecule in the Presence of Crown Ether

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Rotaxanes and pseudorotaxanes¹ have attracted increasing attention because of not only their interlocked structures but also their unique properties that can be applied to molecular shuttles,² molecular wires,³ and drug delivery systems.⁴ The molecular shuttles change the interaction between the stations of the axis and macrocyclic molecules and shift the position of the macrocycle along the axis upon the external stimulation, such as a change in the pH of the solution or electrochemical redox. The application of a stimulus-response system to the formation of pseudorotaxanes results in new preparative reactions of pseudorotaxanes induced by an external stimulus.⁵ Here, we report on the novel reaction of an axis molecule containing a ferrocene moiety which is activated by an electrochemical stimulus and forms a pseudorotaxane with a crown ether.

The electrochemical oxidation of the ferrocene derivatives **1** and **2** having an aminomethyl group at a cyclopentadienyl ligand in the presence of dibenzo[24]crown-8 (DB24C8) and 1-hydroxy-2,2,6,6-tetramethylpiperidine (TEMPOH)⁶ produces pseudorotaxanes composed of a ferrocene-containing axis molecule and macrocyclic DB24C8, as shown in Scheme 1.

Figure 1 shows the linear sweep voltammogram of the reaction of DB24C8 (4 mM) and **1** (2 mM) using a flow cell. It indicates the quantitative one-electron process that converts ferrocene into ferricinium below 0.40 V (vs Ag⁺/Ag) in a high yield (>98%).⁷ The pseudorotaxane **1** produced from the reaction in Scheme 1 was characterized on the basis of the FAB mass spectrum of the solution after flow electrolysis, exhibiting a peak at *m/z* 768.3187 (error −1.5 ppm) corresponding to the cationic pseudorotaxane [DB24C8·1-H]⁺.

The cyclic voltammogram of the solution shows a reversible one-electron transfer at *E*_{1/2} = 0.23 V which is higher than that of **1** (*E*_{1/2} = 0.07 V). No corresponding peak due to residual **1** was observed. The ESR spectrum of the solution shows the characteristic three signals of the TEMPO radical with 92% intensity of the initially charged TEMPOH.⁸ Flow electrolysis of **2** with DB24C8 at 0.4 V also leads to the formation of [DB24C8·2-H]⁺ showing a peak at *m/z* = 748 in the mass spectrum. A mixture of **1**, *n*-Bu₄NPF₆, DB24C8, and TEMPOH did not form a pseudorotaxane without electrochemical oxidation.

The pseudorotaxane [DB24C8·1-H][PF₆] was prepared alternatively by the direct reaction of [1-H][PF₆] with DB24C8, as shown in Scheme 2. X-ray single-crystal analysis of [DB24C8·1-H][PF₆] shows the interlocked structure depicted in Figure 2. The cyclic and axis molecules are associated with each other by N⁺–H···O and C–H···O hydrogen bonds as well as the π – π stacking between the aromatic rings. A solution of [DB24C8·1-H][PF₆] prepared by electrochemical oxidation (Scheme 1) shows a cyclic voltammogram and ¹H NMR and electronic spectra identical with those prepared by Scheme 2.

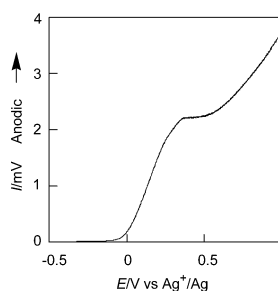


Figure 1. Linear sweep voltammogram of **1** (2 mM) in the presence of DB24C8 (4 mM) in acetonitrile solution of 10 mM *n*-Bu₄NPF₆.

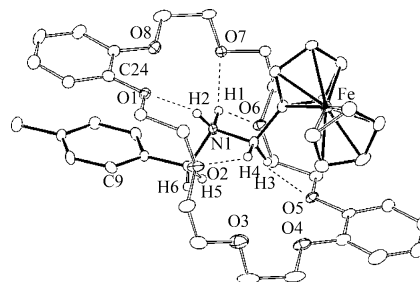
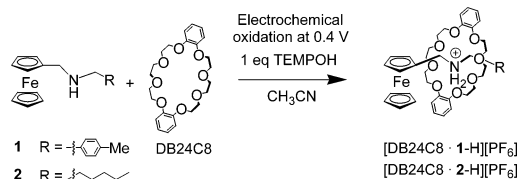
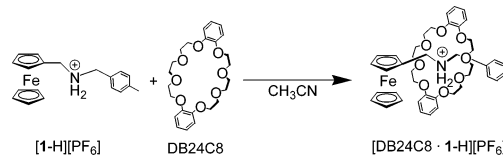


Figure 2. ORTEP drawing of [DB24C8·1-H][PF₆] with 30% ellipsoidal plotting. PF₆[−] anion was omitted.

Scheme 1. Electrochemical Formation of [2]Pseudorotaxane**Scheme 2.** Chemical Formation of [2]Pseudorotaxane

The formation of the pseudorotaxane was investigated by observing the change in the absorption spectra of a mixture of **1** and DB24C8 (1:2–1:20) after electrolysis without TEMPOH. The electrochemical oxidation at constant potentials from −0.4 to 1.0 V by a flow electrolysis technique induces absorption at 630 nm (Figure 3A). It corresponds to the ferricinium species based on the characteristic peak position.⁹ The absorbance at 630 nm decreases gradually as shown in Figure 3B, while the addition of TEMPOH causes its disappearance within 2 s. The change in absorption spectra in the absence of TEMPOH, followed by a decrease in peak height

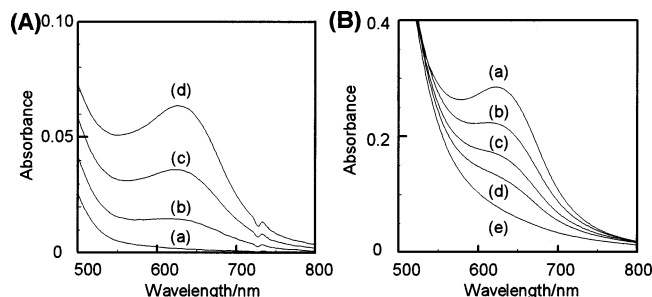


Figure 3. UV-vis spectra of **1** in the presence of DB24C8 in CH_3CN solution of 10 mM $n\text{-Bu}_4\text{NPF}_6$. $[\mathbf{1}]_0 = 2.0$ mM, $[\text{DB24C8}]_0 = 4.0$ mM. (A) Spectra measured immediately after the electrolysis at (a) -0.4 V (vs Ag^+/Ag), (b) 0 V, (c) 0.05 V, (d) 0.1 V. (B) Change in the spectra by flow electrolysis at 0.4 V (293 K) and subsequent reactions. (a) 0 min, (b) 6 min, (c) 12 min, (d) 24 min, and (e) 90 min after electrolysis.

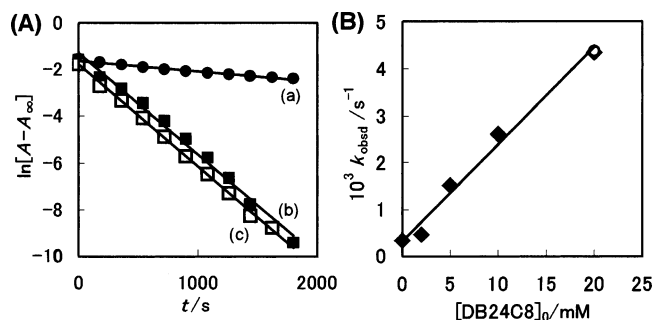
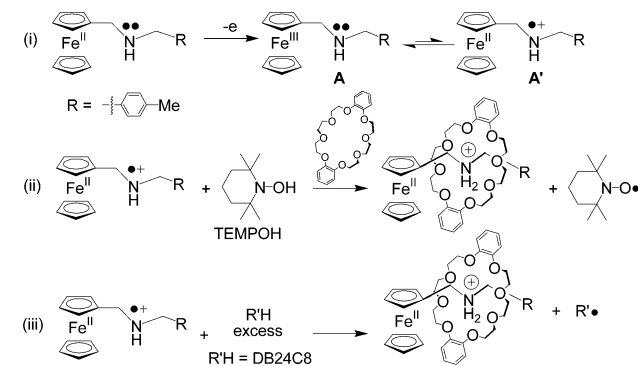


Figure 4. (A) Pseudo-first-order plots of consumption of the ferricinium ion in the presence of DB24C8 of (a) 2 mM ($k_{\text{obsd}} = 4.6 \times 10^{-4} \text{ s}^{-1}$), (b) 20 mM ($k_{\text{obsd}} = 4.4 \times 10^{-3} \text{ s}^{-1}$), (c) 20 mM with 20 mM H_2O ($k_{\text{obsd}} = 4.4 \times 10^{-3} \text{ s}^{-1}$). (B) Change in the observed rate constants with DB24C8 concentration.

Scheme 3



obeys pseudo-first-order kinetics (Figure 4A). The observed rate constant at 20°C increases linearly with increasing DB24C8 concentration, as shown in Figure 4B.¹⁰

These results show that the ferricinium ion formed by the electrochemical oxidation of **1** is rapidly converted into $[\text{DB24C8} \cdot \mathbf{1}\text{-H}]^+$ in the presence of TEMPOH and DB24C8, accompanied by the formation of the TEMPO radical. Without of TEMPOH, a much slower hydrogen transfer from DB24C8 to a cation radical at the nitrogen atom occurs to afford the pseudorotaxane.

Scheme 3 summarizes the mechanism of the pseudorotaxane formation. The electrochemical oxidation of $\text{Fe}(\text{II})$ gives the intermediate **A** which is in rapid equilibrium with **A'**¹⁰ having an $\text{Fe}(\text{II})$ center and the cation radical at the N atom. Analogous 2-aza-

[3]ferrocenophanes and oligoferrocenes with $\text{Fe}-\text{CH}_2-\text{NR}-\text{CH}_2-\text{Fe}$ units also show the intramolecular electron transfer between $\text{Fe}(\text{III})$ centers and the N atom of the ligand.^{11,12} The intermediate **A'** is hydrogenated by TEMPOH or by the CH_2 group of DB24C8 to produce a secondary ammonium cation.

In summary, we report the formation of a pseudorotaxane from a neutral amine axis and crown ether. The reaction occurs by electrochemical oxidation and is completed rapidly in the presence of a suitable hydrogen atom source. It is the first example of the formation of pseudorotaxane induced by an electrochemical stimulus.

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Supporting Information Available: Experimental procedures for synthesis of the complexes and ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data of $[\text{DB24C8} \cdot \mathbf{1}\text{-H}][\text{PF}_6]$ and $[\text{DB24C8} \cdot \mathbf{2}\text{-H}][\text{PF}_6]$ (PDF). X-ray crystallography files in CIF format for pseudorotaxanes. This material is available free of charge via the Internet at <http://pubs.acs.org>. See any current masthead page for ordering information and Web access instructions.

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- (10) **A** and **A'** may not exist as individual equilibrating species because spectroscopic evidences for the presence of **A'** were not obtained.
- (11) Use of 15crown[5]ether (20 mM), having a too small cavity to include the guest molecule, also leads to the formation of $[\mathbf{1}\text{-H}]^+$ ($k_{\text{obsd}} = 2.4 \times 10^{-3} \text{ s}^{-1}$). It suggest that a major part of **1** in Scheme 1 causes the hydrogen transfer followed by complexation with DB24C8. Without addition of DB24C8, the reaction produces $[\mathbf{1}\text{-H}]^+$; however, it is slower than that in the presence of DB24C8 (Figure 4A (a)). This is ascribed to intramolecular hydrogen abstraction that yields the imminium $[-\text{CH}=\text{N}^+-]$ cation. See: (a) Sakano, T.; Horie, M.; Osakada, K.; Nakao, H. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2059. (b) Horie, M.; Sakano, T.; Osakada, K.; Nakao, H. *Organometallics* **2004**, *23*, 18.
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