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Molecule-based system with coexisting conductivity and magnetism and without magnetic inorganic ions

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An ion-radical salt, $(ESBN)_2ClO_4$, obtained from the electrochemical crystallization of an organic donor radical, ESBN, exhibited giant negative magnetoresistance (−70% at 2 K in 9 T) in spite of the absence of metal ions. Furthermore, it was found that the conductivity of $(ESBN)_2ClO_4$ was characterized by a distinct nonlinear temperature dependence and a nonlinear power law of $I \propto V^n$ $(n=12)$. We speculated that such correlated spin-dependent electron transportation is derived from the charge-ordered electronic structure and the strong intramolecular ferromagnetic coupling between π-conduction electrons and π-localized spins in the "spin-polarized donor."

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I. INTRODUCTION

The interplay between magnetic and conducting properties is a key issue in materials science.[1–3] The establishment of a coexisting system of conductivity and magnetism in genuine organic materials is indispensable for developing molecule-based spin-electronic devices. Molecule-based conductors containing magnetic counter ions with a $p\pi$-$d\pi$ interaction between the conduction electrons and localized spins have provided a new class of materials, including paramagnetic[4–6] or ferromagnetic metals,[7] paramagnetic[8] or antiferromagnetic superconductors,[9] and field-induced superconductors,[10] by using (bisethylenedithiotetrathiafulvalene) ET- or (bisethylenedithiotetraselenafulvalene) BETS-based donors. Hitherto, a strategy to construct a molecule-based material with conductivity and magnetism has been limited to the introduction of inorganic magnetic ions into molecular conductors.[4–11] On the other hand, a coexisting system of conductivity and magnetism with an intramolecular ferromagnetic $p\pi$-$p\pi$ interaction that uses a donor radical without magnetic ions has scarcely been explored.[12–14] Although numbers of paramagnetic semiconductors have been prepared by introducing a stable radical unit into the cation radical salts of (tetrathiafulvalene) TTF-based donors as a substituent, the significant interaction between conductivity and magnetism has not been recognized.[15–20] This is because of the lack of an appropriate π conjugation to induce the effective exchange interaction between the conduction electrons and localized spins in these examples. Meanwhile, the negative magnetoresistance of thin films made of π-conjugated molecules without unpaired electrons has been reported.[21–24] However, it originates from a totally different mechanism. Namely, it is caused by the magnetic field effect on the recombination of electrons and holes that are separately injected from the positive and negative electrodes.

To realize the $p\pi$-$p\pi$ spin-transportation coexisting system, we prepared a spin carrying donor molecule, ESBN, which is a diselena analog of BenzoTTF carrying nitronyl nitroxide (NN) in a cross-conjugating manner, and obtained its mixed-valence salt, $(ESBN)_2ClO_4$. The magnetic property of this salt was characterized as a paramagnet (Curie constant of 0.75 emu K mol^{-1}) with a weak antiferromagnetic interaction of $q=-2.5$ K, while its conductivity exhibited a thermally activating behavior. Interestingly, the interaction between the conduction electrons and organic localized spins in $(ESBN)_2ClO_4$ was detected by a preliminary magnetoresistance measurement. In order to more precisely investigate this conductivity and the magnetism coexisting system involving a $p\pi$-$p\pi$ spin-dependent transport, we carried out magnetoresistance measurements down to 2 K by applying an external field of up to 9 T. We also measured the temperature dependence of conductivity and nonlinear I-V characteristics in a wide temperature range (2–300 K). Here, we report a detailed description on the first molecule-based coexisting system of conductivity and magnetism without inorganic magnetic ions on the basis of the intramolecular $p\pi$-$p\pi$ interaction between π-conducting electrons and π-localized spins. It was found that the ion-radical salt of a spin-polarized donor, $(ESBN)_2ClO_4$,[25] exhibits a giant negative magnetoresistance (−70% at 2 K in 9 T), together with a distinct nonlinear temperature dependence and a nonlinear power law of $I \propto V^n$ $(n=12)$. The implication of the experimental results on the strongly correlated electronic structure of $(ESBN)_2ClO_4$ is discussed on the basis of the characteristic electronic structure of ESBN.

II. EXPERIMENT

The synthesis of the spin polarized donor, ESBN, was reported elsewhere.[25] The ion-radical salt of ESBN, $(ESBN)_2ClO_4$, was obtained by electrocrystallization of ESBN in 1,1,1-trichloroethane containing 5% THF in the presence of 0.1M n-$Bu_4N \cdot ClO_4$. For this salt, the magnetic field dependence of magnetization and the temperature dependence of magnetic susceptibility were measured by a superconducting quantum interference device magnetometer

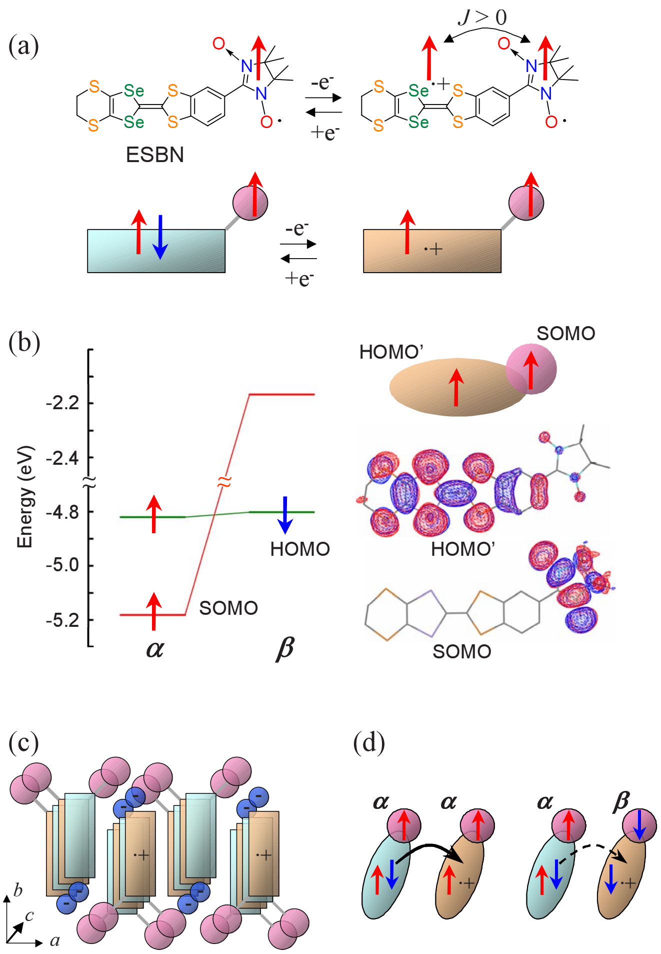

FIG. 1. (Color online) (a) Schematic of the generation of ground-state triplet cation-diradical species of ESBN upon one-electron redox process at the donor moiety. (b) Spin polarized energy diagram of ESBN calculated by a DFT method (B3LYP/6-31G*) and schematic of the space sharing nature of HOMO′ and SOMO. HOMO′ is derived from one-electron oxidation of HOMO. (c) A plausible molecular-packing structure in the $(\mathrm{ESBN})_2\mathrm{ClO}_4$ crystal. (d) Plausible spin-dependent electron transfer in the ESBN/ESBN^+ dimer.

(Quantum Design MPMS-5XL) in the temperature range of 2–300 K and the magnetic field range of 0–5 T.

A conductivity measurement was carried out on a single crystal of $(\mathrm{ESBN})_2\mathrm{ClO}_4$ ($\sim 0.5 \times 0.1 \times 0.02$ mm^3), which was placed on interdigitated Au electrodes and fixed with a paraffin paper. Here, the geometry of the Au electrodes is as follows: The thickness is 100 nm with 5 nm Ti as the adhesive layer, the gap is 2 μm, the electrode width is 2 μm, and the area is 2×2 mm^2 and is fabricated on a quartz substrate sized 5×10 mm^2. Since the crystal has a length of ~ 0.5 mm, it bridged more than 100 teeth of the interdigitated electrodes. The electrode chip was set on a homemade sample holder that was placed in a Quantum Design Physical Property Measurement System (PPMS) cryostat equipped with a superconducting 9 T magnet. A Keithley 6487 picoammeter, which has an internal voltage source, was used to apply constant voltages on the sample and to detect the current through the sample. The temperature dependence of resistance was measured in the temperature range of 2–300 K at constant bias voltages (1–10 V). Current-voltage characteristics were measured at temperature-stabilized conditions. The magnetotransport measurement was also carried out by using the same apparatus under applying magnetic field (−9–9 T) to the parallel direction in reference to the passing current (perpendicular to the tooth), which corresponds to the long crystal axis.

In this study, transport measurements were carried out in the constant voltage mode because the constant current method is not suitable to the present sample with a thermally activating behavior. If the constant current method is used, the voltage on the sample rapidly increases with decreasing temperature, and thus, the resistance of the sample would be influenced by Joule heating.

III. RESULTS

A. Electronic structure of spin-polarized donor (ESBN)

It is worthwhile to first describe the electronic structure of ESBN. As shown in Fig. 1(b), coefficients of the singly occupied molecular orbital (SOMO) are localized on the NN group, while those of the highest occupied molecular orbital (HOMO) are spread over the entire molecule, extending to the NN group. Thus, the space-sharing nature of the relevant molecular orbitals (MOs) guarantees sufficient exchange interactions between the π spins in SOMO and HOMO. The exchange interaction J is estimated as $2J = \sim 200$ K by using B3LYP/6-31G*. Due to this exchange interaction, the π electrons in HOMO feel an exchange field from the π-localized spin in SOMO, and when the SOMO electron has an up spin (α), the highest occupied orbital becomes the down-spin electron (β) in the HOMO, as shown in Fig. 1(b), in a spin-unrestricted description wherein the wave functions of α and β spins are separately expressed. Furthermore, upon one-electron oxidation, the ground state of a cation-diradical species becomes a triplet, as shown in Fig. 1(a).[26–30]

B. Conducting behavior of $(\mathrm{ESBN})_2\mathrm{ClO}_4$ salt

Figure 2(a) shows the temperature dependence of the resistance with an applied voltage of 1 V. As evident from the log R–log T plot in Fig. 2(a), the resistance R is proportional to T^{-7} in a wide temperature range from 300 to 50 K. The origin of this unusual T dependence is not clear at this stage.

Note that the resistance was fitted by the Arrhenius plot in a previous study,[25] and the activation energy was evaluated as $E_a = 47$ meV. However, in the present study, the resistance was measured in the constant voltage mode in a wide range of temperature, and we found that the temperature dependence of resistance could not be fitted by either an Arrhenius model or a variable-range-hopping model.

Figure 2(b) shows the I-V characteristics of $(\mathrm{ESBN})_2\mathrm{ClO}_4$ at various temperatures. One can see distinct nonlinear I-V characteristics at 2 K in the range from 0.1 to 10 V. This nonlinear response becomes evident when $V > 4.5$ V, obeying a power law of $I \propto V^n$ ($n = 12$). The power n gradually decreases from $n = 12.0 \pm 0.5$ at 2 K to $n = 1.4 \pm 0.03$ at 280 K. When 10 V is applied to the crystal across a distance of 2 μm, the applied voltage per molecule is ~ 2 mV, assum-

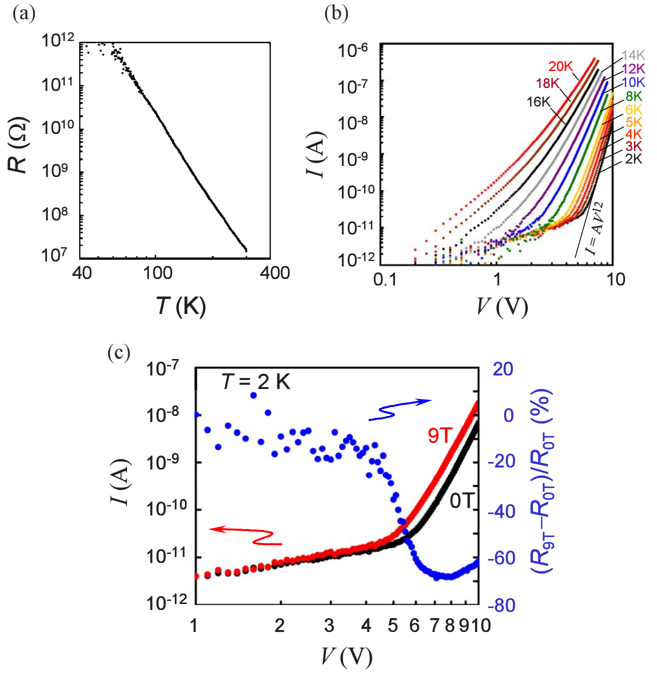

FIG. 2. (Color online) (a) Temperature dependence of the resistance of $(ESBN)_2ClO_4$ at a bias voltage of 1 V. (b) Nonlinear current-voltage characteristics of $(ESBN)_2ClO_4$ at various temperatures. (c) Magnetic field dependence of the current-voltage characteristics at 2 K, together with the voltage dependence of the ratio of negative magnetoresistance.

ing that the depth of the donor radical is 0.4 nm. Since this applied voltage per molecule does not exceed the activation energy for electron migration, the observed nonlinear *I-V* characteristics cannot originate from a Zener breakdown.

C. Magnetotransport properties of $(ESBN)_2ClO_4$ salt

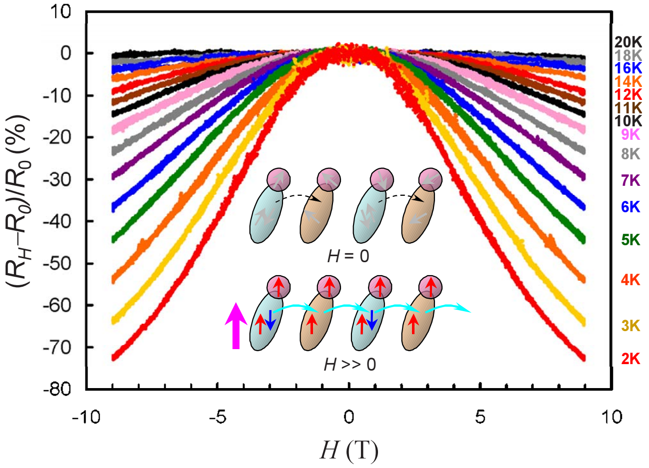

FIG. 3. (Color online) Magnetic field dependence of magnetoresistance of $(ESBN)_2ClO_4$ at various temperatures at a bias voltage of 7 V.

The magnetoresistance of $(ESBN)_2ClO_4$ salt was measured in a single crystal mounted on the interdigitated Au electrodes with a constant bias voltage of 7 V by applying a magnetic field between −9 and 9 T along the parallel direction to the current to suppress the effect of Lorentz force. As shown in Fig. 3, the resistance decreased with increasing magnetic field strength. Here, R_H is the resistance under the magnetic field and R_0 is the resistance at 0 T. Surprisingly, the ratio of the magnetoresistances, $(R_H-R_0)/R_0$, reached −70% under 9 T at 2 K.

As shown in Fig. 4, the magnetic-field dependence of the resistance of $(ESBN)_2ClO_4$ at 2 K is proportional to the square of the magnetization. Therefore, the magnetoresistance reflects the gradual magnetization response of an organic radical (SOMO) with $s=1/2$ to the applied field. We think that the scattering of the conduction electron is suppressed when the localized spins are aligned in the magnetic field. This shows the interplay between π-conduction electrons and π-localized spins. As shown in Fig. 5, the absolute value of $(R_H-R_0)/R_0$ at 9 T monotonously decreased with increasing temperature and it became almost negligible at 20 K. These data indicate that the degree of the exchange interaction between organic localized spins and conduction electrons is ∼20 K, which is smaller than the intramolecular $J(2J\sim 200\text{ K})$ of the cation diradical of $ESBN^+$. This difference can be understood from the fact that the hole is delocalized over several molecules in the ion-radical salt. However, the ratio of negative magnetoresistance of ordinary magnetic metals is several percent at most. Hence, the mechanism of the large magnetoresistance observed in the current salt should be considered.

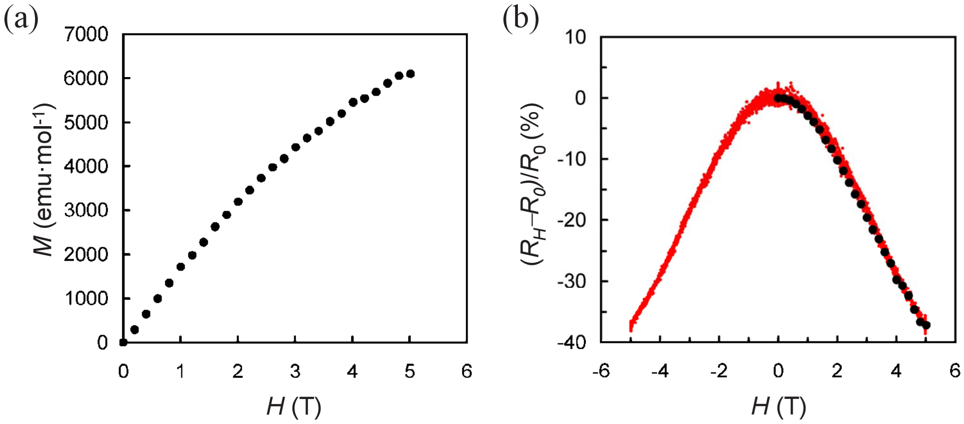

FIG. 4. (Color online) (a) Magnetic field dependence of magnetization of $(ESBN)_2ClO_4$ at 2 K. (b) Magnetic field dependence of magnetoresistance of $(ESBN)_2ClO_4$ at 2 K at a bias voltage of 10 V (red points). The black dots represent the square of the magnetization in (a) with an adjustable prefactor. The field-dependent profile of magnetoresistance can be well reproduced by the square of the magnetization.

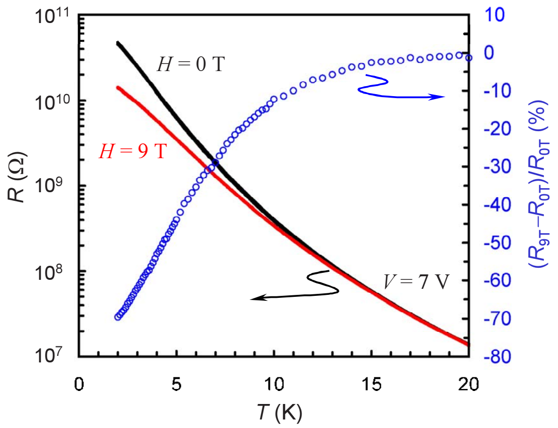

FIG. 5. (Color online) Temperature dependence of magnetoresistance of $(ESBN)_2ClO_4$ at 9 T at a bias voltage of 7 V.

IV. DISCUSSIONS

Let us first discuss the origin of the observed giant negative magnetoresistance in $(ESBN)_2ClO_4$. On the basis of the composition of salt, the conduction column consists of an alternate stack of the singly oxidized spin-polarized donor and the neutral one [Fig. 1(c)]. When the localized spin in SOMO is an up spin (α), the down spin (β) in HOMO tends to be transferred to the adjacent molecule. However, this process is prohibited if the localized spin of the adjacent molecule is down spin, as shown in Fig. 1(d). This mechanism is equivalent to a double-exchange interaction. However, the double-exchange mechanism is based on a metallic band picture and it cannot be applied to our salt because the resistivity is extremely high at temperatures lower than 20 K, at which a negative magnetoresistance is observed.

Alternatively, we can speculate that the electron transport in $(ESBN)_2ClO_4$ is due to a cascade of electron transfer processes between adjacent molecules. In this case, we can assume a paramagnetic state of the localized spins at $H=0$ T and a perfect alignment in $H\rightarrow\infty$ limit. As a result, the maximum value of the negative magnetoresistance should be -50%, although the quantum mechanical interaction between adjacent spins is neglected. However, the observed magnetoresistance amounted to -70% at 2 K and 9 T; furthermore, the magnetization was not saturated even at 2 K. This means that the cascade mechanism is also not applied to our salt.

It is to be noted that the large negative magnetoresistance appeared in the nonlinear conduction region. In fact, $(R_H - R_0)/R_0$ was $\sim -10\%$ in the Ohmic low-voltage region, whereas it increased up to -70% in the nonlinear conduction region (above 6 V), as shown in Fig. 2(c). These results clearly show the correlation between the mechanism of the enhanced negative magnetoresistance and the nonlinear conductivity in this salt. It might be derived from the synergetic effect of electric and magnetic fields applied to the salt, which we will discuss below.

Recently, it was reported that an ion-radical salt with a 2:1 composition of donor and counterion, θ-$(ET)_2CsZn(SCN)_4$, exhibits a similar nonlinear characteristics, obeying the power law of $I \propto V^n$ ($n=8.4$ at 0.29 K).[31] The nonlinear conducting behavior was also found in an ion-radical salt of a dimeric TTF model compound.[32] In the latter system, there is a charge order of the donor units along the stacking direction in the mixed valence state, but this charge order melts when the applied voltage exceeds a threshold value. For the case of θ-$(ET)_2CsZn(SCN)_4$, the nonlinear characteristics were explained by the electric field-induced unbinding of electron-hole pairs with a potential barrier of $\Delta_{(E)}$ in the background of the charge-ordered state. Since the effective potential barrier of $\Delta_{(E)}$ decreases with increasing applied electric field, a high power law in the I-V characteristics emerges.[31] This effect becomes more prominent at lower temperatures. Considering the similarity of the nonlinear I-V characteristics between θ-$(ET)_2CsZn(SCN)_4$ and $(ESBN)_2ClO_4$, we speculate that $(ESBN)_2ClO_4$ also has a charge order, although ESR or NMR experiments should be carried out to confirm the charge order. In fact, Fig. 2(c) shows that the slope in the log−log plot of I-V characteristic was not significantly affected by the magnetic field of 9 T. This supports that the nonlinear conductivity is not of a spin origin.

Assuming that there is a charge order in the present system, the resistance can be expressed by Arrhenius type as[31]

$$R = R_0 \exp(\Delta_{(E)}/k_B T), \tag{1}$$

where $\Delta_{(E)}$ is an effective potential barrier. By using this expression, the strong nonlinear conductivity can be explained.[31] On the other hand, the observed magnetoresistance will be caused by the suppression of the scattering of conduction electrons by paramagnetic (fluctuating) localized spins under the field. This effect is contained in the prefactor R_0 in Eq. (1). In such a case, the power law of the I-V characteristics does not change under the magnetic field in parallel to the appearance of large negative magnetoreistance.

It has been reported that the thermally activated conduction behavior and distinct negative magnetoresistance were also found in the ferric-phtalocyanine complex $TPPP[Fe(Pc)(CN_2)_2]_2$, wherein the origin of the magnetoresistance has not yet been specified.[11] The enhanced magnetoresistance in a nonlinear region of $(ESBN)_2ClO_4$ might be somewhat similar to the spin-dependent tunneling between the nanoparticles in granular systems of magnetic metals. It was recently found that the negative magnetoresistance more pronouncedly emerged in a multiple cotunneling regime, in which a higher-order process of spin-dependent tunneling across several magnetic nanoparticles takes place; the ratio of negative magnetoresistance can be n times larger than that of the theoretical limit of a single magnetic tunnel gap (where n is the number of tunnel gaps involved in the cotunneling process).[33,34] An extension of the correlation length between a conduction electron and localized spins in a nonlinear region might be the cause of the enhanced magnetoresistance in $(ESBN)_2ClO_4$ crystal. Figure 6 schematically shows a plausible mechanism of the appearance of the giant negative magnetoresistance in $(ESBN)_2ClO_4$ at temperatures lower than 20 K, which is associated with a nonlinear conducting behavior. Under the low magnetic field [Fig. 6(a)], the mixed valence donor column falls into the charge-ordered state. In this case, an electron (e.g., β spin) migrates to the neighboring molecule with an α localized spin because

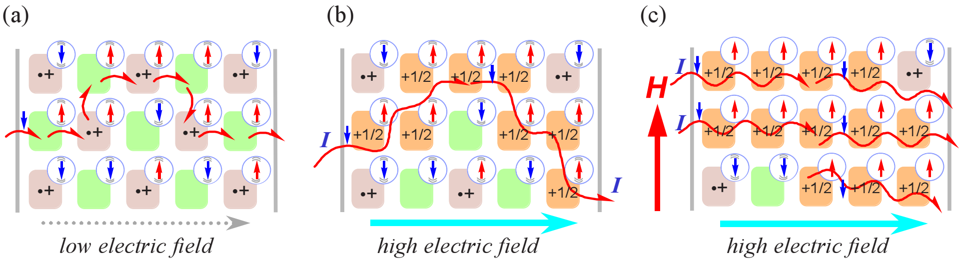

FIG. 6. (Color online) Schematic of a plausible mechanism of the appearance of the giant negative magnetoresistance in $(ESBN)_2ClO_4$ with a nonlinear conducting behavior: under (a) the low electric field, (b) the high electric field, and (c) the high electric field with an application of a high magnetic field.

the molecules with β localized spins do not accept an electron with a β spin. Under the high electric field [Fig. 6(b)], the charge-ordered state partially melts, causing a nonlinear conducting behavior, and then, the coherence length of the conducting electron becomes longer. Finally, when the magnetic field is applied [Fig. 6(c)], most of the localized spins are aligned to suppress the scattering of the conducting electron, causing a negative magnetoresistance.

In summary, it was found that an ion-radical salt of $(ESBN)_2ClO_4$, wherein ESBN is a diselena analog of BenzoTTF carrying NN exhibited both a nonlinear conductivity and a giant negative magnetoresistance as the first $p\pi$-$p\pi$ spin-transport coexisting system. The origin of the nonlinear conductivity is speculated to be derived form the electric field-induced melting of the charge ordered state on the basis of precedent studies exhibiting similar characteristics. Since the giant magnetoresistance reflects the magnetization response of an organic radical ($S=1/2$) to the applied field, it is unequivocally caused by suppression of the scattering of the conduction electron by the localized spin of the organic radical units when local spins are aligned in the magnetic field. We ascribed that such correlated spin-dependent electron transport to the strong intramolecular ferromagnetic coupling between π-conduction electrons and π-localized spins in the spin-polarized donor.

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