

## Electronic Supplementary Information

# Biferrocenium salt with magnetite-like mixed-valence iron: coexistence of Fe<sup>3+</sup> and Fe<sup>2.5+</sup> in the crystal

Tomoyuki Mochida,<sup>\*a,b</sup> Eri Nagabuchi,<sup>b</sup> Masashi Takahashi,<sup>b</sup> and Hatsumi Mori<sup>c</sup>

<sup>a</sup>*Department of Chemistry, Graduate School of Science, Kobe University, Rokkodai, Nada, Hyogo 657-8501, Japan*

*E-mail: tmochida@platinum.kobe-u.ac.jp; Fax: +81 78 803 5679; Tel: +81 78 803 5679*

<sup>b</sup>*Department of Chemistry, Faculty of Science, Toho University, Miyama, Funabashi, Chiba 274-8510, Japan*

<sup>c</sup>*Institute for Solid State Physics, The University of Tokyo, Kashiwanoha, Kashiwa, Chiba 277-8581, Japan*

### 1. General methods

<sup>1</sup>H NMR spectra were measured on a JEOL ECP-400 Fourier-transform spectrometer. Infrared spectra were recorded in the 4000–400 cm<sup>-1</sup> range on a SHIMADZU Prestige-21 FTIR-8400S spectrometer attached to an AIM-8800 microscope. Cyclic voltammograms were recorded with an ALS/chi electrochemical-analyzer model 600A at a scan rate of 0.1 Vs<sup>-1</sup>. Dichloromethane solutions (0.1 mol dm<sup>-3</sup>) containing 0.1 mol dm<sup>-3</sup> nBu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte were used for the measurements with a platinum disk working electrode. The redox potentials were referenced to the Fe(Cp)<sub>2</sub>/Fc(Cp)<sub>2</sub><sup>+</sup> couple. The data for the temperature dependence of the magnetic susceptibilities were collected from 300 to 2 K using a Quantum Design MPMS-XL SQUID magnetometer under a magnetic field of 5000 G. The core diamagnetic components were corrected by a calculation using Pascal's constants. <sup>57</sup>Fe Mössbauer spectra were measured on instruments (MDU-1200, DFG-1200, MVT-1000; Wissel GmbH) using <sup>57</sup>Co/Rh as the source. Isomer shifts are measured with respect to α-Fe foil at 296 K.

### 2. Preparation of 1',1'''-bis(isopropylthio)-1,1''-biferrocene

*n*-Butyl lithium (2.15 mL, 3.41 mmol; hexane solution) was added dropwise over 10 min to a tetrahydrofuran (15 mL) solution of 1,1'-dibromobiferrocene (0.90 g, 1.71 mmol) cooled to -78 °C under a nitrogen atmosphere. After stirring for 1 h at -78 °C, the solution was allowed to warm to room temperature. Diisopropyl disulfide (0.82 mL, 5.12 mmol) dissolved in THF (15 mL) was added to this solution, and the resulting mixture was refluxed for two days. After cooling to room temperature, water was added and the reaction mixture was filtered through Celite. The solution

was extracted with benzene, washed three times with water; the organic layer was then dried over magnesium sulfate. The solvent was removed by evaporation, and the resultant solid was recrystallized from hexane to generate orange crystals (yield 66%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.13$  (d, 12H,  $J = 6.96\text{Hz}$ ), 2.80 (m, 2H), 4.01 (t, 4H,  $J = 1.84\text{ Hz}$ ), 4.08 (t, 4H,  $J = 1.84\text{ Hz}$ ), 4.22 (t, 4H,  $J = 1.84\text{ Hz}$ ), 4.40 (t, 4H,  $J = 1.84\text{ Hz}$ ).

### 3. X-Ray crystallography

Single crystals of **1** were prepared as described in the text. Single crystals of **2** were obtained as dark-purple plates by vapor diffusion of hexane into a 1,2-dichloroethane solution of 1',1'''-bis(isopropylthio)-1,1''-biferrocene and  $[\text{Fe}(\text{C}_5\text{H}_5)_2][\text{Pt}(\text{mnt})_2]$ . Because of the very low yield of **2**, it was only characterized by a structural determination. X-Ray data were collected on a Bruker SMART APEX CCD diffractometer using  $\text{Mo}(\text{K}\alpha)$  radiation ( $\lambda = 0.71069\text{ \AA}$ ) at 173 K. The structures determined at 295 K were unchanged from those at 173 K. The crystal data, data collection parameters, and analysis statistics are listed in Table S1. The structures were solved using direct methods (SHELXS-97<sup>S1</sup>) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at idealized positions and allowed to ride on the relevant heavier atoms. Empirical absorption corrections were applied. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication. The molecular structures and packing diagrams were drawn using ORTEP-3 for Windows<sup>S2</sup> and Mercury 3.1<sup>S3</sup>, respectively.

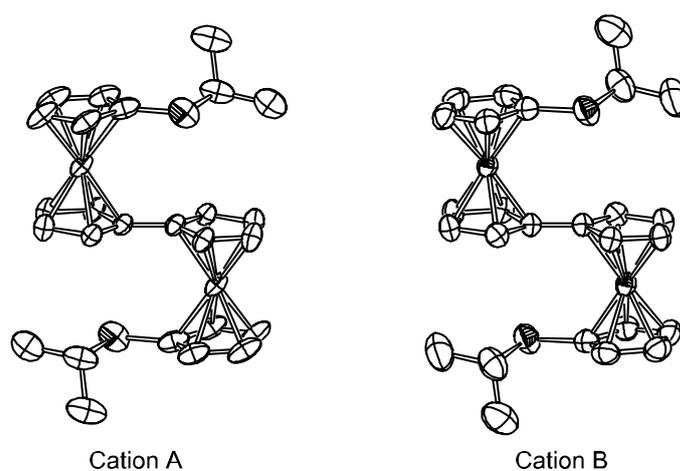
### References

- S1 G. M. Sheldrick, *Acta Crystallogr.* **D64**, 112–122 (2008).  
S2 L. J. Farrugia, *J. Appl. Cryst.* **32**, 837–838 (1999).  
S3 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Cryst.*, **41**, 466–470 (2008).

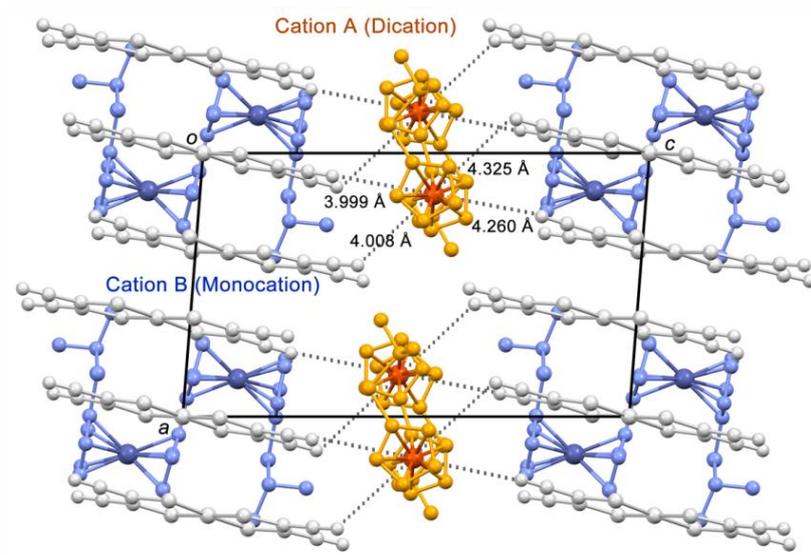
**Table S1.** Crystallographic parameters for **1** and **2**.

	<b>1</b>	<b>2</b>
Formula	C <sub>76</sub> H <sub>60</sub> N <sub>12</sub> Fe <sub>4</sub> Ni <sub>3</sub> S <sub>16</sub>	C <sub>76</sub> H <sub>60</sub> Fe <sub>4</sub> N <sub>12</sub> Pt <sub>3</sub> S <sub>16</sub>
Formula weight	2053.85	2462.99
<i>T</i> / K	173	173
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> / Å	10.4988(14)	11.084(2)
<i>b</i> / Å	12.0318(16)	12.270(3)
<i>c</i> / Å	17.227(2)	17.696(3)
$\alpha$ / °	95.436(3)	100.459(4)
$\beta$ / °	92.971(3)	99.486(4)
$\gamma$ / °	103.641(3)	112.620(4)
<i>V</i> / Å <sup>3</sup>	2099.0(5)	2110.4(7)
<i>Z</i>	1	1
<i>F</i> (000)	1044	1194
Reflections collected	13596	13230
Independent reflections	8525	8560
<i>d</i> <sub>calcd</sub> / g cm <sup>-3</sup>	1.625	1.938
$\mu$ / cm <sup>-1</sup>	17.78	60.66
Refl./Parameter ratio	16.84	16.92
<i>R</i> <sub>1</sub> <sup><i>a</i></sup> , <i>wR</i> <sub>2</sub> <sup><i>b</i></sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0536, 0.1317	0.0625, 0.1284
<i>R</i> <sub>1</sub> <sup><i>a</i></sup> , <i>wR</i> <sub>2</sub> <sup><i>b</i></sup> (all data)	0.0827, 0.1454	0.1349, 0.1562
Goodness of fit	1.020	0.935
Completeness to $\theta = 26.37^\circ$ (%)	99.3	99.3
Parameters	506	506
Largest diff. peak and hole (eÅ <sup>-3</sup> )	1.049 and -0.719	2.768 and -1.637

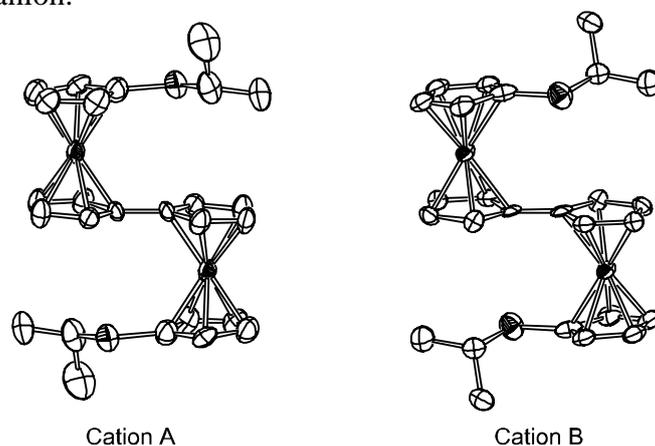
<sup>*a*</sup>  $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$ . <sup>*b*</sup>  $R_w = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}$ .



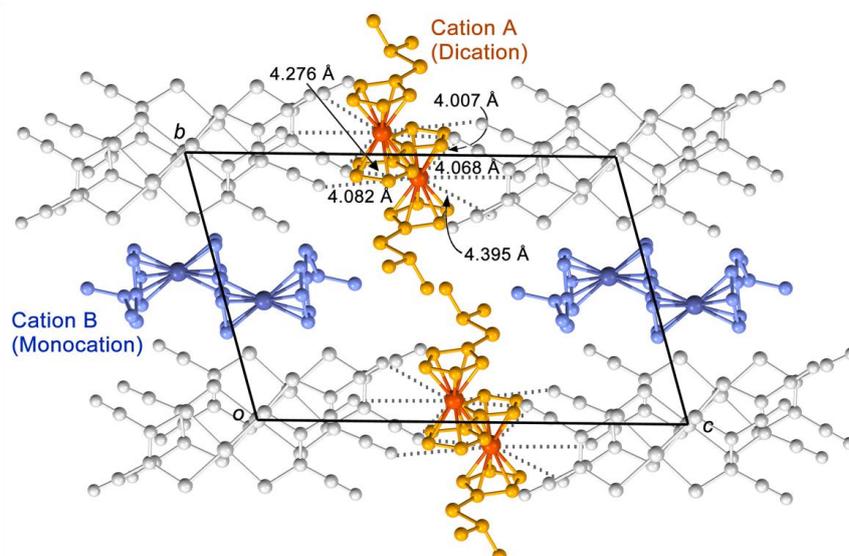
**Fig. S1** ORTEP drawing of the crystallographically independent cations in **1**. Hydrogen atoms are omitted for clarity.



**Fig. S2** Packing diagram of **1** along the *b*-axis. Dotted lines indicate close Fe...NC distances between the cation and anion.



**Fig. S3** ORTEP drawing of the crystallographically independent cations in **2**. Hydrogen atoms are omitted for clarity.



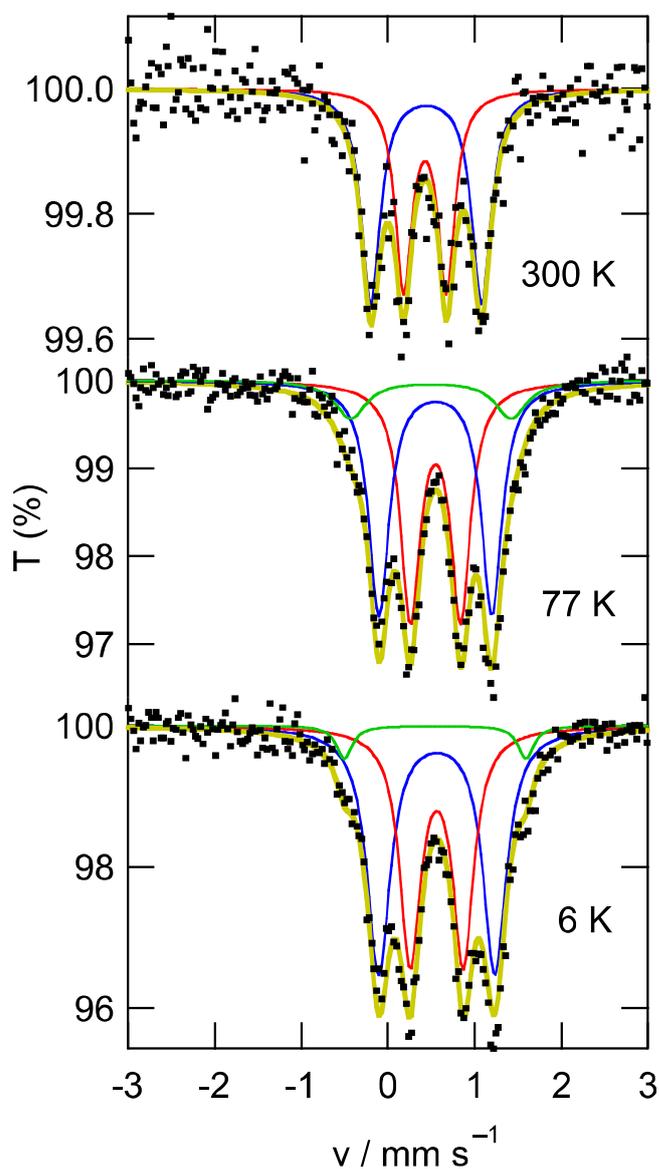
**Fig. S4** Packing diagram of **2** along the *b*-axis. Dotted lines indicate close Fe...NC distances between the cation and anion.

### 3. Mössbauer spectra

**Table S2.** Temperature dependence of the Mössbauer parameters for **1**.

$T$ (K)	$\delta^a$ (mm/s)	$\Delta E_Q$ (mm/s)	$\Gamma^c$ (mm/s)
300	0.43	0.49	0.24
	0.44	1.28	0.26
77	0.55	0.58	0.27
	0.55	1.30	0.29
6	0.56	0.61	0.29
	0.56	1.34	0.33

<sup>a</sup>Isomer shift referenced to iron-foil at room temperature. <sup>b</sup>Quadrupole-splitting. <sup>c</sup>Full width at half-height.



**Fig. S5** Temperature dependence of the Mössbauer spectra of **1**.