Change of magnetic anisotropy induced by a structual transition in a nanochannel molecule-based magnet

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Molecule-based materials are useful candidates to design multi-functional materials.¹ They are flexible as the structural changes can be induced through external stimuli such as light and pressure. In particular, long-range ferromagnetic ordering controlled by molecular adsorption or desorption has been shown as a potential way to develop gas responsive materials.² In this work we designed a flexible molecule-based ferromagnet with molecular formula $Co_7[W(CN)_8]_4Cl_2\cdot24H_2O\cdot3(acetone)$ having tunable crystal structure. This compound has nanochannels in the structures that can change from an open channel form (**open-CoWCl**) to the form of a closed channel (**closed-CoWCl**). The crystal structure and magnetic properties of these two forms were studied.

The red platelet crystals were obtained by adding $Rb^{I}Cl$ and $Rb^{I}_{3}[W^{V}(CN)_{8}]$ aqueous solution dropwise to acetone-water solution of $Co^{II}Cl_{2}$ yielding open form of material. **Open-CoWCl** underwent structural transition and closed the nanochannels when the crystals were exposed to humid air (Figure 1.). Magnetic measurement results revealed that the coercive field of **open-CoWCl** became smaller after this structural transformation. In addition, we confirmed that the magnetic anisotropy of **closed-CoWCl** is smaller than **open-CoWCl** by angulardependent magnetic measurements of the oriented-crystal. Theoretical calculation suggested that the resulting changes in magnetic anisotropy is due to different single-ion anisotropy of cobalt ions and dipole interactions between open and close form.



Figure 1. Crystal structures of **open-CoWCl** and **closed-CoWCl**. (a) View along the *c* axis of **open-CoWCl**. (b) View along the *c* axis of **closed-CoWCl**.

[1] K. Kumar and S. Ohkoshi et al., *Angew. Chem. Int. Ed.*, **2022**, 61, e202201265.
[2] S. Ohkoshi et al., *J. Am. Chem. Soc.*, **2007**, 129, 11, 3084–3085.