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Visible light-induced magnetization change of the cyano-bridged $3d-4f$ heterobimetallic

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Abstract

A visible light-induced magnetization change of the $3d-4f$ heterometallic, $[Nd(DMF)_4(H_2O)_3(\mu\text{-NC})Co(CN)_5] \cdot H_2O$ (DMF = N,N-dimethylformamide), is observed and described. The plots of $\chi_M T$ versus T of the complex showed that the $\chi_M T$ values, after visible light illumination, were enhanced by about 25% as compared to before irradiation in the temperature range of 5–40 K.
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Keywords: Light-induced; Magnetism; Cyano-bridge; $3d-4f$ complex

Photo-induced magnetization has been studied and mainly concentrated on Prussian blue analogs and transition metal complexes [1,2]. However, the photo-control of the magnetic and optical properties remained a challenging topic for material science in view of the possible implementation in optical and memory devices. It was noted that the composite of Prussian blue analogs were generally complicated and crystallization of Prussian blue analogs was difficult, making verification of the proposed structures by X-ray crystallographic analysis impractical [3–12]. In contrast, the synthesis and structural characterization of various cyano-bridged $3d-4f$ heterobimetallics have been reported; driven by the interest in the molecular magnetism [13]. In this report, we focus on developing novel photo-responsive molecule-based magnetic materials. Recently, we discovered the photo-induced magnetization of the cyano-bridged $3d-4f$ hetero-bimetallic assembly $[Nd(DMF)_4(H_2O)_3(\mu\text{-NC})Fe(CN)_5] \cdot H_2O$ (DMF = N,N-dimethylformamide) (**1**) [14]. To further explore the photo-induced magnetization change of the cyano-bridged $3d-4f$ heterobimetallics, another $3d-4f$ het-

erometallic $[Nd(DMF)_4(H_2O)_3(\mu\text{-NC})Co(CN)_5] \cdot H_2O$ (**2**) has been developed and studied with the diamagnetic metal Co^{3+} ions. With this combination, a visible light-induced magnetization change of **2** has been observed. It was observed to be different from the UV light-induced magnetization phenomenon of **1**.

2 was synthesized by the facile reaction of $NdCl_3 \cdot 6H_2O$ and $K_3Co(CN)_6$ following the previous report [13,15]. The crystal structure (Fig. 1) revealed that the Nd^{3+} ions were eight-coordinated in a square anti-prism arrangement, while the Co^{3+} ions were six-coordinated in an octahedral environment. A cyanide bridge linked the Nd^{3+} ion to a $[Co(CN)_6^{3-}]$ moiety. The three-dimensional flexible network of the crystal lattices in **2** (Fig. 2) essentially formed via hydrogen bonds and the van der Waals cohesive forces through the inter-molecular interaction. This flexible network structure played a dominant role in the formation of a long-lived metastable state during the photo-illumination.

The nature of magnetic properties for **2** had been described in previous report [15]. It revealed that the paramagnetic interaction dominated its molecular magnetism in the range of 5–300 K although the weak anti-ferromagnetic interaction was reveled below 7 K. When the photo-induced magnetization change was

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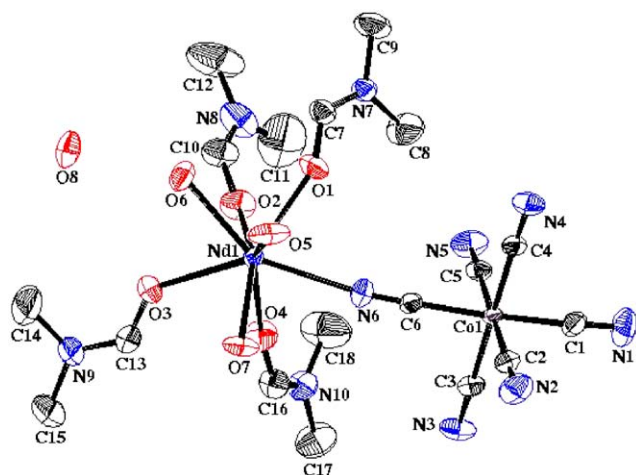E-mail address:* einaga@chem.keio.ac.jp (Y. Einaga).

Fig. 1. The crystal structure of **2**: hydrogen atoms are omitted for clarity and the thermal ellipsoids are drawn at 50% probability level.
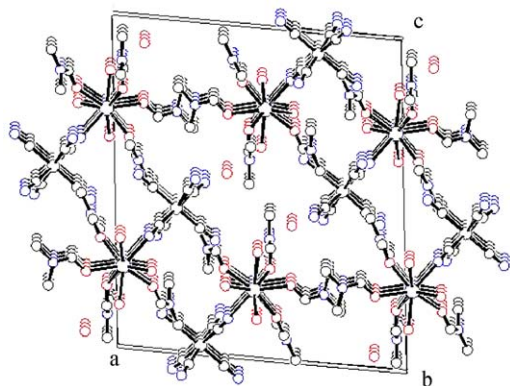

Fig. 2. The three-dimensional packing structure of **2**: viewing from the crystallographic *b*-axis.

Fig. 3. Magnetic susceptibilities ($\chi_M T$) versus temperature (T) curves of **2** at $H = 5000$ G: before (■) and after (□) visible light illumination.

investigated, an Hg–Xe lamp was employed as the light source. The visible light was channeled through an optical fiber into the SQUID magnetometer for the sample illumination. Upon irradiation at 5 K, the magnetization was increased and gradually saturated after several hours. The plots of $\chi_M T$ versus T of **2** (Fig. 3) showed that the $\chi_M T$ values were enhanced by about 25% as compared to those before irradiation in the temperature range of 5–40 K. It was also noted that the change of photo-induced magnetization depended on the sample geometry and the light transmission. The photo-excited state remained for several hours at 5 K. By increase of temperature to 40 K, the photo-induced magnetization had disappeared. This indicated that the photo-excited state had recovered to the ground state. The lower thermal decay temperature of **2** as compared to **1** suggested that the photo-induced magnetization change of **2**, arisen from visible light stimulation, was weaker than **1**. It should be noted that the scale of the photo-induced magnetization change for both **1** and **2**
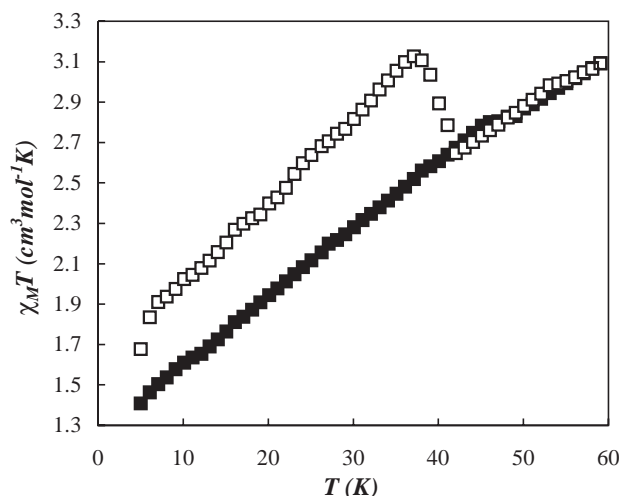
was much smaller as compared to the Prussian blue's. In the former, they were still in a range of paramagnetization although the $\chi_M T$ values were enhanced by about 25–45% after light irradiation. However, for the latter, the paramagnetization had turned to ferrimagnetization after light irradiation.

Photo-induced magnetization for various transition metal compounds has been studied [16–18]. Three outstanding examples were Prussian blue analogs, nitroprusside complexes and spin crossover complexes of Fe^{2+}. The corresponding mechanism of the aforementioned photo-induced magnetic phenomenon was described by several authors. The authors have proposed that photo-switching magnetic properties of Prussian blue analogs follow the mechanism of charge transfer from metal to metal and the electron transfer back and forth was induced by photons at different wavelengths through the cyanide bridge that was created in the related magnetization changes [1]. The charge transfer from metal to ligand was suggested as the mechanism for the photo-induced magnetization change of the nitroprusside complexes [1]. The mechanism of light-induced excited spin state trapping was explained as the transition of electron from LS ($^1A_1$) to HS ($^5T_2$) [1]. In general, three important characteristics coexisted in the photo-induced magnetization phenomena: (1) photo-induced metastable state resulted from charge transformation and/or polarization of electron; (2) photo-induced magnetization change accompanying the structural changes or lattice deformation arose from the photo-excited state; (3) the cooperativity derived from the network, crystal defect and $\pi-\pi$ interaction played an essential role in enhancing the photo-exited state.

In comparison with the aforementioned photo-induced magnetization behaviors, all characteristic factors

were observed in the previous report for the photo-induced magnetization of the cyano-bridged $3d-4f$ heterobimetallic of **1** [14]. It proposed that UV light illumination induced the LMCT transition, accompanied with an increase in the electron population on Fe^{3+} ion. This was followed by the increase in the metal–ligand bond length and a small structural change in the inorganic network. This small structural change was propagated by the molecular interaction in the inorganic network. Further to that, the cooperativity formed by the molecular interaction served to increase the activation energy of the relaxation process, which resulted in the observation of the photo-excited state. It was the cooperativity arising from the flexible network that led to the photo-induced magnetization change.

Since single crystal structures show that **1** and **2** are isomorphous crystals, the same mechanism for the photo-induced magnetization changes should be proposed. Nevertheless, the diamagnetic properties of d^6 electron configuration of Co^{3+} remind that a different mechanism may be possible. In fact, IR spectra revealed the significant differences between **1** and **2** with respect to the changes before and after visible light illumination. Namely, the symmetry or the pattern of the peaks changed significantly in **1** after UV light irradiation, while only small changes occurred in **2** after visible light illumination. The $\nu(CN)$ of IR spectra for **2** (Fig. 4), after visible light irradiation, revealed small red shifts (averaging about $3\,cm^{-1}$) from 2167, 2149 and $2139\,cm^{-1}$ to 2162, 2148 and $2136\,cm^{-1}$. It is an indication of the increase of electron population for the Co^{3+} ions or the rearrangement of d^6 electron configuration. On the basis of the smaller symmetry changes of the peak pattern as compared to that of **1**, the structural distortion of **2** was slightly smaller than **1**. Thus, a different mechanism that may be responsible for this novel photo-responsive behavior is proposed.
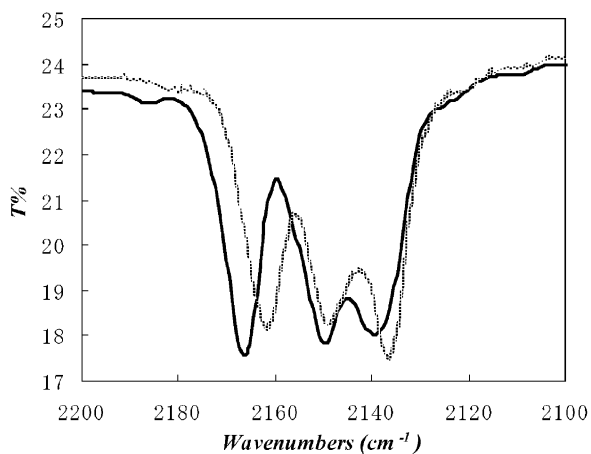

Fig. 4. IR spectra (KBr pallet) of **2** at 8 K: before (—) and after (· · · ·).

On the basis of the above-mentioned findings and previously proposed mechanism for Prussian blue analogs [7], we propose that the visible light irradiation induced a charge transformation from Nd^{3+} to Co^{3+} (MMCT) yielding Nd^{4+} and paramagnetic Co^{2+} (small red shifts of $\nu(CN)$ of IR spectra for **2** showed that the electronic density of cobalt atom increased after light illumination) and/or from charge transformation CN to Co^{3+} (LMCT), followed by the rearrangement of d^6 electronic configuration of Co^{3+} ions and the subtle structural deformation around Co^{3+} ions. In terms of the $4f$ orbitals split under octahedral crystal field, the lowest $fxyz$ orbital is occupied with two electrons, and two electrons reside in the higher triply degenerate set of f-orbital, which is only partially filled and therefore can give up easily an electron. Thus, the charge transformation and/or polarization from Nd^{3+} to diamagnetic Co^{3+} yielding Nd^{4+} and paramagnetic Co^{2+} are possible on the basis of the simple theoretical analysis. These resulted in the transition from the diamagnetic Co^{3+} ions to the excited paramagnetic Co ions through the number of spin or the polarization of spin. Furthermore, this photo-excited state was propagated in the three-dimensional flexible network structure through the intermolecular interaction. It further enhanced the number of spin or the polarization of the spin. Finally, the coopertivity derived from the propagation of the spin or the polarization of spin may have increased the magnetization. However, when treated by thermal effect, the photo-excited paramagnetic Co ions relaxed back to the ground state of the diamagnetic Co^{3+} ions. Thus, the photo-induced magnetization recovered back to normal. It should be emphasized that the evidence for proposing the above-mentioned mechanisms in this report is neither conclusive nor sufficient enough to fully substantiate them. This was due to the difficulty in obtaining several important data. The feasible and better measures require developing.

In summary, the molecule-based magnetization change of **2**, after visible light illumination, showed that the magnetic property for cyano-bridged $3d-4f$ heterobimetallic assembly can be influenced by visible light stimuli in a given temperature range. Our approach for realizing this photo-excited state was by introducing the flexible network structure through the hydrogen bonds in **2**. A flexible network structure was essential to realize such a metastable state. The finding demonstrated that besides UV light, visible light was also capable of inducing the photo-excited state for $3d-4f$ assemblies. In analogy to the paramagnetic Fe^{3+} ions, which are similar to those of Prussian blue analogs, the $3d-4f$ assemblies containing diamagnetic Co^{3+} ions were also found to be photo-responsive. It is obvious that the different photo-induced magnetic properties with respect to different light illumination derive from the differences in the transition metals. This work, together

with the previous findings, presents a new domain for photo-responsive molecule-based magnetic material. Because a number of cyano-bridged $3d-4f$ assemblies have been known, which are of facile synthesis and simple composition as compared to the Prussian blue analogs, novel molecule-based magnetic material with better properties can be developed in the near future. Finally, it will prompt the application in the field of photo-control switch and information storage.

Acknowledgments

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