



Charge-transfer salts of methylferrocenes with DCNQI derivatives (DCNQI = *N,N'*-dicyano-1,4-benzoquinonediimine): Crystal structures and magnetic properties

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ABSTRACT

Organometallic charge-transfer salts composed of decamethyl-, octamethyl-, and dimethylferrocene with *N,N'*-dicyano-1,4-benzoquinonediimine (DCNQI) derivatives were prepared. $[\text{Fe}(\text{C}_5\text{Me}_5)_2][(\text{MeO})_2\text{DCNQI}]$ (**1**) and $[\text{Fe}(\text{C}_5\text{Me}_4\text{H})_2][\text{Me}_2\text{DCNQI}]$ (**2**) were 1:1 DA salts with mixed-stack structures, whereas $[\text{Fe}(\text{C}_5\text{Me}_4\text{H})_2][(\text{MeO})_2\text{DCNQI}]_2$ (**3**) and $[\text{Fe}(\text{C}_5\text{Me}_4\text{H})_2][\text{DCNQI}]_2$ (**4**) were 1:2 DA salts. **3** exhibited a segregated-stack structure, in which charge separation was observed in the acceptor column. **1** became a metamagnet below $T_N = 5.0$ K, whereas the other salts were paramagnets. Valence states and charge-transfer (CT) transitions in these complexes are discussed based on the neutral–ionic (NI) phase diagram.

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1. Introduction

Metallocene-based charge-transfer (CT) complexes have attracted special attention because of their magnetic properties [1]. In particular, decamethylferrocene ($[\text{Fe}(\text{Cp}^*)_2]$) has afforded a variety of CT complexes that are magnetically interesting [1,2]. Among them, the most well-studied example is $[\text{Fe}(\text{Cp}^*)_2][\text{TCNE}]$ (TCNE = tetracyanoethylene), which exhibits ferromagnetic ordering below 4.8 K [3]. To date, many ferrocene-based CT complexes have been synthesized, such as those with TCNQ (tetracyanoquinodimethane), metal-dithiolates, and other anions [1–4]. In our studies, ferrocene-based CT complexes have been investigated in terms of valence states and phase transitions [5]. We recently prepared neutral metallocene complexes with quinone derivatives [6,7] in search of neutral–ionic (NI) transitions in metallocene complexes. The NI transition is a transition from a high-temperature neutral state (D^0A^0) to a low-temperature ionic state (D^+A^-), characteristic of mixed-stack CT complexes that are located near the NI boundary [8]. We extended the NI phase diagram [7] and found that the NI boundary for ferrocene-based CT complexes is located where the difference between the redox

potentials of the donor and acceptor ($\Delta E_{\text{redox}} = E_D - E_A$) is 0.1 V. In the present study, we used donors of $[\text{Fe}(\text{Cp}^*)_2]$ and $[\text{Fe}(\text{C}_5\text{Me}_4\text{H})_2]$ (octamethylferrocene) and acceptors of DCNQI (*N,N'*-dicyano-1,4-benzoquinonediimine) derivatives to search for complexes that are close to this region.

Here, we report the syntheses, magnetic properties, and crystal structures of a series of ferrocene–DCNQI complexes: $[\text{Fe}(\text{Cp}^*)_2][(\text{MeO})_2\text{DCNQI}]$ (**1**), $[\text{Fe}(\text{C}_5\text{Me}_4\text{H})_2][\text{Me}_2\text{DCNQI}]$ (**2**), $[\text{Fe}(\text{C}_5\text{Me}_4\text{H})_2][(\text{MeO})_2\text{DCNQI}]_2$ (**3**), and $[\text{Fe}(\text{C}_5\text{Me}_4\text{H})_2][\text{DCNQI}]_2$ (**4**) (Fig. 1). These are ionic complexes with ΔE_{redox} values close to the NI boundary. Related materials include a mixed-stack complex of $[\text{Fe}(\text{Cp}^*)_2][\text{Me}_2\text{DCNQI}]$ (**1'**), which is a metamagnet below $T_N = 3.9$ K [9], and a few other DCNQI-based metallocenium salts [10]. **1** showed metamagnetic behavior at low temperatures, similar to **1'**, whereas other salts were paramagnets.

2. Results and discussion

2.1. Syntheses and valence states

1–3 were obtained as violet single crystals by recrystallization from acetonitrile or acetone, whereas **4** was obtained as microcrystals. **1** and **2** exhibited a 1:1 DA ratio, whereas **3** and **4** exhibited 1:2 DA ratios. They were ionic complexes consisting of ferrocenium

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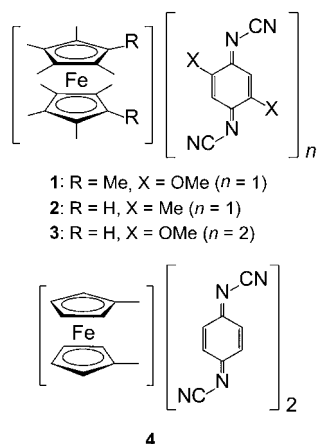


Fig. 1. Chemical formulas of 1–4.

monocations. The average Fe–C(Cp) bond distances in the donors in **1–3**, determined crystallographically (*vide infra*), were 2.096 Å, 2.100 Å, and 2.096 Å, respectively, comparable to those in $[\text{Fe}(\text{Cp}^*)_2]^+$ and $[\text{Fe}(\text{C}_5\text{Me}_4\text{H})_2]^+$ [11]. The degree of CT (ρ) on the acceptors was estimated using $\rho = A[c/(b + d)] + B$, similar to the case of TCNQ complexes [12]. In the equation, b , c , and d represent the bond lengths in the acceptors (Table 1 and Chart 1), and the values of $A = -47.91$ and $B = 22.60$ were tentatively determined based on the geometries of the neutral and anionic forms of Me_2DCNQI [9]. As shown in Table 1, ρ was estimated to be -1 for the acceptors in **1** and **2**, and those for two crystallographically independent acceptors (A1 and A2) in **3** were -1 and 0 , respectively.

The ρ values were also estimated from the $\text{C}\equiv\text{N}$ stretching frequencies of the acceptors in the infrared spectra (Fig. S1), and the result was consistent with the estimation from the bond lengths. In **1** and **2**, the $\text{C}\equiv\text{N}$ stretching vibration, observed at around 2176 cm^{-1} for neutral DCNQI molecules, shifted to lower energy by about 50 cm^{-1} , suggesting the value of $\rho \sim -1$. In **3**, two peaks corresponding to those of the neutral and monoanion species were observed at 2177 cm^{-1} and 2136 cm^{-1} , respectively. In **4**, the low energy shift was about 20 cm^{-1} , suggesting the value of $\rho \sim -0.5$, which is reasonable considering the 1:2 DA ratio.

To investigate CT absorption bands, UV–Vis–NIR spectra of **1–4** and **1'** were measured. As shown in Fig. 2, all the salts exhibited broad absorption bands assignable to CT transitions at around 650–750 nm. The shapes of the CT bands for the 1:1 salts **1**, **2**, and **1'** are almost the same, accompanying a small peak around 800 nm. The band shapes for the 1:2 salts **3** and **4** differed from these. In Fig. 3, the CT energies in these salts are plotted against ΔE_{redox} (Table 2). Theoretical correlations between ΔE_{redox} and $h\nu_{\text{CT}}$ for

Table 1
Selected bond lengths^a and the degree of charge-transfer (ρ) on the acceptors in **1–3** and reference compounds.

Compounds	a (Å)	b (Å)	c (Å)	d (Å)	$c/(b + d)$	ρ^b
$[\text{Fe}(\text{Cp}^*)_2][(\text{MeO})_2\text{DCNQI}]$ (1)	1.365	1.419	1.352	1.321	0.494	-1.0
$[\text{Fe}(\text{C}_5\text{Me}_4\text{H})_2][\text{Me}_2\text{DCNQI}]$ (2)	1.368	1.429	1.354	1.325	0.492	-1.0
$[\text{Fe}(\text{C}_5\text{Me}_4\text{H})_2]$ [($\text{MeO})_2\text{DCNQI}]_2$ (3)	(A1) 1.372 (A2) 1.350	1.416 1.436	1.352 1.306	1.320 1.339	0.494 0.471	-1.1 0.0
$\text{Me}_2\text{DCNQI}^{\text{c,d}}$	1.341	1.447	1.319	1.350	0.472	0.0
$[\text{Fe}(\text{Cp}^*)_2][\text{Me}_2\text{DCNQI}]$ (1') ^e	1.366	1.425	1.352	1.320	0.493	-1.0

^a Definition of a – d are shown in Chart 1.

^b $\rho = A[c/(b + d)] + B$ with $A = -47.91$ and $B = 22.60$.

^c Reference compounds.

^d Ref. [20].

^e Ref. [9].

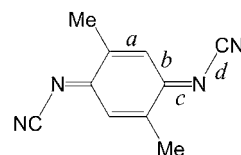


Chart 1.

ferrocene-based 1:1 DA complexes are shown as V-shaped lines [7]. Note that ΔE_{redox} (-0.10 – 0.07 V) of these salts are very close to the NI phase boundary ($\Delta E_{\text{redox}} = 0.1\text{ V}$), and the plots are located near the apex of the theoretical lines. This is reasonable for **1**, **2**, and **1'** and validates our consideration of the theoretical correlation [7]. However, the 1:2 salts **3** and **4** should fall on a different $\Delta E_{\text{redox}}-h\nu_{\text{CT}}$ correlation [7] if they have mixed-stack structures; thus, the result implies that they are not mixed-stack complexes. Consistently, **3** exhibited a segregated-stack structure (*vide infra*), whereas the structure of **4** is unknown. The absorption spectra in **3** likely include CT transitions between the acceptors.

An ionic mixed-stack complex located near the boundary might exhibit an “ionic-to-neutral” transition at high temperatures, which should accompany paramagnetic–diamagnetic changes. However, no such transitions were found in **1–4** by SQUID measurements. No phase transitions could be detected for **1–4** and **1'** by DSC (differential scanning calorimetry) measurements between 100 and 373 K. In terms of ΔE_{redox} , octamethylferrocene complex **2** was located nearer to the NI transition than decamethylferrocene complex **1'**, but an NI transition is less likely to occur in **2** because of its much smaller cell volume compared with **1'** (*vide infra*). We also tried other combinations that fall on the NI boundary using donors of octamethylformyl-, dimethyl-, and non-substituted-ferrocene and acceptors of MeO_2^- , Me_2^- , and non-substituted-DCNQI. However, no complexes were obtained except for **1–4**; in particular, the combinations that might afford neutral complexes were difficult to form. Among the obtained salts, the combination for **3** was the closest to the NI boundary in terms of redox potential, although it did not give a 1:1 mixed-stack structure suitable for an NI transition.

2.2. Crystal structures of **1** and **2**

Packing diagrams of **1** and **2** are shown in Figs. 4 and 5, respectively. Both crystals belong to the space group of $P-1$. The donors and acceptors are stacked alternately in both crystals, and

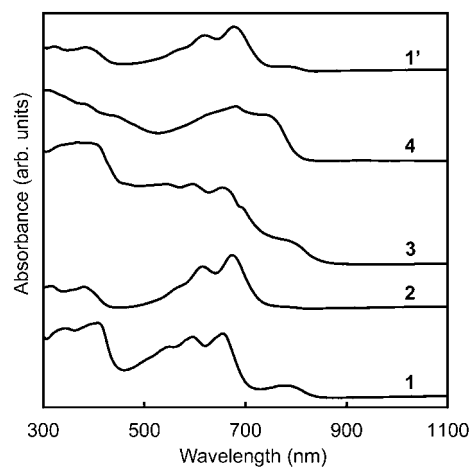


Fig. 2. UV–Vis–NIR spectra of $[\text{Fe}(\text{Cp}^*)_2][(\text{MeO})_2\text{DCNQI}]$ (**1**), $[\text{Fe}(\text{C}_5\text{Me}_4\text{H})_2][\text{Me}_2\text{DCNQI}]$ (**2**), $[\text{Fe}(\text{C}_5\text{Me}_4\text{H})_2][(\text{MeO})_2\text{DCNQI}]_2$ (**3**), $[\text{Fe}(\text{C}_5\text{Me}_4\text{H})_2][\text{DCNQI}]_2$ (**4**), and $[\text{Fe}(\text{Cp}^*)_2][\text{Me}_2\text{DCNQI}]$ (**1'**).

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