2-5-12. Photomagnetic Materials

Overview

Research on photomagnetic materials, whose magnetic states can be altered by light, is of interest not only from fundamental studies of magnetic phenomena but also from possible applications such as optical switching materials. To date, control of magnetic states has been achieved by changing the valence states or spin states by light. In the future, the research field is expected to advance towards interdisciplinary topics, such as multifunctionality and optical dynamics using ultrafast spectroscopy.

Current Status and Frontiers

To control the magnetization using light, it is necessary for the material to have a metastable state with different magnetic properties from the ground state, which can be transformed via a photoexcited state. As materials to satisfy such requirements, metal complexes, whose electronic and magnetic interactions between the metal centers can be controlled, have attracted considerable attention as promising research targets. In Japan, many researchers have led this field since the late 1990s. For an overview up to the mid-2000s, refer to "2-4-9. Photomagnetic Materials" in the Photochemistry Div Report. URL: https://division.csj.jp/div-report/02/0220409.pdf

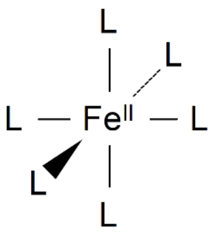

Figure 1. Octahedrally coordinated Fe(II) ions exhibiting the spin-crossover phenomenon.

Recently, research has advanced to photomagnets with multifunctionalities based on charge-transfer metal complexes and spin-crossover metal complexes. Below highlights some examples.

In d^4 to d^7 transition metal complexes with 6-coordinate octahedral structure, a transition from high-spin (HS) to low-spin (LS) states can occur with temperature change, which is known as the spin crossover phenomenon (SCO) (Fig. 1). Additionally, the photoinduced phase transition from LS to HS states is called light-induced spin crossover or Light-Induced Excited Spin-State Trapping (LIESST). In Japan, research on spin crossover has been actively pursued, including studies focused on Fe(II) complexes with so-called Hofmann-type structures (Kitazawa), guest-responsive spin crossover in porous coordination polymers (Ohba), magnetic and spin-state changes induced by gas molecule adsorption (Miyasaka), functionalization of Fe(III) spin-crossover complexes (Hayami, Sato), and spin-crossover-based photomagnetism (Ohkoshi).[1–5]

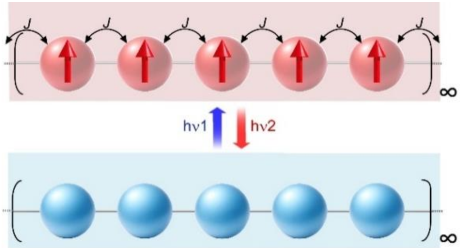

Figure 2. Schematic illustration of photo-reversible SCO ferromagnetism.

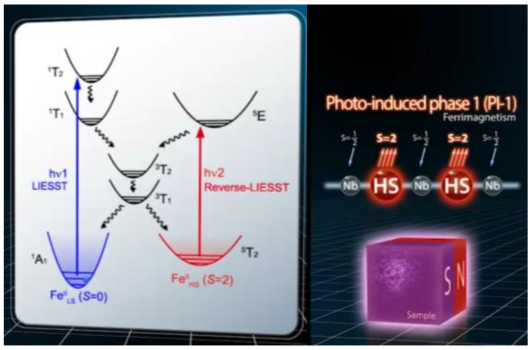

Figure 3. Mechanism of photo-reversible SCO ferromagnetism.

Generally, spin-crossover complexes exhibit magnetic changes within a molecule. If a spin-crossover complex with a 3-dimensional network structure can be constructed, a spontaneous magnetization by long-range magnetic ordering is expected due to strong exchange interactions (J) between the HS sites (Fig. 2). In the compound $Fe_2[Nb(CN)_8](4\text{-pyridinealdoxime})_8 \cdot 2H_2O$, Fe^{II}_{LS} with ${}^1A_1$ ground state is excited to singlet ${}^1T_2$ (or ${}^1T_1$) state by 473 nm light irradiation, and partially proceeds to the metastable quintet state (${}^5T_2$) via triplet states (${}^3T_2$ and ${}^3T_1$). Then, the photo-generated Fe^{II}_{HS} (S = 2) and adjacent Nb^{IV} (S = 1/2) align ferrimagnetically due to superexchange interactions through the cyanide, resulting in a spontaneous magnetization (Fig. 3). This is the light-induced spin-crossover magnet.[4]

Furthermore, $Fe^{II}_2[Nb^{IV}(CN)_8](4\text{-bromopyridine})_8 \cdot 2H_2O$ exhibits photoreversible spin crossover ferromagnetization. Due to its chiral structure, this compound also shows second-harmonic generation (SHG) and magnetization-induced second-harmonic generation (MSHG). Remarkably, alternating irradiation with 473 nm and 785 nm lights induces a 90° optical switching of the polarization plane of the SH light emitted from the crystal.[5] These findings represent the emergence of novel magneto-optical phenomena.

References

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3. S. Hayami, et al., *J. Am. Chem. Soc.*, **123**, 11644–11650 (2001).
4. S. Ohkoshi, et al., *Nature Chemistry*, **3**, 564–569 (2011).
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Future Perspectives and Directions

Challenges within the next ten years: Continued development of novel functionalities through the integration of multiple functionalities is desired. Furthermore, advances in research on optical dynamics using ultrafast spectroscopy are expected.

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