

Redox Behavior of Ferrocene-Containing Rotaxane: Transposition of the Rotaxane Wheel by Redox Reaction of a Ferrocene Moiety Tethered at the End of the Axle

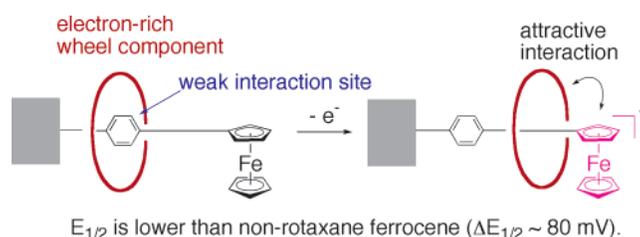
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ABSTRACT



A rotaxane with a ferrocene moiety at the axle terminus was prepared. The redox potential of the ferrocene moiety decreased by ca. 80 mV when the rotaxane had a crown ether wheel capable of moving on the axle. Thus, the stabilization of the oxidized state of the ferrocene moiety is assumed to accompany the transposition of the wheel component on the axle toward the ferrocene moiety.

Interlocked molecules such as rotaxanes and catenanes are characterized by the relative movements of a component against its counterpart.¹ Because these movements are similar to basic mechanical motions, much attention has been paid to the construction and the motion of interlocked-molecule-based molecular machines, which are driven by an intercomponent interaction.² The redox system is one of the most

promising methods to control this interaction because of its compatibility to electric circuits.³ Sauvage et al. demonstrated the redox reactions of copper ions to control the intercomponent metal–ligand interaction, thus inducing drastic conformational changes of the interlocked compounds.⁴ Stoddart et al. demonstrated that the reduction of viologen or oxidation of TTF resulted in a change in intercomponent CT interaction or electrostatic repulsion to induce the transposition of the wheel component on the counterpart axle.^{3,5} Their studies prompted us to investigate the ferrocene-based redox system for the control of component transposition, given that

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(1) (a) Sauvage, J.-P.; Dietrich-Buchecker, C. *Molecular Catenanes, Rotaxanes and Knots*; Wiley-VCH: Weinheim, 1999. (b) Alteri, A.; Gatti, F. G.; Kay, E. R.; Leigh, D. A.; Martel, D.; Paolucci, F.; Slawin, A. M. Z.; Wong, J. K. Y. *J. Am. Chem. Soc.* **2003**, *125*, 8644 and references therein.

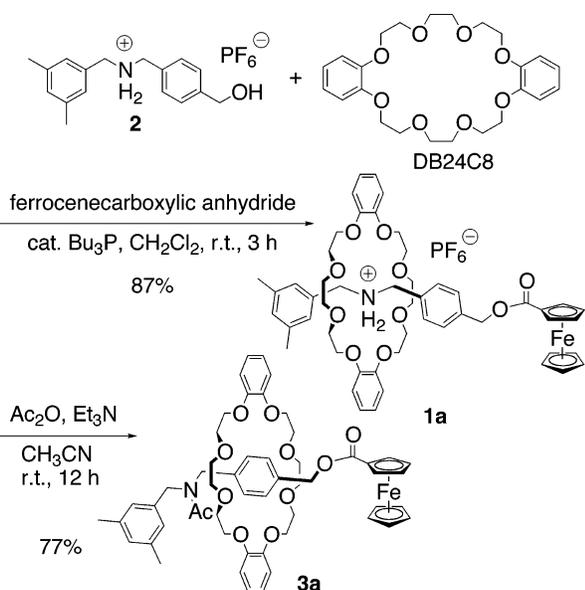
(2) (a) Stoddart, J. F. *Acc. Chem. Res.* **2001**, *34*, 410. (b) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3349. (c) Ashton, P. R.; Ballardini, R.; Balzani, V.; Credi, A.; Dress, K. R.; Ishow, E.; Kleverlaan, C. J.; Kocian, O.; Preece, J. A.; Spencer, N.; Stoddart, J. F.; Venturi, M.; Wenger, S. *Chem. Eur. J.* **2000**, *6*, 3558. Very recently, a supramolecular machine based upon the secondary ammonium ion/crown ether interaction was shown to be driven by the redox properties of a ferrocene unit in a system similar to that reported here; see: Horie, M.; Suzuki, Y.; Osakada, K. *J. Am. Chem. Soc.* **2004**, *126*, 3684.

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Scheme 1



reversible redox systems between ferrocene and ferrocenium cation are well-documented and that the ferrocene group can be a bulky end-cap group.⁶ Therefore, we have designed a novel ferrocene-containing rotaxane (**1**) with a crown ether wheel as an electron-rich component that may interact with the ferrocenium cation.

Rotaxane **1a** was prepared as shown in Scheme 1.⁷ The secondary ammonium salt **2** with a hydroxy group at the terminus was treated with ferrocenecarboxylic anhydride and a catalytic amount of tributylphosphine in the presence of dibenzo-24-crown-8 (DB24C8) to afford **1a** in 87% yield.⁸ The successful preparation of **1a** indicates that the ferrocene moiety is bulky enough to prevent unthreading of DB24C8. The X-ray crystallographic structure of **1a** as a benzene adduct clearly confirmed the rotaxane structure of **1a** (Supporting Information). Because there is a strong intercomponent hydrogen-bonding interaction between the DB24C8 component and the ammonium group in this type of rotaxanes, the transposition of the crown ether component on the axle was not expected. Therefore, **1a** was treated with excess triethylamine and acetic anhydride to convert it to the corresponding nonionic rotaxane **3a**,⁹ in which both components are free from hydrogen-bonding interaction. The X-ray crystallographic structure of **3a** reveals that the weak

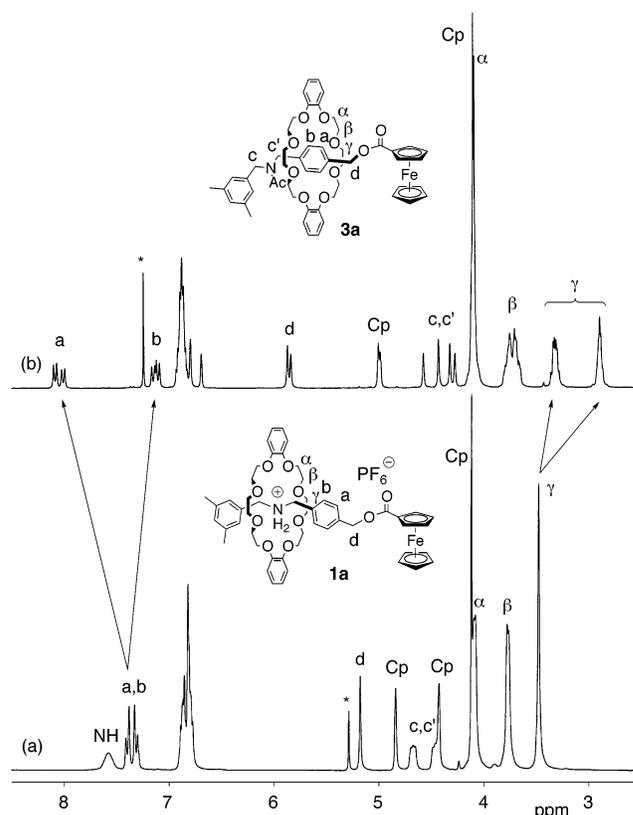


Figure 1. Partial ¹H NMR spectra of (a) **1a** (270 MHz, CDCl₃) and (b) **3a** (270 MHz, CDCl₃). Asterisk (*) denotes the residual CHCl₃ or CH₂Cl₂.

intercomponent interaction became working after the erasure of the strong hydrogen-bonding interaction (Supporting Information). The crown ether component was placed around the *p*-phenylene group, and there was CH/ π interaction between the γ -methylene groups of the DB24C8 component and the *p*-phenylene group.⁹ The ¹H NMR spectrum of **3a** is shown in Figure 1. The considerable downfield shift of the *p*-phenylene group and the split of the γ -methylene groups in the DB24C8 component clearly indicate the presence of CH/ π interaction even in the solution state. Because the CH/ π interaction is rather weak, the DB24C8 component is probably loosely bound on the *p*-phenylene group.

Cyclic voltammetry analyses of **1a** and related compounds were performed in acetonitrile to determine their formal redox potentials ($E_{1/2}$, vs Ag/AgCl). Reversible voltammograms corresponding to the ferrocene moiety were observed for each ferrocene derivative. The results are summarized in Table 1. Rotaxane **1a** showed a $E_{1/2}$ slightly higher than that of benzyl ferrocenecarboxylate and model compound **4** because of the cationic character of **1a**. Because the hydrogen-bonding interaction between the DB24C8 component and the ammonium group prevented the access of the wheel component to the ferrocene moiety of **1a**, the rotaxane structure hardly affected the $E_{1/2}$ of the ferrocene moiety. On the other hand, nonionic rotaxane **3a** showed a

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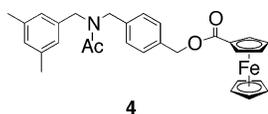
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Table 1. Redox Potentials of Ferrocene-Containing Compounds

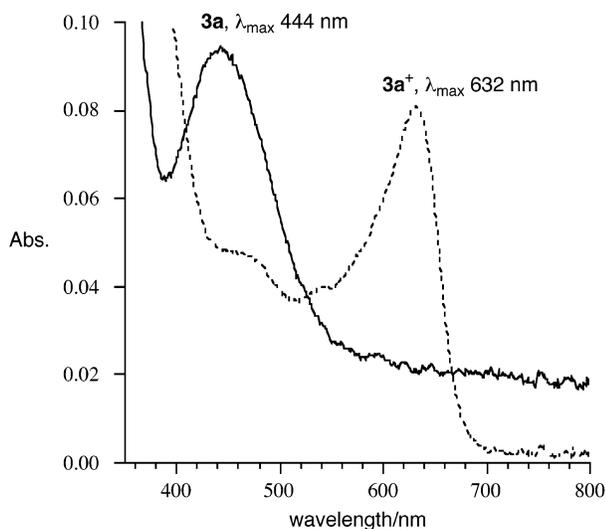
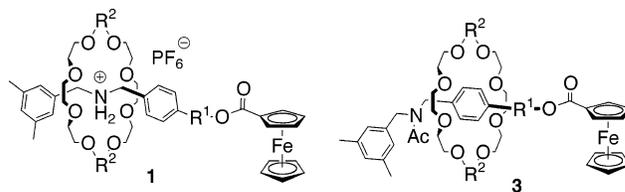
ferrocene derivative	$E_{1/2}^a$ (mV)
benzyl ferrocenecarboxylate	331
4 ^b	335
4 + DB24C8 ^{b,c}	335
1a	353
3a	271

^a Versus Ag/Ag⁺ with glassy carbon electrode at 298 K in 0.1 mol/L tetrabutylammonium perchlorate in acetonitrile (0.5 mmol/L). ^b With 0.1 mol/L tetraethylammonium perchlorate in acetonitrile (5 mmol/L). ^c One equivalent of DB24C8 was added to the solution of **4**.



$E_{1/2}$ ca. 80 mV lower than that of **1a**. The DB24C8 component in **3a** obviously stabilized the oxidized state to reduce its $E_{1/2}$. Because the $E_{1/2}$ of **4** did not change by the addition of DB24C8, it was concluded that the stabilization was induced by the very weak crown ether-ferrocenium cation interaction that occurs when the approach of the crown ether component to the ferrocene moiety is enhanced by the rotaxane structure and feeble intercomponent interaction.

To demonstrate the interaction between the wheel component and the ferrocene group, the electronic spectra of **3a**, **4**, and their oxidized states were measured. One-electron oxidation was chemically carried out with silver tetrafluoroborate in ether under an argon atmosphere. Figure 2 shows the electronic spectra of **3a** and **3a**⁺. The absorption of **3a**

**Figure 2.** Electronic spectra of **3a** (solid line) and **3a**⁺ (dashed line) in CH₂Cl₂ (5.4×10^{-4} mol/L) at room temperature. Although the electronic spectrum of **4** is identical to that of **3a** in the visible region, λ_{\max} of the ferrocenium cation **4**⁺ was observed at 629 nm.**Table 2.** Redox Potentials of Ferrocene Derivatives with Rotaxane Structure

R ¹	R ²	R ¹	R ²
a -CH ₂ -		c -O-(CH ₂) ₂ -	
b -CH ₂ -		d -O-(CH ₂) ₁₂ -	

ammonium rotaxane	$E_{1/2}^a$ (mV)	<i>N</i> -acylated rotaxane	$E_{1/2}^a$ (mV)	$\Delta E_{1/2}$ (mV)
1a	353	3a	271	82
1b	347	3b	267	80
1c	355	3c	291	64
1d	341	3d	297	44

^a Versus Ag/Ag⁺ with glassy carbon electrode at 298 K in 0.1 mol/L tetrabutylammonium perchlorate in acetonitrile (0.5 mmol/L).

at 444 nm corresponding to the ferrocene moiety disappeared by oxidation, while the absorption at 632 nm, which was assigned to the ferrocenium cation moiety,¹⁰ appeared. The reversible redox behavior of **3a** was easily confirmed: the electronic spectrum of the solution of **3a**⁺ readily returned to that of **3a** by exposure to air or water. Although the electronic spectrum of **4** was identical to that of **3a** in the visible region, λ_{\max} of the ferrocenium cation of **4**⁺ was observed at 629 nm. The small but nonetheless significant red shift of the ferrocenium cation of **3a**⁺ as compared to **4**⁺ indicates the presence of attractive interaction between the crown ether and the ferrocenium cation. The ferrocenium cation was obviously stabilized by this interaction. Because there is no perturbation in the reduction state, it can be deduced that the ferrocene group attracted the wheel component by the interaction that emerged during the one-electron oxidation.

What part of the wheel component contributes to the reduction of $E_{1/2}$? Does the wheel component really move on the axle? To answer these questions, some ferrocene derivatives with rotaxane structures were prepared, and their $E_{1/2}$ values were measured. The results are summarized in Table 2. Rotaxanes **1b** and **3b** with dicyclohexano-24-crown-8 as wheel component were prepared to examine the effect of the electron-rich benzene rings of DB24C8. Since the $E_{1/2}$ of **3b** was 80 mV lower than that of **1b**, as also observed for **1a** and **3a**, the ferrocenium cation interacted with the ether oxygen but not with the benzene ring. Further, rotaxanes **1c**, **1d**, **3c**, and **3d** having axles with longer spacers were prepared to confirm the transposition of the wheel component on the axle. The ¹H NMR spectra of **1d** and **3d** are shown in Figure 3. The presence of CH/ π interaction

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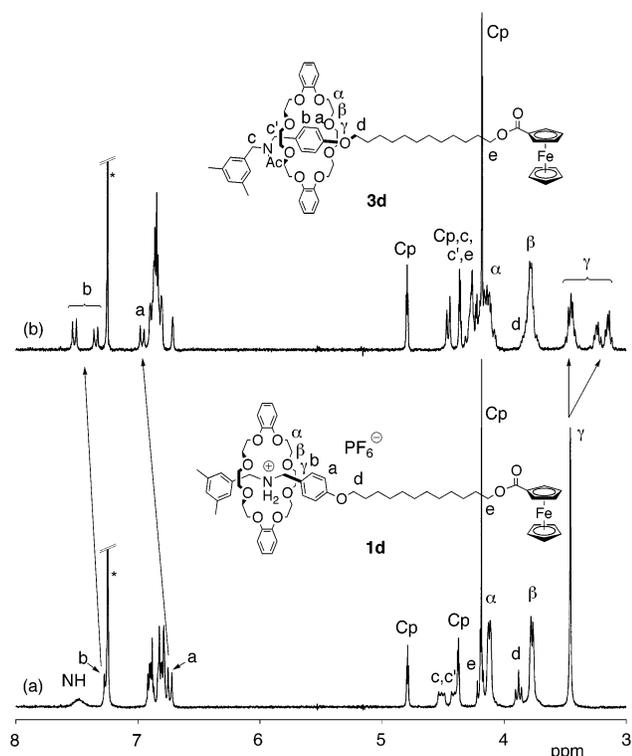


Figure 3. Partial ^1H NMR spectra of (a) **1d** (270 MHz, CDCl_3) and (b) **3d** (270 MHz, CDCl_3). Asterisk (*) denotes the residual CHCl_3 .

between the wheel and the axle in **3d** is evident from the downfield shift of the *p*-phenylene group and the split of the γ -methylene groups in the DB24C8 component, indicating that the DB24C8 wheel is located at the *p*-phenylene group. The $E_{1/2}$ of **3c** was ca. 65 mV lower than that of **1c**, and the $E_{1/2}$ of **3d** was ca. 45 mV lower than that of **1d**. A considerable decrease of $E_{1/2}$ was observed even in **3d**, which has a dodecamethylene spacer between the *p*-phenylene and

ferrocene groups. The large $\Delta E_{1/2}$ cannot be explained without the transposition of the wheel component on the axle that leads it to interact with ferrocenium cation because the *p*-phenylene moiety acts as the station of the wheel. The rather small $\Delta E_{1/2}$ for **3c** and **3d** presumably came from the difference in structure of the *p*-phenylene groups, dialkylbenzene for **3a** and **3b** and alkylalkoxybenzene for **3c** and **3d**.

In the oxidized state, an attractive interaction between the DB24C8 component and the ferrocenium cation moiety is expected to develop. At present, it is not clear if the interaction is a simple ion–dipole interaction or the electrostatic interaction that accompanies electron donation from crown ether oxygen to the ferrocenium cation. When the wheel component was pinned up on the axle by strong interaction such as an intramolecular hydrogen-bonding interaction with the ammonium group in the case of **1a**, weak crown ether–ferrocenium cation interaction did not induce the transposition. However, when the wheel component was labile on the axle, the transposition occurred even by weak attractive intercomponent interaction. As a consequence, the present work demonstrates that rotaxanes with a weak intercomponent interaction such as **3** constitute an excellent scaffold for the construction of a sensitive molecular device.

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Supporting Information Available: Experimental procedures, spectral data, X-ray crystallographic analyses of **1a** and **3a**, cyclic voltammogram of **1**, **3**, and **4**, and electronic spectra of **4** and **4⁺**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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