JOC Article

A General Method for the Synthesis of Alkylenedithio- and Bis(alkylenedithio)tetraselenafulvalenes

Kazuo Takimiya,* Yoshiro Kataoka, Naoto Niihara, Yoshio Aso, and Tetsuo Otsubo*

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi-Hiroshima 739-8527, Japan

ktakimi@hiroshima-u.ac.jp

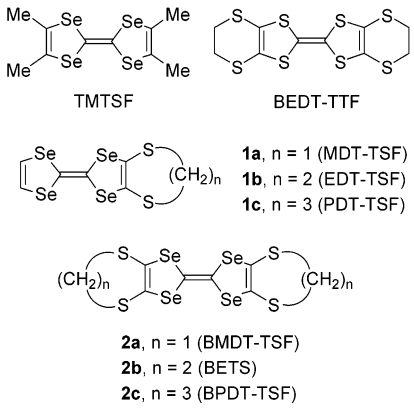
Received February 2, 2003

A general synthetic method toward a series of alkylenedithio- and bis(alkylenedithio)tetraselenafulvalenes, i.e., methylenedithio- (MDT-TSF, **1a**), ethylenedithio- (EDT-TSF, **1b**), propylenedithio- (PDT-TSF, **1c**), bis(methylenedithio)- (BMDT-TSF, **2a**), bis(ethylenedithio)- (BETS, **2b**), and bis(propylenedithio)tetraselenafulvalene (BPDT-TSF, **2c**), as superior electron donors for organic conductors has been developed. This method is advantageous to ready access to a series of compounds from common synthetic intermediates, 2-methylthio-3-(2-methoxycarbonylethylthio)-tetraselenafulvalene (**6**) and 2,6(7′)-bis(methylthio)-3,7(6′)-bis(2-methoxycarbonylethylthio)tetraselenafulvalene (**7**), for the asymmetrical alkylenedithio- and symmetrical bis(alkylenedithio)-TSFs, respectively. These key intermediates are readily prepared by phosphite-promoted coupling reactions of 4-methylthio-5-(2-methoxycarbonylethylthio)-1,3-selenole-2-selone (**5**) or by a reaction of TSF with LDA and methyl 3-thiocyanatopropionate. The latter method provides not only the successful conversion of TSF to these heterocycle derivatives but also a generally acceptable route to them, since TSF is accessible without the toxic and less easily available CSe_2.

Introduction

Tetraselenafulvalene (TSF) derivatives (Chart 1) have been regarded as essential components for the development of superconducting radical cation salts.[1] Historically, the study of organic superconductors was initiated with the discovery of the first superconducting salt, $(TMTSF)_2PF_6$ (TMTSF: tetramethyltetraselenafulvalene), in 1980.[2] Afterward, many superconductors developed were rather based on the sulfur-containing electron donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF). In the past decade, however, not only a series of superconductors[3] but also various intriguing phenomena arising from interplay between conducting electrons and localized spins[4] have been discovered in the radical cation salts of bis(ethylenedithio)tetraselenafulvalene (BETS, **2b**), a TSF analogue of BEDT-TTF. In addition, novel organic superconductors based on the newly developed methylenedithiotetarselenafulvalene (MDT-TSF, **1a**)[5] and its related electron donors[6] have renewed interest in electron donors of the TSF-type.

CHART 1



* To whom correspondence should be addressed. Tel: +81-824-24-7734. Fax: +81-824-24-5494.

(1) For comprehensive reviews on organic superconductors, see: (a) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties, and Theory*; Prentice Hall: Englewood Cliffs, NJ, 1992. (b) Ishiguro, T.; Yamaji, K.; Saito, G. *Organic Superconductors*, 2nd ed.; Springer-Verlag: Berlin, 1998.

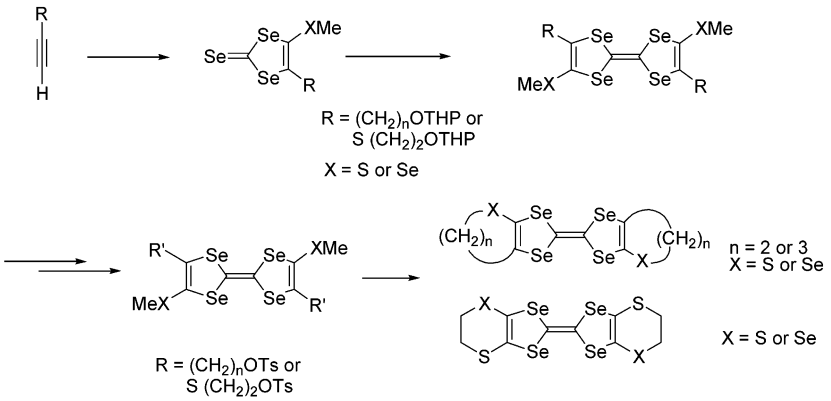
(2) Jérome, D.; Mazaud, A.; Ribault, M.; Bechgaard, K. *J. Phys. Lett.* (*Paris*) **1980**, *41*, L95−L98.

(3) (a) Kobayashi, H.; Udagawa, T.; Tomita, H.; Bun, K.; Naito, T.; Kobayashi, A. *Chem. Lett.* **1993**, 1559−1562. (b) Kobayashi, H.; Tomita, H.; Naito, T.; Kobayashi, A.; Sakai, F.; Watanabe, T.; Cassoux, P. *J. Am. Chem. Soc.* **1996**, *118*, 368−377. (c) Tanaka, H.; Kobayashi, A.; Sato, A.; Akutsu, H.; Kobayashi, H. *J. Am. Chem. Soc.* **1999**, *121*, 760−768. (d) Otsuka, T.; Kobayashi, A.; Miyamoto, Y.; Kiuchi, J.; Wada, N.; Ojima, E.; Fujiwara, H.; Kobayashi, H. *Chem. Lett.* **2000**, 732−733. (e) Kobayashi, H.; Kobayashi, A.; Cassoux, P. *Chem. Soc. Rev.* **2000**, *29*, 325−333. (f) Gritsenko, V.; Tanaka, H.; Kobayashi, H.; Kobayashi, A. *J. Mater. Chem.* **2001**, *11*, 2410−2411. (g) Fujiwara, H.; Fujiwara, E.; Nakazawa, Y.; Narymbetov, B. Z.; Kato, K.; Kobayashi, H.; Kobayashi, A.; Tokumoto, M.; Cassoux, P. *J. Am. Chem. Soc.* **2001**, *123*, 306−314.

(4) (a) Uji, S.; Shinagawa, H.; Terashima, T.; Yakabe, T.; Terai, Y.; Tokumoto, M.; Tanaka, H.; Kobayashi, H. *Nature* **2001**, *410*, 908−910. (b) Balicas, L.; Brooks, J. S.; Storr, K.; Uji, S.; Tokumoto, M.; Tanaka, H.; Kobayashi, H.; Kobayashi, A.; Barzykin, V.; Gor'kov, L. P. *Phys. Rev. Lett.* **2001**, *87*, art. No. 067002. (c) Fujiwara, H.; Kobayashi, H.; Fujiwara, E.; Kobayashi, A. *J. Am. Chem. Soc.* **2002**, *124*, 6816−6817. (d) Zhang, B.; Tanaka, H.; Fujiwara, H.; Kobayashi, H.; Fujiwara, E.; Kobayashi, A. *J. Am. Chem. Soc.* **2002**, *124*, 9982−9983. (d) Fujiwara, E.; Fujiwara, H.; Kobayashi, H.; Otsuka, T.; Kobayashi, A. *Adv. Mater.* **2002**, *14*, 1376−1379.

10.1021/jo034145a CCC: $25.00
Published on Web 05/22/2003

SCHEME 1



From the viewpoint of synthetic chemistry, on the other hand, the synthesis of TSF donors has not been well explored, although a few important methods, for example, a titanocene-involving one for the synthesis of BETS (**2b**),[7] bis(propylenedithio)tetraselenafulvalene (BPDT-TSF, **2c**),[8] and their asymmetrical derivatives,[9] are known. We have thus recognized the importance of developing a versatile synthetic method for preparing TSF derivatives, especially the heterocycle-fused TSFs, and have recently established several reactions suitable for the synthesis of such TSFs. Among them, two breakthrough reactions consist of a one-pot synthesis of 1,3-selenole-2-selones[10] and an outer heterocycle formation via an intramolecular trans-alkylation reaction of a TSF core.[11] A combination of these has opened the way to various heterocycle-fused TSFs; for example, starting from tetrahydropyranyl-protected hydroxyalkyl-[12] or 2-hydroxyethylthioacetylenes,[13] bis(alkylenechalcogeno)- and bis(ethylenedichalcogeno)-TSFs are effectively synthesized, respectively (Scheme 1). The merit of this synthesis is that one can obtain various TSF derivatives possessing the same framework but different chalcogen atoms from the same starting acetylene derivative by choosing the chalcogen reagents in the synthetic sequence.[14]

On the other hand, a drawback of this method is that the size and type of the outer heterocycles attached to the TSF core are exclusively determined by the substituent of the starting acetylene compound, i.e., the R groups in Scheme 1. This means that the method is not necessarily suitable for the synthesis of alkylenedithio- and bis(alkylenedithio)-TSFs with other outer ring sizes.

To solve this problem, we have introduced a deprotection/realkylation procedure on the protected TSF thiolates[15] into the synthetic route described above and found that it provides easy access to a series of alkylenedithio- (**1**) and bis(alkylenedithio)-TSFs (**2**).[16] In this paper, a synthetic method toward these TSF derivatives consisting of the one-pot synthesis of 1,3-selenole-2-selones, deprotection/realkylation of the protected TSF thiolates, and intramolecular trans-alkylation reaction forming the alkylenedithio moiety are described. In addition, an alternative synthetic route to these TSFs from the parent TSF is also mentioned in a carbon diselenide (CSe_2)-free synthesis.

Results and Discussions

Synthesis of Alkylenedithio-TSFs (1a−c). The synthesis of asymmetrical alkylenedithio-TSF is outlined in Scheme 2. In the preliminary report on the synthesis of MDT-TSF (**1a**),[5a] methylthioacetylene (**3**) was used as a starting material, but the preparation and purification of **3** were not very easy owing to its low boiling point (70

(5) (a) Takimiya, K.; Kataoka, Y.; Aso, Y.; Otsubo, T.; Fukuoka, H.; Yamanaka, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 1122−1125. (b) Kawamoto, T.; Mori, T.; Takimiya, K.; Kataoka, Y.; Aso, Y.; Otsubo, T. *Phys. Rev. B* **2002**, *65*, 140508(R). (c) Kawamoto, T.; Mori, T.; Terakura, C.; Terashima, T.; Uji, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *Phys. Rev. B* **2003**, *67*, 020508(R). (d) Takimiya, K.; Kataoka, Y.; Kodani, M.; Aso, Y.; Otsubo, T. *Synth. Met.* **2003**, *133*−*134*, 185−187.

(6) (a) Kodani, M.; Takamori, A.; Takimiya, K.; Aso, Y.; Otsubo, T. *J. Solid State Chem.* **2002**, *168* 582−589. (b) Takimiya, K.; Takamori, A.; Aso, Y.; Otsubo, T.; Kawamoto, T.; Mori, T. *Chem. Mater.* **2003**, *15*, 1225−1227.

(7) (a) Kato, R.; Kobayashi, H.; Kobayashi, A. *Synth. Met.* **1991**, *42*, 2093−2096. (b) Courcet, T.; Malfant, I.; Pokhodnia, K.; Cassoux, P. *N. J. Chem.* **1998**, *5*, 585−589.

(8) (a) Kato, R.; Aonuma, S.; Okano, Y.; Sawa, H.; Kobayashi, A.; Kobayashi, H. *Synth. Met.* **1993**, *55*−*57*, 2084−2089.

(9) (a) Kobayashi, A.; Kato, R.; Naito, T.; Kobayashi, H. *Synth. Met.* **1993**, *55*−*57*, 2078−2083. (b) Kato, R.; Aonuma, S.; Okano, Y.; Sawa, H.; Tamura, M.; Kinoshita, M.; Oshima, K.; Kobayashi, A.; Bun, K.; Kobayashi, H. *Synth. Met.* **1993**, *61*, 199−1162. (c) Okano, Y.; Sawa, H.; Aonuma, S.; Kato, R. *Synth. Met.* **1995**, *70*, 1161−1162. (d) Naito, T.; Kobayashi, H.; Kobayashi, A.; Underhill, A. E. *Chem. Commun.* **1996**, 521−522. (e) Naito, T.; Kobayashi, H.; Kobayashi, A. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 107−114. (f) Imakubo, T.; Sawa, H.; Kato, R. *Synth. Met.* **1997**, *86*, 1883−1884. (g) Ojima, E.; Fujiwara, F.; Kobayashi, H. *Adv. Mater.* **1999**, *11*, 459−462. (h) Sato, A.; Ojima, E.; Kobayashi, H.; Kobayashi, A. *J. Mater. Chem.* **1999**, *9*, 2365−2371. (i) Sakurai, N.; Mori, H.; Tanaka, S.; Moriyama, H. *Chem. Lett.* **1999**, 1191−1192. (j) Imakubo, T.; Tajima, N.; Tamura, M.; Kato, R.; Nishio, Y.; Kajita, K. *J. Mater. Chem.* **2002**, *12*, 159−161.

(10) Takimiya, K.; Morikami, A.; Otsubo, T. *Synlett*, **1997**, 319−321.

(11) Jigami, T.; Takimiya, K.; Aso, Y.; Otsubo, T. *Chem. Lett.* **1997**, 1091−1092.

(12) (a) Jigami, T.; Takimiya, K.; Otsubo, T.; Aso, Y. *J. Org. Chem.* **1998**, *63*, 8865−8872. (b) Jigami, T.; Kodani, M.; Murakami, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *J. Mater. Chem.* **2001**, *11*, 1026−1033.

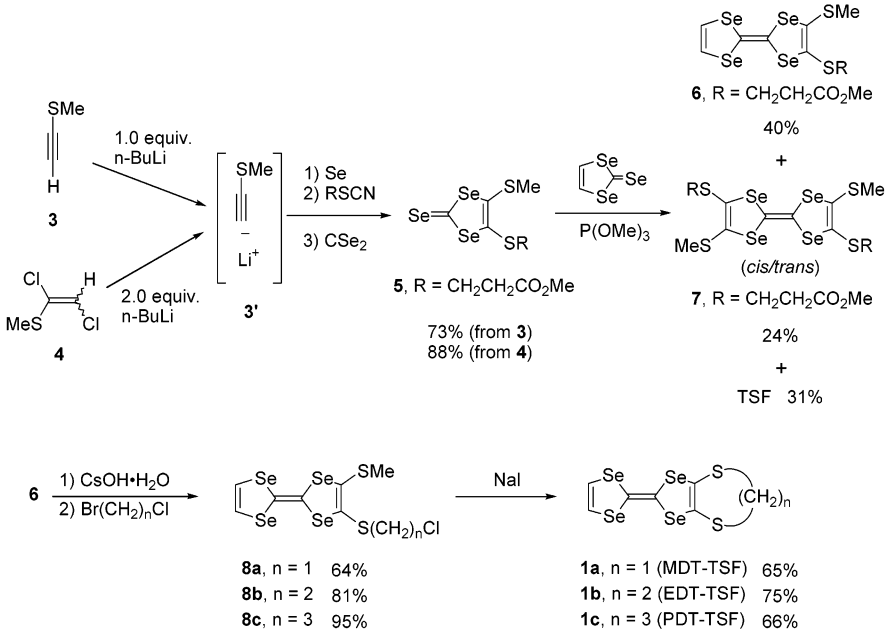
(13) Takimiya, K.; Jigami, T.; Kawashima, M.; Kodani, M. T.; Aso, Y.; Otsubo, T. *J. Org. Chem.* **2002**, *67*, 4218−4227.

(14) Kodani, M.; Murakami, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *Heterocycles* **2001**, *54*, 225−234.

(15) (a) Svenstrup, N.; Rasmussen, K. M.; Hansen, T. K.; Becher, J. *Synthesis* **1994**, 809−812. (b) Simonsen, K. B.; Svenstrup, N.; Lau, J.; Simonsen, O.; Mørk, P.; Kristensen, G. J.; Becher, J. *Synthesis* **1996**, 407−418. (c) Becher, J.; Lau, J.; Leriche, P.; Mørk, P.; Svenstrup, N. *J. Chem. Soc., Chem. Commun.* **1994**, 2715−2716. (d) Takimiya, K.; Oharuda, A.; Morikami, A.; Aso, Y.; Otsubo, T. *Eur. J. Org. Chem.* **2000**, 3013−3019. (e) Kodani, M.; Takimiya, K.; Aso, Y.; Otsubo, T.; Nakayashiki, T.; Misaki, Y. *Synthesis* **2001**, 1614−1618.

(16) The synthesis of MDT-TSF (**1a**) in the present work has been previously reported in ref 5a.

SCHEME 2. Synthesis of Alkylenedithio-TSFs (1a−c)

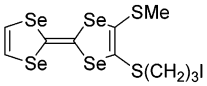


°C at 760 Torr) and thermal instability.[17] Thus, 1,2-dichloro-1-methylthioethane (**4**), which is rather stable and easily accessible from cheap reagents, was examined as a synthetic equivalent of **3**,[18] and it turned out that the synthesis of 4-methylthio-5-(2-methoxycarbonylethylthio)-1,3-selenole-2-selone (**5**) from **4** is very effective: treatment of **4** with 2 equiv of *n*-BuLi in situ generating lithium 2-methylthioacetylide (**3′**), followed by subsequent reactions with selenium, methyl 3-thiocyanatopropionate, and CSe_2 gave **5** in 88% isolated yield.

When an equimolar mixture of **5** and 1,3-diselenole-2-selone in the presence of trimethyl phosphite was allowed to react in refluxing benzene, **6** was obtained in less than 10% yield, and the major products were the unsubstituted TSF and 2,6(7′)-bis(methylthio)-3,7(6′)-bis(2-methoxycarbonylethylthio)tetraselenafulvalene (**7**). Although use of excess 1,3-diselenole-2-selone (3−5-fold) increased the yield of **6** (40−60% yield based on **5**),[5a] a large amount of TSF was concomitantly produced. Alternatively, slow addition of a mixture of **5** and trimethyl phophite in benzene to a refluxing benzene solution of 1,3-diselenole-2-selone improved the yield of **6** (typically 40% isolated yield), even though the ratio of the reactants was 1:1.

Construction of the alkylenedithio moiety was achieved by a two-step reaction. First, the methyl propionate protecting group was cleaved by cesium hydroxide, the resulting TSF thiolate being effectively realkylated with bromochloroalkane.[15] Regardless of the number of methylene moieties, compounds **8a**−**c** were obtained in moderate to good isolated yields. Then, a ring-closing reaction promoted by sodium iodide was carried out. As reported in the previous paper, a reaction of **8a** with sodium iodide in refluxing 2-butanone (bp 80 °C) gave **1a** in 50% yield.[5a] After examinations of several different solvents, it turned out that the yield of **1a** was improved up to 65% in refluxing 2-pentanone (bp 101 °C).

CHART 2



9

We have examined the synthesis of EDT-TSF (**1b**) under the optimal reaction conditions obtained for **1a**. However, **1b** was obtained in only 10% yield together with byproducts that were not easily characterized. By contrast, a similar reaction of **8b** with sodium iodide in DMF was very effective. After examinations of reaction temperature and time, this conversion was optimized (DMF, 90 °C, 15 h) to give **1b** in 75% isolated yield.

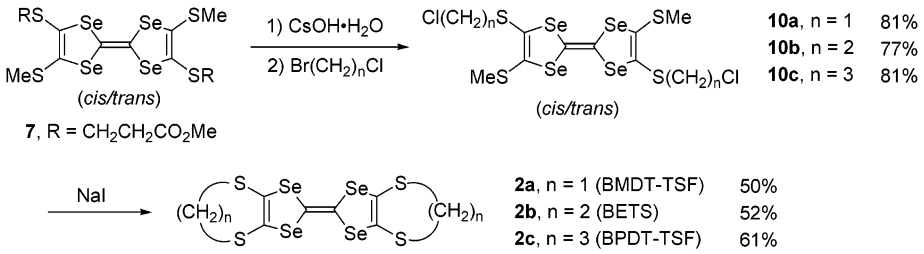
The synthesis of PDT-TSF (**1c**) was rather troublesome; application of the reaction conditions optimized for **1a** (2-pentanone, reflux, 1.5 h) to **8c** did not allow formation of **1c**, and the major product isolated was 2-methylthio-3-iodopropylthio-TSF (**9**, Chart 2). Although a reaction in DMF at 90 °C gave **1c** in 15% yield, concomitant byproducts made it difficult to purify **1c** by column chromatography. Thus, a step-by-step conversion from **8c** to **1c** was examined. Treatment of **8c** with sodium iodide in refluxing 2-butanone gave **9** quantitatively, and then **9** was again treated with sodium iodide in refluxing DMF for 1.5 h effecting the formation of **1c** in 64% yield (two steps).

In these final ring-closing reactions, the optimum reaction conditions depend strongly on the substrates, i.e., the size of the outer alkylenedithio moiety in the products. Generally, the smaller rings form more easily in this series, and the formation of the seven-membered ring in PDT-TSF (**1c**) requires a two-step reaction under harsh reaction conditions. These results are explained

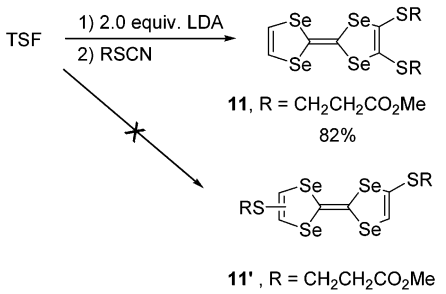
(17) (a) Brandsma, L.; Wijers, H. E.; Jonker, M. C. *Rec. Trav. Chem.* **1963**, *82*, 208−216. (b) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988; pp 172−173.

(18) Delavareme, S. Y.; Viehe, H. G. *Tetrahedron Lett.* **1969**, 4761−4764.

SCHEME 3. Synthesis of Bis(alkylenedithio)-TSFs (2a−c)



SCHEME 4. Selective Difunctionalization of TSF



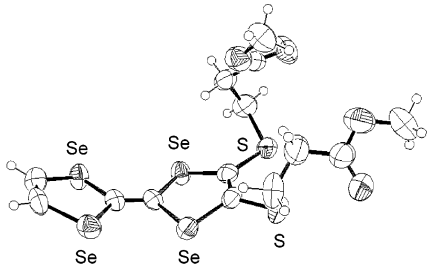


FIGURE 1. Molecular structure of **11**.

by the effects of ring strain and are in accord with the general tendency of ease of ring formation in other cyclization reaction.

Symmetrical TSF Derivatives. The synthesis of the bis(alkylenedithio)-TSFs (**2a**−**c**) by the same method is summarized in Scheme 3. The protected TSF dithiolate (**7**) was readily prepared by a phosphite-promoted coupling of **5** in 77% yield as a cis and trans mixture about the central double bond of the TSF core owing to the two different substituents on each 1,3-diselenole moiety. The ensuing conversion to bis(alkylenedithio)-TSFs (**2a**−**c**) via bis(chloroalkyl) intermediates (**10a**−**c**) was accomplished using the optimized reaction conditions for the corresponding asymmetrical TSFs. The isolated yields of **10** (77−81%) were almost comparable to those of **8**, and the final ring-closing reactions also proceed smoothly in around 50% isolated yields.

CSe_2-Free Synthesis of Asymmetrical and Symmetrical TSFs. In the synthesis of alkylenedithio- (**1**) and bis(alkylenedithio)-TSFs (**2**) described above, one of the key synthetic steps is the preparation of the 1,3-diselenole-2-selone substructure, the synthesis of which requires the toxic and not easily available CSe_2 as a crucial reagent. Because this may be regarded as a disadvantage, we have explored an alternative synthetic route free from CSe_2. One potential approach is to directly functionalize the parent TSF,[19] which is accessible by a CSe_2-free procedure.[20] In fact, there have been several reports on the synthesis of functionalized TSFs such as tetrakis(methylthio)-, tetrakis(methylseleno)-, tetrakis(phenylthio)-, tetrakis(phenylseleno)-, tetrakis(methoxycarbonyl)-, and tetrakis(carboxy)-TSFs[21] via lithiation of TSF with LDA followed by a reaction with appropriate electrophiles.

We first examined the lithiation of TSF with 2 equiv of LDA followed by a reaction with methyl 3-thiocyanatopropionate (Scheme 4). ^1H and ^{13}C NMR spectra of the isolated product were apparently different from those of the known 2,6(7)-bis(2-methoxycarbonylethylthio)tetraselenafulvalene (**11′**),[15d] suggesting the selective formation of 2,3-bis(2-methoxycarbonylethylthio)tetraselenafulvalene (**11**) in this reaction.[6a,22] An unambiguous structural determination was done by an X-ray crystallographic analysis of **11** as shown in Figure 1.

Since **11** is regarded as the synthetic equivalent of the TSF 2,3-dithiolate dianion (**12**), a direct precursor for **1**, a one-step ring formation through the deprotection/realkylation of **11** was attempted as shown in Scheme 5. Contrary to our expectations, reaction of **12**, generated in situ from **11** with 2 equiv of cesium hydroxide, with dihaloalkane resulted in a failed reaction: EDT-TSF (**1b**) and PDT-TSF (**1c**) were isolated in low yields, and no MDT-TSF (**1a**) was obtained at all (Scheme 5).[23]

Instead of the above one-step approach, a stepwise route via a selective monodeprotection of **11** was examined: treatment of **11** with 1 equiv of cesium hydroxide followed by quenching with excess iodomethane gave **6** quantitatively,[15a−c] which was readily converted to the alkylendithio-TSFs (**1a**−**c**) following the reaction sequence depicted in Scheme 2.

Application of the same method to the synthesis of the bis(alkylenedithio)-TSFs (**2**) was also carried out: the protected TSF tetrathiolate **13** obtained in 55% yield from TSF using excess LDA and methyl 3-thiocyanatopropionate was readily converted into **7** in 75% yield by treatment with a controlled amount of the base and excess iodomethane (Scheme 6). Thus, it follows that

(19) A synthetic route to BETS from the parent TSF have been suggested; Montgomery, L. K.; Burgin, T.; Husting, L.; Tilley, L.; Huffman, J. C.; Carlson, K. D.; Dudek, J. D.; Yaconi, G. A.; Geiser, U.; Williams, J. M. *Mol. Cryst. Liq. Cryst.* **1992**, *211*, 283−288.

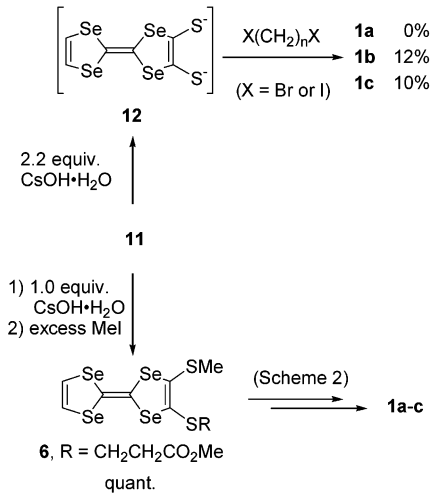
(20) Jackson, Y. A.; White, C. L.; Lakshimikantham, M. V.; Cava, M. P. *Tetrahedron Lett.* **1987**, *28*, 5635−5636.

(21) (a) Iwasawa, N.; Saito, G.; Imaeda, K.; Mori, T.; Inokuchi, H. *Chem. Lett.* **1987**, 2399−2402. (b) Rajeswari, A.; Jackson, Y. A.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1988**, 1089−1090. (c) Zambonius, J. S.; Mayer, C. W. *Tetrahedron Lett.* **1991**, *32*, 2741−2742.

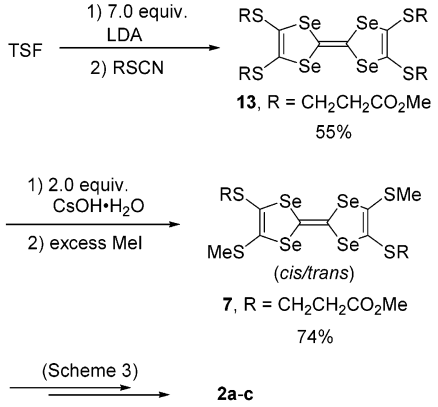
(22) Takimiya, K.; Kataoka, Y.; Morikami, A.; Aso, Y.; Otsubo, T. *Synth. Met.* **2001**, *120*, 875−876.

(23) Successful outer-ring formation of related compounds via similar 2-fold deprotection/realkylation protocol has been reported; for example, Binet L.; Fabre, J. M.; Becher J. *Synthesis* **1997**, 26−28. See also ref 15a,e.

SCHEME 5. Synthesis of Alkylenedithio-TSFs (1a−c) from 11



SCHEME 6. Synthesis of Bis(alkylenedithio)-TSFs (2a−c) from 13



bis(alkylenedithio)-TSFs (**2a**−**c**) can also be synthesized through the functionalization of the parent TSF.

Conclusion

Combining the one-pot synthesis of 1,3-selenole-2-selones, the deprotection/realkylation of the protected TSF thiolates, and the intramolecular trans-alkylation reaction forming alkylenedithio moiety on a TSF core, a general and versatile method for the synthesis of alkylenedithio- (**1**) and bis(alkylenedithio)-TSFs (**2**) is established. The advantage of the present method is that these TSF derivatives can be obtained from the common synthetic intermediates **6** and **7** via the same reaction sequence. These intermediates are conveniently synthesized from 4-methylthio-5-(2-methoxycarbonylethylthio)-1,3-diselenole-2-selones (**5**), prepared from readily available 1,2-dichloro-1-methylthioethane (**4**). For the synthesis of the asymmetrical intermediate **6**, an effective cross-coupling reaction was achieved by slow addition of **5** into a solution of 1,3-diselenole-2-selone. These synthetic improvements enable us to obtain a practical amount of the donors for further complexation studies to develop novel conducting and superconducting radical cation salts.

Furthermore, a CSe_2-free synthesis of the key intermediates **6** and **7** from the parent TSF was also established. This gives a generally acceptable route to alkylenedithio- (**1**) and bis(alkylenedithio)-TSFs (**2**), in particular, MDT-TSF (**1a**) that has been so far impossible to synthesize without CSe_2. Thus, we strongly hope that the present synthetic method will be accepted by many researchers in this field and contribute to the development of novel conducting and superconducting radical cation salts.

Experimental Section

All chemicals and solvents are of reagent grade unless otherwise indicated. All reactions were carried out under a nitrogen atmosphere. THF was purified by distillation from sodium benzophenone ketyl under nitrogen prior to use. Methanol was distilled from Mg under a nitrogen atmosphere. Dry DMF was purchased and used without purification. Carbon diselenide,[24] 1,2-dichloro-1-methylthioethane,[18] methyl 3-thiocyanatopropionate,[25] 1,3-diselenole-2-selone,[10,24b] and TSF (by CSe_2-free method)[20] were synthesized according to the literature procedures.

Column chromatography was carried out with silica gel (63-210 μm). Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, in deuterated chloroform with TMS as internal reference; chemical shifts (δ) are given in parts per million and coupling constants in hertz. MS spectra were obtained using an electron impact ionization procedure (70 eV). The molecular ion peaks of the selenium- and/or chlorine-containing compounds showed a typical isotopic pattern, and all the mass peaks are reported based on ^{80}Se and ^{35}Cl. Preparative gel permeation chromatography (GPC) was performed on a Japan Analytical Industry Co., Ltd. LC-908 equipped with a JAI-GEL 1H, 2H column assembly. Cyclic voltammetry (CV) was carried out in benzonitrile containing tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6; 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.

4-Methylthio-5-(2-methoxycarbonylethylthio)-1,3-diselenole-2-selone (5).[26] To a solution of 1,2-dichloro-1-methylthioethene (**4**, 1.43 g, 10 mmol) in dry THF (40 mL) at −78 °C was added a hexane solution of *n*-BuLi (1.56 M, 13.5 mL, 21 mmol), and the resulting solution was stirred and warmed to −10 °C over a period of 1.5 h. The resulting lithium acetylide solution was cooled again to −78 °C, and then selenium powder (790 mg, 10 mmol) was added in one portion. The reaction mixture was allowed to warm to ice-cooled temperature over the period of 1.5 h. To the resulting selenolate solution were subsequently added methyl 3-thiocyanatopropionate (2.1 g, 14 mmol) and carbon diselenide (0.7 mL, 10 mmol) at −100 °C, and the resulting mixture was kept at −90 °C for 5 min, whereupon water (50 mL) was added, and the mixture was allowed to warm to room temperature. The mixture was poured into diluted HCl aqueous solution (1 M, 200 mL) and extracted with CH_2Cl_2 (100 mL × 3), and the extract was washed with water (100 mL) and then dried over $MgSO_4$. Evaporation of the solvent gave crude **3** as a red viscous oil, which was then purified by column chromatography on silica gel eluted first with dichloromethane−hexane (1:1, v/v) and then with neat dichloromethane. Concentration of the fraction obtained from the latter gave a red solid, which was dissolved in 20 mL of dichloromethane, and the resulting solution was diluted with methanol (50 mL). The solution was cooled in a freezer (−20 °C) to give red crystals of **5** (3.68 g). The second

(24) (a) Pan, W.-H.; Fackler, J. P., Jr. In *Inorganic Syntheses*; Fackler, J. P., Jr., Ed.; John Wiley & Sons: New York, 1982; Vol. 21, pp 6−11. (b) Ogura, F.; Takimiya, K. In *Organoselenium Chemistry; A Practical Approach*, Back, T. G., Ed.; Oxford University Press: New York, 1999; pp 258−260.

(25) Hiskey, R. G.; Carroll, F. I. *J. Am. Chem. Soc.* **1961**, *83*, 4644−4647.

crop (0.18 g) was also collected, and the combined yield amounts to 88%, mp 62−63 °C. The spectroscopic data were identical with the authentic sample.[5a]

2-Methylthio-3-(2-methoxycarbonylethylthio)tetraselenafulvalene (6). To a refluxing solution of 1,3-diselenole-2-selone (2.75 g, 10 mmol) in benzene (80 mL) was added a mixture of **3** (4.39 g, 10 mmol) and trimethyl phosphate (5 mL) in benzene (80 mL) over 30 min, and the resulting mixture was further refluxed for 1 h. After the excess trimethyl phospite and benzene were evaporated off, the residue consisting of the desired asymmetrical TSF (**6**) together with TSF and the symmetrical TSF (**7**) was subjected to column chromatography on silica gel eluted with hexane−dichloromethane (1:1 v/v); after the first fraction (TSF, R_f = 0.9, 0.61 g, 31%), **6** was obtained as a red solid (R_f = 0.5, 2.21 g, 40%), mp 93−94 °C. All the spectroscopic data were identical with those previously reported.[5a] The last fraction eluted with neat dichloromethane contained **7** (R_f = 0.3 with dichloromethane, 0.87 g, 24%).

General Synthetic Procedure for 2-Methylthio-3-chloroalkylthiotetraselenafulvalene (8a−c). To a degassed DMF solution (20 mL) of **6** (513 mg, 1.08 mmol) was added CsOH·H_2O (181 mg, 1.08 mmol) in methanol (5 mL) during 5 min with stirring at room temperature. After the mixture was stirred for further 0.5 h, excess bromochloroalkane (ca. 1.5 mL) was added, and the mixture was stirred for 2 h. The reaction mixture was concentrated in vacuo, and the resulting residue was dissolved in dichloromethane (80 mL). The solution was washed with water (100 mL), dried over Na_2SO_4, and concentrated. The resulting crude product was purified by column chromatography on silica gel eluted with dichloromethane (R_f = 0.8−0.9).

2-Methylthio-3-chloromethylthiotetraselenafulvalene (8a): red plates from dichloromethane−hexane (1:2, v/v); 64% yield; mp 91−92 °C (lit.[5a] mp 91−92 °C).

2-Methylthio-3-(2-chloroethylthio)tetraselenafulvalene (8b): orange powder from dichloromethane−hexane (1:2, v/v); 81% yield; mp 82−84 °C; ^{1}H NMR δ 2.48 (s, 3H), 3.12 (t, J = 7.8 Hz, 2H), 3.69 (t, J = 7.8 Hz, 2H), 7.24 (s, 2H); ^{13}C NMR δ 20.6, 38.8, 42.5, 101.8, 112.9, 122.5, 122.6, 124.2, 137.3; IR (KBr) 3018, 2910 cm^{-1} (CH); MS m/z 536 (M^+). Anal. Calcd for $C_9H_9S_2ClSe_4$: C, 20.30; H, 1.70. Found: C, 20.26; H, 1.69.

2-Methylthio-3-(3-chloropropylthio)tetraselenafulvalene (8c): red powder from dichloromethane−hexane (1:1,v/v); 95% yield; mp 60−61.5 °C; ^{1}H NMR δ 2.10 (quint, J = 6.6 Hz, 2H), 2.47 (s, 3H), 2.98 (t, J = 6.6 Hz, 2H), 3.71 (t, J = 6.6 Hz, 2H), 7.23 (s, 2H); ^{13}C NMR δ 20.6, 31.9, 34.3, 42.9, 102.3, 112.5, 122.5, 122.6, 126.7, 135.3; IR (KBr) 3044, 2914 cm^{-1} (CH); MS m/z 548 (M^+). Anal. Calcd for $C_{10}H_{11}S_2ClSe_4$: C, 21.97; H, 2.03. Found: C, 21.95; H, 1.98.

Methylenedithiotetraselenafulvalene (MDT-TSF, 1a). A mixture of **8a** (104 mg, 0.2 mmol) and sodium iodide (180 mg, 1.2 mmol) in 2-pentanone (5 mL) was refluxed for 1.5 h. The mixture was diluted with water (50 mL), and a resulting precipitate was collected by filtration. The solid was dissolved in carbon disulfide (100 mL), and the solution was washed with water (100 mL × 2), dried over Na_2SO_4, and then concentrated. Recrystallization of the resulting solid from carbon disulfide−hexane (1:1, v/v) gave **1a** (61 mg, 65%) as orange plates: mp 152−153 °C (lit.[5a] mp 152−153 °C); CV $E_{1/2}$ = +0.56, +0.83 V.

Ethylenedithiotetraselenafulvalene (EDT-TSF, 1b). A mixture of **8b** (106 mg, 0.2 mmol) and sodium iodide (90 mg, 0.6 mmol) in DMF (2 mL) was stirred at 90 °C for 15 h. The reaction mixture was concentrated in vacuo, diluted with water (30 mL), and extracted with carbon disulfide (20 mL × 3). The extract was washed with water (50 mL) and dried ($MgSO_4$). Evaporation of the solvent followed by column chromatography on silica gel eluted with carbon disulfide gave **1b** (R_f = 0.5), which was purified by recrystallization from carbon disulfide−hexane to give **1b** as red needles (73 mg, 75% yield): mp 203−204 °C dec; ^{1}H NMR δ 3.30 (s, 4H), 7.25 (s, 2H); IR (KBr) 3075, 3021 cm^{-1} (CH); MS m/z 484 (M^+). Anal. Calcd for $C_8H_6S_2Se_4$: C, 19.93; H, 1.25. Found: C, 19.96; H, 1.30. CV: $E_{1/2}$ = +0.58, +0.90 V.

Propylenedithiotetraselenafulvalene (PDT-TSF, 1c). A mixture of **8c** (109 mg, 0.2 mmol) and sodium iodide (90 mg, 0.6 mmol) in 2-butanone (15 mL) was refluxed for 20 h. The reaction mixture was concentrated, and the residue was treated with dichloromethane (50 mL), which was washed with water (30 mL) and dried (Na_2SO_4). Evaporation of the solvent gave 2-methylthio-3-(3-iodopropylthio)tetraselenafulvalene (**9**, 125 mg, quant). Crude **9** was directly treated with sodium iodide (270 mg, 1.8 mmol) in refluxing DMF (15 mL) for 1.5 h. The reaction mixture was diluted with water (100 mL) and extracted with carbon disulfide (20 mL × 3). The extract was washed with water (50 mL × 3) and dried (Na_2SO_4), and evaporation of the solvent gave crude **1c** as a red solid. Column chromatography on silica gel eluted with carbon disulfide gave a red solid (R_f = 0.5), which was then further purified by recrystallization from carbon disulfide−hexane to give **1c** (64 mg, 66% from **8c**) as red needles: mp 197−198.5 °C dec; ^{1}H NMR δ 2.37 (m, 2H), 2.69 (m, 4H), 7.20 (s, 2H); IR (KBr) 3080, 3030 cm^{-1} (CH); MS m/z 498 (M^+). Anal. Calcd for $C_9H_6S_2Se_4$: C, 21.79; H,1.63. Found: C, 21.99; H, 1.63. CV: $E_{1/2}$ = +0.57V, +0.92.

2-Methylthio-3-(3-iodopropylthio)tetraselenafulvalene (9): red powder from dichloromethane−hexane (1:1, v/v); mp 60−61.5 °C; ^{1}H NMR δ 2.12 (quint, J = 6.8 Hz, 2H), 2.48 (s, 3H), 2.93 (t, J = 6.8 Hz, 2H), 3.35 (t, J = 6.8 Hz, 2H), 7.22 (s, 2H); IR (KBr) 2907 cm^{-1} (C−H); MS m/z 638 (M^+). Anal. Calcd for $C_{10}H_{11}S_2ISe_4$: C, 18.82; H, 1.74. Found: C, 18.81; H, 1.72.

2,6(7′)-Bis(methylthio)-3,7(6′)-bis(2-methoxycarbonylethylthio)tetraselenafulvalene (7). To a refluxing mixture of **5** (907 mg, 2.1 mmol) in benzene (30 mL) was added trimethyl phosphite (1.2 mL), and the mixture was further refluxed for 2.5 h. After evaporation of the solvent and the excess trimethyl phospite, the residue was subjected to a column chromatography on silica gel eluted with dichloromethane to give **7** as a red solid. An analytical sample was obtained by recrystallization from dichloromethane−hexane (1:2, v/v) as red fine crystals (510 mg, 77%): mp 72−73 °C; ^{1}H NMR δ 2.47 (s, 6H), 2.705 and 2.708 (t, J = 7.4 Hz, 4H), 3.07 (t, J = 7.4 Hz, 4H), 3.71 (s, 6H,); ^{13}C NMR δ 20.6, 32.1, 34.5, 51.9, 107.2, 125.8 and 126.1, 135.7 and 135.9, 171.7; IR (KBr) 1732.3 cm^{-1} (C=O); MS m/z 724 (M^+). Anal. Calcd for $C_{16}H_{20}O_4S_4Se_4$: C, 26.67; H 2.80. Found: C, 26.79; H 2.66.

General Synthetic Procedure for 2,6(7′)-Bis(methylthio)-3,7(6′)-bis(chloroalkylthio)tetraselenafulvalene (10a−c). To a degassed DMF solution (20 mL) of **7** (966 mg, 1.5 mmol) was added CsOH·H_2O (586 mg, 3.5 mmol) in methanol (18 mL) during 5 min with stirring at room temperature. After the mixture was stirred for a further 1 h, excess bromochloroalkane (ca. 1.5 mL) was added, and the mixture was stirred for 2 h. The reaction mixture was concentrated in vacuo, and the resulting residue was diluted with water (50 mL) and extracted with dichloromethane (30 mL × 3). The extract was washed with water (50 mL), dried ($MgSO_4$), and concentrated. The resulting crude product was purified by column chromatography on silica gel eluted with dichloromethane (R_f = 0.4−0.5.)

2,6(7′)-Bis(methylthio)-3,7(6′)-bis(chloromethylthio)-tetraselenafulvalene (10a). Red plates from dichloromethane−hexane (1:1, v/v); 81% yield; mp 91−92 °C; ^{1}H NMR δ 2.48 (s, 3H), 4.82 (s, 4H); ^{13}C NMR δ 20.9, 50.9, 107.8, 123.4 and 123.8, 137.9 and 138.2; IR (KBr) 3003, 2915 cm^{-1} (CH); MS m/z 648 (M^+); Anal. Calcd for $C_{10}H_{10}S_4Cl_2Se_4$: C, 18.62; H, 1.56. Found: C, 18.47; H 1.48.

2,6(7′)-Bis(methylthio)-3,7(6′)-bis(2-chloroethylthio)-tetraselenafulvalene (10b): brown plates from dichloromethane−hexane (1:1, v/v); 77% yield; mp 87−89 °C; ^{1}H NMR δ 2.49 (s, 6H), 3.132, 3.134 (t, J = 7.7 Hz, 4H), 3.700 and 3.704 (t, J = 7.7 Hz, 4H); ^{13}C NMR δ 20.7, 38.8 and 38.9, 42.5, 107.4,

123.9 and 124.2, 137.1 and 137.3; IR (KBr) 2970, 2886 cm^{-1} (CH); MS *m/z* 676 (M^+). Anal. Calcd for $C_{12}H_{14}S_4Cl_2Se_4$: C, 21.41, H 2.10. Found: C, 21.44; H 2.11.

2,6(7′)-Bis(methylthio)-3,7(6′)-bis(3-chloropropylthio-tetraselenafulvalene (10c): reddish purple needles from dichloromethane−hexane (1:1, v/v); 81% yield; mp 68−70 °C; ^1H NMR δ 2.09 (m, J = 6.4, 6.8 Hz, 4H), 2.46 (s, 6H), 2.96 (t, J = 6.8 Hz, 4H), 3.687 and 3.689 (t, J = 6.4 Hz, 4H); ^{13}C NMR δ 20.8, 32.1, 34.5, 43.0, 107.5, 126.6 and 126.8, 135.2 and 135.3; IR (KBr) 2921 cm^{-1} (CH); MS *m/z* 704 (M^+). Anal. Calcd for $C_{14}H_{18}S_4Cl_2Se_4$: C, 23.98; H, 2.59. Found: C, 23.93; H 2.54.

Bis(methylenedithio)tetraselenafulvalene (BMDT-TSF, 2a). A mixture of **10a** (130 mg, 0.2 mmol) and sodium iodide (540 mg, 3.6 mmol) in 2-pentanone (15 mL) was refluxed for 1.5 h. The mixture was diluted with water (100 mL), and a resulting precipitate was collected by filtration. The solid was dissolved in carbon disulfide (200 mL), and the solution was washed with water (100 mL × 3), dried (Na_2SO_4), and then concentrated. Column chromatography on silica gel eluted with carbon disulfide gave **2a** (R_f = 0.7), which was then further purified by recrystallization from chlorobenzene to give an analytical pure sample as pale orange plates (55 mg, 50%): mp 209−210 °C; ^1H NMR δ 4.85 (s, 4H); IR (KBr) 3000, 2909 cm^{-1} (CH); MS *m/z* 548 (M^+). Anal. Calcd for $C_8H_4S_4Se_4$: C, 17.66; H, 0.74. Found: C, 17.66; H, 0.80. CV: $E_{1/2}$ = +0.63, 0.88 V.

Bis(ethylenedithio)tetraselenafulvalene (BETS, 2b). A mixture of **10b** (134 mg, 0.2 mmol) and sodium iodide (90 mg, 0.6 mmol) in DMF (2 mL) was stirred at 90 °C for 15 h. The reaction mixture was diluted with water (30 mL), and the resulting precipitate was collected by filtration and dried. The precipitate was dissolved in carbon disulfide (200 mL), and the solution was washed with water (50 mL), dried ($MgSO_4$), and passed through a short column of silica gel. The resulting solution was concentrated to ca. 30 mL, precipitating microcrystals of **2b**, which were collected by filtration, washed with dichloromethane, and dried. Recrystallization from carbon disulfide−hexane gave brown fine crystals of **2b** (59 mg, 52% yield): mp 250 °C dec (lit.[7] mp 250 °C dec). CV: $E_{1/2}$ = +0.69, 0.96 V.

Bis(propylenedithio)tetraselenafulvalene (BPDT-TSF, 2c). A mixture of **10c** (140 mg, 0.2 mmol) and sodium iodide (180 mg, 1.2 mmol) in 2-butanone (15 mL) was refluxed for 18 h. The reaction mixture was concentrated, and the residue was extracted with dichloromethane (50 mL), washed with water (50 mL × 2), and dried (Na_2SO_4). Evaporation of the solvent gave 2,6(7)-bis(methylthio)-3,7(6)-bis(3-iodopropylthio)-tetraselenafulvalene (164 mg, 93%). The crude iodide was allowed to react with sodium iodide (502 mg, 3.34 mmol) in refluxing DMF (20 mL) for 1.5 h. The reaction mixture was diluted with water (100 mL) and extracted with carbon disulfide (30 mL × 3). The extract was washed with water (50 mL × 3) and dried (Na_2SO_4). Evaporation of the solvent gave crude **2c** as a red solid. Column chromatography on silica gel eluted with carbon disulfide gave a red solid (R_f = 0.7), which was then further purified by recrystallization from carbon disulfide−hexane to give **2c** (68 mg, 61% from **10c**) as red plates: mp 288.5−289.5 °C dec; ^1H NMR δ 2.37 (m, 4H), 2.67 (m, 8H); IR (KBr) 2903, 2874 cm^{-1} (CH); MS *m/z* 602 (M^+). Anal. Calcd for $C_{12}H_{12}S_4Se_4$: C, 24.01; H, 2.01. Found: C, 23.93; H 1.95. CV: $E_{1/2}$ = + 0.66, +0.99 V.

2,3-Bis[(2-methoxycarbonyl)ethylthio]tetraselenafulvalene (11). To a solution of TSF[20] (670 mg, 1.7 mmol) in dry THF (60 mL) was added slowly a solution of freshly prepared LDA (3.4 mmol) in THF−hexane (3.4 mL) at −90 °C, and the resulting solution was stirred for 40 min at −78 °C. Methyl thiocyanatopropionate (290 mg, 2.0 mmol) was added via a syringe to the solution, and the mixture was allowed to warm to −50 °C over a period of 1 h and finally quenched by addition of water (60 mL). The mixture was extracted with dichloromethane (20 mL × 4), and the extract was washed with water (60 mL) and dried over $MgSO_4$ (anhydride). The extract was concentrated in vacuo, and the resulting residue containing crude **11** was subjected to column chromatography on silica gel. The first fraction eluted with dichloromethane−hexane (1:1, v/v) contained TSF recovered (R_f 0.9, trace), and the second red band (R_f = 0.3) gave **11** (880 mg, 82%) as a red solid upon concentration in vacuo. Recrystallization from dichloromethane−hexane (1:1, v/v) gave analytically pure and X-ray-quality orange plates of **11**: mp 55−56 °C; ^1H NMR δ 2.68 (t, J = 7.3 Hz, 4H), 3.07 (t, J = 7.3 Hz, 4H), 3.69 (s, 6H), 7.24 (s, 2H); ^{13}C NMR δ 32.2, 34.4, 51.9, 101.7, 112.5, 122.5, 131.4, 171.5; IR (KBr) 1734 (C=O), 1362, 1055 cm^{-1} (CO); MS *m/z* 630 (M^+). Anal. Calcd for $C_{14}H_{16}O_4S_2Se_4$: C, 26.76; H, 2.57. Found: C, 26.67; H, 2.47.

2,3,6,7-Tetrakis[(2-methoxycarbonyl)ethylthio]tetraselenafulvalene (13). A similar procedure for **11** was applied to the synthesis of **13** using 7.0 equiv of LDA. After pretreatment with a short column of silica gel eluted with dichloromethane, the crude product was purified by GPC; the first fraction (V_R = 168 mL) contained the desired product **13** (55% yield) and the second fraction (V_R = 175 mL) the tris-substituted one (30% yield). **13**: red plates from dichloromethane−hexane (1:1, v/v); mp 96−97 °C; ^1H NMR δ 2.70 (t, J = 7.3 Hz, 8H), 3.10 (t, J = 7.3 Hz, 8H), 3.69 (s, 12H); ^{13}C NMR δ 32.3, 34.5, 51.9, 107.0, 131.4, 171.6; IR (KBr) 1732 (C=O), 1363, 1051 cm^{-1} (CO); MS *m/z* 866 (M^+). Anal. Calcd for $C_{22}H_{28}O_8S_4Se_4$: C, 30.56; H, 3.26. Found: C, 30.44; H 3.24.

2-Methylthio-3-(2-methoxycarbonylethylthio)tetraselenafulvalene (6) from 11. To a degassed dry DMF solution (15 mL) of **11** (266 mg, 0.42 mmol) was added CsOH·H_2O (81 mg, 0.42 mmol) in methanol (4 mL) over a period of 10 min with stirring at room temperature. After the mixture was further stirred for 0.5 h, excess iodomethane (0.2 mL) was added, and the mixture was stirred for an additional 2 h. The solvent was evaporated, and the resulting residue was diluted with water and extracted with dichloromethane (30 mL × 3). The extract was washed with water (60 mL), dried over $MgSO_4$ (anhydride), and concentrated in vacuo to give crude **6**, which was purified by silica gel column chromatography eluted with dichloromethane−hexane (1:1, v/v) (R_f = 0.5). Recrystallization from dichloromethane−hexane (1:2, v/v) gave **6** (190 mg, quantitative) as an orange solid, mp 93−94 °C.

2,6(7′)-Bis(methylthio)-3,7(6′)-bis(2-methoxycarbonylethylthio)tetraselenafulvalene (7) from 13. The synthesis of **7** from **13** was carried out in a similar manner as for **6** from **11**: 74% yield; red fine crystals; mp 72−73 °C.

Crystallographic Structure Analysis of 11. X-ray crystal structure analysis was made on a Rigaku AFC7R four-circle diffractometer (Mo Kα radiation, λ = 0.710 69 Å, graphite monochromator, ω scan, $2\theta_{max}$ = 55.0°). The structure was solved by direct methods and refined by full-matrix least-squares on $|F|$. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were not included in the refinement. All calculations were performed using the crystallographic software package teXsan.[27]

Crystal data for **11**: $C_{14}H_{16}O_4S_2Se_4$, M = 628.24, crystal size 0.50 × 0.34 × 0.02 mm, monoclinic, a = 22.502(4) Å, b = 8.811(1) Å, c = 10.208(1) Å, β = 92.73(1)°, V = 2021.6(5) Å^3, space group $P2_1/c$ (no. 14), Z = 4, D_c = 2.064 g cm^{-3}, $F(000)$ = 1200.00, μ = 74.82 cm^{-1}, R = 0.046, R_w = 0.069, 4644 unique reflections (R_{int} = 0.025), 2725 observed reflections [$I > 3.0\sigma(I)$], 218 refined parameters.

Acknowledgment. This work was partially supported by a Grant-in Aid for Scientific Research (No. 13740399) from the Ministry of Education, Culture,

(26) Carbon diselenide is highly toxic and is especially irritating to eyes and respiratory system. It is advisable to avoid direct contact with the skin. Thus, this synthesis must be carried out in an efficient hood with using disposable vinyl or latex gloves and chemical-resistant safety goggles.

(27) teXsan: Single-Crystal Structure Analysis Software, Version 1.11, Molecular Structure Corp., Rigaku Corp., 2000.

Sports, Science and Technology of Japan and Industrial Technology Research Grant Program in '01 from New Energy and Industrial Technology Development Organization (NEDO) of Japan. We also thank Izumi Science and Technology Foundation for financial support.

Supporting Information Available: Procedures for the CSe_2-free synthesis of TSF and a CIF file giving full crystallographic data for **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO034145A