

Bistable Cyanide-Bridged Polynuclear Complexes : Structure, Magnetism and Macroscopic Polarization

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(双安定シアン架橋多核錯体-構造、磁性、及び巨視的分極)

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論 文 の 要 約

In recent years, various materials exhibiting both magnetic and electric polarization bistability have been developed in the field of fundamental and applied solid-state physics. Such materials are in high demand for applications in high-density data storage devices and sensitive switches. Magnetic bistability is well established in systems with electronic spin states tunable at the molecular level, which may arise from metallic ion centers, such as iron, cobalt, and other 3d transition metals. A number of phenomena between metallic ions, including spin crossover (SCO) and charge transfer induced spin transition (CTIST), have been reported. Electric polarization switching, such as that observed in ferroelectric materials, is a form of spontaneous macroscopic electrical polarization, which can be inverted or reoriented according to the external electric field, or tuned into a nonpolar phase via thermal treatment. Hence, the development of materials exhibiting electronic spin-state transition coupled with polarization switching instead of traditional ionic displacement or molecular order-disorder transformation mechanisms has attracted significant attention. A combination of these features enables achievement of tunable bistable magnetic properties as well as electric polarization characteristics using multiple external stimuli. In this thesis, bistability is comprehensively investigated in terms of both SCO and CTIST processes in two families of polynuclear cyanide-bridged complexes. Molecular level polarization changes arise as a result of asymmetric spin transitions, which occur by breaking chirality or spontaneous symmetry with the assistance of molecular packing and intermolecular interactions. Based on this principle, in the present study, thermal- and light-controllable macroscopic polarization switching was successfully achieved. The work was conducted from molecular to crystal scale employing a bottom-up approach as follows:

Chapter 2 focuses on polynuclear chiral SCO compounds. Such molecules are of particular interest for investigating different SCO behaviors resulting from the responses of metal-centered ions to different environments, which in a polar system may give rise to polarization changes. For this purpose, SCO in a chiral tetranuclear complex was thoroughly evaluated. An enantiopure pair $\{[\text{Tp}^*(\text{Fe}^{\text{III}})(\text{CN})_3]_2[\text{Fe}^{\text{II}}(\text{SS}/\text{RR-tzmp})]\}_2 \cdot 2\text{OTf} \cdot 4\text{BN}$ (**2-1**, tzpm = 2-(7,7-dimethyl-5,6,7,8-tetrahydro-6,8-methanoisoquinolin-3-yl)thiazole, OTf = trifluoromethanesulfonic, BN = benzonitrile) was effectively synthesized. The observed half-spin transition of **2-1** was mostly contributed to the SCO of one Fe ion, while the other ion remained high spin. Upon removing the solvent by heating, a gradual, quasi-complete SCO was observed for the solvent-free sample **2-1**, implying that the SCOs of the two Fe ions were inhibited by the interactions between the molecules and lattice in different ways. Regrettably, the small angle between the structural variation and b axis prevented the detection of the polarization changes and the loss of solvents molecules, which led to damage of the bulk crystal in air. However, the existence of polarization changes upon the variation along the polar b axis was strongly indicated, and the challenges associated with the characterization of the compound will be addressed in the future work.

In **Chapter 3**, the successful design and synthesis of complexes with V-shaped cyanide-bridged trinuclear $[\text{Fe}(\text{Tp})(\text{CN})_3]_2(\text{Co}(\text{dpa})_2)$ motifs is discussed. By introducing different aprotic polar solvent molecules into the system, $\{[\text{Fe}(\text{Tp})(\text{CN})_3]_2(\text{Co}(\text{dpa})_2)\} \cdot 2\text{H}_2\text{O}$ (**3-1**) (Tp = hydridotris(pyrazol-1-yl) borate, dpa = 2,2'-dipyridylamine), $\{[\text{Fe}(\text{Tp})(\text{CN})_3]_2(\text{Co}(\text{dpa})_2)\} \cdot 2\text{H}_2\text{O} \cdot 2\text{EtOH}$ (**3-2**), and $\{[\text{Fe}(\text{Tp})(\text{CN})_3]_2(\text{Co}(\text{dpa})_2)\} \cdot 2\text{H}_2\text{O} \cdot 1.5\text{C}_3\text{H}_4\text{OH}$ (**3-3**, $\text{C}_3\text{H}_4\text{OH}$ = allyl alcohol) were effectively synthesized. The CTIST behavior of the materials was assessed by temperature-dependent direct current (dc) magnetic measurements with infrared (IR) spectroscopy. In addition, the field-induced tunable slow magnetic relaxation behavior of the materials was evaluated by performing alternating current (ac) measurements on **3-1**, which is a unique low-temperature (LT) phase with a half-spin ground state $[\text{Fe}^{\text{II}}_{\text{LS}}-\text{Co}^{\text{III}}_{\text{LS}}-\text{Fe}^{\text{III}}_{\text{LS}}]$. Furthermore, the on/off switching of slow magnetic relaxation accompanied by a light-induced CTIST process was achieved by alternating irradiation of 808 and 532 nm sources. Attempts were also made to conduct pyroelectric measurements for **3-1** and **3-2**. Nevertheless, no pyrocurrent peaks were detected for a randomly selected direction of **3-1** in a triclinic *P*-1 system. It is speculated that in such low-symmetry complexes, the removal of the intrinsic *C*2 axis of the $[\text{Fe}_2\text{Co}]$ motif is unfavorable for the construction of a non-polar to polar structural transition via Fe–Co charge transfer. Moreover, a current peak was observed during the measurement of **3-2** during the first cooling process. Although the crystal was fragile during the measurements, the strategy to couple the CTIST process with potential polarization switching is feasible, which is achieved in the following chapter 4.

Chapter 4 is focused on the optically and thermally tunable polarization of the system examined in Chapter 3. Different solvents were used to form two new complexes, specifically $\{[\text{Fe}(\text{Tp})(\text{CN})_3]_2(\text{Co}(\text{dpa})_2)\} \cdot 2\text{H}_2\text{O} \cdot \text{IPA}$ (IPA = isopropanol) (**4-1**) and $\{[\text{Fe}(\text{Tp})(\text{CN})_3]_2(\text{Co}(\text{dpa})_2)\} \cdot 2\text{H}_2\text{O} \cdot \text{MeOH}$ (**4-2**). The HT crystallographic systems belong to a higher symmetry in monoclinic *I*- and *C*-lattices with a structural transition from nonpolar to polar characteristics upon cooling. Such symmetry breaking transition coupled polarization switching was supported by pyroelectric measurements, which were carried out on the obtained crystal samples. As the observed pyrocurrent peaks were nearly in accordance with the CTIST temperature determined by carrying out magnetic susceptibility with IR spectroscopy measurements, the highly cooperative relationship between the two phenomena was confirmed. Additionally, the optical effects on both the magnetic and electric currents of **4-1** were evaluated to establish their relevance. Firstly, the photocurrent in the excitation process was detected by treating the crystalline sample with an 808 nm laser at approximately 5 K, which indicated that a transition from a polar LT phase to a nonpolar metastable (MS) phase took place. This result was in good agreement with the photo-induced crystal structure analysis. Subsequently, the MS phase could be partially off-switched via irradiation utilizing a 532 nm laser source with the current released in the opposite direction. This phenomenon is referred to as the light-electric current conversion effect. Furthermore, upon heating of the long-lifetime MS phase, a current signal was observed at approximately the structural relaxation temperature, as detected by photomagnetic susceptibility measurements, implying that the nonpolar MS phase relaxed back to the polar LT phase. Considering that the current direction, which represents spontaneous polarization, can be reversed utilizing an external electric field, the optical and thermal ferroelectric properties of the studied system were confirmed.

In conclusion, the research described in this thesis focuses on comprehensive evaluation of cyanide-bridged polynuclear complexes. A bistability study based on molecular level SCO and CTIST involved co-crystallization with different guest molecules to adjust the lattice interactions, molecular packing as well as to facilitate the symmetry breaking rearrangement of the crystal lattice with CTIST. Finally, tunable magnetic behavior and polarization switching in the crystalline state were achieved upon treatment with both light and heat.