

# New Magnetic Functionalities Presented by Prussian Blue Analogues

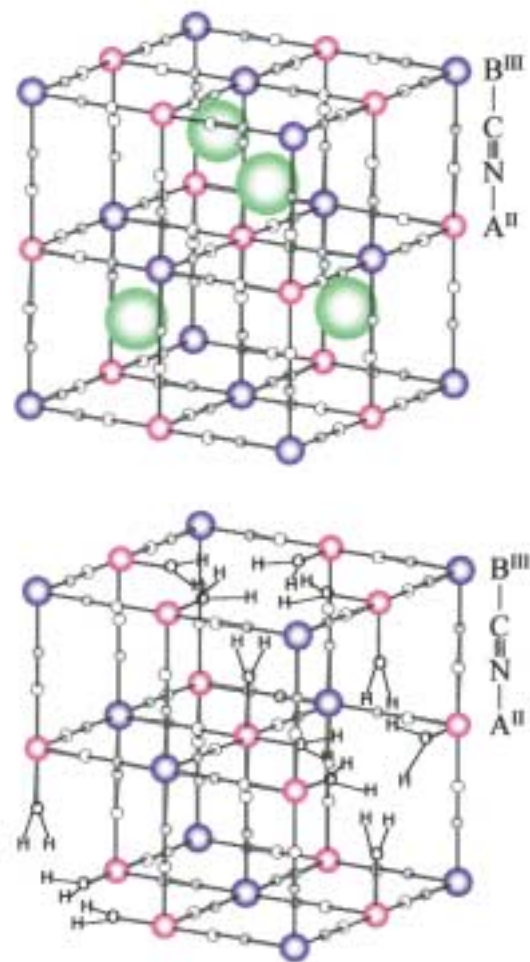
by Shin-ichi Ohkoshi and Kazuhito Hashimoto

Molecular magnetism has been one of the active areas in molecular chemistry for the last 15 years.<sup>1-6</sup> The advantages of molecule-based magnets compared to classical metal and metal oxide ones are that the magnets can be obtained through a selection of proper spin sources (*e.g.*, transition metal ions, organic radicals) and coordinating ligands. One of the attractive targets in this field is the development of functionalized magnets, in which magnetic properties can be controlled by external stimulation. In this article, we introduce various novel functionalities of magnetic materials with electrochemically synthesized Prussian blue analogues, which are one of the classes of molecule-based magnets.

## Molecule-based Magnets

To date, various molecule-based magnets have been obtained with bimetallic, metal-organic, and organic systems. For example,  $\text{Mn}^{\text{II}}\text{Cu}^{\text{II}}$  (pbaOH)  $(\text{H}_2\text{O})_3$  (pba = 2-hydroxy-1,3-propanediylbis(oxamato)) shows one dimensional (1-D) ferrimagnetic behavior below 4.6 K.<sup>2</sup> A series of  $[\text{M}^{\text{II}}\text{Cr}^{\text{III}}(\text{ox})_3]^-$  (ox = oxalato,  $\text{M}^{\text{II}} = \text{Fe}^{\text{II}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}},$  and  $\text{Cu}^{\text{II}}$ ) form 2-D or 3-D network structures, showing spontaneous magnetization.<sup>5</sup> In these two systems, spin sources are unpaired electrons in *d* orbitals of metal ions. A system having unpaired electrons in both *d*-orbitals and *p*-orbitals is also extensively studied. The prepared ionic salt  $[\text{Fe}(\text{Cp}^*)_2]^+[\text{TCNE}]^-$  ( $\text{Cp}^*$  = pentamethylcyclopentadienide, TCNE = tetracyanoethylene) shows a ferromagnetic transition below 4.8 K.<sup>1</sup> Moreover,  $\text{V}(\text{TCNE})_x \cdot y\text{CH}_2\text{Cl}_2$  obtained from the reaction of bisbenzene vanadium with TCNE in dichloromethane exhibits a high magnetic ordering temperature ( $T_c$ ) of *ca.* 400 K.<sup>1</sup> The main targets in the field of molecule-based magnets are classified into the following two at present. One is to obtain magnets with a high  $T_c$  value. Another is to design magnets with novel functionalities. As a proto-

Fig. 1. Schematic crystallographic structures of  $\text{K}^{\text{I}}\text{A}^{\text{II}}[\text{B}^{\text{III}}(\text{CN})_6] \cdot z\text{H}_2\text{O}$  (upper) and  $\text{A}^{\text{II}}_{1.5}[\text{B}^{\text{III}}(\text{CN})_6] \cdot z\text{H}_2\text{O}$  (lower).



type of the system having these properties, Prussian blue analogues are attractive because various types of building blocks  $[\text{B}(\text{CN})_6]^{x-}$  and metal ions A, where B and A are transition metal ions having unpaired electrons, can be assembled in an alternating fashion (Fig. 1).<sup>7</sup>

## Prussian Blue Analogue-based Magnets

Prussian blue,  $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot z\text{H}_2\text{O}$ , is a well-known compound with an extensive history over the past 250 years. This compound shows a blue color and has been used as a dyeing material. Moreover, the electrochromic phenomenon in Prussian blue films

has been studied in the field of electrochemistry.<sup>8</sup> However, Prussian blue's attraction lies not only in its color but also in its magnetic property; it shows long-range ferromagnetic ordering at 5.6 K.<sup>9</sup> In addition, various interesting magnetic properties have been reported recently with its analogues. For example, a series of Prussian blue analogues composed of hexacyanochromate,  $\text{A}^{\text{II}}_{1.5}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot z\text{H}_2\text{O}$  (A = V, Cr, Mn, Ni, Cu), have drawn attention due to their high  $T_c$  values.<sup>10,11</sup> In particular, Verdager *et al.* reported that  $\text{V}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.86} \cdot 2.8\text{H}_2\text{O}$  exhibits a  $T_c$  value of 315 K.<sup>12</sup> Successively, Girolami *et al.* and Miller *et al.* reported crystalline  $\text{K}^{\text{I}}\text{V}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]$  with  $T_c = 103^\circ\text{C}$  and amorphous  $\text{K}^{\text{I}}_{0.058}\text{V}^{\text{II/III}}$

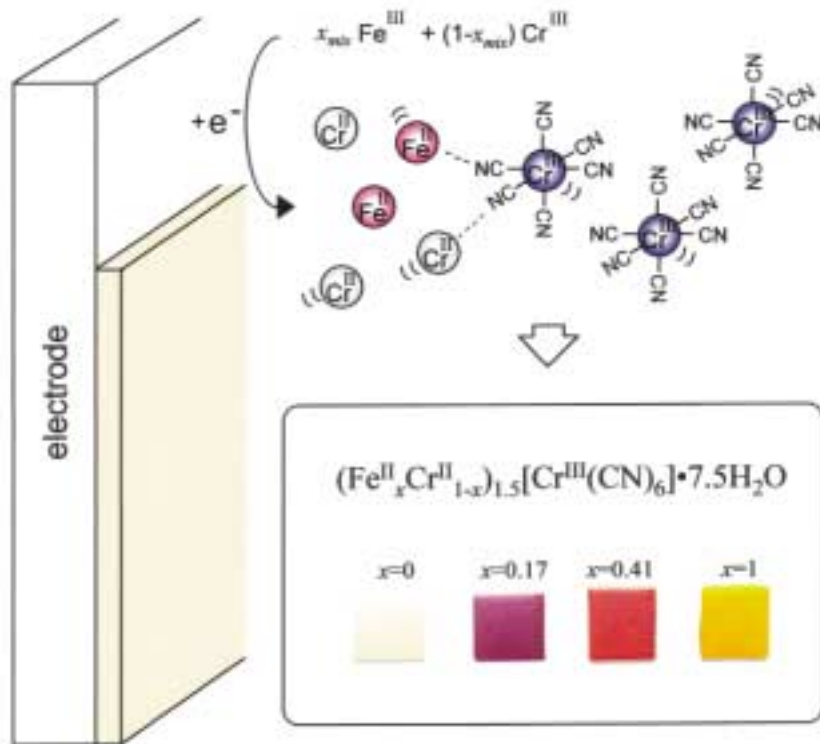


FIG. 2. Schematic diagram illustrating the electrochemical synthesis of binary and ternary metal Prussian blue analogue based-magnetic films. Insert shows photographs of colored magnetic films composed of  $(\text{Fe}^{\text{II}}_x \text{Cr}^{\text{II}}_{1-x})_{1.5} [\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 7.5\text{H}_2\text{O}$ .

$[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.79}(\text{SO}_4)_{0.058} \cdot 0.93\text{H}_2\text{O}$  with  $T_c = 99^\circ\text{C}$ , respectively.<sup>13,14</sup> Furthermore, in multi-metal Prussian blue analogues, the rational design of magnets based on the molecular field theory is possible for the following reasons: (1) metal substitutions induces only small lattice constant changes, and (2) superexchange interactions are essentially effective only between the nearest neighbor metal ions.<sup>15</sup> As an example of the design of novel magnetic properties, we have designed a novel type of magnet exhibiting two compensation temperatures in  $(\text{Ni}^{\text{II}}_{0.22}\text{Mn}^{\text{II}}_{0.60}\text{Fe}^{\text{II}}_{0.18})_{1.5} [\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 7.5\text{H}_2\text{O}$ , *i.e.*, the spontaneous magnetization changes its sign twice with changing temperature.<sup>16</sup>

### Electrochemical Synthesis of Prussian Blue Analogue-based Magnetic Films

The film type of Prussian blue and its analogues can be prepared by electrochemical methods. Itaya *et al.* reported that Prussian blue can be deposited on various substrates includ-

ing transparent  $\text{SnO}_2$  and  $\text{TiO}_2$ .<sup>8</sup> On the basis of this knowledge, we have prepared a high  $T_c$  compound of  $\text{Cr}_{2.12}[\text{Cr}(\text{CN})_6] \cdot z\text{H}_2\text{O}$  ( $T_c = 270\text{ K}$ ) on  $\text{SnO}_2$ -coated glass electrodes by reducing an aqueous solution containing  $\text{Cr}^{\text{III}}\text{Cl}_3$  and  $\text{K}_3[\text{Cr}^{\text{III}}(\text{CN})_6]$  at  $-0.8\text{ V}$  vs. SCE (Fig. 2).<sup>17</sup> Electrochemical switching of magnetic properties was shown between ferrimagnetism and paramagnetism with this film. Ternary metal Prussian blue analogues composed of  $(\text{Fe}^{\text{II}}_x \text{Cr}^{\text{II}}_{1-x})_{1.5} [\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 7.5\text{H}_2\text{O}$  ( $21\text{ K} \leq T_c \leq 220\text{ K}$ ) films were also obtained. Their compositions and colors depended both on the reduction potential and the mixing ratio of trivalent metal ions, *e.g.*, colorless ( $x = 0$ ), violet ( $x = 0.20$ ), red ( $x = 0.42$ ), and orange ( $x = 1$ ) as shown in Fig. 2, and, moreover, their magnetic properties were also rich in variety depending on  $x$ , *e.g.*, disappearance of saturation magnetization and compensation temperatures.<sup>18</sup> Room temperature magnets of  $\text{K}^{\text{I}}_a \text{V}^{\text{II/III}}_x \text{Cr}^{\text{II}}_{1-x} [\text{Cr}^{\text{III}}(\text{CN})_6]_y$  were also prepared by a similar electrochemical method. These films showed green ( $x = 0.23$ ) and blue colors ( $x = 1$ ).

Thus, in Prussian blue analogue films, various bright colored magnetic materials can be obtained by a simple electrochemical method and electrochemical tuning of their colors and magnetic properties is possible.

### Photomagnetism

Research related to the interaction between optical and magnetic properties is one of the attractive topics in the field of magnetic physics. In recent years, as a new functionality of magnetic materials, photoinduced magnetic effects have been extensively studied in a variety of systems such as cyanometalate-based magnets, organic-based magnets, spin crossover complexes, and diluted magnetic semiconductors. As for the optical control of magnetization, one of the possible methods is to change the electron spin state of a magnetic material. For example, the oxidation numbers of transition metal ions in a magnetic material can be varied by photo-irradiation, thus controlling its magnetization. The bistability of the electronic states is also indispensable to obtain photo-induced permanent magnetization because the energy barrier between these bistable states can maintain the photo-produced state even after stopping the photo-irradiation. In this vein, we have demonstrated two novel opto-magnetic processes of photo-induced magnetization and photo-induced magnetic pole inversion in Prussian blue analogues.<sup>19,20</sup>

We observed photo-induced magnetization first in  $\text{K}_{0.2}\text{Co}_{1.4}\text{Fe}(\text{CN})_6 \cdot 6.9\text{H}_2\text{O}$  powder. Its magnetization and  $T_c$  value is increased by red light illumination and the enhanced magnetization is partly reduced by blue light illumination. This photo effect is due to the charge-transfer induced spin transition between  $\text{Fe}^{\text{II}}(t_{2g}^6 e_g^0, S = 0)\text{-CN-Co}^{\text{III}}(t_{2g}^6 e_g^0, S = 0)$  and  $\text{Fe}^{\text{III}}(t_{2g}^5 e_g^1, S = 1/2)\text{-CN-Co}^{\text{II}}(t_{2g}^5 e_g^2, S = 3/2)$  states by the light irradiation. To facilitate potential application of cobalt hexacyanoferrate in future photomagnetic devices, the compound should be available in the form of thin films. In addition, the thin film structure affords electrochemical tuning of the photomagnetic properties at low temperature. Along this line, we demonstrated that the paramagnetic properties of an electrochemically synthesized cobalt hexacyanoferrate thin film composed of  $\text{K}_{0.4}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$  can be changed to ferrimagnetic ( $T_c = 26\text{ K}$ ) by visible light illumina-

tion and the resulting ferrimagnetic properties can be reversed back to paramagnetic by near-IR light illumination (Fig. 3a).<sup>21</sup>

We next designed a magnet exhibiting magnetic pole (“N” and “S”) inversion by photo-stimuli. A ferro-ferrimagnet ( $\text{Fe}^{\text{II}}_x\text{Cr}^{\text{II}}_{1-x})_{1.5}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 7.5\text{H}_2\text{O}$  mixed by ferromagnetic (Fe-Cr system showing the change of magnetization by optical stimuli) site and ferrimagnetic (Mn-Cr system showing no optical response) site showed negative magnetization at a temperature lower than the compensation temperature ( $T_{\text{comp}} = 19 \text{ K}$ ). In this mixed metal cyanide magnet, photo-induced magnetic pole inversion has been achieved (Fig. 3b).

### Magneto-optical Effects

Magneto-optical effects are also based on the interaction between light and magnetism. Faraday effect, which is one of the magneto-optical effects, is observed when linear polarized light propagates through magnetically ordered materials (Figs. 4a and 4b). However, typical magnets such as metal oxides and metal alloys, except for  $\text{FeBO}_3$  and  $\text{K}_2\text{CrCl}_4$ , are usually opaque and thus the application of the Faraday effect is limited. Conversely, electrochemically synthesized Prussian blue analogue films are transparent well into the visible region, and hence, they are useful for the study of the Faraday effect. Thus we measured the Faraday effect in a vanadium hexacyanochromate-based magnetic film with a high

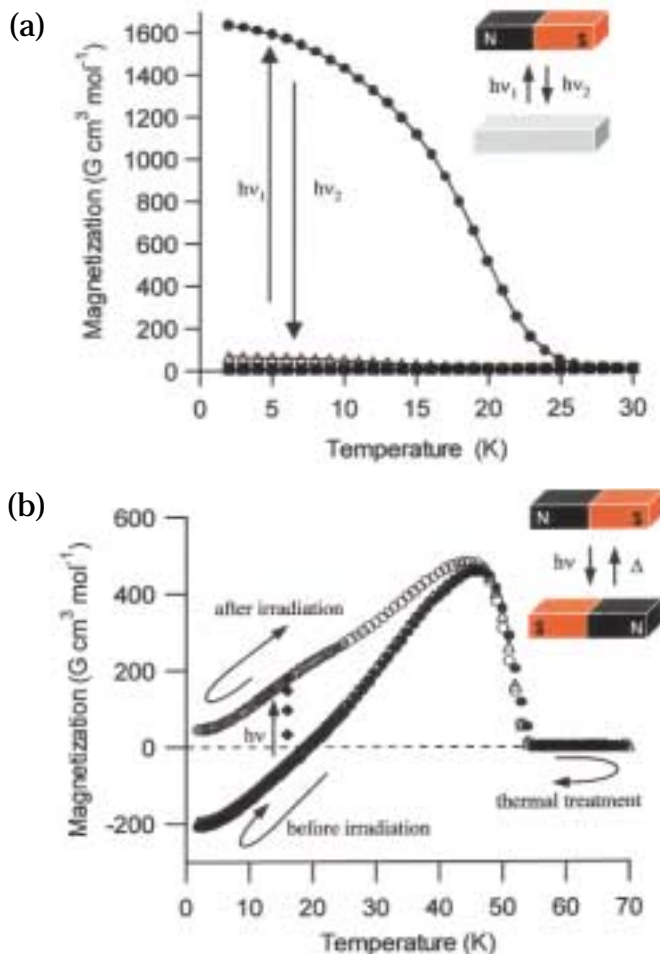


Fig. 3. Photo-induced magnetization and photo-induced magnetic pole inversion. (a) Magnetization versus temperature curves for  $\text{K}_{0.4}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$  at 5G, ■: before illumination, ●: after visible light illumination, ▲: after near IR light illumination. (b) Magnetization versus temperature curves of  $(\text{Fe}^{\text{II}}_{0.40}\text{Mn}^{\text{II}}_{0.60})_{1.5}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 7.5\text{H}_2\text{O}$  observed at 10 G before (●) and after (○) light irradiation at 16 K. The magnetic pole inversion is observed below the compensation temperature of 19 K by the light irradiation and the pole is reversed back again by warming the compound (Δ) to 80 K.

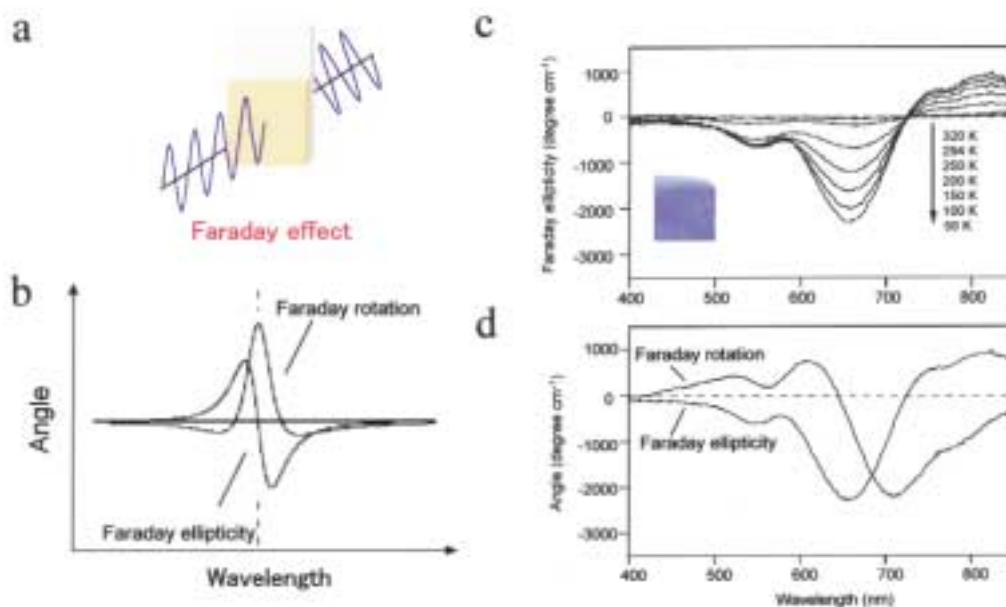


Fig. 4. (a) Faraday effect is observed when linear polarized light propagates through magnetically ordered materials. (b) Faraday rotation and Faraday ellipticity are connected by the Kramers-Kronig relationship at the wavelength of an optical absorption maximum. (c) Faraday ellipticity for  $\text{K}^{\text{I}}_{0.31}\text{V}^{\text{II}}_{0.49}\text{V}^{\text{III}}_{0.51}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.94} \cdot 6.5\text{H}_2\text{O}$  film ( $T_c = 310 \text{ K}$ ) under the external magnetic field of 1 T. (d) The Faraday ellipticity and Faraday rotation spectra in the external magnetic field of 100 G at 50 K.



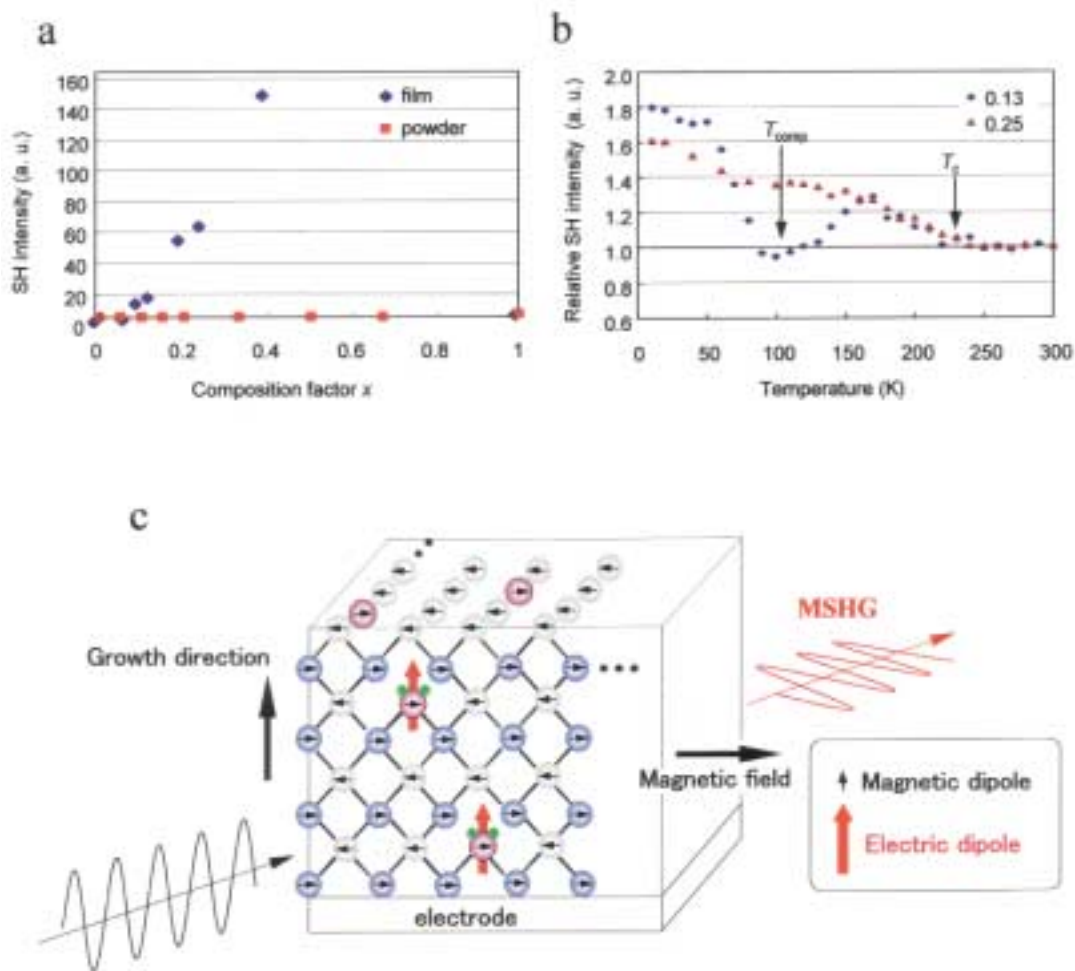


FIG. 5. (a) The SH intensity of  $P_{\text{IN}}\text{-}P_{\text{OUT}}$  polarization combination versus  $x$  in the film and powder forms of  $(\text{Fe}^{\text{II}}_x\text{Cr}^{\text{II}}_{1-x})_{1.5}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 7.5\text{H}_2\text{O}$  (the incident angle:  $45^\circ$ ). The thickness of all films was about  $2 \mu\text{m}$ . (b) Temperature dependences of the SH intensities generated from the films for  $x = 0.13$  and  $0.25$  in a zero applied magnetic field ( $P_{\text{IN}}\text{-}P_{\text{OUT}}$  polarization). (c) Schematic structure of the ternary metal Prussian blue analogue film involving both electric and magnetic dipoles.  $\text{Cr}^{\text{III}}$  (blue spheres) and either  $\text{Fe}^{\text{II}}$  (red spheres) or  $\text{Cr}^{\text{II}}$  (gray spheres), which are randomly incorporated in the lattice, are linked in an alternating fashion. Green spheres are water molecules.

$T_c$  of 310 K (Figs. 4c and 4d).<sup>22</sup> As shown in Fig. 4c, below  $T_c$ , this film shows strong Faraday spectra originating from the intervalence transfer (IT) bands between the vanadium and chromium ions in the visible light region. Thus, colored magnetic films composed of molecule-based magnets exhibit Faraday effects at a particular wavelength in the visible region. Such an IT band can be tuned by mixing metal ions in ternary metal Prussian blue analogues.<sup>17,18</sup> Hence, when such a metal replacement is carried out, the wavelength and magnitude of the Faraday effects can be controlled in the visible region. These materials have the potential to allow us to develop new types of magneto-optical devices such as opto-magnetic memory devices by selecting specific types of laser color.

### Nonlinear Magneto-Optical Effects

Let us focus our attention on nonlinear optical effects in molecule-based

magnets. Recently, second harmonic generation (SHG) from the surface of magnetic materials, so-called magnetization-induced SHG (MSHG), is being actively investigated. This new optical phenomenon is useful for observing surface magnetism because the rotation angle of this effect is much larger than that of the linear Kerr effect. In contrast, SHG arising from bulk magnetic materials has been observed in a limited number of cases to date. This is because most conventional ferromagnetic materials have a centrosymmetric structure, and hence, SHG from their bulk is forbidden in the electric-dipole approximation. However, many of molecule-based magnets are non-centrosymmetric, and hence, they can exhibit SHG. In fact, Gatteschi *et al.* and Nakatani *et al.* reported SHG from a non-centrosymmetric crystal of methoxyphenyl nitronyl-nitroxide radical and from layered materials comprising an organic dye cation and bimetallic oxalate anion ( $[\text{Mn}^{\text{II}}\text{Cr}^{\text{III}}(\text{ox})_3]^-$ ), respectively.<sup>23,24</sup>

Prussian blue analogues should not exhibit SHG due to their centrosymmetric face-centered cubic structures. In fact,  $(\text{Fe}^{\text{II}}_x\text{Cr}^{\text{II}}_{1-x})_{1.5}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 7.5\text{H}_2\text{O}$  ( $0 \leq x \leq 1$ ) powders prepared by coprecipitation do not show SHG. However, electrochemically synthesized  $(\text{Fe}^{\text{II}}_x\text{Cr}^{\text{II}}_{1-x})_{1.5}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 7.5\text{H}_2\text{O}$  ( $0 < x \leq 0.42$ ) magnetic films exhibited strong SHG from their bulk (Fig. 5a).<sup>25</sup> This SH activity was induced by the preferred orientation of the non-centrosymmetric monoclinic structure. In this system, the electric-dipole moment contributing to SHG is the  $\text{CN-Fe}^{\text{II}}\text{-OH}_2$  site. Below the magnetic ordering temperature, the SH intensity changed according to the variation of magnetization values (Fig. 5b). For example, in a film with  $x = 0.13$ , the SH intensity had a minimum value at the compensation temperature of magnetization. These results indicate that magnetic ordering contributes to the nonlinear optical susceptibility. Furthermore, MSHG properties such as the rotation angle and inten-

sity of SH light are expected to be changed by the application of an external magnetic field (Fig. 5c). Such electrochemical induction of second order optical nonlinearity may be applicable to other centrosymmetric materials as well.

Certainly, the novel magnetic functionalities described in this paper are not limited to Prussian blue analogues but most molecule-based magnets are likely to have similar potential. We believe that electrochemistry is a powerful tool for opening new avenues in the field of magnetic materials. ■

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