Optical-switching of second harmonic light in chiral photomagnet

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To control the physical properties and functionalities of materials via optical stimulation is an attractive issue. Spin-crossover phenomenon has been extensively studied because it realizes temperature-, pressure-, or photo-switching of the physical properties and functionalities. In particular, photo-switching from the low-spin (LS) state to the high-spin (HS) state, which is known as light-induced excited spin-state trapping (LIESST), is effective for optical control. Up to date, we have reported various unique photomagnetic mateirals using cyano-bridged bimetallic assemblies.[1,2] For example, we have reported an iron-octacyanoniobate metal complex, $Fe_2[Nb(CN)_8]\cdot$(4-pyridinealdoxime)$_8\cdot 2H_2O$ and a photo-induced ferromagnetism originated by LIESST effect for the first time.[3] In this work, we synthesize a new 3-dimensional chiral cyano-bridged bimetallic assembly of iron-octacyanoniobate, (±)-$Fe_2[Nb(CN)_8]$(4-bromopyridine)$_8\cdot 2H_2O$ (**1**),[4] and firstly observed spin-crossover-induced second harmonic generation (SHG), light-reversible spin-crossover long-range magnetic ordering, and optical-reversible switching of the magnetization-induced second harmonic generation (MSHG) effect.

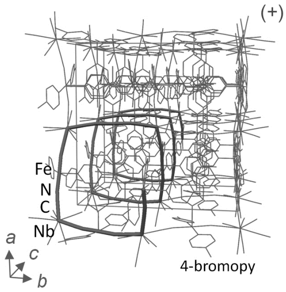

Fig. 1 Crystal structure of **1**.

Cyano-bridged FeNb bimetallic assembly of **1** has a chiral structure in the $I4_122$ space group (Fig.1). The temperature (T) dependence of the molar magnetic susceptibility (χ_M) shows a thermal phase transition between the high-temperature (HT) phase and the low-temperature (LT) phase. The transition temperatures from the HT to LT ($T_{1/2\downarrow}$) and from the LT to HT ($T_{1/2\uparrow}$) are 112 K and 124 K, respectively. The UV-vis absorption spectra exhibits optical absorptions at 430 nm and 560 nm, which are assigned to $^1A_1 \rightarrow {}^1T_2$ and $^1A_1 \rightarrow {}^1T_1$ transitions on the Fe^{II}_{LS} site, respectively. Therefore, the transition from the HT to LT in the $\chi_M T$–T plot is due to spin-crossover from Fe^{II}_{HS} (S = 2) to Fe^{II}_{LS} (S = 0).

Photomagnetic effect of **1** was investigated. Irradiating the LT phase with 473-nm light at 2 K produces large spontaneous magnetization. (Hereafter, called PI-1.) The magnetization (M) versus T curve shows a Curie temperature (T_C) of 15 K. The saturation magnetization (M_s) at 5 T is 7.6 μ_B, close to the expected M_s value of 7.8 μ_B due to ferrimagnetic coupling between Nb^{IV} (S = 1/2) and the photo-produced Fe^{II}_{HS} (S = 2). UV-vis spectrum and Mössbauer spectrum indicated that the observed bulk magnetization is due to the light-induced spin-crossover from Fe^{II}_{LS} to Fe^{II}_{HS}, i.e., LIESST effect. Next, we investigated the optical-switching effect on MSHG. Prior to irradiation, SHG for the LT phase of the paramagnetic state was measured. The SH intensity versus analyzer rotation angle (θ) plot shows that θ_{max} is 0° at $\pm H_0$, which is similar to the θ dependence of the SH intensity observed at 80 K. In the PI-1 phase, which is produced by LIESST effect with 473-nm light irradiation, θ_{max} at $+H_0$ is +88 ± 3° (Fig. 2). In contrast, at $-H_0$, θ_{max} is −86 ± 4°. In the PI-2 phase, produced by Reverse-LIESST effect with 785-nm light irradiation, the θ_{max} values are returned to +3 ± 1° and −3 ± 1° at $+H_0$ and $-H_0$, respectively. In the present system, LIESST and Reverse-LIESST effects control the polarization plane of the output SH light. The photo-reversibility was confirmed by alternative irradiation of 473-nm light and 785-nm light, which showed photo-reversible change in the SH intensity at θ = 0º.

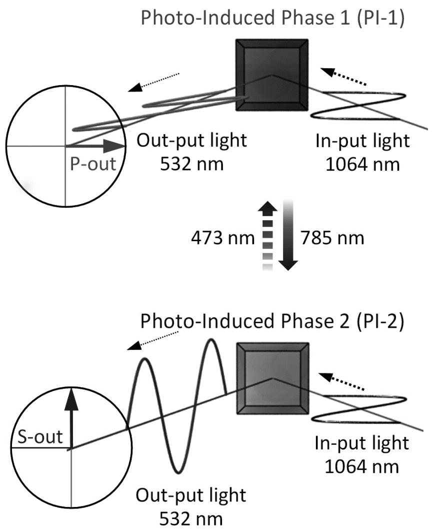

Fig. 2 Optical switching of the polarization plane of the output SH light between the PI-1 and PI-2 phases.

Reference

1) H. Tokoro and S. Ohkoshi, Dalton Trans., **40** (2011) 6825. 2) H. Tokoro and S. Ohkoshi, Bull. Chem. Soc. Jpn., **88** (2015) 227. 3) S. Ohkoshi, K. Imoto, Y. Tsunobuchi, S. Takano, H. Tokoro, Nature Chem., **3** (2011) 564. 4) S. Ohkoshi, S. Takano, K. Imoto, M. Yoshikiyo, A. Namai, H. Tokoro, Nature Photon., **8** (2014) 65.