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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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···S interactions and S···S 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 (Δρ/ρ₀ ≈ −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 crystallographically independent M(dmit)2 anions 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.3,4,5

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 (nBu4N) [Ni(dmit)2] (4.5 mg) with (Et-4BrT)·BF4 (45 mg) as the supporting electrolyte in acetonitrile–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···S short contacts (<3.60 Å) are detected, in addition to a Br···S halogen bond. The lone pair on the thioketone moiety in the anion B points toward the surface area of 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···S 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]2+.8

The anion layers are isolated from each other by the cation layer 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...
The unique nature of \((\text{Et-}4\text{BrT})[\text{Ni(dmit)}_2]_2\) is evident from the magnetic properties (Figure 2b). The \(\chi T\) behavior in the range of 40–300 K was analyzed using the Curie–Weiss law to afford a Curie constant \(C = 0.372\) emu K mol\(^{-1}\) and a Weiss temperature \(\theta = -18\) K. The \(C\) value and room temperature magnetic susceptibility \((1.20 \times 10^{-5}\) emu mol\(^{-1}\)) indicate that one spin of \(S = \frac{1}{2}\) is localized on each \([\text{Ni(dmit)}_2]^{2+}\) unit. This result provides evidence of the bilayer Mott insulating state. The negative \(\theta\) value suggests a dominant AFM interaction between the spins. Interestingly, \(\chi T\) 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 \((\text{Et-}4\text{BrT})[\text{Ni(dmit)}_2]_2\) 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 \(\Delta H_{\text{pp}}\) 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 \((g_{\text{obs}})\) 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.\(^{13}\)

\[
g_{\text{obs}}(T) = \frac{g_A\chi_A(T) + g_B\chi_B(T)}{\chi_A(T) + \chi_B(T)}
\]

The single-crystal g-value anisotropy is coincident with the molecular g-value anisotropy of anion A,\(^{14}\) which corresponds to \(\chi_A(T) \approx 0\) 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 \(g_{\text{obs}}\) in Figure S5c in the SI as well as the change of \(\rho\) and \(E_g\) at this temperature.\(^{15,16}\)

These magnetic studies indicate that \((\text{Et-}4\text{BrT})[\text{Ni(dmit)}_2]_2\) 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. 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\(\text{dmit}\)\]$_2$ 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\(\text{dmit}\)\]$_2$, where the spin degrees of freedom partially “survive.” We expect that, under such conditions, possible interlayer interaction results in intriguing physical properties, as observed in previously prepared bilayer salts. Therefore, the magnetic-field- and pressure-dependent resistance parallel to the anion layers (ac plane) was measured. (Et-4BrT)\[Ni\(\text{dmit}\)\]$_2$ shows large negative magnetoresistance under 1.0 GPa, in which $\rho$ decreases to one-fourth of the initial value ($\Delta \rho/\rho_0 \approx −75\%$) under 70 kOe (inset of Figure 2b). 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. 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. Detailed studies are ongoing to elucidate the mechanism for large negative magnetoresistance.

In conclusion, a novel bilayer Mott system, (Et-4BrT)\[Ni\(\text{dmit}\)\]$_2$, was prepared. The coexistence of FM and AFM SRO layers achieves a FM anomaly and a large negative magnetoresistance. Therefore, the mechanism for large negative magnetoresistance is elucidated by exploiting supramolecular cation--anion interactions as 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, $\rho$, $\chi T$, 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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