Supramolecular Cations of (*S*)-, (*R*)-, and (*RS*)-Indan-1-aminium(dibenzo[18]crown-6) in Magnetic $[Ni(dmit)_2]^-$ Salts

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Magnetic crystals were formed using supramolecular cation structures that consist of (*S*)-AIH^+(dibenzo[18]crown-6), (*R*)-AIH^+(dibenzo[18]crown-6), or (*RS*)-AIH^+(dibenzo[18]crown-6) (AIH^+ = indan-1-aminium) as the counter cation to $[Ni(dmit)_2]^-$ ions ($dmit^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolate), which bear one $S = 1/2$ spin. The resulting salts, (*S*)-AIH^+(dibenzo[18]crown-6)$[Ni(dmit)_2]$ (**1**), (*R*)-AIH^+(dibenzo[18]crown-6)$[Ni(dmit)_2]$ (**2**), and (*RS*)-AIH^+(dibenzo[18]crown-6)$[Ni(dmit)_2]$ (**3**), feature supramolecular cations that are formed through the inclusion of the ammonium moiety of AIH^+ into the cavity of dibenzo[18]crown-6 through N–H···O hydrogen bonds. Salts **1**, **2**, and **3** possess space groups of $P2_1$, $P2_1$, and $P2/m$, respectively, and possess similar molecular packings. Chiral cations (*S*)-AIH^+ (salt **1**) and (*R*)-AIH^+ (salt **2**) yielded chiral crystals, whereas racemic (*RS*)-AIH^+ (salt **3**) afforded a racemic crystal with a mirror plane. Within the crystals, alternating layers of $[Ni(dmit)_2]^-$ ions and (AIH^+)(dibenzo[18]crown-6) cations formed a layered structure along the *b* axis. Since the 2_1 axis of salts **1** and **2** were observed along the *b* axis, effective chiral magnetic interactions between the $[Ni(dmit)_2]^-$ ions were not observed. In the *ac* plane, weak interactions among the $[Ni(dmit)_2]^-$ ions formed a two-dimensional layer. Temperature-dependent magnetic susceptibilities of salts **1**, **2**, and **3** exhibited a Curie–Weiss-type behavior, which shows weak antiferromagnetic interactions between the $[Ni(dmit)_2]^-$ ions, with Weiss temperatures of –2.9, –2.9, and –4.2 K, respectively.

Introduction

Structures of organic ammonium RNH_3^+(crown ether) assemblies in the solid state depend on both the structure of the cation and on the size of the crown ether ring.[1] Various types of RNH_3^+ structures (R = H, CH_3, $C_6H_5CH_2$, NH_2, etc.) have been shown to form stable ammonium(crown ether) complexes in the solid state.[1] In these structures, the $N–H^+···O$ hydrogen bonds and electrostatic interactions play important roles in binding the ammonium moiety into the cavity of the crown ethers.[2] Because it has been shown that the ionic radius of NH_4^+ matches the cavity size of [18]crown-6, it is reasonable to assume that $N–H^+···O$ hydrogen bonds help form stable RNH_3^+([18]crown-6) complexes in the solid state. Although the cation-binding ability of dibenzo[18]crown-6 (1,4,7,10,13,16-hexaoxa-2,3:11,12-dibenzocyclooctadeca-2,11-diene) is similar to that of [18]crown-6,[3] the two benzene rings that are fused onto [18]crown-6 greatly affect the cationic structure of the RNH_3^+(dibenzo[18]crown-6) complexes and the molecular packing within the crystals. Comparatively, the O_6 plane of NH_4^+([18]crown-6) is nearly planar,[4] while the molecular structure of NH_4^+(dibenzo[18]crown-6) can be defined as a V-shaped conformation with the two benzene rings forming a bent structure in relation to the O_6 plane of the [18]crown-6 moiety.[5] The solid-state supramolecular cation structures of RNH_3^+ and dibenzo[18]crown-6, therefore, have the potential to yield a completely different type of cation assembly, as compared to those with [18]crown-6.

We have been involved in preparing supramolecular cationic structures and forming salts with $[Ni(dmit)_2]$ ($dmit^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolate).[6] Such an approach has allowed us to modify the assembled structures of the $[Ni(dmit)_2]^-$ ions, each bearing one $S = 1/2$ spin, and thus adjust the magnetic properties of the $[Ni(dmit)_2]^-$ salts. Among the salts, assembled structures between RNH_3^+ and [18]crown-6, such as anilinium([18]crown-6),[7] *p*-phenylenediammonium([18]crown-6)$_2$,[7] and *p*-xylylenediammonium([18]crown-6)$_2$ supramolecules,[8] yielded a variety of $[Ni(dmit)_2]^-$ ion assemblies that possess magnetic properties such as isolated spins, linear one-dimensional Heisenberg

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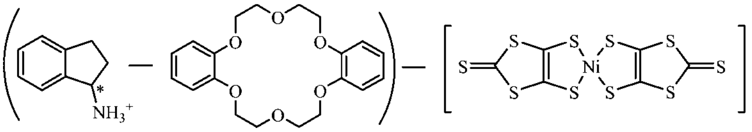

Scheme 1. Chemical structures of (*S*)-, (*R*)-, and (*RS*)-indan-1-aminium(dibenzo[18]crown-6)[Ni(dmit)$_2$] salts.

chains, and spin-ladders, according to the shape of the cationic structures. Introduction of chirality into the RNH$_3^+$ cations can potentially enhance the [Ni(dmit)$_2$]$^-$ ion assemblies within the crystals. A slight chemical modification of the cationic structures, specifically from anilinium([18]-crown-6) to *p*-phenylenediammonium([18]crown-6)$_2$, was found to modulate the [Ni(dmit)$_2$]$^-$ ion assemblies,[7a] and to drastically change the magnetic properties, from that of spin-ladder to that of singlet dimers.[7b] In the present study, we examined the effects of relatively small structural perturbations of the hydrogen-bonded supramolecular cations of RNH$_3^+$(dibenzo[18]crown-6) structures by modifying the chirality of the RNH$_3^+$ units in the [Ni(dmit)$_2$]$^-$ salts. For this purpose, chiral cations (*S*)- and (*R*)-indan-1-aminium [(*R*)-AIH$^+$ and (*S*)-AIH$^+$, respectively] and racemic (*RS*)-indan-1-aminium [(*RS*)-AIH$^+$] were utilized to form the hydrogen-bonded (AIH$^+$)(dibenzo[18]crown-6) structures in the magnetic [Ni(dmit)$_2$] salts (Scheme 1). Because the NH$_3^+$ moiety of AIH$^+$ has the capacity to hydrogen-bond to the six oxygen atoms of the dibenzo[18]crown-6 molecule, it can be suggested that the asymmetric carbon center of (*S*)- and (*R*)-AIH$^+$ may affect the chirality of the crystals.

Results and Discussion

Crystal Structures

As expected, salts of (*S*)-AIH$^+$(dibenzo[18]crown-6)-[Ni(dmit)$_2$] (**1**), (*R*)-AIH$^+$(dibenzo[18]crown-6)[Ni(dmit)$_2$] (**2**), and (*RS*)-AIH$^+$(dibenzo[18]crown-6)[Ni(dmit)$_2$] (**3**) have the same stoichiometry. The data for the X-ray structural analyses for salts **1**, **2**, and **3** were obtained at 297 K (Table 1). The crystal symmetry of salts **1** and **2** were chiral *P*2$_1$ due to the existence of an asymmetric center within the chiral (*S*)- and (*R*)-AIH$^+$ ions, while that of salt **3** was achiral *P*2$_1$/*m* due to the racemic (*RS*)-AIH$^+$ ion. For all the salts, the ammonium moiety of AIH$^+$ lies above the cavity of dibenzo[18]crown-6, thus forming the AIH$^+$(dibenzo-[18]crown-6) cationic structure. Furthermore, the molecular arrangements of the [Ni(dmit)$_2$]$^-$ ions and the AIH$^+$(dibenzo[18]crown-6) cations are similar to each other. Because the LUMO of the [Ni(dmit)$_2$]$^-$ ion is occupied by a single electron, which bears one $S = 1/2$ spin, the salts can be described as magnetic crystals.

The structures of the supramolecular cations of salts **1**–**3** are shown in Figure 1. As shown in Figure 1a, the ammonium moiety of (*S*)-AIH$^+$ lies above the cavity of dibenzo[18]crown-6, which possesses a V-shaped conformation. As a note, X-ray structural analyses confirmed that the absolute chirality of (*S*)-AIH$^+$ (salt **1**) and (*R*)-AIH$^+$ (salt **2**) corresponded to that of the starting (*S*)- and (*R*)-AIH$^+$ ions (Figures 1b and 1c), respectively. For salt **3**, on the other hand, the N1 and C9–C16 atoms define a mirror plane, which allows the isomers (*S*)- and (*R*)-AIH$^+$ ions equal probability (50%) of occupation, thus reflecting the racemic nature of the cation (Figure 1d).

The structural parameters of the cationic structures for salts **1**–**3** are summarized in Table 2. In each case, effective N–H···O hydrogen bonding between the NH$_3^+$ group of AIH$^+$ and the six oxygen atoms of dibenzo[18]crown-6 was observed. The N–O hydrogen bonding distances range from 2.917(6) to 3.132(6) Å, in which the average N–O distance

Table 1. Crystal data, data collection, and reduction parameters of salts **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{35}H_{36}O_6NNiS_{10}$	$C_{35}H_{36}O_6NNiS_{10}$	$C_{35}H_{36}O_6NNiS_{10}$
Formula mass	945.97	945.97	945.97
Space group	*P*2$_1$ (#4)	*P*2$_1$ (#4)	*P*2$_1$/*m* (#11)
a [Å]	8.55(2)	8.57(3)	8.62(2)
b [Å]	20.53(3)	20.57(5)	20.32(4)
c [Å]	11.79(3)	11.81(3)	11.79(2)
β [°]	101.67(7)	101.7(1)	101.35(8)
V [Å^3]	2027(6)	2037(9)	2026(7)
Z	2	2	2
$D_{calcd.}$ [g cm^{-1}]	1.550	1.541	1.550
T [K]	297	297	297
μ [cm^{-1}]	10.4	10.33	10.39
Reflections measured	34337	30802	33339
Independent reflections	8785	8797	4767
Reflections used	5169	5269	3270
R[a]	0.034	0.036	0.034
$R_w(F^2)$[a]	0.074	0.090	0.083
GOF	0.983	0.950	1.128

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = (\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2)^{1/2}$.

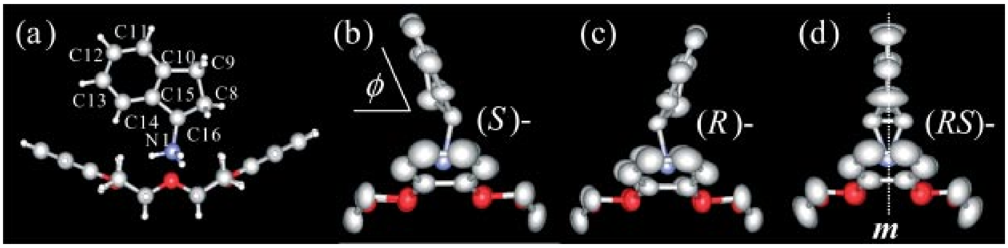

Figure 1. AIH^+(dibenzo[18]crown-6) structures of salts **1**–**3**. (a) Cation unit of salt **1** viewed parallel to the O_6 plane of dibenzo[18]crown-6. Configurations of (b) (*S*)-AIH^+, (c) (*R*)-AIH^+, and (d) (*RS*)-AIH^+ units viewed along the π plane of AIH^+. Hydrogen atoms are omitted for clarity.

for salts **1**, **2**, and **3** are 3.00, 3.02, and 3.02 Å, respectively. The greater average N–O distances, in comparison to the standard distance for the N–O hydrogen bond (2.87 Å),[9] indicate that the AIH^+(dibenzo[18]crown-6) structures involve six weak $NH_3^+\cdots O$ hydrogen-bond interactions. For salts **1** and **2**, the distance between N1 and the O_6 plane of dibenzo[18]crown-6 ($d_{N-O_{plane}}$) is 1.23 Å, while that of racemic salt **3** is slightly longer (1.27 Å). The dihedral angle (φ) between the O_6 plane of dibenzo[18]crown-6 and the C_6 plane of the AIH^+ benzene moiety for salts **1** and **2** is 66.04 and 66.24°, respectively. In contrast, the racemic nature of the (*RS*)-AIH^+ ion of salt **3** exhibits an average structure of 50% probability of each configuration. In this case, the static disorder of the (*R*)-AIH^+ and (*S*)-AIH^+ configuration yields a mirror plane as defined by the N1 and C9–C16 atoms resulting in $\varphi = 90°$. These structural differences in the cations, however, do not affect the $[Ni(dmit)_2]^-$ arrangements within the crystals.

Table 2. Structural parameters of the cations for salts **1**–**3**.[a]

	1	2	3
N1–O1, N1–O4	3.119(6), 3.002(5)	3.131(6), 2.952(5)	2.996(4)
N1–O2, N1–O5	2.963(6), 2.900(6)	2.918(6), 2.958(6)	2.937(3)
N1–O3, N1–O6	2.955(5), 3.110(6)	3.010(5), 3.122(6)	3.119(5)
$N1-O_{AV}$	3.00	3.02	3.02
$d_{N-O_{plane}}$	1.23	1.23	1.27
φ	66.04	66.24	90

[a] The parameters $d_{N-O_{plane}}$ and φ are defined in the text.

The unit cell of salt **1** viewed along the *a* axis is shown in Figure 2. Although the space group of salt **3** is different from those of salts **1** and **2**, the overall molecular packing in crystal **3** is comparable to those of salts **1** and **2**. The AIH^+(dibenzo[18]crown-6) cations and $[Ni(dmit)_2]^-$ ions are independently arranged within the *ac* plane, whereas the cation and anion layers are alternately arranged along the *b* axis. Moreover, the cation layer disrupts the intermolecular interactions between the $[Ni(dmit)_2]^-$ layers along the *b* axis. Since the spiral 2_1 axis is parallel to the *b* axis, effective chiral intermolecular interactions between the $[Ni(dmit)_2]^-$ anions were not expected within the crystals.

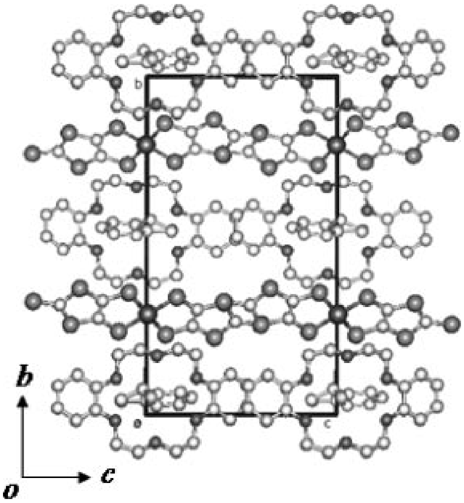

Figure 2. Unit cell of salt **1** viewed along the *a* axis. Hydrogen atoms are omitted.

The arrangements of the cations and anions within the *ac* plane are shown in Figure 3. The AIH^+(dibenzo[18]crown-6) units are stacked along the *a* axis, in which the V-shaped dibenzo[18]crown-6 units in the *ac* plane are arranged in the same direction along the *a* axis. Although a large dipole moment was expected in the *ac* plane, each cationic layer is arranged in a 2_1 symmetry, thus cancelling the dipole moment of the overall crystal. The $[Ni(dmit)_2]^-$ ions within the *ac* plane interact through weak lateral interatomic S···S contacts along the *c* and *a*+*c* axis. Despite the lack of significant π–π overlap between the $[Ni(dmit)_2]^-$ ions, a layered structure is formed by two-dimensional lateral S···S contacts in the *ac* plane. The magnitude of intermolecular interactions between the $[Ni(dmit)_2]^-$ ions was estimated from the calculated values of the transfer integrals (*t*) of LUMO based on extended Hückel molecular orbital calculations (Table 3). The transfer integrals of salts **1**, **2**, and **3** along the *a*+*c* axis (t_1) are 21.8, 21.5, and 26.9 meV, respectively, which are larger than those along the *c* axis (t_2 = 4.04, 4.15, and 4.98 meV for salts **1**, **2**, and **3**, respectively). Since the t_1 interactions are two- or threefold larger than the t_2 interactions, intermolecular interactions between $[Ni(dmit)_2]^-$ ions are dominated by those in the one-dimensional linear chain along the *a*+*c* axis. Each chain is arranged through weak interchain interactions (t_2) along the *c* axis. Because the magnitude of the intrachain interactions (t_1) for salt **3** is roughly 20% greater than those of salts **1** and **2**, slightly larger magnetic interactions should be present for salt **3** than for salts **1** and **2**.

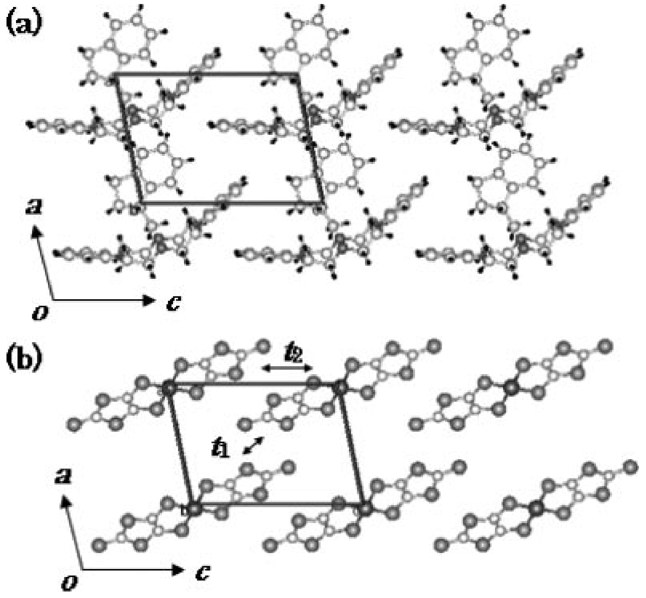

Figure 3. Crystal structures of salt **1**. (a) AIH$^+$(dibenzo[18]crown-6) cation and (b) [Ni(dmit)$_2$]$^-$ ion arrangements within the *ac* plane {intermolecular transfer integrals, t_1 and t_2, between the [Ni(dmit)$_2$]$^-$ ions are shown}.

Table 3. Transfer integral ($t \times 10^{-3}$ eV)[a] and magnetic parameters of salts **1**–**3**.

	1	**2**	**3**
t_1	21.8	21.5	26.9
t_2	4.04	4.15	4.98
C [emu K mol^{-1}]	0.367	0.374	0.372
θ [K]	-2.9	-2.9	-4.2

[a] The transfer integrals (t) were obtained by the LUMO of [Ni(dmit)$_2$]$^-$ based on the extended Hückel calculation ($t = -10S$ eV); S is the overlap integral.

Circular dichroism (CD) spectra of salts **1**–**3** with KBr pellets were measured to confirm the chiral intermolecular interactions between [Ni(dmit)$_2$]$^-$ ions. The intermolecular charge-transfer absorption between [Ni(dmit)$_2$]$^-$ ions has been observed at an energy around 8×10^3 cm^{-1}, while the intramolecular localized excitation bands of the [Ni(dmit)$_2$]$^-$ ion appear in the visible energy region with the absorption maxima around 12, 13, and 18×10^3 cm^{-1}.[10] Weak responses of CD spectra of salts **1** and **2** were observed at ca. 15 and ca. 20×10^3 cm^{-1} as a positive and negative rotation angle, respectively, while there was no meaningful response in the CD spectrum of racemic salt **3**. Therefore, the chiral arrangements of AIH$^+$ ions induced the circular dichroism in the intramolecular localized excitations of [Ni(dmit)$_2$]$^-$ ion along the *b* axis through intermolecular interactions between the [Ni(dmit)$_2$]$^-$ and AIH$^+$ ions.

Magnetic Properties

The magnetism of the crystals were determined by estimating the magnetic exchange energy (J), which is proportional to the square of t, i.e. magnitude of the intermolecular interaction.[11] Each [Ni(dmit)$_2$]$^-$ ion possesses one $S = 1/2$ spin, and therefore the molecular assemblies are directly related to the magnetism. Temperature-dependent magnetic susceptibilities (χ_{mol} vs. T) are similar among salts **1**–**3** (Figure 4 and Table 3); such similarity is also indicated by the comparable [Ni(dmit)$_2$]$^-$ arrangements among the crystals. The χ_{mol} vs. T of salts **1** and **2** exhibit Curie–Weiss behavior, in which the magnetic parameters C and θ are 0.367 emu K mol^{-1} and –2.9 K, respectively. Although salt **3** also exhibits Curie–Weiss behavior, the greater intrachain interactions (t_1 = 26.9 meV) of salt **3**, than those of salts **1** and **2**, provides a slightly larger Weiss constant of θ = –4.2 K (Figure 4b). In salt **3**, the magnitude of intermolecular t_1 and t_2 interactions between [Ni(dmit)$_2$]$^-$ anions are slightly larger than those of salts **1** and **2**, which increases the $|J|$ and $|\theta|$ values. The disordered arrangements of racemic AIH$^+$ ions in salt **3** affects the crystal lattice, which slightly changes the anionic arrangements to increase the intermolecular interactions between the [Ni(dmit)$_2$]$^-$ ions.

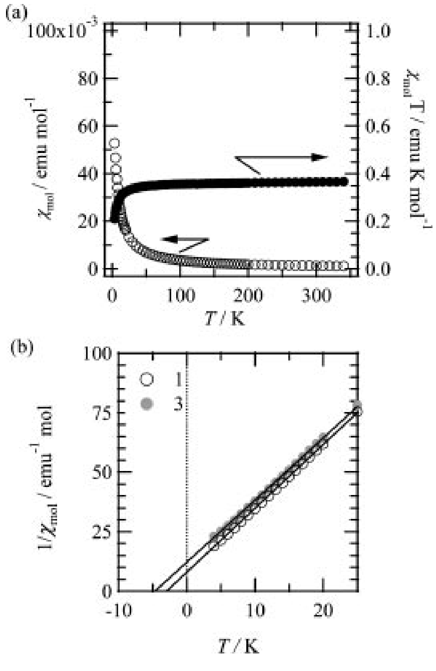

Figure 4. Temperature-dependent molar magnetic susceptibility (χ_{mol}) per one [Ni(dmit)$_2$]$^-$ ion for salts **1**–**3**. (a) χ_{mol} vs. T (left scale) and $\chi_{\text{mol}}T$ vs. T (right scale) plots for salt **1**. (b) $\chi_{\text{mol}}{}^{-1}$ vs. T plots for salts **1** and **3**.

Summary

Supramolecular cationic structures of (S)-AIH$^+$(dibenzo[18]crown-6), (R)-AIH$^+$(dibenzo[18]crown-6), and (RS)-AIH$^+$(dibenzo[18]crown-6) (AIH$^+$ = indan-1-aminium) were incorporated into [Ni(dmit)$_2$]$^-$ salts. Supramolecular assemblies were formed through hydrogen-bond interactions between the NH_3^+ moieties of the AIH^+ ion and the oxygen atoms in the dibenzo[18]crown-6 molecule. Chiral (*S*)-AIH^+ and (*R*)-AIH^+ and racemic (*RS*)-AIH^+ yielded isomorphous crystals with a stoichiometry of AIH^+(dibenzo[18]crown-6)$[Ni(dmit)_2]$. The chiral salts possess a chiral space group of $P2_1$, while the latter salt possesses an achiral $P2_1/m$ space group. However, the molecular packing and temperature-dependent magnetic susceptibilities of the three salts are comparable to each other. The AIH^+(dibenzo[18]crown-6) cations are packed within the *ac* plane, whereas the $[Ni(dmit)_2]^-$ ions form a two-dimensional layer separated by a layer of cations. The transfer integrals in the $[Ni(dmit)_2]$ layer exhibit weak one-dimensional intermolecular interactions between the $[Ni(dmit)_2]$ molecules, which yield weak antiferromagnetic interactions between the $[Ni(dmit)_2]^-$ ions. Chiral cations (*S*)- and (*R*)-AIH^+ were successfully introduced into the supramolecular cationic structures in $[Ni(dmit)_2]$-based molecular magnets. Introduction of chirality into the crown ethers are currently underway in an attempt to achieve chiral intermolecular interaction between the $[Ni(dmit)_2]$ molecules.

Experimental Section

Preparation of $[Ni(dmit)_2]$ Salts: The precursor monovalent salt $nBu_4N[Ni(dmit)_2]$ was prepared according to the literature.[12] The ammonium salts of (*S*)-, (*R*)-, and (*RS*)-$AIH^+BF_4^-$ were prepared by neutralization of commercially available chiral (*S*)-, (*R*)-, and racemic (*RS*)-AIH^+ using 42% aqueous HBF_4. Single crystals of salts **1**–**3** were grown by slow diffusion of $nBu_4N^+[Ni(dmit)_2]^-$ and $AIH^+BF_4^-$ in vials charged with CH_3CN (ca. 20 mL). The compositions of crystals **1**–**3** were determined by X-ray structural analysis and by elemental analysis. Salt **1**: $C_{35}H_{36}NNiO_6S_{10}$ (946.01): calcd. C 44.44, H 3.84, N 1.48; found C 44.11, H 3.69, N 1.24. Salt **2**: $C_{35}H_{36}NNiO_6S_{10}$ (946.01): calcd. C 44.44, H 3.84, N 1.48; found C 44.64, H 3.91, N 1.67. Salt **3**: $C_{35}H_{36}NNiO_6S_{10}$ (946.01): calcd. C 44.44, H 3.84, N 1.48; found C 44.29, H 3.54, N 1.62.

Crystal Structure Determination: Crystallographic data (Table 1) were collected with a Rigaku Raxis-Rapid diffractometer with Mo-K_α (λ = 0.71073 Å) radiation from a graphite monochromator. Structure refinements were performed using the full-matrix least-squares method on F^2. Calculations were carried out using Crystal Structure software packages.[13] Parameters were refined using anisotropic temperature factors with the exception of those for the hydrogen atoms. CCDC-263460 (**1**), -263461 (**2**), and -263462 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic Susceptibility: Temperature-dependent magnetic susceptibilities were measured with a Quantum Design Model MPMS-XL SQUID magnetometer for polycrystalline samples. The applied magnetic field was 1 T for all measurements.

Calculation of Transfer Integrals: Transfer integrals (*t*) were calculated within the tight-binding approximation using the extended Hückel molecular orbital method. The LUMO of the $[Ni(dmit)_2]^-$ ion was used as the basis function.[14] Semi-empirical parameters for Slater-type atomic orbitals were obtained from the literature.[14] The *t* values between each pair of molecules were assumed to be proportional to the overlap integral (*S*) using the equation, $t = -10S$ eV.

Supporting Information (see also footnote on the first page of this article): Preparations of $HAI^+BF_4^-$ and salts **1**–**3**, the atomic numbering scheme, and CD spectra of salts **1–3**.

Acknowledgments

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