

Bilayer Mott System with Cation⋯Anion Supramolecular Interactions Based on a Nickel Dithiolene Anion Radical: Coexistence of Ferro- and Antiferromagnetic Anion Layers and Large Negative Magnetoresistance

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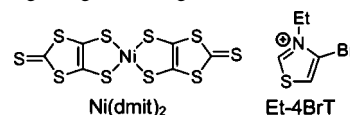
S Supporting Information

ABSTRACT: A novel bilayer Mott system, (Et-4BrT)-[Ni(dmit)₂]₂ (Et-4BrT = ethyl-4-bromothiazolium; dmit = 1,3-dithiole-2-thione-4,5-dithiolate), contains two non-equivalent Ni(dmit)₂ anion layers, where both layers form Mott insulating states. Supramolecular Br_{cation}⋯S_{anion} and S_{cation}⋯S_{anion} interactions play a crucial role in constructing the bilayer structure. The ferro- and antiferromagnetic short-range-ordering layers coexist in the crystal, which achieves large negative magnetoresistance ($\Delta\rho/\rho_0 \approx -75\%$ at 70 kOe) at 5 K under 1 GPa.

The development of exotic physical properties on molecular (super)conductors and magnets based on metal dithiolene complexes M(dmit)₂ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate; M = Ni, Pd, Pt, Au) has attracted much attention because of their capability of exploring the new fields of condensed matter physics and materials science.^{1,2} The electronic structure and physical properties of M(dmit)₂ salts highly depend on the molecular arrangement in the solid state; thus, it is crucial to achieve novel molecular arrangements in order to develop unique electronic structures and physical phenomena. Most Ni(dmit)₂ anion-radical salts contain one type of crystallographically independent anion layer in the unit cell, a so-called *monolayer system*. However, we developed *bilayer* Ni(dmit)₂ anion-radical salts that construct interesting anion arrangements. The bilayer salts contain two crystallographically independent Ni(dmit)₂ anion layers with different anion arrangements in the crystal lattice and exhibit unusual physical properties such as anomalous magnetoresistance.³ It is interesting that, in these bilayer salts, at least one anion layer demonstrates the Mott insulating state. In materials with a narrow and half-filled band (Mott system), strong electron correlation due to the onsite Coulomb repulsion induces unusual electric and magnetic properties.⁴ The electrons in the Mott system are very sensitive to subtle changes in various parameters including interlayer interactions; therefore, the development of a *bilayer Mott system* would be a promising approach to realizing novel electronic structures and physical properties that cannot be obtained in conventional *monolayer systems*. We have revealed that supramolecular cation⋯anion interactions such as halogen bonds play

an important role in the construction of such bilayer structures.^{3a,d}

We report here a new bilayer Mott system, (Et-4BrT)[Ni(dmit)₂]₂ (Et-4BrT = ethyl-4-bromothiazolium), in which the coexistence of antiferromagnetic (AFM) and ferromagnetic (FM) anion layers demonstrates an unusual ferromagnetic anomaly and large negative magnetoresistance.



Single crystals of (Et-4BrT)[Ni(dmit)₂]₂ were obtained by galvanostatic electrolysis from a mixture of (tBu₄N)[Ni(dmit)₂] (4.5 mg) with (Et-4BrT)·BF₄ (45 mg) as the supporting electrolyte in acetone–acetonitrile (3:1, v/v; 20 mL) at 20 °C under argon.

Single-crystal X-ray diffraction (XRD) analysis of (Et-4BrT)[Ni(dmit)₂]₂ revealed that the unit cell contains one crystallographically independent Et-4BrT cation and two crystallographically independent Ni(dmit)₂ anions (A and B; Figure 1).⁶ Each anion independently constructs a layer (layers A and B) with a different anion arrangement, demonstrating that (Et-4BrT)[Ni(dmit)₂]₂ is a new *bilayer system*. Two S_{cation}⋯S_{anion B} short contacts (<3.60 Å) are detected, in addition to a Br_{cation}⋯S_{anion A} halogen bond. The lone pair on the thioketone moiety in the anion B points toward the surface area on the S atom with a highly positive electrostatic potential in the cation, the so-called σ hole,⁷ suggesting that σ holes mediate electrostatically driven supramolecular S_{cation}⋯S_{anion B} interactions. Consequently, a nonsymmetrical steric environment around the cation operates in favor of bilayer structure formation. The similar bond lengths in the anions A and B indicate their equivalent oxidation state, [Ni(dmit)₂]^{0.5-}.

The anion layers are isolated from each other by the cation layers along the *b* axis without interlayer anion⋯anion contacts (<3.60 Å).⁸ The overlap integrals among the lowest unoccupied molecular orbitals (LUMOs) of Ni(dmit)₂ suggest that the anions are strongly dimerized in layer A, whereas the anions in layer B are moderately dimerized and the overlap integrals along the stacking and diagonal directions (*b*, *p*, and *r* in Figure 1d) are

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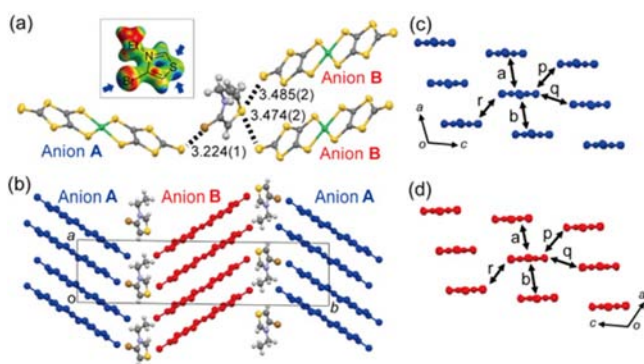


Figure 1. (a) Crystallographically independent cation and anions with short cation-anion distances (Å). The inset shows the calculated electrostatic potential of the Et-4BrT cation, in which arrows indicate σ holes where the electrostatic potential is higher than the other area.⁵ (b) View along the c axis. Anion arrangements viewed along the molecular long axis of anions A (c) and B (d). Overlap integrals among LUMOs ($\times 10^{-3}$) are as follows: (layer A) $a = -17.1$, $b = 0.15$, $p = -0.05$, $q = 0.41$, $r = 1.88$; (layer B) $a = 10.6$, $b = 3.96$, $p = -5.50$, $q = 0.46$, $r = -2.63$.⁸

comparable. The calculated band structure and Fermi surface of each layer indicate that, in both layers, the LUMO band consists of upper and lower branches separated by an energy gap due to dimerization of the anions and each lower band is half-filled (Figure S1 in the Supporting Information, SI). Layer A forms a narrow conduction band with a distorted, one-dimensional (1D) Fermi surface, and layer B constructs a two-dimensional (2D) conduction band with a wider bandwidth. These results indicate that (Et-4BrT)[Ni(dmit)₂]₂ is a *bilayer Mott system*, which was confirmed by measurement of the electrical and magnetic properties (vide infra). It should be emphasized that layer B is a rare example to form a 2D electronic structure because most Ni(dmit)₂ anion-radical salts with conventional stacking structures construct 1D electronic structures because of the b_{2g} symmetry of the LUMO.^{2a}

The temperature-dependent resistivity ρ of (Et-4BrT)[Ni(dmit)₂]₂ is shown in Figure 2a. The room temperature

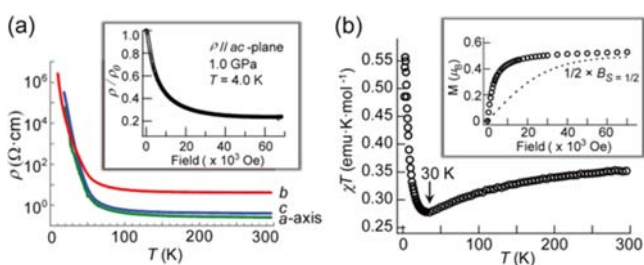


Figure 2. (a) Temperature versus resistivity ρ . ρ is measured along the a (green), b (red), and c (blue) axes. The inset shows magnetic field versus ρ/ρ_0 parallel to the ac plane. ρ_0 indicates resistivity without a magnetic field. (b) Temperature-dependent χT at 10 kOe. The inset shows a magnetization curve at 2 K and half of a Brillouin function for $S = 1/2$ ($B_{S=1/2}$: dotted line).

conductivity ($20 \text{ S}\cdot\text{cm}^{-1}$) is higher than that reported for the bilayer Mott salts (Et-2,5-DBrP)[Ni(dmit)₂]₂ and (Et-2I-5BrP)[Ni(dmit)₂]₂.^{3d} ρ increases gradually with a decrease in temperature from 300 to 60 K. This semiconducting behavior is consistent with the bilayer Mott insulating state of (Et-4BrT)[Ni(dmit)₂]₂. The ρ values along the a and c axes are almost the same and are smaller than that along the b axis, which

suggests 2D electrical character parallel to the ac plane (anion layer); thus, layer B has a main role in the conducting properties. This consideration is supported by a wider conduction bandwidth and a smaller energy gap in layer B than in layer A. Below 60 K, ρ increases abruptly. The activation energy E_a changes at ca. 60 K (from 5.8 to 34 meV) and at ca. 30 K (from 34 to 16 meV) (Figure S2a in the SI). The former change presumably corresponds to the AFM short-range ordering (SRO) of the spins in layer B, and the latter to the FM SRO of the spins in layer A, as discussed later.⁹ The application of pressure suppresses the upturn of ρ , and the system exhibits essentially metallic behavior down to 10 K at 1.4 GPa (Figure S2b in the SI).

The unique nature of (Et-4BrT)[Ni(dmit)₂]₂ is evident from the magnetic properties (Figure 2b). The χT behavior in the range of 40–300 K was analyzed using the Curie–Weiss law to afford a Curie constant C of $0.372 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ and a Weiss temperature θ of -18 K . The C value and room temperature magnetic susceptibility ($1.20 \times 10^{-3} \text{ emu}\cdot\text{mol}^{-1}$) indicate that one spin of $S = 1/2$ is localized on each [Ni(dmit)₂]₂⁻ unit. This result provides evidence of the bilayer Mott insulating state. The negative θ value suggests a dominant AFM interaction between the spins. Interestingly, χT exhibits a FM anomaly below 30 K and noticeable magnetic field dependence (Figure S3a in the SI). The FM anomaly is suppressed below 10 K with an increase in the magnetic field from 2 to 60 kOe, and the AFM behavior appears. Preliminary heat-capacity measurements indicate the absence of 3D magnetic long-range ordering (LRO) above 2 K (Figure S4 in the SI);¹⁰ therefore, FM and/or AFM SRO is expected to occur within the anion layers.¹¹ The magnetization (M) curve (M – H curve) at 2 K can be explained by the fact that, as discussed below, layer B forms AFM SRO and contributes negligibly to M , while layer A forms FM SRO and plays a dominant role in M (inset of Figure 2b).¹²

A single crystal of (Et-4BrT)[Ni(dmit)₂]₂ exhibits a single electron spin resonance (ESR) signal under a magnetic field parallel to the c axis. The signal intensity decreases abruptly below 30 K and finally disappears at 24 K, while ΔH_{pp} increases below 30 K (Figure S3b in the SI). These results indicate that the spins are strongly coupled to form a magnetically correlated state below 30 K, which clearly corresponds to the appearance of the FM anomaly in the SQUID measurement.

The g -value anisotropy of the ESR signal on the bc plane was investigated in an effort to elucidate which anion contributes to the FM anomaly at 30 K. The observed g value (g_{obs}) is related to the g value and magnetic susceptibility of anions A [g_A and $\chi_A(T)$] and B [g_B and $\chi_B(T)$] by eq 1.¹³

$$g_{\text{obs}}(T) = [g_A \chi_A(T) + g_B \chi_B(T)] / [\chi_A(T) + \chi_B(T)] \quad (1)$$

The single-crystal g -value anisotropy is coincident with the molecular g -value anisotropy of anion A,¹⁴ which corresponds to $\chi_B(T) \approx 0$ in eq 1 (Figure S5 in the SI). This result indicates that the ESR signal at 30 K originates from anion A, and thus the spins in layer A form FM SRO. In layer B, AFM SRO is presumably developed below ca. 60 K, as indicated by the decrease of g_{long} in Figure S5c in the SI as well as the change of ρ and E_a at this temperature.^{15,16} These magnetic studies indicate that (Et-4BrT)[Ni(dmit)₂]₂ is a new class of the bilayer Mott system that demonstrates two types of successive magnetic SRO. Coupling between the FM and AFM layers is, for example, widely used to shift the magnetization curve for spin valve devices,¹⁷ but such a structure was achieved on a molecular scale in the present material using supramolecular cation-anion interactions.

The FM interaction between the anions in layer A is interpreted by the spin polarization of the anion, in which intermolecular interaction through opposite spin density induces a net FM interaction.^{18,19} In layer A, FM interactions are expected for the *b*, *p*, and *r* interactions (Figure S6 in the SI for layer B). These FM interactions based on spin polarization compete with weak AFM interactions indicated by the small overlap integrals, and this eventually affords FM SRO. However, in layer B, the efficient overlap integrals with 2D electronic character lead to AFM SRO. It should be emphasized that (Et-4BrT)[Ni(dmit)₂]₂ is the first example of a molecular Mott system that exhibits FM spin interaction and that the mechanism for the FM interaction differs from that of Mott-type inorganic FM oxides, where exchange or superexchange interactions play a main role.

3D magnetic LRO is suppressed down to 1 K in (Et-4BrT)[Ni(dmit)₂]₂, where the spin degrees of freedom partially “survive”.¹⁰ We expect that, under such conditions, possible interlayer interaction results in intriguing physical properties, as observed in previously prepared bilayer salts.^{3a,d} Therefore, the magnetic-field- and pressure-dependent resistance parallel to the anion layers (*ac* plane) was measured. (Et-4BrT)[Ni(dmit)₂]₂ shows large negative magnetoresistance under 1.0 GPa, in which ρ decreases to one-fourth of the initial value ($\Delta\rho/\rho_0 \approx -75\%$) under 70 kOe (inset of Figure 2b).²⁰ Magnetoresistance is a key physical phenomenon in modern electronics and is applied in several electronic devices, such as in the read-and-write head of hard disk drives and in magnetic sensors. Such large magnetoresistance has been rarely found in molecular conductors.²¹ We expect that interaction between the charged carriers in layer B and the spins in the FM layer A play an important role in the magnetoresistance effect.²² Detailed studies are ongoing to elucidate the mechanism for large negative magnetoresistance.

In conclusion, a novel bilayer Mott system, (Et-4BrT)[Ni(dmit)₂]₂, was prepared. The coexistence of FM and AFM SRO layers achieves a FM anomaly and a large negative magnetoresistance effect. These results indicate that the development of bilayer systems by exploiting supramolecular cation⋯anion interactions is a promising approach to realizing unique electronic structures and physical properties.

■ ASSOCIATED CONTENT

Supporting Information

Present addresses of the authors, crystal data, band structures, and Fermi surfaces, ρ , χT , intensity of the ESR signal versus temperature, heat capacity, *g*-value anisotropy, and X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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See the Supporting Information.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) (a) Tamura, M.; Kato, R. *Sci. Technol. Adv. Mater.* **2009**, *10*, 024304. (b) Kanoda, K.; Kato, R. *Annu. Rev. Condens. Matter Phys.* **2011**, *2*, 167–188.
- (2) (a) Kato, R. *Chem. Rev.* **2004**, *104*, 5319–5346. (b) Cassoux, P. *Coord. Chem. Rev.* **1999**, *185–86*, 213–232. (c) Kato, R.; Tajima, A.; Nakao, A.; Tamura, M. *J. Am. Chem. Soc.* **2006**, *128*, 10016–10017.
- (3) (a) Kosaka, Y.; Yamamoto, H. M.; Nakao, A.; Tamura, M.; Kato, R. *J. Am. Chem. Soc.* **2007**, *129*, 3054–3055. (b) Fujiyama, S.; Shitade, A.; Kanoda, K.; Kosaka, Y.; Yamamoto, H. M.; Kato, R. *Phys. Rev. B* **2008**, *77*, 060403. (c) Hazama, K.; Uji, S.; Takahide, Y.; Kimata, M.; Satsukawa, H.; Harada, A.; Terashima, T.; Kosaka, Y.; Yamamoto, H. M.; Kato, R. *Phys. Rev. B* **2011**, *83*, 165129. (d) Kusamoto, T.; Yamamoto, H. M.; Tajima, N.; Oshima, Y.; Yamashita, S.; Kato, R. *Inorg. Chem.* **2012**, *51*, 11645–11654. (e) Kosaka, Y.; Yamamoto, H. M.; Tajima, A.; Nakao, A.; Cui, H.; Kato, R. *CryEngComm* **2013**, in press.
- (4) Imada, M.; Fujimori, A.; Tokura, Y. *Rev. Mod. Phys.* **1998**, *70*, 1039–1263.
- (5) The electrostatic potential is calculated at the B3LYP/6-31g(d) level of theory based on the density functional theory (DFT) method.
- (6) Crystal data for (Et-4BrT)[Ni(dmit)₂]₂ is shown in the SI.
- (7) (a) Murray, J.; Lane, P.; Politzer, P. *J. Mol. Model.* **2009**, *15*, 723–729. (b) Clark, T.; Hennemann, M.; Murray, J.; Politzer, P. *J. Mol. Model.* **2007**, *13*, 291–296.
- (8) The maximum interlayer overlap integral between the anions is 0.56×10^{-3} . Such a weak but nonnegligible interlayer interaction plays a crucial role in the observed negative magnetoresistance.
- (9) Low-temperature single-crystal XRD analysis revealed that this salt exhibits no structural transition down to 10 K.
- (10) As shown in Figure S4 in the SI, temperature-dependent $C_p T^{-1}$ shows a peak at 1 K that suggests magnetic LRO, which means that there is no 3D magnetic LRO above this temperature.
- (11) No crystal-axis anisotropy of χT and *M* was observed by the single-crystal SQUID measurement, suggesting the absence of 3D magnetic LRO.
- (12) It is noted that the *M*–*H* curve in the range of 0–20 kOe can be fitted by $^{1/2}B_S = 8$, suggesting that ca. 16 spins are strongly correlated to form a FM domain (cluster) in layer A at this temperature.
- (13) (a) Tomkiewicz, Y.; Taranko, A. R.; Torrance, J. B. *Phys. Rev. Lett.* **1976**, *36*, 751–754. (b) Iwasa, Y.; Mizuhashi, K.; Koda, T.; Tokura, Y.; Saito, G. *Phys. Rev. B* **1994**, *49*, 3580–3583.
- (14) Kirmse, R.; Stach, J.; Dietzsch, W.; Steimecke, G.; Hoyer, E. *Inorg. Chem.* **1980**, *19*, 2679–2685.
- (15) g_{long} is constant in the high-temperature region, where both anions A and B contribute to g_{long} , but decreases below 60 K (Figure S5c in the SI). This decrease reflects a decrease in the contribution from anion B, according to eq 1.
- (16) Because layer B plays a main role of the conducting property, changing the magnetic state in layer B should affect the observed conducting behavior.
- (17) Diény, B.; Speriosu, V. S.; Parkin, S. S. P.; Gurney, B. A.; Wilhoit, D. R.; Mauri, D. *Phys. Rev. B* **1991**, *43*, 1297–1300.
- (18) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.
- (19) The calculated spin-density distribution based on the DFT method [uB3LYP/6-31g(d) for C and S and /LANL2DZ for Ni].
- (20) This salt maintains the Mott insulating state under 1.0 GPa.
- (21) (a) Hanasaki, N.; Matsuda, M.; Tajima, H.; Ohmichi, E.; Osada, T.; Naito, T.; Inabe, T. *J. Phys. Soc. Jpn.* **2006**, *75*, 033703/1–033703/4. (b) Komatsu, H.; Matsushita, M. M.; Yamamura, S.; Sugawara, Y.; Suzuki, K.; Sugawara, T. *J. Am. Chem. Soc.* **2010**, *132*, 4528–4529. (c) Matsushita, M. M.; Kawakami, H.; Sugawara, T.; Ogata, M. *Phys. Rev. B* **2008**, *77*, 195208-1–195208-6.
- (22) As the magnetic field is increased, all of the spins in layer A tend to align parallel to the field direction, which reduces scattering of the carriers. Eventually, the resistivity decreases upon increasing magnetic field.