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Influence of Magnetic Field upon the Conductance of a Unicomponent Crystal of a Tetrathiafulvalene-Based Nitronyl Nitroxide

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Spintronics, which utilizes not only the charge but also the spin of an electron, has received much attention because of its potential applications in next-generation electronics systems.[1] To achieve this goal, a firm understanding of spin-polarized molecular materials must be established. However, molecular crystals of organic radicals are Mott insulators because of their large on-site Coulomb repulsion, despite the presence of a singly occupied molecular orbital (SOMO). When radicals are partially doped to achieve a mixed-valence state, the unpaired electron of the radical becomes oxidized, forming a spinless cationic species. Therefore, a special electronic structure is required for constructing conductive organic radical crystals. In this regard, we have developed a "spin-polarized donor" in which one-electron oxidation occurs from the HOMO rather than the SOMO, giving rise to a ground-state triplet diradical cation, because of the cross-conjugation between these π-radical and π-donor units (Figure 1).[2] Recently, it was found that a diselena-analogue of the tetrathiafulvalene (TTF)-based spin-polarized donor **ESBN** afforded an ion radical salt of **ESBN**$_2$ClO$_4$ through electrocrystallization. This salt represents the first coexisting system of conductivity and magnetism derived from organic spins without inorganic magnetic ions.[3] Such a donor radical could be a building block for molecular-based spintronic devices if a neutral crystal without counterions manifests interactive conductivity and magnetism upon carrier injection through electrodes. For the present study, we designed and prepared a donor radical consisting of a dibrominated benzo-TTF containing a nitronyl nitroxide (NN) group, 2-[2-(4,5-dibromo-[1,3]dithiol-2-ylidene)-1,3-benzodithiol-5-yl]-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (**BTBN**; Figure 2), by introducing two bromine atoms into the dithiole ring to increase the intermolecular interactions within its crystal (see section SI 1 in the Supporting Information).[4] We found that the unicomponent neutral crystal of **BTBN** was conductive upon hole injection from electrodes, even at low temperatures, and that the conductance of the crystal could be controlled by the application of an external magnetic field.

A differential-pulse voltammogram of **BTBN** measured in benzonitrile in the presence of 0.1 M tetrabutylammonium perchlorate showed redox potentials at 0.82, 0.90, and 1.16 V versus Ag/AgCl. The first and third of these potentials were derived from the donor unit, and the second potential originated from the NN group. Therefore, these data suggest that **BTBN** does indeed possess a spin-polarized electronic structure (section SI 2).[2]

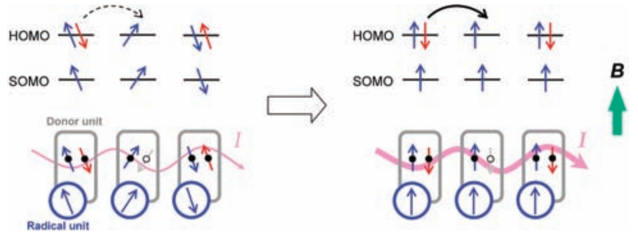

Figure 1. Plausible mechanism for the increase in the conductance of **BTBN** by the application of an external magnetic field.

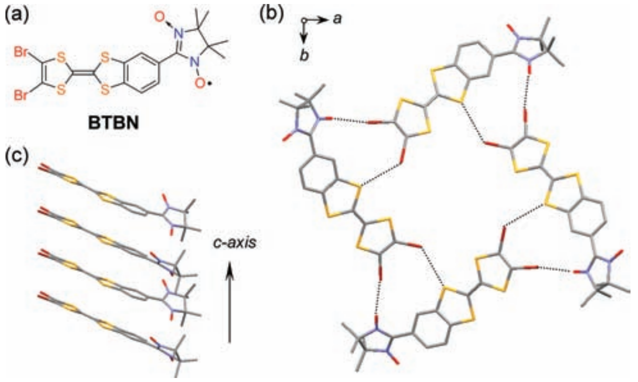

Figure 2. Crystal structure of **BTBN**. (a) Structural formula of **BTBN**. (b) Molecular arrangement viewed along the c axis. (c) Columnar stack along the c axis.

BTBN afforded needle crystals, and its crystal packing is characterized as follows (Figure 2 and section SI3). Four **BTBN** molecules are arranged in a square-like manner with the long molecular axes orthogonal to each other, and the tetrameric **BTBN** units are piled up along the c axis with an interplanar distances of ~3.46 Å. To avoid steric repulsion, the planar donor planes overlap in an inverted manner, placing the NN groups on alternate sides (left or right) of the molecules. Neighboring stacks are connected with close Br···S contacts of ~3.6 Å between one of the bromine atoms of the dithiole ring and a sulfur atom of the benzodithiole ring in the adjacent stack. Each remaining bromine forms a Br···O contact of ~3.0 Å with the oxygen atom of the O−N unit in the NN group of a neighboring molecule. Such a close contact between an O−N unit and a halogen atom has also been observed for crystals of some nitroxide derivatives.[5] Notably, the planar stacking of the donor units in the **BTBN** neutral crystals is appropriate for the conduction of π electrons.

The temperature dependence of the magnetic susceptibility of **BTBN** (Figure S4) was well-explained by a structure involving one-dimensional ferromagnetic chains along the c axis having intrachain interactions with $J_{\mathrm{intra}}/k_B = 6.5$ K and weak antiferromagnetic interchain interactions with $J_{\mathrm{inter}}/k_B = -1.1$ K, where the number of neighboring chains is $z = 2$.[6] The Curie constant (χT) was 0.375

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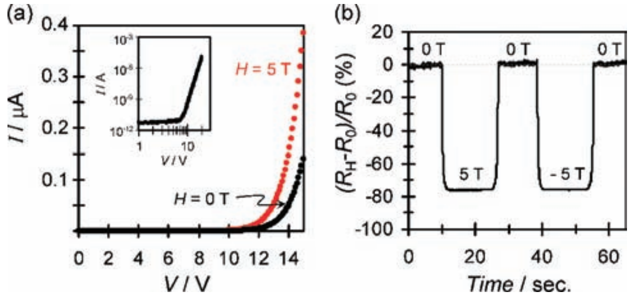

Figure 3. (a) $I-V$ characteristics of **BTBN** at 2 K. Inset: plot of log I vs log V. (b) Magnetoresistance of **BTBN** at 2 K under an applied magnetic field of 5 T. A negative value of the magnetic field corresponds to the direction antiparallel to the previous magnetic field.

emu K mol^{-1} at 290 K. The observed ferromagnetic interaction may be derived from the overlap between NN groups along the chain: the O−N unit of the NN group is close to the central carbon atom of the NN group of an adjacent molecule.

Reflecting the black color of the crystal, the charge-transfer band of a polycrystalline sample extended over to ~1400 cm^{-1} (7100 nm; the band edge was estimated to be ~0.17 eV), suggesting the presence of a narrow gap between the valence and the conduction bands (Figure S5). As a result, the room-temperature conductivity of the neutral single crystal of **BTBN** was as high as 9×10^{-4} S cm^{-1}, as measured by a four-probe method. However, since the neutral crystal was a semiconductor with an activation energy of ~0.28 eV, the degree of resistance of the crystal exceeded the lower limit of the measurement at temperatures below 240 K.

We then fabricated the microcrystalline sample of **BTBN** on interdigitated electrodes with a gap of 2 μm to measure the conductance of crystals at lower temperatures. A field-emission scanning electron microscopy image showed that the thin fabricated layer consisted of needlelike microcrystals with an average length of 13 ± 8 μm. We found that the current−voltage ($I-V$) characteristics of the sample exhibited a distinct nonlinear dependence, particularly when high electric fields were applied to the sample, as shown in Figure 3a. At lower bias voltages, the detected current was very low, but the nonlinear current increased abruptly when the bias voltage exceeded a certain threshold voltage (~8 V at 2 K). This nonlinear $I-V$ characteristic was rationalized in terms of the space-charge-limited conduction (SCLC) mechanism, and the current was driven by carrier injection from the electrode. The situation is similar to the charge transport that takes place in organic electroluminescent devices (section SI 6).[7]

The effect of an external magnetic field on the resistance of **BTBN** microcrystals was measured at a bias voltage of 10 V ($E = 5 \times 10^4$ V cm^{-1}) by applying a magnetic field between −5 and 5 T. The resistance of the sample decreased upon application of a magnetic field at temperatures below 30 K, and the sample exhibited *negative* magnetoresistance of $(R_H - R_0)/R_0 = -76\%$ at 2 K under 5 T (Figure 3b). The temperature at which the magnetoresistance appears, ~30 K, corresponds to the degree of interaction between the conduction electrons and the organic localized spins.[8] When the **BTBN** crystal is hole-doped through the positive electrode, the conduction electrons, which itinerate along the columnar donor stack, are scattered by the thermally fluctuating paramagnetic spins of the radical sites. As the external magnetic field increases, the localized spins align parallel to the external field. Thereafter, on the basis of the double-exchange mechanism, only a conduction electron of the opposite spin can be transferred (Figure 1). Hence, the resistance of the crystal decreases at temperatures lower than 30 K. A control experiment using crystals of the nonradical acetal precursor of **BTBN** exhibited nonlinear conductance attributable to the SCLC mechanism, but the magnetoresistance observed in that case was *positive* (+1.5% at 2 K under 5 T; see section SI 7).

In summary, we have found that unicomponent crystals of **BTBN** become conductive through the injection of holes from an electrode even at low temperatures and that the conductance of the sample is controllable by the external magnetic field at temperatures lower than 30 K. Since the appearance temperature of this magnetoresistance, which is determined by the intramolecular ferromagnetic coupling between unpaired and conduction electrons, is expected to be elevated because of the appropriate molecular design, these findings should be valuable in the development of molecule-based spintronic devices.

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Supporting Information Available: Materials and methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The magnetic field dependence of the magnetoresistance of **BTBN** was appreciably stronger than that of the previously reported compound (Figure S8). This difference presumably occurred because the conduction electrons in **BTBN** interacted with a cluster of ferromagnetically coupled spins of the one-dimensional chain ($J_{intra}/k_B = 6.5$ K), even at lower magnetic fields.

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