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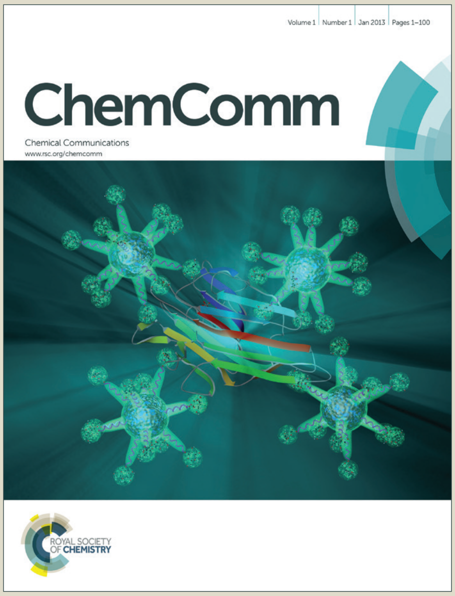

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X-ray Induced Phase Transitions by Selective Excitation of Heterometal ions in a Cyanide-bridged Fe-Co Molecular Square

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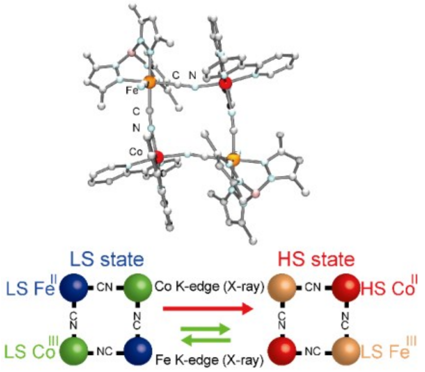
A cyanide-bridged tetranuclear Fe-Co complex showed electron-transfer-coupled spin transitions induced by X-ray irradiation. Single crystal X-ray diffraction measurements and X-ray absorption spectroscopy revealed that the X-ray-induced phase transition ratio was significantly altered by the selective excitation of the metal ions.

The development of systems that exhibit reversible switching of their electronic state upon exposure to light irradiation, is a key approach to the production of functional materials.[1] Cyanide-bridged Prussian blue analogues (PBAs) have been investigated as photo-switchable bistable systems. In 1996, Hashimoto et al. reported the first example of light-induced magnetization in $K_{0.2}Co_{1.4}[Fe(CN)_6]\cdot 6.9H_2O$, in which red light excitation of the $Fe^{II}\rightarrow Co^{III}$ intervalence charge transfer (IVCT) band at low temperature induced phase transition from a diamagnetic ([LS Co^{III} – LS Fe^{II}]) phase to a ferrimagnetic ([HS Co^{II} – LS Fe^{III}]) phase (HS and LS = high and low spin).[1d] The reverse transition was achieved by blue light irradiation. The photomagnetism originates from the light-induced electron transfer between the metal centers and the associated spin transition of the cobalt ions: this phenomenon and its thermally induced equivalent can be described as electron-transfer-coupled spin transition (ETCST; or as charge-transfer-induced spin transition (CTIST)).[2]

In discrete molecular system, the first observation of thermal ETCST behavior was made in a pentanuclear $[Co_3Fe_2]$ cluster,[3a] and was followed by the first report of light-induced ETCST in an octanuclear $[Co_4Fe_4]$ cluster.[3b] Recently, reversible light-induced ETCST was also demonstrated in a $[Co_2Fe_2]$ cluster by alternate irradiations with different wavelengths of light.[3e] The first example of light-induced single molecular magnetism in a hexanuclear $[Co_2Fe_4]$ complex was currently observed by our group,[3d] and was followed by the observation of light-induced single chain magnetism in a cyanide-bridged 1D [CoFe] complex.[1c] In previous work, we have studied a cyanide-bridged molecular square, $[Co_2Fe_2(CN)_6(tp^*)_2(bpy^*)_4](PF_6)_2\cdot 2MeOH$ (**1**) (tp* = hydrotris(dimethylpyrazol-1-yl)borate and bpy* = di-butyl-2,2'-bipyridine), which exhibited thermal and light-induced ETCST between LS ($[(LS\text{-}Co^{III})_2(LS\text{-}Fe^{II})_2]$) and HS ($[(HS\text{-}Co^{II})_2(LS\text{-}Fe^{III})_2]$) states.[3c, 3f]

X-ray absorption spectroscopy (XAS) is a powerful tool to investigate the spin and oxidation states of metal ions. In this work, we performed XAS measurements to investigate the electronic state changes associated with thermal ETCST, and accidentally found X-ray-induced ETCST behavior to occur in **1**. Although X-ray-induced phase transitions have been reported in bulk PBAs, spin-crossover Fe^{II} complexes, and valence tautomeric Co dioxolene complexes,[4,8] complete X-ray-induced phase transitions have never been reported in any discrete molecular system. Complex **1** exhibited the phase transitions as a result of electron transfers between Co and Fe ions; therefore selective excitation of the individual metal ions is predicted to alter the conversion ratio of the X-ray-induced phase transitions. The excitation energy dependence of the phase transition has yet to be investigated in any system. We report here the first example of X-ray-induced ETCST in a discrete molecule, complex **1** (Scheme 1), and propose a mechanism for the ETCST based on our experiments into the X-ray energy dependence of the LS→HS* conversion ratio (HS* = metastable HS state generated by X-ray irradiation).



Scheme 1. Molecular structure of **1** in the X-ray-induced metastable HS* state at 14 K, where the *tert*-butyl groups on bpy* were omitted for clarity (top). The electronic state changes associated with X-ray-induced ETCST in **1** (bottom).

Co and Fe K-edge XAS spectra were recorded on single crystals of **1** to confirm the electronic state changes of the metal ions upon thermal ETCST. The XAS spectra of **1** showed absorption edges at 7.724 (HS Co^{II}) and 7.128 keV (LS Fe^{III}) at 330 K, and the edges shifted to 7.729 (LS Co^{III}) and 7.126 keV (LS Fe^{II}) upon cooling to 15 K, where the absorption edge corresponds to the inflection point at the onset of the K-edge absorption peak (Fig. S1).[5] The K-edge XAS spectra of [Co^{II}(H$_2$O)$_6$](NO$_3$)$_2$ and K$_3$[Co^{III}(CN)$_6$] were reported to show absorption maxima at 7.725 and 7.728 keV for HS Co^{II} and LS Co^{III} ions, while K$_4$[Fe^{II}(CN)$_6$] and K$_3$[Fe^{III}(CN)$_6$] showed them at 7.130 and 7.131 keV for LS Fe^{II} and LS Fe^{III} ions, respectively.[6] Although the spectral change of Fe K-edge absorption in **1** is small (Fig. S1), the observed shift of Fe absorption edge (2 eV) is comparable to the reported values. It is well known that the Fe K-edge spectra for LS Fe(II) and LS Fe(III) ions show only slight differences due to the lack of spin transition upon oxidation state change. These spectral changes upon temperature variation were, therefore, attributable to thermal ETCST between the HS ([(HS-Co^{II})$_2$(LS-Fe^{III})$_2$]) and the ([(LS-Co^{III})$_2$(LS-Fe^{II})$_2$]) LS states.[7]

We noticed that repeated XAS measurements on the LS state at 15 K caused gradual changes in the absorption spectra over time. This result implied the occurrence of some phase transition from the LS phase induced by the incident X-ray irradiation. The Co and Fe K-edge XAS spectral changes were, therefore, recorded at 15 K upon X-ray irradiation at 7.725 keV, an excitation energy close to that of the Co K-edge absorption (Fig. 1, Fig. S2). After X-ray irradiation for 270 mins, differences were observed in both Co and Fe K-edge XAS spectra: the absorption edge shifted from 7.729 to 7.724 keV for the Co K-edge and from 7.126 to 7.128 keV for the Fe K-edge, corresponding to [Co^{III}→Co^{II}] and [Fe^{II}→Fe^{III}] conversions, respectively (Fig. S2). The resultant Co K-edge spectra were deconvoluted using the spectra for the thermally generated pure HS and LS states, and the HS/LS ratio after irradiation for 270 mins was estimated to be 90:10, indicating that almost complete X-ray-induced ETCST from the LS to the HS* state had occurred (Fig. 2, S6, Table S3). It should be noted that the LS profile was recovered by heating the sample to 100 K, indicating that the spectral changes upon X-ray irradiation were not due to radiation damage or decomposition (Fig. S3). The X-ray-induced ETCST was also confirmed by single crystal X-ray diffraction measurements at 14 K after X-ray irradiation (7.725 keV) for 1.5 hours (Scheme 1). The average coordination bond distances for the Co and Fe sites were 1.920(5) and 1.960(5) Å at 24 K before X-ray irradiation, which are characteristic of LS Co(III) and LS Fe(II) ions in the LS state. After the X-ray irradiation, the corresponding distances were 2.039(5) and 1.969(6) Å, respectively. These distance changes are comparable to those observed in the thermally generated HS state (Fig. S4, S5 and Table S1, S2).[3c] The slight deviations are caused by the incomplete conversion of the LS state to the X-ray induced HS state. Further X-ray irradiation led to loss of crystallinity, possibly due to increasing defects in the crystal lattice, which prevented the structural analyses of the completely converted HS state.

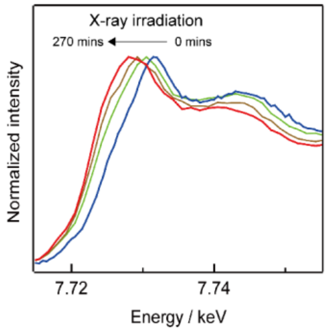


Fig. 1 Co K-edge spectral change upon X-ray irradiation at 7.725 keV for 270mins. The spectral change indicates the electronic state change from the LS to the metastable HS* state in **1** upon X-ray irradiation.

Excitation energy dependence was studied for the X-ray-induced ETCST behavior in **1** using synchrotron radiation with energies of E = 7.129, 7.725, and 12.40 keV, the former two correspond to the Fe and Co K-edges, respectively, and 12.40 keV is greater energy than either K-edge absorption. Fig. 2 shows the time course of the conversion ratios of the LS state to the HS* state when **1** was irradiated with 7.129, 7.725, 12.40 keV X-rays (Fig. S7, Table S3). Upon irradiation of the LS state with 7.129 keV X-rays (Fe K-edge), the HS fraction gradually increased until it reached a saturated conversion ratio of 48% after 10 hours, indicative of partial X-ray-induced ETCST. On the other hand, almost complete conversions to the HS state were achieved by irradiation for ca. 4 hours using both 7.725 keV and 12.40 keV X-rays. Consequently, X-ray-induced ETCST showed significant energy-dependence, and excitation of the Co K-edge was crucial for the complete conversion of the LS state to the HS* state. Again note that the spectra showed the samples to thermally relax back to the LS state upon heating to 100 K (Fig. S8).

The partial X-ray-induced spin transitions in a spin-crossover Fe(II) complex and a valence tautomeric Co dioxolene complex were ascribed to the secondary electrons generated by the X-ray irradiation, which induced the excitation of charge transfer bands to form the metastable state.[8,9] However, the secondary electrons have broad energy distributions, and both forward and reverse phase transitions were simultaneously induced by non-selective excitation. To explain the complete X-ray-induced transition in **1**, we considered the differences between the 3d orbital energy levels in Co and Fe ions. The Co K-edge excitation of the LS state makes a hole in the Co 1s orbital, leading to electronic configurations of Co[$(1s)^1\cdots(3d)^6\cdots(np)^1$] and Fe[$(1s)^2\cdots(3d)^6$].

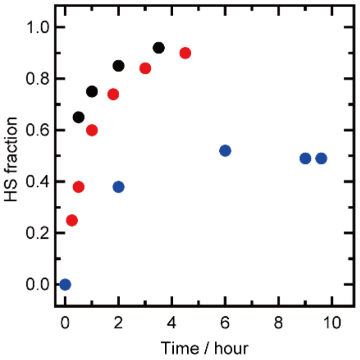


Fig. 2 Time course of the HS fractions upon X-ray irradiation at 7.129 keV (blue), 7.725 keV (red) and 12.40 keV (black).

The electron then de-excites through the radiative or Auger process to form a transient state with a hole in the Co 3d orbital, the configuration of Co[$(1s)^2\cdots(3d)^5\cdots(np)^1$] and Fe[$(1s)^2\cdots(3d)^6$]. In the LS state, the energy of the LS-Fe^{II} t_{2g} orbital is higher than that of the LS-Co^{III} t_{2g} orbital,[10] as confirmed by the redox potentials for the Co^{II}/Co^{III} and Fe^{II}/Fe^{III} processes, respectively (Fig. S9, S10). The electron transfer from Fe^{II} to Co^{III} ions is, therefore, suggested to occur in the transient state.[11] Electron transfer from the Fe^{II} to the Co^{III} ions followed by the relaxation of the excited electrons can lead to the generation of the HS* state. On the other hand, in the transient state generated by the Fe K-edge excitation (Co[$(1s)^2\cdots(3d)^6$] and Fe[$(1s)^1\cdots(3d)^6\cdots(np)^1$]), electron transfer from the Fe^{II} to the Co^{III} ions is likely to be unfavorable because the energy level of the Fe^{II} t_{2g} orbital is higher than that of the Co^{III} t_{2g} orbital.[11] As a result, conversion from the LS to the HS state by Fe K-edge excitation is likely to be very inefficient. Consequently, Co K-edge excitation of the LS state can induce effective conversion to the HS* state, while Fe K-edge excitation leads to only partial conversion, possibly due in part to bi-directional conversion by the secondary electrons (Scheme 1). To investigate the potential for reverse X-ray-induced ETCST by Fe K-edge excitation, we irradiated the HS* state (generated by 12.40 keV X-ray) at 7.129 keV, and found that partial back conversion from the HS* to the LS state occurred, reaching a HS/LS ratio of 75/25 (Fig. S11).

In summary, we investigated the electronic state changes associated with thermal and X-ray-induced ETCST by XAS measurements in a discrete molecular system, complex **1**. The first example of X-ray-induced ETCST in a discrete system was confirmed by single crystal X-ray diffraction and XAS measurements. In addition, it was found that the X-ray-induced ETCST conversion ratio can be significantly altered by the selective excitation of the metal ions.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Experimental and crystallographic details and XAS spectra. CCDC reference numbers 967796 (before irradiation) and 967797 (after X-ray irradiation). See DOI: 10.1039/c000000x/

1 (a) M. Irie, *Chem. Rev.*, 2000, **100**, 1685; (b) O. Sato, J. Tao, Y.-Z. Zhang, *Angew. Chem. Int. Ed.*, 2007, **46**, 2152; (c) N. Hoshino, F. Iijima, G. N. Newton, N. Yoshida, T. Shiga, H. Nojiri, A. Nakao, R. Kumai, Y. Murakami, H. Oshio, *Nat. Chem.*, 2012, **4**, 921; (d) O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, *Science*, 1996, **272**, 704.

2 G. N. Newton, M. Nihei, H. Oshio, *Eur. J. Inorg. Chem.*, *2011*, 3031.

3 (a) C. P. Berlinguette, A. Dragulescu-Andrasi, A. Sieber, J. R. Galán-Mascarós, H.-U. Güdel, C. Achim, K. R. Dunbar, *J. Am. Chem. Soc.*, 2004, **126**, 6222; (b) D. Li, R. Clérac, O. Roubeau, E. Harté, C. Mathonière, R. Le Bris, S. M. Holmes, *J. Am. Chem. Soc.*, 2008, **130**, 252; (c) M. Nihei, Y. Sekine, N. Suganami, H. Oshio, *Chem. Lett.*, 2010, **39**, 978; (d) M. Nihei, Y. Okamoto, Y. Sekine, N. Hoshino, T. Shiga, I. P. Liu, H. Oshio, *Angew. Chem. Int. Ed.*, 2012, **51**, 6361; (e) A. Mondal, Y. Li, M. Seuleiman, M. Julve, L. Toupet, M. Buron-Le Cointe, R. Lescouëzec, *J. Am. Chem. Soc.*, 2013, **135**, 1653; (f) M. Nihei, Y. Sekine, N. Suganami, K. Nakazawa, A. Nakao, H. Nakao, Y. Murakami, H. Oshio, *J. Am. Chem. Soc.*, 2011, **133**, 3592.

4 (a) V. Escax, A. Bleuzen, J. P. Itié, P. Munsch, F. Varret, M. Verdaguer, *J. Phys. Chem.*, 2003, **107**, 4763; (b) D. Papanikolaou, S. Margadonna, W. Kosaka, S-i. Ohkoshi, M. Brunelli, K. Prassides, *J. Am. Chem. Soc.*, 2006, **128**, 8358; (c) T. Yokoyama, K. Okamoto, T. Ohta, S.-i. Ohkoshi, K. Hashimoto, *Phys. Rev. B.*, 2002, **65**, 064438; (d) S. Margadonna, K. Prassides, A. N. Fitch, *Angew. Chem. Int. Ed.*, 2004, **43**, 6316.

5 B. K.Teo, In *EXAFS: Basic Principles and Data Analysis*; Berlin: Springer-Verlag, 1986.

6 A. Bleuzen, C. Lomenech, V. Escax, F. Villain, F. Varret, C. Cartier dit Moulin, M. Verdaguer, *J. Am. Chem. Soc.*, 2000, **122**, 6648.

7 It should be noted that the small energy shift of the Fe K-edges associated with the thermal ETCST was attributed to the small structural change between the LS Fe(III) ion and the LS Fe(II) ion.

8 (a) G. Vankó, F. Renz, G. Molnár, T. Neisius, S. Kárpáti, *Angew. Chem. Int. Ed.*, 2007, **46**, 5306; (b) F. Renz, G. Vankó, P. Homeyama, R. Saadat, Z. Németh, S.; Huotari, *Eur. J. Inorg. Chem.*, 2012, **16**, 2653; (c) G. Poneti, M. Mannini, L. Sorace, P. Sainctavit, M.-A. Arrio, E. Otero, J.C. Cezar, A. Dei, A. *Angew. Chem. Int. Ed.*, 2010, **49**, 1954.

9 (a) B. L. Henke, J. Liesegang, S. D. Smith, *Phys. Rev. B.*, 1979, **19**, 3004; (b) B. L. Henke, J. P. Knauer, K. Premaratne, *J. Appl. Phys.*, 1981, **52**, 1509; (c) H. Henneken, F. Scholze, G. J. Ulm, *J. Appl. Phys.*, 2000, **87**, 257.

10 M. L. Baler, Y. Kitagawa, T. Nakamura, K. Tazoe, Y. Narumi, Y. Kotani, F. Iijima, G. N. Newton, M. Okumura, H. Oshio, H. Nojiri, *Inorg. Chem.*, 2013, **52**, 13956.

11 T. Kawamoto, Y. Asai, S. Abe, *Pys. Rev. B.*, 1999, **60**, 12990.