# Novel $\pi$-Extended Donors Containing a 2,2,5,5-Tetramethylpyrrolin-1-yloxyl Radical Designed for Magnetic Molecular Conductors

Emiko Fujiwara, Akiko Kobayashi,* Hideki Fujiwara,*† Toyonari Sugimoto,† and Hayao Kobayashi††
*Research Centre for Spectrochemistry, Graduate School of Science, The University of Tokyo,*
*Hongo, Bunkyo-ku, Tokyo 113-0033*
†*Research Institute for Advanced Science and Technology, Osaka Prefecture University and CREST, JST,*
*Gakuen-cho, Sakai 599-8570*
††*Institute for Molecular Science and CREST, JST, Myodaiji, Okazaki 444-8585*

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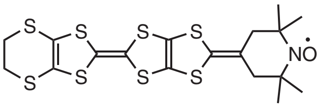
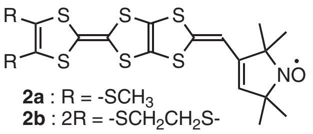
We synthesized $\pi$-extended donors for magnetic conductors that contain a stable 2,2,5,5-tetramethylpyrrolin-1-yloxyl radical, and cleared their structure and physical properties. We also discussed the conducting and magnetic properties of cation radical salts of the synthesized donor.

In the investigation on the multifunctionality of organic conducting materials, the development of magnetic organic conductors is one of the most interesting topics because the interaction between electrical conductivity and magnetism created novel physical phenomena such as field-induced superconductivity in $\pi$–d interacted BETS [=bis(ethylenedithio)tetraselenafulvalene] systems like $\lambda$-(BETS)$_2$FeCl$_4$ and $\kappa$-(BETS)$_2$FeBr$_4$ salts.[1] Among them, we focused on $\pi$-donor molecules that bear stable organic radicals such as TEMPO or PROXYL radicals to develop magnetic organic conductors.[2,3] Thus, we investigated a $\pi$-extended TTF (= tetrathiafulvalene) donor molecules **1** in which a TEMPO radical part directly connects with the donor part through a double bond.[2] However, a magnetic contribution from the localized spins of the TEMPO radical part disappeared in cation radical salts of **1**, and the coexistence of the localized spins and the cation radical moments could not be achieved probably because of singlet formation by very strong intramolecular interaction between them. To adjust the intramolecular interaction, we designed new donor molecules **2** in which one carbon atom is inserted to the connecting bridge of **1** and the TEMPO radical is replaced by a five-membered 2,2,5,5-tetramethylpyrrolin-1-yloxyl radical. Here, we present the synthesis, structure and physical properties of novel $\pi$-extended electron donors that contain a stable radical part **2a**, **2b**. We also discuss the physical properties of cation radical salts based on donor **2b**.

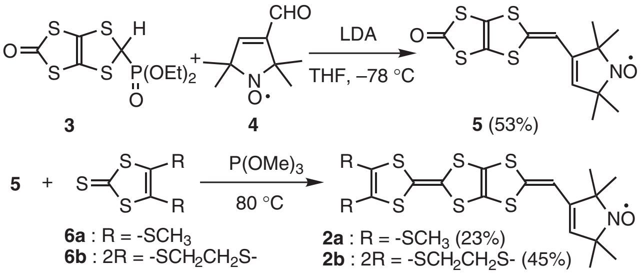


**1**



**2a** : R = -SCH$_3$
**2b** : 2R = -SCH$_2$CH$_2$S-

Synthesis of $\pi$-extended donors **2a**, **2b** was performed according to Scheme 1. Thus, ketone **5** was prepared in 53% yield by the Wittig–Horner reaction between the phosphonate compound **3**[4] and the aldehyde containing a stable radical **4**[5] at −78 °C. Then, a trimethy phosphite-mediated cross coupling reaction was performed between ketone **5**[6] and the corresponding thione compounds **6a**, **6b**. After separation by a column chromatography (deactivated silica gel, eluent: dichloromethane : CS$_2$ = 2:1, v/v), donors **2a**, **2b** were obtained as air-stable microcrystals in the yields of 23 and 45%, respectively.[6] An X-ray crystal structure analysis was performed on a red plate-like single crystal of **2b**, which was recrystallized from CS$_2$/$n$-heptane.[7] Figure 1 shows the molecular structure of donor molecule **2b**. The organic radical part connects with the donor part with a dihedral angle of about 20°. In the unit cell, the donor molecules uniformly stack along the $a$ axis with an interplanar distance of 3.67 Å between TTF parts as shown in Figure 1. Because of a head-to-head overlap mode of the stacking, a slip distance becomes long, 4.68 Å, to avoid the steric hindrance of the bulky organic radical part. There are several S···S contacts (<3.7 Å) along the side-by-side direction, suggesting that donor **2b** can construct the two-dimensional network of intermolecular interactions in cation radical salts. Measurement on the static magnetic susceptibility of **2b** showed a Curie–Weiss temperature dependence with a slight antiferromagnetic interaction ($\theta = -0.7$ K) and a Curie constant ($C = 0.355$ emu K mol$^{-1}$) corresponding to $S = 1/2$ spin per molecule.



**Scheme 1.** Synthesis of donors **2a**, **2b**.

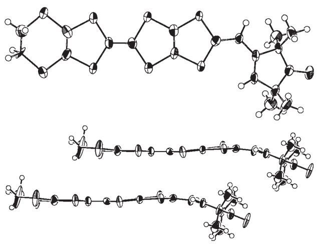


**Figure 1.** Molecular structure of donor **2b**.

The electrochemical properties of donors **2a**, **2b** were measured by cyclic voltammetry (CV) and oxidation potentials are summarized in Table 1. The donors showed four reversible one-electron redox waves corresponding to three 1,3-dithiole rings and one organic radical. Since aldehyde **4** showed an oxidation potential at +0.98 V, the first oxidation of donors **2a**, **2b** around +0.58 V, which is almost the same as that of **1**

(+0.56 V), occurs at the TTF part and the third oxidation occurs at the organic radical part. A molecular orbital calculation was performed by the semiempirical PM3 (UHF) method using MOPAC package. Figure 2 shows the molecular orbitals of donor **2b** below the HOMO level. The highest two orbitals (74$\beta$ and 75$\alpha$) originate from the donor part and the SOMO (74$\alpha$) localizes at the radical part. These results correspond to the CV measurements and indicate that the cation radical spin and the localized radical spin may coexist in the oxidized state.

**Table 1.** Redox potentials of donors **2a**, **2b**, **1** and aldehyde **4**[a]

| Compounds | $E_1$ / V | $E_2$ / V | $E_3$ / V | $E_4$ / V |
|---|---|---|---|---|
| **2a** | +0.58 | +0.86 | +0.95 | +1.67 |
| **2b** | +0.59 | +0.88 | +0.96 | +1.69 |
| **1** | +0.56 | +0.88 | +1.17 | +1.77 |
| **4** | +0.98 | | | |

[a] 0.1 mol dm$^{-3}$ $n$-Bu$_4$N•PF$_6$ in PhCN, Pt electrode, 20 °C, scan rate of 50 mV s$^{-1}$, $V$ vs Ag/AgCl.

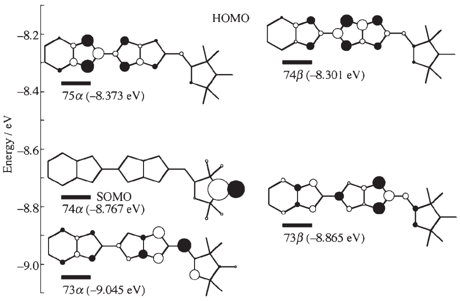


**Figure 2.** Molecular orbitals of donor **2b**.

Preparation of cation radical salts of the radical-containing donors was tried by an electrochemical oxidation with several kinds of supporting electrolytes in chlorobenzene/ethanol (9:1, v/v) under a constant current of 0.8 µA. Only the PF$_6{}^-$ and ReO$_4{}^-$ salts of **2b** were obtained as black microcrystals. Because it was difficult to obtain good crystals that are suitable for structure analyses, D:A composition of the obtained salts was estimated by the electron dispersion spectroscopy (EDS). The magnetic susceptibilities of these salts were measured using a SQUID susceptometer and the electrical conductivities of single crystals were measured by a four-probe method. Although the ReO$_4{}^-$ salt has a 1:1 composition, it shows a relatively high room-temperature conductivity of 0.9 S cm$^{-1}$ and semiconducting behavior with a small activation energy (0.07 eV). As shown in Figure 3, this salt shows a slightly larger room-temperature $\chi T$ value per 1:1 salt (0.40 emu K mol$^{-1}$) than that calculated for $S = 1/2$ system (0.375 emu K mol$^{-1}$), suggesting a quite small contribution from the cation radical moments ($\chi_\pi \approx 1 \times 10^{-4}$ emu mol$^{-1}$ at room temperature). Below ca. 120 K, the $\chi T$ value obeys a Curie–Weiss temperature dependence with a relatively large Weiss temperature ($\theta = -2.8$ K), suggesting that an antiferromagnetic interaction exists between the organic radicals. On the other hand, the PF$_6{}^-$ salt has a 2:1 stoichiometry of the D:A composition. The room temperature conductivity and activation energy have an almost the same order (0.2 S cm$^{-1}$ and 0.10 eV) as the ReO$_4{}^-$ salt. Above ca. 60 K, as Figure 3 indicates, the $\chi T$ values of the PF$_6{}^-$ salt are much larger than the calculated value for two $S = 1/2$ spin per 2:1 salt, suggesting that the cation radical moment of the donor moiety ($\chi_\pi \approx 6 \times 10^{-4}$ emu mol$^{-1}$ at room temperature) and the localized spins of the stable radical coexist. This large susceptibility of the cation radical moments seems to show a strong correlation of conduction electrons. As the temperature decreases, the $\chi T$ value of the PF$_6{}^-$ salt decreases, and obeys a Curie–Weiss temperature dependence below ca. 60 K with a small Weiss temperature of $\theta = -1.3$ K, suggesting that the cation radical moments disappear at low temperature region.

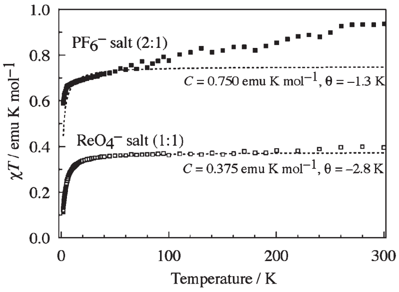


**Figure 3.** Temperature dependence of the $\chi T$ values of the PF$_6{}^-$ (closed square) and ReO$_4{}^-$ (opened square) salts of donor **2b**. Dotted lines are Curie–Weiss fittings on the basis of the indicated parameters in the Figure.

In summary, the modification of the molecular structure in donor **2b** results in the achievement of relatively good conducting properties and the coexistence of the cation radical moments and the localized spins around room temperatures.

### References and Notes

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6 Selected data for **5**: mp 171–172 °C (dec.); IR (KBr) $\nu$ (cm$^{-1}$) 2969, 1663, 1618, 1561, 1357, 1159, 834; $m/z$ 344 [M$^+$], 330, 314; C$_{13}$H$_{14}$NO$_2$S$_4$ (344.52): Found C 45.16, H 4.04, N 4.02; Calcd. C 45.32, H 4.10, N 4.07%; EPR (benzene) $g = 2.0059$, $a_N = 1.43$ mT. Selected data for **2a**: mp 167–168 °C (dec.); IR (KBr) $\nu$ (cm$^{-1}$) 2972, 1564, 1550, 1353, 1159, 968; $m/z$ 522 [M$^+$], 507, 492; C$_{18}$H$_{20}$NOS$_8$ (522.89): Found C 41.59, H 3.96, N 2.75; Calcd. C 41.35, H 3.86, N 2.68%; EPR (benzene) $g = 2.0058$, $a_N = 1.44$ mT. Selected data for **2b**: mp 222–223 °C (dec.); IR (KBr) $\nu$ (cm$^{-1}$) 2970, 1567, 1550, 1354, 1160, 1075; $m/z$ 520 [M$^+$], 505, 490; C$_{18}$H$_{18}$NOS$_8$ (520.87): Found C 41.43, H 3.40, N 2.64; Calcd. C 41.51, H 3.48, N 2.69%; EPR (benzene) $g = 2.0058$, $a_N = 1.44$ mT.

7 Crystal data for **2b**: fw = 520.83, Monoclinic, $P2_1$, $a = 5.949(2)$, $b = 13.028(3)$, $c = 14.661(2)$ Å, $\beta = 98.77(2)°$, $V = 1122.9(4)$ Å$^3$, $Z = 2$, $D_{calcd} = 1.54$ g cm$^{-3}$, 3705 unique reflections, the final $R$ and $R_w$ were 0.066 and 0.064 (1803 reflections [$I > 3.0\sigma(I)$]).

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