JOURNAL OF
Materials
CHEMISTRY

Synthesis and properties of novel heterocycle-fused TTF-type electron donors: bis(propylenethio)tetrathiafulvalene (BPT-TTF), bis(propyleneseleno)tetrathiafulvalene (BPS-TTF), and their tetraselenafulvalene analogues (BPT-TSF and BPS-TSF)†

Tetsuya Jigami, Mie Kodani, Satoshi Murakami, Kazuo Takimiya,* Yoshio Aso and Tetsuo Otsubo*

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan. Tel: +81-824-24-7734; Fax: +81-824-22-7191;
E-mail: ktakimi@hiroshima-u.ac.jp

Received 4th December 2000, Accepted 8th February 2001
First published as an Advance Article on the web 5th March 2001

A series of novel heterocycle-fused TTF-type electron donors, bis(propylenethio)tetrathiafulvalene (BPT-TTF, **5**), bis(propyleneseleno)tetrathiafulvalene (BPS-TTF, **6**), and their tetraselenafulvalene analogues (BPT-TSF, **7** and BPS-TSF, **8**) have been effectively synthesized from a common starting compound, THP-protected pent-4-yn-1-ol. The solution electrochemistry reveals that all the new donors have good electron donating properties. Formation of their radical cation salts by electrocrystallization technique has been successfully achieved. All the radical salts derived from the TTF derivatives (**5** and **6**) are insulating owing to the complete charge transfer. On the other hand, the TSF derivatives (**7** and **8**) afford different types of highly conductive radical cation salts. Of these, **7**·PF_6, **7**·AsF_6 and **7**·$FeCl_4$ remain metallic down to liquid helium temperature.

Introduction

Most of the organic superconductors so far reported are radical cation salts of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, **1**) and related heterocycle-fused TTF type electron donors.[1] The fused outer heterocycles in these donors play a very important role in intermolecular interactions through heteroatomic contacts and accordingly in the solid state properties of the derived radical cation salts. In the search for new electron donors to produce highly conducting and superconducting radical cation salts, potential approaches are to modify the BEDT-TTF framework by (i) changing the number of heteroatoms or ring size of the outer heterocycles and (ii) replacing the sulfur atoms of the inner and outer heterocycles with more polarizable selenium atoms.[2] By a combination of these two guidelines, one may design a wide variety of heterocycle-fused TTF and tetraselenafulvalene (TSF) derivatives, some of which have already been investigated and found to behave as superior electron donors.[1,3,4] Bis(ethylenethio)tetrathiafulvalene (BET-TTF, **2**)[5] possessing five-membered sulfur heterocycles, is such a heterocycle-fused TTF derivative developed early on, and recently Rovira and coworkers reported that it can produce a wide variety of metallic radical cation salts.[5] Our group also synthesized the selenium analogues of **2**, bis(ethyleneseleno)tetrathiafulvalene (BES-TTF, **3**) and bis(ethyleneseleno)tetraselenafulvalene (BES-TSF, **4**) and found that they can form similar conducting radical cation salts but with increasing metallic stability at low temperature due to the introduction of the selenium atoms.[6] The X-ray structural analyses revealed that the radical cation salts of **3** and **4** possess a columnar structure of donor stacks similar to the quasi one-dimensional Bechgaard salts.[1] This feature is in sharp contrast to the quasi two-dimensional salts of BEDT-TTF, which appear in various crystal phases designated as α-, β-, θ-, κ-types, and so on. The planar molecular structures of **3** and **4** unlike non-planar BEDT-TTF are considered to favor simple π-stacking suitable for a columnar structure. With these results in mind, we have designed a new family of six-membered heterocycle fused-TTF type donors, namely bis(propylenethio)tetrathiafulvalene (BPT-TTF, **5**), bis(propyleneseleno)tetrathiafulvalene (BPS-TTF, **6**), and their tetraselenafulvalene analogues (BPT-TSF, **7** and BPS-TSF, **8**). These donors might have flexible outer six-membered rings like BEDT-TTF, and accordingly form radical cation salts with versatile crystal structures. In addition, it should be noted that intermolecular interactions among the donors can be more or less tuned, *i.e.*, decreased by installing only one chalcogen atom in the six-membered ring, but increased by introducing selenium in place of sulfur. In this paper the synthesis and properties of these new TTF-type donors (**5**–**8**) as well as the conductive properties and solid state structures of their radical cation salts are described.

Results and discussion

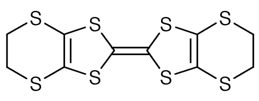
Syntheses of novel electron donors

For the synthesis of the title compounds, we examined a synthetic route similar to that used for BES-TTF **3** and BES-TSF **4**, as shown in Scheme 1.[6] This synthetic route involves two important steps: (1) one-pot formation of the 1,3-dichalcogenole ring[7] from tetrahydropyranyl (THP)-protected pent-4-yn-1-ol[8] and (2) intramolecular transalkylation on a sulfur or selenium atom toward the construction of the outer six-membered heterocycle. The advantage of this method is that an appropriate combination of the sulfur and selenium reagents in the initial formation of 1,3-dichalcogenole ring permits a common access to all the target donors from the same starting material. Thus, BPT-TTF **5** and BPS-TTF **6** were obtained as follows; the acetylene **9** was treated successively with ^{n}BuLi, sulfur and carbon disulfide to generate the vinyl anion intermediate **10**, which was then quenched by methyl

---

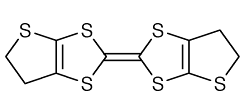
†Electronic supplementary information (ESI) available: further experimental details. See http://www.rsc.org/suppdata/jm/b0/b009700o/

DOI: 10.1039/b009700o



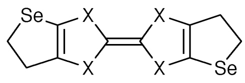
BEDT-TTF or ET

1

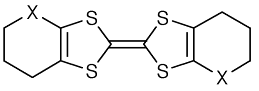


BET-TTF

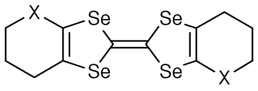
2



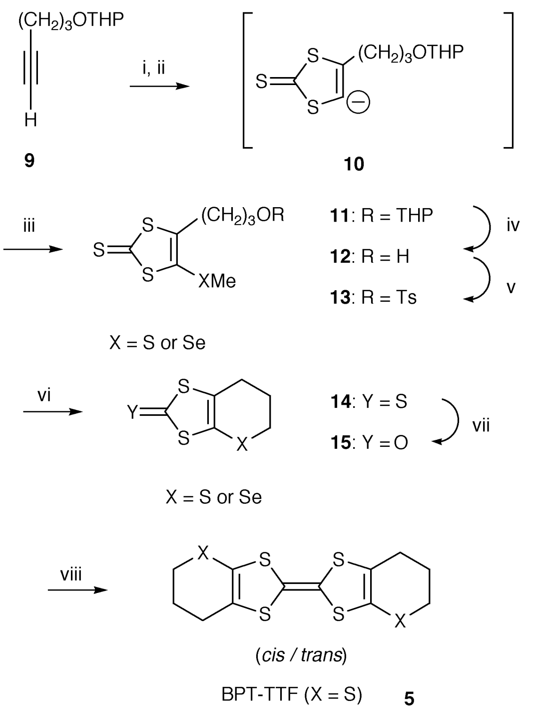
BES-TTF (X = S) **3**
BES-TSF (X = Se) **4**



BPT-TTF (X = S) **5**
BPS-TTF (X = Se) **6**



BPT-TSF (X = S) **7**
BPS-TSF (X = Se) **8**



	11	12	13	14	15	5 or 6
X = S	69%	90%	77%	92%	99%	53% (**5**)
X = Se	83%	79%	80%	98%	87%	34% (**6**)

Scheme 1 Synthesis of BPT-TTF **5** and BPS-TTF **6**. *Reagents*: i, ^{n}BuLi, TMEDA, THF; ii, S, CS_2; iii, MeSCN (for **11** (X = S)) or Se then MeI (for **11** (X = Se)); iv, HCl aq. MeOH–acetone; v, TsCl, pyridine; vi, NaI, DMF; vii, $Hg(OAc)_2$, $CHCl_3$; viii, $P(OMe)_3$.

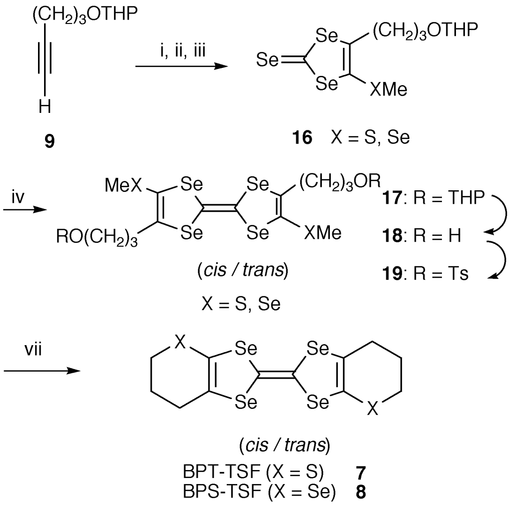
thiocyanate or by a combined reagent of selenium and methyl iodide to afford THP-protected 4-(hydroxypropyl)-5-methylchalcogeno-1,3-dithiole-2-thiones **11** (X = S, 69% yield; X = Se, 83% yield). After deprotection of the THP group (79–90% yield) followed by tosylation under general conditions (77–80% yield), the resulting tosylates **13** were treated with sodium iodide in DMF to afford **14** (X = S, 92% yield; X = Se, 98% yield). It is reasonable to consider that this heterocyclization reaction proceeds *via* intramolecular transalkylation on the chalcogen atom. The transalkylation on sulfur required a higher reaction temperature (120 °C, 3 h), whereas that on the selenium proceeded under somewhat milder conditions (80 °C, 2 h). The conventional transformation of **14** into the ketones **15** with mercury acetate and subsequent trimethyl phosphite-promoted coupling reaction gave BPT-TTF (**5**) and BPS-TTF (**6**) in 52% and 30% yields (two steps), respectively.

For the syntheses of TSF derivatives, BPT-TSF (**7**) and BPS-TSF (**8**), we noticed that it is inexpedient to pursue similar chemical conversions forming the outer six-membered heterocycle on the relatively unstable 1,3-diselenole-2-selone stage,[6] and accordingly a slightly modified route was taken as shown in Scheme 2. Thus the 1,3-diselenole-2-selones **16** were similarly prepared from **9** using a combination of selenium and carbon diselenide instead of sulfur and carbon disulfide, and directly converted into the TSF derivatives **17**, which were then subjected to conversion reactions to give **7** and **8** in moderate yields.

The present donors are expected to exist as a mixture of *cis*- and *trans*-isomers concerning the central double bond as observed for **2**–**4**.[5,6] Unlike the cases of BES-TTF (**3**) and BES-TSF (**4**), ^{1}H NMR spectra of **5**–**8** did not give any helpful information on the existence of the isomers owing to multiplet signals for the outer heterocyclic protons. Alternatively, ^{13}C NMR of readily soluble **5** and **6** showed the three pairs of peaks assignable to the quaternary carbons of the TTF core supporting the existence of *cis*- and *trans*-isomers as expected (see Experimental section). The approximately similar height of each peak in the pairs indicates that the ratio of the *cis*- and *trans*-isomers is roughly 1 : 1.

Electrochemistry

Table 1 summarizes the oxidation potentials of **5**–**8** determined by cyclic voltammetry, together with those of the parent donors, TTF and TSF. All these new donors show two reversible one-electron redox waves, indicating the sequential formation of radical cation and dication species. The first oxidation potentials of **5**–**8** are positively shifted by 10–40 mV with respect to their parent compounds, regardless of the chalcogen type in the outer ring. In addition, the differences between the first and second oxidation potentials, ΔE values, of **5**–**8** are almost same as those of TTF and TSF.



	16	17	18	19	7 or 8
X = S	70%	90%	86%	59%	60% (**7**)
X = Se	76%	98%	95%	64%	30% (**8**)

Scheme 2 Synthesis of BPT-TSF **7** and BPS-TSF **8**. *Reagents*: i, ^{n}BuLi, TMEDA, THF; ii, Se, CSe_2; iii, MeSCN (for **16** X = S) or Se then MeI (for **16** X = Se); iv, $P(OMe)_3$, benzene; v, HCl aq. MeOH–THF; vi, TsCl, NEt_3, CH_2Cl_2; vii, NaI, DMF.

Table 1 Half-wave oxidation potentials[a] of **5**–**8** and related donors

Donor	$E_1^{1/2}$/V	$E_2^{1/2}$/V	ΔE/V
5	0.38	0.76	0.38
6	0.37	0.75	0.38
7	0.53	0.83	0.30
8	0.50	0.80	0.30
TTF	0.34	0.71	0.37
TSF	0.49	0.78	0.29

[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^{-1}, 23 °C.

Radical cation salts

A standard procedure for electrocrystallization was applied to the present new donors, and the obtained radical cation salts are very versatile in composition ratio and conductive behavior, as shown in Table 2. All the salts produced from TTF derivatives **5** and **6** have conductivities lower than 10^{-5} S cm^{-1} at room temperature. This is rationalized in terms of their 1 : 1 composition ratios of donor to anion: since each donor species is in a monocationic state, they are Mott-type insulators.

In contrast, the TSF derivatives **7** and **8** afforded conductive radical cation salts; those of **7** took either 2 : 1 or 3 : 2 stoichiometry, while those of **8** only 3 : 2 stoichiometry. The room temperature conductivities of three 2 : 1 salts of **7**, **7**·PF_6, **7**·AsF_6 and **7**·$FeCl_4$ are very high (38–150 S cm^{-1}), and they are metallic down to liquid helium temperature. The conductivities of **7**·PF_6 and **7**·AsF_6 monotonously increase with lowering temperature, and the maximum values at liquid helium temperature are about twenty times higher than those at room temperature. Fig. 1 demonstrates the temperature-dependent resistivity of **7**·PF_6 as a representative.

Table 2 Radical cation salts of BPT-TTF (**5**), BPS-TTF (**6**), BPT-TSF (**7**) and BPS-TSF (**8**)

Salt	Appearance	D : A[a]	σ_{rt}/S cm^{-1} [c]	Remarks
5·PF_6	Dark blue needles	1 : 1[b]	$<10^{-5}$ [d]	—
5·AsF_6	Black prisms	1 : 1[b]	$<10^{-5}$ [d]	—
6·PF_6	Dark blue needles	1 : 1[b]	$<10^{-5}$ [d]	—
6·AsF_6	Dark blue needles	1 : 1[b]	$<10^{-5}$ [d]	—
6·SbF_6	Dark blue needles	1 : 1[b]	$<10^{-5}$ [d]	—
7·BF_4	Black plates	3 : 2[b]	50	M down to 200 K
7·PF_6	Black prisms	2 : 1	38	M down to 4.2 K
7·AsF_6	Black prisms	2 : 1	150	M down to 4.2 K
7·SbF_6	Black prisms	3 : 2	2.0	M down to 200 K
7·$FeCl_4$	Black plates	2 : 1	98	M down to 4.2 K
8·BF_4	Black prisms	3 : 2	0.5	$E_{act} = 0.027$ eV
8·ClO_4	Black prisms	3 : 2	1.0	$E_{act} = 0.027$ eV
8·PF_6	Black prisms	3 : 2	3.0	$E_{act} = 0.030$ eV
8·AsF_6	Black prisms	3 : 2	5.0	$E_{act} = 0.017$ eV

[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 unless otherwise stated. [d] Measured on a single crystal with a two-probe method.

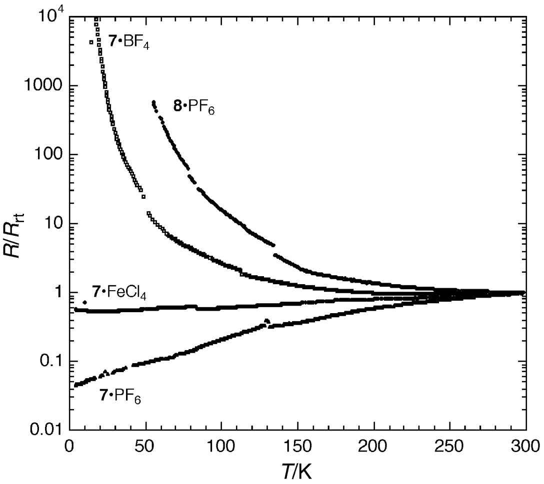


Fig. 1 Temperature dependence of resistivity of radical cation salts derived from **7** and **8**.

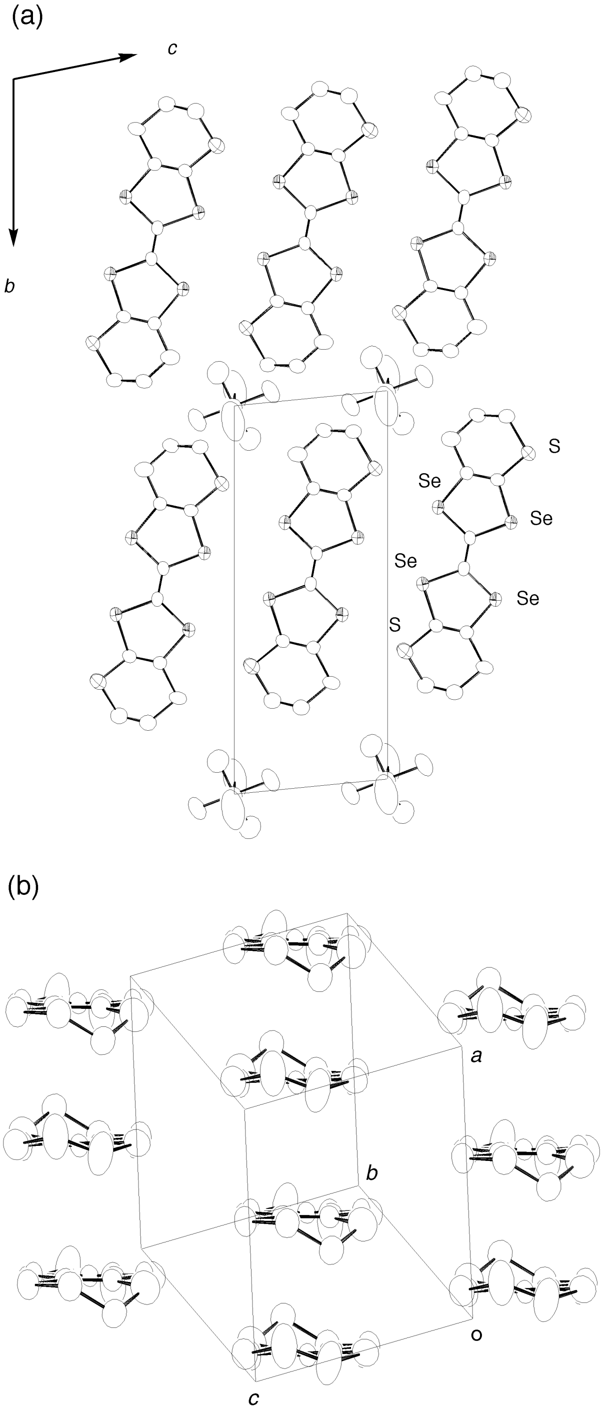


Fig. 2 Crystal structure of **7**·AsF_6: (a) *a*-axis projection, (b) stacking arrangement viewed from the molecular long axis.

The crystal structure of **7**·AsF_6, elucidated by X-ray crystallographic analysis, is shown in Fig. 2.[9] The donor molecules form dimeric pairs, which stack in a columnar manner, resembling β-type BEDT-TTF (**1**) salts.[1] The interplanar distance within the pair is 3.71 Å, and that between the pairs is 4.03 Å. There are many side-by-side interactions

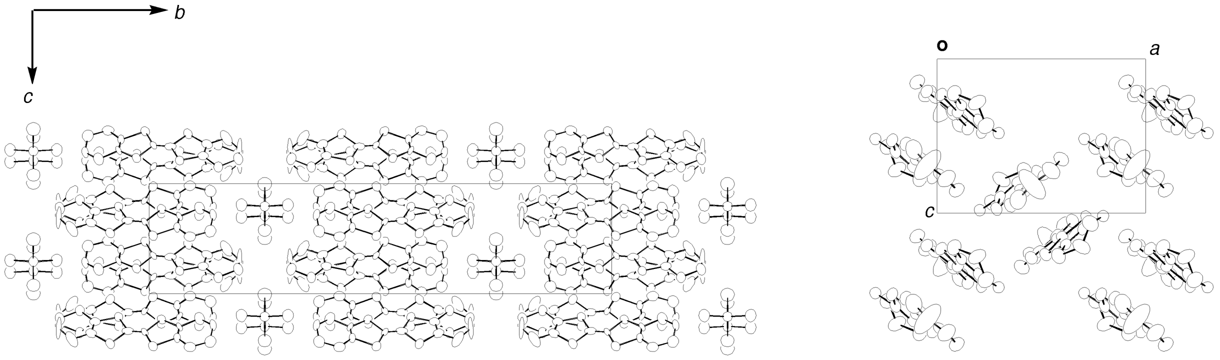


Fig. 3 Crystal structure of **7**·$FeCl_4$: viewed along the *a*-axis (left) and the *b*-axis without anions (right).

between the adjacent stacks through short Se–Se and S–Se contacts, which can enhance the conductivity and stabilize the metallic state down to low temperature.

The temperature dependence of the conductivity of **7**·$FeCl_4$ is not so large as that of **7**·PF_6 and **7**·AsF_6, and its maximum conductivity around 20 K is about double that at room temperature (see also Fig. 1). This different behavior is ascribed to the different crystal structure of **7**·$FeCl_4$, which comprises a so-called κ-type arrangement of the donor, as shown in Fig. 3.

The two 3 : 2 salts of **7** are metallic with a broad maximum of conductivity at a relatively high temperature around 200 K (see also Fig. 1 for **7**·BF_4). The X-ray crystallographic analysis of **7**·BF_4 with a high room temperature conductivity of 50 S cm^{-1} indicated that it belongs to a monoclinic system, but failed in the final refinement of the structure solution because of insufficient data due to serious decay of the crystal during data collection.[10] On the other hand, it turned out that the crystal structure of less conductive **7**·SbF_6 belongs to a triclinic system, which was completely analyzed to be isostructural with 3 : 2 salts of **8** as described below.

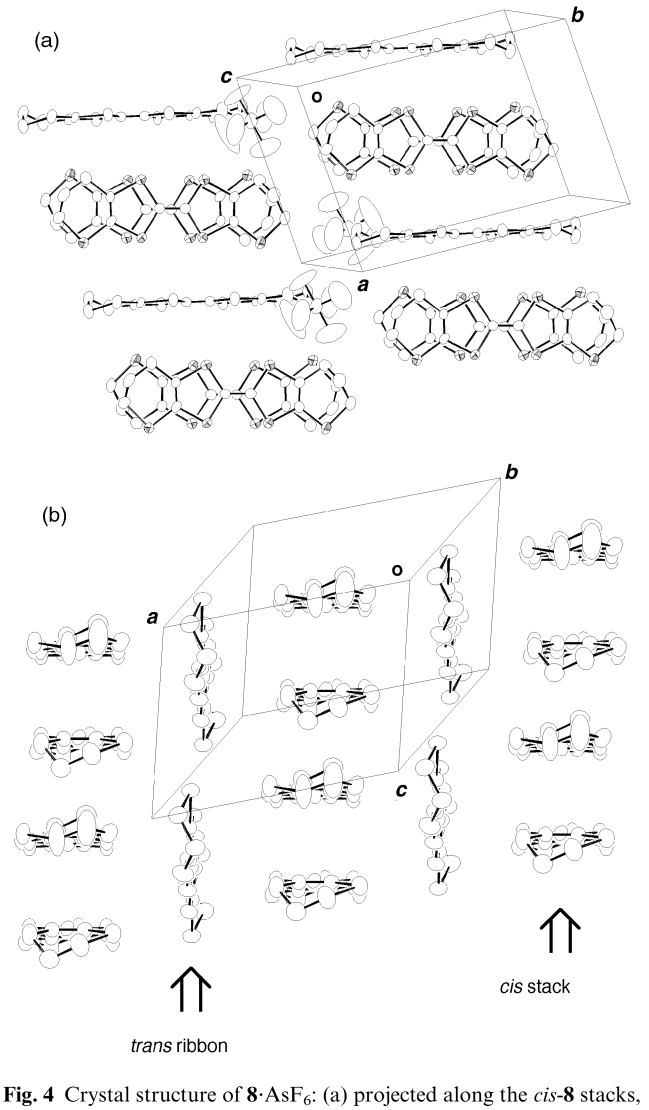


Fig. 4 Crystal structure of **8**·AsF_6: (a) projected along the *cis*-**8** stacks, (b) packing diagram of donor arrays viewed from the molecular long axis of *cis*-**8**.

All the radical cation salts of **8** have 3 : 2 stoichiometry and are moderately conductive (0.5–5.0 S cm^{-1}) at room temperature with semiconductive behavior as represented by **8**·PF_6 shown in Fig. 1. The crystal structures of **8**·PF_6 and **8**·AsF_6 are isostructural with the above **7**·SbF_6.[11] As a representative of this type, the structure of **8**·AsF_6 is shown in Fig. 4. It contains two crystallographically independent donor molecules, one of which takes the *cis* form and the other the *trans* form. The *cis* isomers make face-to-face stacked dimers, which are piled up to construct a columnar structure. In the dimer unit, there are short Se–Se contacts (3.60–3.64 Å), but the shortest Se–Se distance between the neighboring dimers is 4.12 Å, thus indicating alternate interplanar interactions along the column. The *trans* isomer, in contrast, orthogonally exists between the stacking columns of the *cis* isomer. The neighboring *trans* donors interact with each other in an edge-to-edge manner through short Se–Se contacts (3.80–3.89 Å), consequently forming a ribbon-like array. In addition there are many face-to-edge Se–Se interactions (3.70–3.90 Å) between the *cis* isomer and the *trans* isomer, forming a two-dimensional Se–Se contact network.[12] On comparison of the molecular structures, the central double bond of the *cis* isomer (1.38 Å) is longer than that of the *trans* isomer (1.31 Å), suggesting a higher oxidation state of the *cis* isomer than of the *trans* isomer. Taking account of this, the 3 : 2 stoichiometry is elucidated by possibly assigning a monocationic state for the *cis* isomer and a neutral state for the *trans* isomer. This means that the main conduction path occurs through a two-dimensional Se–Se contact network interaction between the *cis* isomer and the *trans* isomer. Such electric conduction over donors with different valence states must suffer a high barrier, being responsible for the semiconductive or weakly metallic behavior of this type of salts.[13]

Conclusion

Bis(propylenethio)- and bis(propyleneseleno)-substituted TTF and TSF (**5**–**8**) have been effectively synthesized from readily available common THP-protected pent-4-yn-1-ol. Electrochemical study showed that they all have moderate electron donating abilities. However, contrary to our initial expectation, no conductive radical cation salts were obtained from the TTF derivatives **5** and **6**. In contrast, the TSF derivatives **7** and **8** gave conductive radical cation salts that were versatile in composition ratio and conductive behavior. In particular, all the salts of **7** were metallic at room temperature but demonstrate different temperature dependence of the conductivities depending on their crystal structures and stoichiometry.

Experimental

General

Melting points are uncorrected. Nuclear magnetic resonance spectra were obtained in the indicated deuterated solvent with a JEOL Lambda 400 spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C with TMS as internal reference; chemical shifts (δ) are reported in parts per million. Mass spectral data were obtained on a Shimadzu QP-2000 spectrometer using an electron impact ionization procedure (70 eV). The molecular ion peaks of the selenium-containing compounds showed a typical selenium isotopic pattern, and all the selenium-containing mass peaks are reported for ^{80}Se. Infrared spectra were obtained on a Shimadzu FTIR-8100A spectrometer. Cyclic voltammetry was carried out on a Hokuto Denko HA-301 potentiostat equipped with a Hokuto Denko HB-104 function generator. 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. All reactions were carried out under a nitrogen atmosphere with dry solvents. Column chromatography was carried out with Daisogel IR-60 (63–210 μm). Preparative gel permeation chromatography (GPC) was performed on Japan Analytical Industry Co., Ltd. LC-908 equipped with a JAI-GEL 1H, 2H column assembly. Selenium powder (red)[14] and carbon diselenide[15] were synthesized according to the literature procedures. All the new compounds were fully characterized by the spectroscopic and elemental analyses, and most of the characterization data are available as Electronic Supplementary Information.†

4-Methylthio-5-[3-(tetrahydropyran-2-yloxy)propyl]-1,3-dithiole-2-thione (11 (X = S))

To a solution of 2-(pent-4-yn-1-yloxy)tetrahydro-2*H*-pyran **9** (2.52 g, 15 mmol) and TMEDA (4.5 mL, 30 mmol) in THF (120 mL) was added a solution of ^{n}BuLi in hexane (1.60 M, 10.5 mL) at −70 °C, and the solution was stirred at the same temperature for 30 min. After addition of sulfur (480 mg, 15 mmol), the mixture was warmed to 0 °C over a period of 1 h and stirred for 2 h at that temperature. The solution was again cooled to −90 °C, and then carbon disulfide (1.8 mL, 30 mmol) and methyl thiocyanate (3.1 mL, 37.5 mmol) were added. The resulting mixture was allowed to warm to 0 °C over a period of 1 h, then diluted with water (50 mL), and extracted with dichloromethane (30 mL × 3). The extract was washed with water and saturated NaCl aqueous solution, dried ($MgSO_4$), and concentrated. The residue was purified with column chromatography on silica gel eluted with dichloromethane to afford practically pure **11** (X = S) as a yellow oil (R_f 0.5, 3.32 g, 69%). An analytical sample was obtained by further purification by preparative GPC.

4-Methylseleno-5-[3-(tetrahydropyran-2-yloxy)propyl]-1,3-dithiole-2-thione (11 (X = Se))

11 (X = Se) was synthesized in the same manner as **11** (X = S) using a combined reagent of selenium powder and methyl iodide instead of methyl thiocyanate as the final quenching reagent. Yellow oil (83% yield).

4-(3-Hydroxypropyl)-5-methylthio-1,3-dithiole-2-thione (12 (X = S))

A mixture of **11** (X = S) (1.61 g, 5.0 mmol), hydrochloric acid (1 M, 3 mL), methanol (50 mL), and acetone (50 mL) was stirred at rt for 12 h. The mixture was diluted with water (100 mL) and then extracted with dichloromethane (30 mL). The extract was washed with brine, dried ($MgSO_4$), and then concentrated. The residue was purified by column chromatography (silica gel, eluent: dichloromethane–AcOEt, 9 : 1 v/v) to give **4** as a yellow oil (1.07 g, 90%). Further purification with preparative GPC gave an analytical sample.

4-(3-Hydroxypropyl)-5-methylseleno-1,3-dithiole-2-thione (12 (X = Se))

12 (X = Se) was synthesized from **11** (X = Se) in the same manner as **12** (X = S). Yellow oil (79% yield).

4-Methylthio-5-(3-tosyloxypropyl)-1,3-dithiole-2-thione (13 (X = S))

To a solution of **12** (X = S) (1.99 g, 7.0 mmol) in pyridine (17.5 mL) was added tosyl chloride (26.7 g, 14.0 mmol) at 0 °C. After being stirred for 6 h, the mixture was poured into ice-containing 1 M hydrochloric acid (50 mL). The mixture was extracted with dichloromethane (50 mL × 3), and the extract was washed successively with 1 M hydrochloric acid (100 mL × 2) and brine (100 mL) and dried ($MgSO_4$). The concentrated extract was purified by column chromatography on silica gel eluting with dichloromethane followed by recrystallization from hexane–chloroform and gave **13** (X = S) as yellow fine needles (2.53 g, 77%).

4-Methylseleno-5-(3-tosyloxypropyl)-1,3-dithiole-2-thione (13 (X = Se))

13 (X = Se) was synthesized from **12** (X = Se) in the same manner as **13** (X = S). Yellow oil (80% yield).

6,7-Dihydro-5*H*-thiino[2,3-*d*]-1,3-dithiole-2-thione (14 (X = S))

A mixture of **13** (X = S) (1.46 g, 3.72 mmol) and sodium iodide (1.12 g, 7.44 mmol) in DMF (16 mL) was heated at 120 °C for 3 h. The mixture was then diluted with water (16 mL) and extracted with carbon disulfide (50 mL × 3), and the extract was successively washed with water (50 mL) and brine (50 mL) and finally dried ($MgSO_4$). Column chromatography of the concentrated extract on silica gel eluted with carbon disulfide gave **14** (X = S) as yellow micro crystals (710 mg, 92%). An analytical sample was obtained by recrystallization from hexane–carbon disulfide as yellow needles.

6,7-Dihydro-5*H*-selenino[2,3-*d*]-1,3-dithiole-2-thione (14 (X = Se))

14 (X = Se) was synthesized from **13** (X = Se) in the same manner as **14** (X = S). Yellow needles from chloroform–hexane (98% yield).

6,7-Dihydro-5*H*-thiino[2,3-*d*]-1,3-dithiol-2-one (15 (X = S))

A mixture of **14** (X = S) (160 mg, 0.79 mmol) and mercury acetate (630 mg, 1.98 mmol) in chloroform (8 mL) was stirred for 8 h at room temperature. The resulting white solid was filtered off and washed with chloroform (10 mL × 3), and the combined filtrate was washed with saturated sodium bicarbonate solution (10 mL × 3) and dried ($MgSO_4$). The concentrated organic layer was subjected to column chromatography on silica gel eluted with dichloromethane to give practically pure **15** (X = S) (150 mg, 99%). Recrystallization from carbon disulfide–hexane gave analytically pure **15** (X = S) as colorless needles.

6,7-Dihydro-5*H*-selenino[2,3-*d*]-1,3-dithiol-2-one (15 (X = Se))

Colorless needles from carbon disulfide–hexane (87% yield).

Bis(propylenethio)tetrathiafulvalene (BPT-TTF, 6,6′,7,7′-tetrahydro-5*H*,5′*H*-$\Delta^{2,2'}$-bi(thiino[2,3-*d*]-1,3-dithiole), 5)

A solution of **15** (X = S) (700 mg, 3.69 mmol) in trimethyl phosphite (15 mL) was heated under reflux for 20 h. After concentration, the residue was purified by column chromatography on silica gel eluted with carbon disulfide followed by recrystallization from benzene–hexane to give **5** as red needles (340 mg, 53%): mp 204–206 °C; ^{1}H NMR ($CDCl_3$) δ 2.13–2.19 (m, 4H, CH_2), 2.37 (t, *J* = 6.3 Hz, 4H, CH_2), 2.97–3.00 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ 23.38, 24.96, 28.36, 108.65 and 108.73, 116.36 and 116.44, 118.04 and 118.12; MS *m*/*z* 348 (M^+). Anal. Calcd for $C_{12}H_{12}S_6$: C, 41.35; H, 3.47%. Found: C, 41.36; H, 3.43%.

Bis(propyleneseleno)tetrathiafulvalene (BPS-TTF, 6,6′,7,7′-tetrahydro-5*H*,5′*H*-$\Delta^{2,2'}$-bi(selenino[2,3-*d*]-1,3-dithiole), 6)

Red needles from benzene–hexane (34% yield): mp 190–191 °C; ^{1}H NMR ($CDCl_3$) δ 2.22–2.28 (m, 2H, CH_2), 2.37–2.40 (m, 2H, CH_2), 3.07–3.10 (m, 2H, CH_2); ^{13}C NMR δ 21.42, 24.12, 26.26, 105.49 and 105.56, 109.65 and 109.69, 119.84 and 119.91; MS *m*/*z* 444 (M^+). Anal. Calcd for $C_{12}H_{12}S_4Se_2$: C, 32.58; H, 2.73%. Found: C, 32.45; H, 2.69%.

4-Methylthio-5-[3-(tetrahydropyran-2-yloxy)propyl]-1,3-diselenole-2-selone (16 (X = S))

To a mixture of **9** (2.52 g, 15 mmol) and TMEDA (4.5 mL, 30 mmol) in THF (120 mL) cooled to −70 °C was added a hexane solution of ^{n}BuLi (1.61 M, 10.2 mL, 16.4 mmol), and the solution was stirred for 30 min to form the lithium acetylide species. Red selenium powder (987 mg, 12.5 mmol) was added in one portion, and the reaction mixture was warmed to 0 °C over a period of 1 h and stirred for an additional 1 h. The mixture was cooled again to −90 °C, and then carbon diselenide (0.8 mL, 12.5 mmol) and methyl thiocyanate (3.09 mL, 37.5 mmol) were added. The resulting mixture was allowed to warm to 0 °C over a period of 1 h and then diluted with water (50 mL), extracted with dichloromethane (30 mL × 3). The extract was washed with water (50 mL) and saturated NaCl aqueous solution (50 mL), dried ($MgSO_4$), and concentrated. The residue was purified with column chromatography on silica gel with dichloromethane to afford **16** (X = S) as a red oil (R_f 0.5, 4.89 g, 70%).

4-Methylseleno-5-[3-(tetrahydropyran-2-yloxy)propyl]-1,3-diselenole-2-selone (16 (X = Se))

16 (X = Se) was synthesized in the same manner as **16** (X = S) using a combined reagent of selenium powder and methyl iodide instead of methyl thiocyanate as the final quenching reagent. Red oil (76% yield).

4,4′(5′)-Bis(methylthio)-5,5′(4′)-bis[3-(tetrahydropyran-2-yloxy)propyl]tetraselenafulvalene (17 (X = S))

Trimethyl phosphite (2.6 mL, 16.6 mmol) was added to a solution of **16** (X = S) (2.57 g, 5.5 mmol) in benzene (30 mL), and the mixture was refluxed for 2 h. Evaporation of the solvent and the excess phosphite gave an oily residue, which was purified by column chromatography on silica gel with dichloromethane as an eluent to give **17** (X = S) as a red oil (R_f 0.4, 1.92 g, 90%).

4,4′(5′)-Bis(methylseleno)-5,5′(4′)-bis[3-(tetrahydropyran-2-yloxy)propyl]tetraselenafulvalene (17 (X = Se))

17 (X = Se) was synthesized from **16** (X = Se) in the same manner as **17** (X = S). Red oil (98% yield).

4,4′(5′)-Bis(3-hydroxypropyl)-5,5′(4′)-bis(methylthio)tetraselenafulvalene (18 (X = S))

A mixture of **17** (X = S) (2.14 g, 2.78 mmol), hydrochloric acid (1.0 M, 1.4 mL), methanol (42 mL), THF (35 mL) and water (50 mL) was stirred at rt for 12 h. The mixture was extracted with dichloromethane (20 mL × 3), and the extract was washed with brine and dried ($MgSO_4$). Evaporation of the solvent gave practically pure **18** (X = S) as a red oil (1.44 g, 86%), which was used for the next reaction without further purification. The analytically pure sample was obtained by further purification with preparative GPC.

4,4′(5′)-Bis(3-hydroxypropyl)-5,5′(4′)-bis(methylseleno)tetraselenafulvalene (18 (X = Se))

18 (X = Se) was synthesized from **17** (X = Se) in the same manner as **18** (X = S). Red powder (95% yield).

4,4′(5′)-Bis(methylthio)-5,5′(4′)-bis[3-(tosyloxy)propyl]tetraselenafulvalene (19 (X = S))

To a solution of **18** (X = S) (360 mg, 0.6 mmol) and triethylamine (0.24 mL, 1.8 mmol) in dichloromethane (6 mL) was added tosyl chloride (336 mg, 1.8 mmol) at 0 °C. The mixture was stirred for 12 h, then quenched by addition of water (3.0 mL) and extracted with dichloromethane (10 mL × 3). The extract was washed with saturated NaCl aqueous solution and dried ($MgSO_4$). Evaporation of the solvent gave **19** (X = S) as a red solid (323 mg, 59%). An analytically pure sample was obtained by the reprecipitation technique: the crude **19** (X = S) was dissolved in dichloromethane (5 mL), and the solution was filtered through filter paper, whereupon hexane (15 mL) was added to the solution to precipitate a microcrystalline solid of pure **19** (X = S).

4,4′(5′)-Bis(methylseleno)-5,5′(4′)-bis[3-(tosyloxy)propyl]tetraselenafulvalene (19 (X = Se))

19 (X = Se) was synthesized from **18** (X = Se) in the same manner as **19** (X = S). Red microcrystalline solid (64% yield).

Bis(propylenethio)tetraselenafulvalene (BPT-TSF, 6,6′,7,7′-tetrahydro-5*H*,5′*H*-$\Delta^{2,2'}$-bi(thiino[2,3-*d*]-1,3-selenole), 7)

A mixture of **19** (X = S) (1.23 g, 1.35 mmol) and sodium iodide (605 mg, 4.05 mmol) in DMF (13 mL) was stirred at 80 °C for 12 h. The reaction mixture was poured into water (50 mL), and the resulting precipitate was collected by filtration and dried *in vacuo*. Column chromatography on silica gel eluting with carbon disulfide gave **7** as a green powder. Recrystallization from hexane–carbon disulfide afforded analytically pure **7** as red plates (430 mg, 60%). mp 181–182 °C (melt with decomposition); ^{1}H NMR ($CDCl_3$) δ 2.14–2.20 (m, 4H, CH_2) 2.46 (t, *J* = 6.0 Hz, 4H, CH_2) 3.02–3.05 (m, 4H, CH_2); MS *m*/*z* 540 (M^+). Anal. Calcd for $C_{12}H_{12}S_2Se_4$: C, 26.88; H, 2.26%. Found: C, 26.82; H, 2.26%.

Bis(propyleneseleno)tetraselenafulvalene (BPS-TSF, 6,6′,7,7′-tetrahydro-5*H*,5′*H*-$\Delta^{2,2'}$-bi(selenino[2,3-*d*]-1,3-selenole), 8)

8 was synthesized from **19** (X = Se) in a similar manner as **7**: the reaction was complete within 1 h at 80 °C. Red plates from hexane–carbon disulfide (30% yield): mp 191–192 °C (melt with decomposition); ^{1}H NMR ($CDCl_3$) δ 2.22–2.28 (m, 4H, CH_2) 2.43–2.46 (m, 4H, CH_2) 3.09–3.12 (m, 4H, CH_2); MS *m*/*z* 636

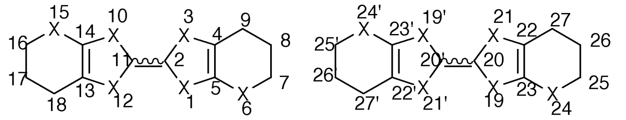


Fig. 5 Numbering scheme of **5**–**8** for structure analyses.

(M^+); Anal. Calcd for $C_{12}H_{12}Se_6$: C, 22.88; H, 1.92%. Found: C, 22.87; H, 1.94%.

Typical electrocrystallization procedure

Into a 20 mL H-shaped glass cell with a fine frit dividing the anolyte and catholyte compartments equipped with platinum wire electrodes were placed 15 mL of chlorobenzene or THF and 3 mL of ethanol containing the appropriate tetrabutylammonium salt ($^nBu_4N^+X^-$, $X^- = BF_4^-$, ClO_4^-, PF_6^-, AsF_6^- and SbF_6^-) or tetraethylammonium salt ($Et_4N^+X^-$, $X^- = FeCl_4^-$) (50–150 mg). The donor (*ca.* 5 mg) was added into the anode compartment. The solution was degassed by passing a dry nitrogen stream and electrolyzed under a constant current of 1–4 μA at 23 °C. Black crystals of radical cation salts gradually grew on the anode electrode within several days. The crystals were collected by filtration, washed with cold dichloromethane, and dried *in vacuo*. The obtained crystals were utilized for the conductivity measurements and X-ray crystallographic analyses. The ratios of donor to anion were determined by the results of crystallographic analyses, except for the following radical cation salts, of which ratios were determined on the basis of combustion microanalysis.

X-Ray crystallographic analyses

X-ray diffraction experiments were performed at room temperature on a Rigaku AFC6S diffractometer with graphite-monochromated Cu Kα radiation ($\lambda = 1.5418$ Å) or a Rigaku AFC7R diffractometer with Mo Kα radiation ($\lambda = 0.7107$ Å). The intensity data were measured using the ω–2θ scan technique. The structures were solved by direct methods or Patterson methods. Hydrogen atoms were located by calculation and not refined. All non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic temperature factors. All the radical cation salt crystals potentially contain the *cis* and *trans* isomers of donors or disordering at S(Se)6–C9, S(Se)15–C18 and S(Se)24–C27 in the outer six-membered rings (see numbering scheme, Fig. 5). The initial positions of the carbon and sulfur (selenium) atoms were determined as usual, and the occupancy of each atom was refined by full-matrix least-squares techniques with population analysis followed by additional cycles of least-squares calculation under the constraints of eqn. (1):

$$Oc_{(C)} = 3.667 - 2.667 \cdot Oc_{(S)}$$

$$Oc_{(C)} = 6.667 - 5.667 \cdot Oc_{(Se)}$$

where $Oc_{(X)}$ = occupancy of the given atom in parenthesis.

Table 3 Crystal data for radical cation salts of **7** and **8**

	$\mathbf{7}_2 \cdot AsF_6$	$\mathbf{7}_2 \cdot FeCl_4$	$\mathbf{8}_3 \cdot (AsF_6)_2$
Chemical formula	$C_{24}H_{24}S_4$-Se_8AsF_6	$C_{24}H_{24}$-$S_4Se_8FeCl_4$	$C_{36}H_{36}Se_{18}$-As_2F_{12}
Formula weight	1261.29	1270.03	2267.79
Crystal system	Triclinic	Orthorhombic	Triclinic
a/Å	7.891(6)	11.733(5)	10.793(4)
b/Å	16.406(5)	35.43(1)	15.769(5)
c/Å	6.629(3)	8.606(5)	8.312(3)
α/°	96.09(3)	—	93.85(3)
β/°	100.43(5)	—	109.43(2)
γ/°	87.10(5)	—	88.04(3)
V/Å^3	838.8(8)	3577(2)	1331.0(8)
T/K	296(1)	296(1)	296(1)
Space group	$P\bar{1}$ (no. 2)	$Pnma$ (no. 62)	$P\bar{1}$ (no. 2)
Z	1	4	1
μ/cm^{-1}	99.95 (Mo Kα)	91.17 (Mo Kα)	136.38 (Mo Kα)
Number of data ($I \geqslant 3.0\sigma(I)$)	2892	2463	3928
R^a, $R_w^{\ b}$	0.028, 0.024	0.064, 0.050	0.040, 0.041

$^a R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $^b R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{\frac{1}{2}}$.

Table 4 Refined probability for atoms in outer six-membered rings

Atom	$\mathbf{7}_2 \cdot AsF_6$	$\mathbf{7}_2 \cdot FeCl_4$	$\mathbf{8}_3 \cdot (AsF_6)_2$
S(Se)6/C9	0.82	0.63	0.89
S(Se)15/C18	0.63	0.81	0.87
S(Se)24/C24	—	—	0.94

Then the probability of atoms are calculated according to eqn. (2):

$$P_{(C)} = (16 - 6 \cdot Oc_{(C)})/10$$

$$P_{(S)} = (16 \cdot Oc_{(S)} - 6)/10$$

$$P_{(Se)} = (34 \cdot Oc_{(Se)} - 6)/10$$

where $P_{(X)}$ = probability of the given atom in parenthesis.

The results for each structural analysis are summarized in Tables 3 and 4.

CCDC 154224–154226. See http://www.rsc.org/suppdata/jm/b0/b009700o/ for crystallographic files in .cif format.

Acknowledgement

This work was partially supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan. We thank the Cryogenic Center, Hiroshima University for supplying cryogen (liquid helium).

References

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

2 For reviews on the synthesis of TTF derivatives, see: G. Schukat, A. M. Richter and E. Fanghänel, *Sulfur Rep.*, 1987, **7**, 155; G. Schukat and E. Fanghänel, *Sulfur Rep.*, 1993, **14**, 245; G. Schukat and E. Fanghänel, *Sulfur Rep.*, 1996, **18**, 1.

3 D. J. Lagouvardos and G. C. Papavassiliou, *Z. Naturforsch.*, 1992, **47b**, 898; T. Naito, H. Kobayashi and A. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 107; S. Golhen, L. Ouahab, A. Lebeuze, M. Bouayed, P. Delhaes, Y. Kashimura, R. Kato, L. Binet and J.-M. Fabre, *J. Mater. Chem.*, 1999, **9**, 387; J. Yamada, H. Nishikawa and K. Kikuchi, *J. Mater. Chem.*, 1999, **9**, 617.

4 A. Kobayashi, T. Udagawa, H. Tomita, T. Naito and H. Kobayashi, *Chem. Lett.*, 1993, 2179; H. Kobayashi, H. Tomita, T. Naito, A. Kobayashi, F. Sakai, T. Watanabe and P. Cassoux, *J. Am. Chem. Soc.*, 1996, **118**, 368; H. Kobayashi, T. Naito, A. Sato, K. Kawano, A. Kobayashi, H. Tanaka, T. Saito, M. Tokumoto and P. Cassoux, *Mol. Cryst. Liq. Cryst.*, 1996, **284**, 61; H. Tanaka, A. Kobayashi, A. Sato, H. Akutsu and H. Kobayashi, *J. Am. Chem. Soc.*, 1999, **121**, 760; E. Ojima, H. Fujiwara, K. Kato and H. Kobayashi, *J. Am. Chem. Soc.*, 1999, **121**, 5581; H. Kobayashi, A. Kobayashi and P. Cassoux, *Chem. Soc. Rev.*, 2000, **29**, 325.

5 E. M. Engler, V. V. Patel, J. R. Andersen, R. R. Schumaker and A. A. Fukushima, *J. Am. Chem. Soc.*, 1978, **100**, 3769; C. Rovira, J. Veciana, N. Santaló, J. Tarrés, J. Cirujeda, E. Molins, J. Llorca and E. Espinosa, *J. Org. Chem.*, 1994, **59**, 3307; J. Tarrés, N. Santaló, M. Mas, E. Molins, J. Veciana, C. Rovira, S. Yang, H. Lee and D. O. Cowan, *Chem. Mater.*, 1995, **7**, 1558; M. C. Rovira, J. J. Novoa, J. Tarrés, C. Rovira, J. Veciana, S. Yang, D. O. Cowan and E. Canadell, *Adv. Mater.*, 1995, **7**, 1023; C. Rovira, J. Veciana, J. Tarrés, E. Molins, M. Mas, D. O. Cowan and S. Yang, *Synth. Met.*, 1995, **70**, 883;

E. Coronado, L. R. Falvello, J. R. Galán-Mascarós, C. Giménez-Saiz, C. J. Gómez-García, V. N. Lauhkin, A. Pérez-Benítez, C. Rovira and J. Veciana, *Adv. Mater.*, 1997, **9**, 984; E. Ribera, C. Rovira, J. Veciana, V. N. Laukhin, E. Canadell, J. Vidal–Gancedo and E. Molins, *Synth. Met.*, 1997, **86**, 1993; C. Rovira, J. Tarrés, E. Ribera, J. Veciana, E. Canadell, E. Molins, M. Mas, V. Laukhin, M.-L. Doublet, D. O. Cowan and S. Yang, *Synth. Met.*, 1997, **86**, 2145; A. Pérez-Benítez, C. Rovira, J. Veciana, J. Vidal-Gancedo, V. N. Laukhin, L. V. Zorina, S. S. Khasanov, B. Z. Narymbetov and R. P. Shibaeva, *Synth. Met.*, 1999, **102**, 1707; E. Laukhina, E. Ribera, J. Vidal-Gancedo, S. Khasanov, L. Zorina, R. Shibaeva, E. Canadell, V. Laukhin, M. Honold, M.-S. Nam, J. Singleton, J. Veciana and C. Rovira, *Adv. Mater.*, 2000, **12**, 54.

6 T. Jigami, K. Takimiya, Y. Aso and T. Otsubo, *Chem. Lett.*, 1997, 1091; T. Jigami, K. Takimiya, T. Otsubo and Y. Aso, *J. Org. Chem.*, 1998, **63**, 8865; T. Jigami, K. Takimiya, Y. Aso and T. Otsubo, *Synth. Met.*, 1999, **102**, 1714.

7 K. Takimiya, A. Morikami and T. Otsubo, *Synlett*, 1997, 319.

8 L. Crombie and A. G. Jacklin, *J. Chem. Soc.*, 1957, 1622.

9 In **7**·AsF_6, the main isomer is *trans*, but orientational disordering of the outer six-membered rings was observed; the probability of sulfur atoms for the *trans* form are approximately 80% for one ring and 60% for the other. For the details, see Experimental section. The crystal data of **7**·PF_6 indicate that the salt is isostructural with **7**·AsF_6. Crystal data for $\mathbf{7}_2\cdot PF_6$: $C_{24}H_{24}S_4Se_8PF_6$, $M=1217.34$, triclinic, $a=7.9230(8)$, $b=16.264(3)$, $c=6.6524(8)$ Å, $\alpha=96.03(1)$, $\beta=100.489(9)$, $\gamma=87.51(1)°$, $V=838.0(2)$ Å^3, space group $P\bar{1}$ (no. 2), $Z=1$, $R=0.043$, $R_w=0.043$.

10 Crystal data for $\mathbf{7}_3\cdot(BF_4)_2$: $C_{36}H_{36}S_{12}Se_6B_2F_8$, $M=2063.58$, monoclinic, $a=31.628(2)$, $b=10.358(2)$, $c=15.369(2)$ Å, $\beta=92.549$ (9)°, $V=5030(1)$ Å^3, space group C_2/c (no. 15), $Z=4$.

11 The final refinements of $\mathbf{8}_3$ $(BF_4)_2$ and $\mathbf{8}_3\cdot(ClO_4)_2$ were not carried out since their cell parameters indicated that they are isostructural with $\mathbf{7}_3\cdot(SbF_6)_2$, $\mathbf{8}_3\cdot(PF_6)_2$and $\mathbf{8}_3\cdot(AsF_6)_2$. Crystal data for $\mathbf{7}_3\cdot(SbF_6)_2$: $C_{36}H_{36}S_6Se_{12}Sb_2F_{12}$, $M=2080.04$, triclinic, $a=10.730(6)$, $b=16.150(9)$, $c=8.162(4)$ Å, $\alpha=92.69(5)$, $\beta=109.82(4)$, $\gamma=88.65(6)°$, $V=1329(1)$ Å^3, space group $P\bar{1}$ (no. 2), $Z=1$, $R=0.078$, $R_w=0.054$. $\mathbf{8}_3\cdot(PF_6)_2$: $C_{36}H_{36}Se_{18}P_2F_{12}$, $M=2179.89$, triclinic, $a=10.80(2)$, $b=15.63(3)$, $c=8.33(1)$ Å, $\alpha=94.0(1)$, $\beta=109.4(1)$, $\gamma=88.2(2)°$, $V=1322(4)$ Å^3, space group $P\bar{1}$ (no. 2), $Z=1$. $\mathbf{8}_3\cdot(BF_4)_2$: $C_{36}H_{36}Se_{18}B_2F_8$, $M=2063.58$, triclinic, $a=10.72(1)$, $b=15.24(7)$, $c=8.27(1)$ Å, $\alpha=94.6(2)$, $\beta=108.88(9)$, $\gamma=87.4(2)°$, $V=1274(7)$ Å^3, space group $P\bar{1}$ (no. 2), $Z=1$. $\mathbf{8}_3\cdot(ClO_4)_2$: $C_{36}H_{36}Se_{18}Cl_2O_8$, $M=2088.87$, triclinic, $a=10.686$ (6), $b=15.274$ (7), $c=8.262$ (3) Å, $\alpha=94.29$ (3), $\beta=108.95$ (3), $\gamma=87.60$ (4)°, $V=1271$ (1) Å^3, $T=296(1)$ K, space group $P\bar{1}$ (no. 2), $Z=1$.

12 Similar packing arrangements have been reported: R. Kato, A. Kobayashi, Y. Sakaki and H. Kobayashi, *Chem. Lett.*, 1984, 993; M. A. Beno, U. Geiser, A. M. Kini, H. H. Wang, K. D. Caarlson, M. M. Miller, T. J. Allen, J. A. Schlueter, R. B. Proksch and J. M. Williams, *Synth. Met.*, 1988, **27**, A209.

13 Generally the bond lengths on the TTF core in TTF-based radical cation salts can be a good probe to evaluate the oxidation stage of the given TTF derivatives. In the present cases, unfortunately the standard deviation of the carbon–carbon bond lengths are relatively large due to the existence of many heavy selenium atoms, and it is very difficult to estimate the exact valences of **8** based on the bond lengths from the structural analysis..

14 J. P. Cornelissen, J. G. Haasnoot, J. Reedijk, C. Faulmann, J.-P. Legros, P. Cassoux and P. J. Nigrey, *Inorg. Chim. Acta*, 1992, **202**, 131.

15 W.-H. Pan and J. P. Fackler Jr., in *Inorganic Syntheses*, Vol. 21, ed. J. P. Fackler Jr., John Wiley & Sons, New York, 1982, pp. 6–11; F. Ogura and K. Takimiya, in *Organoselenium Chemistry; A Practical Approach*, ed. T. G. Back, Oxford University Press, New York, 1999, pp. 258–260.