

# Temperature-dependent XAFS study for guest molecule inserted spin crossover complex: Fe[4-(3-Pentyl)pyridine]<sub>2</sub>[Au(CN)<sub>2</sub>]<sub>2</sub> · n Guest

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Spin crossover (SCO) behavior between high-spin (HS) and low-spin (LS) states in transition metal complexes are derived from the specific electronic configurations between  $3d^4$  and  $3d^7$ , resulting from the external stimuli such as temperature, light, pressure, and guest molecules insertion. There are some reports inserting the clathrates into SCO complexes. One of the clathrate inserted SCO compounds Fe(bpeben)[Pt(CN)<sub>4</sub>] · nH<sub>2</sub>O · 0.5bpeben, bpeben = 1,4-bis(4-pyridylethynyl)benzene, have been synthesized, which exhibits a gradual SCO in  $n = 0$  and an abrupt SCO transition in  $n = 1.5$  [1]. Recently, the spin transition depending on the guest molecules in Fe[4-(3-Pentyl)pyridine]<sub>2</sub>[Au(CN)<sub>2</sub>]<sub>2</sub> · n Guest, where the Guest is 4-(3-Pentyl)pyridine, has been also developed [2]. However, precise electronic and structural properties have not been investigated explicitly. In this study, we aim to investigate the electronic and structural properties across the SCO in Fe[4-(3-Pentyl)pyridine]<sub>2</sub>[Au(CN)<sub>2</sub>]<sub>2</sub> · *o*-xylene by using temperature-dependent X-ray absorption fine structure (XAFS) and extended XAFS (EXAFS).

The guest *o*-xylene inserted complex of Fe[4-(3-Pentyl)pyridine]<sub>2</sub>[Au(CN)<sub>2</sub>]<sub>2</sub> · *o*-xylene was synthesized by the liquid reaction using the Mohr's salt of Fe[(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O], ascorbic acid, K[Au(CN)<sub>2</sub>], *o*-xylene and 4-(3-Pentyl)pyridine, which were mixed with all reagents together. The powder samples were obtained rapidly by this reaction. Temperature-dependent XAFS and EXAFS were performed at BL-9C, Photon Factory (KEK). The sample used for XAFS measurements was diluted by BN powder and formed into pellets. The sample was cooled by the conventional closed He ion cryostat from room temperature to 20 K.

The crystal structure determined by the single-crystal X-ray diffraction (XRD) is shown in the inset of Fig. 1. The magnetic properties measured by superconducting quantum interference device (SQUID) shown in Fig. 1 reveals the SCO transition at 196 K with decreasing temperature and at 200 K with increasing temperature. There was the temperature width for hysteresis of 4 K. Without inserting the clathrates, the HS states are maintained without SCO for all temperature.

Figure 2 shows the temperature-dependent XAFS spectra of Fe[4-(3-Pentyl)pyridine]<sub>2</sub>[Au(CN)<sub>2</sub>]<sub>2</sub> · *o*-xylene for Fe *K*-edge and Au *L*-edge. In the Fe *K*-edge XAFS spectra shown in Fig. 2 (a), the main peak positions shifts toward higher photon energy side with decreasing temperature, which can be explained

by the HS-LS transitions through the changes of the crystal field strength by temperature.

Figure 2 (b) displays the Au *L*-edge XAFS spectra. Contrary to Fe *K*-edge XAFS spectra, the peak positions of the Au *L*-edges remain unchanged across the SCO transition, which suggests that the Au atoms do not contribute to the SCO transition directly.

The insertion of guest molecules into the host complex promotes the SCO because of the increase of chemical pressure from the guest insertion and host-guest interaction. We also found that the spin transition temperature depends on the guest molecule sizes of *o*-, *m*-, *p*- clathrates. In the case of guest molecule of *para*-type, the highest spin transition temperature was achieved, suggesting that the chemical pressure by the largest molecule sizes in the isomers promotes the strong interaction between guest and host molecules.

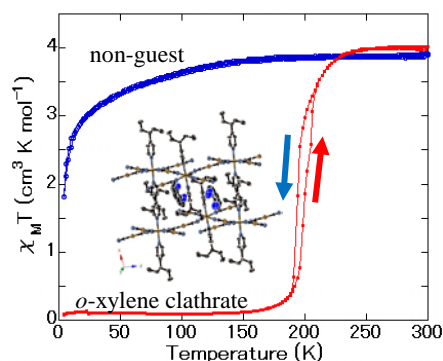


Fig. 1. Magnetic properties of Fe[4-(3-Pentyl)pyridine]<sub>2</sub>[Au(CN)<sub>2</sub>]<sub>2</sub> · n Guest, Guest = non-guest and *o*-xylene, measured by SQUID. Inset shows the crystal structure determined by XRD.

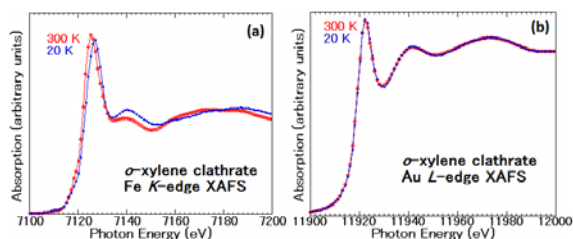


Fig. 2. Temperature-dependent XAFS spectra of Fe[4-(3-Pentyl)pyridine]<sub>2</sub>[Au(CN)<sub>2</sub>]<sub>2</sub> · *o*-xylene, for (a) the Fe *K*-edge and (b) the Au *L*-edge.

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