One-Shot-Laser-Pulse-Induced Cooperative Charge Transfer Accompanied by Spin Transition in a Co-Fe Prussian Blue Analog at Room Temperature

Naonobu Shimamoto,† Shin-ichi Ohkoshi,† Osamu Sato,†† and Kazuhito Hashimoto*†,††
†*Research Center for Advanced Science and Technology, The University of Tokyo, Meguro-ku, Tokyo 153-8904*
††*Kanagawa Academy of Science and Technology, Takatsuku, Kawasaki, Kanagawa 213-0012*

(Received December 26, 2001; CL-011301)

A one-shot-laser-pulse (6 ns) irradiation converted the electronic state of $Na_{0.68}Co_{1.20}[Fe(CN)_6]\cdot3.7H_2O$ from $Fe^{II}(S=0)$-CN-$Co^{III}(S=0)$ to $Fe^{III}(S=1/2)$-CN-$Co^{II}(S=3/2)$ at room temperature. This photochemical reaction was observed only above the power density of 45 mJ pulse^{-1} cm^{-2}, and its quantum yield amounted to about 200%.

Photo-induced spin transition is one of the topics currently under active investigation in the field of metal complex solids; e.g., the light induced excited state trapping in $[Fe(ptz)_6](BF_4)_2$,[1] the photo-induced magnetization[2,3] and the magnetic pole inversion[4] in metal polycyanides. This is because metal complex solids have the advantage of the functionality design, compared to bulk materials such as metal oxides. The photo-induced magnetization was first observed in $K_{0.2}Co_{1.4}[Fe(CN)_6]\cdot6.9H_2O$.[2a] This photo effect is based on the charge-transfer induced spin transition (CTIST) between the $Fe^{II}(t_{2g}{}^6e_g{}^0, S=0)$-CN-$Co^{III}(t_{2g}{}^6e_g{}^0, S=0)$ and the $Fe^{III}(t_{2g}{}^5e_g{}^0, S=1/2)$-CN-$Co^{II}(t_{2g}{}^5e_g{}^2, S=3/2)$ states by the light irradiation. This change was accompanied with a large change in bond length, i.e., the Co-N bond length was longer by about 0.2 Å in Fe^{III}-CN-Co^{II} than in Fe^{II}-CN-Co^{III}.[2c] However, the observation of this phenomenon was limited at low temperature and the quantum yield was not so high.[5] Conversely, it is known that polydiacetylene undergoes a photo-induced structural change with a huge quantum yield of five hundred.[6a] This enhancement of efficiency is due to an avalanche phenomenon in the thermal hysteresis.[6] In this work, our focus was to achieve photo-induced spin transition with a fast response at room temperature. The key in our strategy was to cause a cooperative phase transition between two bistable states using a pulsed laser. For this attempt, we have chosen a Co-Fe polycyanide containing sodium, because its thermal CTIST curve contains a large hysteresis loop and its transition temperature can be tuned by adjusting the atomic composition ratio.[2e] In this paper, we show a phase transition accompanied by a spin transition in the solid of $Na_{0.68}Co_{1.20}[Fe(CN)_6]\cdot3.7H_2O$ at room temperature, induced by only a one-shot-laser-pulse irradiation.

The sample was prepared by mixing an aqueous solution of $CoCl_2$ (2 mM) and NaCl (5 M) to an aqueous solution of $Na_3[Fe(CN)_6]$ (2 mM) and NaCl (5 M), under stirring at 50 °C. The formula of the obtained compound was determined from the results of the induced couple plasma mass spectral (ICP-MS) analysis and the common CHN analysis method, as the follows. Anal. Calcd for $Na_{0.68}Co_{1.20}[Fe(CN)_6]\cdot3.7H_2O$: Na, 3.73; Co, 20.05; Fe, 15.08; C, 19.46; N, 22.70; H, 2.13%. Found: Na, 3.62; Co, 19.67; Fe 14.81; C, 19.26; N, 22.76; H, 2.19%. The infrared (IR) spectra were measured with an FT-IR 8900 (JASCO). Magnetic measurements were carried out using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S). A powder sample was spread on a transparent adhesive tape (sample thickness = about 2 μm) and irradiated by a pulsed Nd^{3+}; YAG laser (wavelength: $\lambda = 532$ nm; pulse width: 6 ns; power density: 0.5–178 mJ pulse^{-1} cm^{-2}). The spot size of the irradiated area was about 2 mmϕ.

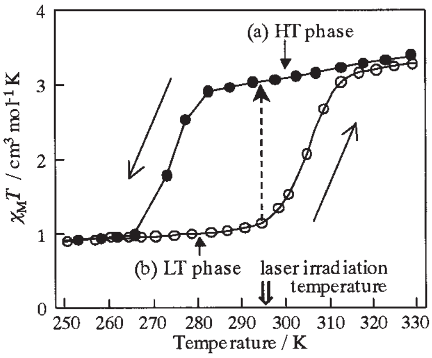

Figure 1. $\chi_M T$ vs T plots for $Na_{0.68}Co_{1.20}[Fe(CN)_6]\cdot3.7H_2O$ at $H = 5000$ G, in the cooling (●) and the warming (○) processes.

The temperature dependence of the molar magnetic susceptibility (χ_M) in the present compound is shown in Figure 1. In the cooling process, the product values of the χ_M and temperature abruptly dropped from 2.9 cm^3 mol^{-1} K at 283 K to 1.0 cm^3 mol^{-1} K at 265 K. The transition temperature from the high-temperature (HT) phase to the low-temperature (LT) phase was 275 K. Conversely, in the warming process, the $\chi_M T$ values abruptly rose from 1.2 cm^3 mol^{-1} K at 298 K to 3.0 cm^3 mol^{-1} K at 310 K. The transition temperature from the LT to the HT phase was 305 K. The width of the observed thermal hysteresis loop was 30 K. The IR absorption spectra showed that the LT phase was composed of only the Fe^{II}-CN-Co^{III} site, but the HT phase was composed of the Fe^{III}-CN-Co^{II}, Fe^{II}-CN-Co^{III} and Fe^{II}-CN-Co^{II} sites.[7] Taking into account the IR absorption intensities of the Fe^{II}-CN-Co^{III} mode and the charge balance of Na^I, Co^{II}, Co^{III}, Fe^{II} and Fe^{III}, the electronic states of the HT and LT phases in this compound were assigned to $Na^I{}_{0.68}Co^{III}{}_{0.39}Co^{II}{}_{0.81}[Fe^{III}(CN)_6]_{0.53}[Fe^{II}(CN)_6]_{0.47}\cdot3.7H_2O$ and $Na^I{}_{0.68}Co^{III}{}_{0.92}Co^{II}{}_{0.28}[Fe^{II}(CN)_6]\cdot3.7H_2O$, respectively.[7]

Figure 2(a) shows the change of the IR spectra before and after the one-shot-laser-pulse irradiation at 295 K, which is the temperature on the inside of the thermal hysteresis loop (see the dot allow in Figure 1). A one-shot-laser-pulse irradiation above a power density of 45 mJ pulse^{-1} cm^{-2} completely changed the IR spectrum of the LT phase to that of the HT phase. Further irradiation with the laser pulses did not change the IR spectra at

Copyright © 2002 The Chemical Society of Japan

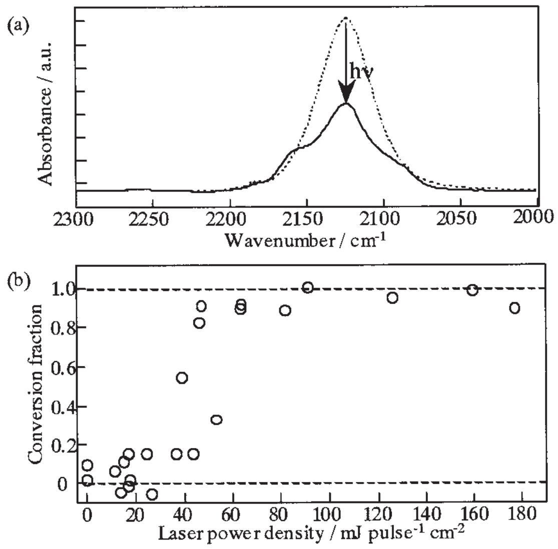

Figure 2. (a) Change of IR spectrum by a one-shot-laser-pulse irradiation of 64.0 mJ pulse^{-1} cm^{-2}. The spectra before and after irradiation are shown as a broken line and a solid line, respectively. (b) Conversion fraction induced by a one-shot-laser-pulse irradiation with different power densities.

all. These results indicate that the CTIST phenomenon was completed by only a one-shot-laser-pulse irradiation. The IR spectrum of this irradiated sample returned to that of the original LT phase by a cooling treatment (295 K → 263 K → 295 K), and changed again to the IR spectrum of the HT phase by a warming treatment (295 K → 323 K → 295 K), suggesting that the present sample was not damaged by the laser irradiation. Conversely, when the laser power density was below 45 mJ pulse^{-1} cm^{-2}, the IR spectrum of the LT phase was maintained even after irradiation by more than 10 shots. The conversion fraction of the IR spectrum of the LT phase to that of the HT phase by a one-shot-laser-pulse irradiation is shown as a function of the laser power density in Figure 2(b). The existence of such a clear threshold in the laser power density suggests that cooperative effects exist in the present photo-induced spin transition. The absorbed photons density under the irradiation with 45 mJ pulse^{-1} cm^{-2} corresponds to about 50% of the transferred electrons from Fe^{II} to Co^{III} on the sample by CTIST from LT to HT, meaning that the threshold value of the laser power corresponds to a quantum yield of about 200% for the present photochemical reaction.

Let us consider a possible mechanism of the observed one-shot-laser-pulse-induced charge transfer accompanied by spin transition.[8] One of the important characteristics of this compound is bistability of the LT and HT phases on the inside of the thermal hysteresis loop. The analysis of the hysteresis loop in Figure 1 gives the free energies of this compound (G) as a function of the HT phase fraction (x) at that temperature region.[9] Figure 3 represents the obtained potential energy curve of this compound at 295 K. The maximum energy appeared at $x = 0.45$ (denoted as $x_{\rm max}$). We can explain the threshold behavior qualitatively by using this potential energy curve as follows. Before irradiation, the system is in the LT phase ($x = 0$). With the laser irradiation, CTIST occurs and the fraction x increases instantaneously. When the fraction x is smaller than $x_{\rm max}$ (arrow (i) in Figure 3), the whole system returns to the original state (arrow (iii)). When x exceeds $x_{\rm max}$ (the arrow (ii)), however, the irradiated sample is completely converted into the HT phase as indicated with arrow (iv). Therefore, we conclude that bistability and strong cooperative interaction in this compound play indispensable roles in the present photo-induced spin transition.

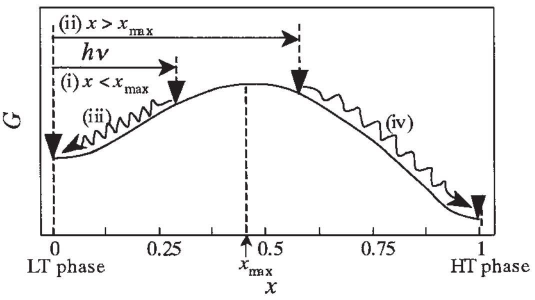

Figure 3. Free energy (G) as a function of the HT phase fraction (x) at 295 K.

This photo-induced phase transition differs from the one previously reported for low temperature[2] in regards to the following points. First, the present reaction is caused above the magnetic ordering temperature, and thus the irradiated sample does not have spontaneous magnetization. Second, the present reaction is a change from the metastable state to the ground state, which is the inverse of the reaction at low temperature. Finally, the quantum yield of the present reaction is much larger than that at low temperature.[5]

References and Notes

1 S. Decurtins, P. Gütlich, C. P. Köhler, and A. Hauser, *Chem. Phys. Lett.*, **105**, 1 (1984).

2 a) O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, *Science*, **272**, 704 (1996). b) O. Sato, Y. Einaga, T. Iyoda, A. Fujishima, and K. Hashimoto, *J. Electrochem. Soc.*, **144**, L11 (1997). c) T. Yokoyama, T. Ohta, O. Sato, and K. Hashimoto, *Phys. Rev. B*, **58**, 8257 (1998). d) O. Sato, Y. Einaga, A. Fujishima, and K. Hashimoto, *Inorg. Chem.*, **38**, 4405 (1999). e) N. Shimamoto, S. Ohkoshi, O. Sato, and K. Hashimoto, *Inorg. Chem.*, **41**, 678 (2002).

3 a) S. Ohkoshi, N. Machida, Y. Abe, Z. J. Zhong, and K. Hashimoto, *Chem. Lett.*, **2001**, 312. b) S. Ohkoshi, N. Machida, Z. J. Zhong, and K. Hashimoto, *Synth. Met.*, **122**, 523 (2001).

4 a) S. Ohkoshi, S. Yorozu, O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, *Appl. Phys. Lett.*, **70**, 1040 (1997). b) S. Ohkoshi and K. Hashimoto, *J. Am. Chem. Soc.*, **121**, 10591 (1999).

5 The quantum yield of the photo-induced magnetization at 5 K with the Xe lamp ($500 \le \lambda \le 750$ nm) at 5 K was c.a. 5%.[2d]

6 a) S. Koshihara, Y. Tokura, K. Takeda, and T. Koda, *Phys. Rev. Lett.*, **68**, 1148 (1992). b) K. Koshino and T. Ogawa, *J. Phys. Soc. Jpn.*, **67**, 2174 (1998).

7 The absorption peaks at 2156, 2123 and 2089 cm^{-1} were assigned to Fe^{III}-CN-Co^{II}, Fe^{II}-CN-Co^{III} and Fe^{II}-CN-Co^{II}, respectively.[2d,e] The electronic states were determined by comparing the peak intensities between the LT and the HT phases.[2e]

8 In a reference experiment carried out using the pulsed-laser with $\lambda = 1001$ nm, the photo-induced phase transition was not induced by even the intensity of 688 mJ pulse^{-1} cm^{-2}. This absorbed photon density corresponded to 6.8 times as large as that of the threshold value at 532 nm, suggesting that the present photo-induced phase transition is due to the photo-induced CTIST phenomenon.

9 O. Kahn, "Molecular Magnetism," VCH, New York (1993).