

The First Crystallographic Study of Stepwise Neutral-Ionic Transitions

An organic metal complex, $[\text{Ru}_2^{\text{III}}(2,3,5,6\text{-F}_4\text{PhCO}_2)_4(\text{DMDCNQI})] \cdot 2(p\text{-xylene})$ ($2,3,5,6\text{-F}_4\text{PhCO}_2^- = 2,3,5,6\text{-tetrafluorobenzoate}$, $\text{DMDCNQI} = 2,5\text{-dimethyl-}N,N'\text{-dicyanoquinonediimine}$), is the first example of a covalently-bonded donor ($[\text{Ru}_2^{\text{III}}(2,3,5,6\text{-F}_4\text{PhCO}_2)_4]$) and acceptor (DMDCNQI) chain system showing neutral-ionic phase transitions. The transitions successively occur at two critical temperatures of $T_1 \sim 270$ K and $T_2 \sim 210$ K. Our crystal structure analysis clarified that neutral chains with $\delta \sim 0$ and ionic chains with $\delta \sim 1$ coexist and these layers are stacked alternately in the intermediate phase ($T_2 < T < T_1$), where δ denotes the degree of charge transfer. This is the first observation of the self-organization of neutral and ionic chains.

Neutral (N)-ionic (I) transitions in organic donor (D)/acceptor (A) charge-transfer complexes are intriguing because a 'reservoir of functions' is available. Accompanying this 'switch of charge', physical properties such as electron transport, magnetism, and dielectric properties drastically change. Therefore, by controlling the transition it is possible to prepare switchable materials. For systematically controlling N-I transitions, tuning the ionization potential of D and the electron affinity of A are important and various successes have been so far achieved in organic stacked DA systems. Meanwhile, the effect of intermolecular Coulomb interactions is a long-standing mystery. It likely causes a number of charge-gap states at once and consequently allows stepwise transitions as predicted theoretically [1, 2]. Although such a two-step N-I transition upon application of pressure to TCNQ has been reported [3], there is not sufficient information for discussing the mechanism of the successive transition, such as spatial arrangement.

$[\text{Ru}_2^{\text{III}}(2,3,5,6\text{-F}_4\text{PhCO}_2)_4(\text{DMDCNQI})] \cdot 2(p\text{-xylene})$ is the first example of a covalently-bonded DA complex exhibiting N-I transitions [4]. $[\text{Ru}_2^{\text{III}}(2,3,5,6\text{-F}_4\text{PhCO}_2)_4]$ ($2,3,5,6\text{-F}_4\text{PhCO}_2^- = 2,3,5,6\text{-tetrafluorobenzoate}$, hereafter abbreviated as $[\text{Ru}_2^{\text{III}}]$) can act as a donor, forming $[\text{Ru}_2^{\text{III}}]^+$ by the oxidation, and DMDCNQI ($= 2,5\text{-dimethyl-}N,N'\text{-dicyanoquinonediimine}$) is a well-known π -acceptor, which becomes a radical anion DMDCNQI^- . The D and A are covalently bound to form a one-dimensional chain as shown in Fig. 1(a). It crystallizes in a monoclinic structure in the space group $P2_1/n$ ($a = 14.760(5)$ Å, $b = 10.519(3)$ Å, $c = 17.152(6)$ Å, $\beta = 97.265(5)^\circ$ at 107 K) where the chains run along the a axis as shown in Figure 1(b). The N-I transitions successively occur at two critical temperatures of $T_1 \sim 270$ K and $T_2 \sim 210$ K. Charge transfer δ on $\text{D}^{\delta+}\text{A}^{\delta-}$ can be empirically estimated from deformation of the D and A. The Ru-O bond length is sensitive to the oxidation state of the $[\text{Ru}_2]$: 2.06–2.07 Å for $[\text{Ru}_2^{\text{III}}]$ and 2.02–2.03 Å for

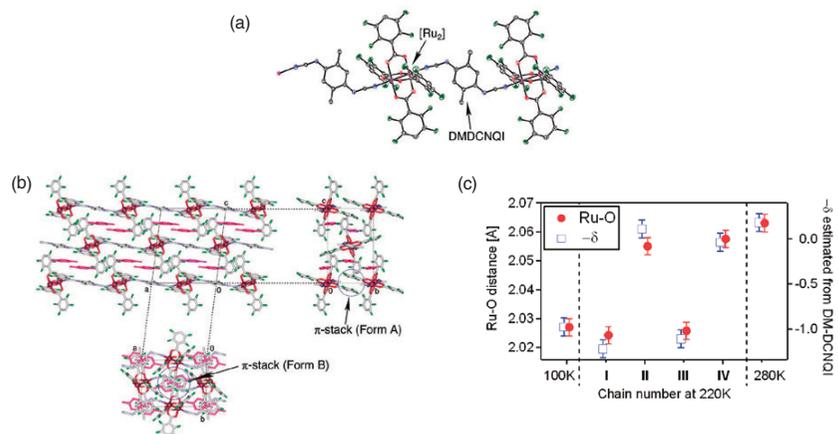


Figure 1 (a) Covalently-bonded $[\text{Ru}_2^{\text{III}}(2,3,5,6\text{-F}_4\text{PhCO}_2)_4]$ and DMDCNQI molecule. (b) Crystal structure of $[\text{Ru}_2^{\text{III}}(2,3,5,6\text{-F}_4\text{PhCO}_2)_4(\text{DMDCNQI})] \cdot 2(p\text{-xylene})$. (c) The Ru-O bond lengths (red solid circles) and estimated $-\delta$ on the DMDCNQI on each chain in the IM phase (240 K). Those values in the I phase (100 K) and N phase (280 K) are also shown for comparison. (Reproduced from Ref. [4])

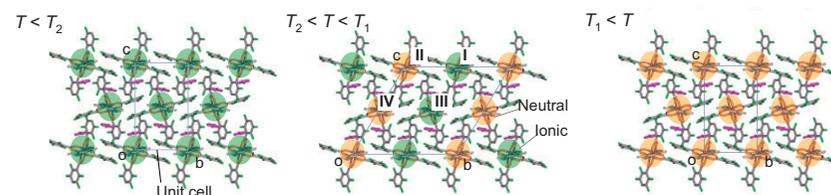


Figure 2 Arrangements of N and I chains in the I phase below T_2 (left), IM phase between T_1 and T_2 (middle), and N phase above T_1 (right) projected onto the bc plane which is perpendicular to the covalently-bonded chain. Yellow and green denote the N and I chains, respectively. (Reproduced from Ref. [4])

$[\text{Ru}_2^{\text{III}}]^+$ [5]. Regarding the DMDCNQI $^{\delta-}$ moiety, δ can be estimated by using the Kistenmacher relationship from the N-C and C-C bond lengths [6]. The results of single-crystal X-ray analysis using a commercial CCD X-ray diffractometer show that δ is almost 0 and 1 in the N phase ($T_1 < T$) and the I phase ($T < T_2$), respectively.

To elucidate the ionic state in the intermediate (IM) phase ($T_2 < T < T_1$), synchrotron X-ray diffraction measurement has been performed on a single crystal using a large cylindrical imaging plate detector at BL-8B. Additional super-lattice reflections with a modulation vector (0 1/2 1/2) were observed and splitting of the fundamental reflections was found in the high-Q range in the IM phase. These results suggest a super-lattice-unit cell ($\mathbf{a}_s = \mathbf{a}$, $\mathbf{b}_s = 2\mathbf{b}$, $\mathbf{c}_s = \mathbf{b} + \mathbf{c}$) in space group $P-1$, containing four independent chains (I–IV). Full crystal structure analysis was performed at 240 K using SHELX by allowing the presence of twins. Details of the refinement are as follows: 30704 reflections (14713 unique), $R_{\text{int}} = 0.0479$, $R_1 = 0.0381$ ($I > 2\sigma(I)$), $R_1 = 0.0663$ (all data) and $wR_2 = 0.1177$ (all data), $S = 0.870$. Figure 1 (c) shows mean Ru-O bond lengths and estimated $-\delta$ on DMDCNQI for chains I–IV, which clearly indicate that two N chains (II and IV) with $\delta \sim 0$ and two I chains (I and III) with $\delta \sim 1$ are aligned to form an alternating stacking, as shown in Fig. 2. This is the first observation of the self-organization of the neutral and ionic moieties.

The arrangement of N and I chains can be explained as follows. Two neighboring chains are aligned in-phase along the b axis as shown in Fig. 1(b). A Coulomb energy cost is necessary for two chains to change

simultaneously from N to I states. On the other hand, since the next-neighbor chains in the [011] direction are aligned antiphase, the two chains can become I chains with an energy gain. The Coulomb interactions probably prevent a uniform N-I transition and instead give rise to a complicated arrangement of N and I chains. Below T_2 , the intrachain energy gain of the I state becomes large enough to overcome the Coulomb energy cost, allowing a uniform I state.

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