

π -다리로 연결된 디-페로센의 전기화학적 특성

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Electrochemical Properties of Di-ferrocenes Linked by π -Bridge

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Ferrocene ($C_{10}H_{10}Fe$: bis(η^5 -cyclopentadienyl)iron: **Fc**) is known as a good electron donor molecule showing one reversible redox cycle.¹ This is one of the reasons why ferrocene is widely used as the main component of electronic, optical and biologically-active materials. Especially, multi-ferrocenyl compounds are frequently studied in the research field of intra-molecular electron-transfer processes. Di-ferrocene compounds linked by a polyethylene moiety ($Fc(CH=CH)_mFc$: **dFcE_m**) are the typical system studied by many researchers.² The number and the geometry of ethylene linkage are the critical factors which control the efficiency of electron-transfer in this system. In this study, we prepared and spectroscopically characterized a di-ferrocenyl compound in which two ferrocenyl groups are linked by an enone moiety ($Fc-C(O)CH=CH-Fc$: **Fc-Fc**). The electron-transfer behavior of this compound was investigated electrochemically and compared with that of 1,2-diferrocenylethylene (**dFcE**). This is a part of series of studies of ferrocenyl chalcones.³

EXPERIMENTAL

General Methods

Acetylferrocene (**ActFc**), ferrocenecarboxaldehyde

(**FcAld**) and HPLC-grade organic solvents were commercially purchased (Aldrich) and used as received.

The FT-IR spectra were recorded on a MIDAC FT-IR spectrometer within the range of 4000 ~ 400 cm^{-1} . The UV-Vis spectra were measured on an HP 8452A diode array spectrophotometer. The 1H NMR spectra were obtained on a Bruker Avance 500 using $CDCl_3$ as a solvent. The mass spectra were obtained on a JMS-700 Mstation by fast atom bombardment (FAB). The electrochemical studies were carried out at room temperature with a CHI 620A Electrochemical Analyzer (CHI Instrument Inc.) under the following conditions: 1.0 mM samples in MeCN containing 0.1 M $n-Bu_4N^+BF_4^-$ using a Pt-button ($r = 1$ mm) working electrode, Ag/AgCl reference electrode and Pt-wire ($\phi = 1$ mm) counter electrode at a scan rate of 50 $mV s^{-1}$. The potentials were referenced to that of Fc/Fc^+ ($E_{1/2} = +0.464$ V vs. Ag/AgCl).

Preparation of Fc-Fc

A mixture of **ActFc** (1 mmol, 228 mg), **FcAld** (1 mmol, 214 mg) and NaOH (5 mmol, 200 mg) was ground with an agate mortar and a pestle. This mixture was allowed to stand in a water bath (85 $^{\circ}C$) for 30 min. The final product was extracted

with CH_2Cl_2 and the solution was dried with MgSO_4 . After filtration, the solvent was removed at reduced pressure and the final product was separated from the residue by column chromatography (SiO_2 , CH_2Cl_2). Yield: 63% (267 mg). Wine-red colored powder. Mp: 208~209°C. Elemental analysis: Cal. (Obs.) for $\text{C}_{23}\text{H}_{20}\text{Fe}_2\text{O}$: C, 65.14 (65.28); H, 4.75 (4.75). FAB-MS(m/z , %): 424.1 (M^+ , 100), 359.1 ($[M-\text{C}_5\text{H}_5]^+$, 17), 307.3 ($[M-\text{Fe}(\text{C}_5\text{H}_5)+4\text{H}]^+$, 10). FT-IR (KBr, cm^{-1}): 3089 (Cp C-H), 1664, 1641 (C=O), 1574, 1448, 1290, 1248 (C=C), 826 (Cp C-H), 674 (C-H), 512, 481 (Cp-Fe). ^1H NMR (500 MHz, CDCl_3 , ppm): 7.71 (1H, CH, d, $J = 15.4$ Hz), 6.75 (1H, CH, d, $J = 15.4$ Hz), 4.88 (2H, C_5H_4 , t, $J = 1.9$ Hz), 4.60 (2H, C_5H_4 , t, $J = 1.8$ Hz), 4.56 (2H, C_5H_4 , t, $J = 1.9$ Hz), 4.47 (2H, C_5H_4 , t, $J = 1.8$ Hz), 4.20 (5H, C_5H_5 , s), 4.19 (5H, C_5H_5 , s). UV-vis (nm): 314, 382, 492 (MeCN); 250, 316, 386, 500 (CHCl_3); 320, 386, 510 (EtOH); 322, 394, 488, 512 (MeOH).

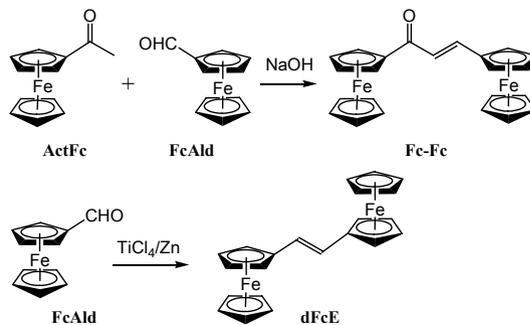
Preparation of dFcE

1,2-Diferrocenylethylene (dFcE) was synthesized by the McMurry coupling method⁴ using **FcAld** and a low-valence titanium compound prepared in a TiCl_4 and Zn powder mixture, as described in a previous report.⁵ This compound was characterized spectroscopically and confirmed to be identical with that prepared before.⁵

RESULTS AND DISCUSSION

Synthesis and Characterization

Fc-Fc was synthesized by solvent-free aldol condensation using **ActFc** and **FcAld** with NaOH as a base catalyst. The purification of **Fc-Fc** was easily achieved by column chromatography using CH_2Cl_2 as the eluent, giving rise to a moderate yield (63%). In this reaction, using stoichiometric amounts of the reactants is important to reduce the amount of side products. For example, the product (**Fc-Fc**) can react further with an excess of the acetyl reactant to produce 1,5-pentadione derivatives via Michael addition reaction.⁶ The purified product was characterized by elemental analysis to-



Scheme 1. Syntheses of **Fc-Fc** and **dFcE**.

gether with the FAB-mass, FT-IR, ^1H -NMR and UV-Vis spectroscopic methods. The FAB-MS data show the mother peak (M^+) at 424.1 for **Fc-Fc** with 100% intensity and the successive loss of the Cp and FeCp moieties at $m/z = 359.1$ and 307.3, respectively. The $\nu(\text{C}=\text{O})$ of **ActFc** was observed at 1663 cm^{-1} , which shifts to a lower frequency (1641 cm^{-1}) for **Fc-Fc**. This is due to the delocalization of the π -electrons on the carbonyl and ethylene moieties in the enon linkage. The NMR spectra measured at room temperature show two doublets at 7.71 ppm ($J = 15.4$ Hz) and 6.75 ppm ($J = 15.4$ Hz) together with other peaks from the ferrocenyl moieties, indicating that the ethylene moiety in the enon linkage is in the *trans*-conformation.⁷

Statistically, four isomers (two *s-cis* and two *s-trans* conformational isomers) are possible as the reaction product, among which the minimized energy structures of **Fc-Fc** with the *s-cis* conformation⁸ are shown in Fig. 1. This may be one of the reasons why the **Fc-Fc** compound was precipitated as a reddish-brown powder, rather than being grown as single crystals, when it was recrystallized in many appropriate solvent pairs such as $\text{CH}_2\text{Cl}_2/n\text{-Hx}$, $\text{CH}_2\text{Cl}_2/\text{ether}$, $\text{CH}_2\text{Cl}_2/\text{EtOH}$, etc. Furthermore, the techniques of electrochemical



Fig. 1. Energy-minimized structures of **Fc-Fc** with *s-cis* conformation calculated by using DMol3 method.

oxidation using an $n\text{-Bu}_4\text{N}^+\text{PF}_6^-$ electrolyte and chemical oxidation with I_2 , TCNQ or F_4TCNQ were not effective to obtain a single crystal of the **Fc-Fc** charge-transfer salt, for the same reason.

Electrochemical Study

The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) results for **Fc-Fc** and **dFcE** are shown in Fig. 2 and 3, respectively. The electrochemical parameters are listed and compared with those of the reactants in Table 1. Both complexes show two reversible and reproducible cycles on a repeated scan between 0~1.3 V, irrespective of the working electrodes (Pt, Au or glassy carbon), corresponding to the two redox processes of the ferrocenyl moieties ($\text{Fc}^+ \leftrightarrow \text{Fc}$). The first

half-wave potential of **dFcE** ($E_{1/2}^1 = 0.404$ V) is smaller than that of **Fc-Fc** ($E_{1/2}^1 = 0.581$ V) and even smaller than those of **ActFc** ($E_{1/2}^1 = 0.712$ V) and **FcAld** ($E_{1/2}^1 = 0.752$ V). Based on the results of the MO calculation⁹ on the simplified compounds (Fig. 4), in which the ferrocenyl moieties were replaced with cyclopentadienyl rings, the electrons in the HOMO are mainly located on the Cp-C(O)CH=CH- part of Cp-C(O)CH=CH-Cp , while they are on the Cp part of Cp-CH=CH-Cp . It can be inferred from this result that the $E_{1/2}^1$ value of **dFcE** is smaller than that of **Fc-Fc**. On the contrary, the difference between $E_{1/2}^1$ and $E_{1/2}^2$ for **dFcE** ($\Delta E^o = 173$ mV) is slightly larger than that for **Fc-Fc** (165 mV). As the ΔE^o value is closely related to the measure of repulsive energy between

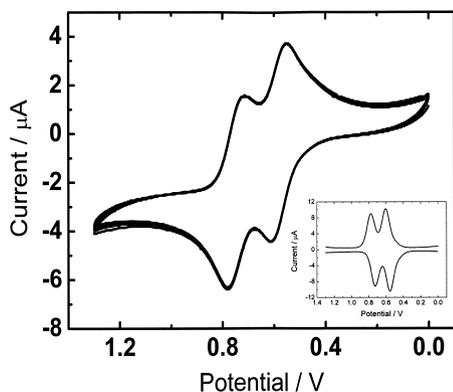


Fig. 2. The cyclic voltammogram (CV) scanned 10 times repeatedly between 0 V and +1.3 V and corresponding differential pulse voltammograms (DPV; inset) of the **Fc-Fc** compound (vs. Ag/AgCl).

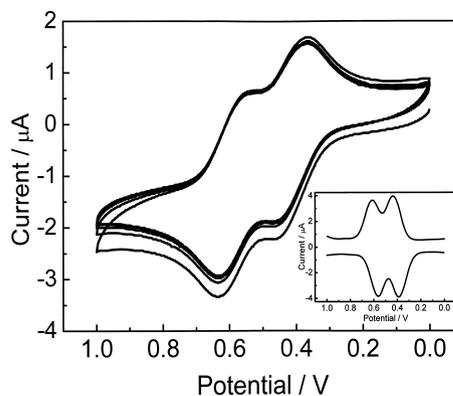


Fig. 3. The cyclic voltammogram (CV) scanned 5 times repeatedly between 0 V and +1.0 V and corresponding differential pulse voltammograms (DPV; inset) of the **dFcE** compound (vs. Ag/AgCl).

Table 1. The cyclic voltammetry parameters for **Fc-Fc**, **dFcE** and their reactants.^a

Compound	Anodic		Cathodic		$E_{1/2}^b$	ΔE^o^c
	E_{pa}^1	E_{pa}^2	E_{pc}^1	E_{pc}^2		
ActFc	0.745		0.679		0.712	
FcAld	0.787		0.717		0.752	
Fc-Fc	0.611			0.551	0.581	0.165
dFcE	0.456	0.781	0.711		0.746	0.173
		0.621	0.532		0.577	

^aThe samples are dissolved in MeCN containing 0.1 M $n\text{-Bu}_4\text{N}^+\text{BF}_4^-$ electrolyte, and the potentials (in volt) are referenced to Fc/Fc^+ ($E_{1/2} = +0.464$ V vs. Ag/AgCl). ^b $E_{1/2} = (E_{pa} + E_{pc})/2$. ^c $\Delta E^o = E_{1/2}^2 - E_{1/2}^1$.

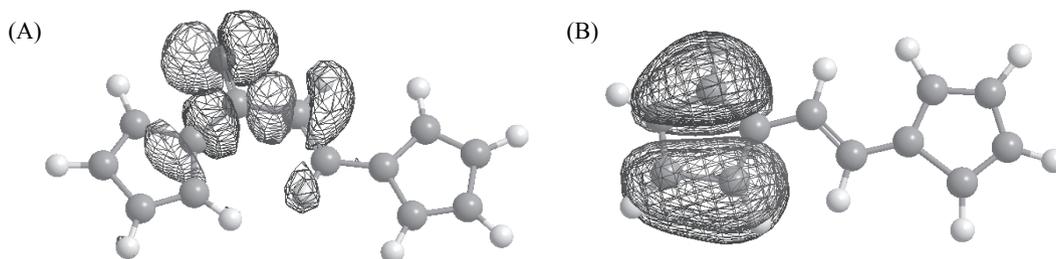


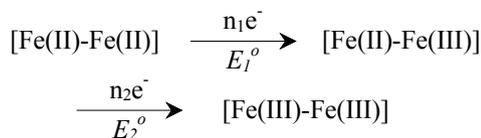
Fig. 4. HOMO of (A) Cp-C(O)CH=CH-Cp ($N = 34$, -11.920 eV) and (B) Cp-CH=CH-Cp ($N = 29$, -12.408 eV). These are the model compounds in which the ferrocenyl moieties in **Fc-Fc** and **dFcE** are replaced with cyclopentadienyl rings for the simplification of the calculation.

Table 2. The comparison of ΔE° (mV) and K_c values of the diferrocenyl compounds.

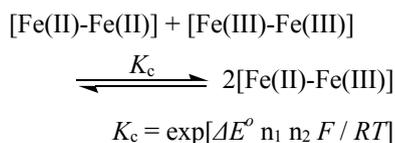
Compound	No. C(sp^2)	ΔE° (mV)	Solvent	K_c^a	ref
dFcE Fc(CH=CH)Fc	2	173	CH ₃ CN	841	This work
	2	170	CH ₂ Cl ₂	748	2b
Fc-Fc FcCO(CH=CH)Fc	3	165	CH ₃ CN	616	This work
dFcE₂ Fc(CH=CH) ₂ Fc	4	129	CH ₂ Cl ₂	151	2b
dFcE₃ Fc(CH=CH) ₃ Fc	6	100	CH ₂ Cl ₂	49	2b

$$^a \Delta E^\circ = (RT/F) \ln K_c = (25.69) \ln K_c \text{ at } 298\text{K.}$$

the two charged centers (that is, the Coulomb repulsion energy), it can be expressed by the disproportionation constant (K_c) of the successive redox processes of the di-ferrocenyl system, as described below:¹⁰



At equilibrium,



where $n_1 = n_2 = 1$, $\Delta E^\circ = E_2^\circ - E_1^\circ$ and $K_c = \exp[\Delta E^\circ / 25.69]$ at 298K. This gives $K_c = \exp(165/25.69) \approx 616$ for **Fc-Fc** and $K_c = \exp(173/25.69) \approx 841$ for **dFcE**. These K_c values are compared with those of **dFcE_m** ($m = 1, 2$ and 3)^{2b} in Table 2. The results clearly show that the number of sp^2 carbon atoms

between the redox active ferrocenyl centers of the **dFcE_m** system is inversely proportional to the K_c value. It is noteworthy that the K_c value for **Fc-Fc** (No. C(sp^2) = 3) is closer to that of **dFcE** (No. C(sp^2) = 2), than that of **dFcE₂** (No. C(sp^2) = 4), even though the enone bridge contains an additional ketone moiety. In other words, we can surmise that the additional antibonding π -orbital on the ketone moiety does not significantly inhibit the intramolecular electron-transfer process. Moreover, it should also be pointed out that the solvents used in the CV measurement (CH₃CN and CH₂Cl₂) do not affect the results seriously enough to cause a deviation from this trend.

In conclusion, it is demonstrated herein that the enone is as effective a bridging group as the ethylene moiety, in terms of its accommodation of electronic communication between the two redox active ferrocenyl groups.

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