Guest-dependent Magnetic and Structural Variations in a Magnetically-bistable 2-D Hollow-Sheet-type Coordination Polymer

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Coordination polymers (CPs) and metal-organic frameworks (MOFs) consisting of metal ions and organic ligands are expected to be chemo-responsive materials, interlocking porous functions and physical properties of the framework.

Here, we prepared a novel CP $\{Fe^{II}(pz)(H_2O)_2[Au^{III}(CN)_4]_2 \cdot H_2O\}$ (pz = pyrazine; **FeAu-H$_2$O**), which formed a 1-D chain-type structure based on cyanide-bridged Au-Fe-Au trinuclear units and pz that bridged between the Fe^{II} sites. **FeAu-H$_2$O** exhibited a dimensional structural conversion to 2-D hollow sheet-type structure of $\{Fe^{II}(pz)[Au^{III}(CN)_4]_2\}$ (**FeAu**) with forming additional Au-CN-Fe bridges accompanying elimination of the coordinated H_2O on the Fe site by dehydration treatment (Fig. 1(a), (b)). The reversible structural change between **FeAu-H$_2$O** and **FeAu** was confirmed by *in situ* PXRD, IR and H_2O adsorption measurements. Furthermore, **FeAu-H$_2$O** and **FeAu** exhibited paramagnetic and cooperative spin transition (ST) behavior, respectively. Thus, H_2O molecules adsorbed in the pore work as a significant factor to break Au-CN-Fe bonds, resulting in the reversible magnetic and structural switching between **FeAu-H$_2$O** and **FeAu**.

We also investigated alcohols (R-OH; R = Me, Et) responsivity for **FeAu**. Rietveld analyses of **FeAu-R-OH** revealed that these compounds maintained the 2-D hollow sheet-type structure with rotation of pillar ligand after uptaking alcohols (Fig.1(c)). Correlation between ST behavior and structural changes were discussed based on the results of temperature dependences of *in situ* magnetic and synchrotron PXRD measurements.

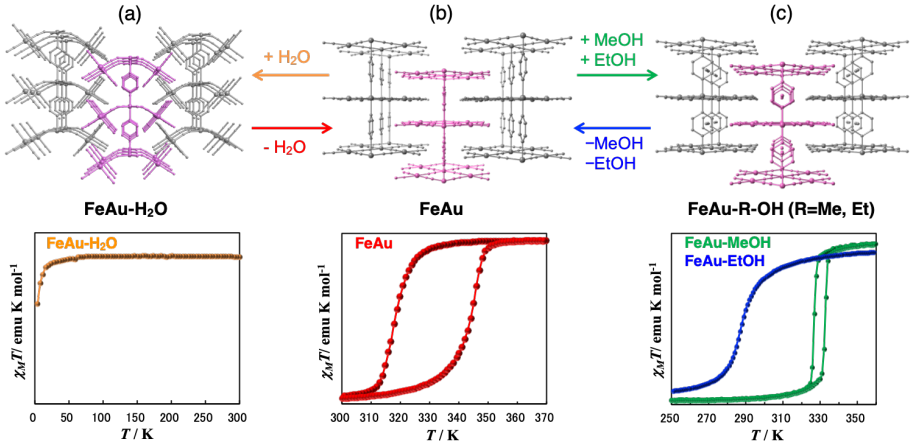

Fig.1 Guest-dependent magnetic and structural change of **FeAu**