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# Dual-Action Molecular Superconductors with Magnetic Anions

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Molecular materials are expected to play an important role in the future in the development of electronic devices. For the realization of molecular electronic devices, it is essential to develop a "dual-action system" [1] whose conducting properties can be sharply controlled by external forces. One of the prospective dual-action molecular systems is a composite system consisting of organic layers responsible for electron conduction and inorganic layers with localized magnetic moments,[1] whose conductivity can be controlled by tuning the magnetic state of the inorganic layers. Here we report two organic superconductors exhibiting remarkable electromagnetic response. One is a superconductor with metamagnetic anion layers, and the other is a system with diluted magnetic moments.

Unprecedented systems such as paramagnetic organic superconductors[2] and ferromagnetic organic metals[3] have been recently developed by combining $\pi$-donor molecules and magnetic anions. We discovered the first antiferromagnetic organic superconductor, $\kappa$-(BETS)$_2$FeBr$_4$ (BETS = bis(ethylenedithio)tetraselenafulvalene).[4] In the crystal, the conduction layers of BETS molecules and magnetic anion layers are arranged alternately along the *b* axis. An indication of field-induced superconductivity has been recently discovered in this system.[5,6] It may be imagined that the superconducting state will be broken if the antiferromagnetic state of anion layers is changed to a ferromagnetic state. It was found that this unprecedented combination of metamagnetism and organic superconductivity is realized in $\kappa$-(BETS)$_2$FeBr$_4$ (Figure 1a,b). The critical field of metamagnetic transition is about 1.6 T.[4] We measured the resistivity of $\kappa$-(BETS)$_2$FeBr$_4$ at 0.59 K with periodically changing external field around 1.6 T and found that the superconducting state can be sharply switched on or off by controlling the metamagnetism of the anion layers by applying an external field (Figure 1c).

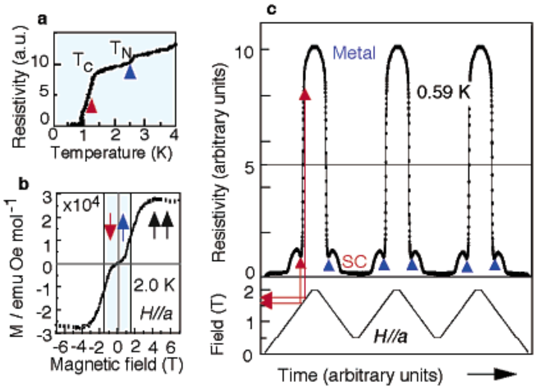

**Figure 1.** Electromagnetic properties and switching behavior of $\kappa$-(BETS)$_2$FeBr$_4$. (a) Successive antiferromagnetic and superconducting transitions: $T_N = 2.5$ K; $T_c = 1.1$ K (ref 4). (b) Magnetization curve at 2.0 K for the magnetic field parallel to *a* (easy axis of antiferromagnetic spin structure) (ref 4). (c) The periodic superconductor → metal switching synchronizing with the periodical modulation of magnetic field ($H||a$) around 1.6 T at 0.59 K. Small resistivity minima (blue triangles) beside the large peaks are due to the Jaccarino−Peter compensation effect (ref 7).

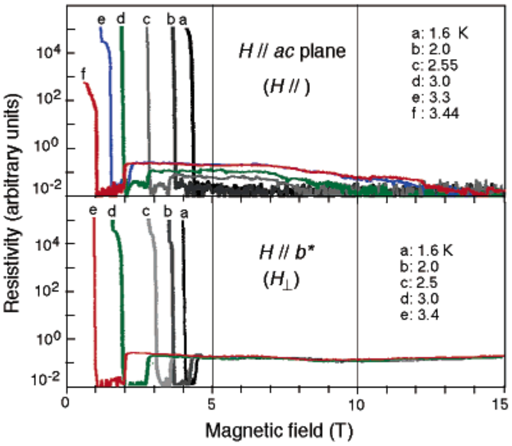

**Figure 2.** Magnetoresistance of $\lambda$-(BETS)$_2$Fe$_{0.4}$Ga$_{0.6}$Cl$_4$ up to 15 T at 1.6−3.4 K for the magnetic fields parallel (upper part, $H||ac$ plane) and perpendicular (lower part, $H||b*$) to the conduction plane.

Recently, a novel realization of field-effect switching between insulating and superconducting states, which is the widest possible variation of electrical properties of materials, has attracted great attention.[8] We have recently found an organic conductor in which superconducting, metallic, and insulating states can be realized selectively by slightly tuning the external magnetic field. Besides $\kappa$-(BETS)$_2$FeBr$_4$, there exists another needle-shaped modification, $\lambda$-(BETS)$_2$FeCl$_4$, which is a remarkable conductor showing surprisingly rich electronic properties.[9] It undergoes an antiferromagnetic insulating transition at 8.5 K;[9a,b] however, under a magnetic field it becomes a metal above 11 T, where Fe$^{3+}$ spins are in the forced-ferromagnetic orientation, and then takes a field-induced superconducting state at 18−42 T for the field parallel to the conduction plane (*ac* plane).[9c−e] In addition, it becomes a superconductor at high pressure.[9f] Furthermore, the diluted magnetic anion systems $\lambda$-(BETS)$_2$Fe$_x$Ga$_{1-x}$Cl$_4$ ($0.35 < x < 0.5$), which are prepared electrochemically from the organic solution containing BETS and mixed electrolyte of [(C$_2$H$_5$)$_4$N]FeCl$_4$/[(C$_2$H$_5$)$_4$N]GaCl$_4$, undergoes an unprecedented superconductor-to-insulator transition.[10] For example, $\lambda$-(BETS)$_2$Fe$_{0.4}$Ga$_{0.6}$Cl$_4$ is superconducting at 4.0−3.4 K and insulating below 3.4 K. We examined the magnetoresistance of this system at 1.6−3.4 K up to 15 T (Figure 2). For the magnetic field applied parallel to the *b** axis (that is, perpendicular to the *ac* conduction plane ($H||b*$, or $H_\perp$)), successive insulator → super-

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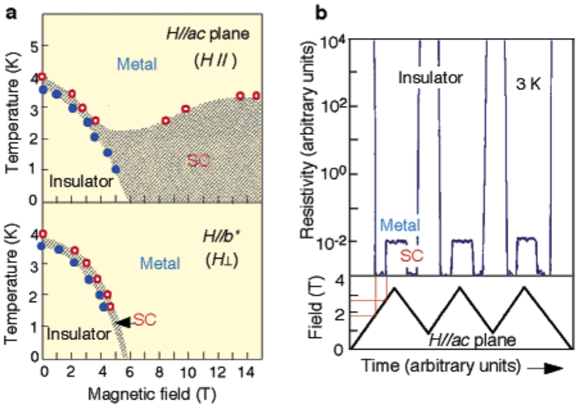

***Figure 3.*** (a) Temperature vs magnetic field phase diagram of λ-$(BETS)_2Fe_{0.4}Ga_{0.6}Cl_4$ for the field parallel (upper part, $H||ac$ plane) and perpendicular (lower part, $H||b^*$) to the conduction plane. The open and closed circles indicate metal-to-superconductor and superconductor-to-insulator transition temperatures, respectively. (b) An example of the insulator → superconductor → metal switching behavior coupled with the periodic modulation of magnetic field around 2.5 T ($H||ac$ plane) at 3 K.

conductor → metal transitions were observed with increasing field. In the hitherto reported two-dimensional organic superconductors, the upper critical field perpendicular to the conduction plane, $H_{c2\perp}$, is much smaller than that parallel to the conduction plane, $H_{c2||}$. In the case of λ-$(BETS)_2GaCl_4$, $H_{c2||}$ and $H_{c2\perp}$ are reported to be about 12 and 2.5 T, respectively at 1.5 K.[11] Therefore, the existence of a superconducting region around $H_\perp = 5$ T is quite unusual. Also for the field parallel to the *ac* plane ($H||ac$ plane, or $H_{||}$), unique behavior was observed. Below 2 K, the insulator → superconductor transition was observed at 3.5−4.5 T, while above 2.5 K, the insulator → superconductor → metal → superconductor transitions take place successively with increasing magnetic field up to 15 T. In contrast to the sharp superconductor → metal transition at lower field, the metal → superconductor transition was very sluggish. The lower-field superconducting phase is considered to be the same superconducting phase as that observed for the field perpendicular to the conduction plane ($H_\perp$), while the high-field superconducting phase observed for the field parallel to the *ac* plane corresponds to the field-induced superconducting phase. Figure 3a shows the $T-H$ phase diagrams of λ-$(BETS)_2Fe_{0.4}Ga_{0.6}Cl_4$ for the fields parallel and perpendicular to the conduction plane. It is natural that the field-induced superconducting phase appears around 14 T, which is much smaller than the internal field on BETS layers ($H_{int}$) of 33 T in λ-$(BETS)_2FeCl_4$,[9e] because $H_{int}$ originating from the antiferromagnetic interaction between localized moments of $Fe^{3+}$ ions and π conduction electrons of BETS molecules will be reduced by the dilution of magnetic ions ($33\ T \times 0.4 = 13$ T). The large reduction of $H_{int}$ has been proved by the examination of the Shubnikov−de Haas oscillation of λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$.[12] If $H_{c2}$ of λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ is approximately equal to that of λ-$(BETS)_2GaCl_4$, then the field-induced superconducting phase can be roughly considered to exist at the range of $H_{int}$ (≈14 T) ± $H_{c2||}(GaCl_4)$ (≈2−26 T). Consequently, the overlapping of low-field and high-field superconducting regions around 5 T will be natural. Due to the antiferromagnetism, $H_{int}$ will be small in the insulating phase. But at low temperature, $H_{int}$ is considered to increase quickly to about 14 T when going out from the insulating region. Thus, there will be a possibility of the existence of a narrow magnetic field region just outside the insulating phase, where the external field ($H_{ext}$) is almost compensated with $H_{int}$ to permit an unusual superconducting state around 5 T for the field perpendicular to the conduction plane ($|H_{ext} - H_{int}| < 2.5\ T \approx H_{c2\perp}(GaCl_4)$). Furthermore, as demonstrated in Figure 3b, owing to the unique phase diagram with narrow superconducting regions neighboring both insulating and metallic phases, the periodic insulator → superconductor → metal changes can be realized in a stepwise manner by periodical modulation of the external field, which means that the widest variation of electrical properties was actualized in this dual-functional molecular material. It is surprising that the unprecedented bulk conductor, whose insulating, metallic, and superconducting states can be selectively realized by slight tuning of the external field, was discovered in the molecular materials.

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