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Structural change and spin-crossover switching triggered by adsorption and desorption of organic molecule for assembled iron complex bridged by 1,3-bis(4-pyridyl)propane

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It is possible to construct various structures for assembled iron complexes bridged by bis(4-pyridyl) type ligand. We have studied iron complexes bridged by 1,2-bis(4-pyridyl)ethane (bpa), and revealed the relation between the isomerism for coordinated bpa and the assembled structure, and the relation between the guest molecule and the spin state of iron.^{1,2)} In the present study, we have studied the magnetic behaviors and structural properties for some assembled complexes with more flexible ligand, 1,3-bis(4-pyridyl)propane (bpp), which has three methylenes, by using single crystal X-ray diffraction analyses, Mössbauer spectroscopy, and SQUID measurements.

We synthesized assembled complexes, $\text{Fe}(\text{NCX})_2(\text{bpp})_2$ ($X = \text{S}$ (**1**), Se (**2**), and BH_3 (**3**)) (bpp = 1,3-bis(4-pyridyl)propane). **1** has a novel 2D interpenetrated structure and shows a temperature-independent high-spin state, while **3** has a 2D interpenetrated structure and shows a spin-crossover phenomenon.³⁾ We synthesized $\text{Fe}(\text{NCBH}_3)_2(\text{bpp})_2 \cdot 2(\text{benzene})$ (**4**) which is a benzene-enclathrated complex of **3**, and studied the magnetic behaviors and structural properties.

$\text{Zn}(\text{NCBH}_3)_2(\text{bpp})_2 \cdot 2(\text{benzene})$ (**4'**) with the same structure as **4** has 1D chain structure. Fresh **4** is in a temperature-independent high-spin state. By releasing benzene molecules in the air, **4** becomes $\text{Fe}(\text{NCBH}_3)_2(\text{bpp})_2$. This guest-free **4** is in a low-spin state at low temperatures, and shows a spin-crossover phenomenon. The guest-free **4** has the same structure with **3**, and enclathrates benzene molecules reversibly by setting it in the benzene atmosphere, returning to the temperature-independent high-spin state. This result and powder X-ray diffraction patterns indicated the change of assembled structure; $\text{Fe}(\text{NCBH}_3)_2(\text{bpp})_2 \cdot 2(\text{benzene})$ [1D chains] \leftrightarrow $\text{Fe}(\text{NCBH}_3)_2(\text{bpp})_2$ [2D interpenetrated structure] (Fig. 1). The change between the two structures reveals the bond cleavage between iron atom and ligand in the transformation. In conclusion, we revealed that the spin-crossover switching in **4** is accompanied by the change of assembled structure.

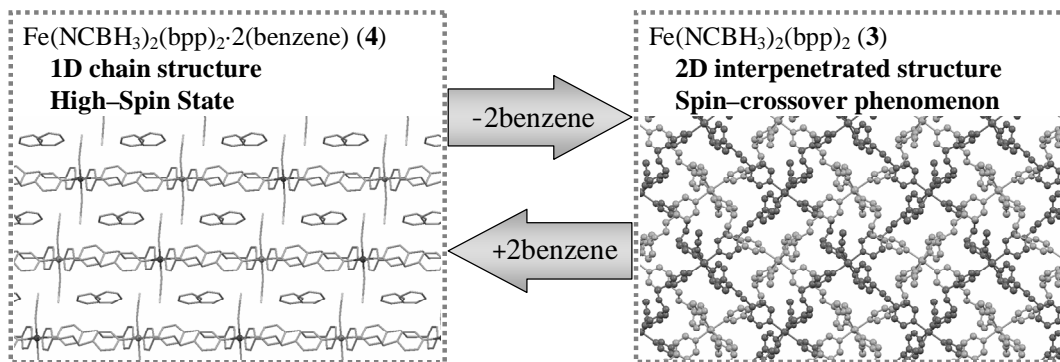


Figure 1. Structural change and spin-crossover switching in **4**.

1) T. Morita et al., *Bull. Chem. Soc. Jpn.*, **2006**, 79, 738. 2) T. Morita et al., *Chem. Lett.*, **2006**, 35, 1042.

3) M. Atsuchi et al., *Chem. Lett.*, **2007**, 36, 1064.