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Crystal Structure and Physical Properties of a Dithiolene Complex Crystal with Adamantane Supramolecular Rotator

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Supramolecular cation salt of adamantane rotator with a dithiolene complex, (fluoroadamantylammonium$^+$)([18]crown-6)[Ni(dmit)$_2$]$^-$ (**1**) was synthesized. The fluorine atom of the adamantane unit showed a large thermal factor elongated latitudinally, suggesting molecular rotation in the solid state. Crystal **1** exhibited a large dielectric response by applying an AC field along the *a* axis.

A large number of artificial molecular machines, such as molecular motors and molecular gyroscope, have been extensively studied.[1,2] We have reported a solid state supramolecular rotator (*m*-FAni$^+$)(DB[18]crown-6)[Ni(dmit)$_2$] (*m*-FAni$^+$ = *m*-fluoroanilinium$^+$, DB[18]crown-6 = dibenzo[18]crwon-6, dmit^{2-} = 2-thioxo-1,3-dithiole-4,5-dithiolate) which exhibited a ferroelectric transition at 346 K due to the flip-flop motion of the *m*-FAni$^+$ cation causing an inversion of the dipole moment in the solid state.[3]

The ferroelectric transition temperature should be affected by the potential energy barrier for the molecular rotation in the solid state. Supramolecular rotators of adamantylammonium$^+$ (AD-NH$_3^+$) cation derivatives with crown-ether stators may have smaller energy barrier for the rotation than that of the flip-flop motion of the anilinium$^+$ cation with C_2 rotation axis, due to the higher symmetry and round shape of the adamantane moiety.[4] In the present study, a supramolecular cation based on a fluorine-substituted adamantylammonium$^+$ cation (F-AD-NH$_3^+$) and [18]crown-6 was introduced into the crystal of [Ni(dmit)$_2$]$^-$ anion in order to develop a molecular ferroelectric material with a smaller energy barrier for molecular rotation. The crystals of (F-AD-NH$_3^+$)([18]crown-6)[Ni(dmit)$_2$]$^-$ (**1**) showed a large dielectric response at higher temperatures, which is discussed based on the molecular packing motif.

Black block single crystals of (F-AD-NH$_3^+$)([18]crown-6)[Ni(dmit)$_2$]$^-$ (**1**) were prepared by the standard diffusion method from acetone (15 mL) solution of (Bu$_4$N)[Ni(dmit)$_2$] (23 mg, 0.034 mmol), [18]crown-6 (100 mg, 0.38 mmol), and (F-AD-NH$_3^+$)Cl$^-$ (37 mg, 0.18 mmol) for one week under nitrogen atmosphere at 30 °C.[4,5] The chemical formula of **1** was confirmed by X-ray crystallographic and elemental analyses.[6-8]

Figure 1 shows a packing motif of crystal **1** at 93 K. In this crystal, one F-AD-NH$_3^+$ cation, one [18]crown-6, and one [Ni(dmit)$_2$]$^-$ were crystallographically asymmetric. The [18]crown-6 and F-AD-NH$_3^+$ cation molecules were arranged parallel to the *a*/(*b*+*c*) plane (Figure 2(a)). The [Ni(dmit)$_2$]$^-$ molecules were arranged to form two dimensional sheets parallel to the *a*/(*b*+*c*) plane. Alternate stacking of the cationic and anionic layers was observed along the *b* direction. In the cationic layer, two [18]crown-6 molecules formed a dimer structure. Distances between the nitrogen atom of the F-AD-NH$_3^+$ cations and the six oxygen atoms of the [18]crown-6 molecule are summarized in Table 1. Atom labels are summarized in Figure S1. The shortest distance between N-H$^+$···O atoms was observed at N(1)-H$^+$···O(4) (2.963(1) Å) in the cation, which is comparable to the standard N-H$^+$···O hydrogen bond distance.[9] Supramolecular cations were formed between F-AD-NH$_3^+$ and [18]crown-6 through the hydrogen bonds in the asymmetric unit. The angle between the mean-plane of the six oxygen atoms and N(1)-C(1) direction was almost perpendicular. In the supramolecular cationic layer, fluorine atoms on the cation arranged anti-parallel along the *a* axis to cancel the dipole moments. No orientational disorder of the fluorine atom was observed by X-ray crystallographic analysis.

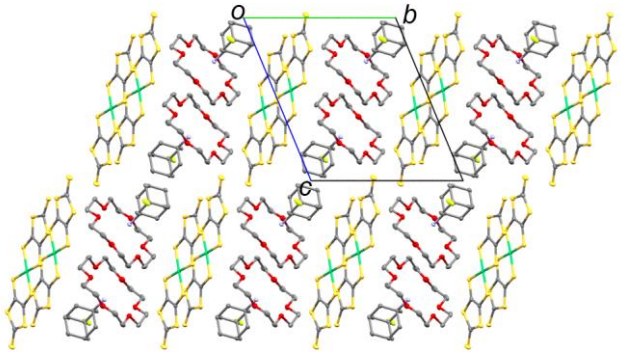

Figure 1. Packing diagram of crystal **1** at 93 K. Thermal ellipsoids indicate 50% of electron densities. Hydrogen atoms are omitted for clarity. Gray: carbon, red: oxygen, yellow: sulfur, green: nickel, light yellow: fluorine, blue, nitrogen.

Table 1. Distances (Å) between the nitrogen atom of F-AD-NH$_3^+$ and the oxygen atoms of [18]crown-6 in the asymmetric unit.

N(1)-O(1)	3.027(1)	N(1)-O(4)	2.963(1)
N(1)-O(2)	2.972(1)	N(1)-O(5)	2.968(1)
N(1)-O(3)	3.031(1)	N(1)-O(6)	2.988(1)

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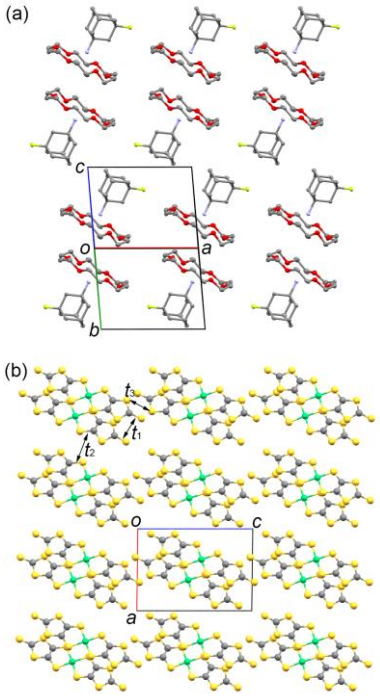

Figure 2. Molecular arrangements in (a) cationic and (b) anionic layers in crystal **1**. In Figure 2(b), t_1 to t_3 indicates molecular interactions between the $[Ni(dmit)_2]^-$ molecules.

To evaluate the molecular motions of the supramolecular cations in crystal **1**, the potential energy barriers for the molecular rotation of the F-AD-NH_3^+ cation was calculated by a restricted Hartree–Fock (RHF) method using the RHF/6-31(d) basis set.[10] The model structure of the supramolecular cations in crystal **1** for the calculation is shown in Figure S2. These structures differed from the real stoichiometry of the salts. The atomic coordinates based on the X-ray crystal structure analyses of the salt at 93 K were used in the calculation. The rotation was performed in 30° steps around the N(1)–C(1) axis. The relative energies were calculated using fixed atomic coordinates. Thus, the results of the calculations overestimated the actual energy barriers. Figure 3 shows the potential energy curves for crystal **1**. A quasi-double-minimum potential curve for the molecular rotation of F-AD-NH_3^+ cation was obtained. The local maxima were observed to be 115 and 105 kJ mol^{-1} at 90 and 270°, respectively. In the case of (AD-NH_3^+)([18]crown-6 derivatives)$[Ni(dmit)_2]^-$, triple-minimum potential curves with the maxima of 13~18 kJ mol^{-1} at 60, 180 and 300° for the molecular rotation of AD-NH_3^+ were obtained.[4] On the other hand, the F-AD-NH_3^+ rotator showed an asymmetric potential curve due to the asymmetric molecular arrangement around the F-AD-NH_3^+ molecules (see Figure S1). The energy barriers were larger than the thermal energy at room temperature (2.5 kJ mol^{-1}) because the relaxation of atoms was not taken into account. The energy barrier was calculated to be 250 kJ mol^{-1} by the same calculation method for (*m*-fluoroanilinium)(DB[18]-crown-6)$[Ni(dmit)_2]$ which showed flip-flop motion.[11-14] Thus, the molecular rotation of the F-AD-NH_3^+ cations in crystal **1** should be possible around room temperature. An elongated thermal factor of the fluorine atom in the circumferential direction already observed at 93 K became much larger at 300 K, suggesting the rotation of F-AD-NH_3^+ in the solid state (see Figure S2).

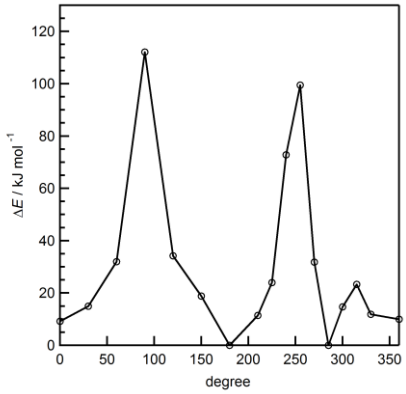

Figure 3. Potential-energy curve of the F-AD group rotation in crystal **1**. The structure unit for the calculation of **1** was (F-AD-NH_3^+)([18]crown-6)$_2$$[Ni(dmit)_2]^-_3$. The solid line is a guide for the eyes.

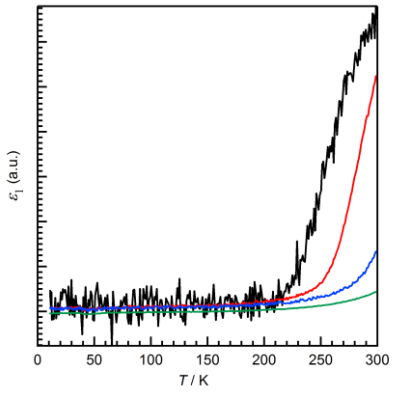

Figure 4. Temperature dependent dielectric constants (ε_1) of crystal **1** along the *a* axis. The electric fields with frequencies of 1 (black), 10 (red), 100 (blue), and 1000 (green) kHz were applied along the *a* axis, which were perpendicular to the rotation axis of the F-AD-NH_3^+ cation.

The result of temperature dependent dielectric constants (ε_1) for crystal **1** supported the molecular motion of the F-AD-NH_3^+ cation in the crystal. Figure 4 exhibits temperature dependent dielectric constants (ε_1) for **1**, applying the external electric field perpendicular to the rotation axis of the F-AD-NH_3^+ with the frequencies of 1, 10, 100, and 1000 kHz. The dielectric responses are affected by molecular motion in the solid state. A large enhancement in the dielectric response may be observed due to the change of dipole moments associated with molecular rotation.[15] From 20 K to 200 K, crystal **1** showed temperature independent ε_1. A rapid increase of ε_1 at all frequencies appeared above 200 K. The higher ε_1 was observed with lower frequency implying that the response originated from molecular motion. In the case of the ferroelectric crystal (*m*-FAni$^+$)(DB[18]crown-6)$[Ni(dmit)_2]$, the increase in dielectric constant with increase in temperature was observed above 250 K.[3] These results suggested that the F-AD-NH_3^+ rotated in the solid state with smaller energy barrier than the *m*-FAni$^+$ rotator.

In the anionic layer, molecular interactions, t_1-t_3, between neighboring $[Ni(dmit)_2]^-$ anions through sulfur-sulfur contacts (3.5669(4)-3.67298(5) Å) shorter than sum of the van der Waals radii (< 3.7 Å) were observed. Transfer integrals, t_1-t_3, calculated by the extended Hückel method were 27.7, -7.76 and 11.2 meV,[16] respectively, which were the same order of the other crystals based on the supramolecular cations and the $[Ni(dmit)_2]^-$ anion showing the Curie-Weiss behavior with antiferromagnetic interactions.[3-4,11-14,17] However, a small amount of isomorphous crystals grew simultaneously with crystal **1** which prevented obtaining reproducible magnetic susceptibilities.

In conclusion, the supramolecular rotator using F-AD-NH_3^+ was successfully introduced into the solid state. Round-shaped rotators such as F-AD-NH_3^+ can realize lower potential energy barriers for the molecular rotation. By combining these rotators with magnetically and electronically active $[M(dmit)_2]^{n-}$ (M = Ni, Pd, Pt; $0 < n \leq 2$) anions will give multifunctional materials such as multiferroic compounds.[11,12,17,18]

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7 *Anal.* $C_{28}H_{41}FNNiO_6S_{10}$ for salt **1**; Calcd, C: 37.90, H: 4.66, N: 1.58, S: 36.19%; Found, C: 37.95, H: 4.64, N: 1.62, S: 36.29%.

8 Crystallographic data of **1**: Chemical formula, $C_{28}H_{41}FNNiO_6S_{10}$; Formula weight, 885.93; Temperature, 93 K; Crystal size, 0.10×0.10×0.10 mm^3; Crystal system, triclinic; Space group, *P*-1; a = 10.1112(3) Å; b = 13.2896(4) Å; c = 15.2796(6) Å; α = 67.3723(9)°; β = 88.047(1)°; γ = 83.204(1)°; V = 1881.7(1) $Å^3$; Z = 2; D_{calc} = 1.564 $g \cdot cm^{-1}$; $F(000)$ = 922; μ = 1.116 cm^{-1}; Measured 2θ range from 6.18° to 54.84°; No. of reflections collected, 18467; Independent reflections, 8486; Observed reflections with $I > 2.00s(I)$, 7808; R_{int}, 0.0202; $R(I > 2\sigma(I))$, 0.0239; R_w (all data), 0.0626; GOF, 1.081; $R(I > 2\sigma(I))$ and R_w (all data) were calculated by following equations. $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $R_w^2 = \Sigma_w(F_o^2 - F_c^2)^2/\Sigma_w(F_o^2)^2$; $w^{-1} = \sigma^2(F_o^2) - (0.0343P)^2 - 0.6657P$, where $P = (F_o^2 - 2F_c^2)/3$. CCDC number: 964569.

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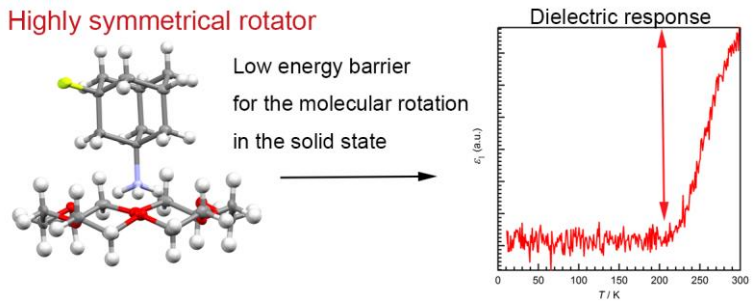
Molecular rotation with low potential energy barrier in the solid state may be realized by using a spherical molecular rotator of adamantane derivatives to show dielectric response.