

XAFS Study of Multistep Spin Crossover in an Iron(II) Family Mediated by Flexible Anion Ordering

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Spin crossover (SCO) is one of the most intriguing properties of molecular-based switching materials. Two distinct spin states of SCO complexes [i.e., high-spin (HS) and low-spin (LS) states] can be accessible by external stimuli, such as temperature, pressure, light, or magnetic field. SCO compounds are also known to exhibit not only one-step LS \leftrightarrow HS conversion but also stepped SCO with various thermal dependencies, such as gradual, abrupt, hysteretic, or a complex combination of them. Abruptness and hysteresis of spin transition are brought by cooperativity between SCO sites through the utilization of bridging ligands in polymeric systems and intermolecular interactions in supramolecular systems for potential applications in data storages, sensors, and display devices.

Here, we report an unprecedented route triggering multistep SCO with hysteresis through strategic regulation of flexible anion ordering related to the substituent modifications by the comprehensive study of a new Fe^{II} family, [FeL^{4-R-Ph}](NTf₂)₂ {where L^{4-R-Ph} = tris[2-([1-(4-R-phenyl)-1H-1,2,3-triazol-4-yl]methylidene)amino-ethyl]amine, where R = Me (**1**), Cl (**2**), Br (**3**), and MeO (**4**)}, including temperature dependencies of magnetic susceptibilities and x-ray absorption fine structure (XAFS) spectra [1].

All the synthetic procedures were performed in air. The fundamental centers around the Fe sites [FeL^{4-R-Ph}]²⁺ are consisted as shown in Fig. 1(a). The samples with different ligand ions depending on the electron negativities are prepared. The powder samples were diluted with BN powders and were formed to pellets for the measurements in the transmission mode at KEK-PF BL-12C. The sample was cooled using a conventional He cryostat. Transmitted X-rays were detected by the ionization chamber filled by Ar gas.

Figure 1(b) shows the magnetic susceptibility of complexes **1-4**. Upon cooling from 300 K, the χ_{MT} value continuously decreases, indicating the complete HS \rightarrow LS spin transition. In this transition, three different steps were observed for **2**: a first gradual decrease between 300 K and 195 K, a second gradual one between 177 K and 151 K, and a third abrupt one between 143 K and 137 K, expected for an approximately two-thirds of Fe^{II} sites are HS state as an intermediate state.

Figure 1(c) shows the temperature-dependent XAFS spectra for **1-4** for Fe K-edge. Spectral line shapes and peak positions confirm the Fe^{II} ionic states for all complexes. Main peak in Fe K-edge shifts toward the higher photon energy side with decreasing temperature through SCO. These shifts are explained by the changes

between HS and LS states, because of the modulation of the ligand field strength by temperature, which is derived from the small ionic radii in LS states determined by XRD. Small but finite intensities in pre-edge structures appear at \sim 7110 eV, which are originated from the transition between 1s and 3d levels through the prohibited transitions. Considering the ligand field symmetry, ⁴T_{1g} and ⁴T_{2g} multiplets in HS states and ²E_g multiplet in LS states become the candidates for the pre-edge structures. The pre-edge structures consist of two types of peaks at 7110 and 7113 eV. At the HS states, higher energy sides are enhanced, which is consistent with the previous analysis. In **1**, line shapes remain unchanged for RT and 60 K. In **2** and **3**, line shapes changed to those in LS states, which is consistent with Mössbauer and magnetic susceptibility measurements. These suggest that the Fe^{II} sites are strongly affected by the ligand field.

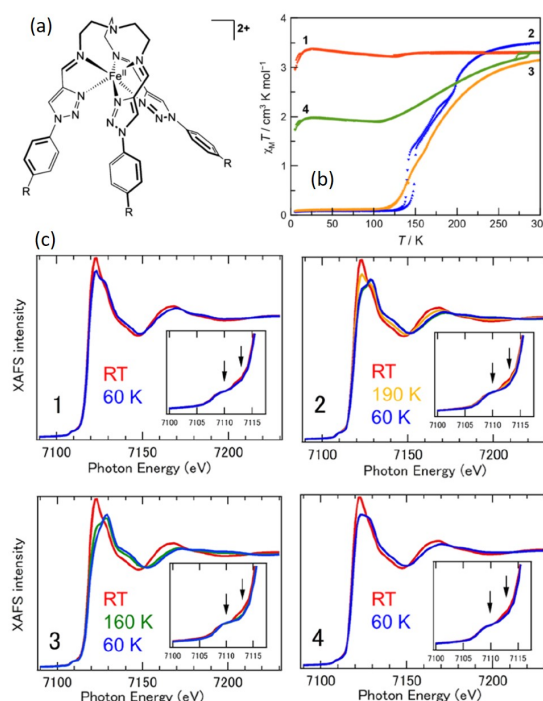


Fig. 1, (a) Structures of [FeL^{4-R-Ph}]²⁺ for samples **1-4**. (b) Magnetic properties, and (c) Fe K-edge XAFS spectra. Insets show the expanded views of pre-edge regions [1].

References

- [1] H. Hagiwara, J. Okabayashi *et al.*, *Inorg. Chem.* **59**, 9866 (2020).