Magnetic Field Effects on Polar Spin Crossover Complexes

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論　文　内　容　の　要　旨

Spin crossover (SCO) systems has been extensively studied regarding their responsiveness to various stimuli such as light, pressure, etc. Development of SCO complexes with polarization change further extends their application to the novel memory devices and sensors. Despite the growing interest in thermal, light, and magnetic field-induced polarization changes accompanied by SCO, the SCO process induced by magnetic fields has not been as thoroughly investigated. This scarcity of research is especially noticeable in molecular magnetoelectric materials, where SCO, when instigated by magnetic fields, is accompanied by a polarization change. Nevertheless, these materials hold substantial significance due to the demand for miniaturization in the memory device, a key application for magnetoelectric materials. From a development perspective, the limited availability of complexes, small polarization changes, and high magnetic field requirements remain significant constraints.

In this thesis, we investigated the magnetoelectric properties of two dinuclear complexes, [(A(*RR*-cth))(B(*SS*-cth))(μ-dhbq)]$(AsF_6)_3$ and [(C(*RR*-cth))(D(*SS*-cth))(μ-dhbq)]$(PF_6)_3$ noted as **1**$(AsF_6)_3$ and **2**$(PF_6)_3$, respectively. Our findings demonstrate the largest polarization change induced by a magnetic field in the **1**$(AsF_6)_3$ and improved sensitivity to the magnetic field in **2**$(PF_6)_3$. We also proposed strategies to design new complexes, potentially resolving the primary limitations in molecular magnetoelectric materials: small polarization change and high magnetic field requirement.

In **Chapter 2**, we report the synthesis and physical properties of the **1**$(AsF_6)_3$ complex. Temperature-dependent measurements of the single crystal structure, Mössbauer spectra, IR spectra, and magnetometry demonstrate an abrupt SCO process followed by a gradual temperature-dependent electron transfer process, similar to the transition behavior observed in the **1**$(PF_6)_3$ complex. Its polar structure, accompanied with the dipole moment change during SCO, results in a significant macroscale polarization change, as validated by pyroelectric

measurements. Nevertheless, the **1**$(AsF_6)_3$ complex exhibits some unique properties compared to the **1**$(PF_6)_3$ complex that make it more suitable for investigating magnetic field-induced polarization switching. These differences mainly relate to the lower SCO transition temperature, larger magnetic susceptibilities difference ($\Delta\chi_m$) at lower temperatures, and narrower SCO transition temperature. Additionally, the asymmetric coordination sphere leads to a significant change in the molecular dipole moment during the SCO process, and the strong metal-ligand covalency allows for a directional shift of electron density toward the metal site. Consequently, the polarization change reaches 0.45 μC cm^{-2} during the SCO process, inducible by both thermal and magnetic fields. To our knowledge, this represents the largest polarization change induced by a magnetic field in molecular systems to date, underscoring the potential of our approach for practical applications.

In **Chapter 3**, we successfully synthesized the isostructural **2**$(PF_6)_3$ complex exhibiting similar electron dynamics, as verified by X-ray crystallography, IR spectroscopy, magnetic, and pyroelectric measurements. After annealing treatment, the **2**$(PF_6)_3$ complex exhibits an SCO process at lower transition temperatures of 35 K (heating) and 15 K (cooling). This SCO process also induces a polarization change, with a maximum value of 0.27 μC cm^{-2} observed in this complex. The **2**$(PF_6)_3$ complex demonstrates higher magnetic field sensitivity due to its larger spin quantum number and lower transition temperature. Furthermore, the complex reacts differently to pulsed and DC magnetic fields due to the slower SCO transition speed compared to the pulsed magnetic field timescale. The pulsed magnetic field induces the largest temperature shift of about 40 K in the SCO system, detected at a temperature of 1.4 K.

The central focus of this thesis is the exploration of magnetic effects on polar SCO complexes, including enhancing the polarization change coupled with SCO induced by the magnetic field and reducing the magnetic field requirement to induce this change. The asymmetric coordination sphere structure and the electron density shift offer a plausible solution for a larger polarization change induced by magnetic fields in the **1**$(AsF_6)_3$ complex. Additionally, increasing spin quantum number in the **2**$(PF_6)_3$ complex enhances the magnetic susceptibilities difference ($\Delta\chi_m$) between low and high spin states, leading to a highly magnetically sensitive complex. These approaches could provide the blueprint for designing magnetoelectric materials with a larger polarization change induced by magnetic fields and higher magnetic field sensitivity, which may help achieving the practical threshold for polarization change and decrease the magnetic field requirement, moving us closer to the development of next-generation magnetoelectric memory devices.