

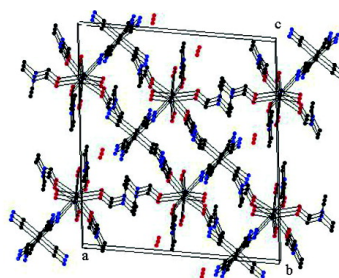
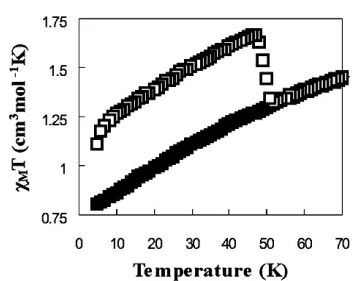
Communication

Photoinduced Magnetization of the Cyano-Bridged 3d–4f Heterobimetallic Assembly $\text{Nd}(\text{DMF})(\text{HO})(\text{CN})\text{Fe}(\text{CN})\cdot\text{HO}$ (DMF = *N,N*-Dimethylformamide)

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Photoinduced Magnetization of the Cyano-Bridged 3d–4f Heterobimetallic Assembly $\text{Nd}(\text{DMF})_4(\text{H}_2\text{O})_3(\mu\text{-CN})\text{Fe}(\text{CN})_5\cdot\text{H}_2\text{O}$ (DMF = *N,N*-Dimethylformamide)

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Photoinduced magnetic and optical properties have attracted much attention,^{1–5} because photocontrol of these properties is a challenging topic of interest in material science in view of the possible implementation in optical and memory devices.^{1b} It is noted that almost all previous reports have focused on Prussian blue analogues or transition metal complexes.^{2–5} However, crystallization of Prussian blue analogues is difficult, making verification of the proposed structures by X-ray crystallographic analysis impractical.^{2–5} In contrast, the synthesis and structural characterization of various cyano-bridged 3d–4f heterobimetallic assemblies have been reported driven by the interest in the molecular magnetism.⁶ Keeping the similarities of the two types of complex in mind, we studied the effects on the magnetic properties of the cyano-bridged 3d–4f heterobimetallic assemblies by light stimulation. As a result, a significant photoinduced magnetization was observed for $\text{Nd}(\text{DMF})_4(\text{H}_2\text{O})_3(\mu\text{-CN})\text{Fe}(\text{CN})_5\cdot\text{H}_2\text{O}$ (DMF = *N,N*-dimethylformamide) (**1**) in a given range of temperature. Herein, we describe the photoinduced magnetization for **1**.

1 was synthesized by a facile reaction of $\text{NdCl}_3\cdot 6\text{H}_2\text{O}$ dissolved in DMF and an equimolar quantity of $\text{K}_3\text{Fe}(\text{CN})_6$ dissolved in deionized water. The crystal structure for **1** (Figure 1) reveals that the Nd^{3+} ions are eight-coordinated in a square-antiprism arrangement, while the Fe^{3+} ions are six-coordinated in an octahedral environment. A cyanide bridge links a Nd^{3+} ion to an Fe^{3+} ion. In addition, a crystalline water molecule is involved in a neutral dinuclear unit. The possible intermolecular bond distances, which are shorter than the sum (3.2 Å) of van der Waals radii,⁷ reveal the presence of hydrogen bonds. Thus, a three-dimensional flexible network of the crystal lattices in **1** (Figure 2) was essentially formed by hydrogen bonds and van der Waals cohesive forces among the intermolecules. It is this flexible network structure that plays a dominant role in the formation of a photoexcited state during light illumination.⁸

A UV lamp was used as the light source in the investigation of photoinduced magnetization changes. The UV light was induced through an optical fiber into the SQUID magnetometer for illumination of the sample. Upon irradiation at 5 K, the magnetization was slowly increased and gradually saturated after several tens of minutes. The plots of $\chi_{\text{M}}T$ versus temperature for **1** (Figure 3) show that the $\chi_{\text{M}}T$ values are enhanced by about 45% as compared to those before irradiation in the temperature range of 5–50 K. However, the UV light induced conversion rate depends on the sample geometry and the light transmission. The photoexcited state could remain for at least several hours at 5 K. When the temperature was increased to 50 K, the photoinduced magnetization was erased.

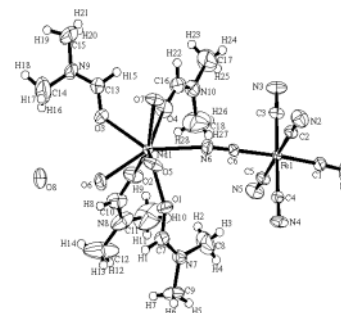


Figure 1. A view of the molecular structure for **1**. Hydrogen atoms are omitted for clarity. Possible hydrogen bond distances: O(8)–O(6) 2.662(7) Å, O(8)–N(1) 2.77(1) Å, O(8)–N(2) 2.85(1) Å. Crystallographic data for **1** ($\text{C}_{18}\text{H}_{36}\text{FeN}_{10}\text{O}_8\text{Nd}$): FW = 720.63, yellow prism (0.40 × 0.30 × 0.30 mm), monoclinic, space group $P2_1/n$ (No. 14), $a = 19.930(9)$ Å, $b = 8.914(5)$ Å, $c = 17.642(7)$ Å, $\beta = 95.87(3)^\circ$, $V = 3117(2)$ Å³, $Z = 4$, $D_c = 1.535$ g cm⁻³, $R_1 = 0.077$, $R_w = 0.112$.

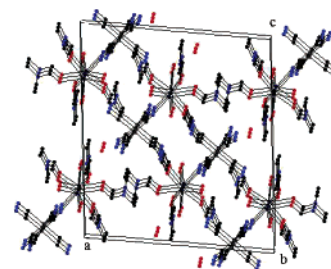


Figure 2. A projection of the three-dimensional crystal packing for **1** formed by hydrogen bondings and van der Waals cohesive forces among the intermolecules.

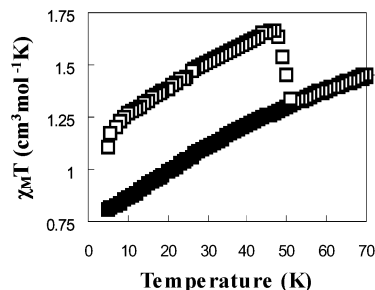


Figure 3. Plot of magnetic susceptibilities ($\chi_{\text{M}}T$) versus temperature (T) for **1** at $H = 5000$ G: before UV light illumination (■); after UV light illumination (□).

This indicates that the photoexcited state had returned to the ground state.

To explain this interesting photoinduced magnetic phenomenon, IR, UV, XRD, and Mössbauer spectra for **1** at lower temperature

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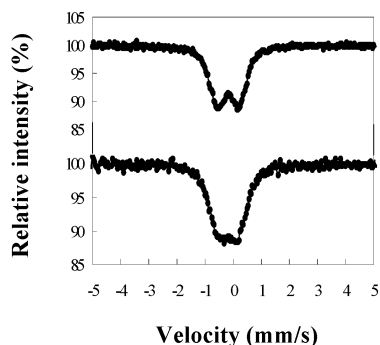


Figure 4. Mössbauer spectra for **1** at 10 K: before UV light illumination (top); after UV illumination (bottom). The affected spectrum recovers after annealing (not shown).

were performed before and after irradiation. Meanwhile, consideration was given to the well-known metal to metal charge-transfer mechanism (redox reaction) which was used to explain photoinduced magnetization for Prussian blue analogues.^{3b,4a} However, Mössbauer spectra of ⁵⁷Fe for **1** at 10 K (Figure 4) show that the doublet absorption peak (isomer shift = -0.18 mm/s) remains after UV light illumination. These reveal that the oxidation state for iron ions remains unchanged.^{5c} In addition, charge transfer involving neodymium ions is unlikely because the valence would remain at +3. Thus, the charge-transfer mechanism for interpreting the photoinduced magnetic phenomenon of **1** was disproved. Nevertheless, the quadrupole splitting shrinks from 0.74 to 0.65 mm/s, suggesting that the ligand–metal bond distance and symmetry of the Fe^{III}(CN)₆ moiety may distort.⁹

Therefore, another mechanism, proposed to explain the photoexcited state for Fe(phen)₂(NCS)₂, is contemplated as being applicable in the present case. This has been proven by single crystallographic analysis of both the irradiated and the nonirradiated states of the photoinduced compound.¹⁰ It demonstrates that the major differences between the ground and the photoexcited states are in the bond lengths and the crystal cell volumes; however, these differences are very small. Thus, on the basis of previous work and our experimental results, we propose that UV illumination of complex **1** induces a LMCT transition. This is supported by the UV spectra¹¹ (Figure S1) and the accompanying increase in the electron density on Fe³⁺ revealed by the IR spectra (Figure S2). It is followed by an increase in the metal–ligand bond length and a small structural change as indicated by IR spectra¹² and X-ray powder diffraction¹³ (Figure S3) for **1**. This small structural change is propagated by molecular interactions in the inorganic network. Furthermore, the cooperativity resulting from the molecular interaction functions to increase the activation energy of the relaxation processes,⁸ which makes observation of the photoexcited state possible. It is the cooperativity arising from the flexible network that leads to the photoinduced magnetization changes. This is in accordance with the photoinduced memory effect which can be triggered by electron excitation in a given material inducing a rearrangement of the lattice and the electronic configuration.¹⁴

In summary, the above-mentioned results clearly show that the magnetic properties of cyano-bridged 3d–4f heterobimetallic compounds can be influenced by external stimuli in a given

temperature range. Our strategy to realize a photoexcited state in **1** is the introduction of a flexible network structure by means of the hydrogen bonds. These findings may open up a new domain for developing molecule-based magnetic materials. Because a number of cyano-bridged 3d–4f assemblies, which are of facile synthesis and simple composition as compared to Prussian blue analogues, are known, novel molecule-based magnetic materials with superior properties may be developed and discovered soon. Finally, this will promote applications in the fields of photocontrolled switches and information storage.

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Supporting Information Available: X-ray crystallographic file for **1** in CIF format, experimental procedures, as well as UV, IR, and XRD spectra for **1** at lower temperature before and after UV light illumination (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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