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COMMUNICATION

Chemical Control of the Monovalent–Divalent Electron-Transfer Phase Transition in Biferrocenium–TCNQ Salts †

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An ionic molecular crystal of (1',1'''-dineopentylbiferrocene)(F₁TCNQ)₃ exhibits a first-order phase transition from a monovalent state (D⁺A₃⁻) to a divalent state (D²⁺A₃²⁻) at around 120 K. The transition was successfully controlled by modulation of the redox potentials using F_nTCNQ (n = 0–2) and by chemical-pressure effects.

Charge-transfer salts comprising donor (D) and acceptor (A) molecules exhibit various phase-transition phenomena, and their solid-state electronic properties have attracted much interest for years.^[1] Many charge-transfer salts containing ferrocenium cations have been reported to date.^[2] Biferrocene, composed of two ferrocene units, produces a monocation (D⁺) and a dication (D²⁺) by oxidation.^[3] During our research on biferrocenium charge-transfer salts,^[4] we found that a charge-transfer salt comprising D = dineopentylbiferrocene (1) and A = fluorotetracyanoquinodimethane (F₁TCNQ), [(1)(F₁TCNQ)₃; Figure 1a], with a CsCl-like arrangement of the cation (D⁺) and anion (A₃⁻, trimer of acceptors), exhibits a phase transition from the monovalent state (D⁺A₃⁻) to the divalent state (D²⁺A₃²⁻) at around 120 K (Figure 1b).^[4a] The phase transition is of the first order and accompanies a two-phase coexistence over a wide temperature range (100–150 K).^[5] To our knowledge, there are no other ionic crystals that undergo phase transitions between the monovalent and divalent phases. There are several interesting electron-transfer phase transitions in metal complexes and charge-transfer complexes,^[6,7] including neutral–ionic transitions between the D⁰A⁰ and D⁺A⁻ states.

This paper reports chemical control of the monovalent–divalent phase transition of (1)(F₁TCNQ)₃ by modification of the components. In analogy to the neutral–ionic transition, this phase transition is likely governed by the balance between (i) the redox potentials of the constituents (D⁺²⁺; A₃⁻²⁻) and (ii) the Coulombic (Madelung) energies of the monovalent and divalent states. The transition to the divalent state is ascribed to thermal contraction of the crystal lattice, which increases the Madelung energy gain of the divalent phase. To control the redox potentials in the current study, we used acceptors with comparable molecular volumes but different electron affinities (F_nTCNQ, n = 0–2).^[8,9] To control the Madelung energy by

chemical-pressure effects, we used donors with different molecular volumes but the same redox potentials [dineopentylbiferrocene (1) or isobutylneopentylbiferrocene (2)^[4c]; Figure 1a]. The phase transition behavior of the salts containing these chemically modified components was investigated by means of magnetic measurements.‡ As shown in Fig. 1c, both phases have two paramagnetic spins per formula unit. However, the total magnetic moment becomes larger in the low temperature phase because of the larger g-value for the ferrocenium species.^[4a]

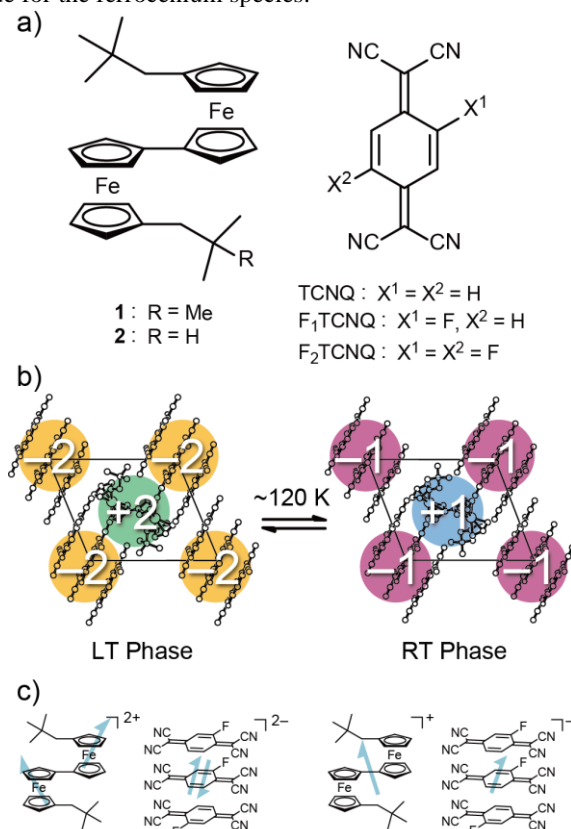


Fig. 1 (a) Chemical formulas of the donors and acceptors used in this study. (b) An illustration of the monovalent–divalent phase transition in $(1)(F_1TCNQ)_{3x}(TCNQ)_{3(1-x)}$. (c) The spin states of the molecules in the divalent (left) and monovalent (right) phases. LT represents low temperature; RT represents room temperature.

First, we used F_nTCNQ ($n = 0, 1, 2$) to control the redox potentials.^[9] TCNQ, with lower electron affinity than F_1TCNQ , yielded isomorphous molecular alloys $(1)(F_1TCNQ)_{3x}(TCNQ)_{3(1-x)}$ over the entire region of x . The temperature dependence of their magnetic susceptibilities ($\chi_m T$) is shown in Figure 2. The magnetic moment increased at the transition temperature owing to the valence transformation. The transition temperatures of the samples decreased with decreasing x , and the phase transition disappeared in the region where $x \leq 0.6$. The phase diagram obtained from the data is shown in the inset. Thus, control of the phase transition temperature was successfully achieved by adding TCNQ. It should be noted that the addition caused not only the decrease in the transition temperature, but also the decrease in magnetic moment in the low-temperature phase. This feature suggests that some portions of the cations remained monovalent (D^+), and hence the $D^+A_3^{2-}$ component was present even in the low-temperature phase. To verify this, we applied ^{57}Fe Mössbauer spectroscopy to the sample with $x = 0.8$. The spectrum at 6 K is shown in Figure 3, which exhibits both the singlet signal of D^{2+} and two pairs of doublet signals of D^+ (corresponding to Fe^{2+} and Fe^{3+}).^[10] This data demonstrate the coexistence of $D^+A_3^{2-}$ and $D^{2+}A_3^{2-}$, and their ratio was determined to be 44:56 from the peak areas. This phenomenon is ascribed to the smaller electron affinity of the acceptor trimers containing TCNQ; namely, only $(F_1TCNQ)_3^-$ had sufficient electron affinity to receive an electron to become A_3^{2-} , whereas the other trimers containing TCNQ ($[(F_1TCNQ)_m(TCNQ)_{3-m}]^-$; $m = 0, 1$, and 2) remained monovalent in the low-temperature phase. The ratio of $(F_1TCNQ)_3^-$ and the other trimers was predicted to be 51:49 ($= x^3:(1-x)^3$) for $x = 0.8$, which is in agreement with the ratio determined by Mössbauer spectroscopy. The low-temperature phase of the molecular alloys is hence regarded as an intermediate phase containing both the monovalent and divalent species. The complete divalent phase comprising only $D^{2+}A_3^{2-}$ was not obtained even at the lowest temperatures under ambient pressure.

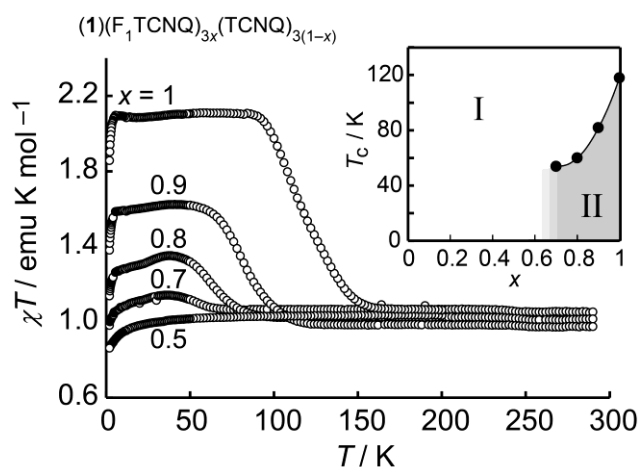


Fig. 2 Temperature dependence of the magnetic susceptibility ($\chi_m T$ values) of $(1)(F_1TCNQ)_{3x}(TCNQ)_{3(1-x)}$ ($x = 1, 0.9, 0.8, 0.7$, and 0.5) measured under a field of 0.5 T. The data are obtained for oriented samples to improve sensitivity, and hence the absolute values in the LT phase are larger than those of non-oriented samples owing to the magnetic anisotropy of the Fe spins. The inset shows the

phase diagram of the molecular alloys, in which $T_{1/2}$ is plotted as a function of the F_1TCNQ ratio (x).

Next, we introduced F_2TCNQ , which has a larger electron affinity than F_1TCNQ . The magnetic susceptibilities of the molecular alloys $(1)(F_1TCNQ)_{3x}(F_2TCNQ)_{3(1-x)}$ ($x = 1, 0.9, 0.8$, and 0.7) are shown in Figure 4a. These salts were isomorphous.^[11] The transition shifted to higher temperature with an increase in F_2TCNQ content. The transition became considerably broadened, and the magnetic susceptibilities in the low-temperature phase were independent of x . Although these features appeared to be in contrast to those observed for the TCNQ-doped alloys, the phenomena in both materials can be explained by the same mechanism. The F_2TCNQ -doped samples were in the divalent phase comprising only $D^{2+}A_3^{2-}$ at low temperatures. With increasing temperature, they transformed successively to intermediate phases in which the $(F_1TCNQ)_m(F_2TCNQ)_{3-m}$ components ($m = 1, 2$, and 3) successively became monoanions, and hence the ratio of $D^+A_3^{2-}$ species increased gradually. This staging phenomenon, becoming continuous because of the quenched disorder, was responsible for the broad transition. In these molecular alloys, doping of acceptor molecules with different electron affinities not only changed the transition temperatures but also led to the appearance of a staging effect.

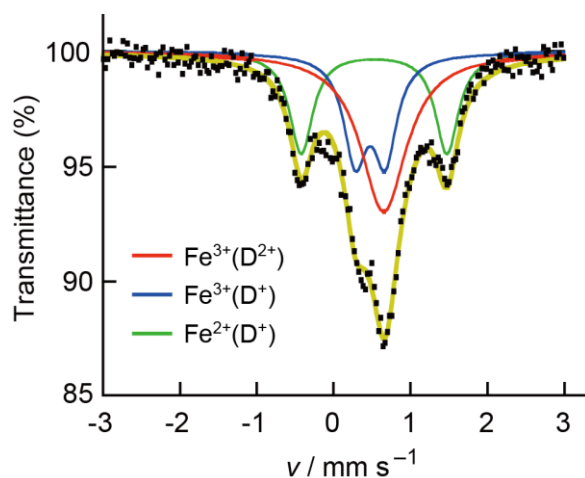


Fig. 3 Mössbauer spectrum of $(1)(F_1TCNQ)_{3x}(TCNQ)_{3(1-x)}$ ($x = 0.8$) measured at 6 K

Finally, the effect of chemical pressure was investigated. Donor **2** has one less methyl group than donor **1**. As shown in Figure 4b, $(2)(F_1TCNQ)_3$ exhibited a phase transition at around 190 K. The cell volume was reduced by 0.99 % relative to $(1)(F_1TCNQ)_3$, which increased the transition temperature by 70 K.^[12] Therefore, the chemical-pressure effects caused a simple shift in the transition temperature.

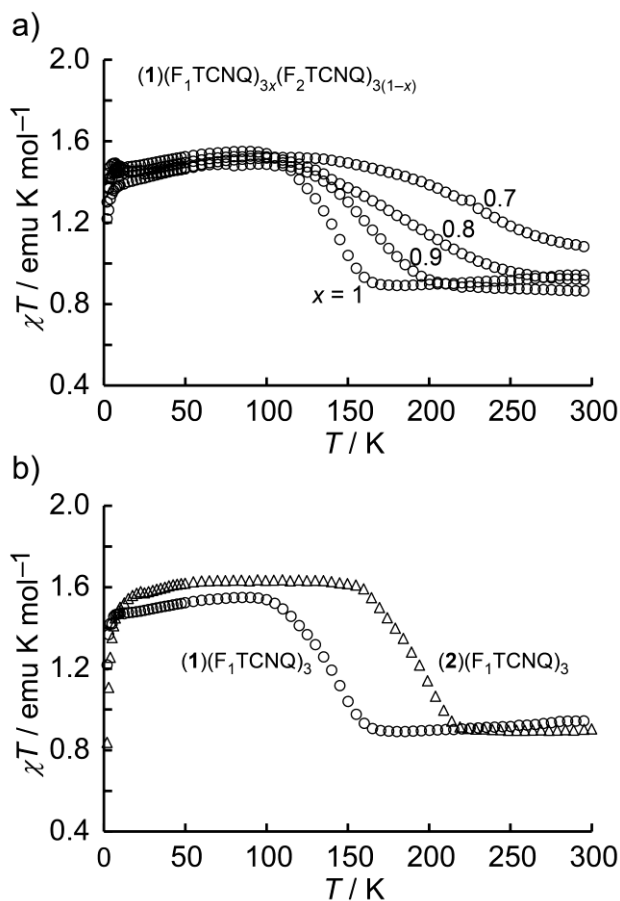


Fig. 4 Temperature dependence of the magnetic susceptibility ($\chi_n T$) of (a) $(1)(F_1TCNQ)_x(F_2TCNQ)_{3(1-x)}$ ($x = 1, 0.9, 0.8,$ and 0.7) and (b) $(1)(F_1TCNQ)_3$, $(1)(Cl_1TCNQ)_3$, and $(2)(F_1TCNQ)_3$.

In summary, the electron-transfer phase transition in the biferrocenium salt $(1)(F_1TCNQ)_3$ was successfully controlled by modulating the redox potentials and the Madelung energies via molecular modification. Molecular alloys that were doped with molecules possessing different redox potentials exhibited phases comprising $D^{2+}A_3^{2-}$ and $D^+A_3^-$. This study has provided us with an understanding of the microscopic mechanism of the monovalent–divalent phase transition. Control of the phase transition by external stimuli such as light and pressure would be an interesting target in future studies. Preparation of general phase diagrams is underway in our laboratories.

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Notes and references

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† Electronic supplementary information (ESI) available: Crystallographic data. CCDC 992759 $[(1)(F_1TCNQ)_{2.1}(F_2TCNQ)_{0.9}]$ and 992760 $[(2)(F_1TCNQ)_3]$. For crystallographic data in CIF or other electronic format see DOI: 10.1039/

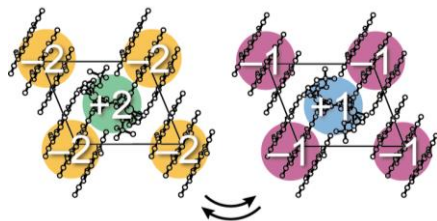
‡ Preparation of $(1)(TCNQ)_{3i}(F_1TCNQ)_{3(1-x)}$ ($x = 0.5$): F_1TCNQ (6.50 mg, 2.94×10^{-2} mmol) and $TCNQ$ (6.00 mg, 2.94×10^{-2} mmol) were dissolved in hot dichloromethane (10 mL), and the solution was added dropwise to a dichloromethane solution (2 mL) of 1',1''-dineopentyl-1,1''-biferrocene^[4c] (30.0 mg, 5.88×10^{-2} mmol). Vapor diffusion of pentane into the solution produced black plate crystals (10.5 mg, yield 16%). Anal. Calcd for $C_{66}H_{48.5}N_{12}F_{1.5}Fe_2$: C, 68.93; H, 4.25; N, 14.62. Found: C, 68.91; H, 4.32; N, 14.69. The samples with $x = 0.6, 0.7, 0.8,$ and 0.9 (nominal values) were prepared by the same methods. Anal. Calcd ($n = 0.6$): C, 68.61; H, 4.21; N, 14.55. Found: C, 68.82; H, 4.40; N, 14.61. Anal. Calcd ($n = 0.7$): C, 68.29; H, 4.16; N, 14.48. Found: C, 68.32; H, 4.29; N, 14.49. Anal. Calcd ($n = 0.8$): C, 67.98; H, 4.11; N, 14.42. Found: C, 67.80; H, 4.22; N, 14.46. Anal. Calcd ($n = 0.9$): C, 67.66; H, 4.07; N, 14.35. Found: C, 67.74; H, 4.36; N, 14.54. The molecular alloys with F_2TCNQ ($x = 0.7, 0.8,$ and 0.9) were prepared similarly. Anal. Calcd ($n = 0.7$): C, 3.88; H, 66.34; N, 14.07. Found: C, 3.84; H, 66.21; N, 13.83. Anal. Calcd ($n = 0.8$): C, 3.93; H, 66.68; N, 14.14. Found: C, 3.89; H, 66.69; N, 14.04. Anal. Calcd ($n = 0.9$): C, 3.98; H, 67.02; N, 14.21. Found: C, 3.94; H, 66.72; N, 14.02. $(2)(F_1TCNQ)_3$ was prepared by the same method, using 1'-isobutyl-1''-neopentyl-1,1''-biferrocene^[4c] and F_1TCNQ . Black-violet block crystals were produced. Anal. Calcd for $C_{65}H_{45}F_3Fe_2N_{12}$: C, 67.14; H, 3.90; N, 14.45. Found: C, 67.31; H, 4.09; N, 14.46.

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- 10 Mössbauer parameters. Fe(III) in D²⁺: δ (isomer shift relative to α -iron) = 0.65 mm s⁻¹, ΔE_Q (quadrupole splitting) = 0 mm s⁻¹; Fe(III) in D⁺: δ = 0.48 mm s⁻¹, ΔE_Q = 0.39 mm s⁻¹; Fe(II) in D⁺: δ = 0.53 mm s⁻¹, ΔE_Q = 1.89 mm s⁻¹.
- 11 Crystallographic parameters for (1)(F₁TCNQ)_{3x}(F₂TCNQ)_{3(1-x)} ($x = 0.7$) at 90 K: triclinic, $P\bar{1}$, $a = 8.7096(17)$ Å, $b = 12.026(2)$ Å, $c = 14.473(3)$ Å, $\alpha = 109.672(2)^\circ$, $\beta = 104.195(3)^\circ$, $\gamma = 98.167(3)^\circ$, $V = 1341.3(4)$ Å³, $R_1 = 0.1107$, and $wR_2 = 0.2783$. Although the salt contains F₂TCNQ, the unit cell volume was smaller by 0.99% than that of (1)(F₁TCNQ)₃. This volume reduction may also affect the transition temperature by chemical pressure effects, but the effects should be smaller for the samples with $x = 0.8$ and 0.9 .
- 12 Cell parameters for (2)(F₁TCNQ)₃ at 295 K: triclinic $P\bar{1}$, $a = 8.7122(7)$ Å, $b = 12.1906(9)$ Å, $c = 14.8007(12)$ Å, $\alpha = 108.481(2)^\circ$, $\beta = 104.862(2)^\circ$, $\gamma = 96.356(2)^\circ$, $V = 1409.03(19)$ Å³. Crystallographic data at 90 K: triclinic, $P\bar{1}$, $a = 8.6943(11)$ Å, $b = 12.0631(16)$ Å, $c = 14.3534(18)$ Å, $\alpha = 109.208(2)^\circ$, $\beta = 105.134(2)^\circ$, $\gamma = 97.578(2)^\circ$, $V = 1332.5(3)$ Å³, $R_1 = 0.0393$, and $wR_2 = 0.1063$. The substituents were disordered in the crystal.

Table of contents entry

An ionic molecular crystal of (dineopentyl-biferrocene)(F₁TCNQ) exhibits a phase transition from a monovalent state (D⁺A₃⁻) to a divalent state (D²⁺A₃²⁻) at around 120 K, which was successfully controlled by modulation of the redox potentials and molecular volumes.



- Chemical pressure control
- Redox potential control