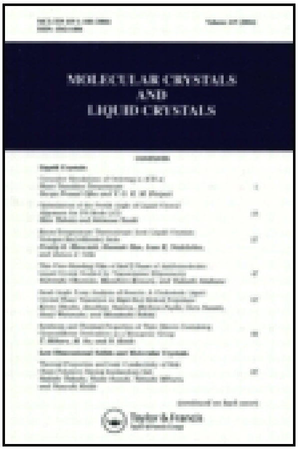

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Synthesis, structures and physical properties of the cation radical salts based on tempo radical containing electron donors

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SYNTHESIS, STRUCTURES AND PHYSICAL PROPERTIES OF THE CATION RADICAL SALTS BASED ON TEMPO RADICAL CONTAINING ELECTRON DONORS

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We have synthesized new electron donors in which one or two TEMPO radical parts connect to the TTF skeleton through a 1,3-dithiol-2-ylidene ring to prevent the steric hindrance of the bulky TEMPO radical for the purpose of the realization of metallic conductivity. Furthermore crystal structure and physical properties of the donors and the cation radical salt have been clarified.

Keywords: organic conductors; molecular magnetism; TEMPO radical; TTF derivatives

INTRODUCTION

In the research for new organic conducting systems, recent studies on the molecular conductors and superconductors containing magnetic transition metal anions, such as the antiferromagnetic superconductor κ-(BETS)$_2$-FeBr$_4$ salt [1], have stimulated the interest for the investigation on the interplay between the conductivity and magnetism. For the development of novel organic conducting-magnetic multifunctional materials and organic ferromagnetic metals, several research groups have synthesized electron donors containing a stable organic radical part to investigate the interaction between the itinerant electrons of conducting band and the localized spins of organic stable radical part [2]. However, no highly conducting salt has been reported from these donors so far because their molecular structures

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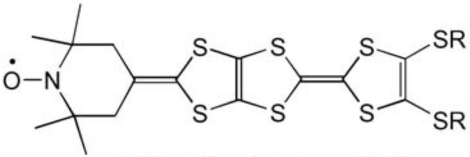
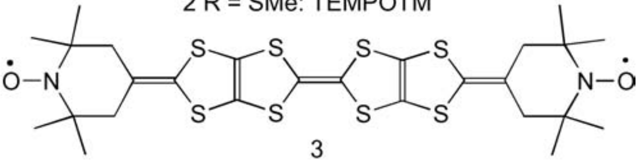
*Address Correspondence to Hideki Fujiwara, Institute for Molecular Science, Department of Molecular Assemblies, Myodaiji-cho, Okazaki, 444 8585, Japan. E-mail: fuji@ims.ac.jp are not suitable for construction of effective conduction path. For the purpose of the realization of metallic conductivity, we have paid attention to the molecular structure as a fusion of a stable TEMPO radical part to the DTET-TTF [methylidene-1,3-dithiolo[4,5-*d*]-4,5-ethylenedithio-TTF] skeleton, which is a promising building block for realizing stable metallic behavior down to low temperature, to prevent the steric hindrance of the bulky TEMPO radical [3]. Herein we report the synthesis and structure of novel electron donors **1** and **2** in which one TEMPO radical part connects to the TTF skeleton through a 1,3-dithiol-2-ylidene ring and physical properties of the obtained donors and a cation radical salt [4a]. Furthermore we have investigated the synthesis and physical properties of biradical molecule **3**.



1 2R = -$(CH_2)_2$-: TEMPOET
2 R = SMe: TEMPOTM



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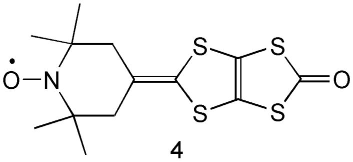
RESULTS AND DISCUSSION

Synthesis

Synthesis of **1** and **2** was performed according to the reported procedures [4]. Namely, the ketone containing TEMPO radical **4** was reacted with the corresponding thiones **5** and **6** by the triethyl phosphite mediated cross-coupling reaction at 75°C. TEMPOTM **2** was obtained as air-stable yellow microcrystals in 20% yield. The symmetrical biradical donor **3** was prepared as air-stable reddish pink powder in the yield of 24% by the triethyl phosphite mediated homo-coupling reaction of **4** at 75°C and is very insoluble to the common organic solvents.



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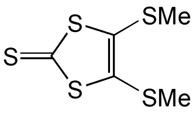

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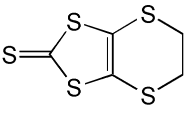

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Structure of TEMPOTM 2

An X-ray crystal structure analysis was performed on a yellow single crystal of TEMPOTM **2** recrystallized from carbon disulfide/*n*-heptane. Crystal data: $C_{18}H_{22}S_8NO$, $M = 524.86$, monoclinic, space group $P2_1/a$, $a = 10.993(2)$, $b = 15.652(2)$, $c = 14.557(1)$ Å, $\beta = 109.824(8)^\circ$, $V = 2356.1(4)$ Å^3, $Z = 4$, $R = 0.038$, $R_W = 0.029$. As shown in Figure 1, the donor **2** has a heavily bent structure at the positions of sulfur atoms of TTF part with dihedral angles of 19.98 and 22.44° as is often observed in neutral TTF derivatives. The TEMPO part adopts a chair-form conformation and the oxygen atom has a slightly large elliptic temperature factor, indicative of some thermal vibration along the axial direction. Figure 2 shows the crystal structure of TEMPOTM. Two molecules are dimerized in a head-to-tail manner with an intradimer interplane distance of 3.548 Å between the tetrathiapentalene moieties [S(4)-C(12)-S(2)-S(3)-C(11)-S(1)] and with a large slip along the molecular long axis due to the large steric hindrance of the bulky TEMPO and bis(methylthio) parts. The dimers are orthogonally arranged in the layers as shown in Figure 2(a). There are several short S-S contacts between the orthogonal molecules (A: 3.566(1) and B: 3.653(1) Å) and between the side-by-side molecules (C: 3.651(1) and 3.705(1) Å), suggesting a possibility of two-dimensional intermolecular interaction in its conducting salts required for the realization of stable metals. The shortest O-O distance (I) is 4.83 Å located between the dimers of the neighboring layers as indicated in Figure 2(b). The second nearest O-O distance (II, 7.36 Å) exists between the orthogonally arranged adjacent molecules. Therefore TEMPO radical spins seem to feel dimerization within the crystal.

Magnetic Properties of Donors

ESR spectrum of benzene solutions of **1** and **2** showed three absorption lines ($g = 2.0061$, $a_N = 15.1$ G) characteristic of the TEMPO radical. Similarly the biradical derivative **3** showed the same three absorption lines

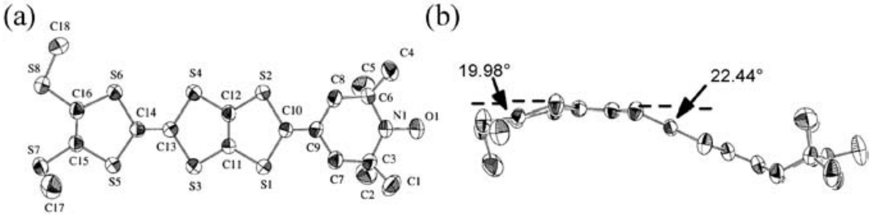

FIGURE 1 (a) Molecular structure of TEMPOTM and (b) the side view.

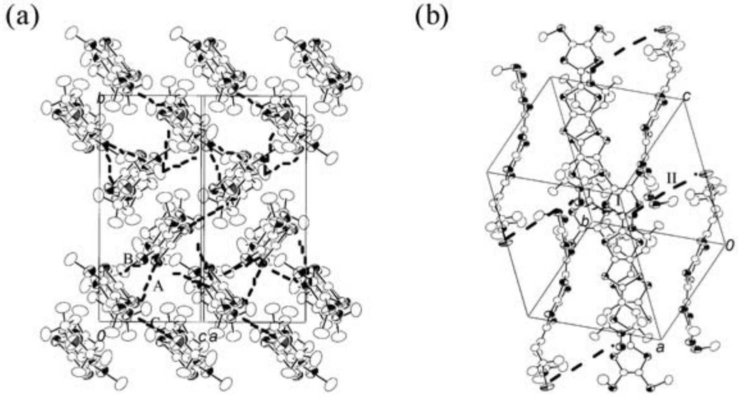

FIGURE 2 Crystal structure of TEMPOTM (a) viewed along the molecular long axis and (b) the top view. O-O distances: I 4.83 and II 7.36 Å. S-S contacts: A 3.566(1), B 3.653(1) and C 3.651(1) and 3.705(1) Å.

in the benzene solution (g = 2.0061, $a_N = 15.1$ G) and one broad signal of the unresolved powders (g = 2.0065, $\Delta H_{pp} = 12.5$ G) because of highly insoluble nature to benzene, however, no superfine structure was observed. The static magnetic susceptibility was measured by the SQUID magnetometer at 1 Tesla. TEMPOET showed paramagnetic susceptibility

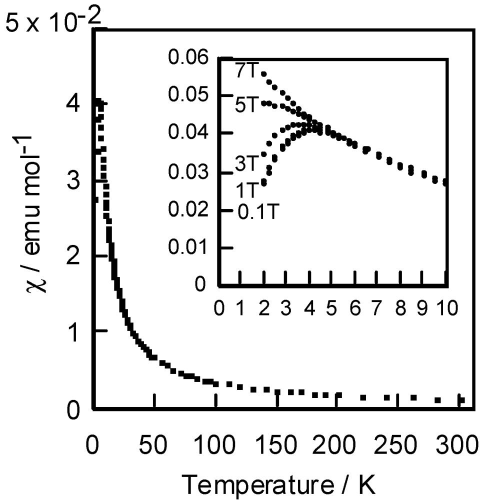

FIGURE 3 χ-T plot of TEMPOTM (inset: χ-T plot under 10 K at several indicated magnetic field).

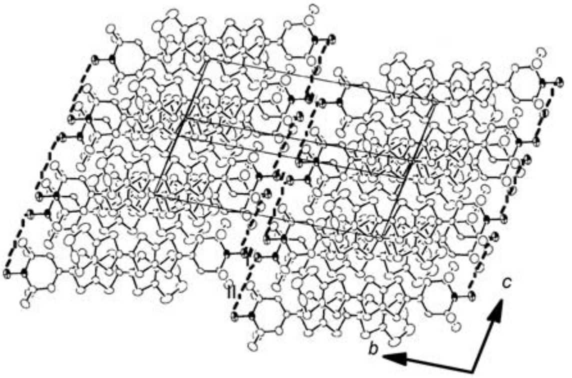

FIGURE 4 Crystal structure of $(TEMPOET)_2[Au(CN)_2]_3$ salt viewed perpendicular to the molecular planes. O-O distances: I 3.24 and II 7.43 Å.

($\chi rt = 1.25 \times 10^{-3}$ emu mol^{-1}) corresponding to one S = 1/2 spin per molecule and Curie-Weiss temperature dependence with a slight antiferromagnetic interaction ($\theta = -1.00$ K). On the other hand, TEMPOTM also showed Curie-Weiss temperature dependence with a slightly strong antiferromagnetic interaction ($\theta = -3.40$ K), however, showed antiferromagnetic ordering at ca. 4.5 K. This antiferromagnetic ordering indicated spin-flop behavior at magnetic field around 3 Tesla and disappeared at 7 Tesla. We think this antiferromagnetic states is originated from the dimerized structure of the TEMPO radical discussed in the crystallographic analysis. The biradical molecule **3** showed Curie-Weiss temperature dependence with a slightly negative Weiss temperature ($\theta = -2.4$ K). The Curie constant is 0.727 K emu mol^{-1} and almost correspond to the value calculated from two independent S = 1/2 spins (0.75 K emu mol^{-1}), suggesting that the interaction between the two TEMPO radical is very weak and they work almost independently in the crystal.

Structure and Physical Properties of the $Au(CN)_2$ salt of 1

The $Au(CN)_2^-$ salt of **1** was electrochemically prepared in 1,2-dichloroethane. Crystal data: $C_{21}H_{20}S_8N_3Au_{1.5}O$, $M = 882.34$, triclinic, space group $P\,\bar{1}$, $a = 11.047(3)$, $b = 18.643(7)$, $c = 7.433(2)$ Å, $\alpha = 90.94(3)$, $\beta = 100.51(2)$, $\gamma = 74.04(2)°$, $V = 1446.2(8)$ Å^3, $Z = 2$, $R = 0.046$, $R_W = 0.047$. The D:A ratio of this salt is revealed to be 2:3 by an X-ray structure analysis and each TEMPOET has +1.5 valence. We consider that the TEMPO radical is not oxidized in this salt, judging by the bent form of the N-O bond from the C-N-C plane of the piperidine ring and N-O bond length. Two donors are dimerized with an interplane distance of 3.53 Å and slipped about 1.62 Å along the molecular short axis and avoid the steric hindrance of the bulky TEMPO part. One of the $Au(CN)_2^-$ anion exists between dimers, indicating no overlap of π-orbitals between dimers in the donor stack. The other $Au(CN)_2^-$ anion is located between the donor layers. Three S-S contacts A (≤ 3.7 Å) exist between the side-by-side molecules. The dimers array along the *c*-axis with shifting molecular long axis (4.84 Å) and form sheet-like structure (Figure 4). There is one very short O-O contact [3.24(2) Å] between the donor sheets, suggesting the possibility of strong spin-spin interaction. The room temperature electrical conductivity of this salt is low value of about 10^{-3} S cm^{-1} due to the highly oxidized state and undesirable stacking of donors. The temperature dependence of resistivity is semiconducting with an activation energy of 0.20 eV. The measurement of the magnetic susceptibility of this salt showed much smaller room temperature value (9.6×10^{-4} emu mol^{-1} for 2:3 salt) than the expected high value from the coexistence of two TEMPO radical spins and one cation radical spin in $(TEMPOET)_2[Au(CN)_2]_3$ salt. This result suggests the existence of intramolecular spin singlet formation and/or intermolecular strong antiferromagnetic spin configuration, which may be derived from the strong spin-spin interaction by very short O-O distance between donor sheets (I). Furthermore the χT value decreases monotonically with decreasing temperature. The temperature dependence of magnetic susceptibility is roughly fitted to a Bleaney-Bowers expression and singlet-triplet gap is estimated to a large value of $-2J = 206\,\mathrm{cm}^{-1}$ except for the lower temperature region probably due to a small amount of paramagnetic impurities and lattice defects. This result suggests the strong antiferromagnetic interaction between two spins and almost singlet ground state.

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