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Charge-disproportionate ordered state with $\delta = 0.75$ in a chemically sensitive donor/acceptor $D^{\delta+}A^{\delta-}$ layered framework†

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A novel charge-disproportionate state with $\delta = 0.75$ was observed in an electron-donor (D)/acceptor (A) $D^{\delta+}A^{\delta-}$ layered framework by chemically tuning the electron-donating affinity of D at the boundary between $D^{0.5+}A^{-}$ and $D^{+}A^{2-}$ phases, which was pressure-sensitive via the formation of the $D^{1+}A^{-}$ oxidation state.

Tuning of the charge-ordered state in a multi-dimensional framework material, which enables the direct control of electrical and magnetic properties of a material, is a challenging theme in solid-state chemistry and materials chemistry. For achieving this purpose, two techniques are commonly available: chemical techniques, i.e. chemical doping or modification and physical techniques, i.e. switching by external stimuli such as temperature, pressure, electric field or photo-irradiation. Some molecular systems have indeed demonstrated intriguing properties associated with the fine-tuning of their charge-ordered state. Among them, a family of metal-organic frameworks (MOFs) constructed from carboxylate-bridged paddlewheel-type diruthium(II, II) complexes (abbreviated as [Ru2(II)]) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) or N,N2-dicyanoquinodiminedime (DCNQI) derivatives, as donor (D)/acceptor (A)-MOFs (D/A-MOFs), provides a good platform, where the electronic/magnetic properties of the MOFs are tuneable as a function of the charge-ordered state of the framework. A variety of oxidation states, including $D^{0}A^{0}$, $D^{0.5+}A^{-}$, and $D^{+}A^{2-}$, have been obtained in a D$_2$A-type MOF, which can be systematically manipulated through the on-demand choice of D and A components on the basis of the relationship of energy gap between HOMO level of D and LUMO level of A: $\Delta E_{HOMO}\text{(DA)} = E_{LUMO}\text{(DA)} - E_{HOMO}\text{(N)}$, with the neutral (N) state and the ionic (I) state as $\Delta E_{HOMO}\text{(DA)} > 0$ and $\Delta E_{HOMO}\text{(DA)} < 0$, respectively (Fig. S1a). When we examine the ionic state of the $[\text{Ru}_2\text{TCNQ}]$ compounds, i.e. D$_2$A-type compounds, with $\Delta E_{HOMO}\text{(I)} < 0$, two types of oxidation states, $D^{0.5+}A^{-}$ and $D^{+}A^{2-}$, which involve one-electron and two-electron transfers to A, respectively, can be considered. These oxidation states provide different magnetic ground states: the $D^{0.5+}A^{-}$ state generally undergoes long-range ordering through TCNQ$^{-}$ with $S = 1/2$, whereas the $D^{+}A^{2-}$ state could lack ordering or have weak ordering because of the presence of diamagnetic TCNQ$^{-}$. Despite the same D$_2$A-type formulation and a common framework structure between them, these oxidation states should be alternated depending mainly on i) the electron-donation affinity of D vs. A used (i.e. the relationship between the ionisation potential of D and the electron affinity of A) and ii) the intrinsic on-site Coulomb repulsion ($U$) of the A species used. Given that the magnitude of $U$ of TCNQ derivatives (TCNQR$_2$, $2,5$- or $2,3,5$-R-substituted 7,7,8,8-tetracyano-p-quinodimethane; R$_2$ = H$_2$, F$_2$, Cl$_2$, Br$_2$, $F\cdotPH$O, $Me\cdotOMe$, (OMe)$_2$; BTDA-TCNQ = bis[1,2,5]dithiazolotetracyanoquinodimethane) is proportional to the potential difference between the first and second redox potentials of TCNQR$_2$ ($\Delta E_1$($A^{-}/A$($solv$)), the order of $U$ for the TCNQR$_2$ compounds is TCNQR$_2$Me$_2$ < TCNQR$_2$ < BTDA-TCNQ < TCNQRBr$_2$ < TCNQ < TCNQCl$_2$ ($\approx$ DCNQI$\text{Me}_2$) < TCNQF$_4$ ≈ TCNQF$_2$ (Fig. S1b). Specifically, $U$ is the smallest in TCNQR(MeO)$_2$ among this group; i.e. the energy window for $\Delta E_{HOMO}\text{(DA)}$, at which TCNQR,$^*$ is stably present, is 0.2–0.3 eV, which is much narrower than the window of 1.2–1.3 eV for TCNQR$_2$ or TCNQF$_2$ (Fig. S1b). This result indicates that the oxidation state of the ionic state between $D^{0.5+}A^{-}$ and $D^{+}A^{2-}$ can be tuned via a small modification or perturbation induced by chemical and/or physical techniques when TCNQR(MeO)$_2$ is used as A.

Here, we demonstrate charge control in layered D$_2$A systems with the TCNQR(MeO)$_2$ acceptor by slightly changing the electron-donating ability of D through modification of the substituent position (e.g. ortho-, meta- and para-positions) of the fluoro group in $[\text{Ru}_2\text{FPhCO}_2]_2$ ([FPhCO] = ortho-, meta- and para-fluorophenyl substituted benzolate). The present compounds are $([\text{Ru}_2\text{(FPhCO}_2)_2]_2\text{TCNQR(MeO}_2)]_n$ (solv) ($x$ = ortho, $n$ (solv) = $4\text{CH}_2\text{Cl}_2$, $1$; $x$ = meta, $n$ (solv) = $4\text{CH}_2\text{Cl}_2$, $2$; $x$ = para, $n$ (solv) = $3\text{CH}_2\text{Cl}_2$; PhNO$_2$, $3$), in which the oxidation state was varied as $D^{0.5+}A^{-}$ for 1, $D^{+}A^{2-}$ for 2, and $D^{0.75+}A^{1.5-}$ for 3. Herein, we focus on the novel charge-ordered state of $D^{0.75+}A^{1.5-}$ in 3, in particular; this novel state was discovered in a superlattice comprising $[\text{Ru}_2\text{FPhCO}_2]_2$, $[\text{Ru}_2\text{I}_2\text{FPhCO}_2]_2$ TCNQR(MeO)$_2$ and TCNQR(MeO)$_2$– components in a formulation ratio of 3:3:1 caused by the disproportionation of intralayer electron transfers. This charge-ordered state can be regarded as an intermediate oxidation state between $D^{0.5+}A^{-}$ for 1 and $D^{+}A^{2-}$ for 2.
All compounds were synthesised by a similar diffusion method of D/A units typically used in relevant compounds (see ESI). Infrared (IR) spectra of compounds are useful for confirming the oxidation state of component units, which were measured by a microscopic technique using a single crystal coated with Paratone-N (HAMPTON Research, Inc.) to remove the effect caused by the elimination of crystallisation solvents. The ν(C≡N) mode for all compounds was observed as red-shifted multiplets: 2109, 2158 and 2202 cm⁻¹ for 1; 2098(br), 2154 and 2190 cm⁻¹ for 2; and 2113(br), 2167, 2191(sh) and 2202 cm⁻¹ for 3 (br = broad; sh = shoulder) (Fig. S2). These results indicate the reduced forms of TCNQ(MeO)₂, where the one-electron reduced form (TCNQ(MeO)₂⁺⁻) and two-electron reduced form (TCNQ(MeO)₂⁻⁻) are assigned for 1 and 2, respectively, and their mixed modes are assigned for 3.

Compounds 1 and 2, which had the D₂A formulation, crystallised in the triclinic P–1 space group (#2), where two kinds of [Ru₃] units and one TCNQ(MeO)₂ unit are structurally characterised as an asymmetric unit, all of which have an inversion centre at the midpoint of the units, resulting in Z = 1 (Fig. S3; Table S1). The TCNQ(MeO)₂ unit acts as a µ₂-bridging ligand to coordinate to the axial sites of [Ru₂] units, forming a two-dimensional (2-D) fishnet-like network spreading over the (101) plane for 1 and over the (100) plane for 2 (Fig. 1 and Fig. S4) (the crystallisation solvent molecules are located at void spaces between layers). On the basis of the trend of Ru–N = 2.22–2.23 Å for [Ru₁II,III] and Ru–N = 2.27–2.28 Å for [Ru₂II,III] (Tables S2 and S3), the oxidation state of [Ru₂] units is suggested as [Ru(1)]II,III⁺⁻ and [Ru(2)]II,III⁺⁻ in 1 and as [Ru₁II,III]⁺⁻ for both [Ru₁] units in 2 (Tables S2 and S3). This charge assignment for [Ru₃] units is supported by a more accurate indication based on a comparison of Ru–O distances (Oeq = equatorial oxygen atoms): 2.06–2.07 Å for [Ru₁II,III] and 2.02–2.03 Å for [Ru₂II,III] in 1, the average Ru–O bond distances for [Ru(1)] and [Ru(2)] units are 2.027 and 2.068 Å, respectively, indicating oxidation states of [Ru₁II,III]⁺⁺ and [Ru₂II,III]⁺⁻, respectively (Table S2). Meanwhile, in 2, the average Ru–O bond distances for both units are 2.023 and 2.026 Å for [Ru(1)] and [Ru(2)], respectively, which are in the range for [Ru₂II,III]⁺⁻ (Table S3).

Correspondingly, the oxidation state of TCNQ(MeO)₂⁻⁻ is assigned as TCNQ(MeO)₂⁻⁻ and TCNQ(MeO)₂⁺⁻ for 1 (2δ = 1.38) and 2 (2δ = 2.20), respectively, on the basis of the Kistenmacher relationship 2δ = ±(A₁c/(b+d)) + B₂, in relation to TCNQ (2δ = 0) with A₁c = –41.667 and B₂ = 19.833 (the bond lengths b, c and d are respective bond distances for 7.9, 1.7- and 1.2-positioned C–C sets in TCNQ(MeO)₂, respectively (Table S4). Specifically, the charge-ordered states for 1 and 2 can be written as [(Ru₁)]II,III⁺⁻–TCNQ(MeO)₂⁻⁻–[Ru(2)]II,III⁺⁻⁺⁻ and [(Ru₁)]II,III⁺⁻–TCNQ(MeO)₂⁺⁻–[Ru(2)]II,III⁺⁻⁺⁻, respectively, leading to the conclusion that 1e and 2e transfer systems, respectively, occur in an identical D₂A system.

In the case of 3, a similar unit cell in the triclinic P–1 space group and with a cell volume similar to that of 1 and 2 was considered; in this unit cell, two kinds of [Ru₂] units and one TCNQ(MeO)₂ unit with respective inversion centres were determined as an asymmetric unit with Z = 1 in an identical 2-D layered fishnet-like network (ESI; Fig. S5; Table S1). This structural analysis is consistent with the charge assignment of D₃h₃, assuming that the presence of such a half-value of charge presumes three possible charge states of charge state in the D₂A system: i) a delocalised charge distributed state, ii) a charge-ordered state as a steady state and iii) a novel charge-disordered state with a superlattice as a steady state. In the present case, model (iii) was adopted because diffraction spots indicating the half-index value for the c-axis q = (0, 0, ½) were observed when X-ray diffraction spots were carefully measured (Fig. 2a), which demonstrates the occurrence of unit-cell doubling such that the c-axis is twice as large as the original minimum cell with Z = 1.

In the superlattice, three types of [Ru₃] units (D₁, D₂ and D₃ in Fig. 2b) and two types of TCNQ(MeO)₂ units (A₁ and A₂ in Fig. 2b) are structurally identified, where D₁ and D₃ and both TCNQ(MeO)₂ units (A₁ and A₂) have an inversion centre at the midpoint of the respective units, whereas all atoms of D₂ are determined as an asymmetric unit; hence, the unit cell has Z = 2. The average Ru–Oeq length is 2.064, 2.025 and 2.027 Å for D₁–D₃, respectively (Table S5): D₂ and D₃ are assigned to [Ru₁II,III]⁺⁻, whereas D₁ is [Ru₂II,III]⁺⁻. The Ru–N lengths agree with these assignments, although the Ru(2)–N(2) bond (2.256(4) Å) was observed as an intermediate value for between [Ru₁II,III]⁺⁻ and [Ru₂II,III]⁺⁻ (Table S5). The Kistenmacher analysis on the two TCNQ(MeO)₂ moieties (A₁ and
Thus, the two types of charge arrangements, D\(^{0.5+}\) and D\(^{1.5-}\) anisotropy, susceptibilities (\(\chi\)) were measured at several different field intensities. a) An \(H-T\) phase diagram, where AF and P indicate antiferromagnetic and paramagnetic phases, respectively. b) Field dependence of the magnetization measured at several temperatures.

The magnetic state of the present \([\text{Ru}_{2}^{II,III}]\)TCNQ system is variable, depending on the charge-ordered states; spin components of \([\text{Ru}_{2}^{II,III}]\) (S = 1) and \([\text{Ru}_{2}^{II,III}]\) (S = 3/2) possess strong magnetic anisotropy, whereas TCNQ\(^{0}\) and TCNQ\(^{-}\) are diamagnetic and paramagnetic (S = 1/2) is paramagnetic. In addition, the magnetic exchange coupling (J) between \([\text{Ru}_{2}^{II,III}]\) and \([\text{Ru}_{2}^{II,III}]\) is known to be very strong, often exceeding 100 K with the support of A \(\rightarrow\) D\(^{+}\) low-energy charge transfer. Furthermore, the magnetically ordered state is known to be strongly affected by interlayer environments associated with interlayer dipole interactions.

The unique charge-ordered state of 3 has two types of TCNQ(MeO)\(^{2-}\), i.e. TCNQ(MeO)\(^{2-}\) and TCNQ(MeO)\(^{2-}\), which are surrounded by two \([\text{Ru}_{2}^{II,III}]\) units and two \([\text{Ru}_{2}^{II,III}]\) units for TCNQ(MeO)\(^{2-}\), as in 1, and four \([\text{Ru}_{2}^{II,III}]\) units for TCNQ(MeO)\(^{2-}\), as in 2, respectively. These situations alternately occur along the c-axis, which appears to be an intermediate state between the 1e\(^{+}\) and 2c\(^{+}\) transfer states, i.e. intermediate between 1 and 2. The \(\chi\) measured at 1 kOe, 1.15 \(\times\) 10\(^{-3}\) cm\(^{3}\) mol\(^{-1}\) at 300 K, gradually increases as the temperature is decreased to approximately 30 K and then abruptly increases without any peak as the temperature is decreased to 1.8 K (3.53 \(\times\) 10\(^{-3}\) cm\(^{3}\) mol\(^{-1}\) at 1.8 K) (Fig. 4a); this basic behaviour is common at lower fields applied at 30 Oe (Fig. S4). Thus, the present compound exhibits a typical magnetic behaviour predicted from the \([\text{Ru}_{2}(1.5-)\text{TCNQ(MeO)}^{2-}\text{–[Ru}(2)_{1.5+}]\) charge-ordered state, which undergoes long-range magnetic ordering that is explained by intralayer ferrimagnetic ordering at \(T_{N} = 88\) K followed by interlayer antiferromagnetic ordering at \(T_{N} = 83\) K (Fig. 3a and Fig. S7). Notably, 1 indeed locates at an antiferromagnetic ground state under the field-cooling condition (Fig. 3b; Fig. 3c shows a phase diagram of 1), but maintains a ferrimagnetic state after undergoing a transition to this state under an applied magnetic field, even at temperatures below the \(T_{N}\), indicating the occurrence of field-induced ferrimagnetic transition. Actually, typical hysteresis curves were observed in the magnetization (M) vs. \(H\) plots obtained under effective coercive fields at temperatures up to the \(T_{N}\) (Fig. 3d).
(Fig. S11). The remnant magnetization value is also small in the same temperature range. In addition, the coercive field is smaller than that for 1; rather, the hysteresis loop for 3 resembles a miniature version of that for 1. This behaviour can be explained by an alternating arrangement of strongly coupled ferrimagnetic domains via TCNQ(MeO)₂ − and weakly coupled paramagnetic species around diamagnetic TCNQ(MeO)₂ ² moieties.

An ‘intermediate’ oxidation state such as that observed in 3 could trigger a phase transition to another stabilised oxidation state (e.g. D₂δA²−, as observed in 2) induced by an external stimulus such as pressure. Hydrostatic pressures up to 7.34 kbar were applied to 3 using a piston-cylinder-type cell fabricated from a Cu–Be alloy, in conjunction with a Pb probe.¹²,¹³ The magnetization at low temperatures, which increases steeply at approximately Tc = 27 K, gradually decreased with increasing pressure and almost disappeared at P = 3 kbar, suggesting a transition to a paramagnetic state (Fig. 5a). This behaviour was confirmed by the M–H curve measured at 1.8 K: the hysteresis curve of 3 disappeared at P = 3 kbar (Fig. 5b). The final M–H feature is almost linear, typical for a paramagnetic state. Thus, the application of pressure to 3 successfully changed its oxidation state from D₂δA²− to D₂A²−. Notably, the original state of 3 was almost recovered when the pressure was released.

![Fig. 5. Pressure-induced changes in the magnetization of 3, as observed in M–T(a) and M–H (b) curves.](image)

In summary, following the prediction based on the ionisation diagram of ΔE_(2A)(DA) vs. (E_(2B)(A) − E_(2A)(A)) (Fig. S1b),¹⁰ D/A sets at around the boundary between D₂δA²− and D₂A²− were investigated; consequently, three types of charge-transfered-state D₂δA²−, with δ = 0.5, 1, and 0.75 for 1–3, respectively, were rationally obtained through modification of the position of the F substituent (i.e. either o-, m- or p-) of [Ru₂(μ₃-FPhCO₂)₆] as D, respectively. Compound 3 has a novel charge-ordered state—a superlattice comprising [Ru₂(μ₃-FPhCO₂)₆], TCNQ(MeO)₂ − and TCNQ(MeO)₂ ² components in a formulation ratio of 1:3:1:1 — caused by the disproportionation of intralayer electron transfers. This oxidation state appears to be an intermediate state between D₂δA²− and D₂A²−. This unique charge-ordered state is sensitive to applied pressure and changes into D₂A²−, demonstrating that the charge-ordered states in D/A frameworks are flexibly controllable via the application of adequate external stimuli. Thus, D/A-MOFs have a strong potential for the design of molecular electronic/magnetic devices with multiple tunability via external stimuli.

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Notes and references

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