Novel π-Electron Donors for Magnetic Conductors Containing a PROXYL Radical

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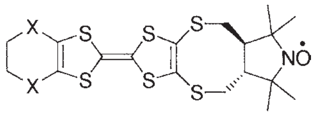
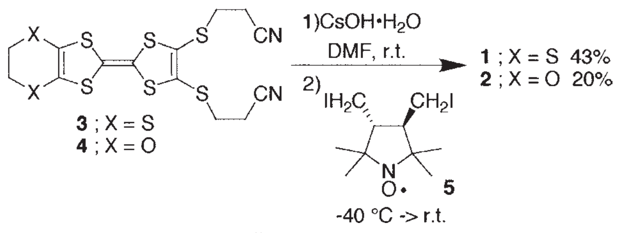
Synthesis, structure and physical properties of novel π-electron donors containing a TTF moiety and a PROXYL radical within a single molecule designed for the development of magnetic conductors are reported. We also clarified the physical properties of the iodine complex of the ethylenedithio derivative.

In the recent progress of molecular conductors, the development of magnetic conductors bearing both conductivity and magnetism has recently played a quite important role in the research of the multifunctionality of organic molecular materials. Several superior examples such as paramagnetic/ferromagnetic metals, antiferromagnetic superconductors and magnetic-field-induced superconductors using magnetic transition metal anions, have been reported as representatives of bifunctional molecular conductors.[1] On the other hand, several trials have been performed to realize organic ferromagnetic metals by using tetrathiafulvalene (TTF) donors containing a stable organic radical as a magnetic center. Several donors have been reported their physical properties to study the relationship between conduction electrons that originated from their cation radical states and localized spins of the stable organic radical part.[2] Recently, we synthesized several new donors containing a TEMPO radical and reported the structures and physical properties of their cation radical salts.[3] Among them, we focused on the donors consisting of a TTF moiety and a PROXYL (2,2,5,5-tetramethylpyrrolidin-1-yloxyl) radical part because the PROXYL radical is quite stable to air and heat and the corresponding donor molecules will have a relatively small steric hindrance due to the symmetrical structure and smaller size of the PROXYL radical than that of the TEMPO radical. In this communication, we present the synthesis, structure and physical properties of novel TTF donors **1** and **2** containing a PROXYL radical. We also clarify the physical properties of the iodine complex of the ethylenedithio derivative **1**.



1 ; X = S, **2** ; X = O

Scheme 1 shows the synthetic method of the TTF donors containing a PROXYL radical **1** and **2**. Thus, 4,5-bis(2′-cyanoethylthio)-TTF derivatives **3** and **4** were treated with $CsOH \cdot H_2O$ in DMF to generate the corresponding dithiolate salts and reacted with bis(iodomethyl) substituted PROXYL radical **5** at −40 °C, which was prepared as a racemic mixture according to the literature.[4] Then, air-stable microcrystals of the TTF derivatives containing a PROXYL radical **1** and **2** were obtained as racemic mixtures in 43 and 20% yields, respectively.[5] An X-ray crystal structure analysis was performed on a needle-like single crystal of **1** prepared by recrystallization from dichloromethane/heptane.[6] Figure 1 shows the molecular and crystal structures of **1**. The TTF moiety has a bent structure as often observed in neutral TTF derivatives. Because the donors were obtained as racemic mixtures, two carbon atoms of the PROXYL radical part (C11–14) are disordered and have two different conformations. The donors overlap each other in a head-to-tail manner and form dimers as shown in Figure 2(b). Though there is one short S-S contact between the dimers (3.55 Å), no contact was observed between the adjacent donors along the side-by-side direction.



Scheme 1.

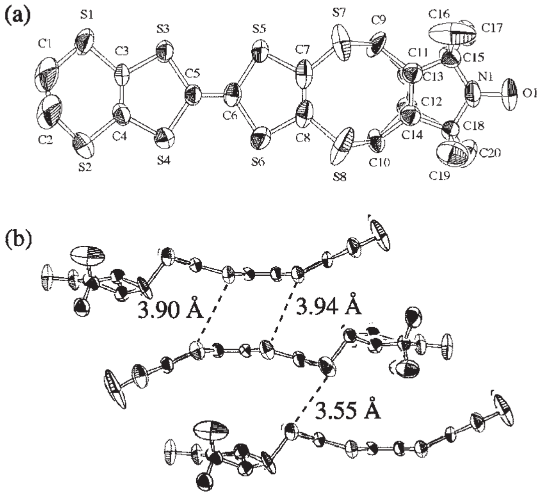


Figure 1. (a) Molecular structure and (b) crystal structure of **1**.

Figure 2 shows the cyclic voltammogram of **1** in benzonitrile at 25 °C (scan rate: $50\,\mathrm{mV\,s^{-1}}$) using tetrabutylammonium hexafluorophosphate as a supporting electrolyte. Both the donors **1** and **2** showed one pair of one-electron reversible redox waves ($E_1{}^{1/2}$: +0.49 and +0.57 V vs Ag/AgCl, respectively) and one pair of broad reversible redox waves wherein two one-electron redox processes are considered to overlap each other ($E_2{}^{1/2}$: +0.89 and +0.92 V, respectively). These results correspond to the existence of three redox-active sites (two 1,3-dithiole rings and one PROXYL radical). The first oxidation is considered to

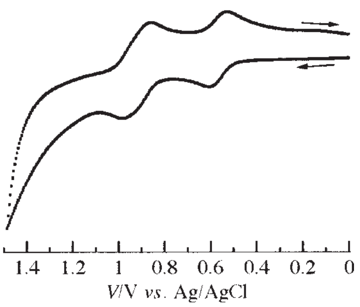


Figure 2. Cyclic voltammogram of **1** in benzonitrile.

originate from the TTF moiety because these first oxidation potentials are almost the same as those of the parent TTF derivatives without a PROXYL radical. The ESR spectra of the donors **1** and **2** showed three absorption lines in benzene characteristic of the PROXYL radical. The static magnetic susceptibilities of these donors were measured on polycrystalline samples by a SQUID magnetometer at 1 T. The room temperature susceptibilities of these donors correspond to the value calculated for one $S = 1/2$ spin per one molecule. The donor **1** indicated the Curie–Weiss behavior with a slight antiferromagnetic interaction ($\theta = -2.1$ K). On the other hand, the donor **2** showed a stronger antiferromagnetic interaction of $\theta = -8.7$ K, which was estimated by the Curie–Weiss fitting above 100 K, and a large decrease of magnetic susceptibilities below 5 K which suggests an antiferromagnetic ordering because the magnetization curve measured at 2.0 K deviated largely from the Brillouin curve and showed a spin-flop behavior around 6 T.

Because we could not obtain any cation radical salts by electrocrystallization, the iodine complex of the donor **1** was prepared as greenish black powder by mixing hot 1,2-dichloroethane solutions of iodine and the donor **1**. We determined the ratio Donor : I_3^- to be 1 : 1.35 by the electron dispersion spectroscopy (EDS) assuming that iodine was included in the salt as I_3^-. This salt is an insulator with a very low room temperature conductivity ($<10^{-5}$ S cm^{-1}) measured on compressed pellets because of such a high oxidation state. The static magnetic susceptibilities of this salt were measured by a SQUID magnetometer at 1 T, and showed that the χT value calculated for 1 : 1.35 salt is almost 0.37 K emu mol^{-1} around room temperatures and obeyed clearly the Curie–Weiss law with a weak antiferromagnetic interaction of $\theta = -2.6$ K. In the ESR measurements of this salt, we observed the same temperature dependence of spin susceptibilities as those of the static susceptibilities. Furthermore, the g-value and peak-to-peak linewidth (ΔHpp) of this salt ($g = 2.0061$, $\Delta H\text{pp} = 1.12$ mT) are almost constant down to 20 K and are close to those of the neutral donor **1** in the solid state ($g = 2.0066$, $\Delta H\text{pp} = 1.26$ mT at room temperature). These results suggest that the actual oxidation state of the donor molecule is $+1$ contrary to the EDS result and all the cation radical moments of the oxidized TTF part disappeared even at room temperature probably because of a strong dimerization and only the PROXYL radical part showed independent behavior with a weak antiferromagnetic interaction. On the other hand, very recently, we synthesized several bis-fused TTF (TTP)[7] derivatives containing a PROXYL radical by utilizing the synthetic method of these TTF derivatives to strengthen the intermolecular interaction indispensable to the realization of metallic conducting behavior. We also clarified that their several cation radical salts showed the coexistence of cation radical moments and localized PROXYL radical spins, and relatively high room temperature conductivity (1 S cm^{-1}) measured on compressed pellet. These results will be reported elsewhere in near future.

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5 Selected data for **1**: yellow powder; mp 207–208 °C (dec.); IR (KBr) ν (cm^{-1}) 2966, 2923, 1461, 1361, 1281, 1248, 879; $C_{18}H_{22}NOS_8$ (524.9): Anal. Calcd C 41.19, H 4.22, N 2.67; Found C 40.89, H 4.15, N 2.35; ESR (benzene) $g = 2.0059$, $a_N = 1.42$ mT. Selected data for **2**: reddish orange powder; mp 193–194 °C (dec.); IR (KBr) ν (cm^{-1}) 2971, 2929, 1654, 1459, 1364, 1161, 1084, 865; $C_{18}H_{22}NO_3S_6$ (492.8): Anal. Calcd C 43.88, H 4.50, N 2.84; Found C 43.99, H 4.43, N 2.52; ESR (benzene) $g = 2.0059$, $a_N = 1.43$ mT.

6 Crystal data for **1**: fw = 524.86, Triclinic, $P\bar{1}$, $a = 9.156(3)$, $b = 15.509(1)$, $c = 8.958(3)$ Å, $\alpha = 95.81(1)$, $\beta = 112.10(2)$, $\gamma = 96.31(1)^\circ$, $V = 1157.3(5)$ Å^3, $D_{\text{calcd}} = 1.506$ g cm^{-3}, 5629 unique reflections, the final R and R_w were 0.079 and 0.086 (2237 reflections $[I > 3.0\sigma(I)]$).

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