

Structure and Electronic Configuration of a Fe(II) Complex in LIESST State – a Pump and Probe Method

Two polymorphs of spin crossover mononuclear six-coordinated iron(II) complexes, trans-Fe(tzpy)₂(NCS)₂ (tzpy = 3-(2-pyridyl)[1,2,3]tri-azolo[1,5-a]pyridine) were isolated and structurally characterized. According to the thermal-dependent magnetic measurements, polymorph A undergoes a gradual spin transition from a paramagnetic high spin state (⁵T₂, S = 2, HS-1) above 200 K to a diamagnetic low spin state (¹A₁, S = 0, LS-1) below 120 K, while polymorph B possesses an abrupt spin transition with T_{1/2} at 102 K. Molecular and crystal structures of polymorph A at HS-1 and LS-1 are studied at 300 and 40 K respectively, significant differences in Fe-N distances and coordination geometries of Fe are found between two spin states as expected. Taking the evidence on X-ray diffraction, X-ray absorption, infra-red absorption and magnetic measurement, the structure and electronic configuration of the light induced excited spin state trapping state (LIESST, HS-2) of polymorph A are firmly established. A single crystal to single crystal transition through irradiation is demonstrated. The changes in structure and electronic configuration due to the spin transition are believed, at the current time frame, to occur concurrently.

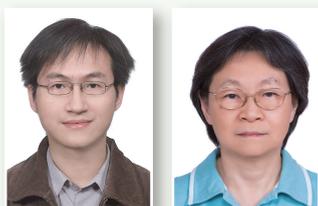
Beamlines

17C1 W20-EXAFS
20A1 BM-(H-SGM)XAS
01C2 SWLS
BL02B1 (SPring-8)

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It is known that many six-coordinated Fe(II) complexes exhibit a spin transition when subjected to external perturbations such as temperature, pressure, light irradiation or even with the inclusion/exclusion of the solvent molecules. This spin transition is often accompanied physical property changes in magnetism, color, and even dielectric constant which make it feasible for the future applications, e.g. molecular memory, molecular switch, molecular sensor, data storage, and display devices etc. The light induced excited spin state trapping (LIESST) phenomenon was commonly observed on Fe(II) spin crossover (SCO) complexes at extremely low temperature using laser light with appropriate wavelength as a pumping source.

The structure at the metastable (LIESST) state is the center of our interest in this work, it may provide significant information concerning the structural changes during the excitation and the relaxation processes; which then lead to the changes in electronic configuration of Fe(II) ion directly. However, the difficulties in measuring the single crystal structure at metastable (MS) state prevent the progress in this respect. To our knowledge, only a handful of structures at LIESST state have been determined so far. More structural information at LIESST state is needed in order to fully understand the detail correlation between the structural variation and the electronic configuration. Furthermore the dynamic behaviour can be approached.

The crystal structures of both HS-1 and LS-1 for polymorph A of Fe(tzpy)₂(NCS)₂ are studied at 300 and 40 K respectively. Significant shortening of Fe-N distances (~0.2 Å) and substantial decreasing in the distortion around Fe octahedron ($\Delta\Sigma \sim 23^\circ$; $\Delta\Theta \sim 100^\circ$) are observed in coordination geometry from HS to LS state (Table 1). The structure of LIESST (HS-2) at 40 K is investigated by pumping the crystal with 532 nm laser and probe with diffraction at wavelength of 0.5886 Å using a vacuum camera device at BL02B1 in SPring-8. The pumping condition is chosen to be the minimal in power and time (11 mW and 30 sec) to fully excite the LS state to HS state, which is monitored by observing one of the frames shown

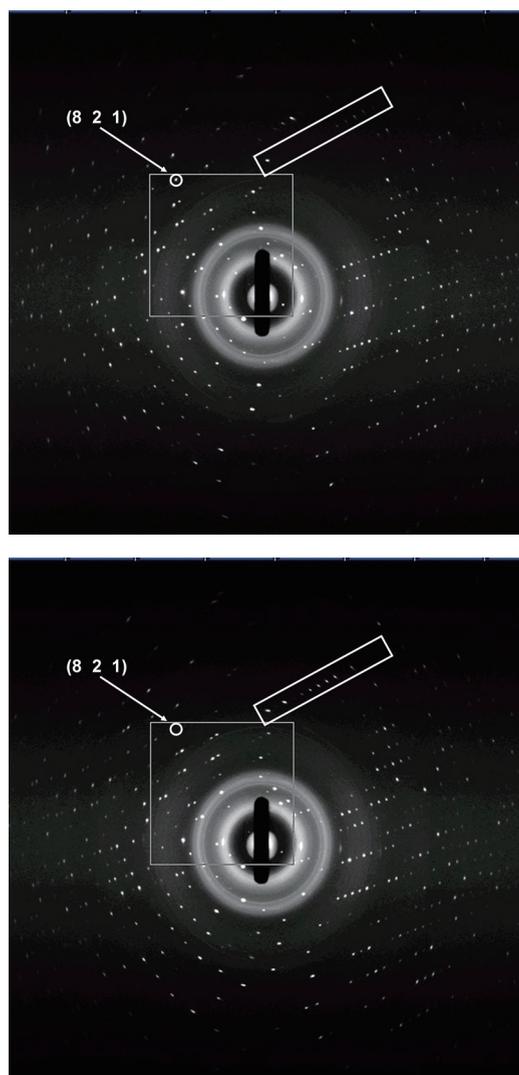


Fig. 1: Diffraction patterns before (a) and after (b) the irradiation at 40 K. Differences between the diffraction pattern are highlighted by circle and thick box.

in Fig. 1. It is apparently different before (Fig. 1a) and after (Fig. 1b) the irradiation. In particular, for example, reflection (8 2 1) is strong at LS, but unobserved at HS; other examples are shown in the area within the thick box. In addition, the peak positions after irradiation (HS-2) are shifted to lower angle indicating a larger unit cell as expected for HS versus LS state. Full data set was collected in such way that each frame was measured after 30 sec of irradiation. A total of 60 frames were measured up to 2θ of 50 deg.

The space group remains unchanged throughout these states. Going from HS-1 at 300 K to LS-1 at 40 K, the volume of unit cell is reduced 6.6 %, but is regained 3.4 % after irradiation to HS-2 at 40 K. Such increase in volume after irradiation is due to the increase in Fe coordination domain from LS to HS states. The bond lengths of Fe-N are shortened $\sim 0.2 \text{ \AA}$ from HS-1 to LS-1 and lengthened about the same amount after irradiation to HS-2. Such changes in Fe-N distances are very typical for the Fe(II) spin transition. The volumes of octahedron are calculated as 13.1, 10.1 and 12.8 \AA^3 for HS-1, LS-1 and HS-2 respectively. The octahedron distortion parameters show that the coordination geometry of the low spin state is much closer to a regular octahedron than that of the high spin state, which is often the case in many other spin crossover systems. Molecular structures before (LS-1) and after (HS-2) the irradiation at 40 K are superimposed in Fig. 2, not only the lengthening of Fe-N is observed but also the slightly twisting of the tzpy ligand is found.

The changes in spin state do not only introduce the change of the Fe coordination geometry but also affect the bond strength of N-C in the NCS ligand. The CN stretching frequency shows a broad band around 2075 cm^{-1} at HS, but a relative sharp absorption at 2116 cm^{-1} for LS state. The fraction of LS can be derived from the IR peak intensity at 2116 cm^{-1} ; thus the complete disappearance

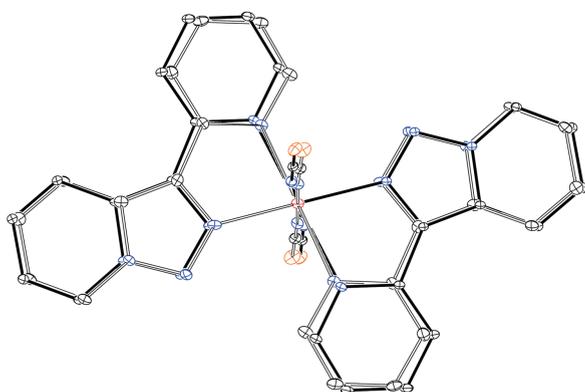


Fig. 2: Superimposed molecular structure at 40 K in the LS-1 and HS-2 (LIESST) states, shown by hollow and solid bonds, respectively.

of the peak at 2116 cm^{-1} indicates the 100% of LS to HS transformation after irradiation. Therefore the life time of the LIESST state can be determined by monitoring the peak intensity at 2116 cm^{-1} ; it is apparent that the lower the temperature is, the slower the relaxation proceeds. However, in this case, even at 30 K, there is more than 10% relaxed in an hour; but we need at least a few hours to complete the single crystal diffraction measurements. In order to make sure that it is in a hundred percent LIESST state and to avoid the possible radiation damage on the sample from the long exposure; a pump and probe experiment is thus designed for the structural determination at LIESST state (HS-2); more structures could be obtained with such design when the life time of the excited state is not long enough to complete the data measurements.

Table 1: FeN_6 octahedron geometry versus spin state

T (K)	Spin State	Fe-N1 (\AA)	Fe-N2 (\AA)	Fe-N5 (\AA)	$\Sigma^{[a]}$ (deg)	$\Theta^{[b]}$ (deg)
Polynorph A						
300	HS-1	2.217(2)	2.181(2)	2.097(3)	74.8	271.5
40	LS-1	2.021(1)	1.973(1)	1.935(1)	52.0	171.4
40 (LIESST)	HS-2	2.211(1)	2.166(1)	2.087(1)	77.0	267.0

[a] The distortion parameter Σ , which is defined as the sum of the absolute values of the deviation from 90° of the 12 *cis* angles in the coordination sphere. [b] The distortion parameter Θ , which is defined as the sum of the deviations from 60° of the 24 possible θ angles on the dihedral angles between two triangular planes.

The changes in spin state or the electronic configuration of Fe(II) can be directly monitored through Fe K- and L-edge absorption spectroscopy, which should be very sensitive to the electron density distribution around the metal, it then reflects exactly the electronic configuration of Fe(II) ion. Previous K- and L-edge absorption spectroscopy have established the fingerprints of HS and LS of Fe(II)

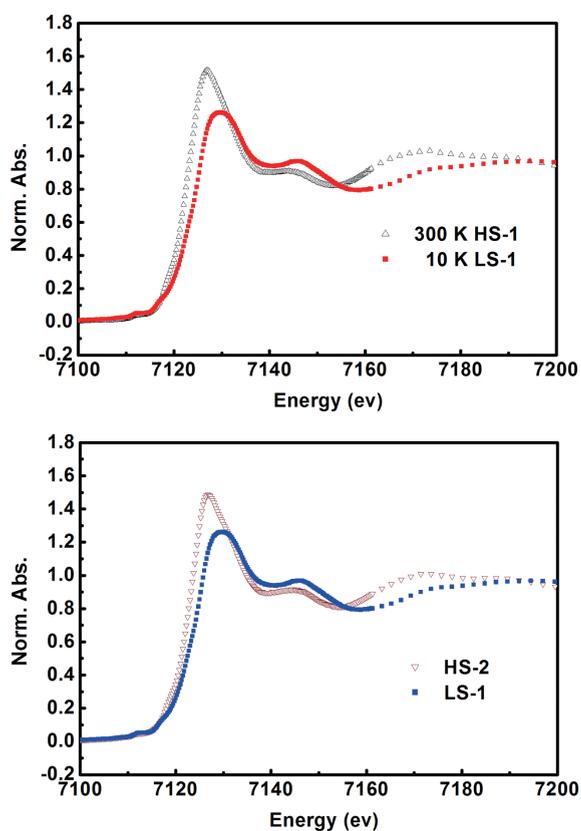


Fig. 3: Fe K-edge absorption spectra: a) HS-1 at 300 K and LS-1 at 10 K; b) before (LS-1) and after laser irradiation (HS-2) at 10 K.

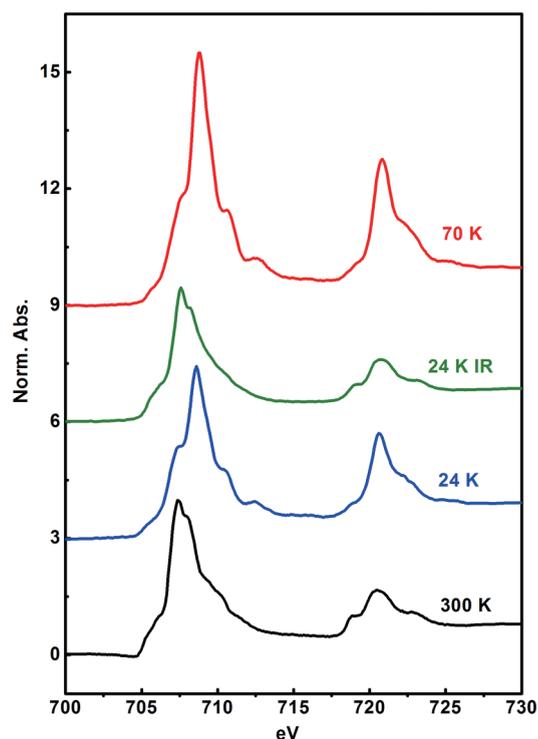


Fig. 4: Fe L-edge absorption at 300 K (HS-1); before (LS-1) and after (HS-2) laser irradiation at 24 K, and after relaxation to LS at 70 K (LS-2).

complexes. The Fe K-edge X-ray near-edge absorption structure (XANES) spectra of polymorph A at 300 K (HS-1) and at 10 K (LS-1) are shown in Fig. 3. Typical spectra of six-coordinated Fe(II) complexes at HS and LS states were well-characterized and a significant shortening in Fe-N distance from HS to LS was found. The Fe $L_{2,3}$ -edge absorption spectra for HS-1 at 300 K and LS-1 at 24 K are shown in Fig. 4. The shift in energy; the changes in spectral fine features as well as the difference in branching ratio between HS and LS states agree well with those of $\text{Fe}^{\text{II}}(\text{phen})_2(\text{NCS})_2$ (phen = 1,10-phenanthroline). The LIESST phenomenon is also investigated, typical spectra of HS can be achieved after irradiation with green laser light at 24 K (Fig. 3 & 4).

In summary, the exact electronic configurations of Fe at HS-1; LS-1 and HS-2 (LIESST) states are clearly confirmed by IR; Fe K- and L-edge absorption spectroscopy. The molecular structure of the LIESST state (HS-2) is successfully obtained by diffraction data with a pump and probe process. By applying such a procedure, the structural determination of any meta-stable excited state with moderate relaxation rate can be achieved. Molecular structure after the irradiation clearly shows the lengthening of the Fe-N bond distance and the slight twist of the coordination geometry in the solid state (Fig. 2). The changes in spin state of Fe ion and the changes in geometry of the complex are believed to be taken place concurrently at the current experimental time scale.

Experimental Stations

X-ray Absorption Spectroscopy end station
Soft X-ray absorption Spectroscopy end station
X-ray powder diffraction end station
Single crystal X-ray diffraction end station

Publications

1. C.-F. Sheu, K. Chen, S.-M. Chen, Y.-S. Wen, G.-H. Lee, J.-M. Chen, J.-F. Lee, B.-M. Cheng, H.-S. Sheu, N. Yasuda, Y. Ozawa, K. Toriumi, and Y. Wang, *Chem.-Eur. J.* **15**, 2384 (2009).
2. C.-F. Sheu, S. Pilllet, Y.-C. Lin, S.-M. Chen, I.-J. Hsu, C. Lecomte, and Y. Wang, *Inorg. Chem.* **47**, 10866 (2008).
3. S. Pilllet, C. Lecomte, C.-F. Sheu, Y.-C. Lin, I.-J. Hsu, and Y. Wang, *J. Phys.-Conf. Ser.* **21**, 221 (2005).
4. J. J. Lee, H. S. Sheu, C. R. Lee, J. M. Chen, J. F. Lee, C. C. Wang, C. H. Huang, and Y. Wang, *J. Am. Chem. Soc.* **122**, 5742 (2000).

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