

論文題目 Photocrystallography Study in Site-Selective Spin Crossover Complexes  
*trans*-[Fe(abpt)<sub>2</sub>(NCS)<sub>2</sub>]

(訳) (放射光単結晶回折によるサイト選択スピנקロスオーバー錯体  
*trans*-[Fe(abpt)<sub>2</sub>(NCS)<sub>2</sub>]の光誘起構造相転移の研究)

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## 1. Introduction

Photocrystallography is regarded as the ultimate method which enables the three dimensional structural determination of molecules in their photo-activated states. Novel photosensitive materials, such as chalcogenides, photochromic organic compounds and charge transfer materials, are interest of their application to optical data storage. One of the photo-active materials: spin crossover (SCO) complexes; have received increasing interest since their potential for the molecular switchable application. The well known LIESST (Light Induced Excited Spin State Trapping) phenomena are evident *via* an extension of the Fe-N bond length by ~0.2 Å which corresponds to the electronic transition <sup>1</sup>A<sub>1</sub> (LS) → <sup>5</sup>T<sub>2</sub> (HS), which the pronounced structural transformation allows us to gain insight into the relationship of Fe-N bonding interactions and magnetic properties based on accurate charge density studies.

The recent discovered SCO complexes; *t*-[Fe(abpt)<sub>2</sub>(NCS)<sub>2</sub>] (abpt = 4-amino-3,5-bis(pyridin-2-yl)1,2,4-triazole) polymorph **C** and **D**, both have two unique Fe atoms in their respective lattices, but only one Fe undergoes the spin transition from high spin (HS) to low spin (LS) and the other stays at HS. Consequently, this type site-selective spin transition may cause unusually concerted structural transition. In general, the LIESST effect would result in the elongation of Fe-N bond length and a substantial increase on the distortion of Fe octahedral coordination geometry due to the spin transition (LS → HS) of Fe ion. The previous discovery of thermal-induced commensurate modulation in polymorph **C** urged us to find out the relationship between structure and magnetic properties. Thus, in attempt to understand the LIESST effect toward this site-selective spin transition compound, the structures and bonding nature of polymorph **C** are investigated at 25 K both before and after the light irradiation.

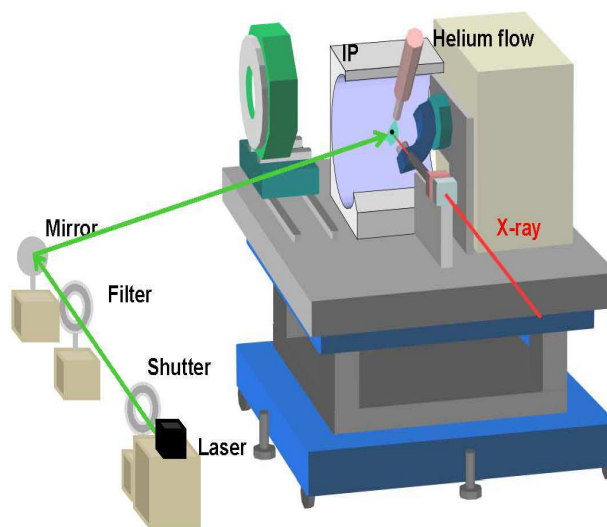
In the case of polymorph **D**, the preliminary SQUID magnetic measurement and infrared (IR) spectroscopic studies indicate that the photo-reaction of **D** involves not only conventional LIESST, but also another photo-reaction. Another photo-reaction product is able to trap metastable HS until warming up to 110 K even after turning off irradiation, which is precedent among SCO complexes. Thus, to fully understand the relationship between molecular structures and physical properties in this fascinating complex, detailed X-ray structural analysis is essential. Single crystal structures of polymorph **D** before irradiation (ground-state, GS), under irradiation (metastable-state 1, MS1), and after irradiation (metastable-state 2, MS2) are investigated by X-ray single crystal diffraction at 25 K. Moreover, the MEM/electrostatic potential are also studied to clarify the chemical bonding nature such as metal-ligand coordination bonding and intermolecular interaction.

The present study is aimed to uncover the structural phase transition associated with site-selective LIESST phenomena in SCO complexes  $t$ -[Fe(abpt)<sub>2</sub>(NCS)<sub>2</sub>] polymorph **C** and **D** by X-ray diffraction using synchrotron radiation. Hopefully, combined with complementary measurements, such as IR spectra and SQUID magnetic measurement, we can obtain comprehensive understanding of these interesting photo-reactions.

## 2. Experimental and Analysis

### 2.1 Synchrotron X-ray Structural Determination

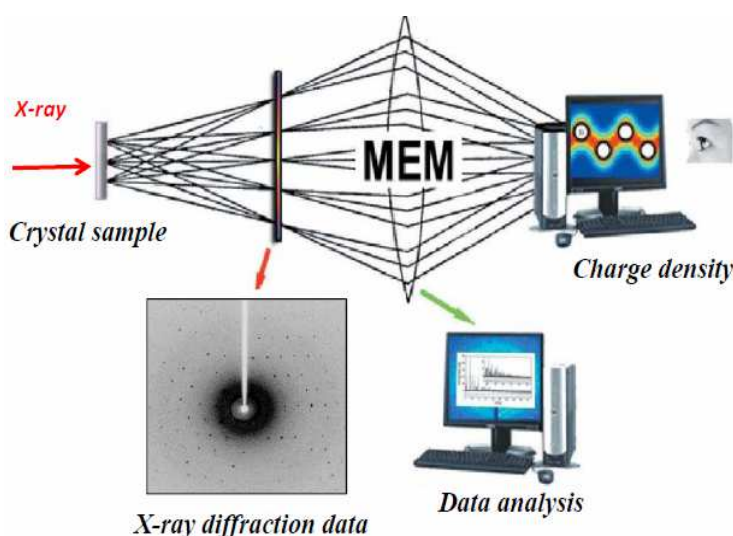
The center of this thesis is the photo-induced X-ray diffraction structural determination and charge density analysis. The study of photo-induced processes in single crystals offers a unique possibility for elucidating detailed single-crystal-to-single-crystal changes at atomic level. To achieve accurate photo-induced structural determination, one of the key points is to make sure the whole single crystal is under laser irradiation without crystal fracture. The excitation wavelength, 532 nm, was chosen at the tail part of the absorption band of 500 nm from UV-Vis spectra. The key on the *in-situ* photoexcitation studies may be the size of the crystal; the smaller the crystal is, the more stable the metastable state seems to be. Under this circumstance, using synchrotron radiation to obtain high resolution data certainly helps a great deal. Thus, the *in-situ* photo-induced X-ray diffraction experiments were performed at BL02B1 in SPring-8 facility, equipped with a Rigaku large cylindrical IP detector.



**Fig 1.** A brief layout of photo-induced experiment at BL02B1/SPring-8.

### 2.3 MEM charge density/electrostatic potential

The MEM charge density enables us to construct the fine structural model from X-ray diffraction data up to charge density level. As the electrostatic potential is an important function for the study of the chemical bonding nature; considerable attention has been paid to its derivation from the X-ray measurements. In this study, the electrostatic potential is evaluated using MEM charge density as an efficient approach to visualize the bonding nature inside materials, especially intermolecular hydrogen bonding.

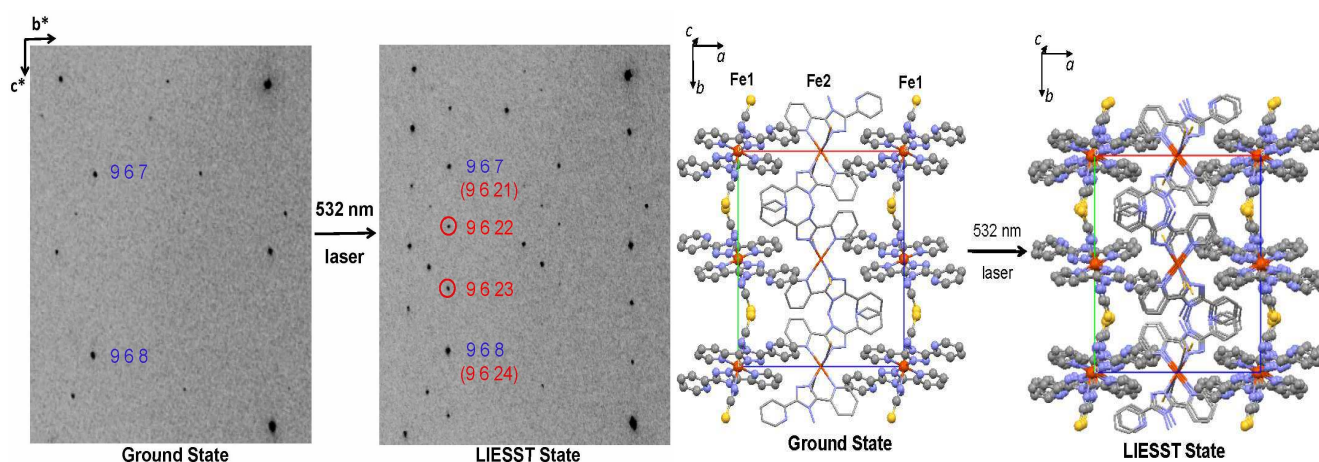


**Fig 2.** Using MEM to visualize the charge density.

### 3. Results and Discussions

#### 3.1 The photo-induced commensurate modulated structure in polymorph C

The structure of **C** at LIESST-state is obtained at 25 K after illuminating the crystal with 532 nm laser. In addition to Bragg peaks of the ground-state, the reflection pattern reveals clearly peaks present at  $l + 1/3$ ,  $l + 2/3$  along  $c^*$  axis as depicted in Fig. 3. A photo-induced commensurate modulated structure is thus detected with a modulated vector,  $q = 1/3 c^*$ . The main difference between the structures at ground and LIESST-states is the two additional molecules designated as Fe12 and Fe22 in the asymmetric unit of the LIESST-state, which can be generated from their non-modulated structure, but with a slight shift of 0.34 and 0.23 Å respectively for Fe1 and Fe2 site. This would give rise to a symmetry breaking and the formation of the modulated structure. Further MEM charge density study reveals the Fe-N coordinated bonding nature related to different spin states. Regarding topological charge density  $\rho(r)$  as a function of Fe-N bond lengths, on going site-selective spin transition from the LS (Fe1 site) to the HS (Fe11 and Fe12 sites) state, the  $\rho(r)$  values at the Fe-N bond critical points decrease, which clearly show the site-selective spin transition in charge density level.



**Fig 3.** (Left) Single crystal diffraction image at  $b^*c^*$  plane at 25 K: left for the ground-state, right for the LIESST-state. Satellite (o) appear at  $l + 1/3$ ,  $l + 2/3$  at the LIESST-state. (Right) Packing diagram of polymorph **C** left for ground-state; right for LIESST-state.

#### 3.2 The photo-induced linkage isomerism in polymorph D

The structures of polymorph **D** before irradiation (ground-state, GS), under irradiation (metastable-state 1, MS1), and after irradiation (metastable-state 2, MS2) were investigated by synchrotron X-ray diffraction at 25 K. This photo-reaction involves both conventional LIESST and photo-induced linkage isomerization. The linkage isomer (LI) molecules are brought by the transformation from isothiocyanato (Fe-NCS) to thiocyanato (Fe-SCN) in the MS1. When it converts to MS2 in light-off environment, the metastable HS molecules relax to LS state, but the LI molecules remain as elucidating in Fig. 4. Furthermore, several reflections only observed with linkage isomer state but unobserved in normal ground-state were monitored through increasing temperature from 25 K MS2. These reflections which only appear with linkage isomer molecules begin weaker through warming up to 100 K, and disappear at 110 K. The full data was collected at this state (110 K) and got pure FeN6 octahedral coordination which proves the linkage isomer molecules disappear through

increasing temperature to 110 K, consistent with the SQUID magnetic measurement results. Moreover, the MEM charge density/electrostatic potential are studied to clarify the intermolecular interaction in GS, MS1, and MS2. It could be concluded that the intermolecular hydrogen bonding plays an important role in stabilizing the metastable state structures.

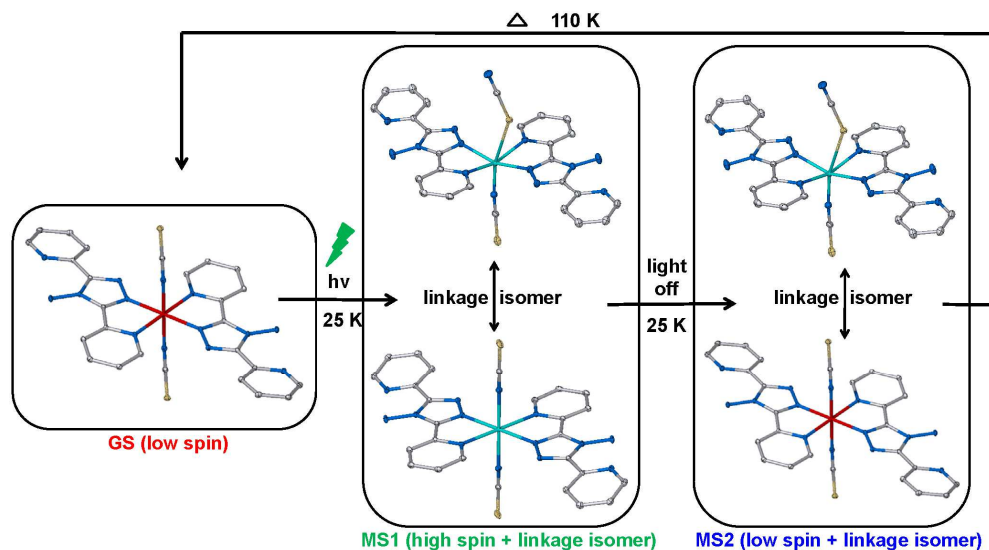


Fig 4. Scheme of photoreaction of polymorph **D** (for photosensitive Fe site).

#### 4. Conclusion

The thesis presents the photocrystallography study of site-selective spin crossover complexes *t*-[Fe(abpt)<sub>2</sub>(NCS)<sub>2</sub>] polymorph **C** and **D** using single crystal X-ray diffraction. With the help of synchrotron radiation X-ray, the *in-situ* photo-induced diffraction experiment can be achieved successfully. (1) Polymorph **C** reveals photo-induced commensurate modulation in crystal structure associated with site-selective spin transition. The Fe-N coordinated bonding strength related to different spin states is studied using MEM charge density with high resolution X-ray diffraction data. Concerning to charge density  $\rho(r)$  as a function of Fe-N bond lengths, it indicates that the charge density  $\rho(r)$  values in BCPs are inverse proportional to the bond lengths. (2) Polymorph **D** reveals intriguing photo-induced linkage isomerization which is brought by the transformation from isothiocyanato (Fe-NCS) to thiocyanato (Fe-SCN). The structural determination in the metastable states is successfully achieved, which give the direct evidence for the precedent existence of linkage isomerization in SCO complexes. The electrostatic potential could be accurately evaluated using MEM charge density. It indicates that the intermolecular hydrogen bonding plays an important role in stabilizing the precedent metastable state structure.

#### Publications

- (1) C. H. Shih, C. F. Sheu, K. Kato, K. Sugimoto, J. Kim, Y. Wang\*, M. Takata\*, The photo-induced commensurate modulated structure in site-selective spin crossover complex *trans*-[Fe(abpt)<sub>2</sub>(NCS)<sub>2</sub>], *Dalton Trans.*, 2010, 39, 7794-7800.
- (2) A. Fujiwara, K. Sugimoto, C. H. Shih, H. Tanaka, J. Tang, Y. Tanabe, J. Xu, S. Heguri, K. Tanigaki, M. Takata, A criterion to characterize rattling behavior provoking phonon-glass states, submitted.