

## Guest molecule inserted spin crossover complexes: Fe[4-(3-Pentyl)pyridine]<sub>2</sub>[Au(CN)<sub>2</sub>]<sub>2</sub> · *n* Guest

Yusuke Ueki,<sup>1</sup> Jun Okabayashi,<sup>2\*</sup> and Takafumi Kitazawa<sup>1</sup>

<sup>1</sup> Department of Chemistry, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan

<sup>2</sup> Research Center for Spectrochemistry, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

The spin crossover (SCO) complexes represent some kinds of functional molecular materials possessing the specific electronic configurations between high-spin (HS) and low-spin (LS) states in transition metals from  $3d^4$  to  $3d^7$  by external stimuli such as temperature, light, pressure, and guest molecules insertion. The Hofmann-type complexes are composed of linear units  $[M^I(\text{CN})_2]$  ( $M^I = \text{Cu}, \text{Ag}, \text{and Au}$ ) or planar units  $[M^{II}(\text{CN})_4]$  ( $M^{II} = \text{Ni}, \text{Pd}, \text{and Pt}$ ), which are investigated by many research groups [1]. Recently, the SCO complex accommodated 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 synthesized [2]. However, precise electronic and structural properties have not been investigated explicitly in the SCO clathrate compound. In this study, we aim to investigate the electronic and structural properties across the spin transition in Fe[4-(3-Pentyl)pyridine]<sub>2</sub>[Au(CN)<sub>2</sub>]<sub>2</sub> · guest (guest = chlorobenzene: **1**, *o*-dichlorobenzene: **2**, *m*-dichlorobenzene: **3**, *p*-dichlorobenzene: **4**) by using temperature-dependent X-ray absorption fine structure (XAFS) and extended XAFS (EXAFS) [3].

The guest molecule inserted complexes into host structure Fe[4-(3-Pentyl)pyridine]<sub>2</sub>[Au(CN)<sub>2</sub>]<sub>2</sub> were synthesized by the liquid reaction using the Mohl'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>], guest molecules and 4-(3-Pentyl)pyridine, which were mixed with all reagents together in air. The powder samples were prepared 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 samples were cooled by the conventional closed He ion cryostat from room temperature to 20 K.

The crystal structures of *o*-dichlorobenzene clathrate (**1**) and *p*-dichlorobenzene clathrate (**4**) were determined by the single-crystal X-ray diffraction (XRD). The magnetic properties measured by superconducting quantum interference device (SQUID) shown in Fig. 1 reveals the spin transition depending on the guest molecule shape. The spin states converted from the HS state at room temperature to the LS state at low temperature around 200 K. The clathrate **4** achieved the highest spin transition 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*-dichlorobenzene for Fe *K*-edge and Au *L*<sub>3</sub>-edge. In the Fe *K*-edge XAFS spectra shown in Fig. 2 (left), the main peak positions shift 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 (right) displays the Au *L*<sub>3</sub>-edge XAFS spectra. Contrary to Fe *K*-edge XAFS spectra, the peak positions of the Au *L*<sub>3</sub>-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 structure promotes the spin transition 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. The guest molecule shape influences the host structure and the spin transition temperature. In the case of *para*-type guest molecule, the highest spin transition temperature was achieved through the host-guest hybridization [3].

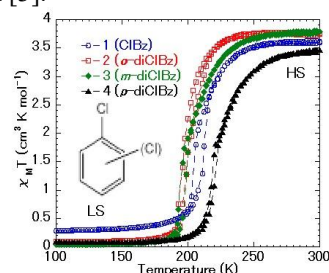


Fig. 1, Magnetic properties of Fe[4-(3-Pentyl)pyridine]<sub>2</sub>[Au(CN)<sub>2</sub>]<sub>2</sub> · *n* Guest, Guest = chlorobenzene: **1**, *o*-dichlorobenzene: **2**, *m*-dichlorobenzene: **3**, *p*-dichlorobenzene: **4**) measured by SQUID.

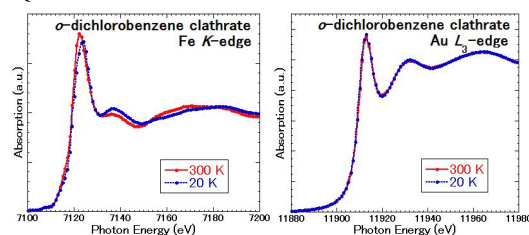


Fig. 2, Temperature-dependent XAFS spectra of Fe[4-(3-Pentyl)pyridine]<sub>2</sub>[Au(CN)<sub>2</sub>]<sub>2</sub> · *o*-dichlorobenzene, for the Fe *K*-edge (left) and the Au *L*<sub>3</sub>-edge (right).

- [1] M. Neville *et al.*, Inorg. Chem., **55**, 10490 (2016).  
 [2] T. Kosone and T. Kitazawa, Inorg. Chim. Acta. **439**, 159 (2016).  
 [3] Y. Ueki, J. Okabayashi, T. Kitazawa, Chem. Lett. **46**, 747 (2017).

\*e-mail: jun@chem.s.u-tokyo.ac.jp