57Fe Mössbauer, UV-visible, and FT-IR Study on Photoinduced Spin Transition of FeII-Triazole Complex

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We have synthesized a novel spin crossover FeII-triazole complex Fe(AZ-trz), where AZ-trz denotes 4-phenylazo-N-[1,2,4]triazole-4-yl-benzamide. 57Fe 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 FeII high-spin, HS, state was induced by exciting a d–d electronic transition band of the FeII low-spin state species. Furthermore, the measurements revealed the lifetime of excited FeII 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. 1 Metal complexes with the electron configuration d4 to d7 can take two different spin states, 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 phenomenon. 2 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 are one of the most well-known spin crossover complexes and general formula is given as below, [FeII(R-trz)]A2±nH2O, 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 FeII ions are triply bridged by triazole ligands through the N atoms occupying the 1- and 2-positions and the FeN6 core is close to a regular octahedron (Figure 1). So far, a lot of triazole complexes which exhibit spin crossover complexes and general formula is given as below, [FeII(R-trz)]A2±nH2O, 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 FeII ions are triply bridged by triazole ligands through the N atoms occupying the 1- and 2-positions and the FeN6 core is close to a regular octahedron (Figure 1). So far, a lot of triazole complexes which exhibit spin crossover phenomena are 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.

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Figure 1. Structure of Fe(AZ-trz). Left shows the molecular structure, while right shows the image of intermolecular structure.

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tered light, $\lambda_{\text{max}} = 450$ 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. $^{57}$Fe Mössbauer spectra were measured by using a Topologic Systems model 222 constant-acceleration spectrometer with a $^{57}$Co/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 Fe$^{II}$-triazole complex Fe(AZ-trz) (Figure 1) were newly synthesized in the method similar to previous reports. They were characterized by means of $^1$H NMR, FT-IR, and elemental analysis. In FT-IR spectroscopy, Fe(AZ-trz) displayed shifts of vibrational bands of $\pi-\pi^*$ transition of azobenzene compared with the ligand AZ-trz, which is due to the intermolecular $\pi-\pi^*$ interaction of azobenzene moiety 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 Fe(AZ-trz) in KBr pellet showed a red shift of the $\pi-\pi^*$ transition band of azobenzene compared with the ligand AZ-trz, which is due to the $\pi-\pi^*$ interaction of azobenzene.

The $\chi_M T$, value, on heating process, gradually increased from about 0.6 cm$^3$ K mol$^{-1}$ at low temperature up to 2.9 cm$^3$ 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 result sample in the HS state was cooled down, the $\chi_M T$ value decreased along with heating process reversibly and hysteresis was not observed. $^{57}$Fe Mössbauer spectra of Fe(AZ-trz) were shown in Figure 3. The temperature dependence of $^{57}$Fe Mössbauer spectra of Fe(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 Fe$^{II}$ with $t_{2g}^3$ electronic configuration, while the wide doublet peak is typical of the HS state of Fe$^{II}$ with $t_{2g}^3 e_g^2$ electronic 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 $\chi_M T$ value and the HS fraction of $^{57}$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 Fe$^{II}$ with HS state, which are hydrated. 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 Fe(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.

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 ($\lambda_{\text{max}} = 450$ nm) (Figure 3d). The HS fraction of the Fe$^{III}$ 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 $^3T_2g$ to $^3T_1g$ levels in the Fe$^{III}$ 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 HS state, induces the LS-to-HS transition by LIESST effect and the relaxation process occurred within 1 min. Furthermore, the LIESST effect of Fe(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 cm$^{-1}$ exhibited the red shift to 1177 cm$^{-1}$ and its intensity decreased. In addition, the intensity of the peak at 1327 cm$^{-1}$ increased, while that at 1342 cm$^{-1}$ decreased relatively and these two peaks slightly underwent red shift. On the other
hand, when the same sample was cooled down, spectrum recovery occurred to the initial one. The peak of 1183 cm$^{-1}$ is assigned to the vibrational band of triazole N–N bond, while the peaks of 1324 cm$^{-1}$ and 1327 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 cm$^{-1}$) and triazole ring (1324 cm$^{-1}$, 1327 cm$^{-1}$) might reflect the thermally induced spin transition. That is, the vibrational band of the triazole ring coordinated with the HS state of Fe$^{II}$ is less influenced by positive charge of Fe$^{II}$ 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 have similar characteristic in the electronic state around the Fe$^{II}$ site. The results demonstrated that the photoinduced LS-to-HS transition induced the elongation of the distance between Fe$^{II}$ ion and N atom of triazole ring.

4. Conclusions

In summary, we have succeeded in synthesizing a novel spin crossover Fe$^{II}$-triazole complex Fe(AZ-trz). From $^{57}$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 Fe$^{II}$ 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 Fe$^{II}$ of the photoinduced metastable form at low temperature was compatible with the electronic state of Fe$^{II}$ at room temperature.

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References


(6) $^{57}$Fe Mössbauer spectra were calibrated using the known hyperfine splitting of $\alpha$-iron.