

## Review

### Switchable molecular magnets

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**Abstract:** Various molecular magnetic compounds whose magnetic properties can be controlled by external stimuli have been developed, including electrochemically, photochemically, and chemically tunable bulk magnets as well as a phototunable antiferromagnetic phase of single chain magnet. In addition, we present tunable paramagnetic mononuclear complexes ranging from spin crossover complexes and valence tautomeric complexes to Co complexes in which orbital angular momentum can be switched. Furthermore, we recently developed several switchable clusters and one-dimensional coordination polymers. The switching of magnetic properties can be achieved by modulating metals, ligands, and molecules/ions in the second sphere of the complexes.

**Keywords:** molecule-based magnets, photomagnets, quantum magnets, switching, clusters, one-dimensional compounds

#### Introduction

The study of magnetic properties of molecular compounds has recently attracted considerable attention.<sup>1)–6)</sup> The development of pure organic magnets has been carried out for a long time, and the first pure organic magnet was reported ca. 20 years ago. This study aimed at developing new molecular magnets having magnetic properties that can be controlled by light, electrochemical reaction, and chemical stimuli.<sup>7),8)</sup> The switchable molecular magnets can be used for future memory and switching devices. In addition, our approach should lead to the development of an interdisciplinary field between molecular magnetism and photochemistry as well as molecular magnetism and electrochemistry.<sup>1)–3),7)</sup>

The magnetic properties of molecular magnets can be controlled by various methods including the direct modulation of metal centers carrying spins. Changes in the redox state and spin multiplicity can be induced by charge transfer, spin crossover, and electrochemical reaction, resulting in the significant modulation of magnetic properties. Moreover, it is possible to control magnetic behavior through the

modulation of ligands located in the first coordination sphere. We used polymerization reactions involving ligand exchange. Furthermore, because the modification of the second sphere is useful to control magnetic properties, we used guest exchange reactions in the magnetic coordination polymers. Although the metal center carrying spins is not directly modulated, it is possible to significantly control magnetic properties when magnetic materials have a bistable nature and possess nearly degenerated electronic states. We applied these techniques to molecular magnets, quantum magnets, paramagnetic mononuclear complexes, clusters, and one-dimensional (1-D) complexes.

This paper is organized as follows: switchable bulk magnets are first described. Next, phototunable quantum magnets are introduced. Finally, switchable paramagnetic mononuclear complexes, clusters, and 1-D complexes are described.

#### Bulk magnets

**Electrochemical reaction.** Prussian blue analogs are redox active complexes (Fig. 1) with a redox labile property that makes these complexes suitable for use as electrochromic materials. The color in electrochromic materials can be switched between two or more colors by electrochemical reduction and oxidation. The color in Prussian blue can be reversibly switched between blue and colorless in the reaction of  $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$  (blue) +  $4\text{K}^+$  +

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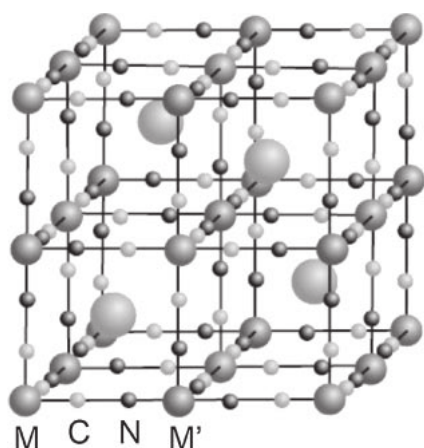


Fig. 1. Structure of the unit cell of a Prussian blue analog (M and M' denote metal ions). Random distribution of  $[M(CN)_6]^{n-}$  vacancies is omitted for clarity.

$4e^- \rightleftharpoons K_4Fe^{II}_4[Fe^{II}(CN)_6]_3$  (colorless). However, Prussian blue has ferromagnetic properties. Therefore, we proposed the development of electrochemically tunable magnets and demonstrated that the magnetic properties can be controlled by the electrochemical reaction,  $Fe^{III}_4[Fe^{II}(CN)_6]_3$  (ferromagnet) +  $4K^+ + 4e^- \rightleftharpoons K_4Fe^{II}_4[Fe^{II}(CN)_6]_3$  (paramagnet).<sup>9</sup> In particular, when the redox state is modulated in a high  $T_c$  (critical temperature) magnet, the change in magnetic properties can be observed at around room temperature. Indeed,  $Cr_{1.43}[Cr(CN)_6]$  exhibited a change in  $T_c$  between 240 and 100 K because of the redox reaction,  $Cr^{III}-CN-Cr^{II} \rightleftharpoons Cr^{II}-CN-Cr^{II}$  (Fig. 2).<sup>10</sup> The magnetic properties could be directly controlled by the modulation of the oxidation state through electrochemistry by using the redox ability of the metal center and the zeolitic property of the Prussian blue framework.

**Photoinduced charge transfer.** We have reported a photochemically tunable magnet on the basis of an FeCo Prussian blue analog.<sup>11–14</sup> At room temperature, the oxidation state in the complex having the formula  $A_{0.4}Co_{1.3}[Fe(CN)_6] \cdot nH_2O$  ( $A =$  alkali cation) can be expressed as  $A^{I}_{0.4}Co^{II-HS}_{1.3}[Fe^{III}(CN)_6] \cdot nH_2O$  (HS = high spin).<sup>12</sup> On cooling, this complex exhibits charge transfer that is coupled to spin crossover. The phase change can be expressed by  $Fe^{III}-CN-Co^{II-HS}$  (high temperature phase)  $\rightleftharpoons$   $Fe^{II}-CN-Co^{III-LS}$  (low temperature phase) (LS = low spin). This is a novel system that exhibits charge transfer coupled to spin transition. The driving force of this phase transition is entropy. It should be noted that the charge transfer coupled to spin transition

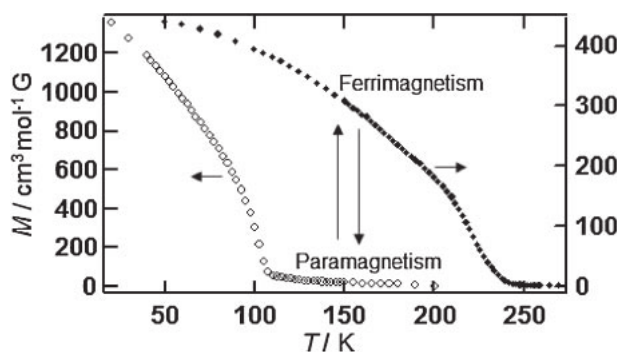


Fig. 2. Field-cooled magnetization versus temperature curves before electrochemical reduction (solid symbols, right axis) and after electrochemical reduction (open symbols, left axis). The material property can be switched from ferrimagnetism and paramagnetism between 100 and 240 K. We should note that although SI unit is recommended to be used in scientific journals, cgs unit “G” is used in this Fig. 2 and Fig. 3. This is because cgs unit is usually used in the field of molecular magnetism.

is frequently called charge transfer induced spin transition (CTIST).

The phase transition temperature depends on the number of vacancies in  $[Fe^{III}(CN)_6]$ . In the case of  $NaCo^{II-HS}[Fe^{III}(CN)_6]$  (Co/Fe = 1.0), Co is fully coordinated by the N atoms of the CN ligands. On the other hand,  $Co^{II-HS}[Fe^{III}(CN)_6]_{2/3}$  (Co/Fe = 1.5) has a vacancy in the  $[Fe^{III}(CN)_6]$  sites. Hence, a Co ion in  $Co^{II-HS}[Fe^{III}(CN)_6]_{2/3}$  is coordinated by 4 N atoms of CN ligands and 2 O atoms of  $H_2O$  ligands on an average. Therefore, the ligand field strength and energy level of Co ions depend on the number of vacancies. Indeed, the phase transition temperature decreases with the increase of the number of vacancies in  $[Fe^{III}(CN)_6]$  sites. In particular,  $Co^{II-HS}[Fe^{III}(CN)_6]_{2/3}$  does not exhibit thermally induced charge transfer. The number of vacancies can be controlled by changing the  $Na^+$  concentration during the synthesis. Hence, we could control the phase transition temperature via a chemical method. In Fig. 3, the magnetic properties for  $Na_{0.07}Co_{1.50}Fe(CN)_6 \cdot 6.3H_2O$  (Co/Fe = 1.50),  $Na_{0.37}Co_{1.37}Fe(CN)_6 \cdot 4.8H_2O$  (Co/Fe = 1.37), and  $Na_{0.94}Co_{1.15}Fe(CN)_6 \cdot 3.0H_2O$  (Co/Fe = 1.15) are depicted.

FeCo Prussian blue has a charge transfer band from  $Fe^{II}$  to  $Co^{III-LS}$  at around 400–600 nm. When the FeCo Prussian blue analog is irradiated with 532-nm light, magnetic properties are switched between ferrimagnetism and paramagnetism. This is because charge transfer is induced by light, and the resultant metastable state could be trapped at low temperature. The photoinduced reaction for  $Na_{0.37}Co_{1.37}Fe(CN)_6 \cdot 4.8H_2O$  is expressed as

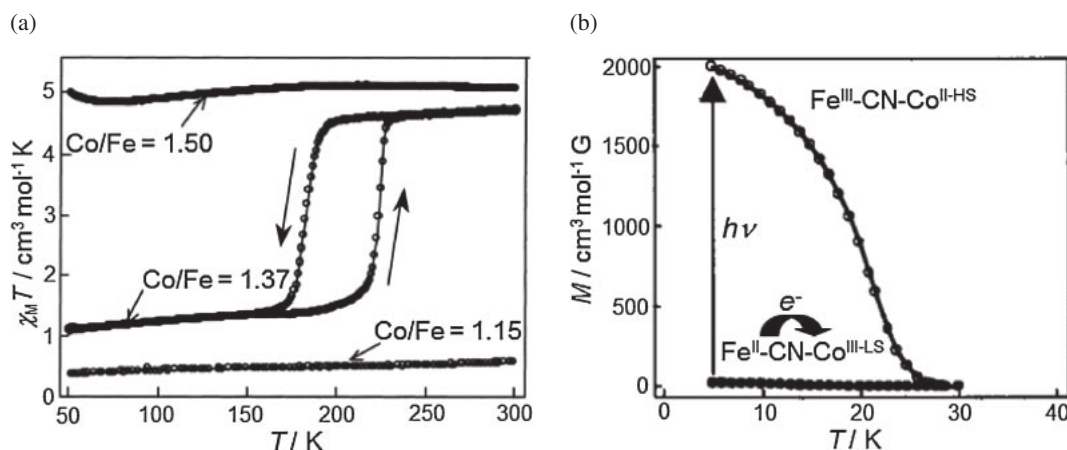
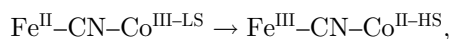


Fig. 3. (a)  $\chi_M T$  versus  $T$  for  $\text{Na}_{0.07}\text{Co}_{1.50}\text{Fe}(\text{CN})_6 \cdot 6.3\text{H}_2\text{O}$  (Co/Fe = 1.50),  $\text{Na}_{0.37}\text{Co}_{1.37}\text{Fe}(\text{CN})_6 \cdot 4.8\text{H}_2\text{O}$  (Co/Fe = 1.37), and  $\text{Na}_{0.94}\text{Co}_{1.15}\text{Fe}(\text{CN})_6 \cdot 3.0\text{H}_2\text{O}$  (Co/Fe = 1.15) during cooling and warming at  $H = 5000$  G. (b) Field-cooled magnetization curves for  $\text{Na}_{0.37}\text{Co}_{1.37}\text{Fe}(\text{CN})_6 \cdot 4.8\text{H}_2\text{O}$  (Co/Fe = 1.37) before (●) and after (○) light irradiation at  $H = 5$  G.



where  $T_c$  after irradiation is 26 K (Fig. 3). Before irradiation,  $\text{Na}_{0.37}\text{Co}_{1.37}\text{Fe}(\text{CN})_6 \cdot 4.8\text{H}_2\text{O}$  contains a large number of diamagnetic  $\text{Co}^{\text{III-LS}}(S = 0)$  and  $\text{Fe}^{\text{II}}(S = 0)$  moieties, which break the magnetic interaction between paramagnetic centers  $\text{Co}^{\text{II-HS}}(S = 3/2)$ . On the other hand, after irradiation, it consists of paramagnetic centers  $\text{Co}^{\text{II-HS}}(S = 3/2, t_{2g}^5 e_g^2)$  and  $\text{Fe}^{\text{III}}(S = 1/2, t_{2g}^5 e_g^0)$ . The unpaired spins interact through the CN bridge.  $t_{2g}$  in  $\text{Fe}^{\text{III}}$  and  $t_{2g}$  in  $\text{Co}^{\text{II-HS}}$  typically give rise to antiferromagnetic interactions, while  $t_{2g}$  in  $\text{Fe}^{\text{III}}$  and  $e_g$  in  $\text{Co}^{\text{II-HS}}$  typically give rise to ferromagnetic interactions due to orthogonality. In the present case, the antiferromagnetic interaction is dominant, leading to the formation of a ferrimagnet after irradiation. When the metastable compound is heated, it recovers the original ground state at approximately 145 K.

Furthermore, photoinduced magnetization was also observed at around the charge transfer phase transition temperature.<sup>15)</sup> When the complex was irradiated within the hysteresis loop at just below the phase transition temperature from  $\text{Fe}^{\text{II}}\text{-CN-Co}^{\text{III-LS}}$  to  $\text{Fe}^{\text{III}}\text{-CN-Co}^{\text{II-HS}}$  and just above the phase transition temperature from  $\text{Fe}^{\text{III}}\text{-CN-Co}^{\text{II-HS}}$  to  $\text{Fe}^{\text{II}}\text{-CN-Co}^{\text{III-LS}}$ , transformation from  $\text{Fe}^{\text{II}}\text{-CN-Co}^{\text{III-LS}}$  to  $\text{Fe}^{\text{III}}\text{-CN-Co}^{\text{II-HS}}$  and  $\text{Fe}^{\text{III}}\text{-CN-Co}^{\text{II-HS}}$  to  $\text{Fe}^{\text{II}}\text{-CN-Co}^{\text{III-LS}}$ , respectively, could be induced with a pulsed laser ( $\lambda = 532$  nm). In contrast to typical photomagnetic properties such as light-induced excited spin state trapping (LIESST) effect, this behavior could be observed even at around room temperature.

In addition, quenching effects called temperature induced excited spin state trapping (TIESST) were observed in the FeCo Prussian blue analog. When the FeCo sample was quickly introduced into the SQUID cavity at 5 K, the high temperature phase with the  $\text{Fe}^{\text{III}}\text{-CN-Co}^{\text{II-HS}}$  structure was trapped without exhibiting phase transition from  $\text{Fe}^{\text{III}}\text{-CN-Co}^{\text{II-HS}}$  to  $\text{Fe}^{\text{II}}\text{-CN-Co}^{\text{III-LS}}$ . This is because the sample is cooled rapidly down to 5 K before the phase change occurs. Furthermore, electric-field-induced conductance switching and reversible electrochemical redox reactions were observed.<sup>12),16)</sup> The electrochemical redox reaction in NaCl aqueous solution is expressed by  $\text{Fe}^{\text{II}}\text{-CN-Co}^{\text{II}} \rightleftharpoons \text{Fe}^{\text{III}}\text{-CN-Co}^{\text{II}} \rightleftharpoons \text{Fe}^{\text{III}}\text{-CN-Co}^{\text{III}}$ .

**Polymerization reaction.** As described above, we could achieve the switching of magnetic properties by using electrochemical reactions and photo-induced metal-to-metal charge transfer. However, another technique called the solid-state polymerization reaction can be used to control the magnetic interaction. We recently revealed that the hexanuclear cluster demonstrates the solid-state reversible polymerization reaction. Because of the formation of the M-CN-M' bridge (M and M' denote metal ions) after the polymerization, long-range magnetic ordering was observed in the polymer structure.

Figure 4 shows the tunable hexanuclear Fe complex,  $[\{\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3\}_4\{\text{Fe}^{\text{II}}(\text{MeCN})(\text{H}_2\text{O})_2\}_2] \cdot 10\text{H}_2\text{O} \cdot 2\text{MeCN}$  (Tp = hydrotris(pyrazolyl)borate).<sup>17)</sup> The cluster has a free CN ligand that serves as a coordination donor site. When the sample was heated to 150 °C, water molecules and coordinated  $\text{CH}_3\text{CN}$  desorbed from the crystal, and the coordination

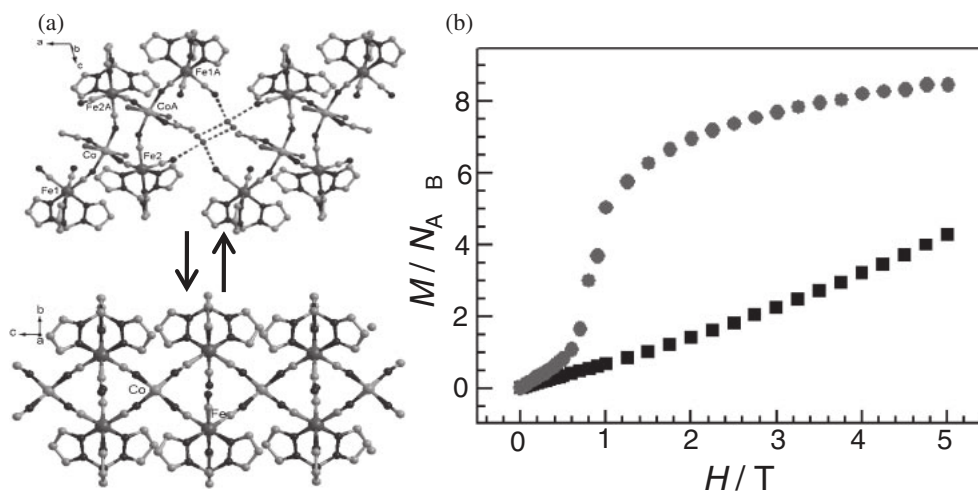


Fig. 4. (a) Top: Side view of  $[\{\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3\}_4\{\text{Fe}^{\text{II}}(\text{MeCN})(\text{H}_2\text{O})_2\}_2] \cdot 10\text{H}_2\text{O} \cdot 2\text{MeCN}$ . Bottom: Side view of  $[\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3]\text{Fe}^{\text{II}}(\text{H}_2\text{O})_2$  with 1-D double zigzag chain structure after heating. (b)  $M$  versus  $H$  plots at 2 K for  $[\{\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3\}_4\{\text{Fe}^{\text{II}}(\text{MeCN})(\text{H}_2\text{O})_2\}_2] \cdot 10\text{H}_2\text{O} \cdot 2\text{MeCN}$  (■) and  $[\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3]\text{Fe}^{\text{II}}(\text{H}_2\text{O})_2$  (●).

reaction proceeded between CN in  $[\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3]^-$  and  $\text{Fe}^{\text{II}}$  in neighboring clusters. Single-crystal analysis shows the 1-D structure formed because of the polymerization reaction. Following this structural change, paramagnetic properties changed to metamagnetic ones because of the formation of magnetically coupled  $-\text{NC}-\text{Fe}^{\text{III}}-\text{CN}-\text{Fe}^{\text{II}}-$  moieties. Furthermore, the original cluster was achiral, while after heating, it changed into a chiral one, indicating that chiral and achiral structures could be switched in this system.

Using this polymerization technique, various magnetic properties can be controlled. Indeed, we could prepare tunable porous magnets for FeCo hexanuclear systems,  $[\{\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3\}_4\{\text{Co}^{\text{II}}(\text{MeCN})(\text{H}_2\text{O})_2\}_2] \cdot 10\text{H}_2\text{O} \cdot 2\text{MeCN}$ .<sup>18)</sup> As in the case of the above complex, the present FeCo complex showed reversible interconversion between clusters and 1-D polymers by heating and exposing the compound to solvent vapors, respectively. The structure after polymerization was microporous, having pores with the channel size of  $1.9 \text{ \AA} \times 3.6 \text{ \AA}$ . Gas adsorption measurements show that  $\text{CO}_2$  and  $\text{H}_2$  were absorbed in the pores while  $\text{N}_2$  was not. This result is consistent with a general correlation between the pore size and kinetic diameters of adsorbates.  $\text{H}_2$  and  $\text{CO}_2$  could be adsorbed because their kinetic diameters, 2.827–2.89  $\text{ \AA}$  for  $\text{H}_2$  and 3.3  $\text{ \AA}$  for  $\text{CO}_2$ , are smaller than the effective channel size. Conversely,  $\text{N}_2$  could not be adsorbed because it has a kinetic diameter (3.64–3.80  $\text{ \AA}$ ) larger than the effective channel size. As in the case of the previous

compounds, magnetic properties switched between paramagnetism and metamagnetism.

**Guest exchange.** Prussian blue analogs are typical examples of porous coordination polymers, containing alkali cations and water molecules in interstitial sites. An important property of Prussian blue analogs is their cation exchange ability. We found that cation exchange in FeCo Prussian blue induces charge transfer between Fe and Co through CN in the framework of the porous coordination polymer.<sup>19)</sup> At room temperature,  $\text{Na}_{0.4}\text{Co}^{\text{II-HS}}_{1.3}[\text{Fe}^{\text{III}}(\text{CN})_6]$  consists of  $\text{Fe}^{\text{III}}-\text{CN}-\text{Co}^{\text{II-HS}}$  moieties. When this is dipped into the solution containing only  $\text{K}^+$  ions, cation exchange from  $\text{Na}^+$  to  $\text{K}^+$  ions is induced in the complex and is expressed as  $\text{Na}_{0.4}\text{Co}^{\text{II-HS}}_{1.3}[\text{Fe}^{\text{III}}(\text{CN})_6] + 0.4\text{K}^+ \rightleftharpoons \text{K}_{0.4}\text{Co}^{\text{II-HS}}_{0.3}\text{Co}^{\text{III-LS}}[\text{Fe}^{\text{II}}(\text{CN})_6] + 0.4\text{Na}^+$ . The interaction between the Prussian blue framework and alkali cations induced the modulation of the electronic structure of the metal center, leading to cation-exchange-induced charge transfer. This suggests that magnetic properties can be controlled by guest ions.

Magnetic properties of the 1-D compound  $[\text{FeTp}(\text{CN})_3]_2\text{Co}(\text{bpe}) \cdot 5\text{H}_2\text{O}$  can also be controlled by guest molecules (Fig. 5).<sup>20)</sup> This complex exhibited reversible temperature-induced charge transfer between  $\text{Fe}^{\text{III}}-\text{CN}-\text{Co}^{\text{II-HS}}$  and  $\text{Fe}^{\text{II}}-\text{CN}-\text{Co}^{\text{III-LS}}$  at around 190 K. Furthermore, when the FeCo complex was irradiated, it exhibited charge transfer from  $\text{Fe}^{\text{II}}-\text{CN}-\text{Co}^{\text{III-LS}}$  to  $\text{Fe}^{\text{III}}-\text{CN}-\text{Co}^{\text{II-HS}}$  states. When the FeCo complex is heated, the dehydrated sample  $[\text{FeTp}(\text{CN})_3]_2\text{Co}(\text{bpe})$  was obtained. The dehydrated

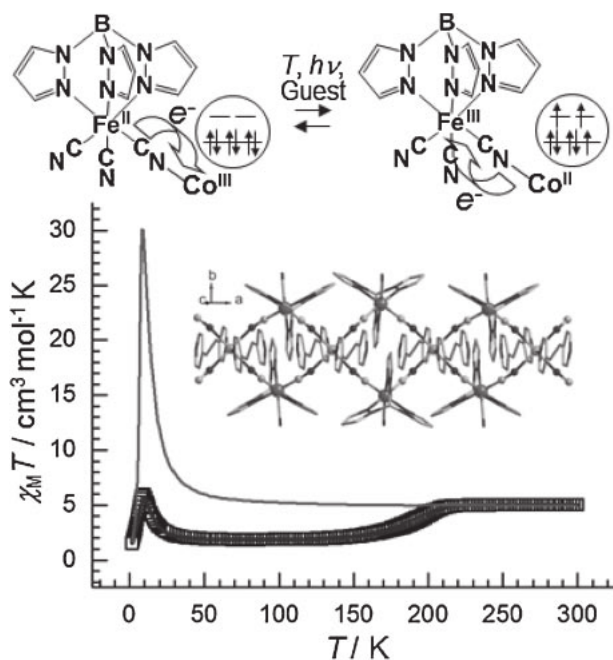


Fig. 5. Temperature-dependent susceptibilities of  $[\text{FeTp}(\text{CN})_3]_2\text{Co}(\text{bpe})$  (line), and  $[\text{FeTp}(\text{CN})_3]_2\text{Co}(\text{bpe})\cdot 5\text{H}_2\text{O}$  ( $\square$ ). (Inset) Side view of the double zigzag chain in  $[\text{FeTp}(\text{CN})_3]_2\text{Co}(\text{bpe})\cdot 5\text{H}_2\text{O}$  along the  $c$  axis.

sample acquires the  $\text{Fe}^{\text{III}}\text{--CN--Co}^{\text{II--HS}}$  state throughout the entire temperature range of 5–300 K. Furthermore, the sample did not exhibit photo-induced magnetization. This indicates that the FeCo complex shows appreciable crystal-water-dependent magnetic and photomagnetic properties. Transformation between the two states involves changes in the switching of hydrogen bonds between uncoordinated water molecules and terminal cyanide nitrogen atoms in  $[\text{Fe}^{\text{III}}\text{Tp}(\text{CN})_3]^-$ . When hydrogen bonds were removed, the redox potential of  $\text{Fe}^{\text{II}}$  shifted toward the negative potential, destabilizing  $\text{Fe}^{\text{II}}\text{--CN--Co}^{\text{III--LS}}$  pairs, while stabilizing  $\text{Fe}^{\text{III}}\text{--CN--Co}^{\text{II--HS}}$  pairs. Therefore, the hydrated compound exhibiting phase transition transformed into the dehydrated complex that does not exhibit metal-to-metal charge transfer.

### Quantum magnets

Recently, the study of quantum magnets has attracted considerable attention.<sup>21)</sup> We synthesized several clusters showing nanomagnetic properties. One of the complexes exhibited photofunctional properties.

The quantum magnets we synthesized were an  $\text{Fe}^{\text{II}}$ -based cyano-bridged linear trinuclear single molecule magnet (SMM),  $\{[\text{Fe}^{\text{II}}(\text{L-N}_3\text{O}_2)(\text{H}_2\text{O})]_2\text{Cr}^{\text{III}}\text{--}$

$(\text{CN})_6][\text{ClO}_4]\}\cdot 3\text{H}_2\text{O}$  ( $\text{L-N}_3\text{O}_2 = \text{azaoxa-macrocycle ligand}$ ),<sup>22)</sup> and a single chain magnet (SCM),  $[\text{Mn}^{\text{III}}_3\text{O}(\text{Meppz})_3(\text{EtOH})_4(\text{OAc})]$  ( $\text{Meppz} = 3\text{-(5-methyl-2-phenolate)pyrazolate}$ ).<sup>23)</sup> In addition, we have synthesized a quantum magnet with a wheel structure (Fig. 6).<sup>24)</sup> When  $[\text{Fe}^{\text{III}}(\text{bpmb})(\text{CN})_2]$  ( $\text{H}_2\text{bpmb} = 1,2\text{-bis(pyridine-2-carboxamido)-4-methylbenzene}$ ) and Mn molecules  $[\text{Mn}^{\text{III}}(\text{salen})]^+$  ( $\text{salen}^{2-} = \text{N,N'ethylenebis(salicylideneaminato)dianion}$ ) are mixed, a CN-bridged dodecanuclear macrocyclic complex,  $\{[\text{Mn}^{\text{III}}(\text{salen})]_6[\text{Fe}^{\text{III}}(\text{bpmb})(\text{CN})_2]_6\}\cdot 7\text{H}_2\text{O}$  ( $S = 15$ ), was obtained. The ac magnetic susceptibility measurements exhibit frequency-dependent behavior below 4 K. Furthermore, the complex showed a magnetic hysteresis loop below 0.5 K.

Unfortunately, the aforementioned complexes did not exhibit photoswitching properties. However, more recently, we have succeeded in synthesizing phototunable SCM (antiferromagnetic phase) by using photoinduced metal-to-metal charge transfer (Fig. 7).<sup>25)</sup> In order to prepare a phototunable SCM, designing of 1-D magnets with negative anisotropy, strong intrachain magnetic interaction, and well-isolated structure between 1-D chains was required. Moreover, 1-D compounds were expected to exhibit charge transfer or spin crossover, which can be achieved by designing the appropriate energy level and ligand field of metal ions. On the basis of this strategy, we synthesized an FeCo complex,  $[\text{Fe}(\text{bpy})(\text{CN})_4]_2\text{Co}(4,4'\text{-bipyridine})\cdot 4\text{H}_2\text{O}$ , with neutral bimetallic layers. The FeCo complex exhibited thermally induced intramolecular charge transfer between  $\text{Fe}^{\text{III}}\text{--CN--Co}^{\text{II--HS}}$  and  $\text{Fe}^{\text{II}}\text{--CN--Co}^{\text{III--LS}}$ . Furthermore, on light irradiation at 5 K, charge transfer from  $\text{Fe}^{\text{II}}$  to  $\text{Co}^{\text{III}}$  was induced and a metastable  $\text{Fe}^{\text{III}}\text{Co}^{\text{II}}$  state was trapped. Variable-temperature ac susceptibility measurements revealed a significant frequency dependence of both in-phase ( $\chi'$ ) and out-of-phase components ( $\chi''$ ), as observed in other SCMs. The pre-exponential factor and the relaxation energy barrier were  $\tau_0 = 1.4 \times 10^{-9}\text{ s}$  and  $\Delta_\tau/k_B = 29\text{ K}$ , respectively. A semicircular Cole–Cole diagram gave an  $\alpha$  value of 0.34. In-phase ac susceptibility showed a frequency-independent peak at 3.8 K, which is due to weak interchain antiferromagnetic interactions. Hence, the magnetic properties after irradiation should be an antiferromagnetic phase of SCM.

### Paramagnetic mononuclear complexes

In addition to magnets and nanomagnets, we have reported several tunable paramagnetic

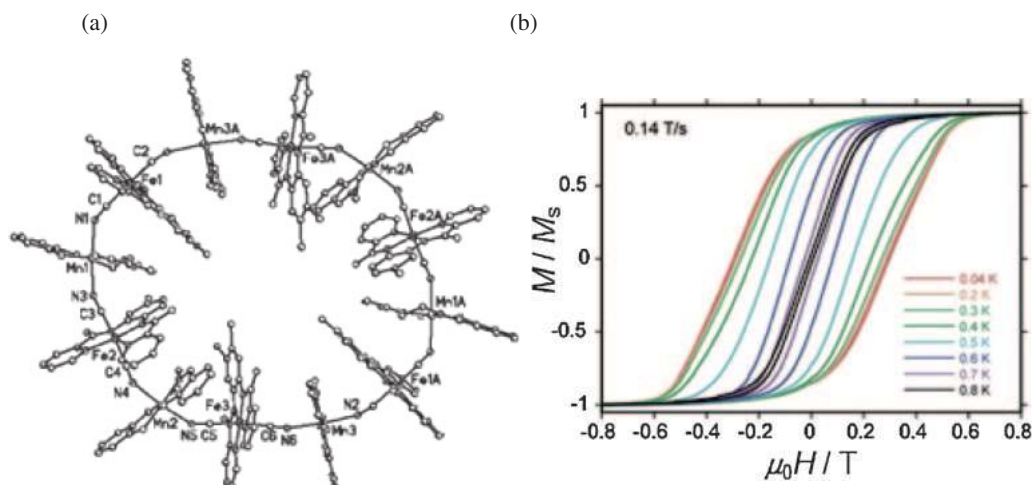


Fig. 6. (a) Molecular structure of  $[\{Mn(salen)\}_6\{Fe(bpmb)(CN)_2\}_6] \cdot 7H_2O$ . (b) Hysteresis loop at different temperatures measured at a scan magnetic field speed of  $0.14 T s^{-1}$ .

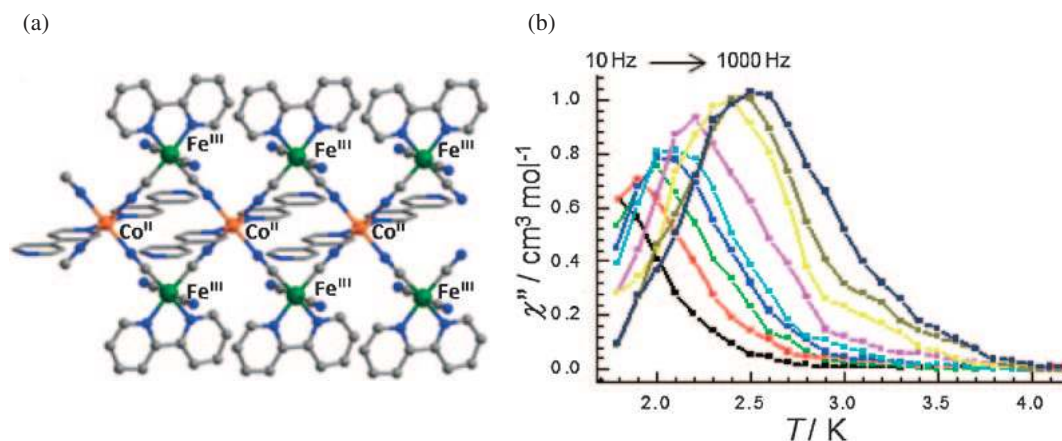


Fig. 7. (a) Side view of the 1-D double zigzag chain of the FeCo complex. (b) Temperature dependence of the imaginary part of ac susceptibility after irradiation in zero dc field at varying ac frequency and a 3 Oe ac field.

mononuclear complexes showing spin crossover, valence tautomerism, and changes in orbital angular momentum.

**Spin crossover.** Metal complexes with a  $d^4-d^7$  configuration can have two different spin states, high spin (HS) and low spin (LS).<sup>26)</sup> When the ligand field is situated in the critical region, the complex exhibits thermally induced spin transition; moreover, LIESST effects have been reported.<sup>27)</sup> Since the first observation of the LIESST effect, many LIESST complexes have been reported. However, the relaxation temperature is typically below ca. 80 K. In contrast, we have recently succeeded in observing a higher relaxation temperature of 130 K for the  $Fe^{II}L(CN)_2$  complex ( $L-N_3O_2 =$  azaoxa-macrocyclic ligand).<sup>28)</sup>

Furthermore, with respect to solid-state samples, only the  $Fe^{II}$  complex showed the LIESST effect to date, and it was believed that LIESST effects did not occur in  $Fe^{III}$  complexes.<sup>26)</sup> However, we have succeeded in observing the LIESST effect in solid-state  $Fe^{III}$  complexes,  $[Fe(pap)_2]ClO_4 \cdot H_2O$  and  $[Fe(pap)_2]PF_6 \cdot MeOH$  ( $Hpap = 2-(2-pyridylmethyleneamino)phenol$ ), as shown in Fig. 8.<sup>29),30)</sup> Magnetization measurements show that spin crossover occurs at approximately 165 K on cooling and at approximately 180 K on warming in  $[Fe(pap)_2]ClO_4 \cdot H_2O$ .<sup>29)</sup> On illumination of ligand-to-metal charge transfer (LMCT) band in the  $Fe^{III}$  complex (400 to 600 nm), Mössbauer spectra clearly show that  $Fe^{III}$  transformed from a LS to HS state. This suggests that LIESST can be induced in an  $Fe^{III}$

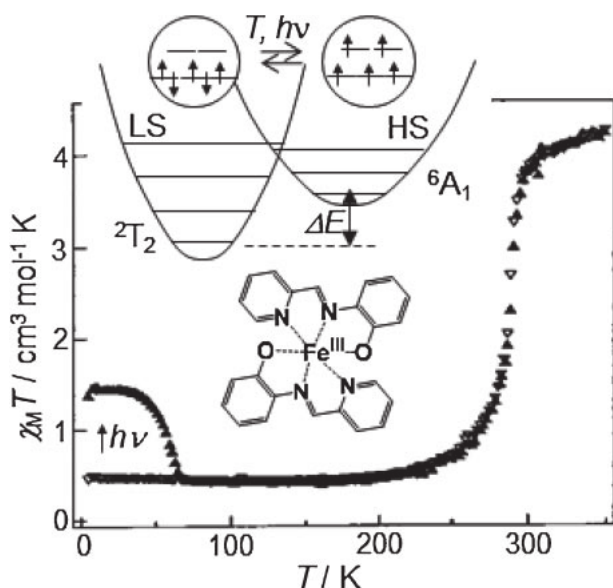


Fig. 8. Photomagnetic behavior:  $\chi_M T$  of  $[\text{Fe}(\text{pap})_2]\text{PF}_6 \cdot \text{MeOH}$  as a function of temperature on cooling ( $\nabla$ ), after irradiated at 5 K and warming up ( $\blacktriangle$ ).<sup>30)</sup>

complex. The LIESST effects were also observed in several other  $\text{Fe}^{\text{III}}$  complexes.<sup>31)</sup>

More recently, a spin crossover conductor,  $[\text{Fe}^{\text{III}}(\text{qsal})_2][\text{Ni}(\text{dmit})_2]_3 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ ,<sup>32)</sup> in which  $[\text{Ni}(\text{dmit})_2]$  ( $\text{dmit}^{2-} = 1,3\text{-dithiole-2-thione-4,5-dithiolato}$ ) is a potential conducting molecule and  $[\text{Fe}(\text{qsal})_2]^+$  ( $\text{qsalH} = N\text{-}(8\text{-quinoly})\text{salicylaldimine}$ ) is a spin crossover complex,<sup>33)</sup> was reported by Takahashi. This indicated an anomaly in conductivity exists at the spin transition temperature of  $[\text{Fe}^{\text{III}}(\text{qsal})_2]^+$ . This anomaly is caused by the chemical pressure to the  $[\text{Ni}(\text{dmit})_2]$  layer, which is induced by the change in the molecular volume involving the spin transition of  $[\text{Fe}(\text{qsal})_2]^+$  in the crystal. Although several attempts have been made to develop spin crossover conductors, this is a first example in which synergy is exhibited between spin crossover and conductivity.  $[\text{Fe}^{\text{III}}(\text{qnal})_2][\text{Pd}(\text{dmit})_2]_5 \cdot \text{acetone}$  [ $\text{qnalH} = N\text{-}(8\text{-quinoly})\text{-2-hydroxy-1-naphthaldimine}$ ] also showed synergistic effects between spin crossover and conductivity.<sup>34)</sup>

**Valence tautomerism.** The observation of a long-lived metastable state for Fe LIESST complexes and FeCo Prussian blue analogs prompted us to explore new complexes showing a photoinduced long-lived metastable state using a different mechanism. We focused on valence tautomeric complexes,<sup>35),36)</sup> and found that several Co compounds show photoinduced magnetization effects because of the long-

lived LMCT.<sup>37),38)</sup> Figure 9 shows the magnetic properties of a switchable complex,  $[\text{Co}^{\text{III-LS}}(3,5\text{-DBSQ})(3,5\text{-DBCat})(\text{tmeda})]$  (3,5-DBSQ = 3,5-di-*tert*-butyl-1,2-semiquinonate; 3,5-DBCat = 3,5-di-*tert*-butyl-1,2-catecholate;  $\text{tmeda} = N,N,N',N'$ -tetramethylethylenediamine).<sup>39)</sup> At high temperature, molecules adopt the HS  $\text{Co}^{\text{II}}$  state and incorporate two semiquinone ligands  $[\text{Co}^{\text{II-HS}}(3,5\text{-DBSQ})_2(\text{tmeda})]$ . On lowering the temperature, an electron is transferred from Co to semiquinone, resulting in a  $\text{Co}^{\text{III-LS}}$  species with catecholate and semiquinone ligands  $[\text{Co}^{\text{III-LS}}(3,5\text{-DBSQ})(3,5\text{-DBCat})(\text{tmeda})]$ . Furthermore, on irradiation to excite the LMCT band, magnetization at 5 K increases significantly. This suggests that the following reaction has occurred:  $[\text{Co}^{\text{III-LS}}(3,5\text{-DBSQ})(3,5\text{-DBCat})(\text{tmeda})] \rightleftharpoons [\text{Co}^{\text{II-HS}}(3,5\text{-DBSQ})_2(\text{tmeda})]$ . The change in magnetization could be maintained below ca. 50 K. Similar photo-effects were also observed in many other Co-valence tautomeric compounds.<sup>38)</sup> The relaxation behavior is the Arrhenius type at high temperature, while it is temperature independent at low temperature, indicating that relaxation is a tunneling process.

**Orbital angular momentum.** Control of magnetic properties can be achieved by changing spin multiplicity. The change in spin multiplicity is realized by inducing charge transfer and spin crossover. However, magnetic susceptibility is also affected by orbital angular momentum. Hence, the bistability of magnetization can be achieved by changing the contribution of the orbital angular momentum term. However, the control of magnetic properties through the modulation of orbital angular momentum has been less investigated thus far. It is well known that the quenching of orbital angular momentum depends on the ligand field and hence on the structure around metal ions. Hence, in order to realize thermally induced change in orbital angular momentum, we synthesized a Co complex,  $[\text{Co}^{\text{II}}(\text{NO}_3)_2(\text{L}')]$  ( $\text{L}' = 2,6\text{-di}(\text{pyrazol-1-yl})\text{pyrazine}$ ), incorporating  $\text{NO}_3$  ligands.<sup>40)</sup> The octahedral HS  $\text{Co}^{\text{II}}$  complex has typically unquenched orbital angular momentum. Furthermore,  $\text{NO}_3$  is a flexible ligand; therefore, we anticipated that the temperature-dependent structural change would be induced in the complex. Indeed, this complex exhibited structural phase transition at approximately 235 K (Fig. 10). As a result, the change in magnetization accompanying the hysteresis loop was clearly observed. Because spin multiplicity does not change, the switching in magnetization can be achieved from the change in orbital contribution, which is induced

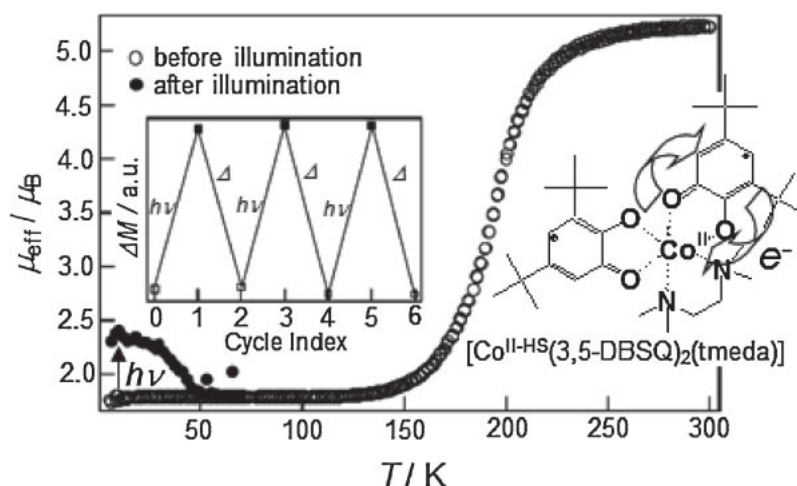


Fig. 9.  $\mu_{\text{eff}}$  versus  $T$  plots before and after illumination. Inset: changes in the magnetization at 5 K. Variables  $h\nu$  and  $\Delta$  represent illumination at 5 K and thermal treatment at 60 K, respectively.

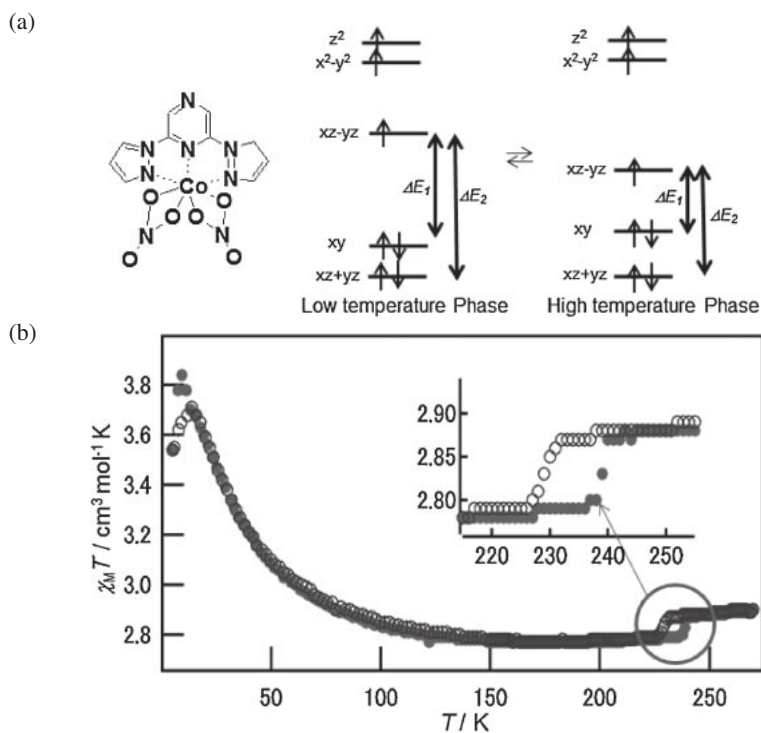


Fig. 10. (a) Splitting of d orbitals of high- and low-temperature phases. (b) Temperature dependence of  $\chi_M T$  in cooling (○) and heating mode (●).

by the modification of the structure around  $\text{Co}^{\text{II-HS}}$  ions. This conclusion is supported by density functional theory calculation.

### Clusters

More recently, we have focused on the development of nanomaterials because, in order to

apply these materials to a high-density recording medium, the bulk materials must be divided into nanometer-scale pieces. Therefore, it is preferable that clusters are synthesized on a nanometer scale from the beginning. Indeed, we synthesized several nanosized clusters that exhibit photofunctional properties.



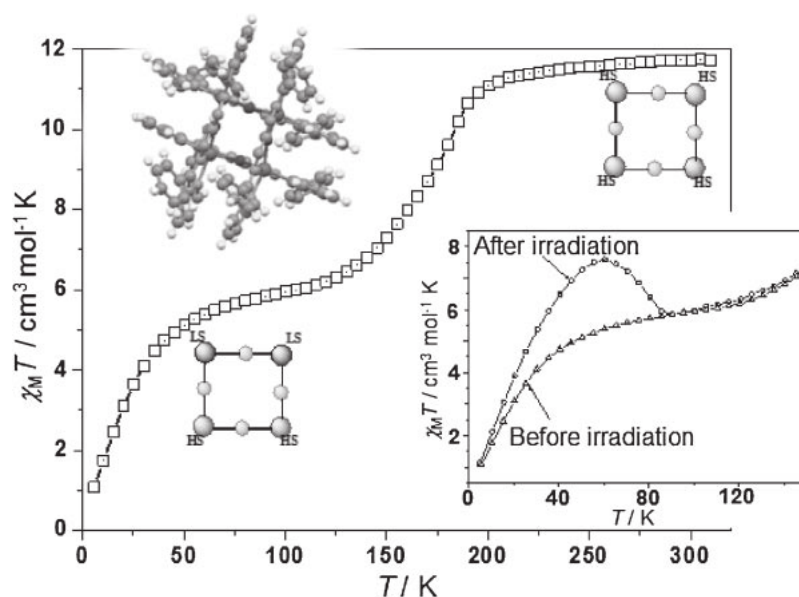


Fig. 11. Temperature dependence of  $\chi_M T$ - $T$  plots and photoinduced changes after irradiation at 532 nm (inset).

**Tetranuclear spin crossover.** We have synthesized a spin-crossover grid,  $[\text{Fe}_4(\text{HL}_1)_4] \cdot (\text{BF}_4)_4 \cdot (\text{H}_2\text{O})_2 \cdot \text{CH}_3\text{OH}$ , showing synergy between spin crossover and the magnetic interaction (Fig. 11).<sup>41)</sup> The magnetic property exhibits a two-step decrease in the magnetization value. On cooling from room temperature, spin crossover occurs from the  $\text{Fe}^{\text{II-HS}}_4$  to  $\text{Fe}^{\text{II-HS}}_2\text{Fe}^{\text{II-LS}}_2$  state at around 170 K. These two  $\text{Fe}^{\text{II-HS}}$  have a *cis*-type arrangement in the cluster. The formation of two HS and LS states results from the presence of intracluster antiferromagnetic interactions. On further cooling, the  $\chi_M T$  value approaches  $0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  with decreasing temperature because of the presence of antiferromagnetic interactions between two  $\text{Fe}^{\text{II-HS}}$  sites. When this complex is irradiated at 5 K by 532-nm light to excite the metal to ligand charge transfer (MLCT) band, only a small increase was observed in magnetization. This is due to the operation of the antiferromagnetic interaction in the cluster. The ground state with an  $\text{Fe}^{\text{II-HS}}_2\text{Fe}^{\text{II-LS}}_2$  structure before irradiation has  $S = 0$  because of the antiferromagnetic interaction between two  $\text{Fe}^{\text{II-HS}}$  ions. Furthermore, the ground state after irradiation also has  $S = 0$  because of the antiferromagnetic interaction between neighboring  $\text{Fe}^{\text{II}}$  ions in the  $\text{Fe}^{\text{II-HS}}_4$  state. Hence, only a small increase in magnetization was observed at low temperatures although two HS species were generated after irradiation. This demonstrated that the grid is a spin-crossover cluster in which the magnetic inter-

action operates between  $\text{Fe}^{\text{II-HS}}$  sites, which is distinguishable from typical spin crossover complexes.

**Dinuclear valence tautomerism.** We have succeeded in preparing a dinuclear Co complex,  $[\{\text{Co}^{\text{III-LS}}(\text{tpa})\}(\text{dhbq})\{\text{Co}^{\text{III-LS}}(\text{tpa})\}] \cdot (\text{PF}_6)_3$  (tpa = tris(2-pyridylmethyl)amine, dhbq = deprotonated 2,5-dihydroxy-1,4-benzoquinone), which exhibits room temperature hysteresis and photomagnetization effects (Fig. 12).<sup>42)</sup> The phase transition temperatures are  $T_{c\downarrow} = 297 \text{ K}$  and  $T_{c\uparrow} = 310 \text{ K}$  with a hysteresis width of 13 K. When the LMCT band around the visible region was irradiated at 5 K, charge transfer from  $(\text{dhbq})^{3-}$  to  $\text{Co}^{\text{III}}$  was induced. The photoprocess that occurred by photoirradiation can be expressed by  $[\{\text{Co}^{\text{III-LS}}(\text{tpa})\}(\text{dhbq})^{3-}\{\text{Co}^{\text{III-LS}}(\text{tpa})\}] \cdot (\text{PF}_6)_3 \rightleftharpoons [\{\text{Co}^{\text{III-LS}}(\text{tpa})\}(\text{dhbq})^{2-}\{\text{Co}^{\text{II-HS}}(\text{tpa})\}] \cdot (\text{PF}_6)_3$ . The change could be reversibly induced.

**Structural isomerism.** Molecule-based magnets are usually composed of metal ions with spin and bridging ligands mediating the magnetic interaction between metal ions. Hence, when the electronic properties of the bridging ligand change, the magnetic interaction between metal ions can be switched. On the basis of this, we constructed a photoswitchable spin device,  $\text{Ni}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}]$ .<sup>43),44)</sup> In the present compound, nickel nitroprusside,  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ , can be regarded as photofunctional bridging complex ligands. It has been reported that when the MLCT band in the visible region in  $\text{Na}_2[\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}]$  is excited, the coordination structure of the

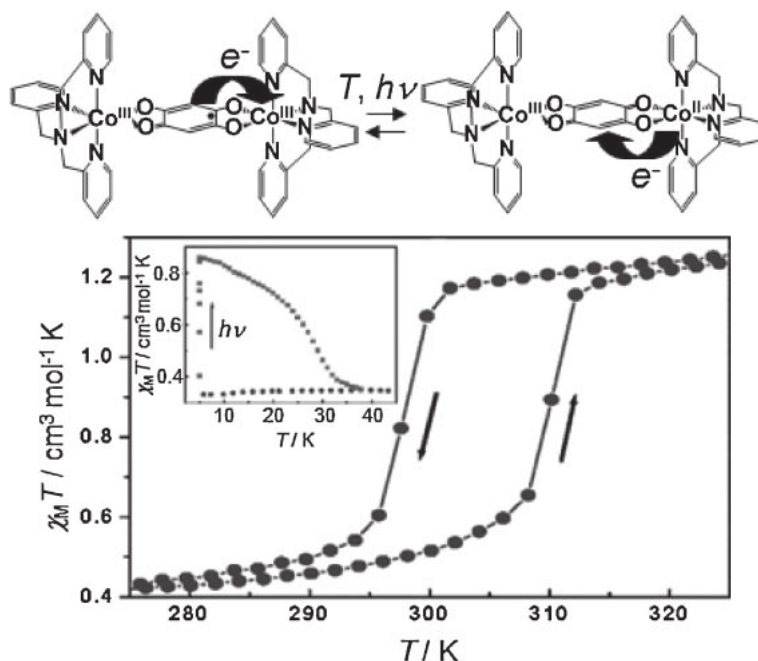


Fig. 12. Temperature dependence of  $\chi_M T$ - $T$  plots and photoinduced changes after irradiation at 532 nm (inset).

nitrosyl group can be modified. Hence, we can expect that the magnetic interaction between  $\text{Ni}^{\text{II}}$  ions through  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$  can be modulated by light. In fact, magnetic coupling in  $\text{Ni}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}]$  could be switched by the excitation of the MLCT band. Photoirradiation finally results in the formation of magnetic clusters with  $S = 5$  in the compound.

### One-dimensional compounds

**Spin crossover.** Only a few examples of magnetically coupled phototunable 1-D compounds have been reported, including one magnetically coupled spin crossover compound. We reported a 1-D LIESST compound,  $[\text{Fe}^{\text{II}}(\text{L})(\text{CN})_2][\text{Mn}^{\text{II}}(\text{hfac})_2]$  ( $\text{L-N}_3\text{O}_2$  = azaoxa macrocycle ligand;  $\text{hfac} = (1,1,1,5,5,5)$ -hexafluoroacetylacetonate), having the  $-\text{NC}-\text{Fe}^{\text{II}}-\text{CN}-\text{Mn}^{\text{II}}-$  heterometallic structure.<sup>45)</sup> The temperature dependence of magnetization showed that on cooling, spin crossover occurs at 110 K, forming 50%  $\text{Fe}^{\text{II-HS}}$  and 50%  $\text{Fe}^{\text{II-LS}}$  at low temperature. When the sample was illuminated at 5 K, a LIESST effect was observed.

**Charge transfer.** Another example is the homochiral  $\text{Mo}^{\text{IV}}\text{Cu}^{\text{II}}$  1-D compound,  $[\text{Cu}^{\text{II}}(\text{tren})][\text{Cu}^{\text{II}}(\text{33})][\text{Mo}^{\text{IV}}(\text{CN})_8] \cdot 4\text{H}_2\text{O}$  ( $\text{tren} = \text{tris}(2\text{-aminoethyl})\text{amine}$ ;  $\text{33} = \text{bis}(3\text{-aminopropyl})\text{amine}$ ).<sup>46)</sup> This compound exhibits spontaneous resolution from achiral components and crystallizes into the chiral

space group  $P2_1$ . On light irradiation, the complexes exhibit reversible photoinduced magnetic properties because of intramolecular charge transfer between  $\text{Mo}^{\text{IV}}$  and  $\text{Cu}^{\text{II}}$  centers. After irradiation, a ferromagnetic interaction occurs between  $\text{Cu}^{\text{II}}$  ( $S = 1/2$ ) and photogenerated  $\text{Mo}^{\text{V}}$  ( $S = 1/2$ ) centers.

### Conclusions

We reported electrochemically switchable molecular magnets. The direct switching of the oxidation state induced a shift in  $T_c$  of the magnets. Furthermore, several compounds showing photoinduced magnetization effects were successfully synthesized, including an FeCo Prussian blue analog, which is the first example of a molecular photomagnet. Furthermore, the 1-D FeCo complex with uniaxial anisotropy exhibited slow magnetization relaxation after irradiation; an antiferromagnetic phase of SCM. Magnetic properties can also be successfully controlled by using polymerization reactions and guest exchange reactions. A considerable change in magnetic properties could be observed even through the modification of the second sphere of the complex. Moreover, we developed  $\text{Fe}^{\text{III}}$  LIESST complexes, phototunable Co-valence tautomeric complexes, and a Co complex exhibiting the change in orbital angular momentum. Furthermore, we extended our work to phototunable clusters and 1-D complexes.

An interesting aspect of our work is the synergy of various properties, in particular the coupling of light and spin. On the other hand, spin electronics have recently attracted considerable attention. Therefore, one challenging issue in molecular magnetism would be the development of a new interdisciplinary field of optospinics and spin electronics. Furthermore, it would be interesting to develop a new field in which light, spin, and polarization show synergistic effects. Indeed, such systems are already being developed with oxides; however, their development is still challenging in terms of molecular compounds. Through the works reported herein, it is expected that new compounds, concepts, fields, and applications will be developed.

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## Profile

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