

Design of Crystalline Spaces for Molecular Rotations in Crystals

Zun-qi Liu,[†] Kazuya Kubo,^{*,†,‡} Shin-ichiro Noro,^{†,‡} Tomoyuki Akutagawa,[§] and Takayoshi Nakamura^{*,†,‡}

[†]Graduate School of Environmental Science, Hokkaido University, N10W5, Kita-ku Sapporo, Hokkaido 060-0810, Japan [‡]Research Institute for Electronic Science, Hokkaido University, N20W10, Kita-ku Sapporo 001-0020, Japan [§]Institute of Multidisciplinaly Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

Supporting Information

ABSTRACT: 4-Methylanilinium derivatives were used to introduce spaces for molecular rotation in crystals. The $[Ni(dmit)_2]^-$ ($dmit^{2-} = 2$ -thioxo-1,3-dithiole-4,5-dithiolate) salts with supramolecular cations of dibenzo[18]crown-6 (DB[18]crown-6) and 4-methylanilinium derivatives, (4-methylanilinium⁺)(DB[18]crown-6)[Ni(dmit)_2]⁻ (1), (2-fluoro-4-methylanilinium⁺)(DB[18]crown-6)[Ni(dmit)_2]⁻ (2), and (3-fluoro-4-methylanilinium⁺)(DB[18]crown-6)[Ni(dmit)_2]⁻ (3) were synthesized. The potential energy curves for the molecular rotations of the cations in the crystals had double minimum shapes with maxima of 100, 210, and 230 kJ mol⁻¹ for crystals 1, 2, and 3,



respectively. Introduction of a methyl substituent at the p-position was effective in reducing the potential energy maxima. For crystals 2 and 3, large dielectric responses originating from the flip-flop motions of the cationic molecules were observed upon applying an AC voltage. The temperature-dependent magnetic susceptibilities of complexes 1, 2, and 3 followed the Curie–Weiss law, showing weak antiferromagnetic interactions.

INTRODUCTION

Solid-state rotators¹ have been used to construct functional molecular materials such as ferroelectrics. A crystal design that provides sufficient space for molecular rotations in the solid state is one of the most important points. Khuong et al. have reported molecular gyroscopes in the solid state based on the pdiethynylbenzene group as the rotator and triphenylmethyl (trityl) and triptycyl groups as the stators connected through covalent bonds.² The molecular gyroscopes ensured sufficient spaces around the diethynylbenzene group through molecular design of the bulky stator moiety. Although the molecular gyroscope approach guarantees molecular rotation in the solid state, advanced organic synthesis of the molecules was required. As an alternative approach, we focused on the supramolecular approach to developing solid-state rotators.³⁻⁶ We have already reported that a ferroelectric crystal of (*m*-fluoroanilinium⁺)- $(DB[18]crown-6)[Ni(dmit)_2]^-$ (DB[18]crown-6) =dibenzo[18]crown-6) exhibited a ferroelectric transition at 348 K, in which the molecular rotator was constructed from an *m*-fluoroanilinium rotator and a DB[18]crown-6 stator connected through hydrogen bonds. The crystal was an order-disorder-type ferroelectric, whose flip-flop motion of the *m*-fluoroanilinium rotator caused an inversion of the dipole moment in the solid state.⁷ Since the *m*-fluoroanilinium rotator has a C2 rotation axis parallel to the C–N bond, the successive flip-flop in the same direction (i.e., molecular rotation) may be possible in the paraelectric phase at higher temperature. The supramolecular approach simplified the synthesis of the solidstate rotators. It is difficult to form adequate void spaces for molecular rotation in the crystal through the supramolecular approach because of the relatively small hydrogen-bonding energy compared with the crystalline energy. The latter usually becomes a maximum in the close-packed structure without void spaces. Thus, careful design of constituent molecules is necessary. One of the strategies was to use spherical molecules instead of planar arylammonium ions. The adamantylammonium cation has a spherical shape with C_3 symmetry. Indeed, the energy barrier for the molecular rotation in the supramolecular cation salt of (adamantylammonium⁺)(DB[18]crown-6)[Ni(dmit)₂]⁻ was considerably smaller than that of $(anilinium^+)(DB[18]crown-6)[Ni(dmit)_2]^{-.8}$ Another approach was the use of heteroaromatics without any substituent at the peri-positions of the ring. The pyridazinium⁺ cation was successfully introduced in (pyridazinium⁺)(DB[18]crown-6)- $[Ni(dmit)_2]^{-9}$ in which the energy barrier for the molecular motion was estimated to be smaller than that for (mfluoroanilinium⁺)(DB[18]crown-6)[Ni(dmit)₂]^{-.10} In the present study, we applied a new strategy for the reduction of the energy barrier for the flip-flop motion of the arylanilinium ion in the solid state. We used 4-methylanilinium⁺ derivatives as the molecular rotator. The methyl group introduced at the para-position of the anilinium⁺ cation parallel to the rotation axis expanded the space for the flip-flop motion of the rotator in the solid state. We synthesized three crystals, (4methylanilinium⁺)(DB[18]crown-6)[Ni(dmit)₂]⁻ (1), (2-fluoro-4-methylanilinium⁺)(DB[18]crown-6)[Ni(dmit)₂]⁻ (2), and

Received:September 4, 2013Revised:November 14, 2013Published:December 16, 2013

Table 1. Crystallographic Data for Salts 1, 2, and 3 at 173 K

	1	2	3
chemical formula	$C_{16.5}H_{17}N_{0.5}Ni_{0.5}O_3S_5$	$C_{16.5}H_{16}F_{0.5}N_{0.5}Ni_{0.5}O_3S_5$	$C_{16.5}H_{16}F_{0.5}N_{0.5}Ni_{0.5}O_{3}S_{5}$
formula weight	459.96	468.45	468.45
crystal size (mm ³)	$0.40 \times 0.20 \times 0.10$	$0.40 \times 0.22 \times 0.10$	$0.38 \times 0.20 \times 0.08$
crystal system	monoclinic	monoclinic	monoclinic
space group	C2/c	C2/c	C2/c
a (Å)	29.1206(15)	28.969(2)	29.2740(11)
b (Å)	9.0225(4)	9.0811(6)	9.0709(3)
c (Å)	20.0291(11)	20.0477(13)	20.0025(9)
β (°)	131.7874(11)	131.4924(14)	131.9151(9)
V (Å ³)	3923.8(3)	3950.5(5)	3952.5(3)
Ζ	8	8	8
$D_{\rm calc}~({\rm g}~{\rm cm}^{-3})$	1.557	1.575	1.574
F(000)	1900	1928	1928
$\mu \text{ (mm}^{-1})$	1.071	1.069	1.068
measured 2θ range (°)	6.18-54.88	6.14-54.88	6.16-54.84
no. of reflections collected	18457	18514	18325
independent reflections	4473	4500	4488
observed reflections with $I > 2.00\sigma(I)$	4158	2767	3591
$R_{ m int}$	0.0251	0.0846	0.0357
$R \left[I > 2\sigma(I) \right]^a$	0.0329	0.0650	0.0446
wR (all data) ^b	0.0790	0.1732	0.1124
GOF	1.159	1.062	1.201
$= \Sigma (F_{o} - F_{c}) / \Sigma F_{o} . {}^{b}R_{w}^{2} = \Sigma_{w} (F_{o}^{2} - F_{c})$	$(E_{\rm o}^2)^2 / \Sigma_w (F_{\rm o}^2)^2; \ w^{-1} = \sigma^2 (F_{\rm o}^2) - (E_{\rm o}^2)^2$	$(0.0466P)^2 - 1.6414P$ for 1, $w^{-1} =$	$\sigma^2(F_o^2) - (0.1398P)^2$ for 2, w ⁻

 $(3-fluoro-4-methylanilinium^+)(DB[18]crown-6)[Ni(dmit)_2]^-$ ter

 $\sigma^2(F_o^2) - (0.0715P)^2 - 17.4945P$ for 3, where $P = (F_o^2 - 2F_c^2)/3$.

(3). The effect of the p-methyl substituent is discussed.

EXPERIMENTAL SECTION

General. Elemental analyses were carried out using a Yanaco CHN Corder MT-6a at the Instrumental Analysis Division, Equipped Management Center, Creative Research Institution, Hokkaido University. IR (400–7800 cm⁻¹) spectra were measured using a Thermo Scientific Nicolet 6700 FT-IR. Thermogravimetric analysis was carried out using a Rigaku Thermoplus TG8120 thermal analysis station employing an Al_2O_3 reference, in the temperature range from 298 to 773 K, with a heating rate of 10 K min⁻¹ under flowing nitrogen gas.

Preparation of (4-Methylanilinium⁺)(DB[18]-crown-6)[Ni- $(dmit)_2^{1-}$ (1), (2-Fluoro-4-methylanilinium⁺)(DB[18]crown-6)₂[Ni(dmit)₂]⁻ (2), and (3-Fluoro-4-methylanilinium⁺)(DB[18]**crown-6)**₂[Ni(dmit)₂]⁻ (3). An acetone solution (20 mL) of $(n-Bu_4N^+)[Ni(dmit)_2]^-$ (20 mg, 0.028 mmol)¹⁰ was added to an acetone solution (20 mL) of (4-methylanilinium⁺) $(BF_4^-)^7$ (50 mg, 0.25 mmol) and DB[18]-crown-6 (200 mg, 0.54 mmol). The solvent was evaporated for one week at room temperature to give crystal 1 as black blocks. Crystals 2 and 3 were obtained as black blocks using similar methods by using $(n-Bu_4N^+)[Ni(dmit)_2]^-$ (20 mg, 0.028 mmol), (2fluoro-4-methylanilinium⁺) (BF_4^{-}) (50 mg, 0.25 mmol) DB[18]crown-6 (200 mg, 0.54 mmol), and $(n-Bu_4N^+)[Ni(dmit)_2]^-$ (20 mg, 0.028 mmol), (2-fluoro-4-methylanilinium⁺)(BF_4^-) (50 mg, 0.25 mmol) DB[18]-crown-6 (200 mg, 0.54 mmol), respectively. The chemical formulas of the salts were determined by elemental and X-ray crystallographic analyses. Anal. Calcd C₃₃H₃₄NO₆S₁₀Ni for salt 1: C, 43.13; H, 3.62; N, 1.52%. Found: C, 43.17; H, 3.76; N, 1.57%. Anal. Calcd C33H34FNO6S10Ni for salt 2: C, 42.26; H, 3.55; N, 1.49%. Found: C, 42.21; H, 3.54; N, 1.30%. Anal. Calcd C₃₃H₃₄FNO₆S₁₀Ni for salt 3: C, 42.26; H, 3.55; N, 1.49%. Found: C, 42.33; H, 3.61; N, 1.32%.

Crystal Structure Determination. Crystallographic data for single crystals of 1, 2, and 3 were collected using a Rigaku R-AXIS RAPID diffractometer with Mo K α radiation ($\lambda = 0.71075$ Å) from a graphite monochromator at 173 and 300 K. The structures were solved by the direct method (SIR 2004) and expanded using Fourier

techniques and refined on F^2 by the full-matrix least-squares method (SHELXL97) compiled into Yadokari-XG.¹¹ The parameters were refined using anisotropic temperature factors, except for the hydrogen atoms, which were refined using the riding model with a fixed C–H bond distance of 0.95 Å. The crystallographic data for salts 1, 2, and 3 at 173 K are summarized in Table 1. The data for 300 K are given in Table S1 of the Supporting Information. CCDC numbers of the crystals are 969609–969614.

Magnetic Susceptibility. The temperature-dependent magnetic susceptibilities of salts 1, 2, and 3 were measured using a Quantum Design MPMS-XL SQUID magnetometer for the polycrystalline samples. The DC magnetic susceptibility was measured at temperatures from 2 to 300 K in an applied field of 1 T.

Calculations. The relative energies of the structures were calculated using a semiempirical method with the RHF/6-31(d) basis set.¹² The nearest-neighboring molecules around the 4-methylanilinium⁺ derivatives were included in the calculation. The structural units of the salts 1, 2, and 3 used in the calculations were (4-methylanilinium⁺)(DB[18]crown-6)₂, (2-fluoro-4-methylanilinium⁺)(DB[18]crown-6)₂, and (3-fluoro-4-methylanilinium⁺)(DB[18]crown-6)₂, respectively, which are different from the real stoichiometries of the salts (Figure S1 of the Supporting Information). The atomic coordinates of the salts based on the X-ray crystal structural analyses at 173 K were used in the calculations. The relative energies of the structures were obtained for rigid rotations around the C(1)–N(1) axes for the flip-flop motion (Figure S2 of the Supporting Information). Rotations were performed in 30° steps.

The overlap integrals (*s*) between the lowest unoccupied molecular orbitals (LUMOs) of the $[Ni(dmit)_2]^-$ anions were calculated with the tight-binding approximation using the extended Hückel method.¹³ Semiempirical parameters for the Slater-type atomic orbitals were obtained from the literature.¹⁴ Transfer integrals (*t*) were obtained from the equation t = -10s.

Dielectric Measurement. The temperature-dependent dielectric constants were measured using the two-probe AC impedance method at frequencies of 1, 10, 100, and 1000 kHz using an Agilent 4294A. A single crystal was placed into a cryogenic refrigerating system (Cryocooler model SRDK-101, Sumitomo Heavy Industries Ltd.).



Figure 1. Packing diagrams of crystal 1 along the *b* axis at 173 K. Thermal ellipsoids of the atoms indicate 50% of electron densities. Hydrogen atoms are omitted for clarity. Gray, carbon; red, oxygen; blue, nitrogen; yellow, sulfur.

The electrical contacts were prepared using gold paste (Tokuriki 8560) to attach the 10 μ m ϕ gold wires to the single crystal.

RESULTS AND DISCUSSION

Crystal Structure. Crystals 1, 2, and 3 contained half the anilinium derivatives, half DB[18]crown-6, and half [Ni- $(dmit)_2$ molecules in the asymmetric unit, which were isostructural with each other and with (m-fluoroanilinium⁺)- $(DB[18]crown-6)[Ni(dmit)_2]^{-.7,8}$ Here, we will describe the structure of crystal 1. Figure 1 shows a packing diagram for crystal 1 along the b axis at 173 K. Anionic and cationic layers are arranged alternately along the c axis. In the cationic layers, the 4-methylanilinium⁺ derivatives and DB[18]crown-6 formed 1:1 adducts of supramolecular cations through the N-H+...O hydrogen bonds with a stand-up configuration of the C-N bond of the phenyl groups with respect to the mean plane of the six oxygen atoms in DB[18]crown-6 (Figure 2). The distances between the nitrogen atoms of the methylanilinium⁺ derivatives and oxygen atoms of DB[18]crown-6 of complexes 1, 2, and 3 are summarized in Table 2. The average distances between the ammonium nitrogen of the cation and the oxygen atoms of the crown ether were 2.7778, 2.9033, and 2.8647 Å for crystals 1, 2, and 3, respectively, indicating formation of typical hydrogen bonding. In the supramolecular cations, the DB[18]crown-6 had a V-shaped conformation. The most distinct difference between crystals 1-3 and the (*m*-fluoroanilinium⁺)- $(DB[18]crown-6)[Ni(dmit)_2]^-$ crystal was that the ammonium moiety of the methylanilinium cation was inserted from outside the V-shaped DB[18]crown-6, whereas the *m*-fluoroanilinium cation was included from inside the V-shaped DB[18]crown-6 (Figure 2).⁷ As a result, the angles between the two benzene rings were 83.54°, 83.71°, and 86.49° in crystals 1, 2, and 3,



Figure 2. Supramolecular cation structures of (a) (4-methylanilinium⁺)(DB[18]crown-6) in 1, (b) (2-fluoro-4-methylanilinium⁺)(DB[18]crown-6) in 2, (c) (3-fluoro-4-methylanilinium⁺)(DB[18]crown-6) in 3, and (d) (*m*-fluoroanilinium⁺)(DB[18]crown-6) in (*m*-fluoroanilinium⁺)(DB[18]crown-6) [Ni(dmit)₂]⁻ viewed parallel to the mean planes of the oxygen atoms of the DB[18]crown-6 molecules. Hydrogen atoms are omitted for clarity.

of the Supporting Information.

Table 2. Distances between the Nitrogen and Oxygen Atoms in Crystals 1, 2, and 3^{a}

	1	2	3
N(1) - O(1)	2.7792(17)	2.791(7)	2.775(5)
N(1) - O(2)	2.9124(10)	2.941(4)	2.893(3)
N(1) - O(3)	2.9460(14)	2.978(6)	2.926(4)
^a Atom numbering sc	hemes of the ator	ns are summariz	ed in Figure S2

respectively, which is much smaller than that of the (mfluoroanilinium⁺) $(DB[18]crown-6)[Ni(dmit)_2]^-$ salt with an angle of 125.75°. 5,7,8 The "anti-V-shape" conformations with sharp dihedral angles in crystals 1-3 played important roles in achieving sufficient crystalline void spaces for the flip-flop motions. The one-dimensional columnar arrangements of the supramolecular cation were constructed in both of the cationic layers of crystals 1-3 as well as $(m-fluoroanilinium^+)(DB[18]$ crown-6)[Ni(dmit)₂]⁻ (Figure 3).^{7,8} The sharp dihedral angles of 1, 2, and 3 directly affected their cell parameters. For example, the parameter c of crystal 3, which was the stacking direction of the cationic and anionic layers, indicated similar magnitudes for the intermolecular interactions between the phenyl rings of the methylanilinium⁺ cation and [Ni(dmit)₂]⁻ anions in $(m-fluoroanilinium^+)(DB[18]crown-6)[Ni(dmit)_2]^$ with a similar cell parameter c.⁷ However, the cell parameters aand b were clearly different from those of (*m*-fluoroanilinium⁺)- $(DB[18]crown-6)[Ni(dmit)_2]^-$. The cell parameter *b* of crystal 3 [9.0709(3) Å], which was the stacking direction of the methylanilinium⁺ cation and DB[18]crown-6, was larger than that of (m-fluoroanilinium)(DB[18]crown-6)[Ni(dmit)₂]⁻ [8.1007(4) Å]. The methyl group expanded the cell parameter b and provided sufficient crystalline void space for the phenyl rings along the b axis, which reduced the energy barriers from

the steric hindrance for the flip-flop motion in the solid state. Noticeable changes for the cell parameter *a* between crystal 3 [29.2740(11) Å] and the *m*-fluoroanilinium⁺ salt [22.9465(10)]Å] were observed.⁷ In the (m-fluoroanilinium⁺)(DB[18]crown- $6)[Ni(dmit)_2]^-$ crystal, the phenyl groups of nearest-neighboring DB[18]crown-6 molecules were slightly overlapped through weak C-H- π interactions along the *a* axis because of the V-shaped conformation with the obtuse folding angle between the phenyl rings of the DB[18]crown-6, causing restriction of the flip-flop motion of the *m*-fluoroanilinium⁺ molecules.⁷ However, no intermolecular interactions between two nearest-neighboring DB[18]crown-6 molecules through the C-H- π interaction of the phenyl rings were observed in the cationic layer of 3 because of the sharp dihedral angle, indicating that the effective intermolecular interactions between the 3-fluoro-4-methylanilinium⁺ cation and DB[18]crown-6 were reduced. Crystals 1 and 2 showed similar cell parameters to crystal 3. Orientational disorder of the fluorine atoms with a large magnitude for the thermal ellipsoids was observed in salts 2 and 3, suggesting flip-flop motions of the arylanilinium⁺ molecules, as observed in (m-fluoroanilinum⁺)(DB[18]crown-6)[Ni(dmit)₂]^{-,7} which further supported the formation of adequate crystalline void space around the rotator molecules.

Potential Energy of Cation Rotations. The potential energy curves for the molecular rotations of the methylanilinium⁺ derivatives in salts 1, 2, and 3 were calculated with a semiempirical method using the RHF/6-31(d) basis set.¹² The model structures for the calculations of 1, 2, and 3 included the nearest-neighboring molecules of $[Ni(dmit)_2]^-$ and DB[18]-crown-6 molecules (Figure S1 of the Supporting Information). The relative energies as a function of the rotation angle ϕ around the C–N bonds of the 4-methylanilium⁺ derivatives were calculated at every 30° rotation. Figure 4 shows the rotation angle dependence of relative energies (ΔE) in salts 1,



Figure 3. Molecular arrangements of the supramolecular cations in crystals (a) 1, (b) 2, (c) 3, and (d) (*m*-fluoroanilinium⁺)(DB[18]crown-6)[Ni(dmit)₂]⁻ viewed along the *c* axis. Hydrogen atoms are omitted for clarity.



Figure 4. Potential energy curves for the 4-methylanilinium⁺ derivatives in the supramolecular cationic structures of (a) 1, (b) 2, and (c) 3. Solid lines are guides for the eye.

2, and 3, where the relative energies at $\phi = 0^{\circ}$ were defined as zero. For crystals 1-3, two potential minima were observed at $\phi = 0^{\circ}$ and 180°. The double minimum potentials with two stable molecular orientations indicated 180° flip-flop motion of the aryl rings in salts 1, 2, and 3, which were the same as those in (m-fluoroanilinium⁺)(DB[18]crown-6)[Ni(dmit)₂]^{-.7,8} The magnitude of maximum ΔE for salt 1 ($\approx 100 \text{ kJ mol}^{-1}$) was about half that for (anilinium⁺)(DB[18]crown-6)[Ni(dmit)₂]⁻ ($\approx 180 \text{ kJ mol}^{-1}$),⁸ indicating that rotation of the 4methylanilinium⁺ cation in 1 was much easier than that in (anilinium⁺)(DB[18]crown-6)[Ni(dmit)₂]⁻. A sufficient crystalline void space was introduced in the crystal by the substitution of the methyl group at the *p*-position of anilinium⁺. The maxima of ΔE for salts 2 and 3 (≈ 200 and ≈ 230 kJ mol⁻¹, respectively) became larger than that of 1 by the introduction of a fluorine atom. However, the values were still smaller than that of (m-fluoroanilinium⁺)(DB[18]crown-6)[Ni(dmit)₂]⁻ $(\approx 270 \text{ kJ mol}^{-1})$.⁷ These results suggested that the introduction of a methyl group at the p-position was effective in providing crystalline spaces for the flip-flop motion in the solid state.

Dielectric Properties. Molecular motions such as the flipflop motion in the solid state can be evaluated by measurements of temperature and frequency dependence of the dielectric constant (ε_1) , where the change in the dipole moment responds to the external electric field resulting in large dielectric constants. In the case of 1, the flip-flop motion of 4methylanilinium⁺ should not cause a change in the dipole moment. Consequently, no change in dielectric response was observed in the temperature- and frequency-dependent dielectric measurement, although adequate crystalline void space for the flip-flop motion of the phenyl group was achieved (Figure S5 of the Supporting Information). The rotator molecules, 2- and 3-fluoro-4-methylanilinium⁺ cations, have dipole moments perpendicular to the C-N rotation axis (Figure S6 of the Supporting Information). Figure 5 shows ε_1 versus T plots for crystals 2 and 3 at measurement frequencies (f) of 1, 10, 100, and 1000 kHz from 10 to 300 K with the electric field applied parallel to the a axis, which was perpendicular to the rotation axis of the rotator. Enhanced dielectric responses (ε_1 = 84 and 37 for crystals 2 and 3, respectively, at 300 K) at 1 kHz were observed, indicating that the response originated from the molecular rotation.¹⁵ Almost no temperature dependence of the dielectric response along the b axis was observed because no dipole inversion occurred by the flip-flop motion.

Magnetic Properties. Figure 6 shows the molecular arrangement of the $[Ni(dmit)_2]^-$ anions in crystal 1. The $[Ni(dmit)_2]^-$ anion formed a two-dimensional layer in the *ab* plane through sulfur–sulfur contacts shorter than the sum of



Figure 5. Temperature and frequency dependence of the dielectric constant ε_1 of salts (a) **2** and (b) **3** measured along the *a* axis. Black, red, blue, and green points indicate measurement frequencies of 1, 10, 100, and 1000 kHz of the electric field, respectively.



Figure 6. Molecular arrangement of the $[Ni(dmit)_2]^-$ anion in crystal 1 viewed along the *c* axis. Green and red dashed lines indicate distances d_1 and d_2 between the sulfur atoms shorter than the sum of the van der Waals radii. The arrowed line indicates the intermolecular interaction t_1 .

the van der Waals radii (<3.7 Å) at d_1 and d_2 with distances of 3.3646(7) and 3.4911(6) Å, respectively. A relatively strong intermolecular interaction between the $[Ni(dmit)_2]^-$ anions, t_1 , was observed along a + b and -a + b. The calculated transfer integral, t_1 , based on the extended Hückel molecular orbital method was 2.62 meV. In crystals **2** and **3**, similar two-dimensional molecular arrangements in the anionic layers were observed with the sulfur–sulfur contacts in the ranges of 3.366(2)–3.475(2) Å and 3.382(2)–3.485(1) Å, respectively.

One S = 1/2 spin was on each $[Ni(dmit)_2]^-$ anion in crystals **1**, **2**, and **3**, where the arrangement of the $[Ni(dmit)_2]^-$ anion directly affected the magnetic properties. The transfer integrals calculated using the extended Hückel molecular orbital method based on the crystallographic analyses of **1**, **2**, and **3** indicated formation of two-dimensional layers through the weak intermolecular interactions (ca. 2 meV), which would lead to a weak antiferromagnetic interaction between $[Ni(dmit)_2]^-$ anions. Plots of χ_{mol} versus *T* for polycrystalline samples of **1**, **2**, and **3** exhibited typical Curie–Weiss behavior with Weiss temperatures (θ) of -3.17, -3.25, and -3.09 K, respectively, indicating weak antiferromagnetic interactions between the $[Ni(dmit)_2]^-$ anions in the salts. Thermal fluctuations of the supramolecular rotators did not affect the magnetic properties of **1**, **2**, and **3**.

CONCLUSION

Hydrogen-bonding molecular assemblies between 4-methylanilinium⁺ derivatives and dibenzo [18] crown-6 (DB [18] crown-6) formed supramolecular rotators, which were introduced into $[Ni(dmit)_2]^-$ crystals (dmit²⁻ = 2-thioxo-1,3-dithiole-4,5dithiolate) to form crystals 1-3. The supramolecular rotator (4-methylanilinium⁺ derivatives)(DB[18]crown-6) arranged in an isostructural manner with (m-fluoroanilinium⁺)(DB[18]- $(rown-6)[Ni(dmit)_2]^-$. The methyl group on the rotator molecule expanded the crystalline space and effectively reduced the potential energy barrier for the 180° flip-flop motion in the solid state compared with that of (*m*-fluoroanilinium⁺)(DB-[18] crown-6) $[Ni(dmit)_2]^-$. The anti-V-shaped conformations of DB[18]crown-6 with a sharp dihedral angle between the terminal phenyl rings in 1-3 provided adequate crystalline void space around the rotator molecules. The molecular flip-flop motions of 2- or 3-fluoro-4-methylanilinium⁺ in the solid state were confirmed by dielectric measurements. Crystals 1-3 exhibited antiferromagnetic behavior following the Curie-Weiss law because of weak intermolecular interactions in the two-dimensional molecular arrangement of $[Ni(dmit)_2]^$ anions. One of our next targets is the introduction of molecular rotators with small potential energy barriers, such as adamantylammonium⁺ derivatives, to achieve molecular rotation in the solid state, which are expected to exhibit a ferroelectric transition at a lower temperature than that of the (m-fluoroanilinium⁺)(DB[18]crown-6)[Ni(dmit)₂]⁻ crystal.^{3,4}

ASSOCIATED CONTENT

Supporting Information

Crystal structures, thermogravimetric analyses, infrared spectra, model structures for the RHF calculation and CIF files of crystals 1, 2, and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: kkubo@es.hokudai.ac.jp.

*E-mail: tnaka@es.hokudai.ac.jp.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

REFERENCES

 (1) (a) Lindoy, L. F.; Atkinson, I. M. Self-Assembly in Supramolecular Systems; Stoddart, J. F., Ed.; RSC: Cambridge, 2000. (b) Molecular Switches; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, Germany, 2001.
 (c) Molecular Machines and Motors; Sauvage, J.-P., Ed.; Springer: Berlin, 2001. (d) Molecular Devices and Machines; Balzani, V., Venturi, M., Credi, A., Eds.; Wiley-VCH: Weinheim, Germany, 2003.
 (e) Bustamante, C., Keller, D., Oster, G. Acc. Chem. Res. 2001, 34, 412–420.

(2) (a) Khuong, T.-A. V.; Nuñez, J. E.; Godinez, C. E.; Garcia-Garibay, M. A. Acc. Chem. Res. 2006, 39, 413–422. (b) Dominguez, Z.; Dang, H.; Jane Strouse, M.; Garcia-Garibay, M. A. J. Am. Chem. Soc. 2002, 124, 2398–2399. (c) Karlen, S. D.; Godinez, C. E.; Garcia-Garibay, M. A. Org. Lett. 2006, 8, 3417–3420. (d) Khuong, T.-A. V.; Dang, H.; Jarowski, P. D.; Maverick, E. F.; Garcia-Garibay, M. A. J. Am. Chem. Soc. 2007, 129, 839–845.

(3) Akutagawa, T.; Nakamura, T. Dalton Trans. 2008, 45, 6335-6345.

(4) (a) Nishihara, S.; Akutagawa, T.; Sato, D.; Takeda, S.; Noro, S.; Nakamura, T. *Chem.–Asian J.* 2007, *2*, 1083–1090. (b) Nishihara, S.; Akutagawa, T.; Hasegawa, T.; Fujiyama, S.; Nakamura, T.; Nakamura, T. *J. Solid State Chem.* 2002, *168*, 661–667. (c) Nishihara, S.; Takutagawa, T.; Hasegawa, T.; Nakamura, T. *Chem. Commun.* 2002, 408–409.

(5) (a) Akutagawa, T.; Sato, D.; Ye, Q.; Noro, S.; Nakamura, T. *Dalton Trans.* **2010**, *39*, 2191–2193. (b) Endo, T.; Akutagawa, T.; Noro, S.; Nakamura, T. *Dalton Trans.* **2011**, *40*, 1491–1496.

(6) (a) Akutagawa, T.; Koshinaka, H.; Ye, Q.; Noro, S.; Kawamata, J.; Yamaki, H.; Nakamura, T. Chem.-Asian J. 2010, 5, 520-529. (b) Akutagawa, T.; Nakamura, T. Dalton Trans. 2008, 6335-6345. (c) Akutagawa, T.; Matsuura, K.; Hashimoto, A.; Nakamura, T. Inorg. Chem. 2005, 44, 4454-4456. (d) Akutagawa, T.; Matsuura, K.; Nishihara, S.; Noro, S.; Nakamura, T. Eur. J. Inorg. Chem. 2005, 3271-3276. (e) Nishihara, S.; Ren, X. M.; Akutagawa, T.; Nakamura, T. Polyhedron 2005, 24, 2844-2848. (f) Akutagawa, T.; Hasegawa, T.; Nakamura, T.; Inabe, T. J. Am. Chem. Soc. 2002, 124, 8903-8911. (g) Akutagawa, T.; Endo, D.; Imai, H.; Noro, S.; Cronin, L.; Nakamura, T. Inorg. Chem. 2006, 45, 8628-8637. (h) Akutagawa, T.; Endo, D.; Noro, S.; Cronin, L.; Nalamura, T. Coord. Chem. Rev. 2007, 251, 2547-2561. (i) Ye, Q.; Akutagawa, T.; Endo, T.; Noro, S.; Nakamura, T.; Xiong, R. Inorg Chem. 2010, 49, 8591-8600. (j) Ye, Q.; Akutagawa, T.; Noro, S.; Nakamura, T.; Xiong, R. Cryst. Growth Des. 2010, 10, 4856-4860.

(7) Akutagawa, T.; Koshinaka, H.; Sato, D.; Takeda, S.; Noro, S.; Takahashi, H.; Kumai, R.; Tokura, Y.; Nakamura, T. *Nat. Mater.* **2009**, *8*, 342–347.

(8) Akutagawa, T.; Sato, D.; Koshinaka, H.; Aonuma, M.; Noro, S.; Takeda, S.; Nakamura, T. *Inorg. Chem.* **2008**, *47*, 5951–5962.

(9) Liu, Z.; Kubo, K.; Lin, L.; Hoshino, N.; Noro, S.; Akutagawa, T.; Nakamura, T. *Dalton Trans.* **2013**, *42*, 2930–2939.

(10) Steimecke, G.; Sieler, H.; Kirmse, R.; Hoyer, E. *Phosphorus Sulfur* **1979**, *7*, 49–55.

(11) (a) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. J. Appl. Crystallogr. 2005, 38, 381–388. (b) Sheldrick, G. M. SHELXL-97 Program of the Refinement of Crystal Structures; University of Göttingen: Germany, 1997. (c) Kabuto, C.; Akine, S.; Nemoto, T.; Kwon, E. J. Cryst. Soc. Jpn. 2009, 51, 218–224.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.;

Crystal Growth & Design

Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M.W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(13) Mori, T.; Kobayashi, A.; Sasaki, Y.; Kobayashi, H.; Saito, G.; Inokuchi, H. Bull. Chem. Soc. Jpn. **1984**, *57*, 627–633.

(14) (a) Albright, T. A.; Hofmann, P.; Hoffmann, R. J. Am. Chem. Soc. 1977, 99, 7546–7557. (b) Joergensen, K. A.; Wheeler, R. A.; Hoffmann, R. J. Am. Chem. Soc. 1987, 109, 3240–3246. (c) Keszler, D. A.; Hoffmann, R. J. Am. Chem. Soc. 1987, 109, 118–124.

(15) Kao, K. C. Dielectric Phenomena in Solids; Elsevier: Amsterdam, 2004.