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SYNTHESIS AND PROPERTIES OF NOVEL UNSYMMETRICAL TETRASELENAFULVALENE DONORS, EDT-PT-TSF AND EDT-PS-TSF

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In order to develop novel electron donors, by structural modification to a superior electron donor, bis(ethylenedithio)-tetraselenafulvalene (BETS **2***), unsymmetrical TSF derivatives ethylenedithio-propylenethio-TSF (EDT-PT-TSF* **5***) and ethylenedithio-propyleneseleno-TSF (EDT-PS-TSF* **6***) have been effectively synthesized. The synthetic method involves a one-pot formation of 1,3-diselenole-2-selones from acetylene derivatives, a cross-coupling to the TSF system, and finally a ring construction of the outer heterocycles. Electrocrystallization of* **5** *affords a series of conductive radical cation salts with* BF_4^-, PF_6^-, AsF_6^-, ClO_4^-, *and* SbF_6^- *anions, which are of the 2:1 or 3:2 composition ratio. All of the salts with 2:1 ratio are stable metals down to 4.2 K without any specific phase transitions. X-ray crystallographic analyses confirm that they have so-called κ-type donor arrangements.*

Keywords: tetraselenafulvalene; radical cation salt; X-ray crystallographic analysis; organic conductor

INTRODUCTION

The development of new molecular metals and superconductors has largely depended on the development of new component organic molecules, mainly tetrathiafulvalene (TTF)-type electron donors. The TTF-type electron donors being able to afford superconducting radical cation salts are rather limited, and many of them are characterized by chemical structures related to bis(ethylendithio)-TTF (BEDT-TTF **1**) [1]. Among such electron donors, a TSF counterpart of BEDT-TTF, BETS (**2**), is of current interest [2].

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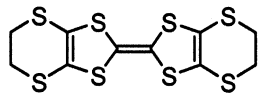
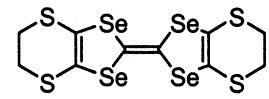
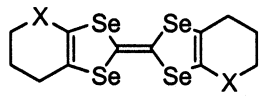
In spite of the widely spreading interest to the analogous TSF-type electron donors, synthetic difficulty of TSF derivatives has been still problematic, and thus only a limited numbers of heterocycle-fused TSF derivatives have been synthesized [3].



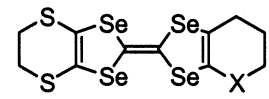
BEDT-TTF **1**



BETS **2**



X = S BPT-TSF **3**
X = Se BPS-TSF **4**



X = S EDT-PT-TSF **5**
X = Se EDT-PS-TSF **6**

As a breakthrough in TSF synthesis, we have recently explored a facile synthetic method for novel TSF derivatives possessing on chalogen-containing outer heterocycles (BPT-TSF **3** and BPS-TSF **4**) [4]. The main features of our procedure are: (1) one-pot preparation of 1,3-diselenole-2-selone derivatives from *O*-tetrahydropyranyl (THP)-protected hydroxyalkyl substituted acetylene derivatives, and (2) ring closure reaction one chalcogen atoms to form outer heterocycles [5,6]. In order to develop new unsymmetric TSF-type electron donors, we have applied this procedure to the synthesis of EDT-PT-TSF (**5**) and EDT-PS-TSF (**6**), hybrids of BETS (**2**) and BPT- (**3**) or BPS-TSF (**4**).

In this article, we like to report their practical syntheses and properties, as well as the crystal structures and conductivities of their radical salts.

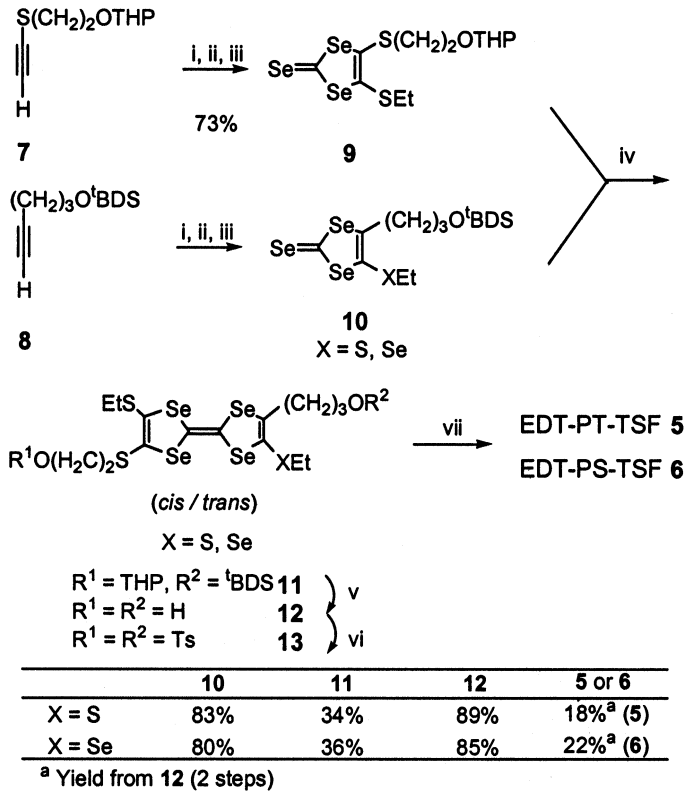
RESULTS AND DISCUSSION

Synthesis

For the synthesis of unsymmetric TTF and TSF derivatives the most general method is a phosphite-mediated cross-coupling reaction of the two half units, 1,3-dichalcogenole-2-chalcogenones. However, isolation of the desired cross-coupling product from the resulting mixture with two homo-coupling ones is often difficult.

In our synthetic strategy for **5** and **6**, the key intermediates are 1,3-diselenole-2-selones with protected hydroxyalkyl substituents. The protecting group we have normally employed is tetrahydropyranyl (THP),

which is highly polar. In the present synthesis, for the sake of facile purification after cross-coupling, we have examined a less polar *tert*-butyldimethylsilyl (^{t}BDS) for the protecting of the second 1,3-diselenole-2-selones. Thus starting from two terminal alkynes, **7**[6] and **8**[7], the corresponding 1,3-diselenole-2-selone derivatives (**9** and **10**) were prepared in good yields. The cross-coupling reaction of **9** and **10** gave the desired **11** together with two homo-coupling products. Thanks to the different polarities of all three TSF derivatives, silica gel column chromatography was very effective to separate **11** from the mixture. The subsequent conversions of **11**, deprotection, tosylation, and finally ring formation via transalkylation on chalcogen atoms, proceeded smoothly to give **5** and **6** in moderate yields (Scheme 1) [8].



	10	11	12	5 or 6
X = S	83%	34%	89%	18%[a] (5)
X = Se	80%	36%	85%	22%[a] (6)

[a] Yield from **12** (2 steps)

SCHEME 1. Synthesis of **5** and **6**. Ragents: i) ^{n}BuLi, TMEDA, THF; ii) Se, CSe_2; iii) EtSCN (for **8** and **10** (X = S)) or Se then EtI (for **10** X = Se); iv) $P(OMe)_3$, benzene; v) HCl aq. MeOH-acetone; vi) TsCl, Et_3N, CH_2Cl_2; vii) NaI, DMF.

TABLE 1 Half-wave Oxidation Potentials[a] of **2**–**6**

Donor	$E_1(1/2)$/V	$E_2(1/2)$/V	ΔE/V
2 (BETS)[b]	+0.69	+0.96	0.27
3 (BPT-TSF)	+0.53	+0.83	0.30
4 (BPS-TSF)	+0.50	+0.80	0.30
5 (EDT-PT-TSF)	+0.57	+0.83	0.26
6 (EDT-PS-TSF)	+0.55	+0.81	0.26

[a] vs. Ag/AgCl electrode, in PhCN containing 0.1 M $^{n}Bu_4NClO_4$ as supporting electrolyte. Pt working and counter electrodes, scan rate 100 mV/s, 23°C.
[b] $^{n}Bu_4NPF_6$ as supporting electrolyte.

Oxidation Potentials

Oxidation potentials of **5** and **6** determined by cyclic voltammetry are summarized in Table 1, together with those of related symmetric TSFs (**2**–**4**). Both of **5** and **6** show two reversible redox couples as normal TSF derivatives do. The first oxidation potentials of **5** and **6** fall in between those of the corresponding symmetrical donors, though the second ones are almost equal to those of **3** and **4**, respectively.

Radical Cation Salts

Electrocrystallization of **5** in chlorobenzene containing tetrabutylammonium salts gave various radical cation salts, although that of **6** only a radical salt with AsF_6^-, as summarized in Table 2. In case of **5** with PF_6^- and AsF_6^- anions, two different phases with different crystal shapes (plates and rods) were obtained. X-ray crystal analysis revealed that the

TABLE 2 Radical Cation Salts of EDT-PT-TSF (**5**) and EDT-PS-TTF (**6**)

Salt[a]	Appearance	Structure	σ/S cm^{-1} [c]	Remarks
$\mathbf{5}_2 \cdot PF_6$	black plates	κ	50	metallic (4.2 K)
$\mathbf{5}_2 \cdot AsF_6$	black plates	κ	22	metallic (4.2 K)
$\mathbf{5}_2 \cdot SbF_6$	black plates	κ	18	metallic (4.2 K)
$\mathbf{5}_3 \cdot (PF_6)_2$	black rods	—	8.6×10^{-4}	semiconductive
$\mathbf{5}_3 \cdot (AsF_6)_2$ [b]	black rods	—	4.7×10^{-4}	semiconductive
$\mathbf{5}_2 \cdot BF_4$	black plates	κ	3.0	metallic (4.2 K)
$\mathbf{5}_2 \cdot ClO_4$	black plate	—	53	—
$\mathbf{6}_3 \cdot (AsF_6)_2$ [b]	black rods	—	5.1×10^{-4}	semiconductive

[a] Determined by X-ray crystallographic analysis unless otherwise stated.
[b] Determined on the basis of elemental analysis.
[c] Measured on a single crystal with a four-probe method.

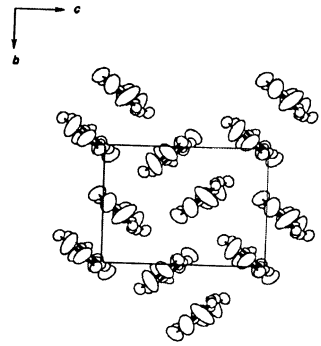


FIGURE 1 Crystal structure of $\mathbf{5}_2{\cdot}AsF_6$.

plate-like crystals have a so-called κ-type donor packing with 2:1 donor to anion ratio [9]. All the plate-like crystals with octahedral anions, namely PF_6^-, AsF_6^-, and SbF_6^- anions are isostructural, and the crystal structure of $\mathbf{5}_2{\cdot}AsF_6$ is shown in Figure 1 as a representative of this series.

On the other hand, X-ray structural analysis of the second phase with rod shape indicated that the phase has a different crystal structure with 3:2 donor to anion ratio as shown in Figure 2 [10]. Judging from the shapes of crystals as well as the donor to anion ratio determined by elemental analyses, the second phase of AsF_6 salt of **5** and $\mathbf{6}{\cdot}AsF_6$ would have the same crystal structure as $\mathbf{5}_3{\cdot}(PF_6)_2$.

The crystal structure of plate-like $\mathbf{5}_2{\cdot}BF_4$ salt was also elucidated by X-ray structural analysis. The salt has a κ-type donor arrangement, but is not isostructural with the above slats with octahedral anions [11].

All the radical cation salts with 2:1 ratio are highly conductive at room temperature (3.0–53 S cm^{-1}), and remain metallic down to liquid helium temperature, except for $\mathbf{5}_2{\cdot}ClO_4$, crystals of which were very fragile and

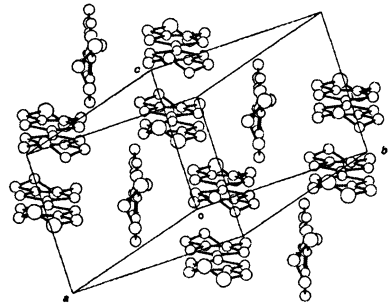


FIGURE 2 Crystal structure of $\mathbf{5}_3{\cdot}(PF_6)_2$.

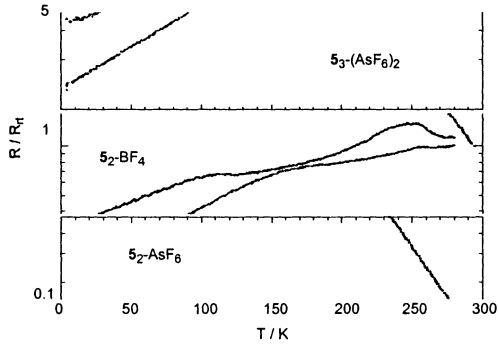


FIGURE 3 Temperature dependence of resistivities.

unequal to low-temperature conductivity measurement. Figure 3 shows temperature dependence of resistivities for $\mathbf{5}_2{\cdot}AsF_6$, $\mathbf{5}_2{\cdot}BF_4$, and $\mathbf{5}_3{\cdot}(AsF_6)_2$, as representatives for three classes of radical salts. In contrast to the metallic 2:1 salts, the conductivities of the 3:2 salts are not so high at room temperature ($10^{-4}\,S\,cm^{-1}$) and semiconductive. This can be explained by the crystal structure; as shown in Figure 2, the structure contains two crystallographycally independent donor molecules, and one of which forms dimeric pairs, and the others is surrounded by the dimer pairs. There is no strong interaction between the dimers or between the dimer and the monomeric donor species, and thus no effective conduction path is constructed. In addition, considering the ratio of 3:2, the oxidation state of each donor molecules is not equal, indicating that a charge localization state would exist.

CONCLUSION

In summary, we have synthesized two new unsymmetrical TSF derivatives (EDT-PT-TSF and EDT-PT-TSF) by utilizing the synthetic method of heterocycle-fused TSFs recently developed by our group. Of them, EDT-PT-TSF has turned out to be a superior electron donor, which, with PF_6^-, AsF_6^-, SbF_6^-, and BF_4^- anions, forms stable metallic salts down to 4.2 K.

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[8] All new compounds were characterized by an elemental analysis, NMR, and MS spectroscopy. Selected physical and spectral data. EDT-PT-TSF (**5**): red needles from carbon disulfide-hexane (1:5, v/v); mp 169–170°C (melt with decomposition); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (m, 2H, CH_2), 2.46 (m, 2H, CH_2), 3.04 (m, 2H, CH_2), 3.30 (s, 4H, SCH_2CH_2S); MS m/z 556 (M^+); Anal. Calcd for $C_{11}H_{10}S_3Se_4$: C, 23.84; H, 1.82%. Found: C, 23.77; H, 1.80%. EDT-PS-TSF (**6**): red needles from carbon disulfide-hexane (1:5, v/v); mp 214–215°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (m, 2H, CH_2), 2.45 (m, 2H, CH_2), 3.11 (m, 2H, CH_2), 3.30 (s, 4H, SCH_2CH_2S); MS m/z 602 (M^+); Anal. Calcd for $C_{11}H_{10}S_2Se_5$: C, 21.98; H, 1.68%. Found: C, 21.78; H, 1.69%.
[9] Crystal data for $\mathbf{5}_2{\cdot}AsF_6$: $C_{22}H_{20}S_6Se_8AsF_6$, M = 1297.36, monoclinic, space group $C2/c$, a = 34.726(7), b = 8.413(4), c = 11.689(4) Å, β = 99.25(3)°, V = 3370(2) Å^3, Z = 4, D_c = 2.557 g cm^{-3}, R = 0.058, R_w = 0.091 for 2836 observed reflections [$I > 3.0\sigma(I)$].
[10] Crystal data for $\mathbf{5}_3{\cdot}(PF_6)_2$: $C_{33}H_{30}S_9Se_{12}P_2F_{12}$, M = 1952.60, monoclinic, space group $P\bar{1}$, a = 9.9134(8), b = 15.710(2), c = 8.7438(8) Å, α = 96.34(1)°, β = 100.732(6)°, γ = 76.667(8)°, V = 1298.6(3) Å^3, Z = 1, D_c = 2.497 g cm^{-3}, R = 0.073, R_w = 0.233 for 3221 observed reflections [$I > 2.0\sigma(I)$].
[11] Crystal data for $\mathbf{5}_2{\cdot}BF_4$: $C_{22}H_{20}S_6Se_8BF_4$, M = 1195.24, monoclinic, space group $C2/c$, a = 35.331(3), b = 11.438(4), c = 8.474(3) Å, β = 93.13(2)°, V = 3419(1) Å^3, Z = 4, D_c = 2.322 g cm^{-3}, R = 0.051, R_w = 0.044 for 1895 observed reflections [$I > 3.0\sigma(I)$].