

Magnetic phase switch accompanied with the suppression of structural disorder by Gas-adsorption in a layered assembly of paddlewheel [Ru₂] units and TCNQ

(¹Department of Chemistry, Graduate School of Science, Tohoku University, ²Institute for Materials Research, Tohoku University, ³Frontier Research Institute for Interdisciplinary Sciences, Tohoku University)

○Yoshie Hiwatashi,¹ Wataru Kosaka,^{1,2} Y Jun Zhang,^{2,3} Hitoshi Miyasaka,^{1,2}

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Charge-transferred metal-organic frameworks composed of electron-donor (D) and -acceptor (A), called as D/A-MOFs, have been attracted much attention because of their high potential applications for tunable electronic/magnetic materials. While the uniformity of pores is usually drawn attention in the class of MOFs, the movability of organic ligands in sufficient interstitial pore spaces, which sometimes results in static/dynamic structural disorders, is one of the intriguing characteristics of MOFs. Such structural disorders are often affected by the guest accommodation, which may cause a modulation of electronic state, consequently physical properties, in the case of D/A-MOFs.

Here, we investigated CO₂ responsibility of magnetic properties of the [Ru₂]-TCNQ layered magnet with $T_c = 56$ K, {[Ru₂(*o*-ClPhCO₂)₄][TCNQ(OMe)₂]} (**1**, *o*-ClPhCO₂[−] = *ortho*-chlorobenzoate), because **1** possesses a static structural disorder at the Cl atom on the benzoate moiety, which could be an origin of partial charge fluctuations, although the charge-distribution was basically classified into the one-electron-transferred ionic state (1e-I) formulated as [Ru₂]^{0.5+}–[TCNQ(OMe)₂]^{•−}–[Ru₂]^{0.5+}.¹

Single-crystal X-ray diffraction (SCXRD) analyses of **1** under CO₂ revealed that the disorder in **1** was disappeared by accommodating one molar amount of CO₂ in a small pore of **1**, forming **1**·CO₂ (Fig. 1a, b). Compound **1**·CO₂ also has the 1e-I state, as well as **1**. Magnetic measurements revealed that T_c largely increased to 100 K under CO₂ sorption from 56 K of **1** (Fig. 1c). The IR spectra for **1** at $P_{\text{CO}_2} = 100$ kPa revealed that the CN stretching peak at the lowest energy in **1** is disappeared in **1**·CO₂, indicating disappearing the partially presented diamagnetic TCNQ(OMe)₂^{2−} species (Fig. 1d). This fact indicates that the electronic state of **1** is not an exact 1e-I state, but is slightly fluctuated as a (1+ δ)e-I state. Thus, a drastic increase of T_c was achieved by the suppression of charge fluctuation (δ), which could be associated with the structural disorder suppressed by the CO₂ adsorption.

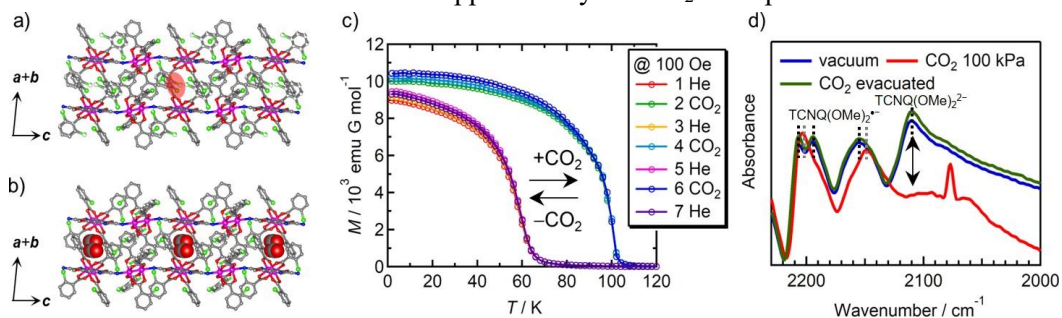


Figure 1. Crystal structure of **1** (a) and **1**·CO₂ (b) along the *a*-axis. (c) Temperature dependence of magnetization at 100 Oe of **1** (under He) and **1**·CO₂. (d) IR spectra under vacuum (blue), 90 kPa CO₂ (red), and evacuated after CO₂ adsorption (green) (200 K).

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