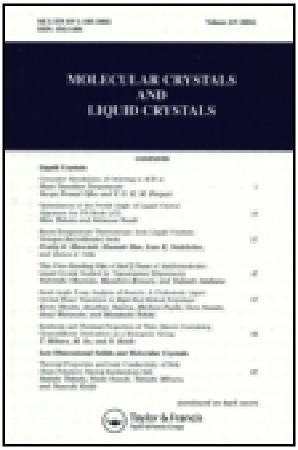

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Ionic(I)–Ionic(II) Phase Transition in a Biferrocenium Charge-Transfer Complex

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An organometallic charge-transfer complex, (dineopentylbiferrocenium) (F_1-TCNQ)$_3$, exhibits an "ionic(I)–ionic(II)" phase transition: a monovalent solid ($D^+A_3^-$) at room temperature, it becomes divalent ($D^{2+}A_3^{2-}$) at low temperatures. Features of the transition are discussed in comparison with those of the N–I transition.

Keywords: biferrocene; charge-transfer complex; F_1TCNQ; phase transition; valence transition

INTRODUCTION

Organic charge-transfer complexes provide an arena for the study of various solid-state physical properties such as electrical conductivity, magnetism, and phase-transition phenomena. The neutral–ionic (N–I) transition – a phase transition between the neutral (D^0A^0) and ionic (D^+A^-) states – has attracted special attention since its discovery in 1981 [1]. However, this phenomenon is limited to several complexes such as tetrathiafulvalene–chloranil (TTF–CA), and no other type of intermolecular valence transition has been reported to date. Here we report the discovery of a new valence transition that can be regarded as "ionic(I)–ionic(II)" (I^I–I^{II}) between the monovalent (D^+A^-) and the divalent states ($D^{2+}A^{2-}$) (Fig. 1a). This phenomenon has

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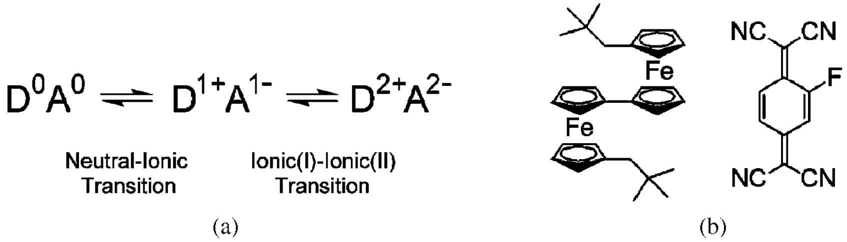

FIGURE 1 (a) Charge-transfer transitions in donor–acceptor complexes. (b) Dineopentylbiferrocene (left) and F_1-TCNQ (right).

been observed in an ionic molecular crystal, (dineopentylbiferrocenium)(fluorotetracyanoquinodimethane)$_3$ (Fig. 1b) [2].

Conventional charge-transfer complexes comprise simple π-conjugated planar molecules, but we have focused on non-planar organometallic molecules [3,4]. Biferrocene has three redox states: neutral, monocation, and dication (Fig. 2); the monocation state involves mixed valency. Therefore, both the first and second electrons can be easily removed. For the N–I transition to occur, it is necessary to have both a mixed-stack structure and matched redox potentials [1]. These requirements may also apply to the I^{I}–I^{II} transition and are met, respectively, by the use of non-planar organometallic donors, which are likely to form mixed-stack structures, and by the use of substituted tetracyanoquinodimethanes, whose redox potentials are controllable. Here we give an overview of the I^{I}–I^{II} transition discovered *via* this approach.

THE IONIC(I)–IONIC(II) PHASE TRANSITION

The charge-transfer complex of dineopentylbiferrocene (D) and fluorotetracyanoquinodimethane (F_1-TCNQ; A) exhibits a phase transition between monovalent and divalent states: at room temperature,

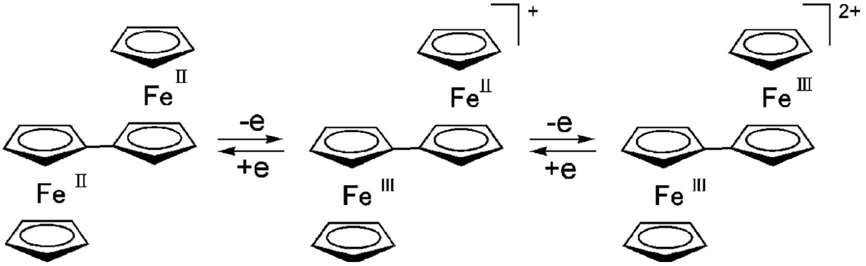

FIGURE 2 Redox states of biferrocene.

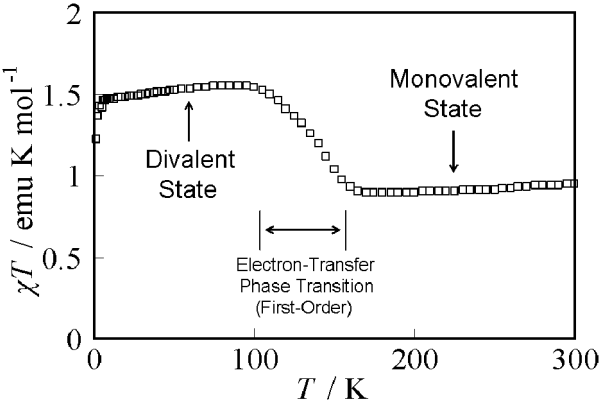

FIGURE 3 Magnetic susceptibilities of polycrystalline samples of (dineopentylbiferrocenium)($F_1TCNQ)_3$ plotted in the form of χT *vs.* T.

biferrocenium cations (D^+) and F_1-TCNQ trimeric anions (A_3^-) crystallize to form a monovalent ionic crystal ($D^+A_3^-$) with a deformed CsCl-type structure. Upon cooling, the crystal exhibits a broad phase transition (100–160 K), becoming divalent ($D^{2+}A_3^{2-}$) at low temperatures. No concomitant change in the space-group (*P*-1) occurs. The Fe valence change has been directly observed by ^{57}Fe Mössbauer spectroscopy, and calorimetric studies revealed the first-order nature of the transition, which accompanies a few Kelvin of hysteresis [2]. The cell volume decreased markedly at the phase transition. The transition is driven by the contraction of the crystal lattice that accompanies the increase in Madelung energy.

The change of magnetism upon transition is remarkable, although both phases are paramagnetic. Figure 3 shows the magnetic susceptibilities for polycrystalline samples, plotted in the form of χT *vs.* T. The molar magnetic susceptibility of the room-temperature phase comes from one Fe(III) spin and one acceptor spin, while that of the low-temperature phase comes from two Fe(III) spins [2]. The χT value is larger in the low-temperature phase, because the ferrocenium spin has a larger magnetic moment than the organic spin.

CHARACTERISTIC FEATURES OF THE TRANSITION

The N–I transition in TTF–CA and the I^I–I^{II} transition in (dineopentylbiferrocenium)(F_1-TCNQ$)_3$ are compared in Table 1. Both are first-order phase transitions but there are some striking differences. In particular, TTF–CA is diamagnetic even in the ionic phase, owing

TABLE 1 Comparison of the Transitions in TTF–CA and (biferrocene) $(F_1TCNQ)_3$

	TTF–CA	(biferrocene)$(F_1TCNQ)_3$
Valence change	Neutral–Ionic	Ionic(I)–Ionic(II)
Magnetic states	Diamagnetic–diamagnetic	Paramagnetic–paramagnetic
Transition type (T_C)	Sharp (81 K)	Gradual (100 ~ 160 K)
Dimensionality	1-Dimensional	3-Dimensional

to spin-Peierls instability of the planar constituents. In contrast, both phases are magnetic in (dineopentylbiferrocene)$(F_1\text{-}TCNQ)_3$; the I^I–I^{II} phase transition is accompanied by significant change in magnetic behavior, as described above. This feature offers the possibility of magnetic control of the phase transition.

There are some other unique characteristics of the I^I–I^{II} transition. Of particular interest is the wide temperature range over which the phase transition occurs, despite its first-order nature. This broad transition is due to coexistence of the domains of the low-temperature and high-temperature phases [5]. Furthermore, the transition is accompanied by a large excess enthalpy [2]. A mechanism for the transition has been proposed [6]; it has been demonstrated that the phase transition between the hard (divalent) state and the soft (monovalent) state can be driven by the difference in entropy i.e., the phonons of the two phases. It is noteworthy that, in striking contrast to usual solid-state phase transitions, this type of transition can occur without changing the lattice symmetry, as observed, similar to the liquid-gas phase transition.

In summary, this study has shown that transformation between the monovalent and divalent states is possible in molecular crystals. A search for the phase diagram for the I^I–I^{II} boundary, analogous to that drawn by Torrance for the N–I boundary [1], is underway.

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