New π-Electron Donors with a 2,2,5,5-Tetramethylpyrrolin-1-yloxyl Radical Designed for Magnetic Molecular Conductors

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For the development of magnetic molecular conductors, we succeeded in the synthesis of new π-electron donors containing TTF (tetrathiafulvalene) or TTP (tetrathiapentalene) framework and a stable 2,2,5,5-tetramethylpyrrolin-1-yloxyl radical within a molecule and clarified the crystal structure and physical properties of these donors. We also discuss the conducting and magnetic properties of a TCNQF$_4$ complex of the synthesized TTF type donor.

Recently, the development of multifunctional molecular materials bearing conductivity and magnetism has attracted a considerable interest. Among them, molecule-based materials consisting of conducting organic layers and magnetic inorganic layers have been intensively studied, and several unprecedented materials such as paramagnetic/ferromagnetic metals, antiferromagnetic superconductors, and organic conductors that exhibit field-induced superconductivity have been discovered.[1] On the other hand, much stronger interaction can be expected for the π-conjugated donors bearing stable organic radical parts, because the conducting electron and localized spin of organic radical part may coexist in their cation radical states. To study the relationship between the conducting electrons and localized spins, physical properties of several donors have been investigated.[2,3] However, it has been difficult to construct the conducting systems based on these donors because the bulky radical moieties tend to interfere with the formation of conduction paths. We have tried to overcome the problem by the selection of an organic radical part with small size.[4] Here, we present the synthesis, structure and physical properties of novel TTF and TTP donors that contain a stable radical part **1a** and **1b** (Chart 1). We also discuss the physical properties of a charge-transfer salt based on donor **1a**.

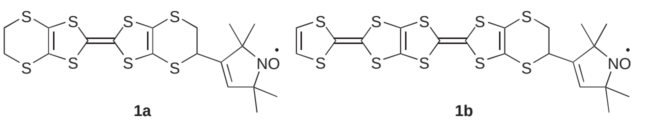
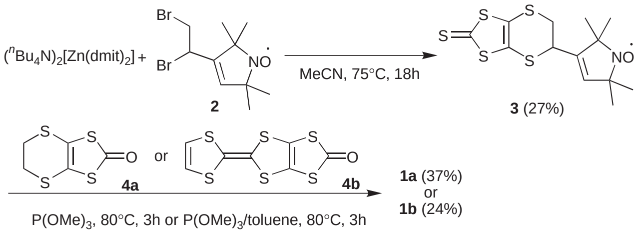


Chart 1.



Scheme 1. Synthesis of donors **1a** and **1b**.

Syntheses of **1a** and **1b** were performed according to Scheme 1. Thus, thione **3** was obtained as yellow microcrystals in 27% yield by the reaction of a zinc complex (^{n}Bu$_4$N)$_2$-[Zn(dmit)$_2$] with the dibromo compound containing a stable radical **2** in MeCN at 75 °C, which was prepared as a racemic mixture according to the literature.[5] Then, a trimethyl phosphite-mediated cross-coupling reaction was performed between thione **3** and the corresponding ketone compounds **4a** and **4b**.[6] After separation by column chromatography (deactivated silica gel, eluent: CS$_2$:AcOEt = 10:1, v/v), donors **1a** and **1b** were obtained as air-stable orange and reddish-brown microcrystals in the yields of 37 and 24%, respectively.[7]

An X-ray crystal structure analysis was performed on a plate-like single crystal of **1a**•MeCN, which was obtained by recrystallization from CS$_2$/MeCN.[8] In the unit cell, there are crystallographically independent one donor molecule and one MeCN molecule (Figure 1a). As shown in Figure 1b, the TTF moiety has a bent structure as often observed in neutral TTF derivatives. The organic radical part connects with the donor part with a dihedral angle of about 90°, suggesting that the conducting electron and localized spin can coexist within a single molecule in the cation radical state. The donors overlap each other in a head-to-tail manner to form a dimer (see Figures 1c and 1d). There is no contact between the adjacent

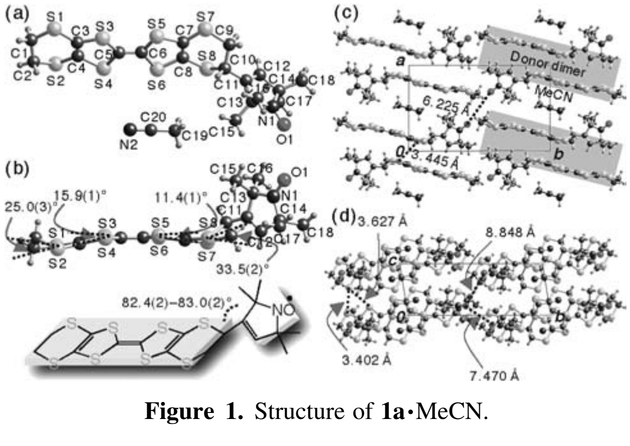


Figure 1. Structure of **1a**•MeCN.

Table 1. Redox potentials of **1a** and **1b** and related compounds[a]

Compounds	E_1	E_2	E_3	E_4	E_5
1a[b]	+0.54	+0.91[d]			
1b[c]	+0.55	+0.78	+0.97	+1.13	+1.32
3[b]	+0.95				
ET[b]	+0.53	+0.88			

[a] 0.1 mol dm^{-3} ^{n}Bu$_4$N•PF$_6$ in PhCN, Pt electrode, scan rate of 50 mV·s^{-1}, V vs. Ag/AgCl. [b] Measured at 20 °C. [c] Measured at 60 °C. [d] Two electron redox process.

dimers along the *a* axis. On the other hand, several S···S contacts (<3.7 Å) were observed both in the dimer and along the side-by-side direction of the donor molecule. The O···O distances between the organic radical parts are long owing to the head-to-tail type overlap mode and solvent-containing stacking structure, suggesting that the magnetic interaction is weak between the NO radicals.

Measurement on the static magnetic susceptibility of **1a**•MeCN and **1b** under 5 kOe showed a Curie–Weiss temperature dependence with slight antiferromagnetic interactions ($\theta = -0.2$ K for **1a**•MeCN and $\theta = -0.6$ K for **1b**) and Curie constants ($C = 0.380$ emu K mol^{-1} for both **1a**•MeCN and **1b**) corresponding to one $S = 1/2$ spin per molecule.

The electrochemical properties of **1a** and **1b** were measured by a CV technique. (Table 1) Donor **1a** shows one pair of reversible one-electron redox waves and one pair of reversible two-electron waves. The first oxidation potential (+0.54 V) is almost the same as that of bis(ethylenedithio)-TTF (ET) (+0.53 V), suggesting similar donating abilities before and after the substitution of the organic radical part. On the other hand, donor **1b** shows five pairs of reversible one-electron waves corresponding to four 1,3-dithiole rings and one organic radical. Since compound **3** shows an oxidation potential at +0.95 V, the second oxidation of **1a**, which is almost the same as that of **3**, occurs at both the TTF and organic radical parts, and the third oxidation of **1b** occurs at the organic radical part. An MO calculation of **1a** was performed by the B3LYP/6-31G* method using Gaussian 98 package. Figure 2 shows the molecular orbitals of donor **1a** below the HOMO level. The highest two orbitals (136α and 135β) originate from the donor part, and the SOMO (135α) localizes at the radical part. These results indicate that the cation radical spin and the localized radical spin can coexist in the oxidized state.

The donor **1a** formed a charge-transfer complex with TCNQF$_4$ in CS$_2$/MeCN by diffusion method.[9] We determined the ratio of donor:acceptor to be 1:1 by the elemental analysis. The degree of charge transfer (Z) of the TCNQF$_4$ complex was estimated to be almost 1 (0.8) by the IR C≡N stretching frequency (2193 cm^{-1}). The compressed pellet sample of the TCNQF$_4$ complex showed semiconducting behavior with an activation energy of 0.28 eV and a very low room temperature electrical conductivity (4×10^{-5} S cm^{-1}). The static magnetic susceptibilities of this complex were measured by a SQUID magnetometer at 5 kOe and showed that the χT value is almost 0.380 emu K mol^{-1} around room temperatures and obeyed clearly the Curie–Weiss law with a weak antiferromagnetic interaction of $\theta = -1.0$ K.

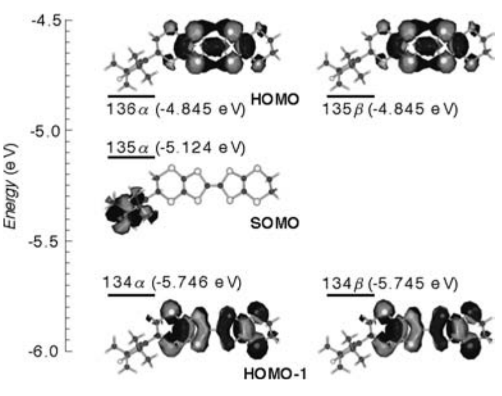


Figure 2. Molecular orbitals of **1a**.

In summary, we have prepared and characterized new TTF- and TTP-type donors with the organic radical part **1a** and **1b**. They suggest the possibility of coexistence of cation radical moment and localized spins of organic radical part in cationic state.

References and Notes

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7 Selected data for **3**: mp 126.5–127.5 °C; IR (KBr) ν (cm^{-1}) 2975, 2926, 1462, 1412, 1358, 1053; m/z 362 [M$^+$]; Calcd for **3**: C, 43.06; H, 4.45; N, 3.86. Found: C, 42.80; H, 4.29; N, 3.61%; ESR (benzene) $g = 2.006$, $a_N = 1.47$ mT. Selected data for **1a**: mp 155.5–156.0 °C (dec.); IR (KBr) ν (cm^{-1}) 2965, 2921, 1460, 1412, 1356; m/z 522 [M$^+$]; Calcd for **1a**•MeCN: C, 41.35; H, 3.86; N, 2.68. Found: C, 41.14; H, 3.89; N, 2.61%; ESR (benzene) $g = 2.006$, $a_N = 1.47$ mT. Selected data for **1b**: mp 197.5–198.5 °C (dec.); IR (KBr) ν (cm^{-1}) 2971, 2924, 1460, 1422, 1356; m/z 607 [M$^+$]; Calcd for **1b** C, 39.44; H, 2.98; N, 2.30. Found: C, 39.12; H, 3.21; N, 2.28%; ESR (benzene) $g = 2.006$, $a_N = 1.47$ mT.

8 Crystal data for **1a**•MeCN: fw 563.89, Triclinic, $P\bar{1}$, $a = 10.962(5)$, $b = 17.938(7)$, $c = 6.670(4)$ Å, $\alpha = 99.25(4)$, $\beta = 100.63(4)$, $\gamma = 87.81(3)°$, $V = 1272(1)$ Å^3, $Z = 2$, $D_{calcd.} = 1.472$ g cm^{-3}, 7439 unique reflections, the final R and R_w were 0.060 and 0.061 (3017 reflections [$I > 2.0\sigma(I)$]).

9 Selected data for **1a**•TCNQF$_4$: mp 158.0–160.0 °C (dec.); IR (KBr) ν (cm^{-1}) 2973, 2929, 2193, 1630, 1536, 1499, 1415, 1385, 1345, 1198, 968; Calcd. for **1a**•TCNQF$_4$: C, 45.10; H, 2.52; N, 8.76. Found: C, 44.80; H, 3.02; N, 8.50%.