Molecular Modifications of Methyleneedithio-Tetraselenafulvalene (MDT-TSF) and Methyleneedithio-Diselenadithiafulvalene (MDT-ST) for Superior Electron Donors

Kazuo Takimiya, Yoshiro Kataoka, Yuki Nakamura, Yoshio Aso, Tetsuo Otsubo
Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8527, Japan
Fax +81(82)4248527; E-mail: ktakimi@hiroshima-u.ac.jp
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This paper is dedicated to Emeritus Professor T. Mukaiyama on the occasion of his 77th birthday

Abstract: The dimethyl-, bis(methylthio)-, and ethylenedithio-derivatives of methylenedithio-tetraselenafulvalene and methyleneedithio-diselenadithiafulvalene have been synthesized as new electron donors. The formation and electrical conductivities of their radical cation salts are examined.

Keywords: tetraselenafulvalenes, selenium, electron donors, organic conductors, crystal structure

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Figure 1

Figure 1

Methylenedithio-tetraselenafulvalene (MDT-TSF), [5H-2-(1,3-disenol-2-ylidene)-1,3-dilena-4,6-dithiapentalene], is a prototypical electron donor capable of producing superconducting radical cation salts with various linear anions such as AuI2 and I3. The related diselenadithiafulvalene donor (MDT-ST), [5H-2-(1,3-dithiol-2-ylidene)-1,3-diselena-4,6-dithiapentalene], also gives superconducting radical cation salts isostructural with the MDT-TSF salts. Among molecular-based superconductors, these are quite unique not only in their relatively high Tc (up to 5.5 K) but also in their unusual structures characteristic of uniform donor stacks and an anion lattice incommensurate with the donor lattice, resulting in a non-integral donor/anion ratio of 1:0.42–0.44. Our special interest in developing new electron donors has focused on the hybrids between MDT-TSF or MDT-ST and other superior electron donors, such as bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) and tetramethyltetraselenafulvalene (TMTSF), forming a number of superconducting radical cation salts. In this paper, we report the synthesis and electrochemical properties of the dimethyl-, bis(methylthio)-, and ethylenedithio-substituted derivatives of MDT-TSF and MDT-ST (1a–e, Figure 1), together with the formation and electrical conductivities of their charge-transfer radical cation salts.

The synthesis of new donors (1a–e) is outlined in Scheme 1. The first of this three-step route is trimethyl phosphite-mediated cross-coupling reactions between 1,3-dichaconenole-2-chalconogens (2a–e) and 4-methylthio-5-(2-methoxy carbonyl ethylidene)-1,3-diselene-2-selene (3a) or 1,3-diselene-2-one (3b). The yields of the cross-coupling reactions are largely dependent on the combinations of the two reactants. The syntheses of the dimethyl and bis(methylthio) derivatives (4a and 4b) of tetraselenafulvalene were accomplished in 42% and 35% yields, respectively, by treatment of the corresponding 1,3-diselenole-2-selene (2a or 2b) with 3a. Similarly, the dimethyl derivative (4c) of diselenadithiafulvalene was obtained in 29% yield by treatment of 4,5-dimethyl-1,3-dithiole-2-selene (2c) with 3a. Improvement of the low yields for the cross-coupling reactions was attempted. However, the cross-coupling reaction of 4,5-dimethyl-1,3-dithiole-2-thione (2d) and 3b gave only a trace amount of 4c. On the other hand, the other diselenadithiafulvalene derivatives (4d and 4e) were obtained by a combination of the corresponding 1,3-dithiole-2-thione (2d or 2e) and the 1,3-diselenolene-2-one (3b, Z = O) in 78% and 73% yields, respectively. In the second step, the thus obtained 4a–e were subjected to the deprotection of 2-methoxy carbonyl ethylidene group with cesium hydroxide in DMF solution to produce the TF- and STF-thiolate anion intermediate (4′), which, on in situ treatment with bromochloromethane, smoothly gave the corresponding 2-methylthio-3-chloromethylthio-DSF and -STF derivatives (5a–c) in 52–87% yields. Finally, the ring-closing reaction via transalkylation on the sulfur atom was initiated by treatment with sodium iodide to afford the MDT-TSF and MDT-ST derivatives (1a–e) in 37–66% yields. All these new compounds are well characterized by spectroscopic measurements as well as combustion elemental analyses. The electrochemical properties of new donors (1a–e) were investigated by means of cyclic voltammetry, and
their half-wave oxidation potentials are summarized in Table 1. All molecules showed two reversible redox couples corresponding to the consecutive formation of radical cation and dication species, as usually seen for tetrachalcogenafulvalenes. When compared to those of the parent MDT-TSF and MDT-ST, the oxidation potentials of the derivatives synthesized here are somewhat lowered by their electron-donating methyl groups and elevated by electron-withdrawing alkylthio groups, but the first oxidation potentials (+0.44–0.61 V vs. Ag/AgCl in PhCN) are still low and roughly comparable with those of TMTSF (+0.45 V) and BEDT-TTF (+0.52 V). That is, they are expected to behave as good electron donors. In a detailed comparison, the MDT-ST derivatives 1c–e show lower oxidation potentials than the corresponding MDT-TSF derivatives 1a and 1b indicating stronger electron donating abilities for the former.

Electrochemical crystallization experiments using these donors were carried out, and four radical cation salts of good crystalline shapes were obtained from the donor 1a and one from 1e, as listed in Table 2. The electrical conductivities of these radical cation salts measured at room temperature were highly varied in the range of 100–103 S cm–1. Most of them showed semi-conducting behavior in the variable temperature conductivity measurements, but the variable temperature conductivities of the ClO4 salt of 1a showing an extraordinarily high room temperature conductivity of 1500 S cm–1 could not be measured, because the crystal was fragile under cooling. Only the crystals of the PF6 salt of 1a showed metallic behavior down to ca. 130 K, and its crystal structure was elucidated by X-ray crystallographic analysis. The crystal contains three crystallographically independent donor molecules (donor A, B, and C), one PF6 anion, and one chlorobenzene molecule as the solvent of crystallization, resulting in the composition of (1a)3(PF6)(PhCl).

Table 1 | Half-Wave Oxidation Potentialsa of Electron Donors (1a–1e)

<table>
<thead>
<tr>
<th>Donor</th>
<th>E1/2 (V)</th>
<th>E2/2 (V)</th>
<th>ΔE (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>0.55</td>
<td>0.82</td>
<td>0.27</td>
</tr>
<tr>
<td>1b</td>
<td>0.61</td>
<td>0.82</td>
<td>0.21</td>
</tr>
<tr>
<td>1c</td>
<td>0.44</td>
<td>0.72</td>
<td>0.28</td>
</tr>
<tr>
<td>1d</td>
<td>0.56</td>
<td>0.76</td>
<td>0.20</td>
</tr>
<tr>
<td>1e</td>
<td>0.55</td>
<td>0.77</td>
<td>0.22</td>
</tr>
<tr>
<td>MDT-TSFB</td>
<td>0.56</td>
<td>0.83</td>
<td>0.23</td>
</tr>
<tr>
<td>MDT-STC</td>
<td>0.50</td>
<td>0.78</td>
<td>0.28</td>
</tr>
</tbody>
</table>

a Vs. Ag/AgCl electrode in PhCN containing 0.1 M n-Bu4ClO4 as supporting electrolyte. Pt working and counter electrodes, scan rate 100 mV/s, 23 °C.

b Ref.5
c Ref.2

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In conclusion, we have successfully synthesized the di-
methyl-, bis(methylthio)-, and bis(ethylenedithio)-derivatives of MDT-TSF and MDT-ST using a three-step synthetic route consisting of cross-coupling, deprotection-realkylation, and hetrocyclization on the sulfur atom. All the new compounds have good electron-donating abilities, and upon electrocrystallization, the dimethyl derivative of MDT-TSF 1a and the ethylenedithio derivative of MDT-ST 1e gave conducting radical cation salts of good crystalline shapes. Among them, the ClO₄ salt of 1a showed a metallic behavior down to ca. 130 K, and its crystal structural analysis revealed a unique donor arrangement consisting of the stacking tetramers and dimers in the ‘face-to-edge’ interrelation manner. These results indicate that the molecular modifications of MDT-TSF and MDT-ST can offer promising electron donors for new intriguing conducting radical cation salts. It should be noticed that in the present synthesis, the key intermediates 4a–e can be utilized for the synthesis of homologous electron donors with different fused rings, such as ethylenedithio- and propylenedithio-rings, on the 1,3-diselenole moiety, provided that the thiolate anion intermediate 4¢ is alkylated with an appropriate chlorobromoalkane reagent. Further study along this direction is now under way.

All chemicals and solvents are of reagent grade. All reactions were carried out under nitrogen atmosphere with anhyd solvents. Column chromatography was carried out with Daisogel IR-60 (63–210 μm). Melting points are uncorrected. NMR spectra were obtained in CDCl₃ with a JEOL Lambda 400 spectrometer operating at 400 MHz for ¹H and 100 MHz for ¹³C with TMS as internal reference; chemical shifts (δ) are reported in ppm. EI–MS spectra were obtained on a Shimadzu QP-2000 or a Shimadzu QP-5050A spectrometer using an electron impact ionization procedure (70 eV). The molecular ion peaks of the selenium-containing compounds showed a typical selenium isotopic pattern, and all the selenium-containing mass peaks are reported for ³²Se. IR spectra were obtained on a Shimadzu FTIR-8100A spectrometer. Elemental analyses were performed by Mr. Hideaki Iwatani, Microanalytical Laboratory in Department of Applied Chemistry, Faculty of Engineering, Hiroshima University. Cyclic voltammetry (CV) was carried out on a Hokuto Denko HA-301 potentiostat equipped with a Hokuto Denko HB-104 function generator using benzonitrile as solvent containing tetrabutylammonium perchlorate (n-Bu₄NClO₄, 0.1 M) as supporting electrolyte with a sweep rate of 100 mV/s. Counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl.

**Table 2** Radical Cation Salts of 1a and 1e  

<table>
<thead>
<tr>
<th>Donor</th>
<th>Anion</th>
<th>Appearance</th>
<th>σ&lt;sub&gt;ac&lt;/sub&gt;/S cm⁻¹</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>IBr</td>
<td>black needles</td>
<td>73</td>
<td>semi-conductive</td>
</tr>
<tr>
<td>1a</td>
<td>ClO₄⁻</td>
<td>black needles</td>
<td>1500</td>
<td>b</td>
</tr>
<tr>
<td>1a</td>
<td>AsF₆⁻</td>
<td>black plates</td>
<td>1.4</td>
<td>semi-conductive</td>
</tr>
<tr>
<td>1a</td>
<td>PF₆⁻</td>
<td>black plates</td>
<td>38</td>
<td>metallic up to 130 K</td>
</tr>
<tr>
<td>1e</td>
<td>AsF₆⁻</td>
<td>black plates</td>
<td>9.4</td>
<td>semi-conductive</td>
</tr>
</tbody>
</table>

* Measured on a single crystal with a standard four probe method.  
* Crystals were too fragile to measure the conductivity under cooling.

Figure 2 | Crystal structure of (1a)(PF₆)(PhCl): (a) a-axis projection (top); (b) donor arrangement in the conducting donor layer (bottom)

Phosphite-Mediated Cross-Coupling Reaction of 4-Methylthio-5-(2-methoxycarboxylthio)-1,3-diselenole-2-chalcogenone (3) and 1,3-Dichalcogenole-2-chalcogenones (2); General Procedure: 2,3-Dimethyl-6-methylthio-7-(2-methoxycarboxylthio)-tetraselenafulvalene (4a) as an Example  

To a refluxing mixture of 4,5-dimethyl-1,3-diselenole-2-selone (2a, 303 mg, 1 mmol) and 4-methylthio-5-(2-methoxycarboxylthio)-1,3-diselenole-2-selone (3a, 1.36 g, 3.1 mmol) in benzene (40 mL) was added trimethyl phosphite (2.4 mL, 5 mmol). After the resulting mixture was refluxed for 3 h, the solvent and the excess phosphite reagent were evaporated off, and the residue was purified by column chromatography (silica gel, CH₂Cl₂); the first less-polar fraction (R<sub>f</sub> = 0.9) consisted of tetramethyldiselenenafulvalene (TMTSF, 62 mg, 28%), and the last fraction (R<sub>f</sub> = 0.3) gave 2,6(7')-bis(methylthio)-3,7(6')-bis(2-methoxycarboxylthio)-tetraselenafulvalene (643 mg, 58%). The middle fraction was again subjected to column chromatography (silica gel, CH₂Cl₂–hexane, 1:1), and the main fraction (R<sub>f</sub> = 0.4–0.5, CH₂Cl₂–hexane, 1:1) gave the desired cross-coupling product, 2,6(7')-bis(methylthio)-7-(2-methoxycarboxylthio)-tetraselenafulvalene (4a). Yield: 242 mg (42%); red solid; mp 103–104 °C.

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13C NMR (CDCl$_3$): $\delta = 1.99$ (s, 6 H), 2.45 (s, 3 H), 2.69 (t, $J = 7.3$ Hz, 2 H), 3.07 (t, $J = 7.3$ Hz, 2 H), 3.70 (s, 3 H).

IR (neat): 1736 cm$^{-1}$ (C=O).

Yield: 35%; dark yellow oil.

Anal. Calcd for C$_{13}$H$_{16}$O$_2$S$_6$Se$_2$: C, 28.15; H, 2.91. Found: C, 28.10; H, 2.45.

Yield: 61%; orange fine needles [CH$_2$Cl$_2$–hexane (1:1)]; mp 127–128 °C.

1H NMR (CDCl$_3$): $\delta = 2.46$ (s, 6 H), 2.47 (s, 3 H), 2.70 (t, $J = 7.3$ Hz, 2 H), 3.07 (t, $J = 7.3$ Hz, 2 H), 3.71 (s, 3 H).

13C NMR (CDCl$_3$): $\delta = 20.46$ (2 $\times$), 20.52, 31.96, 34.35, 51.82, 107.20, 107.44, 125.76, 130.14, 130.44, 136.68, 171.58.

MS (EI): $m/z = 468$ [M$^+$.]

Yield: 35%; dark yellow oil.

Anal. Calcd for C$_{13}$H$_{16}$O$_2$S$_4$Se$_2$: C, 31.84; H, 3.29. Found: C, 31.89; H, 2.45.

Yield: 61%; orange fine needles [CH$_2$Cl$_2$–hexane (1:1)]; mp 127–128 °C.


Yield: 87%; red crystals [CH$_2$Cl$_2$–hexane (1:1)]; mp 135–136 °C.

IR (neat): 1738 cm$^{-1}$ (C=O).

1H NMR (CDCl$_3$): $\delta = 2.36$ (s, 6 H), 2.40 (s, 3 H), 2.63 (t, $J = 7.3$ Hz, 2 H), 3.00 (t, $J = 7.3$ Hz, 2 H), 3.64 (s, 3 H).

13C NMR (CDCl$_3$): $\delta = 19.02$ (2 $\times$), 20.35, 31.73, 34.15, 51.63, 98.99, 118.313, 124.86, 127.36, 127.63, 134.90, 171.32.

MS (EI): $m/z = 556$ [M$^+$.]

Yield: 57%; red needles [CH$_2$Cl$_2$–hexane (1:1)]; mp 94–95 °C.

1H NMR (CDCl$_3$): $\delta = 2.462$ (s, 3 H), 2.464 (s, 3 H), 2.48 (s, 3 H), 4.83 (s, 2 H).

13C NMR (CDCl$_3$): $\delta = 20.54$ (2 $\times$), 20.85, 50.97, 107.11, 108.28, 123.44, 130.21, 130.63, 137.99.

MS (EI): $m/z = 610$ [M$^+$.]

Yield: 52%; red powder [CH$_2$Cl$_2$–hexane (1:1)]; mp 101–102 °C.

1H NMR (CDCl$_3$): $\delta = 2.43$ (s, 6 H), 2.48 (s, 3 H), 4.83 (s, 2 H).

13C NMR (CDCl$_3$): $\delta = 19.24$ (2 $\times$), 20.82, 50.12, 99.00, 119.23, 122.95, 127.73, 128.10, 137.47.

MS (EI): $m/z = 516$ [M$^+$.]

Yield: 52%; red powder [CH$_2$Cl$_2$–hexane (1:1)]; mp 101–102 °C.

1H NMR (CDCl$_3$): $\delta = 2.47$ (s, 3 H), 3.30 (s, 4 H), 4.81 (s, 2 H).

2-Methylthio-3-chloromethylthio-tetraselenafulvalenes or 2-Methylthio-3-chloromethylthio-diselenadithiafulvalenes (5e)

General Procedure: 2-Methylthio-3-chloromethylthio-6,7-dimethyltetraselenafulvalene (5a) as an Example

To a degassed DMF solution (20 mL) of 4a (17 mg, 0.34 mmol) was added CsOH·H$_2$O (57 mg, 0.34 mmol) in MeOH (5 mL) during 5 min with stirring at r.t. After the mixture was stirred for further 0.5 h, excess bromochloromethane (ca. 1 mL) was added, and the mixture was stirred for 2 h. The reaction mixture was diluted with water (100 mL) and extracted with CH$_2$Cl$_2$ (4 × 20 mL). The extract was washed with water (100 mL), dried over Na$_2$SO$_4$, and concentrated. The resulting crude product was purified by column chromatography on silica gel eluted with CH$_2$Cl$_2$–hexane (1:1) to give 2-methylthio-3-chloromethylthio-6,7-dimethyltetraselenafulvalene (5a) (R$_f = 0.6$). Recrystallization from CH$_2$Cl$_2$–hexane (1:1) gave an analytically pure sample. Yield: 158 mg (85%); orange solid; mp 139–140 °C.

Yield: 57%; red needles [CH$_2$Cl$_2$–hexane (1:1)]; mp 94–95 °C.

1H NMR (CDCl$_3$): $\delta = 2.00$ (s, 6 H, CH$_3$), 2.48 (s, 3 H, CH$_3$), 4.82 (s, 2 H, CH$_2$).

13C NMR (CDCl$_3$): $\delta = 16.09, 20.83, 30.88, 50.95, 101.50, 110.28, 123.68, 127.03, 137.18, 138.13.

MS (EI): $m/z = 548$ [M$^+$.]

Yield: 52%; red powder [CH$_2$Cl$_2$–hexane (1:1)]; mp 101–102 °C.

1H NMR (CDCl$_3$): $\delta = 2.462$ (s, 3 H), 2.464 (s, 3 H), 2.48 (s, 3 H), 4.83 (s, 2 H).

13C NMR (CDCl$_3$): $\delta = 20.54$ (2 $\times$), 20.85, 50.97, 107.11, 108.28, 123.44, 130.21, 130.63, 137.99.

MS (EI): $m/z = 610$ [M$^+$.]

Yield: 57%; red needles [CH$_2$Cl$_2$–hexane (1:1)]; mp 94–95 °C.

1H NMR (CDCl$_3$): $\delta = 2.462$ (s, 3 H), 2.464 (s, 3 H), 2.48 (s, 3 H), 4.83 (s, 2 H).

13C NMR (CDCl$_3$): $\delta = 20.54$ (2 $\times$), 20.85, 50.97, 107.11, 108.28, 123.44, 130.21, 130.63, 137.99.

MS (EI): $m/z = 610$ [M$^+$.]

Yield: 52%; red powder [CH$_2$Cl$_2$–hexane (1:1)]; mp 101–102 °C.

1H NMR (CDCl$_3$): $\delta = 2.47$ (s, 3 H), 3.30 (s, 4 H), 4.81 (s, 2 H).
CaCl₂, and then concentrated. Recrystallization of the resulting solution was washed with water (2 × 30 mL), dried over CaCl₂, and then concentrated. Recrystallization of the resulting solid from chlorobenzene gave 1a. Yield: 49 mg (47%); yellow needles [carbon disulfide–hexane (2:1)]; mp 210–213 °C.

**Methylenedithio-tetraselenafulvalene and -diselenadithiafulvalene Derivatives; Dimethyl-methylenedithio-tetraselenafulvalene (1a); General Procedure**

A mixture of 5a (113 mg, 0.21 mmol) and NaI (47 mg, 0.63 mmol) in 2-butanone (20 mL) was refluxed for 13.5 h. The mixture was diluted with water (60 mL), and the resulting precipitate was collected by filtration. The solid was dissolved in carbon disulfide (50 mL) and the solution was washed with water (2 × 30 mL), dried over CaCl₂, and then concentrated. Recrystallization of the resulting solid from chlorobenzene gave 1a. Yield: 66%; reddish purple needles [carbon disulfide–hexane (1:1)]; mp 168–170 °C.

**Preparation of Conducting Radical Cation Salts**

Crystals of radical cation salts summarized in Table 2 were prepared by an electrochemical crystallization method using a two-compartment H-shaped glass cell equipped with a platinum wire as the electrodes. A typical procedure is as follows; donor molecule (3 mg) and tetrabutylammonium salts [(n-Bu₄N)X, X = ClO₄⁻, PF₆⁻, AsF₆⁻, IBr⁻, 20–100 mg] were placed in the anode and the cathode compartment, respectively. Chlorobenzene containing ca. 10% of EtOH (ca. 18 mL) was added, and the resulting solution was deaerated with a dry nitrogen stream. The constant current of 0.1–0.2 μA was applied at 25 °C. Within two weeks, radical cation salts as black plates or needles grew on the anode. The crystals were collected by filtration, washed with CH₂Cl₂, dried, and utilized for the conductivity measurements.

**X-Ray Crystal Structure Analysis of (1a)PF₆(PhCl)**

The X-ray analysis was performed on a Rigaku AFC6S four-circle diffractometer (CuKα radiation, λ = 1.54178 Å, graphite monochromator, 2θ max = 126.2°). The structure was resolved with direct methods (SHELXS-86) and refined by full-matrix least-squares on F². All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were not included in the refinement.

Data for the structure were deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-235172. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336033; e-mail: deposit@chemcrys.cam.ac.uk].

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**References**


