Negative Magneto-resistance Observed on an Ion-radical Salt of a TTF-based Spin-polarized Donor

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A novel diselena analogue of TTF-based spin-polarized donor was synthesized. An ion-radical salt of the donor electro-crystallized on an interdigitated electrode with 2 µm gap showed negative magneto-resistance below 15 K. This is the first example detecting the interaction between localized spin and conducting electron in a genuine organic system.

Coexistence of magnetism and conductivity has drawn considerable interest in materials science.[1] The exchange interaction between a localized spin and a conduction electron leads to various characteristic properties, such as magneto-resistance, Kondo-effect, etc. However, preceding molecule-based materials exhibiting distinct magneto-resistance are limited to d–π interacting molecular conductors composed of a π-organic donor and a magnetic metal ion with a spin or spins in d orbital(s).[2] Construction of a genuine organic system with magnetic interaction between a localized spin and a conduction electron, both of which reside in π-orbitals, has been left as an open question in the field of molecular magnetism.[3,4]

In order to endow a donor radical with a spin-polarized electronic structure,[5] we synthesized TTF-based spin-polarized donors,[6,7] and the magneto-conducting property was studied extensively. Among them, the ion-radical salt of **ETBN** [**(ETBN)**$_2$ClO$_4$] (Chart 1) has become the first example as a genuine organic paramagnetic conductor.[7] However, experimental evidence for the exchange interaction between a localized spin and conduction electrons in this ion-radical salt was not available because of the relatively high activation energy of the ion-radical ($\sigma_{\mathrm{RT}} = 1 \times 10^{-2}$ S·cm^{-1}, $E_{\mathrm{a}} = 0.16$ eV).

In this study, we designed and prepared **ESBN**[8] as a diselena-analogue of **ETBN**. Introduction of heavier chalcogen atoms may increase the overlap among donor planes due to the better contact between chalcogen–chalcogen atoms. Besides, in order to decrease the overall resistance of its ion-radical salt, an interdigitated electrode was applied to the transport measurement of the salt. By virtue of these experimental improvements, here we found the coexistence of conductivity and magnetism in the genuine organic ion-radical salt of **ESBN** for the first time.

The cyclic voltammogram in benzonitrile showed three oxidation waves at 0.76, 0.93, and 1.12 V vs Ag/AgCl: the first wave is assigned to the oxidation process of the donor unit. The ESR spectrum of the singly oxidized **ESBN** in a frozen THF solution gave rise to the ground state triplet species ($|D|/hc = 2.5 \times 10^{-2}$ cm^{-1}, $|E|/hc = 1.8 \times 10^{-3}$ cm^{-1}), confirming the spin-polarized electronic structure. Electro-crystallization of **ESBN** in 1,1,1-trichloroethane containing 5% THF and 0.1 M n-Bu$_4$N·ClO$_4$ afforded an ion-radical salt as black needles. The magnetic susceptibility measurement of the salt showed paramagnetic behavior with Curie constant of 0.75 emu·K·mol^{-1} for the composition of **(ESBN)$_2$ClO$_4$** with a weak antiferromagnetic interaction ($\theta = -2.5$ K). The fact that only two paramagnetic spins are present per unit indicates that the generated π-spins on the π-donor moiety is converted to a conduction electron, pairing tightly with each other in the staking column, while localized spins are left intact. The ion-radical salt showed the activation-type conducting behavior ($\sigma_{\mathrm{RT}} = 6 \times 10^{-4}$ S·cm^{-1}, $E_{\mathrm{a}} = 47$ meV) in the transport measurement (Figure 1), but it is notable that the activation energy of the salt is much smaller than that of **(ETBN)$_2$ClO$_4$**. Thus, the obtained salt showed both conductivity and magnetic property as in the case of the **ETBN** salt.

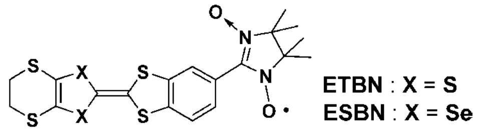

Chart 1.

To decrease the overall resistance of the salt, an interdigitated electrode (IDE) with a gap of 2 µm, which was formed by a platinum plate with the 100-nm thickness on a quartz glass, was used for the low-temperature measurement (Figures 2a and 2b). The electro-crystallization of **ESBN** using IDE as an anode also afforded the ion-radical salt (Figure 2c).

The FE-SEM image showed that the grown crystals with a length of ca. 10 µm bridged several teeth of IDE. The electron dispersion X-ray spectroscopy (EDS) confirmed the composition of the micro-crystal to be **(ESBN)$_2$ClO$_4$** on the basis of the ratio of Se, S, and Cl elements.[9] It was found that the transport behavior of micro-crystals on IDE could be measured down to 10 K as expected (Figure 1 inset).

The effect of an external magnetic field on the resistance of the crystal was examined by applying a field to the parallel direction in reference to the conducting path of the crystal (perpendic-

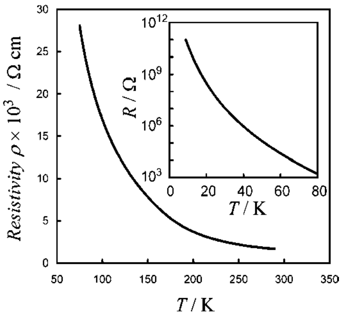

Figure 1. Temperature-dependent transport behavior of a crystalline sample of **(ESBN)$_2$ClO$_4$** and of micro-crystals on an interdigitated electrode (inset).

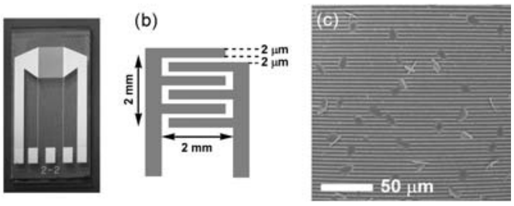

Figure 2. Optical microscopic image (a) and a schematic drawing (b) of an interdigitated electrode. (c) FE-SEM image of micro-crystals of **$(ESBN)_2ClO_4$** on an interdigitated electrode (JEOL JES-6700F, ×500, 10 kV, WD: 8 mm).

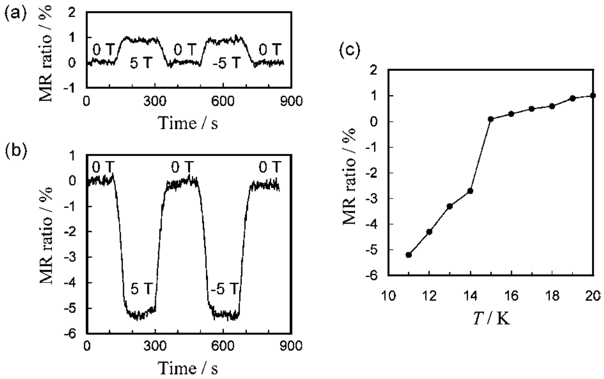

Figure 3. Magneto-resistance of micro-crystals of **$(ESBN)_2ClO_4$** on an interdigitated electrode. Relative magneto-resistance $[(R_{5T} - R_{0T})/R_{0T}]$ at 20 K (a), 11 K (b), and its temperature dependence under the applied magnetic field of 5 T (c).

ular to the tooth) to eliminate the contribution of Lorentz force. The resistance of the sample turned out to be decreased under application of 5 T at 11 K, exhibiting 5% of the negative magneto-resistance, whereas the same sample showed small positive magneto-resistance (ca. 1%) at 20 K (Figures 3a and 3b). When the ratio of the magneto-resistance was plotted against temperatures, the negative magneto-resistance appeared below 15 K as shown in Figure 3c. Since the ratio and the sign of the magneto-resistance did not change by changing the direction of the magnetic field, the magneto-resistance should be the intrinsic nature of this sample.

The above results may be interpreted as follows. Although the conduction electrons along the π-staking will be scattered when the direction of localized spins is random, the scattering of the conduction electron should be suppressed when the localized spins align under a magnetic field. The fact that the sign of the magneto-resistance changed at 15 K means that the exchange interaction (J) between the localized spin and the conduction electron is approximately the same magnitude as the thermal energy at 15 K. This value seems to be too low in reference to the spin–spin interaction observed in the isolated cation diradical salt of a radical-donor with the similar electronic structure.[10] However, it does not conflict with the our result because the conduction electrons are shared by π-staking molecules. The detailed mechanism of the magneto-resistance has to be awaited until ongoing experiments including the determination of the crystal structure have been completed.

Recently, several intriguing investigations on the negative magneto-resistance in organic materials, such as highly doped polyacetylene,[11a] 2-dimensional organic conductors,[11b] and thin film of oligothiophene[11c] were reported. Since these materials do not carry any localized spins, the mechanism of magneto-resistance in these materials must be different from the current case: the magneto-resistance in these materials may be derived from a direct effect of an external magnetic field on the conducting carriers.

In summary, we have detected the negative magneto-resistance in the ion-radical salt of the spin-polarized donor (**ESBN**). Although we have reported the similar result on the network of spin-polarized wire molecules connecting gold nanoparticles,[12] this is the first example of the coexistence system of a localized spin and a conducting electron in the genuine organic system.

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8 Preparation and characterization of **ESBN** are described in Supporting information, which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

9 EDS measurement was carried out using JEOL JED-2200 EDS detector carried by JES-6700F FE-SEM (20 kV). The atomic ratios were determined by the averaged values over 20 pieces of micro crystals: S/Se = 2.02(10); Cl/Se = 0.24(2); Cl/S = 0.12(1). Calcd. for $(ESBN)_2ClO_4$ ($C_{38}H_{38}ClN_4O_8S_8Se_4$): S/Se = 2; Cl/Se = 0.25; Cl/S = 0.125.

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