Investigation of Magnetoelectric Effects in μ_3-oxo-bridged Polynuclear Transition Metal Complexes

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論 文 名　：　Investigation of Magnetoelectric Effects in μ_3-oxo-bridged Polynuclear Transition Metal Complexes
（μ_3-オキソ架橋遷移金属多核錯体の電気磁気効果）

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論　文　内　容　の　要　旨

Materials which show the polarization switching properties under external stimuli have garnered significant interests in recent era as advanced functional materials. Ferroelectric materials are those that demonstrate spontaneous polarization changes and with hysteretic behavior under application of electric fields, which are deployed in various devices including memory units and capacitive storages. In recent years, many studies focusing on controlling the polarization of materials via different stimuli, e.g., temperature, light, and pressure, have been conducted, offering novel concepts for developing next-generation functional materials. Among them, the crystalline molecular materials have become an important branch due to their easily modulated dynamic electronic structures and potential multi responsiveness.

Recently, there have been reports on polarization switching induced by magnetic fields, which promoted related research on molecular materials. The reported molecules can be tentatively classified into two groups with different coupling mechanism, (1) molecules with spin-crossover properties, (2) molecules with dynamic Jahn-Teller axis distortion. However, these propose relatively strong restrictions to the molecular design, e.g., a sophisticated engineering of the molecular potential energy surfaces. To extend molecular crystals with magnetoelectric coupling, this thesis suggests two alternative approaches based on valence delocalization in class II/III mixed valence (MV) complexes and polynuclear complex with non-collinear spin configuration dictated by local magnetic anisotropy.

In Chapter 2, we developed a mixed-valence trinuclear iron compound crystallized in a polar $P2_1$ space group. The thermally induced electron delocalization/localization transition is confirmed by temperature dependent single X-ray diffraction and Mössbauer spectra. During the electron redistribution process, the release of pyroelectric current has been clearly observed with temperature scan. Through density functional theory calculations, the contribution from the rotation of coordinated pyridine and the free tert-butyl groups to the molecular dipole moment to be less significant compared to that from the valence separation. Notably, the intramolecular magnetic coupling is antiferromagnetic based on magnetic characterizations. As magnetic fields tend to stabilize the electronic configurations through Zeeman effect, a ground state with a larger spin quantum number could be expected when magnetic fields are applied. Owing to the dependence of electron delocalization on the net spin quantum number for class II

MV systems, a polarization change induced by magnetic field is therefore expected.

In Chapter 3, the magnetoelectric effect in a pentanuclear [Mn_3Zn_2] single-molecule magnet (SMM) with a [Mn3O]$^{7+}$ magnetic core is investigated. This newly synthesized trinuclear compound is crystallized in a polar *R*3*c* space group with a the crystallographic 3-fold rotational axis coinciding with the molecular C_3 axis, and the three Mn^{3+} ions are symmetrically equivalent. The Jahn-Teller axes, hence the local magnetic easy axes, are slightly tilted from each other, and the easy axis of the molecule is parallel to the polar axis. This, together with the ferromagnetic coupling among Mn^{3+} ions, makes it a SMM, and the magnetic hysteresis becomes evident below 2.4 K. The magnetic properties were performed from different angles to characterize the magnetic anisotropy. During the electric measurements along the polar axis, the magnetic field was directed to the parallel and perpendicular directions separately. While magnetic fields were manipulated between −5 T and +5 T, the induced current was clearly detected and was found to be correlated with both direction and variation of the applied magnetic fields. Moreover, the compound exhibits different polarization switching features in the low- and high-field limit with high sensitivity to magnetic fields. The potential origin of the polarization switching is also discussed in the thesis.

In conclusion, to achieve the goal of developing novel materials featuring magnetic field induced polarization changes, this thesis investigates two distinct magnetoelectric coupling mechanisms that operate at molecular level. By crystallizing the corresponding compounds in polar space groups, the switching behavior of the molecular dipole moments in magnetic fields can be extended to a single-crystal level. The characterization of two distinct molecular systems broadens the scope of crystalline molecular materials with magnetic field-induced polarization switching behavior. The study proposed novel concepts for the development of magnetoelectric materials and multifunctional SMMs in future. Furthermore, it introduces promising prospects for the implementation of magnetoelectric materials in future.