A Molecular Pyroelectric Using a Chiral Zinc(II) Complex: High Pyroelectric Coefficient by Second-order Pyroelectricity

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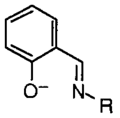
A chiral zinc complex [Zn(R-salphet)$_2$] [R-salphet$^-$ = N-(R)-1-phenylethylsalicylideneiminate(1–)] showed second-order pyroelectricity in a starch matrix. The pyroelectric coefficient was found to be 2.0 ± 1.5 mC m^{-2} K^{-1}, which is much greater than that of practical pyroelectric materials. The resonance and antiresonance frequencies were found to be 50 kHz and 90 kHz, respectively, from the admittance measurement. The electromechanical coupling factor was calculated to be 0.95.

Pyroelectric materials generate electricity when temperature is changed. Their applications include areas such as infrared sensors.[1–4] There is interest in developing new materials with better performance from the aspect of material science. A pyroelectric effect is strongly dependent on the symmetry of materials, and 10 pyroelectric point groups are theoretically predicted as C_1, C_2, C_s, C_{2v}, C_4, C_{4v}, C_3, C_{3v}, C_6, and C_{6v} among 32 point groups.[5] At this stage, the pyroelectric effect is expected to be achieved by controlling the symmetry of the materials, and a fundamental study about the relationship between the structure and the magnitude of the pyroelectric effect is of course interesting. One promising way to control the symmetry of a material is to use a building molecule with a characteristic symmetry. Recently, Krebs and coworkers used a C_{3v} organic molecule and successfully made a C_{3v} molecular pyroelectric, whose space group was R_{3m}.[6] On the contrary, our purpose is to develop molecular pyroelectrics using metal complexes as building units and to find the relationship between the crystal structure and the pyroelectricity. The coordination geometries found in metal complexes have a wide variety and include the following: octahedral, tetrahedral, square pyramidal, trigonal bipyramidal, square planar, and so on. However, the geometries in organic compounds are most of the time tetrahedral or trigonal planar. It may be an efficient approach to control the crystal structure by using metal complexes as building molecules for the purpose of developing molecular pyroelectrics.

In this study, a chiral zinc(II) complex [Zn(R-salphet)$_2$] (**1**) [R-salphet$^-$ = N-(R)-1-phenylethylsalicylideneiminate(1–)] was used as a builing molecule to exclude centrosymmetry with the aim of making a molecular pyroelectric. This complex has been reported[7] to crystallize in the space group $P2_12_12_1$, and the crystal group is D_2. An achiral zinc(II) complex [Zn(salipr)$_2$] (**2**) [salipr$^-$ = N-2-propylsalicylideneiminate(1–)] was also used for comparison. Crystal structure of the complex **2** has also been determined. The space group is P_{bca}, and the crystal group is D_{2h}.[8]

The chiral and achiral zinc(II) complexes were synthesized according to the literature.[7,8] The powder of each complex mixed in an aqueous starch matrix was put between a pair of flat aluminum electrodes and dried at ~70 °C to make a capacitor plate. Several plates were made by the same procedure and used for the following measurements.



R-salphet$^-$: R = (R)-1-phenylethyl
salipr$^-$: R = i-Pr

Before the pyroelectric measurement, spontaneous polarization of the plates was examined. Since the crystal group of the complex **1** is D_2, there is no permanent electric dipole moment in the unit cell. However, some of the plates showed unexpected spontaneous polarization. Examples of the discharge behavior are shown in Figure 1. Each line represents the time-course of the potential between the electrodes after a certain potential was applied. The applied potential was –1.0, 0.0, and 1.0 V. All the time-course curves reached the same residual potential, indicating that a spontaneous polarization existed between the electrodes. For example, when the residual potential was 38 mV, as shown in the Figure 1, the spontaneous polarization was calculated as 7.8 nC m^{-2}, but it was much smaller (< 10^{-5}) than that of the general polarized materials, which fall in the range of 10–10^3 mC m^{-2}.[9]

No spontaneous polarization of the plates was detected for the complex **2**.

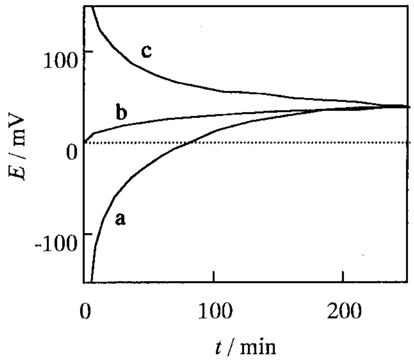


Figure 1. Discharge behavior of a capacitor plate of the complex **1**. The applied potential was (a) –1.0, (b) 0.0, and (c) 1.0 V.

When the powder sample of the D_2 crystal is put between a pair of parallel electrodes, macroscopic symmetry is increased to D_4, and spontaneous polarization is not expected to occur. However, if the concentration gradient of the complex emerges between the electrodes, the symmetry decreases to C_4, generating spontaneous polarization. The fact that spontaneous polarization occured by the concentration gradient is an important finding when the crystal group is not a polarized one. However, unpolarized plates were selected for further measurement since the polarized plates may not be favorable for the pyroelectric measurement.

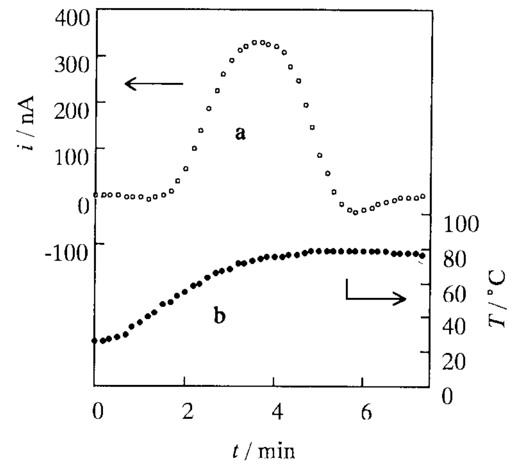


Figure 2. Time-courses of (a) pyroelectric current of a capacitor plate of the complex **1** and (b) temperature.

The pyroelectric property of the plates was estimated by measuring the electric current using an electrometer. When the plate containing the complex **1** was heated, pyroelectric current was observed. An example of the time-course of the electric current is shown in Figure 2 together with a time-course of the temperature. While the temperature was increasing, pyroelectric current was observed. However, when the temperature became constant, the pyroelectric current gradually disappeared. This is consistent with the fact that pyroelectric current is proportional to temperature change (Equation 1).[10] Strictly speaking, the current curve is not so simple in its shape and deviates from the differentiated form of the temperature. This is probably because the generated charge would not be quenched so quickly.

$$i_p = p\,S\,(dT/dt) \tag{1}$$

where i_p is the pyroelectric current, p is the pyroelectric coefficient, S is the area of the electrodes, T is the temperature, and t is the time. The pyroelectric coefficient is calculated as 2000 ± 1500 μC m^{-2} K^{-1}. This value is much larger than that of existing materials. The pyroelectric coefficients of some representative pyroelectric materials are 200 μC m^{-2} K^{-1} for $BaTiO_3$,[11,12] 600 μC m^{-2} K^{-1} for $PbTiO_3$,[12] 350–400 μC m^{-2} K^{-1} for TGS (triglycine sulfide),[12] and 180–1790 μC m^{-2} K^{-1} for PZT ($PbZrO_3$–$PbTiO_3$ system).[12]

Judging from the crystal group of the complex **1**, pyroelectricity can not be expected, and the observed pyroelectric current must be different from the usual one. Although D_2 complexes cannot be expected to posess pyroelectricity, they can be expected to have piezoelecricity that generates electricity by compression or strain. At this stage, the observed current can be concluded to be second-order pyroelectricity, in which thermal expansion and piezoelectricity are coupled.

In order to reveal the existence of piezoelectricity, admittance of the plate was measured at room temperature adopting a sine wave in the frequency range of 1 Hz to 120 kHz (Figure 3). The resonance frequency f_S and antiresonance frequency f_P were 50 kHz and 90 kHz, respectively, and they can be considered as the transverse effect of piezoelectricity in the plate.[13] Equation 2[14] can calculate the electromechanical coupling factor K as 0.95.

$$1/K^2 = 0.405\{f_S/(f_P - f_S)\} + 0.595 \tag{2}$$

This value is higher than that of typical piezoelectrics such as quarts (0.137),[15] $BaTiO_3$ (0.45),[15] and PZT #5 (0.70).[15]

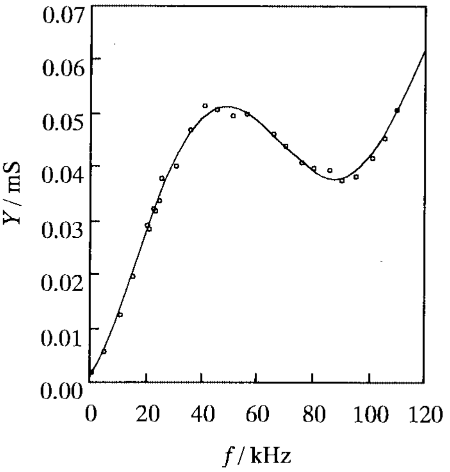


Figure 3. Admittance vs frequency of a capacitor plate of the complex **1**.

To the best of our knowledge, this is the first study on a chiral-complex-based molecular pyroelectric that shows second-order pyroelectricity.

References and Notes

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