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Multirotations of (Anilinium)([18]Crown-6) Supramolecular Cation Structure in Magnetic Salt of $[Ni(dmit)_2]^-$

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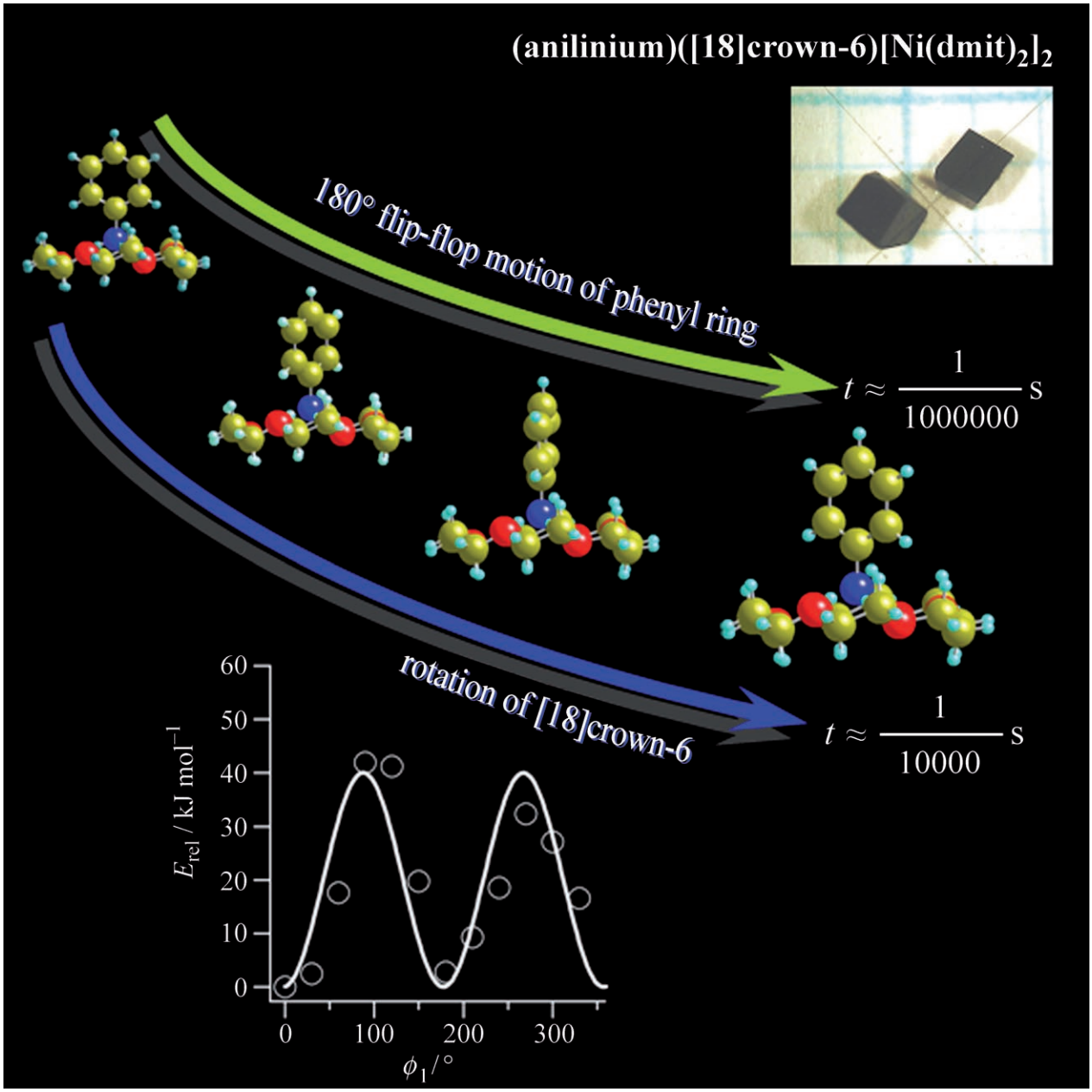

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Abstract: A solid-state dynamic supramolecular structure consisting of (anilinium)([18]crown-6) was arranged as the cation in a salt of $[Ni(dmit)_2]^-$ (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate). With the ammonium moiety of anilinium located within the cavity of [18]crown-6, a hydrogen-bonded supramolecular structure is formed, with an orthogonal arrangement between the π plane of anilinium and the mean O6 plane of [18]crown-6. In this supramolecular cation, both anilinium and [18]crown-6 act as dynamic units with different rotational modes in the solid state. The uniform stacks of cations form an antiparallel arrangement, thus producing a layer structure. Sufficient space for the 180° flip-flop motion of the phenyl ring and the rotation of [18]crown-6 was observed in the cation layer. Thermally activated 180° flip-flop motions, with a frequency of 6 MHz at room temperature and an activation energy of 31 kJ mol^{-1}, were confirmed by temperature-dependent ^{2}H NMR spectra of ([D_5]anilinium)-([18]crown-6)[$Ni(dmit)_2$]. A double-minimum potential for the molecular rotation of anilinium, with a barrier of approximately 40 kJ mol^{-1}, was indicated by ab initio calculations. The wide-line ^{1}H NMR spectra indicated a thermally activated rotation of [18]crown-6 at temperatures above 250 K. Therefore, multiple molecular motions of the 180° flip-flop motion of the phenyl ring and the rotation of [18]crown-6 occur simultaneously in the solid state. The temperature-dependent dielectric constants revealed that the molecular motion of [18]crown-6, other than the flip-flop motion, dominates the dielectric response in the measured temperature and frequency range.

Keywords: anilinium · crown compounds · molecular machines · molecular motors · supramolecular chemistry

Introduction

A large number of artificial molecular machines, involving molecules such as rotaxanes and catenanes, have been synthesized and studied.[1,2] Although the structures and functions of such molecular machines are far from those of biological molecular machines,[3] a few fundamental and significant functions have been attained in artificial molecular rotors, for example, unidirectional molecular rotation has been proposed with triptycyl[4]helicene, biphenanthrylidene, and catenane derivatives, in which combinations of thermo-, photo-, and chemical energy are utilized to interconvert their molecular structures and conformations through stepwise structural isomerizations in solution.[4] From the theoretical aspect, the transduction of kinetic energy into work has been discussed as the Brownian ratchet mechanism, which indicates the importance of the saw-tooth-type asymmetric potential for and the biasing mechanism of molecular rotation.[5]

Solid-state molecular motion, in which arrangements of the molecules are fixed within a crystal in accordance with crystal symmetry, is important for device applications of molecular mechanical machines. Several attempts to construct molecular motion in the solid state have been carried out to array dynamic molecular systems in molecular assemblies.[6,7] In general, however, molecules are closely packed in the crystal and often do not have sufficient space to allow molecular rotation; therefore, molecular design and crystal engineering are essential for realizing solid-state dynamic molecular systems. For example, derivatives of 1,4-bis(3,3,3-triphenylpropynyl)benzene have been defined as gyroscope molecules that function as molecular rotators in the solid state, in which a phenylene rotator is connected to the bulky triphenylpropynyl stators.[7] In the solid state, the phenylene moiety exhibits a 180° flip-flop motion with a rotational frequency of roughly 100 MHz.[7]

We have employed the supramolecular-cation approach to realize dynamic molecular systems in the solid state; supramolecular cations were introduced into magnetic $[Ni(dmit)_2]$ salts (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate).[8] Because

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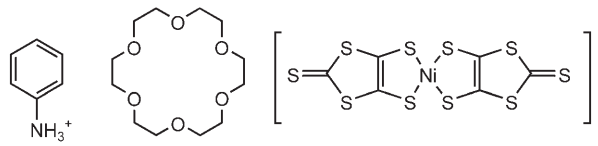
the supramolecular cations are structurally diverse and flexible, various combinations of the cations and crown ethers can yield molecular-assembly structures with a variety of sizes and shapes.[9] Among these supramolecular cations, the dynamic molecular structure in the salt Cs_2([18]crown-6)$_3$[Ni(dmit)$_2$]$_2$ demonstrated the synergetic rotation of [18]crown-6 molecules.[10] In this salt, the rotation of [18]crown-6 was coupled with the magnetic properties of [Ni(dmit)$_2$]$^-$ anions. The biasing of the molecular rotation was achieved by applying an external stimulus (hydrostatic pressure), which functioned as a brake for the molecular motion. Although the molecular rotation of [18]crown-6 is random owing to the symmetric rotational potential, the supramolecular-cation approach can be employed to develop a new type of dynamic molecular system in the solid state. We recently reported the molecular rotation of (adamantylammonium)([18]crown-6) in the salt of [Ni(dmit)$_2$]$^-$.[6e] As adamantane is known to form a plastic crystal, the rotation of the molecule was performed at lower temperatures due to the high symmetry of the adamantyl group. The supramolecular cation of (anilinium)([18]crown-6) in the salt of [Ni(dmit)$_2$]$^-$ (Scheme 1) is therefore a promising candidate for constructing new types of dynamic molecular systems in the solid state.[11] In the crystal of (anilinium)([18]crown-6)[Ni(dmit)$_2$], the molecular spins of [Ni(dmit)$_2$]$^-$ form a spin-ladder structure.[11a] The (anilinium)([18]crown-6) supramolecular cation is formed through the N–H···O hydrogen-bonding interactions between the ammonium moieties and the oxygen atoms of the [18]crown-6 molecules. In these cation structures, the phenyl group and [18]crown-6 molecule act as the dynamic and static parts, respectively, while [18]crown-6 itself has the potential to form a rotational molecular system as shown in Cs_2([18]crown-6)$_3$[Ni(dmit)$_2$]$_2$. Herein, we report the multimode molecular rotations of the 180° flip-flop motion of the phenyl ring and the rotation of [18]crown-6 in a single crystal of (anilinium)([18]crown-6)[Ni(dmit)$_2$].



Scheme 1. The (anilinium)([18]crown-6)[Ni(dmit)$_2$] salt.

Abstract in Japanese:

動的な (anilinium)([18]crown-6)超分子カチオン構造を、[Ni(dmit)$_2$]塩にカウンターカチオンとして導入した (anilinium)([18]crown-6)[Ni(dmit)$_2$]塩を作製した。Anilinium カチオンのアンモニウム基と [18]crown-6 分子の酸素原子間で N–H···O 水素結合を形成する事で、anilinium カチオンのπ-平面が [18]crown-6 の酸素原子平面に対して垂直に配置した超分子カチオン構造を形成し、anilinium と[18]crown-6 分子は、固体中でそれぞれ異なる回転モードで運動を行っていた。均一に積層したカチオン構造が横方向に配列することで、層状構造を形成していた。カチオン層内では、フェニル基の 180 度フリップ–フロップ運動と[18]crown-6 の回転運動を可能とする空間が確保されていた。重水素置換した([D$_5$]anilinium) ([18]crown-6)[Ni(dmit)$_2$]塩の固体 ^{2}H NMR の温度依存性から、室温において約 6 MHz の周波数で 180 度フリップ–フロップ運動が生じていることが確認され、その活性化エネルギーは 31 kJmol^{-1} であった。これは、ab initio 計算から見積もられる約 40 kJmol^{-1} のエネルギー障壁を有する 2 極小ポテンシャルの存在と一致する。また、広幅 ^{1}H NMR の温度依存性から、約 250 K 以上の温度領域で[18]crown-6 分子の回転運動が存在する事が示された。以上の結果から、フェニル基の 180 度フリップ–フロップ運動と[18]crown-6 分子の回転運動が、固体中で同時に実現していることが解った。また、誘電率の温度依存性には、これらの分子運動を反映した誘電応答が観測された。

Results and Discussion

To confirm the molecular motions of anilinium and [18]crown-6 independently, a deuterated salt of ([D$_5$]anilinium)([18]crown-6)[Ni(dmit)$_2$] (**1**) was prepared by the diffusion method with $C_6D_5NH_3^+$ cations. The crystal structure of **1** (Figure 1) is isostructural with that of (anilinium)([18]crown-6)[Ni(dmit)$_2$] (**2**).[11a] The π dimers of the [Ni(dmit)$_2$]$^-$ anions interact through effective intermolecular interactions of the lateral S–S contacts along the *c* axis (Fig-

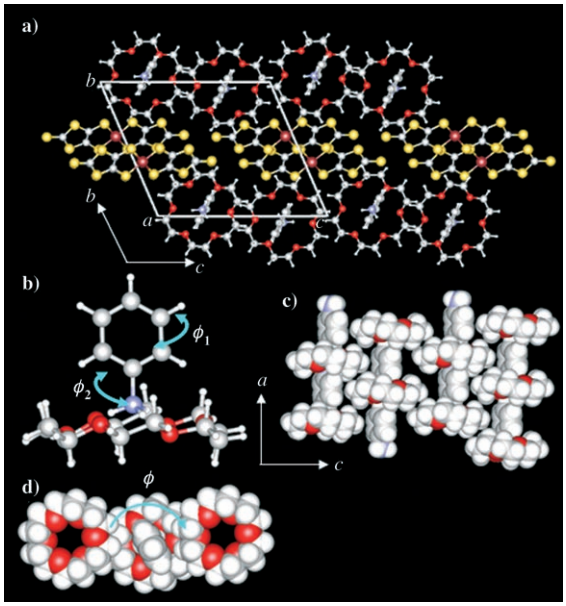


Figure 1. Crystal structure of **1**. a) Unit cell viewed along the *a* axis. b) Supramolecular-cation structure of ([D$_5$]anilinium)([18]crown-6) viewed normal to the π plane of anilinium. The rotational angles ϕ_1 and ϕ_2 correspond to the rotations of the phenyl ring and the NH_3^+ moiety around the C–N bond, respectively (see text). c) CPK representation of the cation layer within the *ac* plane, viewed along the *b* axis. d) CPK representation of the ([D$_5$]anilinium)([18]crown-6) structure surrounded by its nearest two [18]crown-6 molecules, viewed along the long axis of anilinium.

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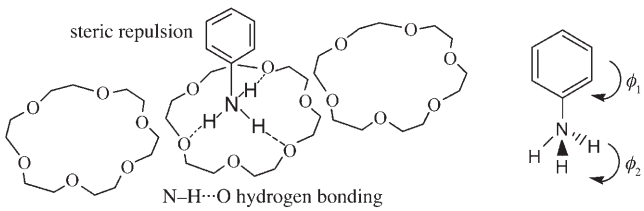
ure 1 a). Regular π-dimer arrangements of the anions along the long axis of $[Ni(dmit)_2]^-$ form a ladder chain, in which the ladder-leg and -rung directions correspond to the $a+c$ and the a axes, respectively.[11a] Furthermore, weak interladder interactions through the lateral S–S contacts along the a axis were observed within the ac plane. The ($[D_5]$anilinium)([18]crown-6) cations are sandwiched between the $[Ni(dmit)_2]^-$ anion layers to form a two-dimensional cationic layer. An alternating arrangement of cation and anion layers was observed along the b axis. The lack of intermolecular interactions between the cation and anion layers, within the limit of the van der Waals contacts, indicates the isolation of the cation structures from the $[Ni(dmit)_2]^-$ anion layer.

The supramolecular cation ($[D_5]$anilinium)([18]crown-6) in the crystal is formed by one crystallographically asymmetrical $[D_5]$anilinium cation and one [18]crown-6 molecule. Orientational disorder along the long axis of anilinium and [18]crown-6 was not observed in the X-ray crystal-structure analysis of **1** at 298 K. The N–H···O hydrogen-bonding interactions between the ammonium moiety of $[D_5]$anilinium and the six oxygen atoms of [18]crown-6 yield the supramolecular-cation structure (Figure 1 b). As the dihedral angle (θ) between the mean π plane of $[D_5]$anilinium and the mean O6 plane of [18]crown-6 is close to perpendicular ($\theta=85°$), the phenyl ring of $[D_5]$anilinium and the [18]crown-6 molecule can be regarded as the dynamic and static moiety, respectively. The average N–O distance in the hydrogen bonds (2.92 Å; N1–O1 = 2.891(2), N1–O2 = 2.926(2), N1–O3 = 2.876(2), N1–O4 = 2.979(2), N1–O5 = 2.935(2), N1–O6 = 2.944(2) Å) is comparable to the standard N–H···O hydrogen-bonding distance of 2.90 Å.[12]

The Corey–Pauling–Koltun (CPK) representation of the cation layer, viewed along the b axis, is shown in Figure 1 c. Although the uniform stack of ($[D_5]$anilinium)([18]crown-6) cations along the a axis gives rise to a unidirectional dipole arrangement, the antiparallel array of the cation chains along the c axis cancels out the net dipole moment of the crystal (Figure 1 c). As shown in Figure 1 c and d, the CPK representation of the cation layer indicates sufficient space for the molecular rotation of the phenyl ring and [18]crown-6 in the crystal. The π planes of $[D_5]$anilinium in the cation stack are parallel to each other and are related by translation through the unit cell. Along the c axis, the π plane of $[D_5]$anilinium is sandwiched between two [18]crown-6 molecules (Figure 1 d).

The motion of the phenyl ring of anilinium in the solid state is determined by the potential-energy curve and the magnitude of the potential-energy barrier (ΔE). The potential-energy curve of the molecular rotation of anilinium in **1** was calculated by using the RHF/6-31(d) basis set.[13] Because the phenyl ring of anilinium was sandwiched between two [18]crown-6 molecules of adjacent supramolecular units (Figure 1 d), a model structure of (anilinium)([18]crown-6)$_3$ was employed to calculate the relative energies as a function of the rotational angles ϕ_1 and ϕ_2 around the C–N bond of anilinium (Scheme 2). The rotation of anilinium should be



Scheme 2. Schematic representation of the model structure of (anilinium)([18]crown-6)$_3$. Two types of intermolecular interactions, steric repulsion and N–H···O hydrogen bonding, are important; the corresponding rotational angles ϕ_1 and ϕ_2, respectively, were employed for the evaluation of potential energies. Rotational angle ϕ_1 represents the rotation of the phenyl ring with fixed atomic coordinates for the NH_3^+ moiety, whereas rotational angle ϕ_2 describes the rotation of the NH_3^+ moiety with fixed coordinates for the phenyl ring.

affected by two types of intermolecular interactions: 1) N–H···O hydrogen bonding between the NH_3^+ moiety and the six oxygen atoms of [18]crown-6, and 2) steric repulsion between the π plane of the phenyl ring and its two nearest-neighbor [18]crown-6 molecules (Scheme 2). Accordingly, three rotational modes were considered: 1) rotation of the phenyl ring, with angle ϕ_1 around the C–N bond at $\phi_2=0°$, which is dominated by steric repulsion from two [18]crown-6 molecules, 2) rotation of the NH_3^+ moiety, with angle ϕ_2 around the C–N bond at $\phi_1=0°$, which is affected by N–H···O hydrogen-bonding interactions, and 3) rotations of ϕ_1 and ϕ_2 around the C–N bond ($\phi_1=\phi_2$) corresponding to the total contribution of molecular rotation. The structure determined by single-crystal X-ray structure analysis was defined as $\phi_1=\phi_2=0°$.

Figure 2 shows the dependence of the relative energy of the (anilinium)([18]crown-6)$_3$ structure on the rotational angle; the relative energy at $\phi=0°$ is defined as zero. For rotational angle ϕ_1, the initial atomic coordinates from the X-

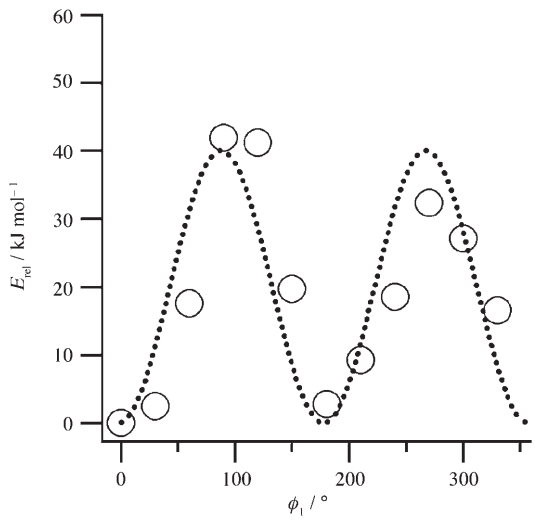


Figure 2. Potential-energy curve of phenyl-ring rotation in the (anilinium)([18]crown-6)$_3$ structure. The relative energy of (anilinium)([18]crown-6)$_3$ was obtained by the ab initio method of the RHF/6-31G(d) basis set. The rotational angle (ϕ_1) around the C–N bond of anilinium was incremented by 30° steps, and the single-point energy was calculated at each angle. The dashed curve is a guide for the eye (see text).

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ray crystal-structure analysis correspond to the first potential-energy minimum at $\phi_1 = 0°$, whereas the second potential-energy minimum was observed at around $\phi_1 = 180°$. The double-minimum potential with two stable molecular orientations was in good agreement with the 180° flip-flop motion of the phenyl ring, as confirmed by ^{2}H NMR measurements (see below). A nearly symmetrical shape was observed for the potential-energy curve of the 180° flip-flop motion. The values of ΔE at around $\phi_1 = 90$ and 270° were slightly dissimilar (Figure 2). The observation of only one position for the phenyl ring in the crystal-structure analysis should indicate a 180° periodicity for the potential curve. The difference between the calculated potentials at $\phi_1 = 90$ and 270° is attributed to the crystallographically asymmetric unit of (anilinium)([18]crown-6), as we employed fixed atomic coordinates from the X-ray crystal-structure analysis for the calculation. The atomic coordinates of the anilinium cation should relax during the rotation to the original positions at $\phi_1 = 180°$ to minimize the total energy of the crystal packing. A symmetrical potential-energy curve with 180° periodicity, therefore, is the most reasonable description for the 180° flip-flop motion of the anilinium cation in the crystal (dashed line in Figure 2).

The rotation of the NH_3^+ moiety (ϕ_2) should also affect the relative energy of the (anilinium)([18]crown-6) system. As one of the six oxygen atoms of [18]crown-6 appears every 60° for a 360° rotation of angle ϕ_2, the potential-energy curve as a function of ϕ_2 shows six minima for 360° rotation of the NH_3^+ moiety. However, ΔE here was less than 2 kJ mol^{-1}, which is about 5% of ΔE for the phenyl rotation. The results of the theoretical calculations for the rotation under the condition $\phi_1 = \phi_2$ provided a similar potential-energy curve to that shown in Figure 2, thus suggesting an almost-negligible rotational barrier of the NH_3^+ moiety for the 180° flip-flop motion of the anilinium cation.

Solid-state molecular rotation of the phenyl ring of anilinium was directly observed with solid-state ^{2}H NMR spectroscopy of **1**. X-ray crystal-structure analysis and ab initio calculations indicate the possibility of the 180° flip-flop motion of the phenyl ring of anilinium. The temperature dependence of the lineshape of wide-line ^{2}H NMR spectra is shown in Figure 3. Temperature-dependent changes in the lineshapes clearly confirmed the 180° flip-flop motion of the phenyl ring. Simulation of the lineshape for each spectrum,[14] measured at different temperatures, reveals that the flip-flop motion has a frequency of roughly 6 MHz at 293 K and that it is motionless below 185 K (within the limits of the NMR timescale).

The frequency (τ^{-1}) of the flip-flop motion as a function of T^{-1} is shown in Figure 3b. From this linear plot, the activation energy of 31 kJ mol^{-1} was deduced by using the Arrhenius equation, $\tau^{-1} = \tau_0^{-1}\exp(-E_a/k_B T)$. The experimentally determined activation energy (E_a) is similar to the calculated ΔE values of about 40 kJ mol^{-1}.

Temperature-dependent wide-line ^{1}H NMR spectra of **1** were obtained to evaluate the dynamic properties of the [18]crown-6 molecules. These spectra are evidently composed of two types of signals: wide and narrow (Figure 4a). The full width at half maximum (ΔH) and peak-to-peak linewidth (ΔH_p) of the differential spectra (blue lines) were plotted against temperature, which correspond to the wide and narrow signals, respectively. As the protons of both [18]crown-6 (24 H) and NH_3^+ (3 H) of **1** are detected in the ^{1}H NMR spectra, the spectrum is largely dominated by the components of [18]crown-6. ΔH_p corresponds to the linewidth of the sharp signal of the motional protons in NH_3^+ (closed circles in Figure 4b). A temperature-independent narrow line was observed at $\Delta H_p \approx 10$ kHz in the entire measured temperature range, thus suggesting that the molecular rotation of the ammonium moiety occurred at 120 K. By lowering the temperature to 120 K, a broadening of ΔH was observed at around 260 K (open circles in Figure 4b). The ΔH values at temperatures below 200 K were almost constant at about 50 kHz, whereas those above 300 K reached at a constant value of about 18 kHz, which corresponds to the thermally activated rotation of [18]crown-6 in **1**. About 30 kHz change of ΔH values by lowering the tem-

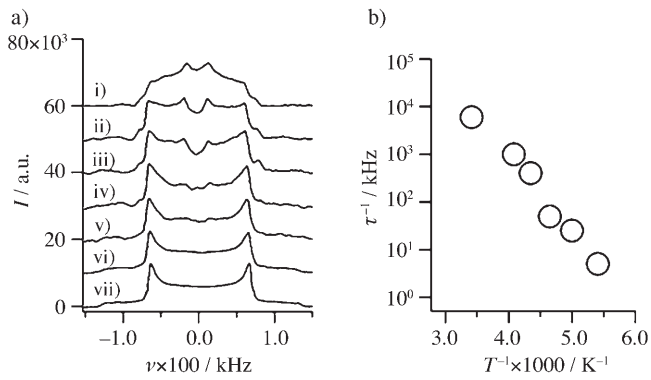

Figure 3. Solid-state ^{2}H NMR spectra of **1**. a) Temperature-dependent lineshapes at i) $T = 293$, ii) 245, iii) 230, iv) 215, v) 200, vi) 185, and vii) 170 K. b) Plot of frequency of flip-flop motion (τ^{-1}) versus T^{-1}.

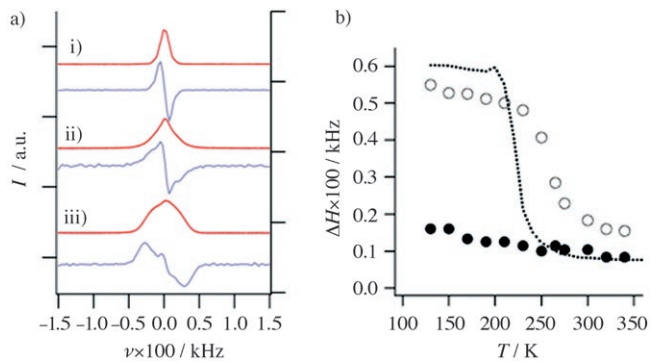

Figure 4. Solid-state wide-line ^{1}H NMR spectra of **1**. a) Temperature-dependent lineshapes at i) $T = 340$, ii) 265, and iii) 190 K. b) Temperature dependence of i) full-width at half-maximum (open circles: ΔH), ii) peak-to-peak linewidth of the narrow component in the differential spectra (filled circles: ΔH_p) of **1**, and iii) ΔH of the reference salt $Cs_2([18]crown\text{-}6)_3[Ni(dmit)_2]_2$ (dotted line).

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perature was almost the same with that of molecular rotation of [18]crown-6 in Cs_2([18]crown-6)$_3$[Ni(dmit)$_2$]$_2$ (dotted line in Figure 4b).[10] The rotational frequency of [18]crown-6 in **1** was estimated to be several tenths of a kilohertz at around 250 K.

Although the thermally activated 180° flip-flop motion of the phenyl ring of [D_5]anilinium and the rotation of [18]crown-6 were confirmed by temperature-dependent NMR spectroscopy, the magnetic properties of the crystal were not affected by the molecular rotation. The temperature dependence of the magnetic susceptibility was that of the [Ni(dmit)$_2$]$^-$ spin ladder,[11] which did not exhibit any anomaly associated with the molecular rotation. On the other hand, the 180° flip-flop motion of the phenyl ring and the rotation of [18]crown-6 affected the dielectric response of the crystal. When the frequency of the molecular motion is higher than that of the applied AC electric field, the molecular motion can follow the outer AC field without dielectric loss.[15] On the other hand, application of a significantly higher AC electric-field frequency than the frequency of molecular motion does result in dielectric loss. On the basis of the crystal symmetry, the dipole moments of the crystal would cancel each other. However, it is possible that the temperature-dependent changes in the molecular motion of anilinium and [18]crown-6 can influence the dielectric responses.

The plots of dielectric constant (ε_1) versus T for **1** at fixed frequencies of 1, 10, 100, and 1000 kHz are shown in Figure 5. The absolute ε_1 value for **1** at 300 K is dependent

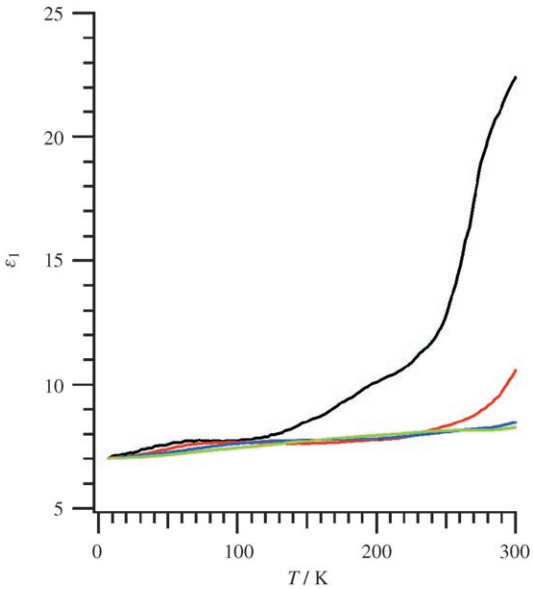

Figure 5. Plot of ε_1 versus T for **1** at fixed frequencies of 1 (black), 10 (red), 100 (blue), and 1000 kHz (green).

on the frequency of the applied AC electric field. The values for ε_1 at 300 K decreased from 22 to 11, 9, and 8 when the AC frequencies were increased from 1 to 10, 100, and 1000 kHz, respectively. The magnitude of ε_1 at 1 kHz (T = 300 K) was about three times that at 1000 kHz. These results strongly suggest that a relaxation process of the molecular motion that is comparable to the rotation frequency of [18]crown-6 (several tenths of a kilohertz at room temperature) affected the frequency-dependent values of ε_1. By decreasing the temperature from 300 K, the absolute values of ε_1 at 1 kHz decreased gradually and exhibited a broad maximum at around 200 K. The values for ε_1 at 1, 10, 100, and 1000 kHz merged at around 100 K, at which point the molecular rotation in the cation structure was completely suppressed within the limits of the timescale of measurement of the dielectric constant. From the temperature-dependent wide-line ^{1}H NMR spectrum, the rotational frequency of [18]crown-6 at about 200 K was estimated to be less than 10 kHz, and the broad anomaly of ε_1 at about 200 K should be reflected by the molecular rotation of [18]crown-6. Therefore, the dielectric responses at temperatures above 100 K may be related to the thermally activated rotation of [18]crown-6.

Conclusions

A dual-mode molecular motion was observed in the (anilinium)([18]crown-6) supramolecule, which was introduced as the countercation structure of a [Ni(dmit)$_2$]$^-$ salt. The two-dimensional arrangements of the cations were sandwiched between the [Ni(dmit)$_2$]$^-$ anion layers, where alternating layers of cations and anions suppressed the intermolecular interactions between the layers. In the cation layer, sufficient space to allow the 180° flip-flop motion of anilinium and the random rotation of [18]crown-6 was observed. Temperature-dependent ^{2}H NMR spectroscopy revealed a thermally activated 180° flip-flop motion of the phenyl ring of [D_5]anilinium above 200 K, whose activation energy is about 31 kJ mol^{-1}, whereas the wide-line ^{1}H NMR spectrum indicated a thermally activated rotation of [18]crown-6 at temperatures above 250 K. Therefore, dual molecular motions of the 180° flip-flop of the phenyl ring and the rotation of [18]crown-6 occur simultaneously in the solid state. The lower rotational barrier of the NH_3^+ moiety ($\Delta E \approx 2$ kJ mol^{-1}) relative to that of the phenyl ring (ΔE = 30–40 kJ mol^{-1}) in anilinium allows NH_3^+ rotation to lower temperatures. Factors such as the frequency, symmetry, and activation energy of each rotation are important points in the development of supramolecular rotators. Supramolecular designs of multimode molecular motions allow us to develop novel solid-state dynamic molecular systems for electromagnetic or dielectric applications.

Experimental Section

Preparation of [Ni(dmit)$_2$]$^-$ Salts

Crystals of **1** were obtained by the standard diffusion method in a vial (≈20 mL) and were used for X-ray crystal-structure analysis and solid-state ^{1}H and ^{2}H NMR spectroscopy. ([D_5]anilinium)(BF_4) was prepared from aqueous tetrafluoroboric acid (HBF_4; 54%) and 2,3,4,5,6-deuterated aniline in CH_3CN. The green solution of (nBu$_4$N)[Ni(dmit)$_2$] (20 mg in

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CH_3CN ($\approx$20 mL)) was poured into a solution of ([D_5]anilinium)(BF_4) (50 mg) and [18]crown-6 (200 mg) in CH_3CN ($\approx$20 mL). The difference in the densities of the solutions allowed for the slow diffusion of the two solutions. After one week, single crystals (typical dimensions $0.5\times0.5\times0.4$ mm^3) were obtained as black blocks. The stoichiometry of the crystals was determined by X-ray structural and elemental analyses. Elemental analysis: calcd (%) for $C_{24}H_{32}N_1O_6S_{10}Ni$: C 35.59, H 3.98, N 1.73; found: C 35.99, H 4.17, N 1.82.

Crystal-Structure Determination

Crystallographic data of **1** were collected on a Rigaku Raxis-Rapid diffractometer with $Mo_{K\alpha}$ ($\lambda=0.71073$ Å) radiation and a graphite monochromator. Structural refinements were performed by using the full-matrix least-squares method on F^2. Calculations were carried out with the Crystal Structure software packages.[16] Parameters at ambient pressure were refined by using anisotropic temperature factors except for the hydrogen atom. Crystal data of **1**: Space group $P\bar{1}$ (No. 2), $a=8.092(3)$, $b=14.241(7)$, $c=16.645(7)$ Å, $\alpha=113.074(18)$, $\beta=97.040(15)$, $\gamma=92.670(19)°$, $V=1742.12(13)$ Å^3, $Z=2$, $D_{calcd}=1.544$ g cm^{-3}, $\mu=1.544$ cm^{-1}, $T=298$ K, 16590 reflections, 7829 independent reflections, 6847 reflections for structural refinement, $R=0.040$, $R_w(F_2)=0.038$, GOF$=1.01$. CCDC-625767 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Electrical Measurements

Temperature-dependent dielectric constants were measured by the two-probe AC impedance method over the frequency range 100–10×10^6 Hz (HP4194A). A single crystal was placed in a cryogenic refrigeration system (Daikin PS24SS). The electrical contacts were prepared by using gold paste (Tokuriki 8560) to attach the 10-μm-diameter gold wires to the crystal along the *b* axis.

Calculation of Potential Energy

Atomic coordinates based on the X-ray crystal-structure analysis were used for the calculations. The relative energy of the (anilinium)([18]-crown-6)$_3$ model structure was calculated by using the RHF/6-31(d) basis set.[13] The relative energy of the (anilinium)([18]crown-6)$_3$ system was obtained by evaluating three types of rotation modes: 1) rigid rotation of anilinium around the C–N bond, 2) rotation of the NH_3^+ moiety around the C–N bond with fixed atomic coordinates of the phenyl ring, and 3) rotation of the phenyl ring around the C–N bond with fixed atomic coordinates of the C–NH_3^+ moiety. The rotations were performed at 30° intervals, and the relative energies were calculated by using fixed atomic coordinates.

Solid-State NMR Spectroscopy

Solid-state wide-line ^{2}H NMR spectra were obtained by the solid-echo pulse sequence $\pi/2_x$–τ–$\pi/2_y$ on a Bruker DSX 300 spectrometer; the $\pi/2$ pulse width and τ were 2.3 and 13 μs, respectively. The temperature was controlled by cold N_2 gas with a VT1000 control unit and was maintained constant within ±1 K during the acquisition of the signal. Solid-state wide-line ^{1}H NMR spectra under the static conditions of the sample were obtained by the above solid-echo pulse sequence (the $\pi/2$ pulse width and τ were 1.3 and 10 μs, respectively) on a Bruker DSX 300 spectrometer with an operating frequency of 300 MHz for protons.

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