

New π -extended organic donor containing a stable TEMPO radical as a candidate for conducting magnetic multifunctional materials

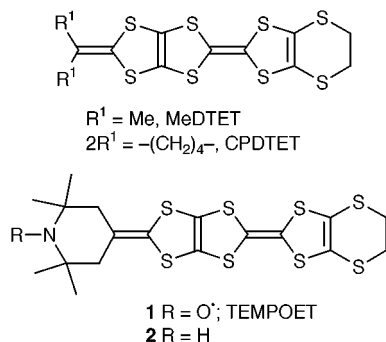
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A novel organic electron donor containing a stable TEMPO radical (TEMPOET) was synthesized and its magnetic and electrochemical properties were investigated; furthermore, the crystal structure and physical properties of the $\text{Au}(\text{CN})_2^-$ salt of TEMPOET were clarified.

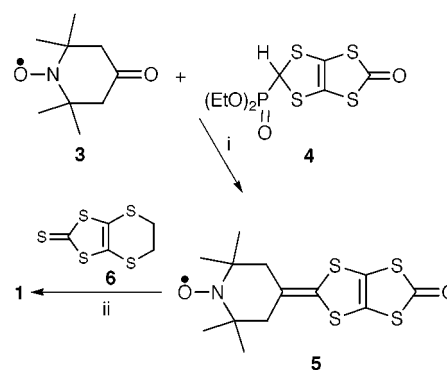
Organic molecular magnetism has become a very active field of research since the discovery of the first pure organic ferromagnet, *p*-nitrophenyl nitronyl nitroxide (β -NPNN), in 1991 and the subsequent development of several ferromagnets based on aminoxy radicals.^{1,2} On the other hand, recent studies on molecular conductors and superconductors containing magnetic transition metal anions, such as the $(\text{ET})_2(\text{H}_2\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot \text{PhCN}$ salt, a series of λ -(BETS)₂Fe_xGa_{1-x}Cl₄ alloy salts and the κ -(BETS)₂FeBr₄ salt³ [where ET is bis(ethylenedithio)-TTF and BETS is bis(ethylenedithio)tetraselenafulvalene], have stimulated interest in the interplay between conductivity and magnetism in the search for new organic conductors. Among them, several donors containing a stable aminoxy radical have been prepared by several research groups for the development of novel organic conducting magnetic multifunctional materials and organic ferromagnetic metals.^{4,5} However, no highly conducting salt has been obtained from these donors so far. From the view point of the realization of metallic conductivity, we designed a molecular structure as the fusion of a stable TEMPO radical moiety to a DTET-TTF skeleton, which is a promising building block for realizing stable metallic behavior, as reported in the cases of MeDTET



and CPDTET salts.^{6,7} Here we present the synthesis, structure and physical properties of novel organic donor TEMPOET **1**. Furthermore, we report here the structure and physical properties of its $\text{Au}(\text{CN})_2^-$ salt as the first X-ray structure analysis of a cation radical salt based on a TEMPO radical-containing donor.

TEMPOET **1** was synthesized as shown in Scheme 1. Thus, the ketone **5** was obtained in 52% yield by the Wittig–Horner reaction of **4**⁸ and 4-oxo-TEMPO **3**. It was then reacted with thione **6** by a cross-coupling reaction. TEMPOET was obtained as air-stable microcrystals in 45% yield.[†]

As shown in Fig. 1, TEMPOET presents four waves at +0.56, +0.88, +1.17 and +1.77 V vs. Ag/AgCl, the first and third ones are slightly reversible, the second one is completely reversible and the fourth one irreversible. The first oxidation potential, +0.56 V, is almost the same as that of ET (+0.53 V). On the other hand, the corresponding piperidine analogue **2** showed



Scheme 1 Reagents and conditions: i, 0.5 M LDA (1.1 equiv.), THF, -78°C , 15 min; ii, $\text{P}(\text{OEt})_3$ (100 equiv.), 75°C , 45 min.

three redox waves. Comparing the redox potentials of **1** to those of **2**, three (+0.56, +0.88 and +1.77 V) of the four potentials of **1** are almost equivalent to the three potentials of **2** (+0.55, +0.87 and +1.74 V). Therefore, the oxidation of the TEMPO radical part is considered to occur at the third oxidation process (+1.17 V), suggesting the possibility of the formation of the cation radical salts with an active TEMPO radical spin. However, the almost complete loss of reversibility of the first redox wave of **1** might indicate the existence of some further reaction in the reductive process of the cation radical state of **1** dissimilar to the case of **2**. The static magnetic susceptibility measurement of **1** showed a paramagnetic value ($\chi_{\text{rt}} = 1.25 \times 10^{-3} \text{ emu mol}^{-1}$) corresponding to one $S = 1/2$ spin per molecule and a Curie–Weiss temperature dependence ($\theta = -1.00 \text{ K}$).

The $\text{Au}(\text{CN})_2^-$ salt of **1** was electrochemically prepared in 1,2-dichloroethane. An X-ray structure analysis revealed that the D:A ratio of this salt is 2:3 and each TEMPOET has +1.5 valence.[‡] The N–O bond length of the TEMPO radical part is 1.42(1) Å and is a little longer than that of the reported neutral TEMPO radicals (1.27–1.30 Å).⁹ When a TEMPO radical is oxidized, the N–O bond length becomes shorter than the neutral one because of $\text{N}^+=\text{O}$ double bond formation, as in the case of TEMPO•TCNQF₄ complex [1.195(5) Å].¹⁰ Furthermore, judging from the bent form of the N–O bond from the C–N–C plane

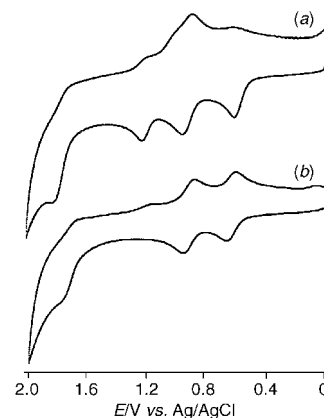


Fig. 1 Cyclic voltammograms of (a) **1** and (b) **2** in PhCN (scan rate 50 mV s^{-1}).

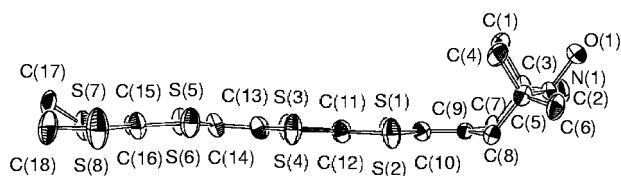


Fig. 2 Structure of the donor molecule in the $(1)_2[\text{Au}(\text{CN})_2]_3$ salt.

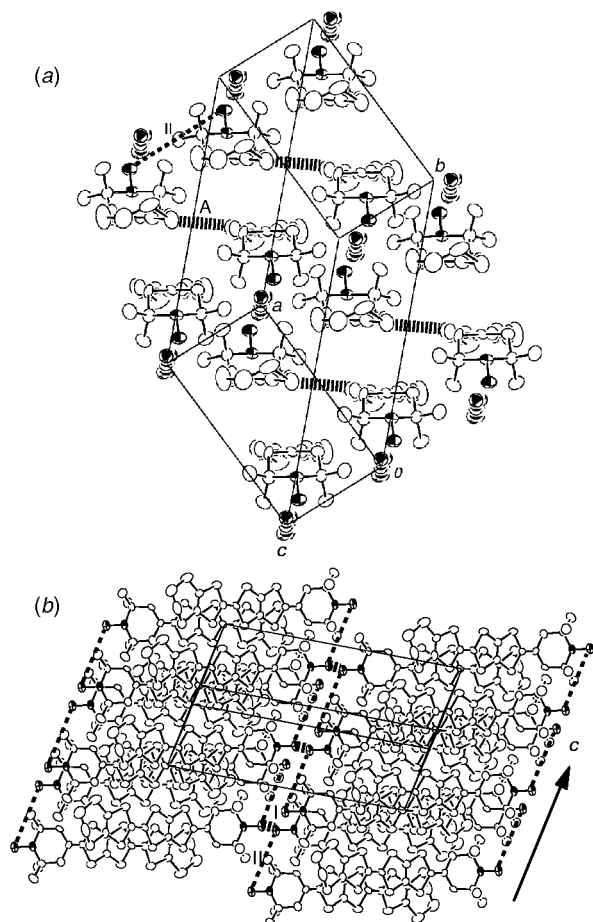


Fig. 3 Crystal structure of $(1)_2[\text{Au}(\text{CN})_2]_3$ salt viewed (a) along the molecular long axis and (b) perpendicular to the molecular planes. S–S contacts: A S(1)–S(7) 3.624(5), S(3)–S(5) 3.658(5) and S(3)–S(7) 3.529(5) Å. O–O distances: I 3.24 and II 7.43 Å.

and the redox behavior of this donor discussed above, we think that the TEMPO radical part is not oxidized in this $\text{Au}(\text{CN})_2^-$ salt. The framework of TEMPOET is almost flat except for the chair-formed TEMPO part, suggesting the oxidation of the donor part (Fig. 2). One of the $\text{Au}(\text{CN})_2^-$ anions exists between the donor dimers, indicating no overlap of π -orbitals between dimers in the donor stack [Fig. 3(a)]. The dimers array along the c -axis with an offset of the molecular long axis (4.84 Å) and form sheet-like structure [Fig. 3(b)]. There is one very short O...O contact [3.24(2) Å] between the donor sheets. The room temperature electrical conductivity of this salt is low, with a value of about $10^{-3} \text{ S cm}^{-1}$, due to the highly oxidized state and undesirable stacking of donors. The temperature dependence of the resistivity produces semiconducting behaviour with an activation energy of 0.20 eV. The measurement of the magnetic susceptibility of this salt showed a much smaller room temperature value ($9.6 \times 10^{-4} \text{ emu mol}^{-1}$ for a 2:3 salt) than the expected high value from the coexistence of two TEMPO radical spins and one cation radical spin in the $(1)_2[\text{Au}(\text{CN})_2]_3$ 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 *via* the very short O–O distances between donor sheets (I). Furthermore the χT value decreases monotonically with decreasing temperature, as shown in Fig. 4. The

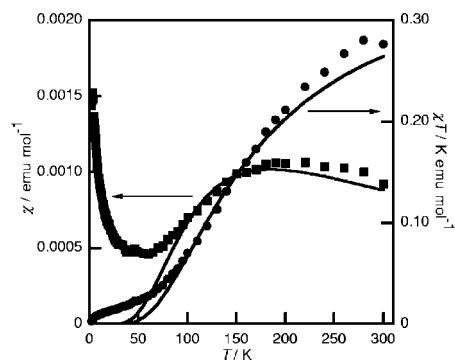


Fig. 4 χT (■) and $\chi T-T$ (●) plots for the $(1)_2[\text{Au}(\text{CN})_2]_3$ salt. Solid lines are calculated on the basis of a Bleaney–Bowers expression.

temperature dependence of the magnetic susceptibility is roughly fitted to a Bleaney–Bowers expression¹¹ and the singlet–triplet gap is estimated to be large, with a value of $-2J = 206 \text{ cm}^{-1}$, 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 an almost singlet ground state.

Notes and references

† Selected data for 1: mp 206–207 °C (decomp.); m/z (70 eV, EI) 523 (100%) [$M^+ + 1$], 525 (24) [$\text{C}_{18}\text{H}_{20}\text{NOS}_8$ (522.84): calc. C, 41.35; H, 3.86; N, 2.68. Found: C, 41.27; H, 3.71; N, 2.64%]; EPR (benzene) $g = 2.0061$, $a_N = 15.1 \text{ G}$.

‡ Crystal data for $1_2[\text{Au}(\text{CN})_2]_3$: $\text{C}_{21}\text{H}_{20}\text{S}_8\text{N}_4\text{Au}_{1.5}\text{O}$, $M = 896.34$, triclinic, space group $P\bar{1}$, $a = 11.047(3)$, $b = 18.643(7)$, $c = 7.433(2) \text{ Å}$, $\alpha = 90.94(3)$, $\beta = 100.51(2)$, $\gamma = 74.04(2)^\circ$, $U = 1446.2(8) \text{ Å}^3$, $T = 293 \text{ K}$, $Z = 2$, μ (Mo–K α) = 8.237 mm^{-1} , 6561 reflections measured, 6259 independent ($R_{\text{int}} = 0.040$). The final R and R_w were 0.046 and 0.047 (3413 reflections [$I > 3.0\sigma(I)$]). One of the $\text{Au}(\text{CN})_2^-$ anions is disordered over an inversion centre. CCDC 182/158. See <http://www.rsc.org/suppdata/cc/1999/2417/> for crystallographic data in .cif format.

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