

# Fundamental study of electronic pyroelectricity on valence-tautomeric molecular crystals

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(原子価異性分子結晶の電子焦電性に関する基礎研究)

## 論 文 内 容 の 要 旨

Pyroelectricity plays an important role in sensors and energy conversion devices. Conventional pyroelectric materials utilize the collective modes of ion displacement or reorientation of polar molecules to drive the change in polarization which is manifested as the redistribution of surface charge resulting electronic pyroelectricity. However, this approach mainly focuses on the chemical modification of standard ferroelectric materials and lacks the structural diversity and chemical designability for desired functional properties. Molecular systems, on the other hand, always promises better diversity and chemical tailorability than the condensed matter systems. Incorporating the intramolecular redistribution of electronic density in molecular crystals as the source for the polarization change, we can expect designable exotic pyroelectric behaviors from the molecular origin rather than the collective modes. Moreover, in the last decades, versatile ways of direct energy conversion received tantalizing attention and among them energy harvesting from low-grade thermal energy and light are the most encouraging and promising solution in terms of cleaner and more sustainable energy sources.

In this regard, we innovated novel molecular magnetic systems by employing bistable dynamic molecules where two or more nearly degenerate labile electronic states can be interconverted by thermal or light perturbations, resulting polarization based pyroelectric current without any external electric field. Interestingly, this electronic pyroelectricity not only operates at unit-cell level but also getting manifested at macroscopic single-crystal level due to chirality-assisted polar crystal engineering strategy. These external stimuli induced currents and magnetism might be considered as a promising strategy for low-power and high-speed switches and might set a revolutionary benchmark in the field of polarization switching as well as energy conversion.

Along this line, in chapter 2, a dinuclear pseudo-symmetric polar [FeCo] complex, [(Fe(*RR*-cth))(Co(*SS*-cth))( $\mu$ -dhbq)](PF<sub>6</sub>)<sub>3</sub> (where, cth = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; dhbq = deprotonated di-hydroxy benzoquinone) is introduced where both the metal centers, Iron and Cobalt are in distorted octahedral environment. Approximately at 90 K, an abrupt spin transition from highly covalent Fe<sup>3+</sup><sub>LS</sub> to Fe<sup>3+</sup><sub>HS</sub> occurs (LS = low spin, HS = high spin) accompanied by partial ligand-to-metal charge redistribution, which is followed by a temperature-induced continuous population change between two redox isomers with the structure of [Fe<sup>3+</sup><sub>HS</sub>-dhbq<sup>3-</sup>-Co<sup>3+</sup><sub>LS</sub>] and [Fe<sup>2+</sup><sub>HS</sub>-dhbq<sup>2-</sup>-Co<sup>3+</sup><sub>LS</sub>]. Thus, two different types of pyroelectric effects emerge because of the dynamic change in spin and charge in the polar [FeCo] crystal.

A pyroelectric current peak is observed at the spin transition temperature because of charge redistribution between Fe and the dhbq ligand, whereas an approximately constant and relatively large pyroelectric current is observed above the spin transition temperature due to the successive population of the electron-transferred  $[\text{Fe}^{2+}_{\text{HS}}\text{-dhbq}^{2-}\text{-Co}^{3+}_{\text{LS}}]$  state. A thorough analysis including single-crystal X-ray diffraction, temperature-dependent high-resolution X-ray near-edge absorption, Mössbauer spectroscopy, IR spectroscopy and DFT calculations reveals the unprecedented mechanism behind such peculiar phenomenon that represents an intricate and ingenious example of electronic pyroelectricity, to which three electronic structures contribute. Interestingly, pyroelectric coefficient remains at approximately  $3.4 \text{ nC cm}^{-2} \text{ K}^{-1}$  at 300 K, which is as large as that of polyvinylidene difluoride (PVDF).

In chapter 3, in order to manipulate polarization-based properties at molecular scale by light perturbations, we reported a dinuclear polar [CoGa] complex,  $[(\text{Co}(\text{RR-cth}))(\text{Ga}(\text{SS-cth}))(\mu\text{-dhbq})](\text{PF}_6)_3$  where two nearly degenerate electronic states of labile nature with different dipole moments can be interconverted by photon energy. The cobalt centre of the complex experiencing magnetic bistability where intramolecular charge transfer nominally involves the transfer of an electron from the redox-active bridging ligand ( $\text{dhbq}^{3-}$ ) to the low-spin  $\text{Co}^{\text{III}}$  centre to form a ( $\text{dhbq}^{2-}$ ) and a high-spin  $\text{Co}^{\text{II}}$  driven by 532 nm light irradiations. Moreover, the complex can also harvest thermal energy in terms of temperature dependent polarization change, which is quantitatively described by the sharp peak of pyroelectric coefficient at the phase transition temperature ( $\sim 220 \text{ K}$ ). A thorough analysis including single crystal X-ray diffraction, magnetometry, temperature dependent XAS, IR spectroscopy and DFT calculations providing a way to establish a correlation of molecular structure with macroscopic polarization in terms of interconversion between two distinct electronic states  $[\text{Co}^{3+}_{\text{LS}}\text{-dhsq-Ga}^{3+}]$  and  $[\text{Co}^{2+}_{\text{HS}}\text{-dhbq-Ga}^{3+}]$ .

In Chapter 4, a pseudo-racemic heterometallic co-crystal is introduced as a novel crystal engineering strategy to realize macroscopic polarization change via electron transfer in a valence tautomeric cobalt complex. Primarily, we investigated thermal and photo-induced valence tautomerism in the crystal of a mononuclear complex,  $[\text{Co}(\text{phendiox})(\text{rac-cth})] (\text{AsF}_6)$  (where,  $\text{H}_2\text{-phendiox} = 9, 10\text{-dihydroxyphenanthrene}$ ), which crystallizes in polar space group  $Pca2_1$  and undergoes phase-transition approximately at 230 K. As there persists pseudo-cancellation of polarization along the crystallographic- $c$  axis, we synthesized [FeCo] co-crystals using enantiopure ligands in pursuit of obtaining a net polarization along the polarization axis (where,  $[\text{FeCo}] = \{[\text{Fe}(\text{phendiox})(\text{SS-cth})] [\text{Co}(\text{phendiox})(\text{RR-cth})]\}(\text{AsF}_6)_2$ ). A thorough analysis including single crystal X-ray diffraction, magnetometry, IR spectroscopy and DFT calculations demonstrate valence tautomerism behaviour in these systems. Unfortunately, electronic pyroelectricity measurement on these complexes could not be obtained due to very small crystal dimensions.

Overall, the research in this thesis presents several novel results of molecular pyroelectricity using bistable dynamic magnetic molecules and molecular level dipole reorientation that further lead to macroscopic tunable polarization, were realized. The achieved rapid manipulation of collective polarization switching described in this work will contribute towards modern molecule-based materials science and allow potential high-performance devices to be fabricated.