Visible Light-Induced Reversible Photomagnetism in Copper(II) Octacyanomolybdate(IV)

Shin-ichi Ohkoshi,[†] Naoko Machida,[†] Yukinori Abe,[†] Zhuang J. Zhong,[††] and Kazuhito Hashimoto*[†,††]
[†]*Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904*
[††]*Kanagawa Academy of Science and Technology, 3-2-1 Sakato, Takatsu-ku, Kawasaki, Kanagawa 213-0012*

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We report a visible light-induced reversible photomagnetism in $Cu^{II}_2[Mo^{IV}(CN)_8]·8H_2O$ (**1**). By the irradiation with a 480-nm laser light, the compound **1** showed a spontaneous magnetization with a magnetic ordering temperature (T_c) of 30 K. Conversely, the magnetization and T_c values were reduced by the irradiation with a 600-nm laser light. This photomagnetism is due to the reversible photo-induced electron transfer between paramagnetic **1** and its valence isomer exhibiting ferromagnetism.

One of the targets in the field of molecule-based magnets[1] is to develop novel types of functionalized magnets. In particular, the optical control of magnetic properties is the research that has attracted considerable attention. We have first reported a photo-induced magnetization in the system of $K_{0.4}Co^{II}_{0.3}Co^{III}[Fe^{II}(CN)_6]·5H_2O$.[2] Moreover, we have demonstrated a photo-induced magnetic pole inversion in a mixed ferro-ferrimagnet $(Fe^{II}_xMn^{II}_{1-x})_{1.5}[Cr^{III}(CN)_6]·7.5H_2O$.[3] In the present work, to survey new magnetic substances exhibiting a photo-induced magnetization, we have focused our attention on the photochemistry of mixed-valence compounds.[4] To date, for many class II mixed-valence compounds, the photo-induced electron transfer reactions have been observed in their solution states.[5,6] Hence, we considered that solids of class II mixed-valence compounds are potential materials exhibiting a photo-induced magnetization. From this point of view, we have studied the photomagnetism of $Cu^{II}_2[Mo^{IV}(CN)_8]·8H_2O$ (Cu^{II}; $3d^9$, $S = 1/2$, Mo^{IV}; $4d^2$, $S = 0$) (**1**) and observed the photo-induced magnetization effect.[7,8] We here report a visible light-induced reversibility of the photomagnetism in the compound **1**.

The prepared compound **1** is a violet powder.[9] The CN stretching frequency for **1** was observed at 2162 cm^{-1} in the IR spectra. The X-ray powder diffraction pattern spectra showed complicated many peaks, indicating that the morphology of **1** is not amorphous but crystalline. The UV–vis spectrum showed the intervalence transfer (IT) band between Mo^{IV}–CN–Cu^{II} and Mo^{V}–CN–Cu^{I} around 500 nm. This observed UV–vis spectrum almost corresponded to the optical absorption spectra in the solution of Cu^{II} / $[Mo^{IV}(CN)_8]^{4-}$.[5a,6] Magnetic measurements showed that the compound **1** is paramagnetic in the temperature region of $1.7\ K \le T \le 350\ K$ (Figure 1a, open circles).

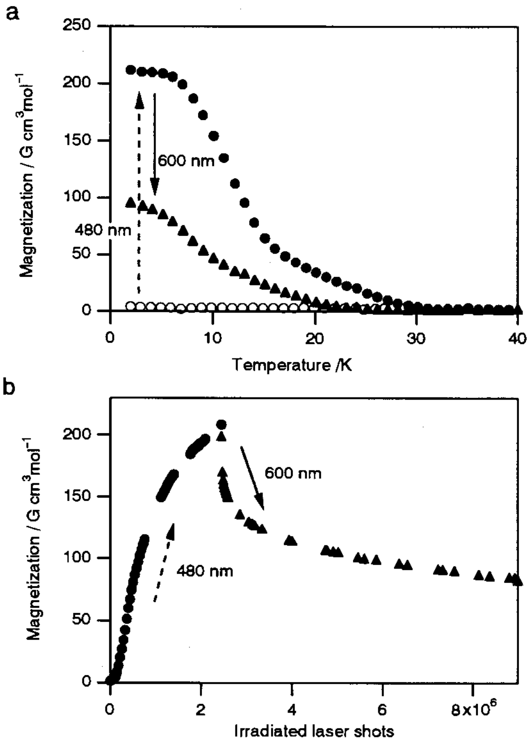

Figure 1. (a) Visible light-induced reversible magnetization in the compound 1 under the field of 10 G at 5 K; (○) before irradiation; (●) after irradiation of 480 nm; (▲) after irradiation of 600 nm. (b) Magnetization vs irradiated laser shots plots in the compound 1 under the field of 10 G at 5 K using the laser lights of (●) 480 nm and (▲) 600 nm.

The photomagnetic effect in the compound **1** was investigated using various laser lights between 430 and 650 nm.[10] By the irradiation with the 480 nm laser light (0.25 mJ cm^{-1} $pulse^{-1}$) at 5 K, the compound **1** showed the spontaneous magnetization with the Curie temperature (T_c) of 30 K (Figure 1a, closed circles). This induced magnetization persisted for a period of two days at 5 K after turning off the light. In contrast, when the irradiation light was switched to 600 nm (0.40 mJ cm^{-1} $pulse^{-1}$), the magnetization decreased and the T_c value was reduced to 22 K after the irradiation of 6.5×10^6 shots (Figure 1a, closed triangles). In the present measurement, the photo-reduced magnetization was not complete (Figure 1b). One of the reasons of this is as follows: The IT band of **1** is very broad (ca. 350–650 nm) and hence the complex **1** slightly absorbs the 600 nm laser light, resulting that the equilibrium between photo-reduced magnetization and photo-induced magnetization is established. The present visible light reversibility of **1** could be repeated at least for 10 times. From the result of the wavelength of the laser light vs the change in the magnetization, the magnetization of **1** is induced by the irradiation of the laser light with $430 \le \lambda < 520$ nm and, conversely, the magnetization is reduced by the laser light with $520 \le \lambda \le 650$ nm. We have thus observed the visible light-induced reversible change between the paramagnetic and ferromagnetic states by the irradiation with different laser lights.

In the light of the photo-induced electron transfer reaction in an aqueous solution of Cu^{II} / $[Mo^{IV}(CN)_8]^{4-}$,[5,6] the present reversible photomagnetism could be explained as follows. In

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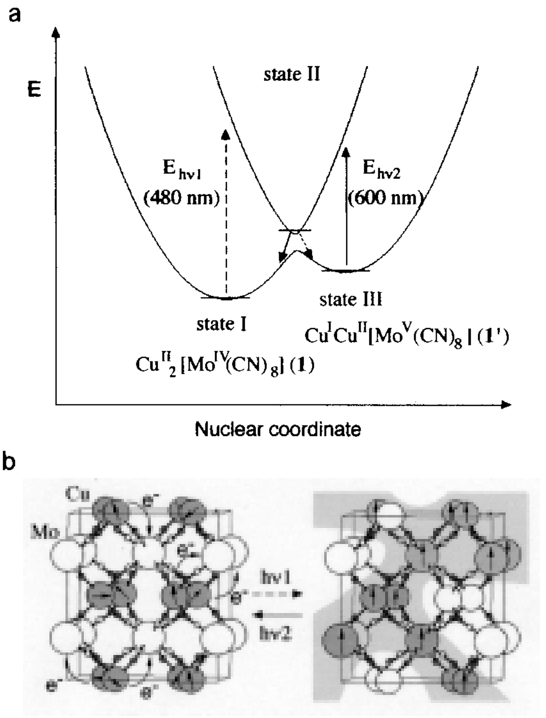

Figure 2. (a) Potential energy diagrams in the solid state of the class II mixed-valence compound **1**. (b) Schematic illustration of possible magnetic spin coupling in the solid state of **1** by the irradiation. Gray shadow shows the route of the possible ferromagnetic spin alignment. The schematic structure is represented based on the crystal structure of $Mn^{II}_2[Mo^{IV}(CN)_8]\cdot 4H_2O$.[12] Large circle is Mo ion, middle circle is Cu ion, small black circle is carbon atom, and small white circle is nitrogen atom.

general, the schematic potential diagram of class II mixed-valence compound **1** is represented as shown in Figure 2a. The compound **1** in the initial state (state I) is paramagnetic. By the irradiation with 480 nm laser light, compound **1** is excited to the charge transfer state (state II). The **1** in the state II immediately relaxes to the state I or forms the mixed valence isomer (Mo^V–CN–Cu^I) (state III). In this valence isomer state, Mo^V ion ($4d^1$, $S = 1/2$) has an unpaired electron but Cu^I ion ($3d^{10}$, $S = 0$) has no unpaired electron. However, half of the copper ions should remain as Cu^{II} ion due to the stoichiometric limitation in the present compound. Therefore, the irradiated **1** will be expressed as $Cu^ICu^{II}[Mo^V(CN)_8]\cdot 8H_2O$ (**1'**). Because the magnetic coupling between unpaired electrons on Cu^{II} and Mo^V ions in $Cu^{II}_{1.5}[Mo^V(CN)_8]\cdot 3H_2O$ is ferromagnetic,[7] the unpaired electrons on Mo^V (S=1/2) and Cu^{II} (S=1/2) ions of **1'** are expected to interact ferromagnetically. The possible routes of the spin alignment are schematically shown in Figure 2b. Conversely, when **1'** is irradiated by the 600-nm laser light, the back electron transfer occurs via the state II, and hence **1'** returns to the paramagnetic original **1**. Experimentally, the photon energy (E) for the photo-reduced magnetization process ($520 \le \lambda \le 650$ nm) was lower than that for the photo-induced magnetization process ($430 \le \lambda < 520$ nm). This result is also consistent with the relationship of $E_{h\nu 2} < E_{h\nu 1}$ in the schematic potential diagram of the compound **1**.

In summary, we could switch between the paramagnetic and ferromagnetic states reversibly by the visible light-irradiations in the $Cu^{II}_2[Mo^{IV}(CN)_8]\cdot 8H_2O$ solid, which is one of the class II mixed-valence compounds.[5] One of the reasons of this success is that the electronic structure of class II mixed-valence compounds meets the conditions of the reversible photo-induced electron transfer. In many class II mixed-valence compounds, the photo-induced electron transfers have been already observed in their solution state.[4–6] Therefore, the class II compounds will be potential materials exhibiting the photo-reversible magnetic effect. We believe that the present work shows the promising route for preparing the photomagnetic materials.

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References and Notes

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6 Henning et al. reported that $[Mo^{IV}(CN)_8]^{4-}$ and Cu^{2+} ions form a mixed-valence compound in an aqueous solution, which exhibits IT band around 500 nm (ref 5a,b). By the excitation of this band, the electron transfer proceeds from Mo^{IV} to Cu^{II} ions, producing the valence isomers Cu^I / $[Mo^V(CN)_8]^{3-}$. It is also reported that the Cu^I / $[Mo^V(CN)_8]^{3-}$ possess a very long lifetime of 3.65×10^3 s at 93 K (ref 5c).

7 S. Ohkoshi, N. Machida, Z. J. Zhong, and K. Hashimoto, accepted to the special issue for J. S. Miller's recipient of the 2000 ACS Chemistry of Materials Award in *Synth. Metal*. In this topical paper, we showed the photo-induced magnetization of **1** as follows: When the paramagnetic compound **1** was irradiated by a filtered blue light (400–430 nm, 3 mW /cm^2) of a Xe lamp at 5 K, the irradiated sample exhibited a spontaneous magnetization with a T_c value of 17 K. The magnetization after the irradiation indicated that the irradiated sample is a ferromagnet. By annealing the irradiated sample above 200 K, the magnetic property of this sample returned to the initial state.

8 C. Mathonière group is also studying the photomagnetic effect of the same compound: G. Rombaut, M. Verelst, S. Golhen, L. Ouahab, C.Mathonière, and O. Kahn, *Inorg. Chem.* in press.

9 The title compound **1** was obtained by the following minor modified methods of ref 11. An aqueous solution of $K_4[Mo(CN)_8]\cdot 2H_2O$ (0.2 mol dm^{-3}) was added to an aqueous solution of $CuCl_2\cdot 2H_2O$ (0.2 mol dm^{-3}). Elemental analyses of the prepared sample showed that a formula for **1** is $Cu^{II}_2[Mo^{IV}(CN)_8]\cdot 8H_2O$: Calcd for $Cu^{II}_2[Mo^{IV}(CN)_8]\cdot 8H_2O$: Cu, 22.09; Mo, 16.68; C, 16.70; N, 19.48; H, 2.80 %. Found: Cu, 22.0; Mo, 16.2; C, 17.6; N, 19.5; H, 2.9 %.

10 Magnetic susceptibility and magnetization measurements before and after irradiation were carried out using a Quantum Design MPMS 7 superconducting quantum interference device (SQUID) magnetometer. A sample (~ 0.1 mg) supported on a commercial transparent adhesive tape was placed on the edge of an optical fiber. As exciting light sources, the OPO laser (Surelight OPO; HOYA-continum, $410 \le \lambda \le 2500$ nm) pumped by Nd-YAG laser (Surelight II; HOYA-continum, $\lambda = 355$ nm, repetition = 10 Hz, pulse width = 5 ns) was used.

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