

IV-G Progress of Conjugated Phenomena Coupled with Spin and Photon for Assembled Hetero-Molecular System

Intercalation of photochromic molecule into magnetic system provides fascinating multi-functionalities such as photo-magnetism, which gains much attention for their application to devices. The main subjects in this project are the development of photo-induced spin-crossover phenomena at room temperature by using the photo-isomerization of intercalated molecule, and the development of the transformation of magnetism for two-dimensional ferromagnetic system coupled with photochromic molecule.

IV-G-1 Reversible Photomagnetism in a Cobalt Layered Compound Coupled with Photo-Chromic Diarylethene

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Photomagnetism is one of the most attractive topics in recent research on molecular solids. In order to produce a photo-controllable magnet, we have synthesized a novel organic-inorganic hybrid system coupled with a photochromic diarylethene anion, 2,2'-dimethyl-3,3'-(perfluorocyclopentene-1,2-diyl)bis(benzo [b]thiophene-6-sulfonate) (**1a**) and cobalt LDHs (layered double hydroxides). The anion exchange reaction between the diarylethene anion, **1a**, and the layered double hydroxide, $\text{Co}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$ (**2**), takes place successfully (Figure 1), which was elucidated by powder X-ray diffraction analysis and IR spectra. Based on the elemental analysis, the title compound synthesized by the anion exchange reaction between **2** and **1a** has the chemical composition, $\text{Co}_4(\text{OH})_7(\text{1a})_{0.5}\cdot\text{H}_2\text{O}$ (**3**). Powder X-ray diffraction analysis revealed the interlayer distance of $c = 27.8 \text{ \AA}$. The magnetic susceptibility measurements elucidated the ferromagnetic intra- and inter-layer interactions and the Curie temperature of $T_c = 9 \text{ K}$.

In order to investigate the photo-irradiation effect on the magnetism, we carried out light irradiation on **3** spread thin on a glass plate in the dark at room temperature. After the irradiation, we measured the temperature dependence of the AC and DC susceptibilities and the hysteresis loop at 2 K. Although there is no light irradiation effect on the Curie temperature, the hysteresis loop shows a photomagnetic effect. The coercive field as well as the remnant magnetization decreases from 940 Gauss to 550 Gauss after light irradiation of 313 nm. The initial hard magnet is switched to a soft magnet by light irradiation of 313 nm. In addition, the soft magnet is almost reversibly returned to the initial hard magnet by the light irradiation of 550 nm. As plotted in Figure 2, both the coercive field and the remnant magnetization change almost reversibly by light irradiation of 313 nm and 550 nm. By UV irradiation of 313 nm, **3** shows the photo-isomerization of diarylethene anion from the open form to the closed one in solid state, which leads to the decreases in the coercive field and the remnant magnetization. Furthermore, the photo-excited state is returned to the initial state (open form) almost reversibly by

visible-light irradiation of 550 nm. In this manner, we have succeeded in controlling the magnetic properties reversibly by two kinds of photo-irradiation for the organic-inorganic hybrid system, **3**.¹⁾

Reference

- 1) M. Okubo, M. Enomoto and N. Kojima, *Solid State Commun.* **134**, 777–782 (2005).



Figure 1. Schematic representation of the anion exchange reaction and the structure of **3**.

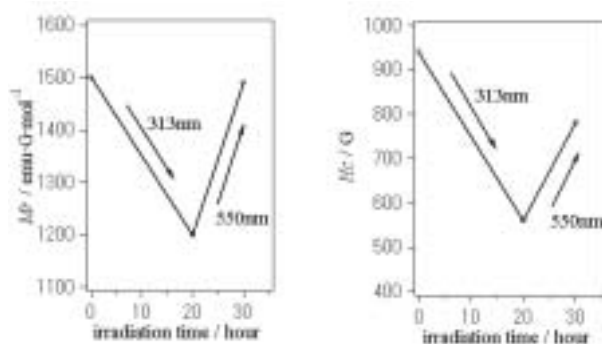


Figure 2. Photo-irradiation effects on the coercive field (H_c) and the remnant magnetization (M_r) of **3** at 2 K.