A Magnetic Organic Conductor Based on a π Donor with a Stable Radical and a Magnetic Anion—A Step to Magnetic Organic Metals with Two Kinds of Localized Spin Systems

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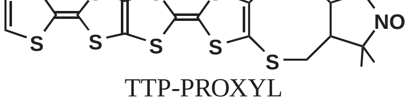
(TTP-PROXYL)$FeCl_4$, where TTP-PROXYL is 2,5-bis-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (TTP) incorporating the 2,2,5,5-tetramethyl-1-pyrrolidinyloxy (PROXYL) radical, is a semiconductor with two kinds of localized spin systems, that is, the systems of organic radical spins and 3d spins of magnetic $FeCl_4^-$ ions. The π spin of the TTP-PROXYL radical cation disappears due to dimerization but the χT-value of $4.65\,\mathrm{K\,emu\,mol^{-1}}$ indicates the coexistence of high-spin Fe^{3+} ($S = 5/2$) and PROXYL radical ($S = 1/2$) in this salt. (TTP-PROXYL)$GaCl_4$ is isostructural to the $FeCl_4$ salt and exhibited similar semiconducting properties.

The synergetic action of magnetism and conductivity in the magnetic organic conductor consisting of π donor molecules and magnetic anions has recently attracted a considerable attention.[1] Among the magnetic organic conductors hitherto reported, BETS systems have been known to exhibit novel electro-magnetic properties such as the field-induced insulator–metal transition, which can be regarded as a kind of colossal magnetoresistance first observed in the organic conductors,[2a] and the field-induced superconductivity of λ-$(BETS)_2FeCl_4$,[2b] the insulator–superconductor–metal switching of λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$,[2c] and the competition between metamagnetism and superconductivity of κ-$(BETS)_2FeBr_4$[2d] [BETS = bis(ethylenedithio)tetraselenafulvalene]. These properties are originated from the coupling between π metallic electrons of organic layers and localized magnetic moments of transition-metal complex anions. Although even the possibility of a new type of the magnetic conductor exhibiting photo-induced spin transition has been reported recently,[3] there remains the long-standing target, that is, the magnetic organic conductor based on π donors having a stable organic radical part in the development of magnetic organic conductors.[4] It was not easy to construct the conducting systems based on these π donors because the bulky radical moieties tend to interfere with the formation of conduction paths. Recently, Fujiwara et al. have determined the crystal structure of fairly high-conducting system based on TTP derivative containing the stable PROXYL radical moiety, (CP-TTP-PROXYL)$_4AsF_6$ [CP-TTP-PROXYL = 4,5-cyclopenteno-TTP-PROXYL] (Scheme 1),[5] which encouraged us to try to develop the organic metals based on π donors with localized radical spins. It should be noted that the organic conductors based on the π donors with stable radical parts have a great advantage in the development of the magnetic organic conductors with much stronger magnetic interactions. In the organic conductors consisting of usual TTF-like π-donors and magnetic anions, the enhancement of magnetic interactions between conducting electrons and localized spins does not seem to take place easily. However, if the organic conductors based on π donors with localized radical spins and magnetic anions such as $FeCl_4^-$ can be prepared, the magnetic interaction between organic radical spin and magnetic moment of Fe^{3+} ions would occur, which will open a way to realize a new type of the magnetic organic conductors such as ferrimagnetic organic conductors. In this paper, we report the crystal structures and physical properties of (TTP-PROXYL)$FeCl_4$ and isostructural (TTP-PROXYL)$GaCl_4$.



TTP-PROXYL

Scheme 1.

TTP-PROXYL was prepared according to the literature.[5,6] The black crystals of (TTP-PROXYL)MCl_4 (M = Fe and Ga) were prepared electrochemically. The X-ray crystal structure analyses revealed that the $FeCl_4$ salt was isostructural to the $GaCl_4$ salt and belonged to the triclinic system.[7] The crystals have the donor:anion ratio of 1:1. As shown Figure 1, there are two crystallographically independent donors (A and B) and anions (C and D). Unlike usual organic conductors, the crystal of (TTP-PROXYL)MCl_4 has not two-dimensional donor layer. Two TTP-PROXYL molecules interrelated by inversion symmetry are dimerized in a head-to-tail manner (Figure 2). There are many intradimer short S···S contacts. The TTP-PROXYL dimers A and B are loosely stacked to form columns along the *b* and *a* directions, respectively, and the TTP-PROXYL columns and MCl_4^- anions are arranged alternately along the *a* and *b*

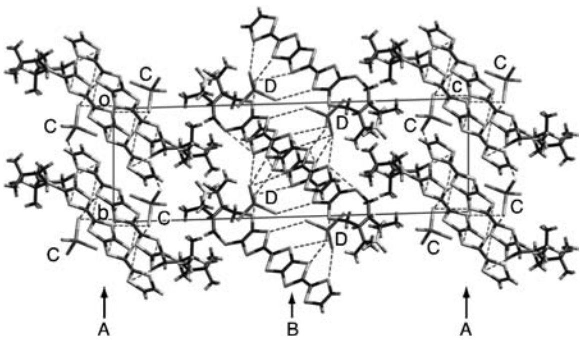


Figure 1. The crystal structure of (TTP-PROXYL)$FeCl_4$. A, B and C, D are crystallographically independent TTP-PROXYL molecules and $FeCl_4^-$ ions, respectively. The broken lines indicate the intermolecular S···Cl and S···S contacts shorter than the corresponding van der Waals distances.

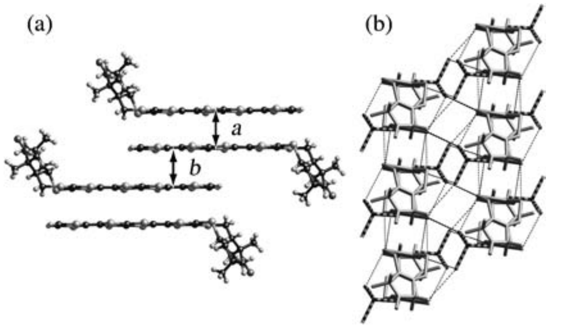


Figure 2. (a) Column composed of TTP-PROXYL A. Overlap integrals ($\times 10^3$): $a = 17.6$, $b = 1.36$. (b) End-on projection of the arrangement of TTP-PROXYL molecules and $FeCl_4^-$ ions.

directions, respectively. TTP-PROXYL molecules (A and B) are almost planar except PROXYL moieties. There is no short contact between NO• radicals and between NO• radicals and Cl atoms of the anions. The shortest C···Cl distance of neighboring anions is 3.49 Å. There are many short Cl···S contacts between donors and anions (e.g. 3.314, 3.331, 3.408, 3.444, and 3.446 Å). Essentially the same structural properties were also observed in (TTP-PROXYL)$GaCl_4$.

The semiconducting properties of (TTP-PROXYL)$FeCl_4$ are shown in Figure 3a ($\rho(\mathrm{rt}) = 1 \times 10^3\,\Omega\,\mathrm{cm}$, $E_a = 0.13\,\mathrm{eV}$). (TTP-PROXYL)$GaCl_4$ showed almost the same electrical properties. Since TTP-PROXYL molecule is in the mono-cation state, there is the probability that π radical spin and NO• radical spin coexist in a TTP-PROXYL molecule. Therefore, it might be imagined that the spin state of TTP-PROXYL is either in the singlet or triplet. However, the χT-value ($0.38\,\mathrm{K\,emu\,mol^{-1}}$) of (TTP-PROXYL)$GaCl_4$ showed that TTP-PROXYL has one $S = 1/2$ spin (Figure 3b), which is consistent with the observed narrow ESR signal ($g = 2.006$, $\Delta H \approx 14\,\mathrm{G}$) (Figure 3c). This is easily understood from the strongly dimerized structure of TTP-PROXYL molecules. Since the intradimer transfer integrals were calculated to be about 0.18 eV (dimer A) and 0.17 eV (dimer B), the crystal structure can be sufficiently stabilized by the dimer formation (Figure 2). Then the excess π electrons on the TTP-moieties form non-magnetic state and the NO• radical spin survives to give Curie paramagnetism. Thus, the intramolecular magnetic interaction between the π donor and the NO• radical parts is considered to be much smaller than the intradimer $\pi\cdots\pi$ interaction. The weaker intramolecular interaction between radical orbital and π orbital and the stronger intermolecular $\pi\cdots\pi$ interaction could be important to obtain the system where localized radical moments and π conduction band coexist. Similar situation was also observed in (TTP-PROXYL)-$FeCl_4$. The π radical spins disappeared by the dimer formation and the χT-value of $4.65\,\mathrm{K\,emu\,mol^{-1}}$ can be explained by simple addition of the susceptibilities due to localized high spin Fe^{3+} and NO• spins. The broad ESR signal ($g = 2.07$, $\Delta H \approx 800\,\mathrm{G}$ at 3.5 K) with a shoulder at 3390 G (as indicated by *arrow* in Figure 3c) also suggested the coexistence of Fe^{3+} spins and NO• spins. The small Weiss temperature ($\theta = -0.7\,\mathrm{K}$ for both salts) is consistent with the lack of short intermolecular contacts between NO• radicals and/or $FeCl_4^-$ ions. Anyway, to our knowledge, (TTP-PROXYL)$FeCl_4$ is the first organic semiconductor with two kinds of localized spin systems, though the significant coupling between two spin systems was not observed in this salt.

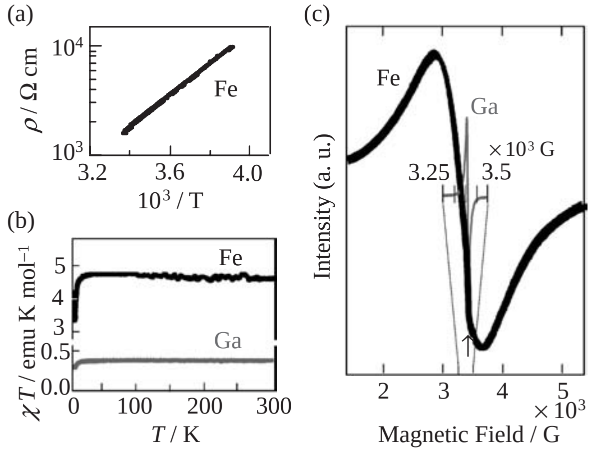


Figure 3. (a) Temperature dependence of the resistivity of (TTP-PROXYL)$FeCl_4$. (b) The χT–T plots of (TTP-PROXYL)-MCl_4 (M = Fe and Ga). (c) ESR spectra of (TTP-PROXYL)-MCl_4 at 3.5 K.

In summary, we have prepared and characterized the novel organic conductor, (TTP-PROXYL)$FeCl_4$, with two kinds of localized spin systems, which provides an important hint to realize a new type of the magnetic organic conductors.

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7 The crystal data are as follows: (TTP-PROXYL)$FeCl_4$, triclinic, $P\bar{1}$, $a = 9.755(4)$, $b = 10.262(4)$, $c = 32.275(13)$ Å, $\alpha = 91.66(1)$, $\beta = 94.71(2)$, $\gamma = 90{,}18(1)^\circ$, $V = 3218(3)$ Å^3, $Z = 4$, $R = 0.068$, $R\mathrm{w} = 0.050$; (TTP-PROXYL)$GaCl_4$, triclinic, $P\bar{1}$, $a = 9.778(5)$, $b = 10.2625(5)$, $c = 32.33(2)$ Å, $\alpha = 91.57(2)$, $\beta = 94.69(2)$, $\gamma = 90{,}30(2)^\circ$, $V = 3235(3)$ Å^3, $Z = 4$, $R = 0.064$, $R\mathrm{w} = 0.067$.

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