

**$^{57}\text{Fe}$  Mössbauer, UV-visible, and FT-IR Study on Photoinduced Spin Transition of  $\text{Fe}^{\text{II}}$ -Triazole Complex**Tadashi Mitsuoka,<sup>a</sup> Masaru Nakagawa,<sup>b</sup> Tomokazu Iyoda,<sup>b</sup> and Yasuaki Einaga<sup>\*,a</sup><sup>a</sup>Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Yokohama 223-8522, Japan<sup>b</sup>Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama 226-8503, Japan

Received: January 23, 2007; In Final Form: February 25, 2007

We have synthesized a novel spin crossover  $\text{Fe}^{\text{II}}$ -triazole complex  $\text{Fe}(\text{AZ-trz})$ , where AZ-trz denotes 4-phenylazo-*N*-[1,2,4]triazole-4-yl-benzamide.  $^{57}\text{Fe}$  Mössbauer spectra and magnetic susceptibility measurements of this compound exhibited a gradual spin crossover behavior by thermal change and also a light-induced excited spin state trapping (LIESST) effect. Both UV-visible absorption spectra and IR spectra confirmed the phenomena. The  $\text{Fe}^{\text{II}}$  high-spin, HS, state was induced by exciting a d-d electronic transition band of the  $\text{Fe}^{\text{II}}$  low-spin state species. Furthermore, the measurements revealed the lifetime of excited  $\text{Fe}^{\text{II}}$  HS state to be 1 min.

**1. Introduction**

The developments of new magnetic materials whose magnetic properties can be controlled by photoillumination have been attracting great interest.<sup>1</sup> Metal complexes with the electron configuration  $d^4$  to  $d^7$  can take two different spin state, i.e., the high-spin (HS) and low-spin (LS) states and they have been investigated because some of them can exhibit the spin crossover phenomena.<sup>2</sup> A long-lived photoinduced spin transition phenomenon is called a light-induced excited spin state trapping (LIESST) effect and attracting extensively attention from the viewpoint of the development of optically switchable magnetic materials because of their possible applications for optical memories or other switch devices.

Triazole complexes is one of the most well-known spin crossover complexes and general formula is given as below,  $[\text{Fe}^{\text{II}}(\text{R-trz})_3]\text{A}_2 \cdot n\text{H}_2\text{O}$ , where R-trz is 4-R-substituted-1,2,4-triazole and A is anion. The structure consists of linear chains in which the neighboring  $\text{Fe}^{2+}$  ions are triply bridged by triazole R-trz ligands through the N atoms occupying the 1- and 2-positions and the  $\text{FeN}_6$  core is close to a regular octahedron<sup>3</sup> (Figure 1). So far, a lot of triazole complexes which exhibit spin crossover phenomena have been designed and synthesized by modifying side chain R- or changing counter anion A. Recently, some researches in an attempt to finding other functions such as gel-like networks and self-assembled macromolecules by using the advantage of polymeric coordination of triazole complexes have also been reported.<sup>4</sup> However, the

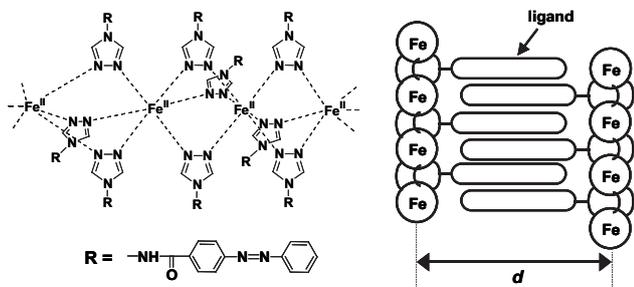
number of the studies on photoinduced spin transition of triazole complexes or combining spin crossover of triazole complex with photochemistry are very few.<sup>5</sup> In the present work, we designed a novel triazole complex  $\text{Fe}(\text{AZ-trz})$  for the purpose of realizing LIESST effects. As a result, we could confirm the LIESST effect of  $\text{Fe}^{\text{II}}$  in  $\text{Fe}(\text{AZ-trz})$  complex by means of  $^{57}\text{Fe}$  Mössbauer, FT-IR, and UV-visible absorption spectroscopies. This may open the possibility to the development of triazole complexes for the purpose of the LIESST materials.

**2. Experimental**

**2.1. Synthesis of Azobenzene Ligand.**<sup>4a,4b</sup> Triazole ligand AZ-trz (4-phenylazo-*N*-[1,2,4]triazole-4-yl-benzamide) was synthesized as follows. To a THF (200 mL) solution of 4-phenylazo benzoic acid (508 mg), triethylamine (500  $\mu\text{L}$ ), and diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP, 1.20 g), 4-amino-1,2,4-triazole (205 mg) was added at room temperature. The mixture was refluxed for 2 hours and allowed to cool to room temperature. After the reaction mixture was evaporated to dryness, the residue was washed by chloroform and recrystallized by ethanol to give an orange product (407 mg, 61% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.64 (m, 3H, ArH), 7.95 (d, 2H, ArH), 8.05 (d, 2H, ArH), 8.16 (d, 2H, ArH), 8.81 (s, 2H, triazole-H); FT-IR (KBr;  $\text{cm}^{-1}$ )  $\nu$  (C=O) 1685,  $\nu$  (trz-ring) 1562, 1320,  $\nu$  (N-N) 1155,  $\delta$  (trz-ring) 618.

**2.2. Synthesis of  $\text{Fe}^{\text{II}}$ -triazole complex.**<sup>3b,3e,4a,4b</sup> To a THF (50 mL) solution of AZ-trz (198 mg) was added a THF (10 mL) solution of  $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (98 mg) containing a small amount of ascorbic acid to prevent the partial oxidation of  $\text{Fe}^{\text{II}}$ , and the reaction mixture was refluxed for 10 minutes under nitrogen atmosphere. Then, a pale orange precipitate was obtained immediately and collected by filtration, washed by methanol and THF, and dried under reduced pressure to give an orange powder (193 mg, 61% yield). FT-IR (KBr;  $\text{cm}^{-1}$ )  $\nu$  (C=O) 1688,  $\nu$  (trz-ring) 1553, 1339,  $\nu$  (N-N) 1183,  $\delta$  (trz-ring) 623; Anal. Calcd for  $\text{C}_{45}\text{H}_{36}\text{N}_{18}\text{O}_{11}\text{Cl}_2\text{Fe} \cdot 2\text{H}_2\text{O}$ : C, 46.29; H, 3.45; N, 21.59. Found C, 45.74; H, 3.61; N, 21.05.

**2.3. Instruments.** FT-IR and UV-visible absorption spectra were recorded on an FT/IR-660 spectrometer (JASCO) and a V-560 spectrometer (JASCO), respectively. The magnetic properties were investigated with the SQUID magnetometer (MPMS-XL, Quantum Design). Visible light illumination (fil-



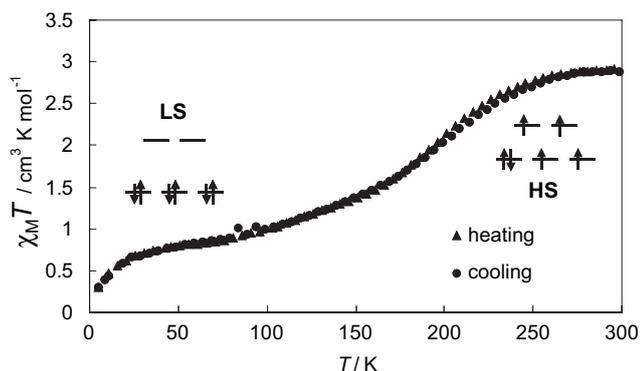
**Figure 1.** Structure of  $\text{Fe}(\text{AZ-trz})$ . Left shows the molecular structure, while right shows the image of intermolecular structure.

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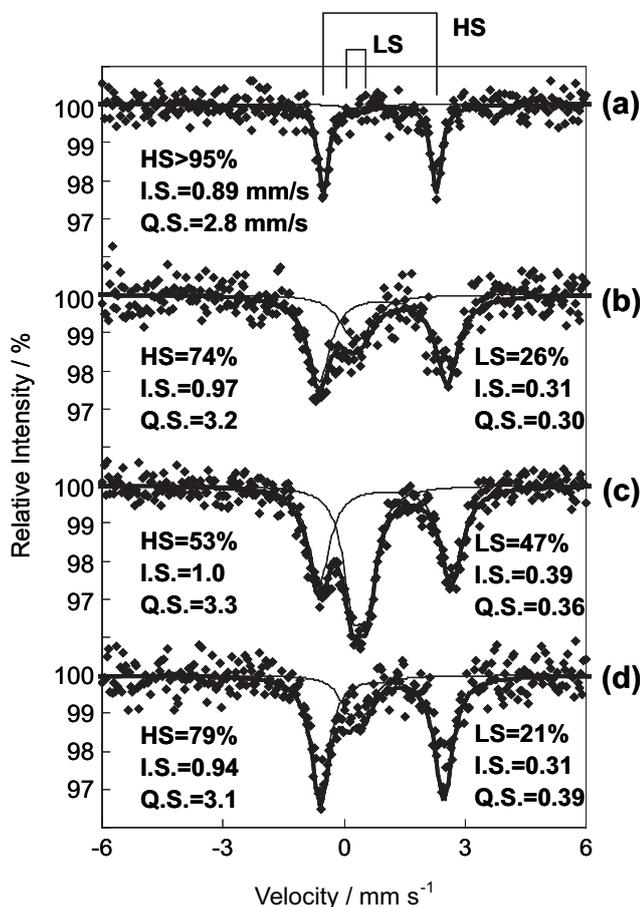
tered light,  $\lambda_{\max} = 450$  nm) was carried out using a xenon light source (BA-X500, USHIO). XRD patterns were recorded on RINT RAD-RC (Rigaku) with Cu  $K_{\alpha}$  radiation.  $^{57}\text{Fe}$  Mössbauer spectra were measured by using a Topologic Systems model 222 constant-acceleration spectrometer with a  $^{57}\text{Co}/\text{Rh}$  source in transmission mode. When we measured the spectra at low temperature, a closed-cycle helium refrigerator (Nagase Electronic Equipments Service Co., Ltd.) was used.

### 3. Results and Discussion

The azobenzene ligand AZ-trz and  $\text{Fe}^{\text{II}}$ -triazole complex  $\text{Fe}(\text{AZ-trz})$  (Figure 1) were newly synthesized in the method similar to previous reports.<sup>4a, 4b</sup> They were characterized by means of  $^1\text{H}$  NMR, FT-IR, and elemental analysis. In FT-IR spectroscopy,  $\text{Fe}(\text{AZ-trz})$  displayed shifts of vibrational bands of C=O (1688  $\text{cm}^{-1}$ ) and triazole ring (1553, 1339, 1183  $\text{cm}^{-1}$ ) by reference to AZ-trz, indicating that  $\text{Fe}^{2+}$  ion coordinated with



**Figure 2.**  $\chi_{\text{M}}T$  vs.  $T$  plots for  $\text{Fe}(\text{AZ-trz})$ . The sample was warmed from 5 to 300 K and then cooled from 300 to 5 K at a rate of 10 K  $\text{min}^{-1}$ .



**Figure 3.**  $^{57}\text{Fe}$  Mössbauer spectra of  $\text{Fe}(\text{AZ-trz})$  at room temperature (a), 150 K (b), 10 K (c), and under visible light illumination at 10 K (d).

triazole ligand.<sup>3b,3e,4a,4b</sup>

The X-ray diffraction (XRD) pattern of  $\text{Fe}(\text{AZ-trz})$  at room temperature showed a diffraction peak at  $2\theta = 3.74^\circ$  with a  $d$  spacing 23.6 Å. This value indicates an interdigitation of the azobenzene side chain to give parallel-aligned polynuclear  $\text{Fe}^{\text{II}}$  chains, whose center-to-center separation is the same as  $d$  spacing value.<sup>4a-c</sup> Moreover, the  $d$  spacing value also suggests an intermolecular  $\pi$ - $\pi$  interaction of azobenzene moieties because the  $d$  spacing value (23.6 Å) is larger than the length of the azobenzene side chain (about 15 Å) (Figure 1). UV-visible absorption spectrum of the complex  $\text{Fe}(\text{AZ-trz})$  in KBr pellet showed a red shift of the  $\pi$ - $\pi^*$  transition band of *trans*-form azobenzene compared with the ligand AZ-trz, which is due to  $\pi$ - $\pi$  interaction of azobenzene.

The  $\chi_{\text{M}}T$  value, on heating process, gradually increased from about 0.6  $\text{cm}^3 \text{K mol}^{-1}$  at low temperature up to 2.9  $\text{cm}^3 \text{K mol}^{-1}$  above 250 K. That is, characteristic of the LS-to-HS transition was observed (Figure 2). On the other hand, when the resulting sample in the HS state was cooled down, the  $\chi_{\text{M}}T$  value decreased along with heating process reversibly and hysteresis was not observed.  $^{57}\text{Fe}$  Mössbauer spectra of  $\text{Fe}(\text{AZ-trz})$  were shown<sup>6</sup> in Figure 3. The temperature dependence of  $^{57}\text{Fe}$  Mössbauer spectra of  $\text{Fe}(\text{AZ-trz})$  were consistent with magnetic data. Typically two doublet peaks were observed. The very narrow doublet peak is typical of the LS state of  $\text{Fe}^{\text{II}}$  with  $t_{2g}^6$  electron configuration, while the wide doublet peak is typical of the HS state of  $\text{Fe}^{\text{II}}$  with  $t_{2g}^4 e_g^2$  electron configuration. Spectrum at 10 K showed that the LS fraction was 47% and the rest was HS fraction (Figure 3c). When sample was heated, the LS fraction decreased to 26% and below 5%, at 150 K and room temperature, respectively (Figure 3a, b). The Mössbauer spectra also indicated the spin crossover phenomena. The  $\chi_{\text{M}}T$  value and the HS fraction of  $^{57}\text{Fe}$  Mössbauer spectrum at low temperature before the LS-to-HS transition was not zero. It is suggested that the existence of HS fraction even at low temperature is due to the chain-end  $\text{Fe}^{\text{II}}$  with HS state, which are hydrated.<sup>4b</sup> From the HS fraction (53%) in the Mössbauer spectrum at 10 K (Figure 3c), we can know that this compound have a lot of terminals. The reason for the small degree of polymerization in  $\text{Fe}(\text{AZ-trz})$  was the large size of the AZ-trz ligand, because it is known that the size of 4-position's functional groups of triazole ligand influenced the polymerization of the triazole complexes.<sup>4b</sup>

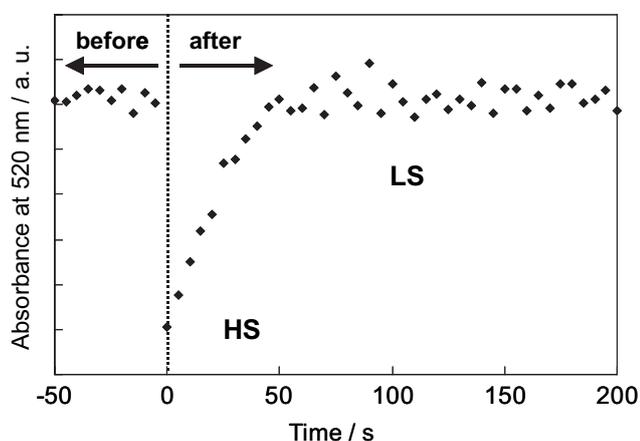
A xenon lamp was used as the visible light source to investigate photoinduced spin transition. Mössbauer spectrum was measured while being illuminated with the filtered light ( $\lambda_{\max} = 450$  nm) (Figure 3d). The HS fraction of the  $\text{Fe}^{\text{II}}$  complex under illumination drastically increased up to 79%. However, this increased value returned to the initial state by turning off the illumination. That is, the LIESST effect was observed although the lifetime of the photoinduced excited state (HS) was not long.

In order to estimate the lifetime of the HS state, the absorption band at 520 nm, corresponding to the d-d electronic transition from  $^1A_{1g}$  to  $^1T_{1g}$  levels in the  $\text{Fe}^{\text{II}}$  LS state was monitored at 10 K (Figure 4). After visible light illumination for 3 min, the absorbance decreased immediately and recovered to the former value after 1 min. These indicate that the visible light illumination, which selectively excited the LS state, induces the LS-to-HS transition by LIESST effect and the relaxation process occurred within 1 min. Furthermore, the LIESST effect of  $\text{Fe}(\text{AZ-trz})$  could be repeated several times.

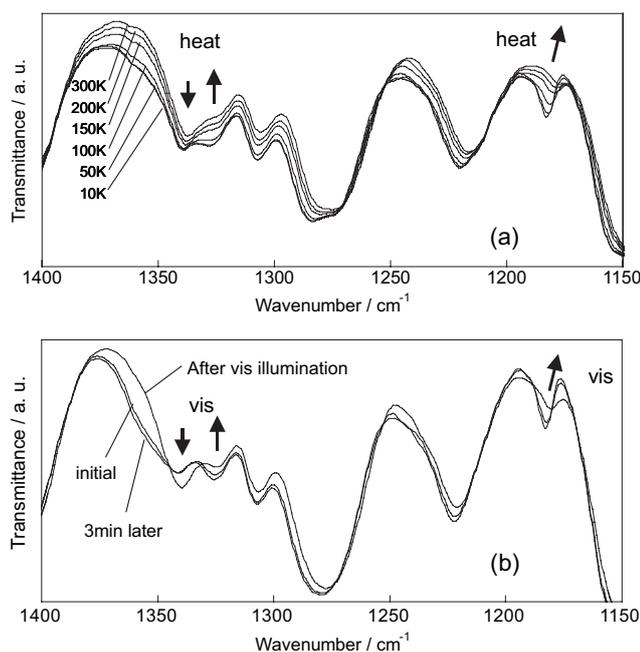
The spin crossover phenomena were also monitored by FT-IR spectra. Figure 5a illustrated thermal changes of the spectra respectively. When the sample was heated, the peak at 1183  $\text{cm}^{-1}$  exhibited the red shift to 1177  $\text{cm}^{-1}$  and its intensity decreased. In addition, the intensity of the peak at 1342  $\text{cm}^{-1}$  increased, while that at 1327  $\text{cm}^{-1}$  decreased relatively and these two peaks slightly underwent red shift. On the other

hand, when the same sample was cooled down, spectrum recovered to the initial one. The peak of  $1183\text{ cm}^{-1}$  is assigned to the vibrational band of triazole N–N bond, while the peaks of  $1342\text{ cm}^{-1}$  and  $1327\text{ cm}^{-1}$  is assigned to the vibrational band of triazole ring. Generally, the distance in the metal-to-ligand bond length of the HS state is longer than that of the LS state. It means that the thermal change of the vibrational band of triazole N–N bond ( $1183\text{ cm}^{-1}$ ) and triazole ring ( $1324\text{ cm}^{-1}$ ,  $1327\text{ cm}^{-1}$ ) might reflect the thermally induced spin transition.<sup>3b</sup> That is, the vibrational band of the triazole ring coordinated with the HS state of  $\text{Fe}^{\text{II}}$  is less influenced by positive charge of  $\text{Fe}^{\text{II}}$  than the one coordinated with the LS state because of the difference of the distance between metal and ligand. In this case, some vibrational bands in the triazole ring exhibited the shift or the change of intensity by thermal LS-to-HS spin transition.

Moreover, FT-IR spectra were also consistent with the LIESST effects. Figure 5b showed that some vibrational bands of ligands exhibited the reversible peak shifts and the changes of peak intensities by visible light illumination. It is also recognized that the FT-IR spectrum at 10 K soon after illumination is almost compatible with that at 300 K, indicating that the photoinduced metastable state and the room temperature state



**Figure 4.** The absorbance change of Fe(AZ-trz) at 520 nm after visible light illumination for 3 min at 10 K. (The minus area shows the absorbance before illumination, while the plus area shows after illumination.)



**Figure 5.** The FT-IR spectra changes of Fe(AZ-trz). (a) Thermal change. (b) Photoinduced change at 10 K. (Spectra were obtained before illumination, right after illumination, and 3 min after illumination.)

have similar characteristic in the electronic state around the  $\text{Fe}^{\text{II}}$  site. The results demonstrated that the photoinduced LS-to-HS transition induced the elongation of the distance between  $\text{Fe}^{\text{II}}$  ion and N atom of triazole ring.

#### 4. Conclusions

In summary, we have succeeded in synthesizing a novel spin crossover  $\text{Fe}^{\text{II}}$ -triazole complex Fe(AZ-trz). From  $^{57}\text{Fe}$  Mössbauer spectra, we could have directly observed the photoinduced spin transition of Fe(AZ-trz) by visible light illumination at low temperature. It was confirmed that the photoinduced spin transition occurred by exciting a d–d electronic transition band of the  $\text{Fe}^{\text{II}}$  LS state species and the LIESST effect continued for 1 min by monitoring the absorption change at 520 nm. Moreover, the photoinduced spin transition phenomenon was also confirmed by monitoring the change of FT-IR spectra, and the result indicated that the electronic state around  $\text{Fe}^{\text{II}}$  of the photoinduced metastable form at low temperature was compatible with the electronic state of  $\text{Fe}^{\text{II}}$  at room temperature.

**Acknowledgement.** This work was supported by Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sport, Science, and Technology (MEXT) of Japan, and by New Energy and Industrial Technology Development Organization (NEDO) program (Japan).

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