Budding Researchers Support Proposal Report

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Title of Project: Study of photo-induced commensurate modulated structure in Fe(II) spin crossover system: *t*-[Fe(abpt)$_2$(NCS)$_2$] polymorph **C**

Beam line used: BL02B1

Purpose of the experiment: The materials with light-triggered and/or -driven function have been attractive in creating a novel conceptual function. To investigate those structures not only understand the mechanism of photo-induced phenomena but also lead new design of optical functional materials. For reasons detailed below, we focus on one of spin crossover complexes *t*-[Fe(abpt)$_2$(NCS)$_2$] polymorph **C** as a proto type of a photo-active molecular material. Recently we successfully synthesized the title complex. In a preliminary study it exhibits thermal spin transition at Tc = 86 K. The most interesting point in preliminary work is: By monitoring cell parameter in the range of 25-300 K, we found out that title complex exhibits not only spin transition at 86 K, but also intriguing commensurate modulated structure with cell parameter *c* tripled between the spin transition temperature 86 K and 170 K (Figure. 4). It remained a question whether after photo irradiation, the photo-induced structure of title complex also occurs commensurate modulated structure or not. Undoubtedly, X-ray diffraction provides an ultimate method to determine the photo-induced structure. However, suffering from conventional laboratory setup, we had several limitations, such as: (1) longer data collection time is difficult to completely keep in metastable state during data collection, and (2) the less laser penetration depth because of using relatively larger single crystal. Thus, to explore the origin of the photoreaction process, we carried out the single crystal structure analysis using high-brilliance and high-resolution synchrotron X-ray at BL02B1/SPring-8 (Figure. 1).

Experimental method: Molecular and crystal structures of polymorph **C** both at ground and at LIESST states were investigated by X-ray single crystal diffraction at 25 K. Diffraction data were measured at beamline BL02B1 in SPring-8 synchrotron facility, with monochromatic (λ = 0.4959 Å) radiation, equipped with a Rigaku large cylindrical image-plate detector. A crystal of 0.10 × 0.08 × 0.05 mm was cooled slowly to 25 K using open flow helium cryosystem, a full Ewald sphere diffraction data was collected by means of ω scan, with 6° frame width and 6

minutes exposure time per frame in dark. The crystal was then illuminated with a 532 nm laser while continuing rotate the crystal with respect to the laser beam for 5 minutes in order to ensure a spatially homogeneous excitation. The excitation wavelength, 532 nm, was chosen at the tail part of the absorption band of 500 nm.

Summary of the result: In this experiment, we successfully performed the structural determination of the photo-induced state of title complex in BL02B1, we found that after irradiating this sample by λ = 532 nm green light laser, this complex undergoes both **LIESST** (Light Induced Excited Spin State Trapping) and photo-induced commensurate modulated structure with cell parameter *c* tripled. The extra reflection along *c** generated from photo-irradiation could be easily found out in reciprocal space plane (Figure. 2). We collected the full data of **LIESST** state at 25 K and the commensurate modulated structure is discovered by means of structure determination (Figure. 3). Furthermore, we monitored the cell parameter after irradiating sample at 25 K in the range of 20-60 K, and the relaxation of this LIESST metastable state takes place at 52-57 K. (Figure. 4).

Conclusion: In summary, the detail crystal and molecular structures of polymorph **C** of *t*-[$Fe(abpt)_2(NCS)_2$] at 25 K both at ground and at LIESST state were successfully characterized. The photo-induced commensurate modulated structure and spin transition from ground (LS-HS) to metastable LIESST (HS-HS-HS-HS) state were firmly illustrated. The change in lattice from (*a*, *b*, *c*) to (*a*, *b*, 3*c*) due to either the photo-excitation (LIESST) or thermally quenching (TIESST) is roughly the same, which is obviously different from that of the room temperature. Such unusual molecular multi-stability could be understood as highly related with the intermolecular π-π interactions and site-selective LS → HS excitation. The relaxation of this LIESST metastable state takes place at 52-57 K.

Future Plan: For the future work, since the metastable structure reveals both photo-induced spin transition and commensurate modulated structure, it is intriguing to study the origins of photo-induced commensurate modulation. Perhaps it could be further conducted by means of time-resolved X-ray diffraction in order to better understand the underlying mechanism. For example, it could be able to capture images or "molecular movies" that visualize the step-by-step evolution in these fascinating photo-reactions. As the XFEL (X-ray Free Electron Laser) technique is developing which provides much higher-brilliance X-ray pulse. Hopefully, the XFEL time-resolved X-ray diffraction is accessible to study it in the near future.

Expected Impact: This result reveals photo-induced commensurate modulated structure in spin crossover complexes, where the photo-induced metastable structure is obviously different from that of the room temperature. To the best of my knowledge, it is the first case in the world, which may create a new possibility of photoswitchable materials.

Project Organization: In this project, I was responsible for writing experimental proposal, designing and coordinating this study under the supervision of Prof. M. Takata at the University of Tokyo. This project is cooperated with Prof. Y. Wang and C-F. Sheu at National Taiwan University which is conducted by me under the supervision of Prof. M. Takata.

Publication: Che-Hsiu Shih, Chou-Fu Sheu, Kenichi Kato, Kunihisa Sugimoto, Jungeun Kim, Yu Wang*, Masaki Takata*, The photo-induced commensurate modulated structure in site-selective spin crossover complex *trans*-[Fe(abpt)$_2$(NCS)$_2$], *Dalton Trans*., 2010, ASAP.

Conference: (1) Oral Presentation: Che Hsiu Shih, Chou Fu Sheu, Kunihisa Sugimoto, Jungeun Kim, Kenichi Kato, Yu Wang*, Masaki Takata*, Photo-induced structure determination and electron density study by MEM of Spin Crossover complex [Fe(abpt)$_2$(NCS)$_2$] AsCA'09 (Asian Crystallography Conference Association), China, Beijing, 2009, October 22- 25.

(2) Poster presentation: Che-Hsiu Shih, Chou-Fu Sheu, Kenichi Kato, Kunihisa Sugimoto, Jungeun Kim, Masaki Takata*, Yu Wang*, The photo-induced superstructure in a spin crossover complex *trans*-[Fe(abpt)$_2$(NCS)$_2$] polymorph **C** by synchrotron X-ray diffraction. Fourth Taiwan-Japan Joint Conference on Neutron and X-ray Scattering, Taiwan, 2010, March 8-10.

List of figures:

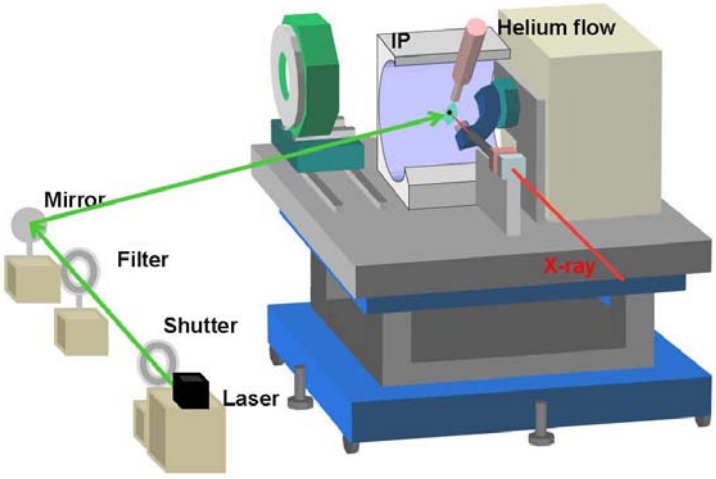

Figure 1: The design of photo-induced experimental configuration at BL02B1/SPring-8

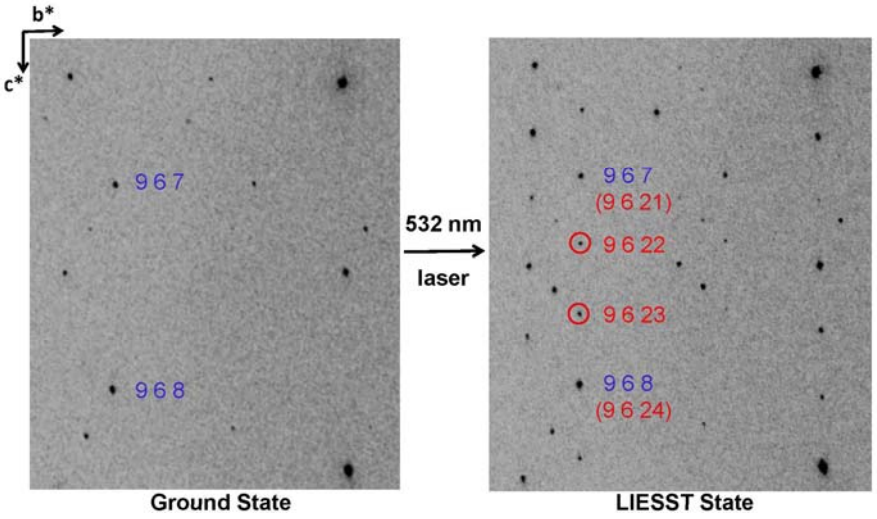

Figure 2: Single crystal diffraction image at the b^*c^* plane at 25 K: left for the ground state, right for the LIESST state. Satellite peaks (o) appear at $l + 1/3$, $l + 2/3$ at the LIESST state.

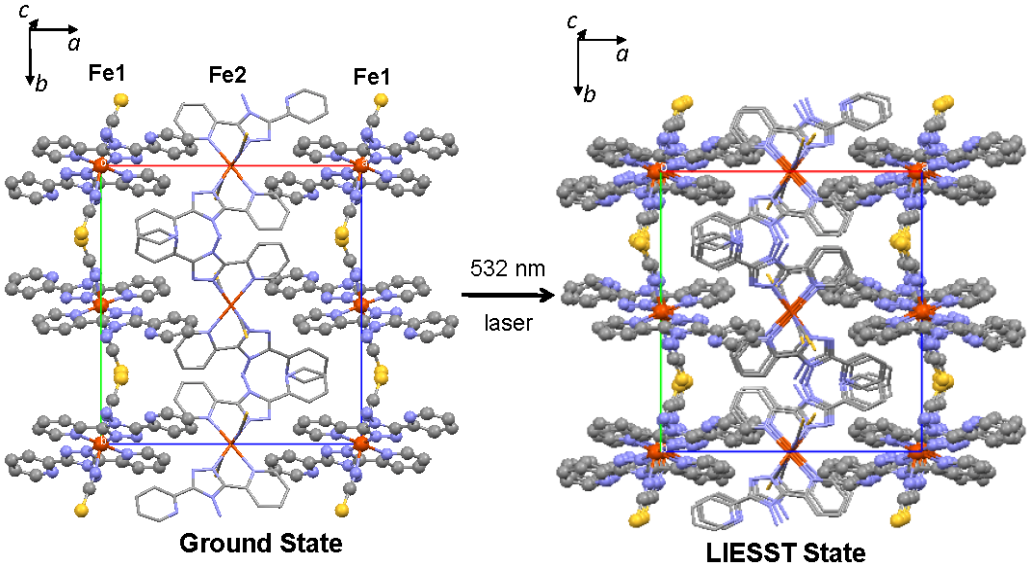

Figure 3: Packing diagram of polymorph **C**. (left) ground state; (right) LIESST state.

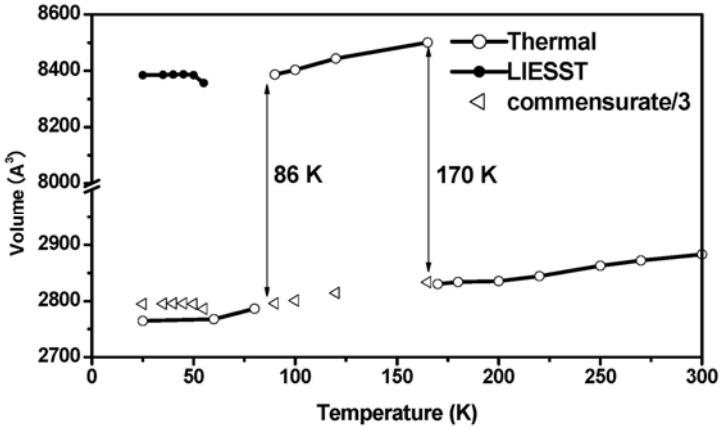

Figure 4: Temperature dependent of unit cell volume of polymorph **C**