New Spiro Donor Molecules: Bis(tetrathiafulvalenyldithio)-methane and -germane

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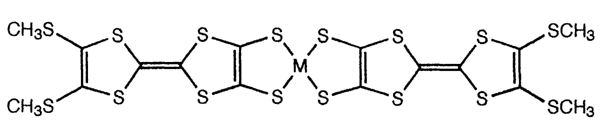
As a new tetrathiafulvalene (TTF)-based donor molecule were synthesized spiro carbon and germanium compounds substituted with two tetrathiafulvalenyldithiolate groups. The redox processes were composed of two pairs of broad and reversible waves, each of which involves two electron transfer. The radical cations or bis(radical cation)'s generated by one- or two-electron oxidation were characterized by ESR.

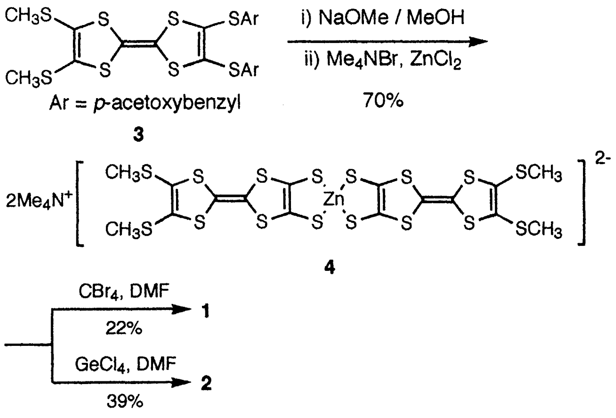
New donor molecules are essential to further development of organic conductors and superconductors.[1] To this end a number of TTF derivatives continue to play an important role.[2,3] We had much interest in a special TTF-based donor molecule, where two TTF groups are arranged by a spiro bond. In crystals obtained from this donor it is expected that each TTF group can be separately stacked to form a two-dimensional column and π- and/or σ-interaction can occur between two columns through a spiro bond.[4] Eventually, a metallic state might maintain at higher temperature as a result of increased dimensionality of conduction columns. Furthermore, if two columns are perfectly perpendicular to each other, ferromagnetic interaction might occur between conduction electrons in each column, giving an unprecedented organic ferromagnetic metal. Now we succeeded in the synthesis of spiro carbon (**1**) and germanium compounds (**2**) substituted with two dimethylthiotetrathiafulvalenyldithio groups, which might come up to our expectations. In this report we disclose the redox behavior of **1** and **2**, and the spin distribution in the radical cations ($1^{+\bullet}$ and $2^{+\bullet}$) or bis(radical cation)'s ($1^{+\bullet,+\bullet}$ and $2^{+\bullet,+\bullet}$).



1 : M = C, **2** : M = Ge

According to Scheme 1, **1** and **2** were successfully synthesized. The 4,5-bis(*p*-acetoxybenzylthio)-1,3-dithiole-2-[(4,5-dimethylthio)-1,3-dithiole]-2-ylidene (**3**)[5] already known was reacted with sodium methoxide (2 equiv.), followed by treatment with zinc chloride (1 equiv.) and tetramethylammonium bromide (1 equiv.) to afford bis(tetramethylammonium) bis(2,3-dimethylthio-6,7-dithiolato) zinc complex (**4**) as a pale orange crystal in 70% yield. The reaction of **4** with carbon tetrabromide (1 equiv.) in DMF at -40 °C gave **1** as a black powder (mp 273-274 °C) in 22% yield. By the similar reaction using germanium tetrachloride in place of carbon tetrabromide, **2** was obtained as a dark brown powder (mp 265-266 °C) in 39% yield. The elemental analyses gave satisfactory results (**1**: Anal. Found: H, 1.71; C, 27.72%. Calcd for $C_{17}H_{12}S_{16}$: H, 1.66; C, 28.00%; **2**: Anal. Found: H, 1.53; C, 24.53%. Calcd for $C_{16}H_{12}S_{16}Ge$: H, 1.53; C, 24.33%). The ^{1}H-NMR spectra of **1** and **2** in $CS_2/CDCl_3$ showed a singlet peak at 2.43 ppm. The molecular structures are not solved yet, since it was unsuccessful to get their single crystals suitable to X-ray structure analysis.

Scheme 1.



The redox behavior of **1** and **2** was investigated using cyclic voltammetry. Figure 1 shows their cyclic voltammograms measured in DMF containing a supporting electrolyte, $Et_4N^{+}\bullet ClO_4^{-}$ at 0 °C. For both **1** and **2** apparently two pairs of broad and reversible waves were observed, and the redox potentials are +0.52 and +0.77 V vs. SCE for **1** and +0.51 and +0.77 V vs. SCE for **2**. The separation between oxidation and

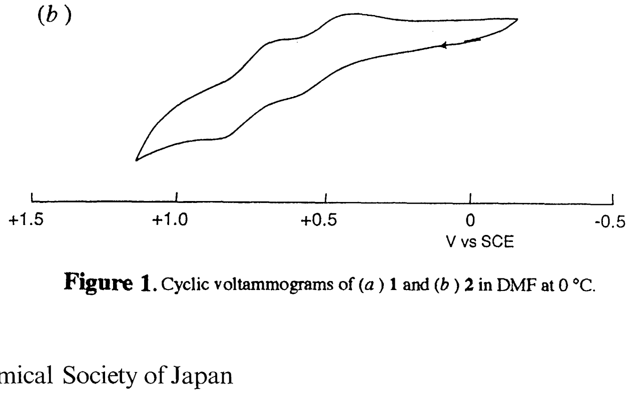


Figure 1. Cyclic voltammograms of (*a*) 1 and (*b*) 2 in DMF at 0 °C.

reduction potentials in each pair of waves is about 100 mV, irrespective of a sweep rate in the range from 50 to 200 mV/sec. This value is larger than that usually obtained in one-electron redox process (60 mV).[6] Accordingly, each pair of waves is actually composed of two pairs of redoxes between **1** (**2**) and $\mathbf{1}^{+\bullet}$ ($\mathbf{2}^{+\bullet}$) and between $\mathbf{1}^{+\bullet}$ ($\mathbf{2}^{+\bullet}$) and $\mathbf{1}^{+\bullet,+\bullet}$ ($\mathbf{2}^{+\bullet,+\bullet}$) at the lower potential, and of two pairs of redoxes between $\mathbf{1}^{+\bullet,+\bullet}$ ($\mathbf{2}^{+\bullet,+\bullet}$) and the radical cation/dication's ($\mathbf{1}^{+\bullet,2+}$ and $\mathbf{2}^{+\bullet,2+}$) and between $\mathbf{1}^{+\bullet,2+}$ ($\mathbf{2}^{+\bullet,2+}$) and the bis(dication)'s ($\mathbf{1}^{2+,2+}$ and $\mathbf{2}^{2+,2+}$) at the higher potential, respectively. The two species, $\mathbf{1}^{+\bullet}$ ($\mathbf{1}^{+\bullet,+\bullet}$) and $\mathbf{2}^{+\bullet}$ ($\mathbf{2}^{+\bullet,+\bullet}$) generated by one- or two-electron oxidation of **1** and **2** were characterized by ESR. To generate these species electrochemical oxidation method was used. Thus, when **1** was electrochemically oxidized with a gradual increase in potential in CS_2/DMF (1:2 (v/v)) containing $Et_4N^+{\bullet}ClO_4^-$ at -40 °C, a group of seven signals was observed at g = 2.0071 in the ESR spectrum (see Figure 2a). The hyperfine splitting constant (a_H) is 0.026 mT. This spectrum can be well understood as hyperfine splitting of an unpaired electron with six equivalent hydrogen atoms, suggesting that either an unpaired electron in $\mathbf{1}^{+\bullet}$ produced by one-electron oxidation of **1** resides in the one TTF moiety or two unpaired electrons in $\mathbf{1}^{+\bullet,+\bullet}$ produced by two-electron oxidation of **1** are separately localized at the two TTF moieties without significant interaction between them. The $\mathbf{1}^{+\bullet}$ or $\mathbf{1}^{+\bullet,+\bullet}$ was stable under these potential and temperature conditions. By further increase in potential the signals only decreased intensity and finally disappeared. The similar spectrum was also obtained in the electrochemical oxidation of **2** under the conditions as above (see Figure 2b), although the g (2.0074) and a_H (0.048 mT) values are slightly different from those of $\mathbf{1}^{+\bullet}$ or $\mathbf{1}^{+\bullet,+\bullet}$. Accordingly, also for $\mathbf{2}^{+\bullet}$ or $\mathbf{2}^{+\bullet,+\bullet}$ one or two unpaired electrons are not delocalized on the whole molecule, but reside in the one- or two-TTF moieties.

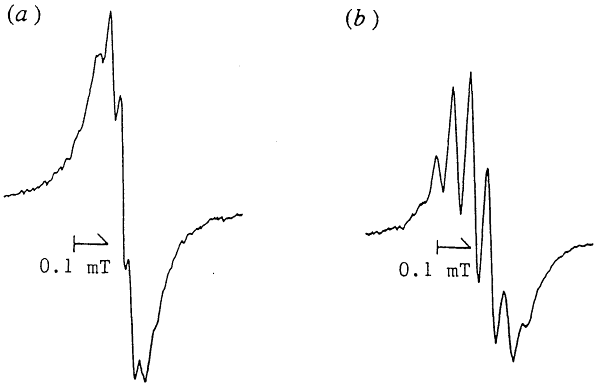


Figure 2. The ESR spectra of (*a*) $\mathbf{1}^{+\bullet}$ (or $\mathbf{1}^{+\bullet,+\bullet}$) and (*b*) $\mathbf{2}^{+\bullet}$ (or $\mathbf{2}^{+\bullet,+\bullet}$) in CS_2 / DMF (1:2 (v/v)) at -40 °C.

In conclusion, π interaction between two TTF moieties through tetrathiamethane and tetrathiagermane spacers in **1** and **2** is quite small in solution, as is obvious from both cyclic voltammetry and ESR results. This main cause might be due to markedly decreased spiro conjugation as a result of large distortion of 1,3-dithiacyclopentene and 1,3-dithia-2-germacyclopentene rings in spiro bond out of a plane, in view of the crystal structure of 2,2'-spirobi[1,3-benzodithiole].[7] However, supposedly such a distortion can be suppressed by significant steric influence of molecules in close proximity in solid, bringing about stronger intramolecular interaction between the two TTF moieties through a spiro bond as well as stronger intermolecular interaction within the TTF columns. We are now attempting to get single crystal salts of $\mathbf{1}^{+\bullet}$ ($\mathbf{1}^{+\bullet,+\bullet}$) and $\mathbf{2}^{+\bullet}$ ($\mathbf{2}^{+\bullet,+\bullet}$) using electrocrystallization method.

References

1 J. M. Williams, U. Geiser, T. Mori, and J. E. Eldridge, Proceedings of the Symposium on *Advances and Properties of Novel Low-dimensional and Conducting or Superconducting Solids*, Honolulu, Hawaii (1995) (published as *Mol. Cryst. Liq. Cryst.*, vol. 284 in 1996).

2 M. R. Bryce, *J. Mater. Chem.*, **5**, 1481 (1995).

3 T. Otsubo, Y. Aso, and K. Takimiya, *Adv. Mater.*, **8**, 203 (1996).

4 H. Durr and R. Gleiter, *Angew. Chem., Int. Ed. Engl.*, **17**, 559 (1978).

5 C. Gemmell, J. D. Kilburn, H. Veck, A. E. Underhill, *Tetrahedron Lett.*, **1992**, 3293; Y. Misaki, H. Nishikawa, K. Kawakami, S. Koyanagi, T. Yamabe, and M. Shiro, *Chem. Lett.*, **1992**, 2321.

6 A. J. Bard and L. R. Faulkner, "*Electrochemical Methods. Fundamentals and Applications*," John Wiley & Sons, New York (1980).

7 K. Ueda, T. Sugimoto, H. Fujita, M. Iwamatsu, and A. Nishinaga, unpublished result.