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Applied and Materials Chemistry

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

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Supramolecular cation salt of adamantane rotator with a dithiolenic complex, (fluoroadamantylammonium<sup>+</sup>)([18]crown-6)[Ni(dmit)<sub>2</sub>]<sup>-</sup> (**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.

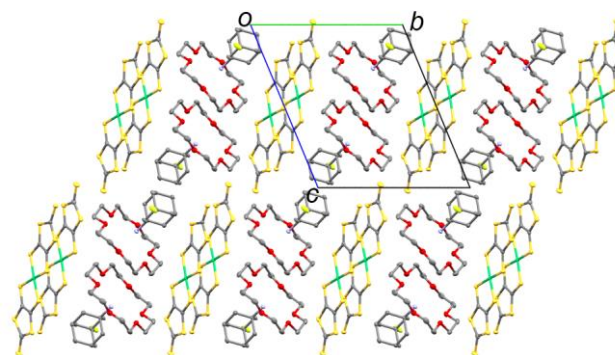
A large number of artificial molecular machines, such as molecular motors and molecular gyroscope, have been extensively studied.<sup>1,2</sup> We have reported a solid state supramolecular rotator (*m*-FAni<sup>+</sup>)(DB[18]crown-6)[Ni(dmit)<sub>2</sub>] (*m*-FAni<sup>+</sup> = *m*-fluoroanilinium<sup>+</sup>, DB[18]crown-6 = dibenzo[18]crown-6, dmit<sup>2-</sup> = 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<sup>+</sup> cation causing an inversion of the dipole moment in the solid state.<sup>3</sup>

The ferroelectric transition temperature should be affected by the potential energy barrier for the molecular rotation in the solid state. Supramolecular rotators of adamantylammonium<sup>+</sup> (AD-NH<sub>3</sub><sup>+</sup>) cation derivatives with crown-ether stators may have smaller energy barrier for the rotation than that of the flip-flop motion of the anilinium<sup>+</sup> cation with C<sub>2</sub> rotation axis, due to the higher symmetry and round shape of the adamantane moiety.<sup>4</sup> In the present study, a supramolecular cation based on a fluorine-substituted adamantylammonium<sup>+</sup> cation (F-AD-NH<sub>3</sub><sup>+</sup>) and [18]crown-6 was introduced into the crystal of [Ni(dmit)<sub>2</sub>]<sup>-</sup> anion in order to develop a molecular ferroelectric material with a smaller energy barrier for molecular rotation. The crystals of (F-AD-NH<sub>3</sub><sup>+</sup>)([18]crown-6)[Ni(dmit)<sub>2</sub>]<sup>-</sup> (**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<sub>3</sub><sup>+</sup>)([18]crown-6)[Ni(dmit)<sub>2</sub>]<sup>-</sup> (**1**) were prepared by the standard diffusion method from acetone (15 mL) solution of (Bu<sub>4</sub>N)[Ni(dmit)<sub>2</sub>] (23 mg, 0.034 mmol), [18]crown-6 (100 mg, 0.38 mmol), and (F-AD-NH<sub>3</sub><sup>+</sup>)Cl<sup>-</sup> (37 mg, 0.18 mmol) for one week under nitrogen atmosphere at 30 °C.<sup>4,5</sup> The chemical formula of **1** was confirmed by X-ray crystallographic and elemental analyses.<sup>6-8</sup>

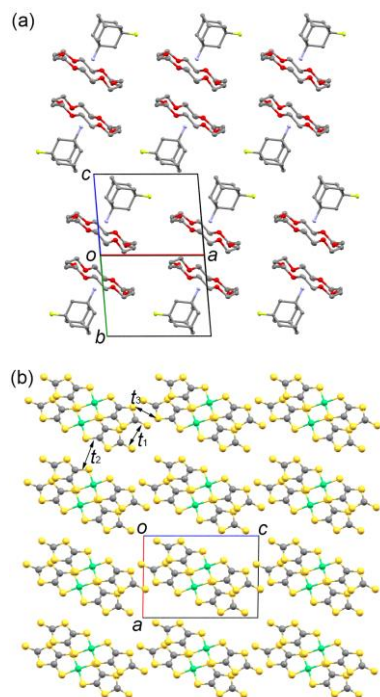
Figure 1 shows a packing motif of crystal **1** at 93 K. In this crystal, one F-AD-NH<sub>3</sub><sup>+</sup> cation, one [18]crown-6, and one [Ni(dmit)<sub>2</sub>]<sup>-</sup> were crystallographically asymmetric. The [18]crown-6 and F-AD-NH<sub>3</sub><sup>+</sup> cation molecules were arranged parallel to the *a*/(*b*+*c*) plane (Figure 2(a)). The [Ni(dmit)<sub>2</sub>]<sup>-</sup> 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<sub>3</sub><sup>+</sup> 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<sup>+</sup>...O atoms was observed at N(1)-H<sup>+</sup>...O(4) (2.963(1) Å) in the cation, which is comparable to the standard N-H<sup>+</sup>...O hydrogen bond distance.<sup>9</sup> Supramolecular cations were formed between F-AD-NH<sub>3</sub><sup>+</sup> 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<sub>3</sub><sup>+</sup> and the oxygen atoms of [18]crown-6 in the asymmetric unit.

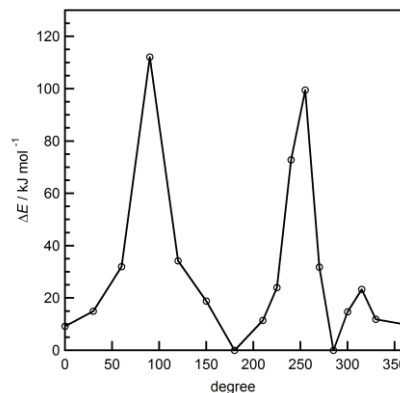
N(1)-O(1)	3.027(1)	N(1)-O(4)	2.963(1)
N(1)-O(2)	2.972(1)	N(1)-O(5)	2.968(1)
N(1)-O(3)	3.031(1)	N(1)-O(6)	2.988(1)



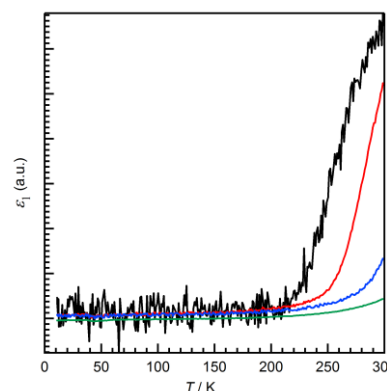
**Figure 2.** Molecular arrangements in (a) cationic and (b) anionic layers in crystal **1**. In Figure 2(b),  $t_1$  to  $t_3$  indicates molecular interactions between the  $[\text{Ni}(\text{dmit})_2]^-$  molecules.

To evaluate the molecular motions of the supramolecular cations in crystal **1**, the potential energy barriers for the molecular rotation of the  $\text{F-AD-NH}_3^+$  cation was calculated by a restricted Hartree–Fock (RHF) method using the RHF/6-31(d) basis set.<sup>10</sup> 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  $30^\circ$  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  $\text{F-AD-NH}_3^+$  cation was obtained. The local maxima were observed to be 115 and 105  $\text{kJ mol}^{-1}$  at  $90^\circ$  and  $270^\circ$ , respectively. In the case of  $(\text{AD-NH}_3^+)([\text{18}]\text{crown-6 derivatives})[\text{Ni}(\text{dmit})_2]^-$ , triple-minimum potential curves with the maxima of 13–18  $\text{kJ mol}^{-1}$  at  $60^\circ$ ,  $180^\circ$  and  $300^\circ$  for the molecular rotation of  $\text{AD-NH}_3^+$  were obtained.<sup>4</sup> On the other hand, the  $\text{F-AD-NH}_3^+$  rotator showed an asymmetric potential curve due to the asymmetric molecular arrangement around the  $\text{F-AD-NH}_3^+$  molecules (see Figure S1). The energy barriers were larger than the thermal energy at room temperature ( $2.5 \text{ kJ mol}^{-1}$ ) because the relaxation of atoms was not taken into account. The energy barrier was calculated to be  $250 \text{ kJ mol}^{-1}$  by the same calculation method for  $(m\text{-fluoroanilinium})(\text{DB}[\text{18}]\text{-crown-6})[\text{Ni}(\text{dmit})_2]^-$  which showed flip-flop motion.<sup>11–14</sup> Thus, the molecular rotation of the  $\text{F-AD-NH}_3^+$  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  $\text{F-AD-NH}_3^+$  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  $(\text{F-AD-NH}_3^+)([\text{18}]\text{crown-6})_2[\text{Ni}(\text{dmit})_2]_3^-$ . The solid line is a guide for the eyes.



**Figure 4.** Temperature dependent dielectric constants ( $\epsilon_1$ ) 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  $\text{F-AD-NH}_3^+$  cation.

The result of temperature dependent dielectric constants ( $\epsilon_1$ ) for crystal **1** supported the molecular motion of the  $\text{F-AD-NH}_3^+$  cation in the crystal. Figure 4 exhibits temperature dependent dielectric constants ( $\epsilon_1$ ) for **1**, applying the external electric field perpendicular to the rotation axis of the  $\text{F-AD-NH}_3^+$  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.<sup>15</sup> From 20 K to 200 K, crystal **1** showed temperature independent  $\epsilon_1$ . A rapid increase of  $\epsilon_1$  at all frequencies appeared above 200 K. The higher  $\epsilon_1$  was observed with lower frequency implying that the response originated from molecular motion. In the case of the ferroelectric crystal  $(m\text{-FAni}^+)(\text{DB}[\text{18}]\text{-crown-6})[\text{Ni}(\text{dmit})_2]^-$ , the increase in dielectric constant with increase in temperature was observed above 250 K.<sup>3</sup> These results suggested that the  $\text{F-AD-NH}_3^+$  rotated in the solid state with smaller energy barrier than the  $m\text{-FAni}^+$  rotator.

In the anionic layer, molecular interactions,  $t_1$ - $t_3$ , between neighboring [Ni(dmit)<sub>2</sub>] 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,<sup>16</sup> respectively, which were the same order of the other crystals based on the supramolecular cations and the [Ni(dmit)<sub>2</sub>] anion showing the Curie-Weiss behavior with antiferromagnetic interactions.<sup>3-4,11-14,17</sup> 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<sub>3</sub><sup>+</sup> was successfully introduced into the solid state. Round-shaped rotators such as F-AD-NH<sub>3</sub><sup>+</sup> can realize lower potential energy barriers for the molecular rotation. By combining these rotators with magnetically and electronically active [M(dmit)<sub>2</sub>]<sup>n-</sup> (M = Ni, Pd, Pt; 0 < n ≤ 2) anions will give multifunctional materials such as multiferroic compounds.<sup>11,12,17,18</sup>

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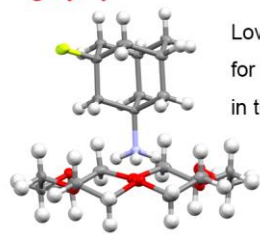
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- 7 *Anal.* C<sub>28</sub>H<sub>41</sub>FNNiO<sub>6</sub>S<sub>10</sub> for salt **1**; Calcd, C: 37.90, H: 4.66, N: 1.58, S: 36.19%; Found, C: 37.95, H: 4.64, N: 1.62, S: 36.29%.
- 8 Crystallographic data of **1**: Chemical formula, C<sub>28</sub>H<sub>41</sub>FNNiO<sub>6</sub>S<sub>10</sub>; Formula weight, 885.93; Temperature, 93 K; Crystal size, 0.10×0.10×0.10 mm<sup>3</sup>; Crystal system, triclinic; Space group, P-1;  $a = 10.1112(3)$  Å;  $b = 13.2896(4)$  Å;  $c = 15.2796(6)$  Å;  $\alpha = 67.3723(9)^\circ$ ;  $\beta = 88.047(1)^\circ$ ;  $\gamma = 83.204(1)^\circ$ ;  $V = 1881.7(1)$  Å<sup>3</sup>;  $Z = 2$ ;  $D_{\text{calc}} = 1.564$  g·cm<sup>-3</sup>;  $F(000) = 922$ ;  $\mu = 1.116$  cm<sup>-1</sup>; Measured  $2\theta$  range from 6.18° to 54.84°; No. of reflections collected, 18467; Independent reflections, 8486; Observed reflections with  $I > 2.00\sigma(I)$ , 7808;  $R_{\text{int}}$ , 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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## Crystal Structure and Physical Property of Dithiolene Complex Crystal with Adamantane Supramolecular Rotator

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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.

### Highly symmetrical rotator



Low energy barrier  
for the molecular rotation  
in the solid state

