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Lately, a number of studies have been made on photo-induced cooperative phenomena from both theoretical and experimental viewpoints. These photo-effects can be named as a photo-induced phase transition (PIPT) and PIPT materials are attractive and potential candidates of photo-memory with high sensitivity. We focus on spin-crossover complexes as a typical example of the PIPT and report exotic characteristics of it.

Keywords: photo-induced phase transition; spin-crossover complex

INTRODUCTION

Cooperative phenomenon is an important target for the physics and chemistry. Recently, extensive study has been started on a dynamical process of the phase transition. If photo-irradiation can trigger the phase transition, many advantages are brought into the dynamical study of the phase transition. For example, we will be able to measure accurately a generation and growth of the domain by femto-second spectroscopy, and also be able to control a direction of the phase transition by changing a wavelength of irradiated light. In this decade, it has been reported that π-conjugated polymer, charge transfer complex, and

magnetic semiconductor really show the phase transition triggered by photo-irradiation [1]. Here, we report a photo-induced spin state phase transition (PIPT) in spin-crossover complexes $[Fe(2\text{-pic})_3]Cl_2 \cdot EtOH$ (2-pic=2-aminomethyl-pyridine) as a typical example.

SPIN-CROSSOVER COMPLEX

In spin-crossover complex ($[Fe(2\text{-pic})_3]Cl_2 \cdot EtOH$), Fe^{2+} ion and six nitrogen atoms of three 2-pic molecules take quasi-octahedral construction, and every complex is combined with three other ones via hydrogen bonds which is an origin of the cooperative interaction (spin-lattice interaction)(fig. 1(a)) [2]. In quasi-octahedral ligand field, six d-electrons of Fe^{2+} ion can take two kinds of spin configurations; high spin (HS; S=2) and low spin (LS; S=0) configurations (see fig. 1(b)). Indeed the $[Fe(2\text{-pic})_3]Cl_2 \cdot EtOH$ shows the two step first order phase transition (T_c=114 K and 121 K) between the HS and LS phases [3]. This change of the spin configurations can be probed by magnetic, NMR, and spectroscopic measurements. Figure 2 shows temperature dependence of the absorption spectrum. In the HS state, a weak $^5T_2 \rightarrow {}^5E$ absorption band has been observed around 1.5 eV. In the LS state, strong singlet-singlet transition $^1A_1 \rightarrow {}^1T_1$ appears around 2.0 eV. Thus we can estimate the fraction of the HS and LS states using the absorption intensity at the specific photon energy.

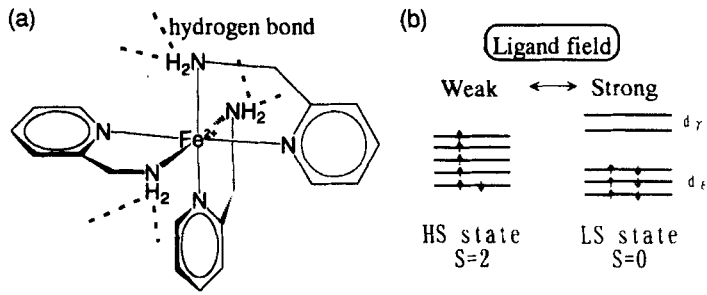

FIGURE 1, (a) The structure of $[Fe(2\text{-pic})_3]Cl_2 \cdot EtOH$ (2-pic=2-aminomethyl-pyridine). Metal-ligand complexes are combined via hydrogen bonds, as indicated by the dashed line. (b) High spin (HS; S=2) and low spin (LS; S=0) configuration of six d-electrons of Fe^{2+} ion under the weak and strong ligand fields.

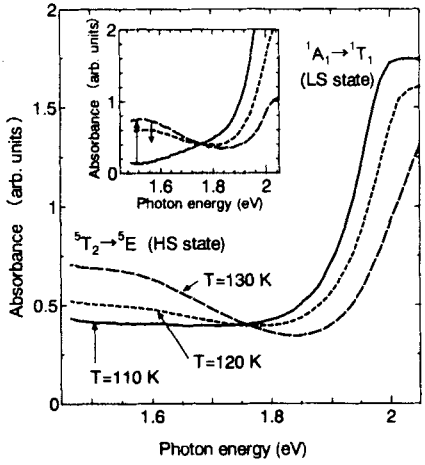

FIGURE 2, Temperature dependence of the absorption spectra observed at 130 K (dashed line), 120 K (dotted line), and 110 K (solid line). Inset; spectral changes accompanied with bi-directional photo-conversion between LS and HS states at 2.2 K.

In addition to the thermal transition, it has been reported that photo-irradiation can induce the bi-directional changes between the HS and LS states in this crystal [4]. At low temperature, the thermodynamically stable LS state can be converted to the metastable HS state by irradiating the continuous light of which photon energy is resonant to the $^1A_1 \rightarrow {}^1T_1$ absorption band (about 2.0 eV). This photo-converted HS state was trapped in this state and its lifetime was very long ($>10^4$ second). Furthermore, it was also possible that the trapped HS state goes back to the LS state by irradiating the light with the photon energy of 1.5 eV which was resonant to the $^5T_2 \rightarrow {}^5E$ absorption band (see the inset to Fig. 2). The observed bi-directional photo-conversion and very long lifetime of the trapped HS state assure that the observed photo-induced spin-crossover transition is not due to a thermal effect.

DYNAMICAL PROCESS OF PHOTO-INDUCED PHASE TRANSITION IN SPIN-CROSSOVER COMPLEX

Figure 3 shows the dynamical process of the photo-conversion from the LS to HS state under continuously irradiating 1.8 eV light with various intensities at 2.2 K. The crystal absorbed only less than 2-3% of the irradiated light, so the whole sample was excited homogeneously.

The first notable point is that an efficiency of the photo-conversion strongly depends on photon flux (I). Hereafter, I denotes the photon number absorbed by a fraction of the crystal with one cubic centimeter for every second. With I weaker than 9.0×10^{17} $cm^{-3}s^{-1}$ (I_{th}), the crystal remained in the LS state. If I became stronger than I_{th}, the occurrence of the photo-transformation from the LS to HS phases was confirmed.

The second important characteristic is the existence of incubation period (τ_{incu}). Just after the starting of the photo-excitation ($\tau<\tau_{incu}$), the LS phase gradually changed into the HS state with the same conversion speed (see the inset to Fig. 3). However, when the converted HS fraction exceeded 5% ($\tau>\tau_{incu}$), the conversion speed increased abruptly though I was kept constant value. A conversion efficiency Φ (the number of photo-converted Fe^{2+} ions by absorption of one photon) also increased after τ_{incu}. For example, with $I=1.0\times10^{18}$ $cm^{-3}s^{-1}$, Φ was 2.9 before τ_{incu} and it increased until 34 after τ_{incu}.

In addition to these features, the crystal converted to the HS state step-by-step. This step-like behavior suggests the occurrence of the phase separation. To confirm the phase separation in the dynamical process of photo-conversion, we directly observed the growth of the HS domain at 6.4 K under uniform irradiation of 1.9 eV continuous light by

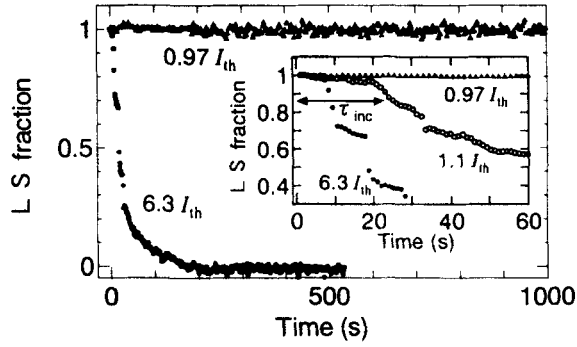

FIGURE 3, Photo-transformation process from LS to HS state under the continuous irradiation of 1.8 eV light. Excitation photon-flux I was the same as the value in inset. Inset; the early stage of photo-conversion process. Filled circles, open circles, and filled triangles are for I of 5.7×10^{13} (6.3 I_{th}), 1.0×10^{13}(1.1 I_{th}), 8.0×10^{13} $cm^{-3}s^{-1}$ (0.97 I_{th}), respectively. (Redraw based on the data shown in ref. 5)

microscope. The area of each photograph in Fig. 4 is 67×67 μm^2 and the wavelength region of the monitor light was 2.17-2.25 eV. The white and black parts show the HS and LS states, respectively (see Fig. 2). Before τ_{incu}, no change has been observed. However after τ_{incu}, the HS domain of about 20 μm in size abruptly appeared. As irradiation time increased, it grew up and other new HS domains appeared. Birth and growth of the HS domains is the origin of the step-like behavior.

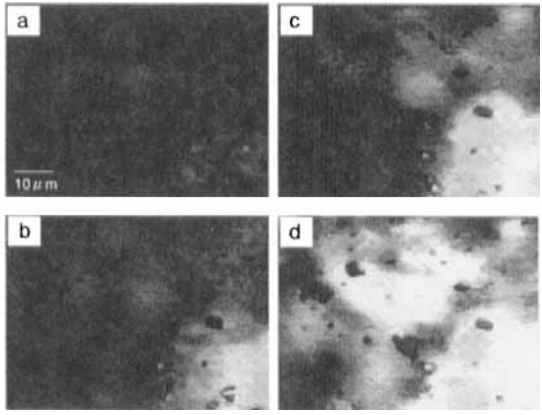

FIGURE 4, Transparent photograph of the photo-conversion from LS (black part) to HS (white part) state under the continuous irradiation of 1.95 eV light at 6.4 K. (a), (b), (c), and (d) shows the $0.8\tau_{incu}$, τ_{incu}, $1.3\tau_{incu}$, and $1.7\tau_{incu}$ after starting the irradiation. Images are 60×67μm^2

We consider that the observed natures of the PIPT dynamics, i.e. the threshold-like behavior, existence of incubation period, and phase separation, reflect the cooperative spin-lattice interaction among complexes [5]. It is a reasonable expectation that another weak external field affects the dynamical process of the spin state PIPT. Indeed, the photo-converted fraction of HS state from original LS state really shows the strong dependence on the magnetic field. Figure 5 is a converted HS fraction observed after photo-irradiation of 1800-seconds. The powdered crystals of $[Fe(2\text{-pic})_3]Cl_2 \cdot EtOH$ were excited at 10 K under various magnetic field. As enhancing the external magnetic field, the value of Φ increased nonlinearly. The magnetic field induced spin state transition from LS to HS states has not been observed without photo-excitation. Of course, additional experiment utilizing good single

crystal is necessary for more precise discussion on the magnetic field effect in PIPT dynamics.

CONCLUSION

In this present study, we reported several exotic phenomena in the dynamical process of the photo-induced phase transition (PIPT) of spin-crossover complex $[Fe(2\text{-}pic)_3]Cl_2 \cdot EtOH$. The characteristic behavior observed in this study will provide an important knowledge for the study of cooperative phenomena under nonequilibrium conditions and the application for optical memories. The theoretical analysis of this phenomena and more precise experiment using good single crystals under rather high magnetic field are now in progress.

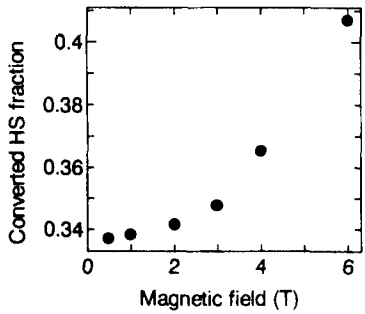

FIGURE 5, Converted HS fraction observed at 10 K after 1800-second photo-irradiation under various external magnetic fields.

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