Budding Researchers Support Proposal Report

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Beam line used: BL02B1

Title of experiment: Study of photo sensitive material with linkage isomer in Fe(II) spin crossover system: $Fe(abpt)_2(NCS)_2$ polymorph D (abpt = 4-Amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole)

Research summary

Purpose of the experiment: The materials with light-triggered and/or -driven function have been attractive in creating a novel conceptual optical function. To investigate those structures not only understand the mechanism of photo-induced phenomena but also can lead new optical functional materials. For reasons detailed below, We focus on one of spin crossover complex $Fe(abpt)_2(NCS)_2$ as a proto type of a photo- active molecular material. According to infrared spectroscopy and SQUID magnetic measurement, this complex undergoes gradually thermal spin transition from a high spin (HS, S=2, t_{2g}^4 e_g^2) to low spin (LS, S=0, t_{2g}^6 e_g^0) electronic configuration at 162 K. Below 50 K, $Fe(abpt)_2(NCS)_2$ exhibits the well known Light Induced Excited Spin State Trapping (LIESST) phenomenon pumping by λ=532nm green light laser. However, after turning off laser, according to infrared spectroscopy and SQUID magnetic results, this complex doesn't completely relax to LS ground state but remains about 6% HS. From conventional laboratory X-ray diffraction, we had preliminary structural information of $Fe(abpt)_2(NCS)_2$ at photo-induced state (HS). If we fit the X-ray diffraction data with regular high spin FeN6 octahedral coordination model, we could observe that here is still some strong residual electron density surrounding Fe atom (Q_1=12.8 e/Å^3, figure 1). We suppose that besides LIESST phenomenon, the photo-induced linkage isomer reaction also happens after photo irradiation. However, suffering from conventional laboratory X-ray setup, we had several limitations, such as longer data collection time which is difficult to completely keep in meta-stable state during data collection, and the less laser penetration depth because of using relatively larger single crystal. We didn't have well enough structural data to perform the structural determination. To explore the origin of the process we carried out the single crystal structure analysis using high-brilliance and high-resolution synchrotron radiation X-ray at BL02B1/SPring-8.

Summary of the result: In this experiment, we successfully performed the structural determination of the photo-excited state (MS1) of $Fe(abpt)_2(NCS)_2$ in BL02B1, we found that after irradiating this sample by λ=532 nm green light laser, this complex undergoes both LIESST and light-induced linkage isomerism which is brought by the transformation from thiocyanato (Fe-SCN) to isothiocyanato (Fe-NCS) (figure 2). Because this material comprises both photo induced high spin state (Fe-NCS) and linkage isomerism (Fe-SCN), after turning off laser, the relaxation state (MS2) comprises not just ground low spin state(Fe-NCS) but also linkage isomer high spin state(Fe-SCN) (figure 2). We were also curious if the isothiocyanato (Fe-SCN) would transforms back to thiocyanato(Fe-NCS) through temperature increasing or not. Therefore, we monitored several reflections which are observed in linkage isomer state but unobserved in normal ground state by increasing temperature from 20 K MS2 state. In figure 3, one could easily see that the reflection (h, k, l) = (4, 9, 5) which belongs to linkage isomer state reflection begins weaker around 100 K, and disappears at 110K. We collected full data at this state (110 K) and got a pure FeN6 octahedral coordination which proves the linkage isomer disappears through increasing temperature to 110 K.

Experimental method: This single crystal experiment was performed by Rigaku large cylindrical image plate camera in BL02B1 (ref 1) with 0.49812Å wavelength synchrotron radiation X-ray, SPring-8. The photo source is 532nm diode green light laser.

Experimental data: The crystal structures were refined with SHELX97 (ref 2). Non-hydrogen atoms were refined anisotropically, hydrogen atoms were refined isotropically. More details on data collection and structural refinement results are collected in Table 1.

Conclusion: To conclude, in view of our results, we succeed in the first observation of photo-induced both spin transition and linkage isomerism by crystallographic identification of spin crossover material: $Fe(abpt)_2(NCS)_2$ polymorph D. The structural results (MS1, MS2) are consistent with our previous infrared spectroscopy and SQUID magnetic measurement. We also found out that the linkage isomer phenomena disappear when temperature increases from 20 K to 110 K. The experimental conditions were optimized to yield diffraction data of acceptable resolution and quality. Numerous experimental difficulties have been overcome in BL02B1/SPring-8.

(i) Under the combined influence of cooling He flux, X-ray and laser beams, the mosaicity of the single crystal samples unavoidably increases. In the present work, the use of synchrotron radiation enabled the collection data at higher angular resolution, and this greatly improved the deconvolution of thermal motion.

(ii) Even at very low temperature, well below T_{LIESST}, the meta-stable to ground state relaxation is not completely negligible. However, thanks to continuous laser excitation and shorter collection time due to high-brilliance synchrotron radiation during diffraction measurement, a photo-stationary state was achieved with complete photo-conversion.

Reference: (1) http://www.spring8.or.jp/wkg/BL02B1/instrument/lang-en/INS-0000001502/instrument_view

(2) George M. Sheldrick, Acta Cryst. (2008). A64, 112–122

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Figure1: F_{obs}-F_{cal} residual mapping of $Fe(abpt)_2(NCS)_2$

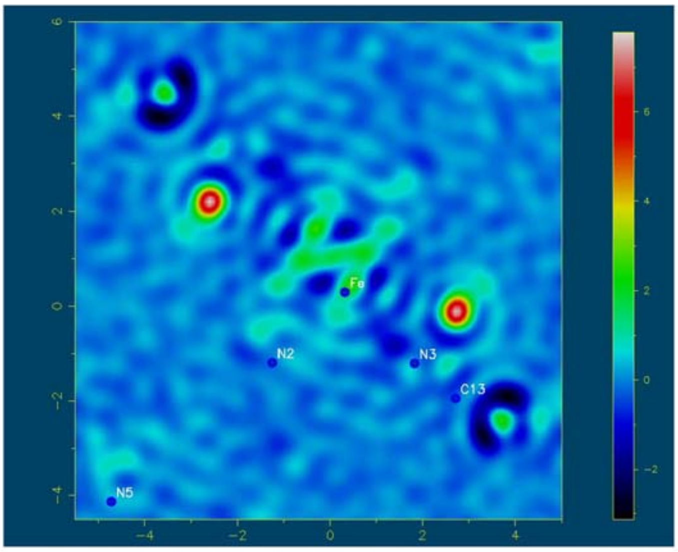


Figure2: The phase transition diagram of spin state and bond length of GR, MS1, MS2 at 20K

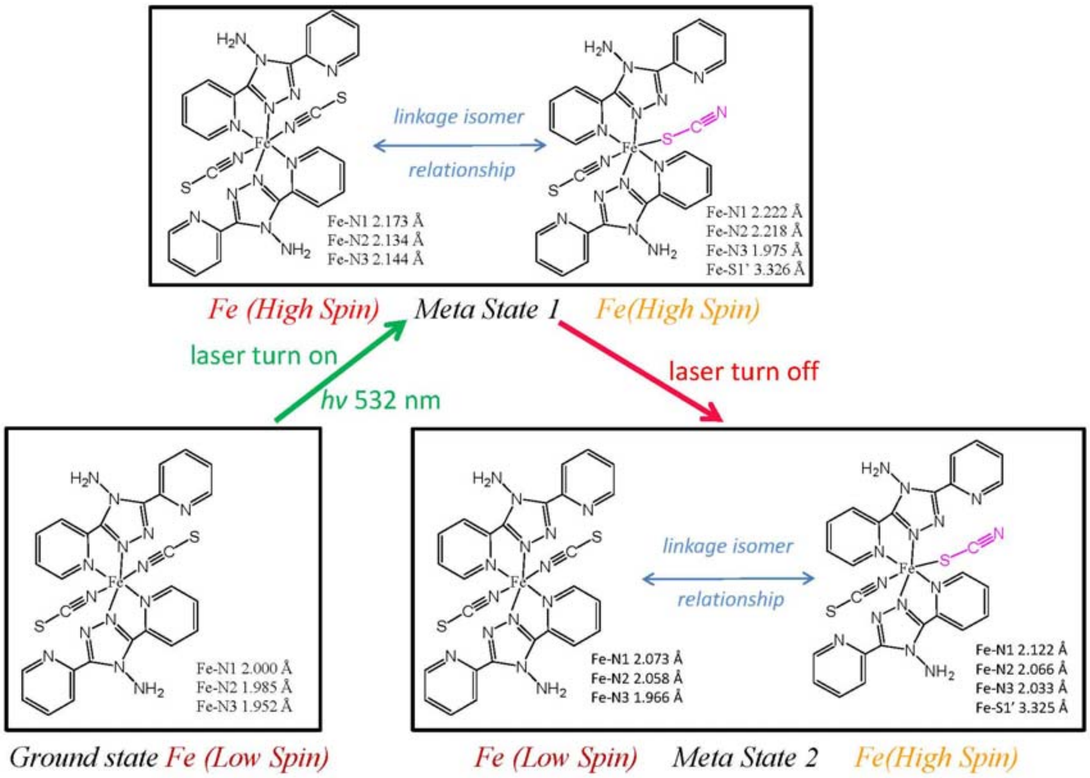


Figure 3: Monitor reflection (4, 9, 5) by increasing temperature (MS2 at 20K to 110K)

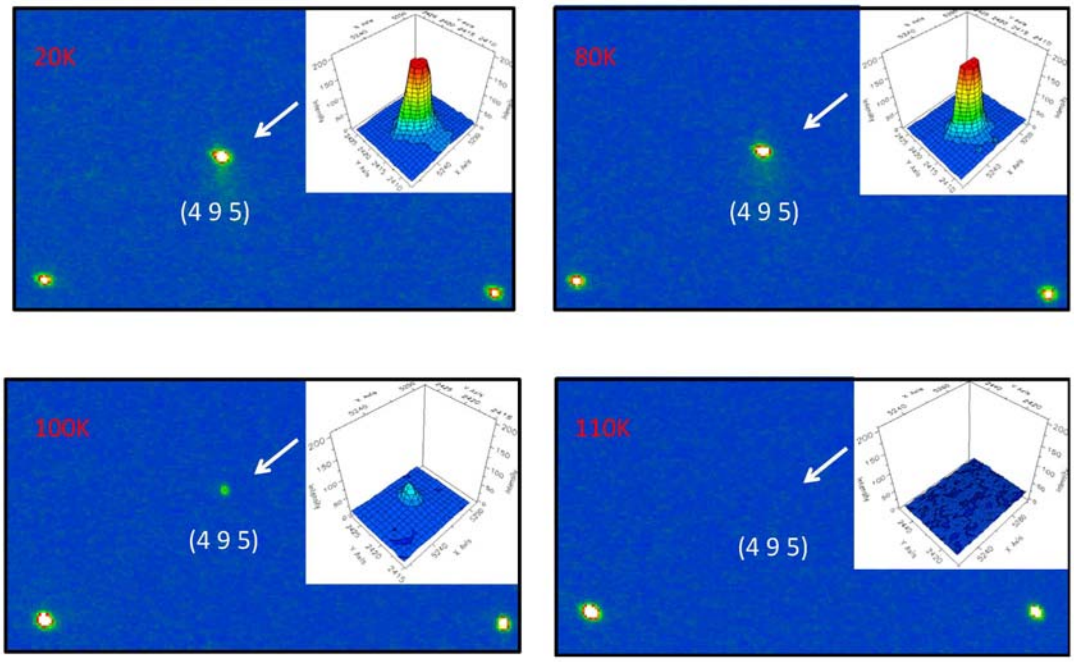
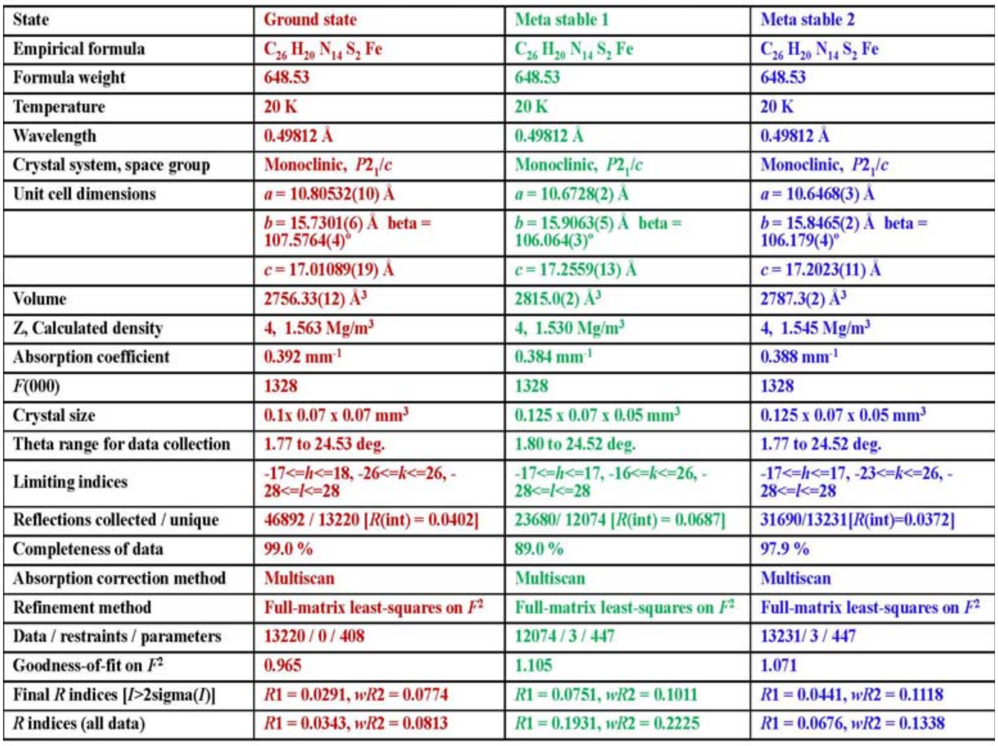


Table 1: Crystal data for *trans*-[Fe(abpt)$_2$(NCS)$_2$] at GS, MS1, and MS2 at 20K



State	Ground state	Meta stable 1	Meta stable 2
Empirical formula	C_{26} H_{20} N_{14} S_2 Fe	C_{26} H_{20} N_{14} S_2 Fe	C_{26} H_{20} N_{14} S_2 Fe
Formula weight	648.53	648.53	648.53
Temperature	20 K	20 K	20 K
Wavelength	0.49812 Å	0.49812 Å	0.49812 Å
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 10.80532(10) Å	a = 10.6728(2) Å	a = 10.6468(3) Å
	b = 15.7301(6) Å beta = 107.5764(4)°	b = 15.9063(5) Å beta = 106.064(3)°	b = 15.8465(2) Å beta = 106.179(4)°
	c = 17.01089(19) Å	c = 17.2559(13) Å	c = 17.2023(11) Å
Volume	2756.33(12) Å^3	2815.0(2) Å^3	2787.3(2) Å^3
Z, Calculated density	4, 1.563 Mg/m^3	4, 1.530 Mg/m^3	4, 1.545 Mg/m^3
Absorption coefficient	0.392 mm^{-1}	0.384 mm^{-1}	0.388 mm^{-1}
F(000)	1328	1328	1328
Crystal size	0.1x 0.07 x 0.07 mm^3	0.125 x 0.07 x 0.05 mm^3	0.125 x 0.07 x 0.05 mm^3
Theta range for data collection	1.77 to 24.53 deg.	1.80 to 24.52 deg.	1.77 to 24.52 deg.
Limiting indices	-17<=h<=18, -26<=k<=26, -28<=l<=28	-17<=h<=17, -16<=k<=26, -28<=l<=28	-17<=h<=17, -23<=k<=26, -28<=l<=28
Reflections collected / unique	46892 / 13220 [R(int) = 0.0402]	23680/ 12074 [R(int) = 0.0687]	31690/13231[R(int)=0.0372]
Completeness of data	99.0 %	89.0 %	97.9 %
Absorption correction method	Multiscan	Multiscan	Multiscan
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	13220 / 0 / 408	12074 / 3 / 447	13231/ 3 / 447
Goodness-of-fit on F^2	0.965	1.105	1.071
Final R indices [I>2sigma(I)]	$R1$ = 0.0291, $wR2$ = 0.0774	$R1$ = 0.0751, $wR2$ = 0.1011	$R1$ = 0.0441, $wR2$ = 0.1118
R indices (all data)	$R1$ = 0.0343, $wR2$ = 0.0813	$R1$ = 0.1931, $wR2$ = 0.2225	$R1$ = 0.0676, $wR2$ = 0.1338