

Photomagnetism in Cyano-Bridged Bimetal Assemblies

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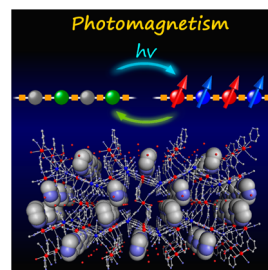
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CONSPECTUS

The study of photoinduced phase-transition materials has implications for the fields of inorganic chemistry, solid-state chemistry, and materials science. Cyano-bridged bimetal assemblies are promising photomagnetic materials. Because cyano-bridged bimetal assemblies possess various absorption bands in the visible light region, their electronic and spin states can be controlled by visible light irradiation. Moreover, the selection of magnetic metal ions and organic ligands provide a way of controlling spin–spin interactions through a cyano bridge.

In this Account, we describe cyano-bridged bimetal assemblies developed in our laboratory. $\text{Cu}^{\text{II}}_2[\text{Mo}^{\text{IV}}(\text{CN})_8] \cdot 8\text{H}_2\text{O}$ (CuMo), $\text{Rb}^{\text{I}}\text{Mn}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ (RbMnFe), and $\text{Co}^{\text{II}}_3[\text{W}^{\text{V}}(\text{CN})_8]_2 \cdot (\text{pyrimidine})_4 \cdot 6\text{H}_2\text{O}$ (CoW) induce photomagnetism via photoinduced metal-to-metal charge transfers (MM'CT), while $\text{Fe}^{\text{II}}_2[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot (4\text{-pyridinealdoxime})_8 \cdot 2\text{H}_2\text{O}$ (FeNb) exhibits a photoinduced magnetization via a photoinduced spin crossover. Irradiation with 473 nm light causes the CuMo system to exhibit a spontaneous magnetization with a Curie temperature (T_c) of 25 K, but irradiation with 532, 785, and 840 nm light reduces the magnetization. In this reversible photomagnetic process, excitation of the MM'CT from Mo^{IV} to Cu^{II} produces a ferromagnetic mixed-valence isomer of $\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}[\text{Mo}^{\text{V}}(\text{CN})_8] \cdot 8\text{H}_2\text{O}$ (CuMo'). CuMo' returns to CuMo upon irradiation in the reverse-M'MCT band. RbMnFe shows a charge transfer (CT)-induced phase transition from the $\text{Mn}^{\text{II}}\text{–Fe}^{\text{III}}$ phase to the $\text{Mn}^{\text{III}}\text{–Fe}^{\text{II}}$ phase. Irradiation with 532 nm light converts the $\text{Mn}^{\text{III}}\text{–Fe}^{\text{II}}$ phase into the $\text{Mn}^{\text{II}}\text{–Fe}^{\text{III}}$ phase, and we observe photodemagnetization. In contrast, irradiation of the $\text{Mn}^{\text{II}}\text{–Fe}^{\text{III}}$ phase with 410 nm light causes the reverse phase transition. A CT-induced Jahn–Teller distortion is responsible for this visible light-induced reversible photomagnetic effect. In the CoW system, a CT-induced spin transition causes the thermal phase transition from the $\text{Co}^{\text{II}}\text{–W}^{\text{V}}$ phase to the $\text{Co}^{\text{III}}\text{–W}^{\text{IV}}$ phase. Irradiation of the $\text{Co}^{\text{III}}\text{–W}^{\text{IV}}$ phase with 840 nm light causes ferromagnetism with a T_c of 40 K and magnetic coercive field (H_c) of 12 000 Oe, but excitation of the back M'MCT ($\text{Co}^{\text{II}} \rightarrow \text{W}^{\text{V}}$) with 532 nm light leads to the reverse phase transition.

These examples of the photomagnetic effect have occurred by exciting MM'CT bands. In the fields of inorganic chemistry and materials science, researchers have studied extensively the photoinduced phase transitions between low-spin (LS) and high-spin (HS) transition metal ions. Recently, we have observed the first example of photoinduced spin crossover ferromagnetism with a FeNb system ($T_c = 20$ K and $H_c = 240$ Oe), in which a strong superexchange interaction between photoproducted $\text{Fe}^{\text{II}}(\text{HS})$ and neighboring paramagnetic Nb^{IV} operates through a CN bridge. The optical switching magnets described in this Account may lead to novel optical recording technologies such as optomagnetic memories and optical computers.



1. Introduction

Research on photoinduced phase-transition materials is an attractive subject in the fields of inorganic chemistry, solid-state chemistry, and materials science.^{1–4} Some of the applicative results have been utilized in industrial applications, including optical recording materials such as digital versatile discs (DVDs) and Blu-ray discs.^{5,6} In addition,

magnetic materials have a longer industrial history as magnetic recording materials in tapes and discs. For example, magneto-optical disks, in which recording is performed by heating using light a magnetic material beyond its Curie temperature (T_c), are still being utilized to this day. Unlike these conventional magnetic recording materials, photomagnetic materials (optical switching magnets) described

herein switch their physical properties when exposed to light, thereby leading to the potential development of novel optical recording technologies such as opto-magnetic memories and optical computers. Photomagnetic materials, therefore, have been receiving not only scholarly attention from the perspective of nonequilibrium phase transition, but also extensive industrial attention.

As candidate materials that demonstrate photomagnetism, metal assembled complexes are thought to be promising. Since metal complexes possess various absorption bands in the visible light region, there is a possibility of controlling their electronic states and spin states using visible light. Moreover, magnetic metal ions and organic ligands can be selected in view of spin–spin interactions, and thus material design suitable for each research objective can be conducted. Additionally, when a cyanometalate is bonded to a transition metal, the ligand field of the cyanometalate, that is, the energy levels of the d-orbitals, is influenced. For example, in an octacyanometalate building block, it takes various coordination geometries, for example, square antiprism, bicapped trigonal prism, dodecahedron, resulting in that various crystal structures can be formed. Motivated by these characteristics, various cyano-bridged metal-complex magnetic materials with zero-dimensional high-spin clusters, one-, two-, and three-dimensional (3D) magnetic structures have been designed and synthesized.^{7–35} By focusing on the various coordination structures of metal ions and the structural flexibility of cyano groups, several studies have reported on functional metal complex magnetic materials that respond to physical stimuli such as light,^{36–57} pressure,^{58,59} and electric field,^{60,61} as well as chemical stimuli such as humidity⁶² and gaseous adsorption.^{63,64} In particular, we have developed several magnetic functional cyano-bridged metal complexes, for example, photomagnetic materials,^{38,39,46–56} magnetic materials exhibiting two compensation temperatures,⁶⁵ ferroelectric ferromagnetic metal complex,⁶⁰ piezoelectric ferromagnetic material exhibiting magnetization-induced second harmonic generation (MSHG),^{66,67} humidity and solvent vapor sensitive magnetic materials,^{62,64} and so on. Herein, we describe cyano-bridged magnetic metal complexes that we have developed: (i) $\text{Cu}^{\text{II}}_2[\text{Mo}^{\text{IV}}(\text{CN})_8] \cdot 8\text{H}_2\text{O}$, (ii) $\text{Rb}^{\text{I}}\text{Mn}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$, and (iii) $\text{Co}^{\text{II}}_3[\text{W}^{\text{V}}(\text{CN})_8]_2 \cdot (\text{pyrimidine})_4 \cdot 6\text{H}_2\text{O}$, which induce photomagnetic phenomena via photoinduced charge-transfer transition, and (iv) $\text{Fe}^{\text{II}}_2[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot (4\text{-pyridinealdoxime})_8 \cdot 2\text{H}_2\text{O}$, which exhibits photoinduced spin-crossover ferromagnet.

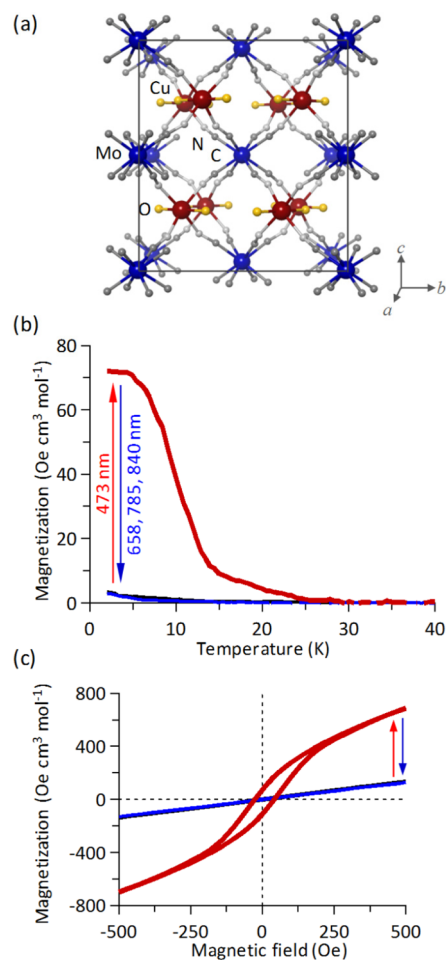


FIGURE 1. Visible-light-induced reversible photomagnetism in the CuMo octacyano-complex. (a) Schematic crystal structure. (b) Magnetization vs temperature curves before (black line) and after light irradiation with 473 nm light (red line), after irradiation with 658, 785, or 840 nm light (blue line). (c) Magnetic hysteresis loops at 3 K before (black line) and after irradiating with 473 nm light (red line), after thermal treatment of 250 K (blue line).

2. Visible-Light-Induced Reversible Photomagnetism of a CuMo Octacyano-Complex Based on Photoinduced Charge Transfer

In mixed-valence metal complexes, metal-to-metal charge transfer (MM'CT) absorption bands are observed in the visible region. If charge transfer can be induced by the photoexcitation of the MM'CT, the electronic states of mixed-valence metal complexes can be changed. Herein, the visible-light-induced reversible magnetism of CuMo octacyano mixed valence metal complex,^{53,55} $\text{Cu}_2[\text{Mo}(\text{CN})_8] \cdot 8\text{H}_2\text{O}$, is described.

This complex, obtained as a purple powder, has a 3D structure where Cu and Mo are alternately bridged via a cyano group (Figure 1a). Magnetization vs temperature curves of this complex before and after irradiation are

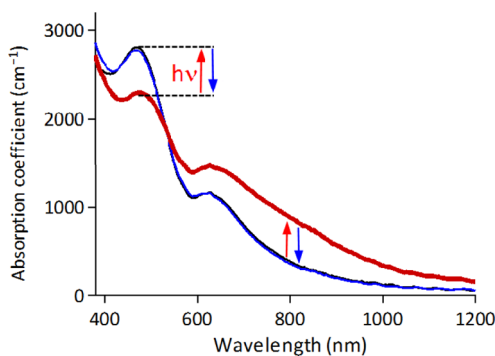


FIGURE 2. UV–vis absorption spectra of the CuMo octacyano-complex at 3 K before (black line) and after irradiation with 473 nm light (red line) and after thermal treatment of 250 K (blue line).

shown in Figure 1b. Before irradiation, the paramagnetic behavior with Cu^{II} ($S = 1/2$) was observed. Upon exposure to a 473 nm continuous wave (cw) laser light, spontaneous magnetization was induced, resulting in a ferromagnetic state with $T_c = 25$ K. Magnetization vs magnetic field curve after irradiation indicated magnetic coercive field (H_c) of photoinduced phase is 30 Oe (Figure 1c). Conversely, when this photoinduced ferromagnetic phase was irradiated with laser light with $\lambda \geq 520$ nm, we observed decreases in magnetization. Figure 1b depicts such decreases in magnetization upon light irradiation with a wavelength of 658, 785, or 840 nm. The UV–vis absorption spectrum of film-type of $\text{Cu}_2[\text{Mo}(\text{CN})_8] \cdot 8\text{H}_2\text{O}$ showed the MM'CT band from Mo^{IV} to Cu^{II} around 480 nm (Figure 2). After irradiation with 473 nm light, reverse-M'CT band from Cu^{I} to Mo^{V} was observed around 710 nm. The photoinduced spontaneous magnetization is thought to be induced by the photoinduced charge-transfer transition from Mo^{IV} ($S = 0$) to Cu^{II} ($S = 1/2$). After the charge transfer was completed, the composition of its valence isomer became $\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}[\text{Mo}^{\text{V}}(\text{CN})_8] \cdot 8\text{H}_2\text{O}$, with unreacted Cu^{II} remaining. It is thought that a superexchange interaction was induced between the unreacted Cu^{II} and the photoproducted Mo^{V} ($S = 1/2$) via cyano groups, which lead the ferromagnetism (Figure 3a). In contrast, photoinduced demagnetization indicates that the laser irradiations of 658, 785, or 840 nm caused the photoinduced back charge transfer from Cu^{I} to Mo^{V} , thereby restoring the initial state. It is worth noting that this photoinduced magnetization also disappeared upon a thermal treatment (250 K) and reverted to the initial state. The consideration of this reversible photomagnetic phenomenon in terms of the energy diagram of mixed-valence metal complexes^{68–71} suggests that irradiation to MM'CT absorption bands with a 473 nm laser light produced a valence isomer. Irradiation to the back photoinduced charge transfer absorption bands with a

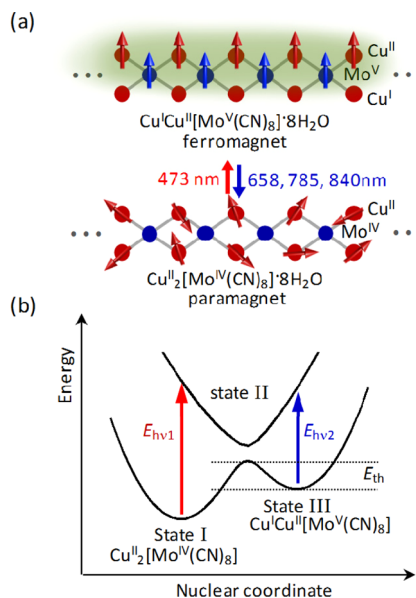


FIGURE 3. (a) Mechanism of magnetic ordering of photomagnetic phenomena in the CuMo octacyano-complex. (b) Mechanism of photoinduced charge transfer in a class II mixed-valence complex.

658, 785, or 840 nm laser light converted the valence isomer to the initial state with light (Figure 3b). This photomagnetic effect was repeatedly observed, indicating that this complex is a visible-light-induced, reversible photomagnetic material. Moreover, an analogue of this complex, $\text{Cs}_2\text{Cu}^{\text{II}}_7[\text{Mo}^{\text{IV}}(\text{CN})_8]_4 \cdot 6\text{H}_2\text{O}$, can be electrochemically synthesized as a thin film, with similar photomagnetic properties.⁵⁴

3. Visible-Light-Induced Reversible Photomagnetism of a RbMnFe Hexacyano-Complex Based on Photoinduced Charge-Transfer-Induced Jahn–Teller Distortion

Photomagnetism can be achieved by light irradiation onto magnetic materials which have a bistability. In bistable materials, the energy barrier between bistable states maintains a photoinduced state, resulting the observation of the persistent photoinduced magnetic state. From this perspective, RbMnFe hexacyano complex (Figure 4a),^{46–48,72–77} one of a Prussian blue analogue, is suitable for observing photomagnetism. It is known to exhibit a charge-transfer phase transition from Mn^{II} ($S = 5/2$)– NC – Fe^{III} ($S = 1/2$) [high-temperature (HT)] phase to Mn^{III} ($S = 2$)– NC – Fe^{II} ($S = 0$) [low-temperature (LT)] phase accompanying Jahn-teller distortion on Mn^{III} .

To excite an MM'CT band, the LT phase was exposed to a 532 nm laser light. Before light irradiation, magnetization vs temperature curve of the LT phase revealed that this phase

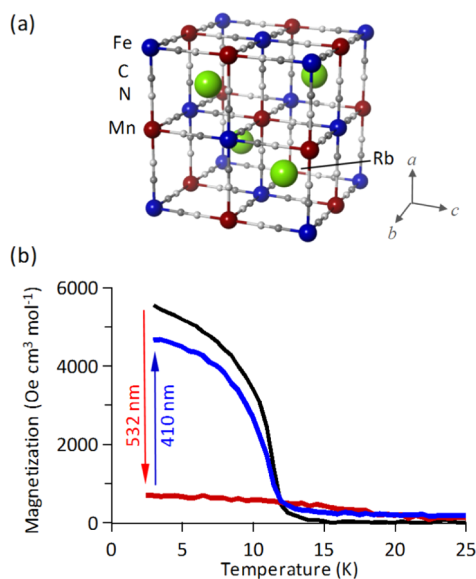


FIGURE 4. Visible-light-induced reversible photomagnetism in the RbMnFe hexacyano-complex. (a) Crystal structure. (b) Magnetization vs temperature curves before and after light irradiation. Before irradiation (black line), after irradiation with 532 nm light (red line), after irradiation with 410 nm light (blue line).

was ferromagnet with $T_C = 12$ K (Figure 4b). Additionally, upon exposure to a 532 nm laser light, a decrease in magnetization was observed, and upon subsequent exposure to a 410 nm laser light, an increase in magnetization was observed. Such a change phenomenon in magnetization was repeatedly observed by alternately irradiating the LT phase with 532 and 410 nm lasers.

This reversible photomagnetism can be explained by the following. Exposure to a 532 nm laser light excited the MM'CT ($\text{Fe}^{\text{II}} \rightarrow \text{Mn}^{\text{III}}$) band, inducing a photoinduced phase with the same electronic state as the HT phase. The relaxation of the metastable photoinduced phase to the stable LT phase was suppressed by thermal energy. In contrast, the ligand-to-metal charge transfer (LMCT) ($\text{CN}^- \rightarrow \text{Fe}^{\text{III}}$) band excitation of $[\text{Fe}(\text{CN})_6]^{3-}$ induced by irradiation with a 410 nm laser light resulted in the different photoexcited state, resulting in the transition to the initial LT phase. To our knowledge, this is the first observation of such an optical switching between a ferromagnetism and an antiferromagnetism.

4. Photoinduced Gigantic Coercivity of a CoW Octacyano-Complex Based on Photoinduced Charge-Transfer-Induced Spin Transition

Octacyano metal complexes can have various coordination structures that depend on the chemical environment, e.g., square antiprism (D_{4h}), dodecahedron (D_{2d}), and bicapped

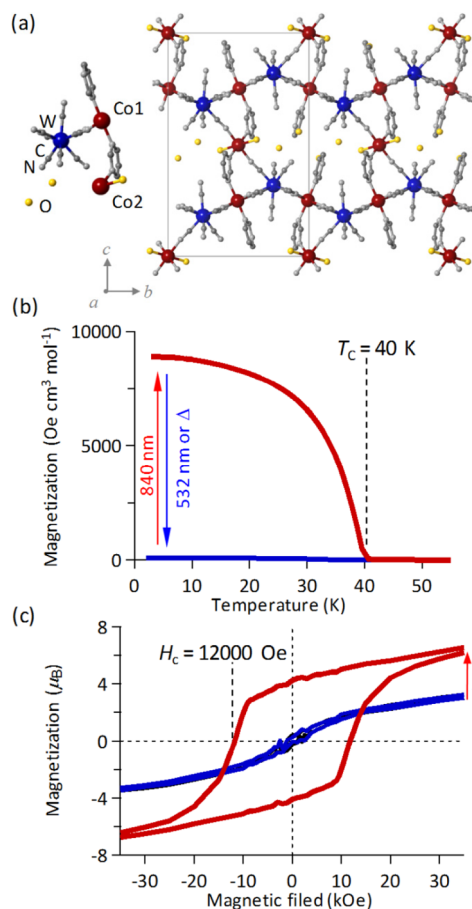


FIGURE 5. Crystal structure of the CoWprm octacyano-complex. (a) Asymmetric unit (left) and view along the a -axis (right). (b) Magnetization vs temperature curves before and after light irradiation. (c) Magnetic hysteresis loops before and after light irradiation (at 2 K). Before irradiation (black lines), after irradiation with 840 nm light (red lines), and after thermal treatment of 150 K or irradiation with 532 nm light (blue lines).

trigonal prism (C_{2v}). Therefore, octacyano metal complexes have the potential to sensitively respond to external stimuli. Here we discuss photomagnetic phenomena exhibiting gigantic coercivity, which are observed in $\text{Co}_3[\text{W}(\text{CN})_8]_2(\text{prm})_4 \cdot 6\text{H}_2\text{O}$ (CoWprm complex),^{51,52} a 3D structure containing pyrimidine (prm) as an organic ligand.

The crystal structure of a CoWprm complex, obtained as a red powder, belongs to the monoclinic system ($P2_1/n$) where Co and W are alternatively bridged via cyano ligands to form a 3D network structure (Figure 5a). This complex showed a charge-transfer-induced spin transition as a function of temperature. The electronic state of the HT phase is $\text{Co}^{\text{II}}(\text{HS}; S = 3/2)_3 - \text{W}^{\text{V}}(S = 1/2)_2$ and that of the LT phase is $\text{Co}^{\text{III}}(\text{LS}; S = 0)_2 - \text{W}^{\text{IV}}(S = 0)_2 - \text{Co}^{\text{II}}(\text{HS}; S = 3/2)$. This transition is induced by the MM'CT between Co and W and the spin transition in Co^{III} . Ultraviolet–visible (UV–vis) absorption spectra revealed a peak around 500 nm assigned to MM'CT,

$\text{Co}^{\text{II}} \rightarrow \text{W}^{\text{V}}$, in the HT phase and a peak around 750 nm assigned to $\text{M}^{\text{I}}\text{MCT}$, $\text{W}^{\text{IV}} \rightarrow \text{Co}^{\text{III}}$, in the LT phase.

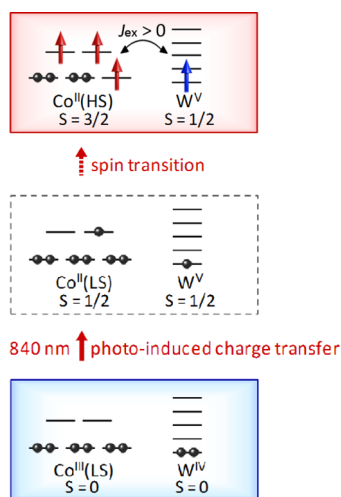


FIGURE 6. Mechanism of the photomagnetic phenomenon in the CoWprm octacyano-complex due to photoinduced charge-transfer-induced spin transition.

The LT phase of the CoWprm complex is paramagnetic. Upon light irradiating ($\lambda = 840$ nm), the sample exhibits spontaneous magnetization (Figure 5b). T_{C} and H_{C} of this photoinduced magnetic phase are 40 K and 12 000 Oe, respectively (Figure 5c). With the subsequent irradiation by a laser light ($\lambda = 532$ nm), the magnetization was decreased. Such a change in magnetization was repeatedly observed by alternatively irradiating the CoWprm complex with 840 and 532 nm lasers. Investigation of the electronic states of the CoWprm complex using infrared (IR) absorption spectra revealed that the visible-light reversible photomagnetic phenomenon observed was induced by the reversible charge-transfer-induced spin transition between the LT phase, $\text{Co}^{\text{III}}(\text{LS})_2\text{-W}^{\text{IV}}_2\text{-Co}^{\text{II}}(\text{HS})$, and the photoinduced phase, $\text{Co}^{\text{II}}(\text{HS})_3\text{-W}^{\text{V}}_2$ (Figure 6).

5. Photoinduced Spin Crossover Ferromagnetism of a FeNb Octacyano-Complex

Transition metal complexes (from d^4 to d^7) with octahedral coordination can transit from a high-spin (HS) state to a

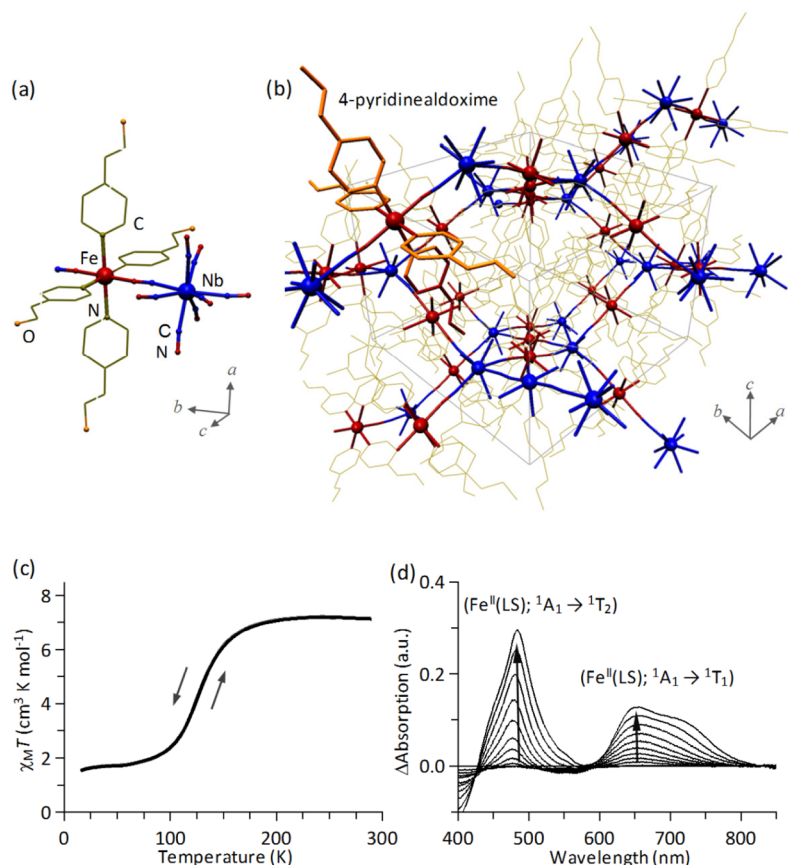


FIGURE 7. Crystal structure of the FeNb(4-pyoxm) octacyano-complex. (a) Asymmetric unit and (b) cyano-bridged Fe–Nb three-dimensional framework. (c) $\chi_{\text{M}}T$ – T curves of the FeNb(4-pyoxm) octacyano-complex. (d) Temperature dependence of UV–vis differential spectra. Spectra are depicted from 300 to 100 K at 20 K intervals by setting a spectrum at 300 K as the standard.

low-spin (LS) as temperature decreases, which is called a “spin crossover transition”. This phenomenon was first discovered in an Fe^{III} complex, and many spin crossover complexes have been reported since then.^{78–80} Transition phenomena from the LS state to the HS state by light irradiation are termed “light-induced excited spin-state trapping (LIESST)” and have been studied as a technique to control paramagnetic states using light. Since its first discovery in an Fe^{II} complex (Fe^{II}(1-propyltetrazole)₆(BF₄)₂),⁸¹ a wide variety of studies have been conducted.^{78,80} Spin crossover complexes that have been reported are mostly those composed of molecular crystals, where molecules gather to crystallize via the van der Waals force. However, if spin crossover complexes that have 3D network structures can be synthesized and HS sites can form a magnetic ordering with each other, then the spontaneous magnetization can be expected. From this perspective, we synthesized a new octacyano metal complex, Fe₂[Nb(CN)₈·(4-pyoxm)₈·2H₂O (FeNb(4-pyoxm) complex), which contains Fe, Nb, and 4-pyridinealdoxime (4-pyoxm) as the organic ligand and then discovered ferromagnetism caused by photoinduced spin crossover,⁴⁹ which is described below.

The crystal structure of an FeNb(4-pyoxm) complex is tetragonal (space group: *I4*₁/*a*) as shown in Figure 7a and b, where an Fe^{II} ion is connected to two N atoms of cyano groups and to four N atoms of 4-pyoxm. In addition, four cyano groups of Nb^{IV}(CN)₈ are bridged with Fe ions, and the other four are not bridged. Fe and Nb ions are continually bridged via cyano groups to form a 3D network structure.

A measurement of the temperature dependence of the molar magnetic susceptibility (χ_M) of an FeNb(4-pyoxm) complex revealed a drastic decrease in the $\chi_M T$ around 130 K (Figure 7c). In the UV–vis absorption spectra, absorption assigned to the d–d transitions (¹A₁→¹T₂, ¹A₁→¹T₁) of Fe^{II}(LS) (*S* = 0) that was absent at room temperature was observed around 480 and 650 nm at low temperature region (Figure 7d). Additionally, in the ⁵⁷Fe Mössbauer spectra, Fe^{II}(LS) was observed at low temperature. These results suggest that a decrease in $\chi_M T$ around 130 K is induced by the spin crossover transition from Fe^{II}(HS) (*S* = 2) to Fe^{II}(LS) (*S* = 0).

Next we discuss photomagnetic effects in an FeNb(4-pyoxm) complex. Prior to light irradiation, the LT phase of an FeNb(4-pyoxm) complex is paramagnetic, while after light irradiation with a 473 nm cw laser light, spontaneous magnetization and magnetic hysteresis appear, suggesting that the paramagnetic phase changes ferromagnetic phase

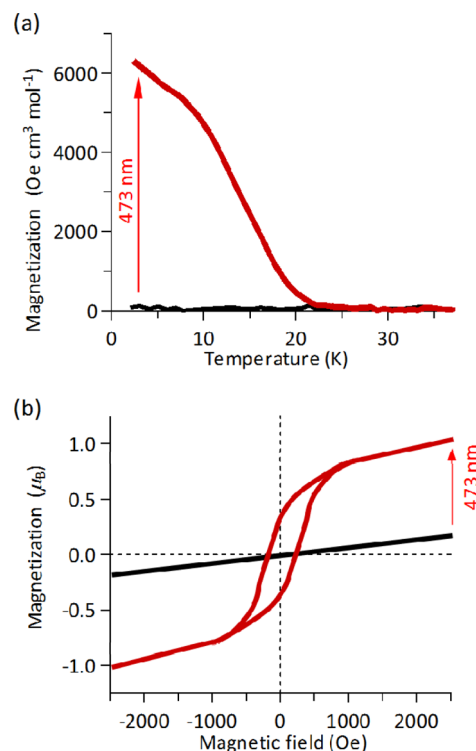


FIGURE 8. Photomagnetism in the FeNb(4-pyoxm) octacyano-complex due to photoinduced spin crossover. (a) Magnetization vs temperature curves before and after light irradiation. (b) Magnetic hysteresis loops before and after light irradiation at 2 K. Before irradiation (black lines) and after irradiation with 473 nm light (red lines).

(Figure 8). In the photoinduced ferromagnetic phase, T_C , H_C and saturation magnetization (M_S) are 20 K, 240 Oe, and 7.4 μ_B , respectively. The M_S value of 7.4 μ_B agrees well with a calculated value of 7.7 μ_B obtained in a case where the spins of photoinduced Fe^{II}(HS) (*S* = 2, $g_{\text{Fe}^{\text{II}}(\text{HS})} = 2.17$) and Nb^{IV} (*S* = 1/2, $g_{\text{Nb}^{\text{IV}}} = 1.99$) are antiparallel to each other. Before and after light irradiation with a 473 nm laser light, a UV–vis spectra at 3 K revealed a decrease in the absorption of ¹A₁→¹T₂ and ¹A₁→¹T₁ of Fe^{II}(LS), while Mössbauer spectra revealed a decrease in the Fe^{II}(LS) peak and an increase in Fe^{II}(HS) peak. These results suggest that the observed photomagnetic phenomenon was induced by the photoinduced spin crossover from Fe^{II}(LS) to Fe^{II}(HS).

The photomagnetism of FeNb(4-pyoxm) complexes can be explained by a scheme described below. First, in the LT phase before light irradiation, a paramagnetic ion Nb^{IV} and a diamagnetic ion Fe^{II}(LS) are alternately bridged via a cyano group, and thus the spin source is physically remote, leading paramagnetism. Upon irradiation with a 473 nm light, Fe^{II}(LS), whose ground state is ¹A₁, is excited to a singlet state ¹T₂ (or ¹T₁), a part of which subsequently transits to a quintet state, ⁵T₂, through a triplet state ³T₂ or ³T₁ (Figure 9).

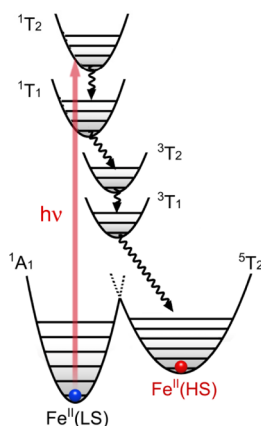


FIGURE 9. Schematic illustration of light-induced excited spin-state trapping (LIESST) phenomenon.

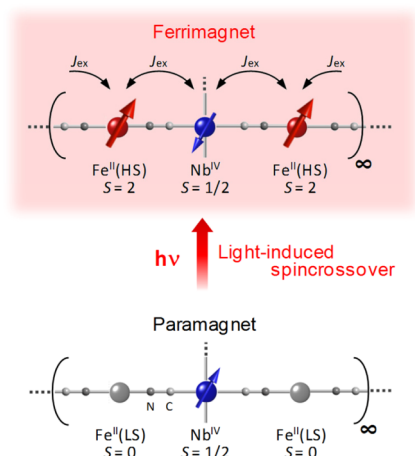


FIGURE 10. Schematic illustration of the mechanism of ferromagnetic ordering due to photoinduced spin crossover in the FeNb(4-pyoxm) octacyano-complex.

In a photoinduced phase, which is metastable, the spins of photoinduced $\text{Fe}^{\text{II}}(\text{HS})$ and those of neighboring Nb^{IV} are antiferromagnetically aligned by the superexchange interaction via cyano groups, leading to spontaneous magnetization (Figure 10). Note that the superexchange interaction constant (J_{ex}) between $\text{Fe}^{\text{II}}(\text{HS})$ and Nb^{IV} is calculated by molecular field theory,^{39,49} that is, $|J_{\text{ex}}| = 3k_{\text{B}}T_{\text{C}}\{Z_{\text{Nb}^{\text{IV}}\text{Fe}^{\text{II}}(\text{HS})}Z_{\text{Fe}^{\text{II}}(\text{HS})\text{Nb}^{\text{IV}}}S_{\text{Fe}^{\text{II}}(\text{HS})}(S_{\text{Fe}^{\text{II}}(\text{HS})} + 1)S_{\text{Nb}^{\text{IV}}}(S_{\text{Nb}^{\text{IV}}} + 1)\}^{-1/2}$, where the spin quantum numbers are $S_{\text{Nb}^{\text{IV}}} = 1/2$ and $S_{\text{Fe}^{\text{II}}(\text{HS})} = 2$, the numbers of the nearest neighbor are $Z_{\text{Nb}^{\text{IV}}\text{Fe}^{\text{II}}(\text{HS})} = 4$ and $Z_{\text{Fe}^{\text{II}}(\text{HS})\text{Nb}^{\text{IV}}} = 2$, k_{B} is the Boltzmann constant, and $T_{\text{C}} = 20$ K. Consequently, J_{ex} was estimated to be -6.9 cm^{-1} .

In the present study, we have synthesized a new 3D network metal complex $\text{Fe}_2[\text{Nb}(\text{CN})_8](4\text{-pyridinealdoxime})_8 \cdot 2\text{H}_2\text{O}$ and succeeded in the observation of a photoinduced spin crossover ferromagnetism for the first time. This photomagnetic effect is induced by the LIESST and the

superexchange interaction between $\text{Fe}^{\text{II}}(\text{HS})$ and Nb^{IV} . In the previous work, we reported $\text{Fe}_2[\text{Nb}(\text{CN})_8] \cdot (3\text{-pyCH}_2\text{OH})_8 \cdot 4.6\text{H}_2\text{O}$,²⁵ in which spin-crossover and ferrimagnetism coexist, but this compound did not show the light-induced spin-crossover ferromagnetism. This is because the crystal structure is very highly symmetric (cubic: $Ia\bar{3}d$) and results in a very stable alternating arrangement of $\cdots\text{Fe}^{\text{II}}(\text{HS})\text{--Fe}^{\text{II}}(\text{LS})\text{--}\cdots$, and consequently, photoinduced $\text{Fe}^{\text{II}}(\text{HS})$ domains cannot be formed. Hence, a somewhat low-symmetrical crystal structure is effective to produce photoinduced $\text{Fe}^{\text{II}}(\text{HS})$ domains, which is necessary to realize LIESST-induced bulk magnetization.

6. Conclusions

In addition to the materials described herein, we are conducting research on the photoinduced magnetic pole inversion in a hexacyanometal complex system, $(\text{Fe}^{\text{III}}_{0.4}\text{Mn}^{\text{II}}_{0.6})_{1.5}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 7.5\text{H}_2\text{O}$,^{38,39} and photomagnetism in octacyanometal complex systems, $\text{Cs}^{\text{I}}_2\text{Cu}^{\text{II}}_7[\text{Mo}^{\text{IV}}(\text{CN})_8]_4 \cdot 6\text{H}_2\text{O}$,⁵⁴ $[\text{Cu}^{\text{II}}(1,4,8,11\text{-tetraazacyclodecane})_2][\text{Mo}^{\text{IV}}(\text{CN})_8] \cdot 10\text{H}_2\text{O}$,⁵⁶ and $\text{Cs}^{\text{I}}\text{Co}^{\text{II}}(3\text{-cyanopyridine})_2[\text{W}^{\text{V}}(\text{CN})_8] \cdot \text{H}_2\text{O}$.⁵⁰ In hexacyanometal complexes, the photomagnetic phenomena of a $\text{K}_{0.2}\text{Co}_{1.4}[\text{Fe}(\text{CN})_6] \cdot 6.9\text{H}_2\text{O}$ system and the photoinduced change of magnetic susceptibility in a $\text{K}_{1.54}\text{V}^{\text{II}}_{0.77}\text{V}^{\text{III}}_{0.08}[\text{Cr}^{\text{III}}(\text{CN})_6](\text{SO}_4)_{0.16} \cdot 3.1\text{H}_2\text{O}$ system are known.^{42,82} In systems where photochromic molecules are introduced into magnetic complexes such as oxalate metal complexes and single-molecule magnets, changes in magnetic coercive field and alternating current (ac) magnetic susceptibility induced by photoisomerization are observed.^{83–85}

Besides these molecular magnetic materials, photomagnetic effects are also reported in dilute magnetic semiconductors and perovskite-type manganese oxides.^{86,87} Furthermore, theoretical studies on photoinduced phase transition are actively being conducted.^{88–93} Metal complexes are superior as a model material to explore novel functional materials. By taking advantage of the knowledge that has been obtained through our previous studies, we have recently discovered a novel metal oxide, λ -tritanium pentoxide ($\lambda\text{-Ti}_3\text{O}_5$), which exhibits photoreversible metal–semiconductor phase transition at room temperature,⁹⁴ suggesting the possibility of developing room-temperature photomagnetism by concurrently studying magnetism.

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FOOTNOTES

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REFERENCES

- Verdaguer, M.; Bleuzen, A.; Marvaud, V.; Vaissermann, J.; Seuleiman, M.; Desplanches, C.; Scullier, A.; Train, C.; Garde, R.; Gelly, G.; Lomenech, C.; Rosenman, I.; Veillet, P.; Cartier, C.; Villain, F. Molecules to build solids: high T_C molecule-based magnets by design and recent revival of cyano complexes chemistry. *Coord. Chem. Rev.* **1999**, *190*–192, 1023–1047.
- Nasu, K., Ed. *Relaxations of Excited States and Photo-Induced Structural Phase Transitions*; Springer: Berlin, 1997.
- Dei, A. Photomagnetic effects in polycyanometallate compounds: an intriguing future chemically based technology? *Angew. Chem., Int. Ed.* **2005**, *44*, 1160–1163.
- Ohkoshi, S.; Hashimoto, K. Photo-magnetic and magneto-optical effects of functionalized metal polycyanides. *J. Photochem. Photobiol. C* **2001**, *2*, 71–88.
- Meinders, E. R.; Mijritskii, A. V.; Pieterse, L. V.; Wuttig, M. *Optical Data Storage: Phase Change Media and Recording*; Springer: Berlin, 2006.
- Wuttig, M.; Yamada, N. Phase-change materials for rewriteable data storage. *Nat. Mater.* **2007**, *6*, 824–832.
- Ludi, A.; Güdel, H. U. Structural chemistry of polynuclear transition metal cyanides. *Struct. Bonding (Berlin)* **1973**, *14*, 1–21.
- Mallah, T.; Thiébaud, S.; Verdaguer, M.; Veillet, P. High- T_C molecular-based magnets: ferrimagnetic mixed-valence chromium(III)-chromium(II) cyanides with T_C at 240 and 190 K. *Science* **1993**, *262*, 1554–1557.
- Ferlay, S.; Mallah, T.; Ouahès, R.; Veillet, P.; Verdaguer, M. A room-temperature organometallic magnet based on Prussian blue. *Nature* **1995**, *378*, 701–703.
- Entley, W. R.; Girolami, G. S. High-temperature molecular magnets based on cyanovanadate building blocks: spontaneous magnetization at 230 K. *Science* **1995**, *268*, 397–400.
- Buschmann, W. E.; Paulson, S. C.; Wynn, C. M.; Girtu, M. A.; Epstein, A. J.; White, H. S.; Miller, J. S. Magnetic Field Induced Reversed (Negative) Magnetization for Electrochemically Deposited $T_C = 260$ K Oxidized Films of Chromium Cyanide Magnets. *Adv. Mater.* **1997**, *9*, 645–647.
- Holmes, S. M.; Girolami, G. S. Sol-Gel Synthesis of $KV^I[Cr^{III}(CN)_6] \cdot 2H_2O$: A Crystalline Molecule-Based Magnet with a Magnetic Ordering Temperature above 100 °C. *J. Am. Chem. Soc.* **1999**, *121*, 5593–5594.
- Mizuno, M.; Ohkoshi, S.; Hashimoto, K. Electrochemical Synthesis of High- T_C , Colored, Magnetic Thin Films Composed of Vanadium(III)–Chromium(II) Hexacyanochromate(III). *Adv. Mater.* **2000**, *12*, 1955–1958.
- Larionova, J.; Clérac, R.; Sanchiz, J.; Kahn, O.; Golhen, S.; Ouahab, L. Ferromagnetic Ordering, Anisotropy, and Spin Reorientation for the Cyano-Bridged Bimetallic Compound $Mn_2(H_2O)_5Mo(CN)_7 \cdot 4H_2O$ (α Phase). *J. Am. Chem. Soc.* **1998**, *120*, 13088–13095.
- Sra, A. K.; Andruh, M.; Kahn, O.; Golhen, S.; Ouahab, L.; Yakhmi, J. V. A Mixed-Valence and Mixed-Spin Molecular Magnetic Material: $[Mn^{II}]_6[Mo^{III}(CN)_7][Mo^{IV}(CN)_6]_2 \cdot 19.5H_2O$. *Angew. Chem., Int. Ed.* **1999**, *38*, 2606–2609.
- Tanase, S.; Tuna, F.; Guionneau, P.; Maris, T.; Rombaut, G.; Mathonière, C.; Andruh, M.; Kahn, O.; Sutter, J.-P. Substantial Increase of the Ordering Temperature for $\{Mn^{II}/Mo^{IV}(CN)_7\}$ -Based Magnets as a Function of the 3d Ion Site Geometry: Example of Two Supramolecular Materials with $T_C = 75$ and 106 K. *Inorg. Chem.* **2003**, *42*, 1625–1631.
- Milon, J.; Daniel, M.-C.; Kaiba, A.; Guionneau, P.; Brandès, S.; Sutter, J.-P. Nanoporous Magnets of Chiral and Racemic $\{[Mn(HL)]_2Mn\{Mo(CN)_7\}_2\}$ with Switchable Ordering Temperatures ($T_C = 85$ K \leftrightarrow 106 K) Driven by H_2O Sorption (L = N,N-Dimethylalaninol). *J. Am. Chem. Soc.* **2007**, *129*, 13872–13878.
- Tomono, K.; Tsunobuchi, Y.; Nakabayashi, K.; Ohkoshi, S. Vanadium(II) Heptacyanomolybdate(III)-Based Magnet Exhibiting a High Curie Temperature of 110 K. *Inorg. Chem.* **2010**, *49*, 1298–1300.
- Wang, X.-Y.; Prosvirnin, A. V.; Dunbar, K. R. A Dicosanuclear $\{Mo_9Mn_{14}\}$ Cluster Based on $[Mo(CN)_7]^{4-}$. *Angew. Chem., Int. Ed.* **2010**, *49*, 5081–5084.
- Garde, R.; Desplanches, C.; Bleuzen, A.; Veillet, P.; Verdaguer, M. New Molecule-Based Magnets: from Hexacyano to Octacyanometalates. *Mol. Cryst. Liq. Cryst.* **1999**, *334*, 587–595.
- Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hidai, M.; Fujishima, A.; Ohkoshi, S.; Hashimoto, K. A High-Spin Cyanide-Bridged Mn_9W_6 Cluster ($S = 39/2$) with a Full-Capped Cubane Structure. *J. Am. Chem. Soc.* **2000**, *122*, 2952–2953.
- Pradhan, R.; Desplanches, C.; Guionneau, P.; Sutter, J.-P. Octadecanuclear Cluster or 1D Polymer with $\{[ML]_2Nb(CN)_8\}_n$ Motifs as a Function of $\{ML\}$ (M = Ni(II), n = 6; M = Mn(II), n = ∞ ; L = Macrocyclic). *Inorg. Chem.* **2003**, *42*, 6607–6609.
- Freedman, D. E.; Bennett, M. V.; Long, J. R. Symmetry-breaking substitutions of $[Re(CN)_6]^{3-}$ into the centered, face-capped octahedral clusters $(CH_3OH)_{24}M'_9M''_6(CN)_{48}$ (M = Mn, Co; M' = Mo, W). *Dalton Trans.* **2006**, 2829–2834.
- Herrera, J. M.; Franz, P.; Podgajny, R.; Pilkington, M.; Biner, M.; Decurtins, S.; Stoeckli-Evans, H.; Neels, A.; Garde, R.; Dromzée, Y.; Julve, M.; Sieklucka, B.; Hashimoto, K.; Ohkoshi, S.; Verdaguer, M. Three-dimensional bimetallic octacyanidometalates $[M^{IV}\{\mu-CN\}_4Mn^{II}(H_2O)_2\}_2 \cdot 4H_2O)_n$ (M = Nb, Mo, W): Synthesis, single-crystal X-ray diffraction and magnetism. *C. R. Chim.* **2008**, *11*, 1192–1199.
- Arai, M.; Kosaka, W.; Matsuda, T.; Ohkoshi, S. Observation of an Iron(II) Spin-Crossover in an Iron Octacyanoniobate-Based Magnet. *Angew. Chem., Int. Ed.* **2008**, *47*, 6885–6887.
- Sieklucka, B.; Podgajny, R.; Pinkowicz, D.; Nowicka, B.; Korzeniak, T.; Bałanda, M.; Wasiutyński, T.; Pełka, R.; Makarewicz, M.; Czaplak, M.; Rams, M.; Gawel, B.; Łasocha, W. Towards high T_C octacyanometalate-based networks. *CrystEngComm* **2009**, *11*, 2032–2039.
- Imoto, K.; Takemura, M.; Tokoro, H.; Ohkoshi, S. A Cyano-Bridged Vanadium-Niobium Bimetal Assembly Exhibiting a High Curie Temperature of 210 K. *Eur. J. Inorg. Chem.* in press.
- Bennett, M. V.; Beauvais, L. G.; Shores, M. P.; Long, J. R. Expanded Prussian Blue Analogues Incorporating $[Re_6Se_8(CN)_6]^{3-4-}$ Clusters: Adjusting Porosity via Charge Balance. *J. Am. Chem. Soc.* **2001**, *123*, 8022–8032.
- Berlinguette, C. P.; Dragulescu-Andrasi, A.; Sieber, A.; Galán-Mascarós, J. R.; Güdel, H.-U.; Achim, C.; Dunbar, K. R. A Charge-Transfer-Induced Spin Transition in the Discrete Cyanide-Bridged Complex $[[Co(tmphen)]_2][Fe(CN)_6]_2$. *J. Am. Chem. Soc.* **2004**, *126*, 6222–6223.
- Nihei, M.; Ui, M.; Yokota, M.; Han, L.; Maeda, A.; Kishida, H.; Okamoto, H.; Oshio, H. Two-Step Spin Conversion in a Cyanide-Bridged Ferrous Square. *Angew. Chem., Int. Ed.* **2005**, *44*, 6484–6487.

- 31 Schelter, E. J.; Karadas, F.; Avendano, C.; Prosvirin, A. V.; Wernsdorfer, W.; Dunbar, K. R. A Family of Mixed-Metal Cyanide Cubes with Alternating Octahedral and Tetrahedral Corners Exhibiting a Variety of Magnetic Behaviors Including Single Molecule Magnetism. *J. Am. Chem. Soc.* **2007**, *129*, 8139–8149.
- 32 Li, D.; Clérac, R.; Roubeau, O.; Harté, E.; Mathonière, C.; Bris, R. L.; Holmes, S. M. Magnetic and Optical Bistability Driven by Thermally and Photoinduced Intramolecular Electron Transfer in a Molecular Cobalt-Iron Prussian Blue Analogue. *J. Am. Chem. Soc.* **2008**, *130*, 252–258.
- 33 Nihei, M.; Sekine, Y.; Suganami, N.; Oshio, H. Thermally Two-Stepped Spin Transitions Induced by Intramolecular Electron Transfers in a Cyanide-bridged Molecular Square. *Chem. Lett.* **2010**, *39*, 978–979.
- 34 Hilfiger, M. G.; Chen, M.; Brinzari, T. V.; Nocera, T. M.; Shatruk, M.; Petasis, D. T.; Musfeldt, J. L.; Achim, C.; Dunbar, K. R. An Unprecedented Charge Transfer Induced Spin Transition in an Fe-Os Cluster. *Angew. Chem., Int. Ed.* **2010**, *49*, 1410–1413.
- 35 Zhang, Y.; Li, D.; Clérac, R.; Kalisz, M.; Mathonière, C.; Holmes, S. M. Reversible Thermally and Photoinduced Electron Transfer in a Cyano-Bridged $\{Fe_2Co_2\}$ Square Complex. *Angew. Chem., Int. Ed.* **2010**, *49*, 3752–3756.
- 36 Bleuzen, A.; Marvaud, V.; Mathoniere, C.; Sieklucka, B.; Verdaguer, M. Photomagnetism in Clusters and Extended Molecule-Based Magnets. *Inorg. Chem.* **2009**, *48*, 3453–3466.
- 37 Tokoro, H.; Ohkoshi, S. Novel Magnetic functionalities of Prussian blue analogs. *Dalton. Trans.* **2011**, *40*, 6825–6833.
- 38 Ohkoshi, S.; Yorozu, S.; Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. Photoinduced magnetic pole inversion in a ferro-ferrimagnet: $(Fe^{II}_{0.40}Mn^{II}_{0.60})_{1.5}Cr^{III}(CN)_6$. *Appl. Phys. Lett.* **1997**, *70*, 1040–1042.
- 39 Ohkoshi, S.; Hashimoto, K. Design of a Novel Magnet Exhibiting Photoinduced Magnetic Pole Inversion Based on Molecular Field Theory. *J. Am. Chem. Soc.* **1999**, *121*, 10591–10597.
- 40 Avendano, C.; Hilfiger, M. G.; Prosvirin, A.; Sanders, C.; Stepien, D.; Dunbar, K. R. Temperature and Light Induced Bistability in a $Co_3[Os(CN)_6]_2 \cdot 6H_2O$ Prussian Blue Analog. *J. Am. Chem. Soc.* **2010**, *132*, 13123–13125.
- 41 Pajerowski, D. M.; Andrus, M. J.; Gardner, J. E.; Knowles, E. S.; Meisel, M. W.; Talham, D. R. Persistent Photoinduced Magnetism in Heterostructures of Prussian Blue Analogues. *J. Am. Chem. Soc.* **2010**, *132*, 4058–4059.
- 42 Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. Photoinduced Magnetization of a Cobalt-iron Cyanide. *Science* **1996**, *272*, 704–705.
- 43 Bleuzen, A.; Lomenech, C.; Escax, V.; Villain, F.; Varret, F.; Moulin, C. C. D.; Verdaguer, M. Photoinduced Ferrimagnetic Systems in Prussian Blue Analogues $C'_xCo'_y[Fe(CN)_6]_z$ (C' = Alkali Cation). 1. Conditions to Observe the Phenomenon. *J. Am. Chem. Soc.* **2000**, *122*, 6648–6652.
- 44 Pejakovic, D. A.; Manson, J. L.; Miller, J. S.; Epstein, A. J. Photoinduced Magnetism, Dynamics, and Cluster Glass Behavior of a Molecule-Based Magnet. *Phys. Rev. Lett.* **2000**, *85*, 1994–1997.
- 45 Moore, J. G.; Lochner, E. J.; Ramsey, C.; Dalal, N. S.; Stiegman, A. E. Transparent, Superparamagnetic $K'_xCo'_y[Fe(CN)_6]_z$ -Silica Nanocomposites with Tunable Photomagnetism. *Angew. Chem., Int. Ed.* **2003**, *42*, 2741–2743.
- 46 Tokoro, H.; Ohkoshi, S.; Hashimoto, K. One-shot-laser-pulse-induced demagnetization in rubidium manganese hexacyanoferrate. *Appl. Phys. Lett.* **2003**, *82*, 1245–1247.
- 47 Tokoro, H.; Matsuda, T.; Nuida, T.; Moritomo, Y.; Ohoyama, K.; Loutete-Dangui, E. D.; Boukheddaden, K.; Ohkoshi, S. Visible-Light-Induced Reversible Photomagnetism in Rubidium Manganese Hexacyanoferrate. *Chem. Mater.* **2008**, *20*, 423–428.
- 48 Tokoro, H.; Ohkoshi, S. Phase collapse caused by blue-light irradiation in a cyanobridged coordination polymer. *Appl. Phys. Lett.* **2008**, *93*, 021906/1–3.
- 49 Ohkoshi, S.; Imoto, K.; Tsunobuchi, Y.; Takano, S.; Tokoro, H. Light-induced spin-cross-over magnet. *Nat. Chem.* **2011**, *3*, 564–569.
- 50 Arimoto, Y.; Ohkoshi, S.; Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hashimoto, K. Photoinduced Magnetization in a Two-Dimensional Cobalt Octacyanotungstate. *J. Am. Chem. Soc.* **2003**, *125*, 9240–9241.
- 51 Ohkoshi, S.; Ikeda, S.; Hozumi, T.; Kashiwagi, T.; Hashimoto, K. Photoinduced Magnetization with a High Curie Temperature and a Large Coercive Field in a Cyano-Bridged Cobalt-Tungstate Bimetallic Assembly. *J. Am. Chem. Soc.* **2006**, *128*, 5320–5321.
- 52 Ohkoshi, S.; Hamada, Y.; Matsuda, T.; Tsunobuchi, Y.; Tokoro, H. Crystal Structure, Charge-Transfer-Induced Spin Transition, and Photoreversible Magnetism in a Cyano-Bridged Cobalt-Tungstate Bimetallic Assembly. *Chem. Mater.* **2008**, *20*, 3048–3054.
- 53 Ohkoshi, S.; Machida, N.; Zhong, Z. J.; Hashimoto, K. Photo-induced Magnetization in Copper(II) Octacyanomolybdate(IV). *Synth. Met.* **2001**, *122*, 523–527.
- 54 Hozumi, T.; Hashimoto, K.; Ohkoshi, S. Electrochemical Synthesis, Crystal Structure, and Photomagnetic Properties of a Three-Dimensional Cyano-Bridged Copper-Molybdenum Complex. *J. Am. Chem. Soc.* **2005**, *127*, 3864–3869.
- 55 Ohkoshi, S.; Tokoro, H.; Hozumi, T.; Zhang, Y.; Hashimoto, K.; Mathonière, C.; Bord, I.; Rombaut, G.; Verelst, M.; Moulin, C. C. D.; Villain, F. Photoinduced Magnetization in Copper Octacyanomolybdate. *J. Am. Chem. Soc.* **2006**, *128*, 270–277.
- 56 Tokoro, H.; Nakagawa, K.; Nakabayashi, K.; Kashiwagi, T.; Hashimoto, K.; Ohkoshi, S. Photoreversible Switching of Magnetic Coupling in a Two-dimensional Copper Octacyanomolybdate. *Chem. Lett.* **2009**, *38*, 338–339.
- 57 Herrera, J. M.; Marvaud, V.; Verdaguer, M.; Marrot, J.; Kalisz, M. Reversible Photoinduced Magnetic in the Heptanuclear Complex $[Mo^V(CN)_2(CN-Cu)_6]^{8+}$: A Photomagnetic High-Spin Molecule. *Angew. Chem., Int. Ed.* **2004**, *43*, 5468–5471.
- 58 Coronado, E.; Giménez-López, M. C.; Levchenko, G.; Romero, F. M.; García-Baonza, V.; Milner, A.; Paz-Pasternak, M. Pressure-Tuning of Magnetism and Linkage Isomerism in Iron(II) Hexacyanochromate. *J. Am. Chem. Soc.* **2005**, *127*, 4580–4581.
- 59 Egan, L.; Kamenev, K.; Papanikolaou, D.; Takabayashi, Y.; Margadonna, S. Pressure-Induced Sequential Magnetic Pole Inversion and Antiferromagnetic-Ferromagnetic Crossover in a Trimetallic Prussian Blue Analogue. *J. Am. Chem. Soc.* **2006**, *128*, 6034–6035.
- 60 Ohkoshi, S.; Tokoro, H.; Matsuda, T.; Takahashi, H.; Irie, H.; Hashimoto, K. Coexistence of ferroelectricity and ferromagnetism in a rubidium manganese hexacyanoferrate. *Angew. Chem., Int. Ed.* **2007**, *46*, 3238–3241.
- 61 Mahfoud, T.; Molnár, G.; Bonhommeau, S.; Cobo, S.; Salmon, L.; Demont, P.; Tokoro, H.; Ohkoshi, S.; Boukheddaden, K.; Bousseksou, A. Electric-Field-Induced Charge-Transfer Phase Transition: A Promising Approach Toward Electrically Switchable Devices. *J. Am. Chem. Soc.* **2009**, *131*, 15049–15054.
- 62 Ohkoshi, S.; Arai, K.; Sato, Y.; Hashimoto, K. Humidity-induced magnetization and magnetic pole inversion in a cyano-bridged metal assembly. *Nat. Mater.* **2004**, *3*, 857–861.
- 63 Kaye, S. S.; Long, J. R. Hydrogen Storage in the Dehydrated Prussian Blue Analogues $M_3[Co(CN)_6]_2$ ($M = Mn, Fe, Co, Ni, Cu, Zn$). *J. Am. Chem. Soc.* **2005**, *127*, 6506–6507.
- 64 Ohkoshi, S.; Tsunobuchi, Y.; Takahashi, H.; Hozumi, T.; Shiro, M.; Hashimoto, K. Synthesis and Alcohol Vapor Sensitivity of a Ferromagnetic Copper-Tungsten Bimetallic Assembly. *J. Am. Chem. Soc.* **2007**, *129*, 3084–3085.
- 65 Ohkoshi, S.; Abe, Y.; Fujishima, A.; Hashimoto, K. Design and Preparation of a Novel Magnet Exhibiting Two Compensation Temperatures Based on Molecular Field Theory. *Phys. Rev. Lett.* **1999**, *82*, 1285–1288.
- 66 Nuida, T.; Matsuda, T.; Tokoro, H.; Sakurai, S.; Hashimoto, K.; Ohkoshi, S. Nonlinear Magneto-optical Effects Caused by Piezoelectric Ferromagnetism in F43m-type Prussian Blue Analogues. *J. Am. Chem. Soc.* **2005**, *127*, 11604–11605.
- 67 Train, C.; Nuida, T.; Gheorghe, R.; Gruselle, M.; Ohkoshi, S. Large Magnetization-Induced Second Harmonic Generation in an Enantiopure Chiral Magnet. *J. Am. Chem. Soc.* **2009**, *131*, 16838–16843.
- 68 Brown, D. B., Ed. *Mixed-valence Compounds*; D. Reidel: Dordrecht, 1980.
- 69 Prassides, K., Ed. *Mixed Valency Systems: Applications in Chemistry, Physics and Biology*; NATO ASI 343; Kluwer Academic Publishers: Dordrecht, 1991.
- 70 Robin, M. B.; Day, P. Mixed Valence Chemistry-A Survey and Classification. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247–422.
- 71 Hush, N. S. Intervalence-Transfer Absorption. Part 2. Theoretical Considerations and Spectroscopic Data. *Prog. Inorg. Chem.* **1967**, *8*, 391–444.
- 72 Ohkoshi, S.; Tokoro, H.; Utsunomiya, M.; Mizuno, M.; Abe, M.; Hashimoto, K. Observation of Spin Transition in an Octahedrally Coordinated Manganese(II) Compound. *J. Phys. Chem. B* **2002**, *106*, 2423–2425.
- 73 Kato, K.; Moritomo, Y.; Sakata, M.; Umekawa, M.; Hamada, N.; Ohkoshi, S.; Tokoro, H.; Hashimoto, K. Direct observation of charge transfer in double-perovskite-like $RbMn[Fe(CN)_6]$. *Phys. Rev. Lett.* **2003**, *91*, 255502/1–4.
- 74 Margadonna, S.; Prassides, K.; Fitch, A. N. Large Lattice Responses in a Mixed-Valence Prussian Blue Analogue Owing to Electronic and Spin Transitions Induced by X-ray Irradiation. *Angew. Chem., Int. Ed.* **2004**, *43*, 6316–6319.
- 75 Tokoro, H.; Ohkoshi, S.; Matsuda, T.; Hashimoto, K. A Large Thermal Hysteresis Loop Produced by a Charge-Transfer Phase Transition in a Rubidium Manganese Hexacyanoferrate. *Inorg. Chem.* **2004**, *43*, 5231–5236.
- 76 Ohkoshi, S.; Nuida, T.; Matsuda, T.; Tokoro, H.; Hashimoto, K. The dielectric constant in a thermal phase transition magnetic material composed of rubidium manganese hexacyanoferrate observed by spectroscopic ellipsometry. *J. Mater. Chem.* **2005**, *15*, 3291–3295.
- 77 Vertelman, E. J. M.; Lummen, T. T. A.; Meetsma, A.; Bouwkamp, M. W.; Molnar, G.; Loosdrecht, P. H. M. V.; Koningsbruggen, P. J. V. Light- and Temperature-Induced Electron Transfer in Single Crystals of $RbMn[Fe(CN)_6] \cdot H_2O$. *Chem. Mater.* **2008**, *20*, 1236–1238.
- 78 Güttlich, P.; Goodwin, H. A., Eds. *Spin crossover in transition metal compounds I, II, III*, Topics in Current Chemistry 233–235; Springer: Berlin, 2004.
- 79 König, E. Structural changes accompanying continuous and discontinuous spin-state transitions. *Prog. Inorg. Chem.* **1987**, *35*, 527–622.
- 80 Güttlich, P.; Hauser, A.; Spiering, H. Thermal and Optical Switching of Iron(II) Complexes. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2024–2054.
- 81 Decurtins, S.; Güttlich, P.; Köhler, C. P.; Spiering, H.; Hauser, A. Light-Induced Excited Spin State Trapping in a Transition-Metal Complex: The Hexa-1-Propyltetrazole-Iron(II) Tetrafluoroborate Spin-Crossover System. *Chem. Phys. Lett.* **1984**, *105*, 1–4.
- 82 Bozdag, K. D.; Yoo, J.-W.; Raju, N. P.; McConnell, A. C.; Miller, J. S.; Epstein, A. J. Optical control of magnetization in a room-temperature magnet: V-Cr Prussian blue analog. *Phys. Rev. B* **2010**, *82*, 094449–094453.

- 83 Bénard, S.; Rivière, E.; Yu, P.; Nakatani, K.; Delouis, J. F. A Photochromic Molecule-Based Magnet. *Chem. Mater.* **2001**, *13*, 159–162.
- 84 Kida, N.; Hikita, M.; Kashima, I.; Okubo, M.; Itoi, M.; Enomoto, M.; Kato, K.; Takata, M.; Kojima, N. Control of charge transfer phase transition and ferromagnetism by photoisomerization of spiropyran for an organic-inorganic hybrid system, (SP)[Fe^{II}Fe^{III}(dto)₃] (SP = spiropyran, dto = C₂O₂S₂). *J. Am. Chem. Soc.* **2009**, *131*, 212–220.
- 85 Morimoto, M.; Miyasaka, H.; Yamashita, M.; Irie, M. Coordination Assemblies of [Mn₄] Single-Molecule Magnets Linked by Photochromic Ligands: Photochemical Control of the Magnetic Properties. *J. Am. Chem. Soc.* **2009**, *131*, 9823–9835.
- 86 Koshihara, S.; Oiwa, A.; Hirasawa, M.; Katsumoto, S.; Iye, Y.; Urano, C.; Takagi, H.; Munekata, H. Ferromagnetic Order Induced by Photogenerated Carriers in Magnetic III-V Semiconductor Heterostructures of (In, Mn) As/GaSb. *Phys. Rev. Lett.* **1997**, *78*, 4617–4620.
- 87 Fiebig, M.; Miyano, K.; Tomioka, Y.; Tokura, Y. Visualization of the Local Insulator-Metal Transition in Pr_{0.7}Ca_{0.3}MnO₃. *Science* **1998**, *280*, 1925–1928.
- 88 Nagaosa, N.; Ogawa, T. Theory of photoinduced structure changes. *Phys. Rev. B* **1989**, *39*, 4472–4483.
- 89 Boukheddaden, K.; Shteto, I.; Hôo, B.; Varret, F. Dynamical model for spin-crossover solids. II. Static and dynamic effects of light in the mean-field approach. *Phys. Rev. B* **2000**, *62*, 14806–14817.
- 90 Sun, X.; Fu, R. L.; Yonemitsu, K.; Nasu, K. Photoinduced Polarization Inversion in a Polymeric Molecule. *Phys. Rev. Lett.* **2000**, *84*, 2830–2832.
- 91 Nasu, K.; Ping, H.; Mizouchi, H. Photoinduced structural phase transitions and their dynamics. *J. Phys.: Condens. Matter* **2001**, *13*, R693–R721.
- 92 Miyashita, S.; Konishi, Y.; Tokoro, H.; Nishino, M.; Boukheddaden, K.; Varret, F. Structures of Metastable States in Phase Transitions with a High-Spin Low-Spin Degree of Freedom. *Prog. Theor. Phys.* **2005**, *114*, 719–735.
- 93 Miyashita, S.; Rikvold, P. A.; Mori, T.; Konishi, Y.; Nishino, M.; Tokoro, H. Threshold phenomena under photoexcitation of spin-crossover materials with cooperativity due to elastic interactions. *Phys. Rev. B* **2009**, *80*, 064414/1–6.
- 94 Ohkoshi, S.; Tsunobuchi, Y.; Matsuda, T.; Hashimoto, K.; Namai, A.; Hakoe, F.; Tokoro, H. Synthesis of a metal oxide with a room-temperature photoreversible phase transition. *Nat. Chem.* **2010**, *2*, 539–545.