

## Control of spin transition by interface strain in heterostructured metal-organic framework thin film

Metal-organic frameworks (MOFs) are formed by the self-assembly of metal ions and ligands, and thus have a tailor-made framework structure. MOFs show various physical properties (gas separation, switching, catalysis, and so on). For future practical applications of MOFs such as high performance catalysts or chemical sensors, crystalline oriented MOF thin films have been intensively pursued in recent years. Among the proposed thin film fabrication techniques, layer-by-layer method is one of the most well-established bottom-up approaches. In this method, substrates with self-assembled monolayers (SAMs) are fabricated by alternately immersing them in a solution of building blocks. However, during the fabrication process, step-by-step growth at the surface sometimes result in unconventional structures that are not seen in the bulk. For example, heterostructured MOF thin films, in which one MOF is epitaxially grown on top of another MOF, are known to exhibit unique gas separation ability. It should be noted that the heterostructured MOF thin films have tunable interfaces between different MOFs. Thus, the heterostructured MOF thin films have the ability to realize the rational design of MOF interfaces and provide a new research platform.

As a research platform for the heterostructured MOF thin films, Hoffmann-type MOF  $\{Fe(pz)[M(CN)_4]\}$  [ $pz = \text{pyrazine}$ ;  $M = Ni$  ( $Nipz$ ),  $M = Pt$  ( $Ptpz$ )] is a very attractive candidate because it is an iron(II) coordination compound with a  $3d^6$  electron configuration and exhibits spin transitions induced by temperature, light, and so on [1]. These electronic configurations can move between paramagnetic high-spin (HS) and diamagnetic low-spin (LS) states, with accompanying structural changes.

In this study, we show the first example of strain-controlled spin transition in a heterostructured MOF thin film [2]. As shown in Fig. 1, we fabricated a heterostructured MOF thin film **Nipz5L-Ptpz30L**, composed of 5 layers of **Nipz** (bottom buffer layer) and 30 layers of **Ptpz** (upper layer), using the layer-by-layer method to control the spin transition behavior. **Nipz5L-Ptpz30L** showed a remarkable increase in the spin transition temperature.

In order to confirm the structure and orientation of **Nipz5L-Ptpz30L**, synchrotron XRD measurements were carried out using SPing-8 BL13XU ( $\lambda = 1.550 \text{ \AA}$ , room temperature). Figure 2 shows the synchrotron XRD profiles of different scattering geometries of **Nipz5L-Ptpz30L** in horizontal (in-plane) and vertical (out-of-plane) directions with respect to the substrate.

The in-plane XRD pattern shows peaks indexed as  $hk0$ , showing periodic ordering of cyano-bridged 2D layers. However, the out-of-plane pattern shows two peaks, 001 and 002, showing interlayer ordering through pyrazine.  $hk0$  and  $00l$  diffraction peaks are observed separately in the in-plane and out-of-plane patterns. The data clearly show that **Nipz5L-Ptpz30L** has high crystallinity and well-controlled orientations of crystal growth in both in-plane and out-of-plane directions. Furthermore, the lattice constants of **Nipz5L-Ptpz30L** (tetragonal,  $P4/mmm$ ,  $a = 7.28 \text{ \AA}$ ,  $c = 7.08 \text{ \AA}$ ) were determined from the XRD results. These lattice constants are significantly smaller than the bulk **Ptpz** in the HS state ( $a = 7.53 \text{ \AA}$ ,  $c = 7.32 \text{ \AA}$ , 293 K), but similar to the bulk **Ptpz** in the LS state ( $a = 7.33 \text{ \AA}$ ,  $c = 6.94 \text{ \AA}$ , 293 K) [1], which indicates that **Nipz5L-Ptpz30L** is in LS state at room temperature.

The Raman spectrum of MOF shows a strong pyrazine internal vibration mode between  $600$  and  $1600 \text{ cm}^{-1}$ . As a probe of the change in spin state, it is well known that the strong intensity enhancement of the pyrazine stretching mode  $\nu(\text{ring})$  at  $1030 \text{ cm}^{-1}$  is a useful marker for the transition from the LS state to the HS state. When  $\nu(\text{ring})$  is normalized to the intensity of the CH bending mode  $\delta(\text{CH})$  at  $1230 \text{ cm}^{-1}$ , the  $\nu(\text{ring})$  mode becomes a quantitative measure of the spin state. Therefore, VT Raman spectra were measured in order to investigate the spin transition behavior. As shown in Fig. 3(a), the intensity ratio between the  $\nu(\text{ring})$  and  $\delta(\text{CH})$  modes clearly explains the spin transition behavior. During the heating process, **Nipz5L-Ptpz30L** shows a spin transition from 370 K to 400 K, and during the cooling process, it shows

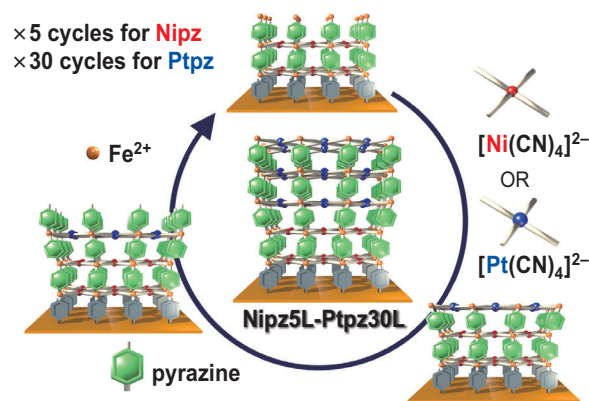


Fig. 1. Fabrication process of heterostructured thin film (**Nipz5L-Ptpz30L**).

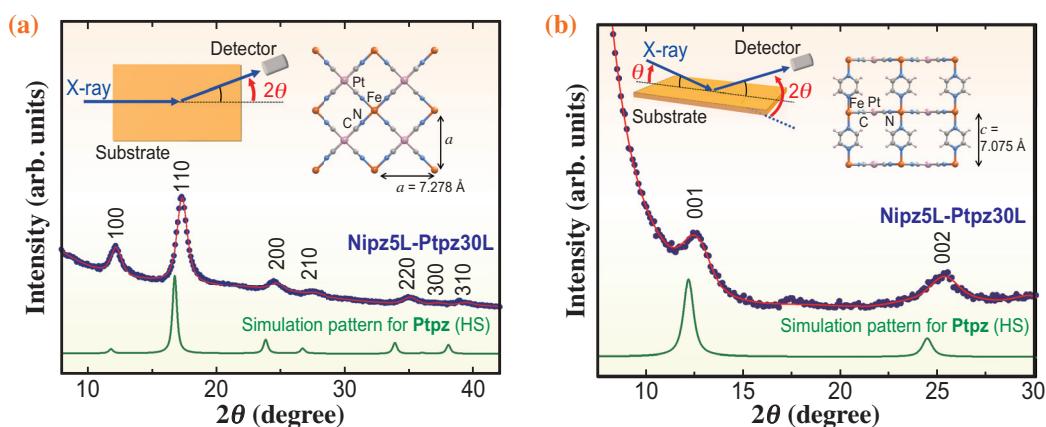


Fig. 2. Synchrotron XRD profiles of **Nipz5L-Ptpz30L**. (a) In-plane XRD patterns. (b) Out-of-plane XRD patterns.

hysteresis at  $\sim 380\text{K}$ , indicating that a first-order spin transition occurs. The spin transition temperatures ( $T_c$ ) of **Nipz5L-Ptpz30L** during the cooling process ( $T_c^\downarrow$ ) and heating ( $T_c^\uparrow$ ) were  $362\text{K}$  and  $388\text{K}$ , respectively, where  $T_c$  is defined as the intermediate temperature at which the normalized intensity ratio reaches 0.65. **Ptpz30L** showed little change compared to bulk **Ptpz**. On the other hand, **Nipz5L-Ptpz30L** showed an increase in  $T_c$  of  $\sim 80\text{K}$ .

In the case of spin-transition compounds such as Hoffmann-type MOFs, a strong ligand field stabilizes the LS state: compressive strain on the **Ptpz** layer brings the CN ligand closer to  $\text{Fe}^{2+}$  (Fig. 3(b)), the level

of  $d_{x^2-y^2}$  orbitals increases due to  $\sigma$ -donation from CN ligand to  $\text{Fe}^{2+}$ , and the level of  $t_{2g}$  orbitals decreases due to  $\pi$ -back donation from  $\text{Fe}^{2+}$  to CN ligand. As a result, the ligand field around  $\text{Fe}^{2+}$  becomes stronger and the LS state becomes more stable.

Therefore, we have demonstrated for the first time that the spin transition behavior of MOFs can be controlled by fabricating nanometer-sized heterostructured thin films. These results provide useful insights into basic science for the future practical application of MOFs with various physical properties by rationally verifying the interfacial strain of heterostructured thin films.

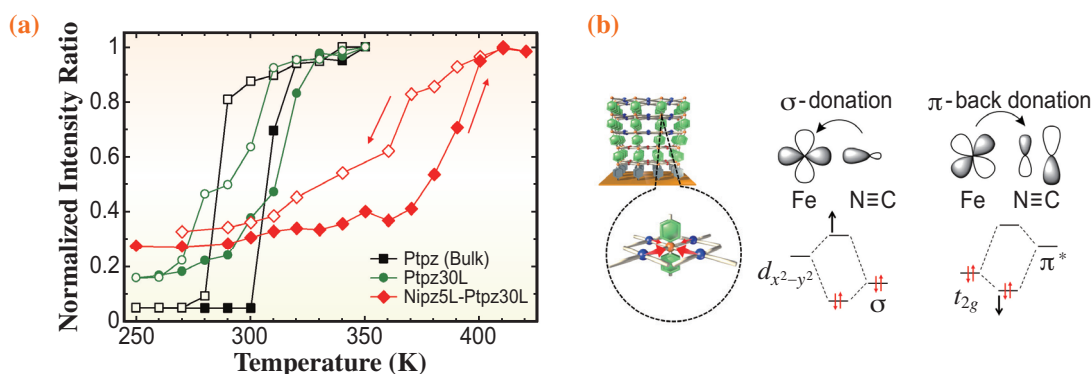


Fig. 3. (a) Temperature dependence of the normalized Raman intensity ratio. (b) Schematic representations of increase in spin transition temperature induced by compressive strain.

Tomoyuki Haraguchi

Department of Chemistry, Tokyo University of Science

Email: haraguchi@rs.tus.ac.jp

### References

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- [2] T. Haraguchi, K. Otsubo, O. Sakata, A. Fujiwara, H. Kitagawa: *J. Am. Chem. Soc.* **143** (2021) 16128.