Magneto-Ionic Phase Switching in an Electron-Donor/-Acceptor Metal-Organic Framework using a Li-Ion Battery System

Magnetic phase switching between the paramagnetic and ferrimagnetic states in a neutral electron-donor/-acceptor metal-organic framework (D/A-MOF) has been demonstrated by electron-filling control using a Li-ion battery (LIB) system, in which a D/A-MOF is incorporated as a cathode. Selective electron-doping to the acceptor sites of the framework, accompanied by insertion of Li ions into pores in the material, has been achieved by tuning the battery voltage. X-ray diffraction measurements indicate that Li ions are inserted into the void spaces prepared by removing the crystal solvent, accompanied by expansion of the flexible framework without significant collapse of coordination bonds.

Electrical control of magnetism has attracted great interest in the field of materials science and spintronics [1]. In these research fields, various approaches for electrical magnetism control, such as magnetic domain reversal by polarized spin-current flow and electric-field modulation of magnetic anisotropy, have been suggested and demonstrated. Electron-filling control using a field effect transistor (FET) in correlated electron systems is also a representative approach to modulate magnetic properties by electrical means. In diluted magnetic semiconductors, the stability of the ferromagnetic phase is successfully controlled by tuning electron density using FET systems. However, the application of FET systems is inevitably limited to thin films or materials interfaces because of the electrostatic screening effect of electric-field-induced carriers, which prevents penetration of the electric field into the bulk region.

Recently, Li-ion battery (LIB) systems have been attracting attention as another type of device for filling control, which is applicable to bulk materials [2-4]. In an LIB system, Li-ion migration accompanied by a redox reaction in electrodes is used for energy storage. This mechanism can be used to control the electron density of the electrode materials, because equal numbers of electrons and Li$^+$ ions are introduced to the electrode materials to maintain charge neutrality. In our recent study, taking advantage of this LIB characteristic, we attempted to control the magnetism in bulk compounds by

the Li-ion migration that accompanies redox reactions, i.e. 'magneto-ionic control' [5].

As a target material, we selected an electron-donor/-acceptor metal-organic framework (D/A-MOF), which is composed of paddlewheel-type diruthenium(II, II) complex as a donor (D) unit, and 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) derivative as an acceptor (A) unit. Since the D/A-MOFs are porous redox-active compounds, they are suitable for the electrodes of LIB systems. A notable characteristic of the D/A-MOF is that the magnetic order appears when A is in a radical state with an unpaired spin. Focusing on this characteristic, we carried out selective electron-filling control of the A sites in the paramagnetic neutral D/A-MOF, in which A sites have no radical spin, by tuning the battery voltage in discharge/charge cycles (**Fig. 1a**). In this study, to obtain a neutral system for magnetism control, a combination of [Ru$_2$^{II,II}(CF$_3$CO$_2$)$_4$(THF)$_2$] and BTDA-TCNQ, which have a positive $\Delta E_{H\text{-}L}(DA) \equiv E_{LUMO}(A) - E_{HOMO}(D)$ value, was chosen to suppress electron transfer from D to A. Indeed, this D/A combination resulted in a new neutral D$_2$A-type layered MOF, [{Ru$_2$^{II,II}(CF$_3$CO$_2$)$_4$}$_2$(BTDA-TCNQ)]·nCH$_2$Cl$_2$·(p-xylene) (**1**) (**Fig. 2a**). In the electron-filling control by an LIB system, since Li-ion insertion into the target material is necessary, we removed the crystal solvent CH$_2$Cl$_2$ by evacuating **1** to produce a space for accommodating Li ions. For the CH$_2$Cl$_2$ removed compound, [{Ru$_2$^{II,II}(CF$_3$CO$_2$)$_4$}$_2$(BTDA-TCNQ)]·(p-xylene) (**1'**)

(**Fig. 2b**), we attempted electron-doping through Li-ion insertion. **Figure 1b** shows the temperature dependence of magnetization of pristine (**1'**) and Li-ion-inserted samples, Li$_x$[{Ru$_2$^{II,II}(CF$_3$CO$_2$)$_4$}$_2$(BTDA-TCNQ)]·(p-xylene). A rapid increase of magnetization around 80 K is observed for the Li-ion-inserted sample at 2.66 V vs. Li/Li$^+$ ($x = 1$). This result indicates that ferrimagnetic order is induced from the paramagnetic state by electron-filling of BTDA-TCNQ units through Li-ion insertion (**Fig. 1a**). Furthermore, we succeeded in reversible phase switching with the discharge/charge cycle of an LIB system between the paramagnetic and ferrimagnetic states (**Fig. 1a**).

The structural variation driven by the accommodation of Li ions in **1'** was confirmed by synchrotron X-ray diffraction measurements. **Figure 2c** shows the powder X-ray diffraction (PXRD) patterns of the pristine sample (**1'**) ($x = 0$) and the Li-ion-inserted sample at 2.66 V vs. Li/Li$^+$ ($x = 1$). The PXRD pattern of the Li-ion-inserted sample is different from that of **1'**, which crystallizes in the triclinic space group P–1 (**Fig. 2b**). Notably, the PXRD pattern of the Li-ion-inserted sample can be indexed to the monoclinic space group C2/m, which is the same as that of the as-synthesized compound **1** containing CH$_2$Cl$_2$ (**Fig. 2a**). These facts indicate that

the crystal structure of **1'** is modified during the process of Li-ion insertion and, ultimately, the material adopts a structure similar to that of the CH$_2$Cl$_2$ solvated sample (**1**). Li ions seem to be inserted into the void spaces located in **1'**, which is produced by removal of CH$_2$Cl$_2$ from **1**, accompanied by expansion of the flexible framework, like recovering to the structure of **1**, without significant collapse of the coordination bonds in the layered framework.

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K. Taniguchi[1], K. Narushima[1], H. Sagayama[2], W. Kosaka[1], N. Shito[1] and H. Miyasaka[1] ([1]Tohoku Univ., [2]KEK-IMSS-PF)

Figure 2: (a) The crystal structure of as-synthesized sample containing CH$_2$Cl$_2$ (**1**). **(b)** The crystal structure of dried sample (**1'**) after removing CH$_2$Cl$_2$. **(c)** The PXRD patterns for the pristine (**1'**) (red line) and the Li-ion-inserted material (2.66 V vs. Li/Li$^+$) (blue line). The pattern of **1** is shown for comparison (black line).
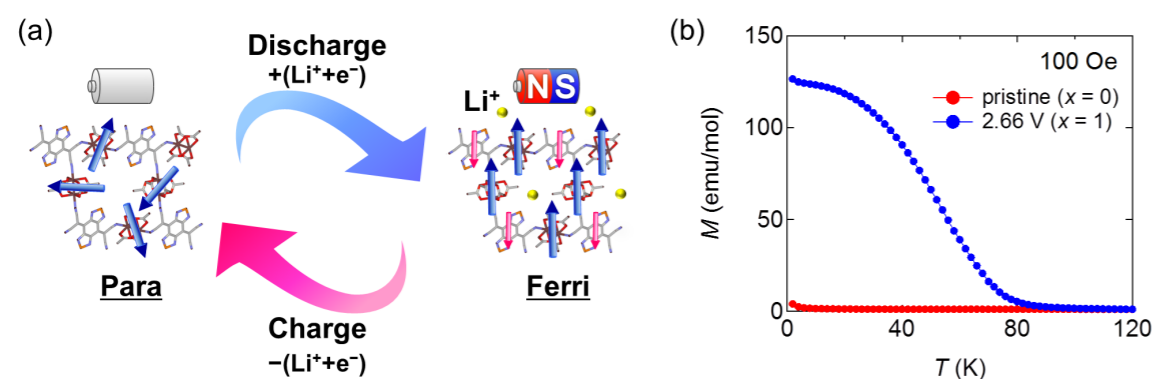

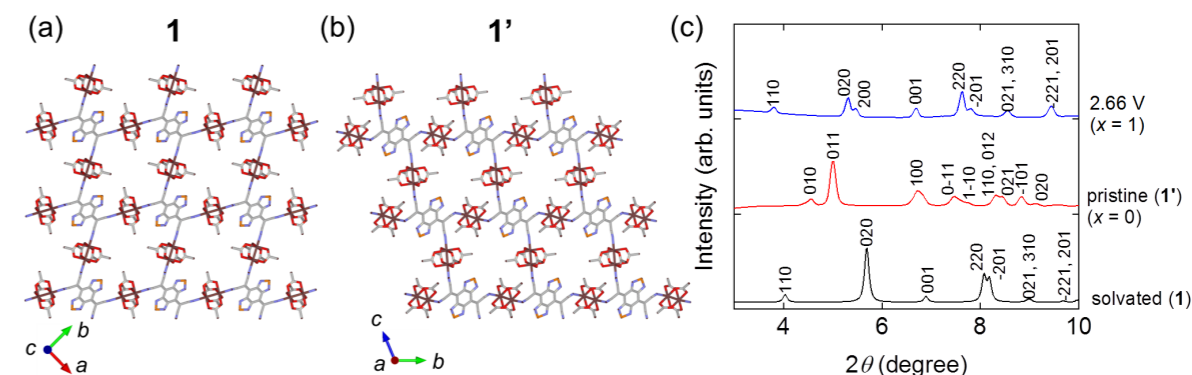**Figure 1: (a)** Schematic figure of magnetism control in D/A-MOF by an LIB system. **(b)** Magnetic phase switching by Li-ion insertion.