A Novel TTP Donor Containing a PROXYL Radical for Magnetic Molecular Conductors

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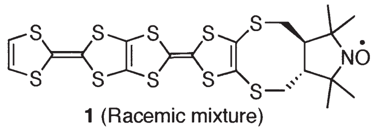
(Received February 24, 2003; CL-030149)

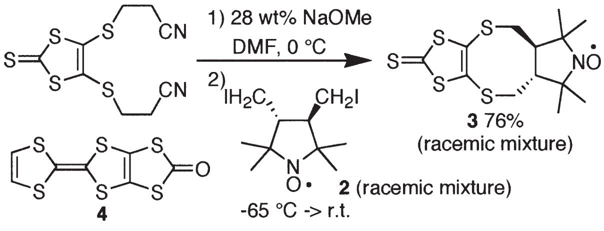
A TTP donor containing a stable PROXYL radical was synthesized to develop conducting-magnetic bifunctional materials and its structure and physical properties were investigated. Furthermore its cation radical salts were prepared and revealed their conducting and magnetic properties.

The development of new electron donors for molecule-based conductors involving a magnetic centre is of quite interest in order to investigate the interplay between the π conducting electrons generated by oxidation and the localized radical spins, and several donors containing a stable radical have been synthesized to try for novel conducting-magnetic bifunctional materials.[1,2] Among them, we have also developed several donor molecules containing a stable TEMPO radical based on π-extended tetrathiafulvalene (TTF) frameworks,[3] however, it is difficult to obtain highly conductive cation radical salts using the TTF skeleton because the TTF framework is too small to overcome the steric hindrance of bulky organic radicals and to accomplish strong intermolecular interactions indispensable for metallic behavior. Therefore, to realize the metallic conductivity, we focused on the molecules with TTP skeleton [TTP = 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene], which were regarded as a series of promising donors for the realization of stable metallic states.[4] In this communication, we present the synthesis, structure and physical properties of a novel electron donor consisting of the TTP framework and a stable PROXYL (2,2,5,5-tetramethyl-pyrrolidin-1-yloxyl) radical part (**1**).[5] Furthermore, we report here the physical properties of its ClO_4^- and $FeCl_4^-$ salts as the highest-conductive cation radical salts based on the donors containing a localized radical spin.



1 (Racemic mixture)

The TTP derivative containing a PROXYL radical **1** was synthesized as shown in Scheme 1. The thione (**3**) was prepared as a racemic mixture in 76% yield by the reaction between the generated 1,3-dithiole-2-thione-4,5-dithiolate and bis(iodomethyl)-substituted PROXYL radical derivative (**2**).[6] Then, the thione **3** was reacted with the ketone (**4**)[4] by the trimethyl phosphite mediated cross-coupling reaction at 80 °C. Air-stable orange needles of the TTP derivative **1** were obtained as a racemic mixture in 30% yield.[7] An X-ray crystal structure analysis was performed on a single crystal of **1** obtained by recrystallization from CS_2/ethyl acetate.[8] In the unit cell, there are a half of crystallographically independent donor molecule and a half of CS_2 as an interstitial solvent. Figure 1 shows the molecular structure of the donor molecule **1**. Because the donor molecule lies on the mirror plane, the racemic structure of the PROXYL radical part was observed as an averaged structure. The donor molecules stack along the *a* axis and several S···S contacts (≈ 3.7 Å) were observed both in the stack and between the stacks, suggesting the possibility of the construction of two-dimensional network of intermolecular interactions in its cation radical salts.



Scheme 1.

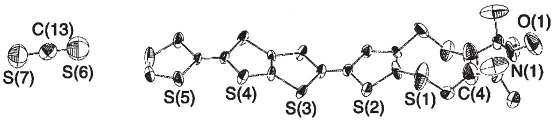


Figure 1. Molecular structure of $1{\cdot}CS_2$ with selected atom numbers.

The cyclic voltammogram of **1** was measured at 40 °C. The donor **1** showed five reversible one-electron redox waves at +0.53, +0.79, +0.90, +1.16 and +1.34 V vs Ag/AgCl, corresponding to the existence of four redox active 1,3-dithiole ring and one PROXYL radical. The first oxidation potential of **1**, +0.53 V, is close to that of 4,5-bis(methylthio)-TTP (+0.50 V) and is quite different from that of **2** (+0.89 V) under the identical conditions. These results indicate that the first oxidation occured at the TTP skeleton and the coexistence of a cation radical moment and a localized spin in one molecule will be possible. The temperature dependence of static magnetic susceptibility of **1** was well fitted with the Curie-Weiss law with slight antiferromagnetic interaction ($\theta = -1.9$ K) and the Curie constant ($C = 0.373\,\mathrm{emu\,K\,mol^{-1}}$) corresponding to one spin per one molecule.

The ClO_4^- and $FeCl_4^-$ salts of **1** were electrochemically prepared in benzonitrile/ethanol (9:1) solution. Since we could not obtain their good single crystals suitable for X-ray structure analysis, their D:A compositions were determined by the electron dispersion spectroscopy (EDS) from the ratio of sulfur and chlorine or iron. We performed the EDS measurements for each 10 different microcrystalline samples and confirmed that these two salts have an isomorphous composition. The ClO_4^- salt was obtained as black microcrystals and the D:A ratio was determined to be 1:0.64. The magnetic susceptibility was measured by SQUID at 1 T and the temperature dependence of the χT values per 1:0.64 salt is shown in Figure 2a. The χT values of this salt around room temperature are almost

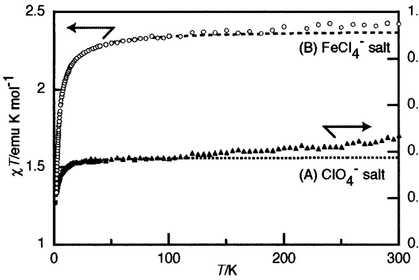


Figure 2. Temperature dependence of the χT values of (A) the ClO_4^- and (B) the $FeCl_4^-$ salts. The dotted lines show the Curie-Weiss fitting curves for (A) the ClO_4^- ($C = 0.375\,\mathrm{emu\,K\,mol^{-1}}$ and $\theta = -1.2\,\mathrm{K}$) and (B) the $FeCl_4^-$ ($C = 2.39\,\mathrm{emu\,K\,mol^{-1}}$ and $\theta = -1.7\,\mathrm{K}$) salts.

$0.45\,\mathrm{emu\,K\,mol^{-1}}$ and exceed the value for one $S = 1/2$ spin per one molecule, suggesting the coexistence of the cation radical moment of the TTP moiety and the localized spin of the PROXYL radical part. With decreasing the temperature, the χT value decreased slowly to the value corresponding to one spin per one molecule ($0.375\,\mathrm{emu\,K\,mol^{-1}}$) around 100 K, probably indicating the disappearance of the contribution from the cation radical moments. Then, it obeyed the Curie-Weiss law with slight negative Weiss temperature ($\theta = -1.2\,\mathrm{K}$), suggesting an antiferromagnetic interaction between the localized PROXYL radical spins. The electrical conductivity of this salt was measured on compressed pellets. The room temperature conductivity is relatively high value of $10^{-1}\,\mathrm{S\,cm^{-1}}$ for compressed pellets. The temperature dependence of resistivities is semiconducting with an activation energy of 0.14 eV. The coexistence of the conducting electrons and the localized spins indicates that this salt is a paramagnetic semiconductor. On the other hand, we tried the preparation of cation radical salts using magnetic anions to realize magnetic transitions through the PROXYL (n) - magnetic anion (d) interaction. Then, we obtained the $FeCl_4^-$ salt of **1** as black microcrystals and also cleared the D:A ratio to be 1:0.46. The temperature dependence of the χT values per 1:0.46 salt is also plotted in Figure 2a. The χT values around room temperature are $2.43\,\mathrm{emu\,K\,mol^{-1}}$ and correspond to the sum of the contributions from one PROXYL radical ($0.375\,\mathrm{emu\,K\,mol^{-1}}$), high spin Fe^{3+} ($0.46 \times 4.375\,\mathrm{emu\,K\,mol^{-1}} = 2.01\,\mathrm{emu\,K\,mol^{-1}}$) and a small amount of π conducting electrons from the cation radical moments (approximately $0.04\,\mathrm{emu\,K\,mol^{-1}}$), suggesting the coexistence of these three different magnetic moments. At low temperature region, the χT value decreased according to the Curie-Weiss law with small negative Weiss temperature ($\theta = -1.7\,\mathrm{K}$), indicating the existence of antiferromagnetic interactions between these spins. However, we could not observe any magnetic transition down to 2 K. The electrical conductivity of this salt was measured on compressed pellets. The room temperature value is $1.1\,\mathrm{S\,cm^{-1}}$ and is the highest record in the cation radical salts based on the donors containing stable organic radicals reported so far, even though it was measured on compressed pellets, to our knowledge. This salt showed semiconducting behavior, however, the activation energy is quite small value of 0.02 eV. Therefore, the electrical conductivity of this salt can be considered to be essentially metallic if we could measure the conductivity using its single crystals. Furthermore, the almost linear tendency of χT decrease at high temperature region also seems to suggest the temperature independent term of the metallic π-conducting electrons. These results indicate that this salt is almost paramagnetic metal with the coexistence of the conducting electrons and two kinds of the localized spins. The further investigations, in particular, synthesis of the other derivatives and preparation of cation radical salts are actively in progress.

The authors thank Prof. Y. Misaki for his kind suggestions to synthesize the TTP derivative.

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7 Selected data for **1**: mp 242–243 °C (dec.); IR (KBr) ν ($\mathrm{cm^{-1}}$) 2971, 1508, 1363, 766; $C_{20}H_{20}NOS_{10}{\cdot}CS_2$ (687.18): Calcd. C 36.70, H 2.93, N 2.04; Found C 36.58, H 2.92, N 1.84; ESR (benzene) $g = 2.0059$, $a_N = 1.42\,\mathrm{mT}$. Selected data for **3**: mp 158–159 °C (dec.); IR (KBr) ν ($\mathrm{cm^{-1}}$) 2966, 1467, 1364, 1071; m/z 364 [M^+]; Found C 42.45, H 4.81, N 3.47: Calcd. for $C_{13}H_{18}NOS_5$ (364.62) C 42.83, H 4.98, N 3.84; EPR (benzene) $g = 2.0059$, $a_N = 1.42\,\mathrm{mT}$.

8 Crystal data for $\mathbf{1}{\cdot}CS_2$: fw = 343.56, Monoclinic, $P2_1/m$, $a = 8.939(4)$, $b = 12.082(6)$, $c = 13.399(7)\,\text{Å}$, $\beta = 95.47(1)^\circ$, $V = 1440(1)\,\text{Å}^3$, $Z = 4$, $D_{\mathrm{calcd.}} = 1.584\,\mathrm{g\,cm^{-3}}$, 3429 unique reflections, the final R and R_w were 0.098 and 0.142 (1108 reflections [$I > 4.0\sigma(I)$]).

Published on the web (Advance View) May 6, 2003; DOI 10.1246/cl.2003.482