Novel Selenocycle-Fused TTF-Type of Electron Donors Forming Conducting Molecular Complexes: Bis(ethyleneseleno)tetrathiafulvalene (BES-TTF), Diselenolotetrathiafulvalene (DS-TTF), and Bis(ethyleneseleno)tetraselenafulvalene (BES-TSF)

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The title selenocycle-fused tetrathiafulvalene derivatives (BES-TTF and DS-TTF) and tetraselenafulvalene derivative (BES-TSF) have been synthesized as novel electron donors, and their conducting molecular complexes have been studied. Although DS-TTF formed only semiconducting complexes, BES-TTF and BES-TSF gave metallic complexes with various electron acceptors, such as TCNQ, ClO_4^-, PF_6^-, and AsF_6^-. Among them, the TCNQ complex of BES-TSF showed an extraordinarily high room-temperature conductivity of 2700 ± 500 S cm^{-1}, which is of the highest class for a molecular complex. The complexes of BES-TTF underwent a typical metal-to-insulator transition at low temperature, characteristic of one-dimensional organic metals. On the other hand, complexes of BES-TSF were less temperature-dependent and remained highly conducting, even down to cryogenic temperature. The different behaviors of the three donors are discussed on the basis of the crystal structures of their representative complexes as elucidated by X-ray crystallographic analyses.

Introduction

Since the discovery of numbers of superconductors based on bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF),[1] much attention has centered on the heterocycle-fused modifications of TTF-type electron donors.[2] The fused heterocyclic rings play a considerably important role in the intermolecular interactions and, accordingly, conductivities of the derived charge-transfer complexes. Bis(ethylenethio)tetrathiafulvalene (BET-TTF) and dithienotetrathiafulvalene (DT-TTF), developed early by Engler's group,[3] may have been among such potential heterocycle-fused TTF donors, but their complexes were studied only with TCNQ. Recently Rovira and coworkers have reported that BET-TTF behaves as a superior electron donor, forming metallic radical cation salts.[4] It is well-known that replacement of the sulfur atoms of TTF donors with selenium is one of the most promising modifications for searching for novel potential electron donors, because the incorporated selenium atoms can serve to make advantageous organic metals that are endowed with increased bandwidth and enhanced dimensionality owing to stronger heteroatomic interactions.[5] In this connection, the heretofore unknown selenocyclic analogues of BET-TTF and DT-TTF, bis(ethyleneseleno)tetrathiafulvalene (BES-TTF) and diselenolotetrathiafulvalene (DS-TTF), are of great interest. Moreover, bis(ethyleneseleno)tetraselenafulvalene (BES-TSF) is expected to be a more promising electron donor. Concerning selenophene-annulated TTF derivatives, there have been two reports on symmetrical DS-TTF[6] and selenolo-bisTTF;[7] however, the former described no complex, and the latter described only a conducting complex with TCNQ. We now report the synthesis and properties of the three selenocycle-fused TTF-type electron donors and their conducting complexes.[8]

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(1) For a comprehensive review on organic superconductors, see: 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: New Jersey, 1992.

(2) For excellent reviews on the structural modifications of TTF, see: (a) Schukat, G.; Richter, A. M.; Fanghänel, E. *Sulfur Rep.* **1987**, *7*, 155−240. (b) Schukat, G.; Fanghänel, E. *Sulfur Rep.* **1993**, *14*, 245−390. (c) Schukat, G.; Fanghänel, E. *Sulfur Rep.* **1996**, *18*, 1−294.

(3) Engler, E. M.; Patel, V. V.; Andersen, J. R.; Schumaker, R. R.; Fukushima, A. A. *J. Am. Chem. Soc.* **1978**, *100*, 3769−3776.

(4) (a) Rovira, C.; Veciana, J.; Santaló, N.; Tarrés, J.; Cirujeda, J.; Molins, E.; Llorca, J.; Espinosa, E. *J. Org. Chem.* **1994**, *59*, 3307−3313. (b) Tarrés, J.; Santaló, N.; Mas, M.; Molins, E.; Veciana, J.; Rovira, C.; Yang, S.; Lee, H.; Cowan, D. O. *Chem. Mater.* **1995**, *7*, 1558−1567. (c) Rovira, M. C.; Novoa, J. J.; Tarrés, J.; Rovira, C.; Veciana, J.; Yang, S.; Cowan, D. O.; Canadell, E. *Adv. Mater.* **1995**, *7*, 1023−1027. (d) Rovira, C.; Veciana, J.; Tarrés, J.; Molins, E.; Mas, M.; Cowan, D. O.; Yang, S. *Synth. Met.* **1995**, *70*, 883−886. (e) Ribera, E.; Rovira, C.; Veciana, J.; Laukhin, V. N.; Canadell, E.; Vidal-Gancedo, J.; Molins, E. *Synth. Met.* **1997**, *86*, 1993−1994. (f) Rovira, C.; Tarrés, J.; Ribera, E.; Veciana, J.; Canadell, E.; Molins, E.; Mas, M.; Laukhin, V.; Doublet, M.-L.; Cowan, D. O.; Yang, S. *Synth. Met.* **1997**, *86*, 2145−2146.

(5) Cowan, D.; Kini, A. In *The Chemistry of Organic Selenium and Tellurium*; Patai, S., Ed.; John Wiley & Sons: New York, 1987; Vol. 2, Chapter 12.

(6) Ketcham, R.; Hörnfeldt, A.-B.; Gronowitz, S. *J. Org. Chem.* **1984**, *49*, 1117−1119.

(7) Wang, C.; Ellern, A.; Becker, J. Y.; Bernstein, J. *Adv. Mater.* **1995**, *7*, 644−646.

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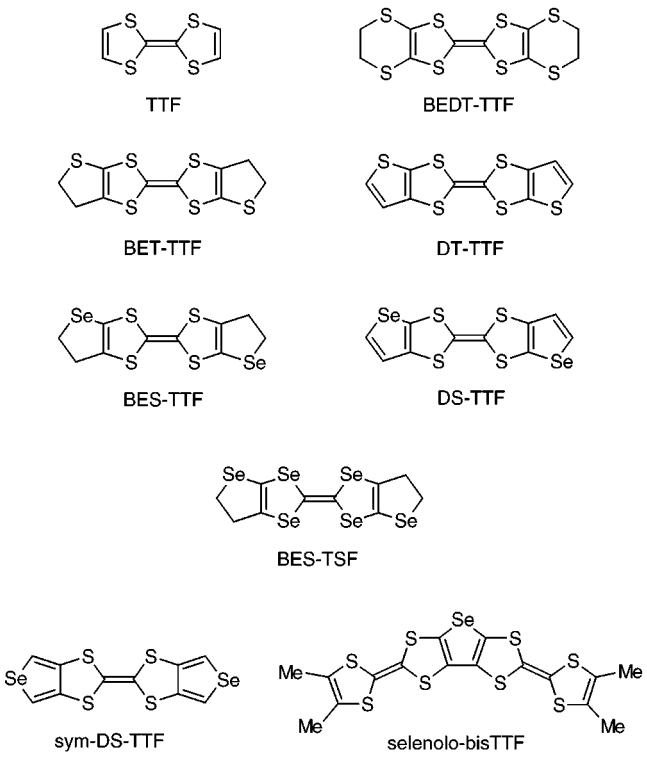
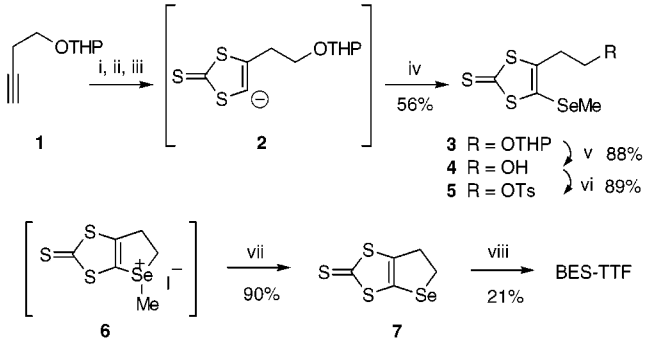


Results and Discussion

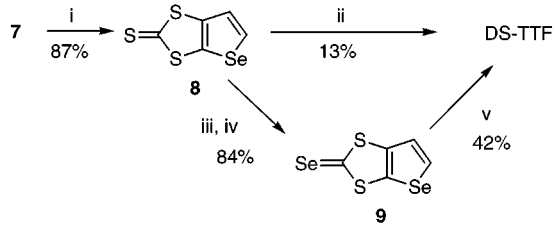
Synthesis. Based on the general synthetic strategy of TTF molecules, the key intermediates for the syntheses of BES-TTF and DS-TTF are 5,6-dihydroselenolo[2,3-*d*]-1,3-dithiole-2-thione (**7**) and selenolo[2,3-*d*]-1,3-dithiole-2-thione (**8**), respectively. Although the reported syntheses of similar sulfur intermediates for BET-TTF and DT-TTF involve the construction of the 1,3-dithiole-2-thione ring by conventional methods starting with thiolan-2-one[3] or thiolan-3-one,[4a] these methods are not suitable for the synthesis of the present system, because the corresponding starting selenocyclic materials are not readily accessible. Instead, we have developed a convenient route which involves the construction of the 1,3-dithiole-2-thione ring via cyclization reaction of a terminal acetylene with sulfur and carbon disulfide,[9] followed by the construction of the selenocyclic ring, as shown in Scheme 1. Thus, commercially available tetrahydropyranyl (THP)-protected 3-butyn-1-ol (**1**) was treated with *n*-BuLi at −70 °C in THF to generate the lithium acetylide, which was successively reacted with elemental sulfur and carbon disulfide. The resulting vinyl anion **2** was then reacted with selenium and subsequently quenched by addition of methyl iodide to give THP-protected 4-(2-hydroxyethyl)-5-methylseleno-1,3-dithiole-2-thione (**3**) in 56% yield. After the THP protecting group was removed by treatment with dilute hydrochloric acid (88% yield), the resulting alcohol **4** was converted into the tosylate **5** in 89% yield. The second ring formation was achieved by a unique transalkylation reaction from **5** via a hypervalent selenium intermediate **6** promoted by sodium iodide in DMF, giving rise to the key intermediate **7** in high yield (90%). The conventional desulfurization self-coupling of **7** promoted by trimethyl phosphite gave BES-TTF in 21% yield.

Scheme 1[a]



[a] Reagents and conditions: (i) *n*-BuLi, TMEDA, THF, −70 °C; (ii) S, 0 °C; (iii) CS_2, −85 °C; (iv) Se powder, then MeI, 0 °C; (v) HCl (aq), acetone/MeOH, rt; (vi) TsCl, pyridine, 0 °C; (vii) NaI, DMF, 80 °C; (viii) $P(OMe)_3$, reflux.

Scheme 2[a]



[a] Reagents and conditions: (i) DDQ, toluene, reflux; (ii) $P(OMe)_3$, reflux; (iii) $(MeO)_2SO_2$, 80 °C, then HBF_4 (aq), 0 °C; (iv) NaHSe, MeOH, rt; (v) $P(OMe)_3$, benzene, reflux.

The precursor **8** of DS-TTF was readily prepared in 87% yield by dehydrogenation of **7** with DDQ in refluxing toluene (Scheme 2). The subsequent self-coupling reaction of **8** gave DS-TTF in 13% yield. The poor yield of the coupling reaction was fairly improved to 42% by alternatively using the corresponding selone **9**, which was obtained from **8** by a well-established procedure (84%).

The above synthetic method for BES-TTF and DS-TTF was also found to be successfully applicable to the syntheses of the sulfur counterparts, BET-TTF and DT-TTF, as shown in Scheme 3. Although the overall yield is nearly equal, this new approach complements the preceding two methods[3,4a] in terms of a large preparative scale.

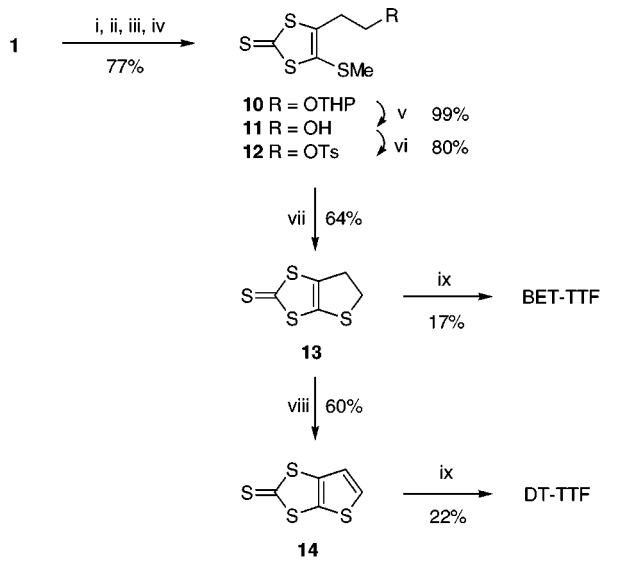
The synthesis of BES-TSF was performed by a modified method, as shown in Scheme 4. Successive treatment of **1** with elemental selenium, carbon diselenide, again selenium, and finally methyl iodide similarly gave THP-protected 4-(2-hydroxyethyl)-5-methylseleno-1,3-diselenole-2-selone (**15**) in 70% yield. Differently from BES-TTF, however, the subsequent approach from **15** to BES-TSF failed because of the instability of the intermediate, 5,6-dihydroselenolo[2,3-*d*]-1,3-diselenole-2-selone (**16**). Alternatively, **15** was prior to the second ring formation, coupled to the TSF derivative **17** in 93% yield; after the THP group was deprotected by dilute hydrochloric acid (94% yield), the resulting diol **18** was converted into the ditosylate **19** in 95% yield, which was then subjected to the transalkylation reaction to give BES-TSF in 39% yield.

Molecular Structures. As seen in the case of the sulfur analogues,[3,4a] BES-TTF, DS-TTF, and BES-TSF

(8) A preliminary report on BES-TTF and DS-TTF appeared: Jigami, T.; Takimiya, K.; Aso, Y.; Otsubo, T. *Chem. Lett.* **1997**, 1091−1092.

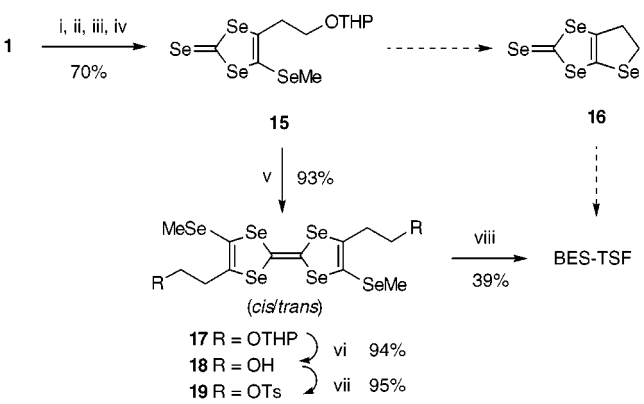
(9) (a) Mayer, R.; Gebhardt, B. *Chem. Ber.* **1964**, *97*, 1298. (b) Engler, E. M.; Patel, V. V. *J. Org. Chem.* **1975**, *40*, 387. (c) Takimiya, K.; Morikami, A.; Otsubo, T. *Synlett* **1997**, 319−321.

Scheme 3[a]



[a] Reagents and conditions: (i) *n*-BuLi, TMEDA, THF, −70 °C; (ii) S, 0 °C; (iii) CS_2, −85 °C; (iv) MeSCN, 0 °C; (v) HCl (aq), acetone/MeOH, rt; (vi) TsCl, pyridine, 0 °C; (vii) NaI, DMF, 120 °C; (viii) DDQ, toluene, reflux; (ix) $P(OMe)_3$, reflux.

Scheme 4[a]



[a] Reagents and conditions: (i) *n*-BuLi, TMEDA, THF, −70 °C; (ii) Se, 0 °C; (iii) CSe_2, Se, −70 °C; (iv) MeI, 0 °C; (v) $P(OMe)_3$, benzene, reflux; (vi) HCl (aq), THF/MeOH, rt; (vii) TsCl, pyridine, 0 °C; (viii) NaI, DMF, 80 °C.

consist of a mixture of two structural isomers with different symmetry, i.e., cis (C_{2v}) and trans (C_{2h}). This was confirmed by the observation of two kinds of signals (1:1 integral ratio) with slightly different chemical shifts for the methylene protons in the ^{1}H NMR spectra of BES-TTF and BES-TSF; however, the isomeric selenophene proton signals of DS-TTF were indistinguishable. The isomeric separation of BES-TTF and DS-TTF with chromatographic and fractional crystallization techniques failed, whereas recrystallization of the isomeric mixture of BES-TSF from chlorobenzene gave two kinds of crystals, reddish orange plates and dark red needles, which corresponded to each of the structural isomers. Both isomers are stable in the crystal state, but readily convertible into each other in solution.[10] An X-ray crystallographic analysis confirmed the reddish orange plate to be the trans isomer, as shown in Figure 1. From this, it follows that the dark red needle is the cis isomer,

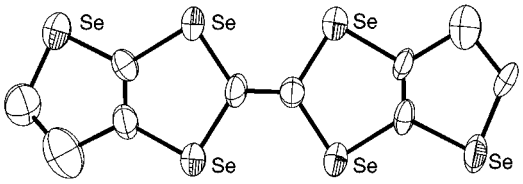


Figure 1. Molecular structure of *trans*-BES-TSF.

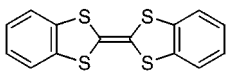
Table 1. Half-Wave Oxidation Potentials (V)[a]

donor	$E_{1/2}(1)$	$E_{1/2}(2)$	ΔE
BES-TTF	0.32	0.66	0.34
BET-TTF	0.36	0.68	0.32
DS-TTF	0.38	0.71	0.33
DT-TTF	0.46	0.79	0.33
BES-TSF	0.47	0.74	0.27
TTF	0.34	0.71	0.37
DB-TTF	0.60	0.98	0.38
TSF	0.49	0.78	0.29

[a] Cyclic voltammetry was carried out at a scan rate of 400 mV s^{-1} with Pt working and counter electrodes and an Ag/AgCl reference electrode in 10^{-3} mol dm^{-3} benzonitrile solution containing 10^{-1} mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte.

but its structural confirmation by an X-ray crystallographic analysis was fruitless because the crystal was found to comprise orientationally disordered molecules.

Cyclic Voltammetry. The cyclic voltammetry of BES-TTF, DS-TTF, and BES-TSF showed two reversible, one-electron redox waves. The half-wave oxidation potentials are summarized together with those of the related compounds in Table 1. BES-TTF has slightly lower oxidation potentials than TTF and BET-TTF, indicating the enhancement of its electron-donating ability by fusion of the dihydroselenolo rings. This is the case with the electron-donating ability of BES-TSF relative to TSF. The fused selenolo rings of DS-TTF, on the contrary, serve to heighten the oxidation potentials. This is in harmony with a general tendency that the fusion of aromatic rings to TTF leads to weaken its donor ability, as exemplified by the oxidation potentials of DT-TTF and dibenzotetrathiafulvalene (DB-TTF). However,



DB-TTF

the perturbation effect of the fused selenolo rings is not so marked, since the aromaticity of selenophene is not so large as those of benzene and thiophene; thus, DS-TTF still stays in a strong class of electron donors.

Molecular Complexes. BES-TTF formed crystalline molecular complexes with TCNQ by a diffusion method and with inorganic anions, such as ClO_4^-, PF_6^-, and AsF_6^-, by an electrocrystallization method. The properties of the resulting complexes are summarized together with those of the complexes of the other donors in Table 2. The TCNQ complex shows a high conductivity of 150 S cm^{-1} at room temperature. In variable-temperature measurements, the conductivity increases with lowering temperature, reaches a maximum (270 S cm^{-1}) at 110 K, where a typical metal-to-insulator transition observed for the TTF-TCNQ family[11] occurs, and then falls mono-

(10) Souizi, A.; Robert, A.; Batail, P.; Ouahab, L. *J. Org. Chem.* **1987**, *52*, 1610−1611.

(11) Etemad, S.; Penney, T.; Engler, E. M.; Scott, B. A.; Seiden, P. E. *Phys. Rev. Lett.* **1975**, *34*, 741−744 and references therein.

Table 2. Conductivities of Molecular Complexes of BES-TTF, DS-TTF, and BES-TSF[a]

donor	acceptor	appearance	D:A[b]	σ_{rt} (S cm^{-1})	remark	T_{max}[c] (K)	σ_{max} (S cm^{-1})	$\sigma_{4.2K}$ (S cm^{-1})
BES-TTF	TCNQ	black needles	1:1	150	metallic	110	270	6.4×10^{-2}
BES-TTF	ClO_4^-	black plates	2:1	280	metallic	110	530	$<10^{-4}$
BES-TTF	PF_6^-	black plates	2:1	200	metallic	240	240	$<10^{-4}$
BES-TTF	AsF_6^-	black plates	2:1	60	metallic	50	150	1.7
DS-TTF	TCNQ	black needles	1:1	0.2	semiconductive ($E_a = 0.064$ eV)			
DS-TTF	ClO_4^-	black needles	1:1	5×10^{-5}	semiconductive			
BES-TSF	TCNQ	black plates	1:1	2700	metallic	40	9800	4700
BES-TSF	ClO_4^-	red brown leaflets	3:2:1(PhCl)[d]	100	metallic	50	190	140
BES-TSF	AsF_6^-	red brown leaflets	2:1:1(PhCl)[d]	100	metallic	100	110	11

[a] Conductivities were measured on a single crystal with a four-probe method. [b] Determined on the basis of elemental analyses or X-ray crystallographic analyses. [c] Temperature for the highest conductivity. [d] Additional inclusion of a chlorobenzene from solvent.

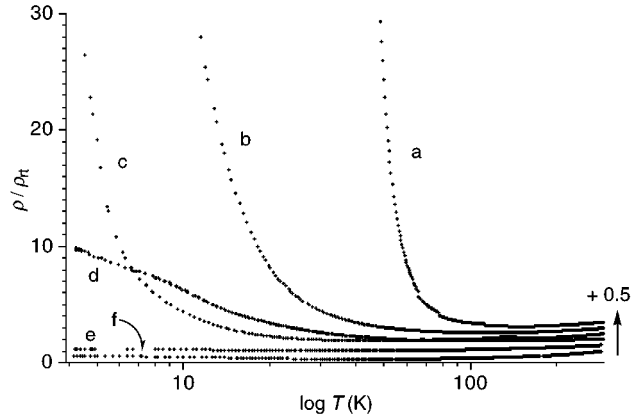
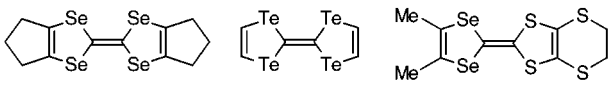


Figure 2. Normalized resistance vs temperature plots for the complexes of BES-TTF (a−c) and BES-TSF (d−f) with acceptors: (a) ClO_4, (b) TCNQ, (c) AsF_6, (d) AsF_6, (e) ClO_4, (f) TCNQ. The plots are displaced upward successively by 0.5 ρ/ρ_{rt} unit from the bottom plot.

tonically at further lower temperatures (Figure 2). The radical cation salts also show high conductivities with similar temperature-dependent behavior. The magnitude of these conductivities is roughly close to that for the complexes of BET-TTF.[4] This indicates that, against our expectation, BES-TTF exerts no selenium substitution effect on the formation of its conducting complexes.

In contrast to BES-TTF, DS-TTF formed semiconducting complexes with TCNQ and ClO_4^-. The room-temperature conductivity (0.20 S cm^{-1}) of the TCNQ complex is much lower, by an order of 10^3 in magnitude, than the value of BES-TTF·TCNQ. In addition, the ClO_4^- salt shows a poor conductivity of 10^{-5} S cm^{-1}. These results suggest different crystal structures between the DS-TTF complexes and the above BES-TTF complexes (vide infra).

BES-TSF, like BES-TTF, formed metallic complexes with TCNQ, ClO_4^-, and AsF_6^-. In particular, the BES-TSF·TCNQ complex shows a remarkably high room-temperature conductivity of 2700 ± 500 S cm^{-1} (10 samples). Although great interest has been placed on the discovery of novel superconductors based on the TTF family, the development of molecular complexes with the highest conductivities under ambient conditions is also very important. The room-temperature conductivities of molecular complexes, even superconductive ones, are still very low as compared to those of the metal elements and rarely exceed 10^3 S cm^{-1}. To the best of our knowledge, the highest conductivities of molecular complexes ever reported have been for HMTSF·TNAP (2400 ± 600 S cm^{-1}),[12] TTeF·TCNQ (2200 ± 300 S cm^{-1}),[13] and $(DMET)_2$·$Au(CN)_2$ (2500 S cm^{-1}).[14] The present conductivity of BES-TSF·TCNQ is comparable to or more than these values. A comparison with the conductivity of HMTSF·TCNQ[15] (1391−2178 S cm^{-1}) suggests contribution of the outer selenium atoms of BES-TSF to the high conductivity. As the temperature is lowered, the conductivity rises steadily and reaches a maximum at around 40 K, which is about 3 times as large as the room-temperature value. With further cooling, the conductivity drops gradually, but still remains higher, even at 4.2 K, than the room-temperature value (see also Figure 2). The ClO_4^- and AsF_6^- complexes of BES-TSF show room-temperature conductivities, whose magnitudes are similar to those of the radical cation salts of BES-TTF, but also less temperature-dependent and highly conducting down to cryogenic temperature. This low-temperature, semimetallic behavior is reminiscent of similar behavior previously found for the TNAP[12] and TCNQ[15] complexes of HMTSF.



Crystal Structures of Molecular Complexes. To understand the different conductivity behaviors of the molecular complexes of the three present donors, the crystal structures of their representative complexes, $(BES\text{-}TTF)_2$·AsF_6, DS-TTF·TCNQ, and BES-TSF·TCNQ, were elucidated by X-ray crystallographic analyses. The crystal structure of the $(BES\text{-}TTF)_2$·AsF_6 complex comprises segregated stacking columns along the *b*-axis; the donor molecules, trans-rich in 70% and disordered in 30%, are stacked in a zigzag fashion with alternate average intervals of 3.62 and 3.65 Å (Figure 3a). This crystal structure is essentially isostructural to that of $(BET\text{-}TTF)_2$·AsF_6 reported by Rovira and co-workers.[4b] However, there are subtle differences in intermolecular interactions between the two structures: the average stacking distances of the BES-TTF salt are a little greater than those (3.55 and 3.62 Å) of the BET-TTF salt. In addition, nonbonded S···S contacts (3.79, 3.65, and 3.78 Å) between the neighboring BES-TTF donors in the transverse direction are a little greater than the corresponding contacts (3.51, 3.56, 3.58, and 3.62 Å) of the

(12) Bechgaard, K.; Jacobsen, C. S.; Andersen, N. H. *Solid State Commun.* **1978**, *25*, 875−879.
(13) Cowan, D. O.; Mays, M. D.; Kistenmacher, T. J.; Poehler, T. O.; Beno, M. A.; Kini, A. M.; Williams, J. M.; Kwok, Y.-K.; Carlson, K. D.; Xiao, L.; Novoa, J. J.; Whangbo, M.-H. *Mol. Cryst. Liq. Cryst.* **1990**, *181*, 43−58.
(14) Kikuchi, K.; Kikuchi, M.; Namiki, T.; Saito, G.; Ikemoto, I.; Murata, K.; Ishiguro, T.; Kobayashi, K. *Chem. Lett.* **1987**, 931−934.
(15) Bloch, A. N.; Cowan, D. O.; Bechgaard, K.; Pyle, R. E.; Banks, R. H.; Poehler, T. O. *Phys. Rev. Lett.* **1975**, *34*, 1561−1564.

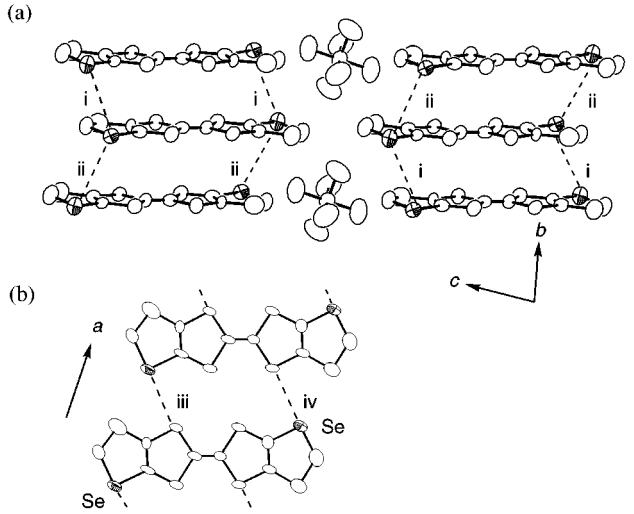


Figure 3. Crystal structure of $(BES\text{-}TTF)_2{\cdot}AsF_6$: (a) *a*-axis projection and (b) interstacking contacts. Selected nonbonded interactions are (i) 3.95, (ii) 4.01, (iii) 3.62, and (iv) 3.57 Å.

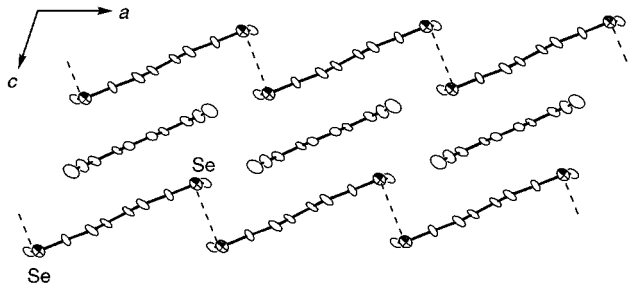


Figure 4. Crystal structure of DS-TTF·TCNQ: Se···Se contacts (3.80 Å) are depicted by dotted lines.

BET-TTF salt. However, the BES-TTF complex benefits from additional Se···Se contacts (3.95 and 4.01 Å) between the dihydroselenolo rings along the stacking direction (Figure 3a) and close Se···S contacts (3.57 and 3.62 Å) along the transverse direction (Figure 3b). A balance between the two opposing factors for the intermolecular interaction of the BES-TTF system as a whole accounts for no selenium substitution effect for the BES-TTF complexes.

The crystal structure of the DS-TTF·TCNQ complex is characterized by a mixed-stacking arrangement, where the donor and acceptor molecules are alternately stacked with sliding and at intervals of 3.5 Å along the *c*-axis (Figure 4). This unfavorable arrangement is responsible for the low conductivity; the value (0.2 S cm^{-1}) is, however, rather marked for a mixed-stacking molecular complex, and in fact, much higher, by 2 orders of magnitude, than that (10^{-3} S cm^{-1}) of the DT-TTF·TCNQ complex, which was also estimated to take a mixed-stacking crystal structure.[3] This is best understood by the presence of nonbonded Se···Se interactions (3.80 Å) between the donor molecules of neighboring columns along the *a*-axis.

The crystal structure of the BES-TSF·TCNQ complex with an unusually high conductivity was confirmed to adopt segregated stacking columns (Figure 5a). The BES-TSF molecules are uniformly stacked with sliding and at intervals of 3.65 Å along the *c*-axis, and the TCNQ molecules at intervals of 3.30 Å. The planes of both components are tilted in opposite directions relative to

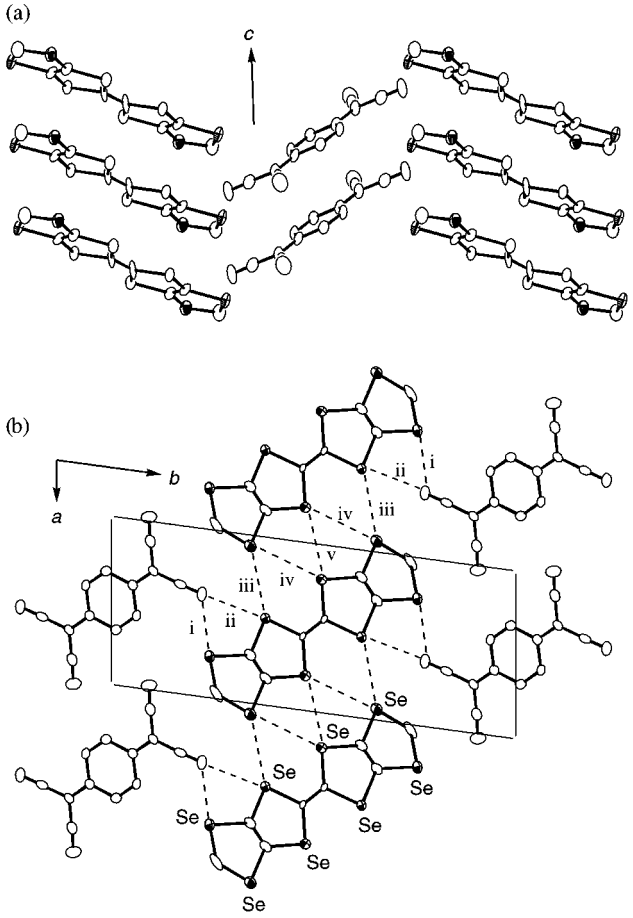


Figure 5. Crystal structure of BES-TSF·TCNQ: (a) *a*-axis projection and (b) *c*-axis projection. Selected nonbonded interactions are (i) 3.02, (ii) 3.10, (iii) 3.87, (iv) 3.67, and (v) 3.84 Å.

the *c*-axis (69.7° for BES-TTF and 56.9° for TCNQ). An important feature of this crystal structure is that the donor molecules strongly interact with the neighboring molecules in a side-by-side arrangement: the selenium atom of the TSF moiety of BES-TSF has a short transverse Se···Se contact (3.84 Å) with that of another BES-TSF and a Se···N contact (3.10 Å) with the nitrogen atom of the TCNQ acceptor (Figure 5b). In addition, the outer selenium atom, though locationally disordered, has short contacts either with the selenium atoms of the TSF moiety (3.67 and 3.87 Å) or with the nitrogen atom of the acceptor (3.02 Å). This kind of arrangement mode is quite different from that of the less conducting HMTSF-TCNQ complex with transverse Se···N interactions.[16] It is thus understandable that the high conductivity of BES-TSF·TCNQ is induced by strong heteroatomic interactions not only along the stacking direction but also along the transverse direction, which are enhanced by the additional outer selenium atoms of BES-TSF.

Conclusion

Among the present selenocycle-fused electron donors developed, BES-TTF and BES-TSF have turned out to be superior electron donors, forming various metallic molecular complexes. Although the complexes of BES-TTF undergo a typical metal-to-insulator transition at

(16) Phillips, T. E.; Kistenmacher, T. J.; Bloch, A. N.; Cowan, D. O. *J. Chem. Soc., Chem. Commun.* **1976**, 334−335.

low temperature, complexes of BES-TSF show semimetallic behavior down to cryogenic temperature. It is noteworthy that the TCNQ complex of BES-TSF has an extraordinarily high room-temperature conductivity of 2700 ± 500 S cm^{-1}, which is of the highest class for a molecular complex.

Experimental Section

General. Melting points are uncorrected. Nuclear magnetic resonance spectra were measured at 400 MHz for ^1H and 100 MHz for ^{13}C with TMS as internal reference. Mass spectral data were obtained using an electron impact ionization procedure (70 eV). The molecular ion peaks of the selenium-containing compounds showed a typical selenium isotropic pattern. Elemental analyses were performed by Mr. Hideaki Iwatani, Microanalytical Laboratory in Department of Applied Chemistry, Faculty of Engineering, Hiroshima University. All chemicals and solvents are of reagent grade and were purified by conventional methods. All reactions were carried out under a nitrogen atmosphere with dry solvents. 2-(3-Butynyloxy)tetrahydro-2*H*-pyran (**1**) was purchased from Aldrich. Selenium powder[17] and carbon diselenide[18] were prepared according to the literature procedures.

4-Methylseleno-5-[2-(tetrahydropyran-2-yloxy)ethyl]-1,3-dithiole-2-thione (3). To a solution of **1** (3.1 mL, 20 mmol) and TMEDA (6.0 mL, 40 mmol) in THF (120 mL) was added a solution of *n*-BuLi in hexane (1.54 M, 14 mL) at −70 °C, and the solution was stirred at the same temperature for 30 min. After addition of sulfur (640 mg, 20 mmol), the mixture was warmed to 0 °C over a period of 1 h and stirred for 2 h at the same temperature. The solution was again cooled to −85 °C, and MeOH (80 mL, 2 mol), carbon disulfide (1.2 mL, 20 mmol), and selenium powder (1.6 g, 20 mmol) were successively added. The reaction mixture was warmed to 0 °C over a period of 2 h, stirred for 1 h, and quenched with methyl iodide (1.25 mL, 20 mmol). After addition of water (30 mL), the mixture was extracted with CH_2Cl_2, and the extract was washed with brine and dried ($MgSO_4$). After concentration, column chromatography of the residue on silica gel with CH_2Cl_2 gave 3.99 g (56%) of **3** as a yellow oil. An analytical sample was obtained by further purification with preparative GPC using $CHCl_3$ as eluent: ^1H NMR ($CDCl_3$) δ 1.5−1.9 (m, 6H), 2.32 (s, 3H), 3.07 (m, 2H), 3.52 (m, 2H), 3.78 (m, 1H), 3.91 (m, 1H), and 4.62 (br t, J = 3.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.9, 19.2, 25.3, 30.4, 32.1, 62.1, 65.8, 98.8, 121.7, 146.8, and 214.7; MS m/z 356 (M^+); IR (neat) 1063 cm^{-1} (C═S). Anal. Calcd for $C_{11}H_{16}O_2S_3Se$: C, 37.18; H, 4.54. Found: C, 37.42; H, 4.39.

4-(2-Hydroxyethyl)-5-methylseleno-1,3-dithiole-2-thione (4). A mixture of **3** (6.2 g, 17.5 mmol), 2 N hydrochloric acid (20 mL), methanol (100 mL), and acetone (100 mL) was stirred at rt for 12 h. Water (150 mL) was introduced, and the mixture was extracted with CH_2Cl_2. The extract was washed with brine, dried ($MgSO_4$), and then concentrated. The residue was subjected to column chromatography (silica gel, 9:1 CH_2Cl_2/AcOEt) to give 4.2 g (88%) of **4** as a yellow oil. Further purification with preparative GPC gave an analytical sample: ^1H NMR ($CDCl_3$) δ 1.84 (br s, 1H), 2.34 (s, 3H), 3.04 (t, J = 5.9 Hz, 2H), and 3.84 (t, J = 5.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.0, 34.4, 61.7, 122.2, 146.2, and 214.3; MS m/z 272 (M^+); IR (neat) 1059 (C═S) and 3400 cm^{-1} (OH). Anal. Calcd for $C_6H_8OS_3Se$: C, 26.57; H, 2.97. Found: C, 26.59; H, 2.94.

4-Methylseleno-5-(2-tosyloxyethyl)-1,3-dithiole-2-thione (5). To a solution of **4** (2.9 g, 10.7 mmol) in pyridine (18 mL) was added tosyl chloride (4.1 g, 21 mmol) at 0 °C. After being stirred for 12 h, the mixture was poured into ice-containing 1 N hydrochloric acid (20 mL). The mixture was extracted with CH_2Cl_2, and the extract was washed with 1 N hydrochloric acid and then with brine and dried ($MgSO_4$). After concentration, column chromatography of the residue on silica gel (CH_2Cl_2) followed by recrystallization from hexane/$CHCl_3$ gave 4.0 g (89%) of **5** as yellow fine needles: mp 84−85 °C; ^1H NMR ($CDCl_3$) δ 2.30 (s, 3H), 2.45 (s, 3H), 3.09 (t, J = 5.9 Hz, 2H), 4.16 (t, J = 5.9 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), and 7.72 (d, J = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.0, 21.6, 30.6, 67.9, 123.6, 127.6, 129.9, 131.8, 142.9, 145.4, and 213.0; MS m/z 426 (M^+); IR (KBr) 1063 cm^{-1} (C═S). Anal. Calcd for $C_{13}H_{14}O_3S_4Se$: C, 36.70; H, 3.32. Found: C, 36.47; H, 3.29.

5,6-Dihydroselenolo[2,3-*d*]-1,3-dithiole-2-thione (7). A mixture of **5** (3.03 g, 7.13 mmol) and NaI (2.14 g, 14.2 mmol) in DMF (30 mL) was heated at 80 °C for 0.5 h. Water (30 mL) was added to the cooled mixture, which was then extracted with CS_2, and the extract was successively washed with water and brine and finally dried ($MgSO_4$). After concentration, column chromatography of the residue on silica gel with CS_2 followed by recrystallization from hexane/$CHCl_3$ gave 1.54 g (90%) of **7** as yellow needles: mp 117−117.5 °C; ^1H NMR ($CDCl_3$) δ 3.16 (t, J = 7.8 Hz, 2H) and 3.84 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 30.4, 35.0, 125.7, 135.9, and 216.8; MS m/z 240 (M^+); IR (KBr) 1053 cm^{-1} (C═S). Anal. Calcd for $C_5H_4S_3Se$: C, 25.10; H, 1.69. Found: C, 25.34; H, 1.67.

5,5′,6,6′-Tetrahydro-$\Delta^{2,2'}$-biselenolo[2,3-*d*]-1,3-dithiole (BES-TTF). A solution of **7** (1.35 g, 5.64 mmol) in trimethyl phosphite (22 mL) was heated under reflux for 2 h. After concentration, the residue was purified by column chromatography on silica gel with CS_2 followed by recrystallization from toluene to give 251 mg (21%) of BES-TTF as reddish orange needles: mp 209−210 °C dec; ^1H NMR of the 1:1 cis and trans isomeric mixture (CS_2/$CDCl_3$) δ 2.86 and 2.87 (each t, J = 7.8 Hz, 4H) and 3.78 (t, J = 7.8 Hz, 8H); MS m/z 414 (M^+). Anal. Calcd for $C_{10}H_8S_4Se_2$: C, 28.99; H, 1.95. Found: C, 29.13; H, 1.99.

Selenolo[2,3-*d*]-1,3-dithiole-2-thione (8). A solution of **7** (82 mg, 0.34 mmol) and DDQ (160 mg, 0.70 mmol) in toluene (5 mL) was refluxed for 20 h. After evaporation of the solvent, the residue was purified by column chromatography on silica gel with CH_2Cl_2 followed by recrystallization from hexane/$CHCl_3$ to give 70 mg (87%) of **8** as yellow prisms: mp 150−150.5 °C; ^1H NMR ($CDCl_3$) δ 7.30 (d, J = 5.8 Hz, 1H) and 8.29 (d, J = 5.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 122.2, 132.7, 135.1, 140.3, and 216.0; MS m/z 238 (M^+); IR (KBr) 1063 cm^{-1} (C═S). Anal. Calcd for $C_5H_2S_3Se$: C, 25.32; H, 0.85. Found: C, 25.37; H, 0.84.

Selenolo[2,3-*d*]-1,3-dithiole-2-selone (9). A mixture of **8** (69 mg, 0.29 mmol) and dimethyl sulfate (0.4 mL) was stirred at 80 °C for 0.5 h. With cooling to 0 °C in an ice bath, 42% fluoroboric acid (1 mL) was added, and the resulting mixture was stirred for 5 min. To the reaction mixture were successively added anhydrous acetic acid (1 mL) and ethyl ether (10 mL). The resulting yellow precipitate was collected by filtration, washed with ethyl ether, and then dried in vacuo. It was added in one portion to a solution of sodium hydrogenselenide generated from $NaBH_4$ (25 mg, 0.65 mmol) and selenium powder (30 mg, 0.38 mmol) in MeOH (2 mL) at 0 °C. The resulting mixture was stirred for 1 h at rt and then poured into water (5 mL). The product was extracted with CH_2Cl_2, and the extract was washed with brine and dried ($MgSO_4$). After concentration, column chromatography of the residue on silica gel with CS_2 followed by recrystallization from hexane/$CHCl_3$ gave 69 mg (84%) of **9** as orange needles: mp 160−161 °C; ^1H NMR (CS_2/$CDCl_3$) δ 7.29 (d, J = 5.8 Hz, 1H) and 8.37 (d, J = 5.8 Hz, 1H); ^{13}C NMR (CS_2/$CDCl_3$) δ 121.4, 135.8, 136.9, 145.0, and 204.4; MS m/z 286 (M^+); IR (KBr) 932 cm^{-1} (C═Se). Anal. Calcd for $C_5H_2S_2Se_2$: C, 21.14; H, 0.71. Found: C, 21.15; H, 0.72.

$\Delta^{2,2'}$-Biselenolo[2,3-*d*]-1,3-dithiole (DS-TTF). A solution of **9** (294 mg, 1.0 mmol) and trimethyl phosphite (0.4 mL) in benzene (6 mL) was refluxed for 1 h. After concentration, the residue was purified by column chromatography on silica gel with CS_2 and subsequent recrystallization from toluene to give 90 mg (42%) of DS-TTF as golden yellow leaflets: mp 237−

(17) Cornelissen, J. P.; Haasnoot, J. G.; Reedijk, J.; Faulmann, C.; Legros, J.-P.; Cassoux, P.; Nigrey, P. J. *Inorg. Chim. Acta* **1992**, *202*, 131−139.

(18) Pan, W.-H.; Fackler, J. P., Jr. In *Inorganic Syntheses*; Fackler, J. P., Jr., Ed.; John Wiley & Sons: New York, 1982; Vol. 21, p 6−11.

237.5 °C with dec; ^{1}H NMR (CS_2/$CDCl_3$) δ 7.00 (d, J = 5.7 Hz, 2H) and 7.86 (d, J = 5.7 Hz, 2H); MS m/z 412 (M^+). Anal. Calcd for $C_{10}H_4S_4Se_2$: C, 29.27; H, 0.98. Found: C, 29.29; H, 0.96.

Alternatively, the coupling reaction of **8** in trimethyl phosphite under reflux for 2 h gave DS-TTF in 13% yield.

4-Methylthio-5-[2-(tetrahydropyran-2-yloxy)ethyl]-1,3-dithiole-2-thione (10). To a solution of **1** (6.28 mL, 40 mmol) and TMEDA (6.04 mL, 40 mmol) in THF (150 mL) was added a solution of *n*-BuLi in hexane (1.61 M, 26.1 mL) at −70 °C, and the solution was stirred at the same temperature for 30 min. After addition of sulfur (1.28 g, 40 mmol), the mixture was warmed to 0 °C over a period of 1 h and stirred for 2 h. Into the solution, again cooled to −85 °C, were successively added carbon disulfide (2.53 mL, 42 mmol) and methyl thiocyanate (4.1 mL, 60 mmol). The reaction mixture was warmed to 0 °C over a period of 2 h and stirred for 1 h. After being quenched with water (100 mL), the mixture was extracted with CH_2Cl_2, and the extract was washed with brine and dried ($MgSO_4$). After concentration, chromatography of the residue on silica gel with CH_2Cl_2 gave 9.55 g (77%) of **10** as a yellow oil. An analytical sample was obtained by further purification with preparative GPC using $CHCl_3$ as eluent: ^{1}H NMR ($CDCl_3$) δ 1.5−1.9 (m, 6H), 2.40 (s, 3H), 3.07 (m, 2H), 3.52(m, 1H), 3.79 (m, 1H), 3.91 (m, 1H), and 4.63 (br t, J = 3.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.2, 20.5, 25.3, 30.3, 30.6, 62.1, 65.7, 98.8, 131.7, 146.6, and 212.6; MS m/z 308 (M^+); IR (neat) 1065 cm^{-1} (C═S). Anal. Calcd for $C_{11}H_{16}O_2S_4$: C, 42.83; H, 5.23. Found: C, 42.96; H, 5.29.

4-(2-Hydroxyethyl)-5-methylthio-1,3-dithiole-2-thione (11). Compound **11** was obtained as a yellow solid in 99% yield from **10** by the same procedure as described for the preparation of **4**: mp 33−33.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 1H), 2.44 (s, 3H), 3.03 (t, J = 6.1 Hz, 2H), and 3.84 (t, J = 6.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.5, 32.9, 61.6, 132.3, 145.8, and 212.2; MS m/z 224 (M^+); IR (neat) 3400 (OH) and 1061 cm^{-1} (C═S). Anal. Calcd for $C_6H_8OS_4$: C, 32.12; H, 3.59. Found: C, 32.10; H, 3.54.

4-Methylthio-5-(2-tosyloxyethyl)-1,3-dithiole-2-thione (12). The tosylation of **11** to **12** was accomplished in 80% yield by the same procedure as described for the preparation of **5**: yellow needles from hexane/$CHCl_3$; mp 61−62 °C; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H), 2.45 (s, 3H), 3.08 (t, J = 6.0 Hz, 2H), 4.16 (t, J = 6.0 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), and 7.73 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.2, 21.6, 29.0, 67.8, 127.7, 129.9, 131.9, 133.6, 142.3, 145.4, and 210.7; MS m/z 378 (M^+); IR (neat) 1071 cm^{-1} (C═S). Anal. Calcd for $C_{13}H_{14}O_3S_5$: C, 41.25; H, 3.75. Found: C, 41.29; H, 3.72.

5,6-Dihydrothieno[2,3-*d*]-1,3-dithiole-2-thione (13). Compound **12** was converted in 64% yield to **13** by the same procedure as described for the preparation of **7**, except that the mixture was heated at 120 °C for 2 h: yellow needles from hexane/$CHCl_3$; mp 116−117 °C (lit.[3] mp 110−111 °C); ^{1}H NMR ($CDCl_3$) δ 3.09 (t, J = 7.7 Hz, 2H) and 3.75 (t, J = 7.7 Hz, 2H); MS m/z 192 (M^+).

Thieno[2,3-*d*]-1,3-dithiole-2-thione (14). Conversion of **13** to **14** was carried out in 60% yield by the same procedure as described for the preparation of **8**: red needles from hexane/$CHCl_3$; mp 130.5−131 °C (lit.[3] mp 125−125.5 °C); ^{1}H NMR ($CDCl_3$) δ 7.09 (d, J = 5.4 Hz, 1H) and 7.67 (d, J = 5.4 Hz, 1H); MS m/z 190 (M^+).

5,5′,6,6′-Tetrahydro-$\Delta^{2,2'}$-bithieno[2,3-*d*]-1,3-thiole (BET-TTF). Compound **13** was coupled with trimethyl phosphite to BET-TTF in a manner similar to that described for BES-TTF (17% yield): reddish orange crystals from toluene; mp 196−197 °C with dec (lit.[3] trans mp 195−196 °C, cis mp 184−186 °C; lit.[4a] mp 191−193 °C dec); ^{1}H NMR (CS_2/$CDCl_3$) δ 2.826 (isomer 2.833) (t, J = 8.1 Hz, 4H) and 3.72 (t, J = 8.1 Hz, 4H); MS m/z 320 (M^+).

$\Delta^{2,2'}$-Bithieno[2,3-*d*]-1,3-thiole (DT-TTF). Compound **14** was coupled with trimethyl phosphite to DT-TTF in a similar manner as described for BES-TTF (22% yield): golden orange leaflets from toluene; mp 228−229 °C (lit.[3] mp 214−215 °C; lit.[4a] mp 213−214 °C dec); ^{1}H NMR (CS_2/$CDCl_3$) δ 6.85 (d, J = 5.1 Hz, 2H) and 7.28 (d, J = 5.1 Hz, 2H); MS m/z 316 (M^+).

4-Methylseleno-5-[2-(tetrahydropyran-2-yloxy)ethyl]-1,3-diselenole-2-selone (15). To a mixture of **1** (1.57 mL, 10 mmol) and TMEDA (3.0 mL, 20 mmol) in THF (80 mL) cooled to −70 °C was added a hexane solution of *n*-BuLi (1.54 M, 6.5 mL), and the solution was stirred at the same temperature for 30 min. Selenium (790 mg, 10 mmol) was added in one portion, and the reaction mixture was warmed to 0 °C over a period of 2 h and stirred for additional 2 h. Then the mixture was cooled again to −90 °C, and selenium powder (790 mg, 10 mmol) was added. To the mixture was slowly added a THF (20 mL) solution of carbon diselenide (0.64 mL, 10 mmol) over a period of 1 h, while the temperature was maintained around −70 °C, and then the mixture was warmed to 0 °C over a period of 1 h. The mixture was quenched by MeI (0.70 mL, 11 mmol) and stirred for an additional 1 h. After water (50 mL) was added, the mixture was extracted with CH_2Cl_2, and the extract was washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was subjected to column chromatography on silica gel with CH_2Cl_2 to afford 3.47 g (70%) of **15** as a red oil: ^{1}H NMR ($CDCl_3$) δ 1.5−1.9 (m, 6H), 2.34 (s, 3H), 3.15 (m, 1H), 3.27 (m, 1H), 3.50 (m, 2H), 3.80 (m, 1H), 3.92 (m, 1H), and 4.63 (br t, J = 3.4 Hz, 1H); ^{13}C NMR ($CDCl_3$)-δ 11.9, 19.1, 25.2, 30.3, 34.8, 62.1, 65.9, 98.8, 129.1, 157.5, and 212.8; MS m/z 496 (M^+); IR (neat) 903 cm^{-1} (C═Se). Anal. Calcd for $C_{11}H_{16}O_2Se_4$: C, 26.63; H, 3.25. Found: C, 26.58; H, 3.24.

4,4′(5′)-Bis(methylseleno)-5,5′(4′)-bis[2-(tetrahydropyran-2-yloxy)ethyl]tetraselenafulvalene (17). A solution of **15** (1.5 g, 3.0 mmol) and trimethyl phosphite (1.1 mL, 9 mmol) in benzene (14 mL) was refluxed for 2 h. After evaporation of the solvent, the residue was purified by column chromatography on silica gel with CH_2Cl_2 to give 1.18 g (93%) of **17** as a red oil: ^{1}H NMR ($CDCl_3$) δ 1.5−1.9 (m, 12H), 2.252 (isomer 2.255) (s, 6H), 2.95 (m, 4H), 3.48 (m, 4H), 3.85 (m, 4H), and 4.63 (br t, J = 3.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 10.9 (isomer 11.0), 19.2, 25.4, 30.5, 35.0, 62.0, 66.3, 98.6 (isomer 98.8), 114.1 (isomer 114.3), and 140.3 (isomer 140.4); MS m/z 836 (M^+). Anal. Calcd for $C_{22}H_{32}Se_6O_4$: C, 31.67; H, 3.87. Found: C, 31.80; H, 3.87.

4,4′(5′)-Bis(2-hydroxyethyl)-5,5′(4′)-bis(methylseleno)-tetraselenafulvalene (18). A mixture of **17** (382 mg, 0.46 mmol), 2 N hydrochloric acid (0.2 mL), methanol (6 mL), and THF (10 mL) was stirred at rt for 12 h. Water (12 mL) was introduced, and then the mixture was extracted with CH_2Cl_2. The extract was washed with brine, dried ($MgSO_4$), and then concentrated. The residue was washed with a small amount of CH_2Cl_2 to give 288 mg (94%) of **18** as a reddish brown solid: mp 110−112 °C; ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 6H), 2.86 (t, J = 5.9 Hz, 4H), and 3.75 (t, J = 5.9 Hz, 4H); MS m/z 668 (M^+); IR (KBr) 3300 cm^{-1} (OH). Anal. Calcd for $C_{12}H_{16}O_2Se_6$: C, 21.64; H, 2.42. Found: C, 21.55; H, 2.37.

4,4′(5′)-Bis(methylseleno)-5,5′(4′)-bis[2-(tosyloxy)ethyl]-tetraselenafulvalene (19). To a solution of **18** (890 mg, 1.34 mmol) in pyridine (9 mL) was added tosyl chloride (1.53 g, 8.04 mmol) at 0 °C. After being stirred for 12 h, the resulting mixture was poured into ice-containing 1 N HCl solution (5 mL). The precipitate was collected by filtration and washed with a small amount of MeOH to give 1.24 g (95%) of **19** as a light red solid: mp 155 °C dec; ^{1}H NMR ($CDCl_3$) δ 2.21 (s, 6H), 2.43 (s, 6H), 2.93 (t, J = 6.2 Hz, 4H), 4.09 (t, J = 6.2 Hz, 4H), 7.29 (d, J = 8.3 Hz, 4H), and 7.75 (d, J = 8.3 Hz, 4H). Anal. Calcd for $C_{26}H_{28}O_6S_2Se_6$: C, 32.05; H, 2.90. Found: C, 32.07; H, 2.95.

5,5′,6,6′-Tetrahydro-$\Delta^{2,2'}$-biselenolo[2,3-*d*]-1,3-selenole (BES-TSF). A mixture of **19** (1.24 g, 1.27 mmol) and NaI (762 mg, 5.08 mmol) in DMF (25 mL) was stirred at 80 °C for 0.5 h. The reaction mixture was poured into water (50 mL), and the precipitate was collected by filtration, washed with small amount of MeOH, and dried in vacuo. The brown solid was recrystallized from PhCl to give 295 mg (39%) of BES−TSF as a mixture of two kinds of crystals. For the trans isomer: reddish orange plates; mp 205−207 °C with dec; ^{1}H NMR (CS_2/$CDCl_3$) δ 2.88 (t, J = 7.8 Hz, 4H) and 3.69 (t, J = 7.8 Hz, 4H); MS m/z 604 (M^+). For the cis isomer: dark red needles; mp 199−201 °C dec; ^{1}H NMR (CS_2−$CDCl_3$) δ 2.87 (t,

J = 7.8 Hz, 4H) and 3.69 (t, J = 7.8 Hz, 4H); MS m/z 604 (M^+). Anal. Calcd for $C_{10}H_8Se_6$: C, 19.95; H, 1.34. Found: C, 20.13; H, 1.20.

Complexation. The TCNQ complexes of BES-TTF and DS-TTF were prepared by a conventional diffusion method using acetonitrile as solvent, while that of BES-TSF was obtained by gradual growth of the crystals from an interface between a carbon disulfide solution of the donor and an acetonitrile solution of the acceptor. All the radical cation salts were prepared by electrocrystallization under galvanostatic conditions (0.5−1.0 μA) in the presence of n-$Bu_4N^+X^-$ ($X^- = ClO_4^-$, PF_6^-, and AsF_6^-) as the supporting electrolyte. The most suitable solvent was chlorobenzene containing about 5% ethanol.

X-ray Crystallographic Analyses.[19] X-ray diffraction experiments were performed at rt on a Rigaku AFC6S diffractometer or a Rigaku AFC7R diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.5418 Å) or Mo Kα radiation (λ = 0.7107 Å), respectively. The intensity data were measured using the $\omega-2\theta$ scan technique. The structures were solved by direct methods or Patterson methods and refined by full-matrix least-squares techniques with anisotropic temperature factors for the non-hydrogen atoms.

(19) Fully refined data for these structures have been deposited at the Cambridge Crystallographic Data Centre. The data can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

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Supporting Information Available: X-ray data for trans BES-TSF, $(BES\text{-}TTF)_2{\cdot}AsF_6$, DS-TTF·TCNQ, and BES-TSF·TCNQ (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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