

Macroscopic Polarization Switching in Mononuclear Valence Tautomeric Cobalt Complexes

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(原子価異性単核コバルト錯体における分極スイッチング)

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論 文 内 容 の 要 旨

Materials exhibiting polarization switching induced by directional charge transfer under external stimuli have attracted significant attention due to their fast-switching capabilities and potential applications. Our group recently reported two strategies for preparing polar compounds that exhibit polarization switching. The first involves the introduction of a chiral ligand, while the second replaces one of the homometal centers with a different metal—referred to as pseudo-symmetric co-crystallization (S. Kanegawa, *J. Am. Chem. Soc.* 138, 14170, 2025). Although numerous non-ferroelectric materials exhibiting polarization switching have been reported recently, most are ionic complexes, some of which include crystal solvents. These ionic systems present several limitations: they are water-soluble, poorly suited for polar film fabrication, and lack robustness. Moreover, complexes containing crystal solvents are unstable under high-temperature and vacuum conditions, potentially leading to film damage. In contrast, neutral materials are advantageous as they are stable in vacuum and at elevated temperatures. Such materials are promising candidates for investigating polarization inversion, molecular energy harvesting, and molecular-scale polarization switching. While the second strategy has successfully produced polar crystals, macroscopic polarization change has not been detected. This is primarily due to the small net dipole moments along the polar axis, which result from poor molecular orientation, and the limited crystal size, which impedes pyroelectric measurements. Although macroscopic polarization inversion is a crucial property of ferroelectrics—relevant for applications in energy harvesting, memory devices, sensors, and catalysis—it is rarely observed in non-ferroelectrics. Given this background, this thesis focuses on three main objectives: (i) the synthesis of a solvent-free and neutral complex exhibiting polarization switching, (ii) the realization of macroscopic polarization switching via the pseudo-symmetric co-crystallization technique, and (iii) the achievement of polarization inversion in non-ferroelectric compounds.

In Chapter 2, the goal was to synthesize a solvent-free and neutral complex exhibiting polarization switching. A neutral cobalt complex demonstrating electronic pyroelectricity was designed and synthesized using a ligand substitution strategy. According to previous reports, the redox-active ligand employed often yields neutral polar crystals, although typically in the presence of crystal solvents.

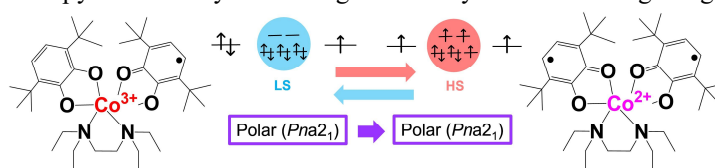


Figure 1. Polarization switching in a solvent-free neutral cobalt complex.

To address this, the (N–N) ligand was substituted (Figure 1), leading to the formation of a solvent-free, neutral, and polar crystal. The charge transfer properties were confirmed through multiple techniques, including magnetization measurements. Furthermore, the complex undergoes a polar-to-polar phase transition during the valence tautomerism (VT) process, during which a pyroelectric current was observed. Theoretical calculations indicate that the primary origin of the polarization switching lies in intramolecular charge transfer. These findings suggest that the complex is a promising candidate for the development of new VT compounds capable of reversible and stable polarization switching, even at temperatures above ambient.

In Chapter 3, the objective was to achieve macroscopic polarization switching and polarization inversion. This study was inspired by previous work in our group on [Zn][Co] and [Ga][Co] complexes prepared via the pseudo-symmetric co-crystallization technique, as reported by Kanegawa. Although these systems yielded polar compounds, macroscopic polarization change was not observed due to poor molecular orientation within the crystals. Additionally, those studies did not incorporate a design aimed at achieving polarization inversion. In this work, attention was focused on an [Fe][Co] complex (Figure 2). The [Fe] moieties exhibit strong covalency with the redox-active ligands, and the oxidation state of the Fe ion lies between Fe^{3+} and Fe^{2+} . Consequently, the dipole moment magnitude of $[\text{Fe}_{\text{HS}}(\text{phencat})(\text{RR-cth})]^+$ is expected to lie between those of $[\text{Co}^{\text{III}}_{\text{LS}}(\text{phencat})(\text{RR-cth})]^+$ and $[\text{Co}^{\text{II}}_{\text{HS}}(\text{phensq})(\text{RR-cth})]^+$, thus making polarization inversion a feasible outcome. To enable detectable macroscopic polarization change, a halogen substitution strategy was employed, aiming to enhance molecular orientation and thereby amplify the net dipole moment. Based on this approach, we synthesized [Fe][Co] complexes exhibiting polar crystal structures (Figure 2). Pyroelectric measurements confirmed the presence of pyroelectric current, indicating that the [Fe][Co] complexes exhibit macroscopic polarization switching. Furthermore, density functional theory (DFT) calculations revealed that polarization inversion could occur when all Co complexes undergo VT. However, the VT transition temperature of these complexes was too high, and full tautomerism was not observed even at 400 K. As a result, polarization inversion was not achieved under the experimental conditions.

In Chapter 4, the study advanced toward achieving macroscopic polarization inversion, building upon the findings of Chapter 3. To this end, efforts were directed at lowering the VT transition temperature by modulating the energy levels of the redox-active ligands. A reduction in the transition temperature would enable all Co complexes to undergo VT below 400 K, a prerequisite for observing polarization inversion. By chemically modifying the redox-active ligands, a novel [Fe][Co] complex, $[\text{Co}(\text{pyrene-4,5-diox})(\text{RR-cth})][\text{Fe}(\text{pyrene-4,5-diox})(\text{SS-cth})](\text{AsF}_6)_2$, was successfully synthesized (Figure 3). This complex exhibits a VT transition temperature of 211 K. Pyroelectric current was detected, confirming that macroscopic polarization change occurs in this [Fe][Co] complex. However, polarization inversion as originally anticipated was not observed, as only half of the Co ions exhibited valence tautomeric behavior. Interestingly, pyroelectric current inversion was nonetheless detected. This phenomenon is likely due to the opposing directions of intramolecular electron transfer and displacement of $[\text{AsF}_6]^-$ anions within the crystal lattice.

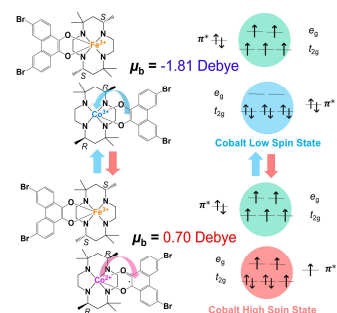


Figure 2. Polarization inversion in a mononuclear complex.

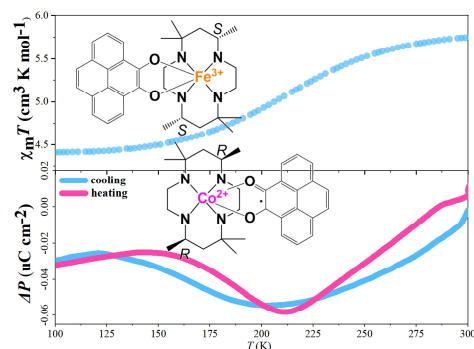


Figure 3. Macroscopic pyroelectric currents inversion in a mononuclear complex