

Polarization Switching in Valence Tautomeric Complexes with Enantiopure Ligands

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(エナンチオピュア配位子を有する原子価異性錯体の分極スイッチング)

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論 文 内 容 の 要 旨

Dynamic polar materials, capable of switching between different polarization states in response to external stimuli, are attracting significant attention due to their potential applications in molecular sensors, memory devices, and energy harvesting systems. Non-ferroelectric materials with versatile electron dynamics, such as spin crossover, valence tautomerism, and double exchange, have emerged as promising candidates for achieving polarization switching. By rational molecular design and crystal engineering, several complexes exhibiting polarization switching by spin crossover and valence tautomerism have been developed in our laboratory. Among them, the light-induced polarization switching phenomenon holds the potential in the next-generation optoelectronic memory devices. However, the magnitude of light-induced polarization change remains limited with a record of *ca.* 0.3 $\mu\text{C cm}^{-2}$, which is far from the practical threshold (1 $\mu\text{C cm}^{-2}$) for capacitive memory. Addressing this limitation by discovering new non-ferroelectric materials capable of achieving significant light-induced polarization changes represents a critical challenge for future research.

In this thesis, we aim to enhance the efficiency of light-induced polarization change by rational molecular design. By density functional theory (DFT) screening based on a previously reported polarization switching material, $[\text{Cr}(\text{RR-cth})(\mu\text{-dhibq})\text{Co}(\text{SS-cth})_3](\text{PF}_6)_3$ (cth = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, dhibq = 3,5-dihydroxy-1,4-benzoquinone), we noticed that the modification by introduction of the enantiopure cth ligand induces distortion in the molecular structure, leading to the significant stabilization of the metastable $[\text{CoHS}^{2+}\text{-dhibq}^{2-}\text{-Cr}^{3+}]$ state. This feature could potentially enhance the lifetime of such a metastable state, thereby improving the photoconversion ratio and the induced polarization change. Moreover, as the introduction of chirality interrupts the crystallographic symmetry, the possibility of the molecules being packed in a polar space group would be largely increased even for the homometallic systems. Following this approach, several polar crystals, including $[\text{Cr}(\text{SS-cth})(\mu\text{-dhibq})\text{Co}(\text{SS-cth})_3](\text{PF}_6)_3 \cdot 2.5\text{H}_2\text{O} \cdot 0.5\text{MeOH}$ (**2-1**), $[\text{Cr}(\text{SS-cth})(\mu\text{-dhibq})\text{Co}(\text{SS-cth})_3](\text{AsF}_6)_3$ (**3-1**), and two dinuclear Fe complexes (**4-1** and **4-2**), were synthesized and thoroughly characterized.

In **Chapter 2**, we investigated the synthesis of physical properties of complex **3-1**. The key challenge in obtaining the pure dinuclear $[\text{CoCr}]$ complex with enantiopure ligand lies in the lack of chiral recognition, resulting in contamination of homometallic species. To address this issue, we propose a stepwise synthetic strategy by firstly binding the bridging dhibq ligand with the kinetically inert Cr^{3+} site. In this way, we successfully obtained the desired pure heterometallic species, as confirmed through mass spectrometry. Interestingly, the complex exhibits solvent-dependent valence tautomerism (VT). Magnetization measurements, UV-Vis spectroscopy, and IR spectroscopy in the pristine form revealed partial valence tautomerism with a transition temperature of approximately 170 K. Upon solvent

removal, the electron transfer process became nearly complete, and the process was reversible upon reabsorption of the corresponding solvents. X-ray single-crystal structural analyses demonstrated that both forms, before and after the removal of crystalline solvents, are packed in the polar $P2_1$ space group, plausible for polarization switching behavior. Pyroelectric measurements revealed a thermally induced polarization change of approximately $0.27 \mu\text{C cm}^{-2}$ in the pristine form, while a shift in the transition temperature upon solvent removal could also be detected. These results clearly indicate the capability of this stepwise synthetic methodology in obtaining the dinuclear complexes with an enantiopure ligand and the solvent-dependent polarization switching behavior in such a system.

In **Chapter 3**, we investigated a photoinduced polarization switching behavior in **3-1**. Based on the results in Chapter 2, we proposed enhancing the efficiency of light-induced valence tautomerism (LIVT) by replacing the counterion with a larger anion, AsF_6^- , to further stabilize the $[\text{Co}_{\text{HS}}^{2+}\text{-d}^{\text{h}}\text{bq}^{2-}\text{-Cr}^{3+}]$ configuration. Additionally, by recrystallization the product in ethanol, we obtained an optimized molecular orientation in the new crystalline phase. Magnetization analysis confirmed valence tautomerism with a reduced transition temperature of 123 K. Notably, this compound exhibits wavelength-dependent photomagnetization conversion. Remarkably, the efficiency of LIVT under 1340 nm reached virtually complete. This represents the first reported near-infrared light-excited valence tautomeric transition from $[\text{Co}_{\text{LS}}^{3+}\text{-Cr}^{3+}]$ to $[\text{Co}_{\text{HS}}^{2+}\text{-Cr}^{3+}]$ with full photoconversion. This feature might be related to the presence of a broad ligand-to-metal charge transfer (LMCT) band centered at 1400 nm of $[\text{Co}_{\text{LS}}^{3+}\text{-d}^{\text{h}}\text{sq}^{3-}\text{-Cr}^{3+}]$ configuration. Pyroelectric measurements after light irradiation revealed an exceptional light-induced polarization change of $2.25 \mu\text{C cm}^{-2}$, a value significantly higher than that induced thermally. To clarify the potential differences between light- and thermally-induced states, low-temperature single-crystal structural analyses were conducted before and after 1340 nm irradiation. The post-irradiation results revealed a hidden phase characterized by breaking of translational symmetry, reorientation of host molecules, and directional ion displacement. This phenomenon underpins the larger light-induced polarization change and highlights a novel mechanism for near-infrared light-induced polarization changes via the hidden phase.

In **Chapter 4**, we extend our synthetic strategy to homometallic $[\text{Fe}_2]$ complexes and discuss the potential photoinduced inversion of molecular dipole moments in such a system. Preliminary spectroscopic studies suggest the presence of a spin-delocalized ground state in this family of compounds. However, the introduction of enantiopure ligands leads to crystallization in the polar $P2_1$ space group with a slightly asymmetric chemical environments of the two Fe centers. DFT calculations revealed that opposite change in the electron densities on the two Fe sites would occur under irradiation with different wavelengths of light. This intriguing behavior suggests the potential for achieving the unprecedented light-induced polarization inversion using lasers of varying wavelengths.

The objective of this thesis is to design and develop versatile polar crystals exhibiting valence tautomerism through rational molecular design, innovative synthetic strategies, and crystal engineering. These efforts focus on achieving significant macroscopic polarization under controllable conditions. The introduction of the enantiopure cth ligand has been pivotal in breaking molecular symmetry and obtaining polar crystals. The purification of $[\text{CrCo}](\text{PF}_6)_3$ demonstrates the effectiveness of a stepwise synthetic approach in minimizing contamination, which could be extended to other systems with achiral ligands, enriching non-ferroelectric systems and enabling macroscopic polarization changes. Additionally, the synthesis of $[\text{CrCo}](\text{AsF}_6)_3$ exemplifies how molecular design and advanced crystal growth techniques can enhance light-induced polarization changes. The polar homometallic $[\text{Fe}_2]$ introduces a novel pathway for polarization inversion by controlling directional electron redistribution between two Fe centers in electron-delocalized complexes. These findings open new avenues for exploring polar crystals with macroscopic polarization-switching capabilities, emphasizing the diversity and modifiability of non-ferroelectric crystals.