On-off optical switching of the magnetic and structural properties in a spin-crossover complex

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On-off optical switching of the magnetic and structural properties in a spin-crossover complex

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A photoexcitation is one of the promising external fields to control the material phases. Here, the authors have demonstrated that the magnetic and structural properties of a spin-crossover complex, Fe(phen)$_2$(NCS)$_2$ (phen = 1,10-phenanthroline), can be reversibly switched by the on-off action of the continuous photoexcitation at the same temperature. The structural data suggest that the density of the high-spin Fe$^{2+}$ in the photoinduced phase is about 0.88. Suppressed atomic vibrations of the photoinduced phase exclude the conventional heating effect as the origin for the observed optical switching. © 2007 American Institute of Physics. [DOI: 10.1063/1.2736213]

The photoexcitation is one of the most promising methods to reversibly control the material phase/property of organic and metal-organic compounds, which may be utilized as an optical switching device. Among the materials, iron(II) spin-crossover complexes\textsuperscript{1-8} is one of the most interesting systems, as they are known to show the photoinduced low-spin (LS) to high-spin (HS) transition. However, this light-induced excited spin state trapping\textsuperscript{1} (LIESST) is a long-lasting phenomenon, and we need a troublesome thermal annealing and/or another photoexcitation to restore the material. This is a serious limitation for the development of optical switching device based on the spin-crossover complexes. In this letter, we report on a fast on-off optical switching of the magnetic and structural properties of Fe(phen)$_2$(NCS)$_2$ (phen = 1,10-phenanthroline) at the same temperature by a single continuous-wave laser at 532 nm. There exists a threshold excitation light intensity $I_{th}$ for the on-off optical switching phenomenon, suggesting that some cooperative interaction among the photoinduced HS species plays a crucial role.

The spin-crossover complex, Fe(phen)$_2$(NCS)$_2$, consists of the neutral Fe(phen)$_2$(NCS)$_2$ molecules within the orthorhombic (Pbcn; $Z=4$) cell.\textsuperscript{9} In the Fe(phen)$_2$(NCS)$_2$ molecule, the iron(II) is surrounded by four N atoms belonging to 1,10-phenanthrolines and two N atoms of (NCS)$^-\$ groups. The synthesis procedure of Fe(phen)$_2$(NCS)$_2$ was described elsewhere.\textsuperscript{9} The compound shows a thermally induced phase transition from the LS phase to the HS phase at $T_C = 176$ K. The thermally induced phase transition is accompanied by a volume expansion, reflecting the elongation of the Fe–N bond distances by 0.10–0.20 Å. At low temperature ($T < 60$ K), the compound shows the LIESST phenomenon\textsuperscript{10} by the photoirradiation of a He/Ne laser (633 nm).

Figure 1(a) shows an example of the on-off optical switching of Fe(phen)$_2$(NCS)$_2$ at 100 K, where no LIESST phenomenon is observed. The vertical axis is the density of the high-spin species ($n_{HS}$). The magnitude of $n_{HS}$ is estimated by the magnetic susceptibility measured in a Quantum Design magnetic properties measuring system (MPMS) superconducting quantum interference device magnetometer operated at 1000 Oe. The $n_{HS}$ value shows a clear binary response to the on-off action of the continuous-wave laser irradiation at 532 nm. The transition speed is about 10 s. Hereafter, we will call the phase under photoirradiation as “on phase.” In this phase, the creation process of the HS species overwhelms the thermal relaxation process of them. In Fig. 1(b), we plotted the $n_{HS}$ value in the on phase against the excitation powder ($I$). The $n_{HS}$ value begins to increase when $I$ reaches a threshold value ($I_{th} = 6$ mW/mm$^2$), and then reaches around 0.8 at $I = 20$ mW/mm$^2$. Such a threshold behavior is absent in the conventional LIESST phenomenon. Désaix et al.\textsuperscript{11} reported a similar threshold behavior, but with much slower transition time of order of hour, in a mixed crystal Fe$_{0.5}$Co$_{0.5}$NCS$_2$ brt)$_2$(NCS)$_2$H$_2$O. They attributed the behavior to the cooperative effect of the relaxation. In order to explain much faster switching time as observed in this letter, however, we need an additional cooperative effect in the creation process of the HS species. We think that the internal pressure\textsuperscript{6} induced by the photoinduced HS species, whose

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FIG. 1. (a) On-off optical switching of the density of the high-spin species ($n_{HS}$) measured at 100 K. The gray horizontal bar represents the on-off action of the excitation light at 532 nm. (b) Excitation power density ($I$) dependence of $n_{HS}$ in the “on phase” at 100 K.
ionic radius (=0.74 Å) is much larger than that (=0.61 Å) of the LS Fe$^{2+}$, causes a structural phase transition into the HS-rich phase. This argument is further supported by the fact that the cell volume of the photoinduced phase is much larger than that of the LS phase (vide infra).

In order to reveal the structural feature of the on phase, we have performed a synchrotron-radiation x-ray powder diffraction measurement at the SPring-8 BL02B2 beamline. A 532 nm laser beam was weakly focused onto the capillary with a convex lens (f=20 cm); the laser spot size (about 2 mm) is larger than the x-ray beam size (1×0.5 mm$^2$). The reflections were collected on an imaging plate, installed in a large Debye-Scherrer camera. The reflections were collected on an imaging plate in the 2θ range of 3°–76°. Figure 2 shows a part of the powder diffraction pattern at 92 K: black (gray) curve without photoexcitation is well reproduced by the grey curve with (without) photoexcitation. Even though the photoexcitation considerably changes the powder diffraction patterns, the pattern change is reversible for a repeated on-off action of the laser irradiation. The sample under photoexcitation is stable for more than 11 h, without any deterioration of the diffraction pattern. The gray curve without photoexcitation is well reproduced by the Rietveld refinement with the single orthorhombic (Pbcn; Z =4) phase, that is, the LS phase. On the other hand, we need an additional photoinduced phase to reproduce the black curve. The space group of the photoinduced phase is found to be the same as that of the LS phase. We ascribe the additional phase to the on phase, as observed in Fig. 1(a). Here, we emphasize that the formation of the photoinduced phase cannot be ascribed to the conventional thermal heating effects. Because the degree of the thermal atomic vibrations of the photoinduced phase, which was estimated by the so-called Wilson plot, is nearly the same as that at 92 K and is much smaller than that at 260 K.

Figure 3(a) shows the cell volume ($V$) of the LS phase (filled circles) and the photoinduced phase (open circles) against $I$. The $V$ value of both the phases shows negligible change against $I$. The cell volume ($V$=2.28 nm$^3$) of the photoinduced phase is about 4% larger than that ($=2.20$ nm$^3$) of the LS phase, reflecting the larger ionic radius of the HS Fe$^{2+}$. In Fig. 3(b), we plotted the mass fraction ($\delta$) of the photoinduced phase. As shown by the eye-guided broken line, the formation of the photoinduced phase shows the threshold behavior, consistently with the magnetic behavior [see Fig. 1(b)].

Here, let us compare the microscopic structure of the on phase with the other HS phases, that is, the low-temperature LIESST phase and the thermally induced HS phase. We listed in Table I the geometrical features of the FeN$_6$ octahedron of Fe(phen)$_2$(NCS)$_2$ molecule. The FeN$_6$ octahedron in the LS phase has larger distortion ($\Sigma$) and larger volume ($V$) as compared with those of the LS phase. At the bottom of Table I, we listed the relative volume ($V$/$V_0$) of the FeN$_6$ octahedron normalized by the cell volume. In spite of the 3% thermal shrinkage, the magnitude of $V$/$V_0$ (=0.006 35) in the LIESST phase at 30 K (Marchivie et al.\textsuperscript{16}) is nearly the same as that (=0.006 39) at 260 K. This is probably because the LIESST phase is a metastable HS phase, which can be produced also by the thermal quenching. Here, we emphasize that the magnitude of $V$/$V_0$ (=0.006 22) in the on phase is smaller than the other HS phases. If we postulate a linear relation between $n_{\text{HS}}$ and $V$/$V_0$, $n_{\text{HS}}$ of the on phase is estimated to be about 0.88. Such a suppressed $n_{\text{HS}}$ value should be ascribed to the dynamical nature of the on phase, where the creation process of the HS species balances with the thermal relaxation process of them.

Finally, let us investigate the charge density distribution of the Fe(phen)$_2$(NCS)$_2$ molecule. Figures 4(b)–4(d) show the isodensity surface contours (0.45 e Å$^{-3}$) of the molecule determined by the maximum entropy method (MEM) Rietveld analysis.\textsuperscript{14–17} on the x-ray powder diffraction patterns. The isodensity surface contour is sharp at 92 K [the LS phase: Fig. 4(b)] and in the on phase [Fig. 4(c)], while it is

![FIG. 2. X-ray powder diffraction patterns of Fe(phen)$_2$(NCS)$_2$ at 92 K under photoexcitation ($I$=64 mW/mm$^2$; black curve) and without photoexcitation (gray curve).](image)

![FIG. 3. (a) Cell volume ($V$) of Fe(phen)$_2$(NCS)$_2$ at 92 K against excitation power density ($I$). Closed and open circles stand for the LS phase and the on phase, respectively. (b) Mass fraction ($\delta$) of the on phase against $I$. A broken straight line is merely the guide for the eyes.](image)

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<th>Table I. Geometry of the FeN$_6$ octahedron of Fe(phen)$_2$(NCS)$<em>2$. $d</em>{\text{Fe-N}}$ ($i=1, 2, 3$) is the Fe–N$^2$ bond distance, $\Sigma$ is defined by the sum of the absolute values of the deviation from 90° of the 12 cis angles of the FeN$_6$ octahedron. $V$ and $v$ are the cell volume and the volume of the FeN$_6$ octahedron, respectively. These values were determined by the Rietveld analysis of the x-ray powder diffraction patterns. N$_1$ and N$_3$ atoms are located on 1,10-phenanthroline, while N$_3$ are on NCS$^-$ ion.</th>
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Reference 10.
Isodensity surface contour repeats the photoexcitation and thermal relaxation processes.

Fig. 4 rather blurred at 260 K/H20849 Fig. 4. (Color) (a) Ball and stick picture of the Fe(phen)$_2$(NCS)$_2$ molecule. Isodensity surface contour (0.45 Å$^{-3}$) of the Fe(phen)$_2$(NCS)$_2$ molecule in (b) the LS phase at 92 K, (c) the on phase at 92 K, and (d) the HS phase at 260 K, determined by the MEM/Rietveld analysis.

rather blurred at 260 K [the thermally induced HS phase; Fig. 4(d)]. This again indicates that the degree of the thermal atomic vibrations of the photoinduced phase is nearly the same as that at 92 K. Here, we emphasize that the respective Fe(phen)$_2$(NCS)$_2$ molecule in the photoinduced phase repeats the photoexcitation and thermal relaxation processes. The iron ion of the on phase [Fig. 4(c)] is more isolated as compared with the LS phase [Fig. 4(b)], reflecting the longer Fe–N bond distance.

In conclusion, we demonstrated the on-off optical control of the magnetic and structural properties of a molecular solid. The photoinduced phase, in which the creation process of the HS species balances with the thermal relaxation process of them, exists only under photoexcitation. Based on the structural analysis, we concluded that the photoinduced phase is a cold phase with suppressed HS density and long-range periodicity. Thus, the photoexcitation is a promising external field to control the material phase, especially when it is coupled with material parameters such as the spin state or the internal pressure.

This work was supported by a Grant-In-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology and Japan Science and Technology Agency (CREST “X-ray Pinpoint Structural Measurement-Development of the Spatial- and Time-resolved Structural Study Technique for Nano-materials and Devices”). The synchrotron-radiation x-ray powder diffraction experiments were performed at the SPring-8 BL02B2 beamline with approval of the Japan Synchrotron Radiation Research Institute (JASRI).

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13See EPAPS Document No. E-APPLAB-90-077718 for magnitude of the thermal atomic vibrations estimated by the Wilson plot. This document can be reached via a direct link in the online's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).
17The diffraction data were collected for 11 h at 92 K (the LS phase and the on phase), 260 K (the HS phase). The number of the structural factors derived by the Rietveld analysis was 672, 700, and 706 for the LS phase, the on phase, and the thermally induced HS phase, respectively. The maximum (minimum) $d$ values were 8.6 (1.2), 8.7 (1.2), and 8.7 A (1.2 A) for the off state, the on state, and the HS phases. The MEM analyses were carried out with a program ENIGMA (Ref. 16) using $132 \times 100 \times 172$ pixels. The $R_F$ factors based on the MEM charge densities are 3.5%, 2.7%, and 4.3% for the LS phase, the on phase, and the HS phase, respectively.