Improved Synthesis of Double-Bridged Tetraselenafulvalenophanes and Formation of Their Conductive Radical Cation Salts

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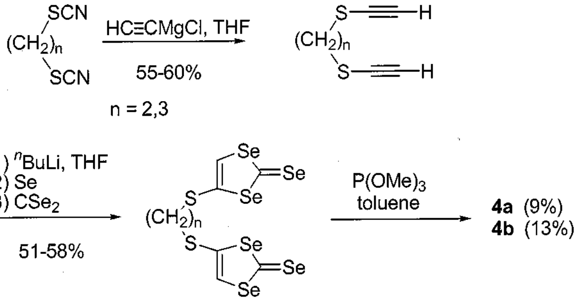
The double-bridged tetraselenafulvalenophanes (TSF-phanes, **4**) were efficiently synthesized by a new method using the deprotection/realkylation sequence of the TSF bisthiolate building block **7**. Electrocrystallization of **4b** with the Au(CN)$_2^-$ counter-anion gave a radical cation salt that showed a very high conductivity of 53 S cm^{-1} at room temperature. X-ray crystallographic analysis revealed that the crystal structure contained many intra- and intermolecular Se–Se contacts; favorable for high conductivity.

Introduction

Since the discovery of the first organic metal, tetrathiafulvalene (TTF) tetracyano-*p*-quinodimethane (TCNQ) complex,[1] much effort has been devoted to the structural modification of the TTF donor molecule. One of these potential modifications is to develop multi-redox systems containing two or more TTF units, which can undergo intra- and intermolecular electronic interactions between themselves, thereby allowing control over the crystal structures and/or electronic structures of their molecular complexes.[2] The most intriguing example is of the cyclophane type (the so-called TTF phane), in which two TTF units are stacked in a double-decker manner.[3] In such a dimeric structure, effective through-space interaction between the two TTF units can be expected. Thus, TTF phanes are a good model for studying the electronic structure of stacked TTFs in conductive TTF-based molecular salts.

Interested in investigating the most suitable type of TTF phane, we have studied various TTF phanes, including the quadruple-bridged ones with crisscross-oriented overlap, **1**,[3e,3h] and with parallel-oriented overlap, **2**,[3d] and the double-bridged **3**.[4] Results revealed that only the flexible double-bridged TTF phanes **3** can form highly conductive radical cation salts. As expected, the nonbonded interactions between the sulfur atoms of the TTF phanes play an important role in the conductivities of these salts. Since the nonbonded interaction of selenium is generally accepted to be much stronger than that of sulfur, we recently developed the selenium analogue of **3**, namely double-bridged tetraselenafulvalenophanes (TSF-phanes, **4**).[5]



Scheme 1. The first synthesis of TSF-phanes **4a** and **4b**

A preliminary complexation study revealed that **4a** can form a more conductive salt with ClO$_4^-$ than can **3a**. However, the detailed study of **4** has been hampered by a shortage of material, because the three-stage synthesis of **4**, involving as the last step the dimeric coupling of bis(1,3-diselenole-2-selones), promoted by trimethyl phosphite, was problematic (Scheme 1);[5] the coupling yield was very low and not reproducible when the scale of the reaction was increased. This has prompted us to explore an alternative synthesis of **4**, making large-scale preparation possible. We would now like to report an effective synthesis of compounds **4** − using a deprotection/realkylation sequence based on the newly developed TSF bisthiolate building block − as well as the initial study of their conductive radical cation salts.

Results and Discussion

Synthesis

This improved method for producing **4** is based on the coupling at the crucial cyclization step of two TSF bisthiolates **5** with two α,ω-dibromoalkanes. Becher and co-

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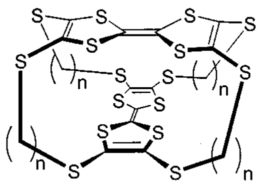
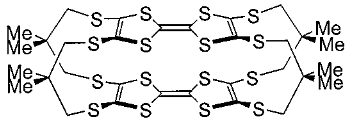


1 n = 2 ~ 5



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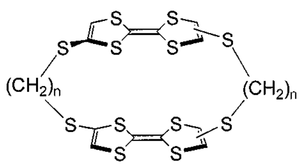
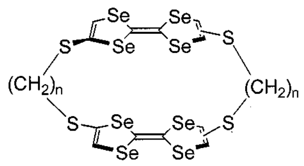
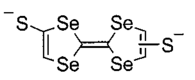


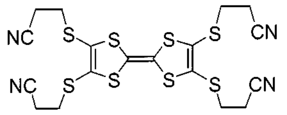
3a n = 2 (*cis / trans*)
3b n = 3 (*cis / trans*)



4a n = 2 (*cis / trans*)
4b n = 3 (*cis / trans*)



5 (*cis / trans*)



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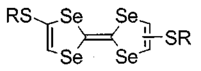
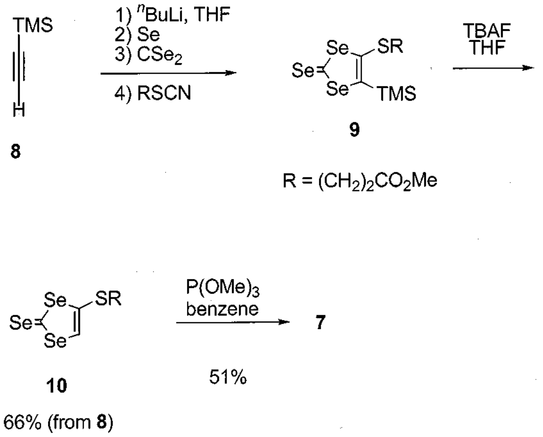


R = $(CH_2)_2CO_2Me$

7 (*cis / trans*)

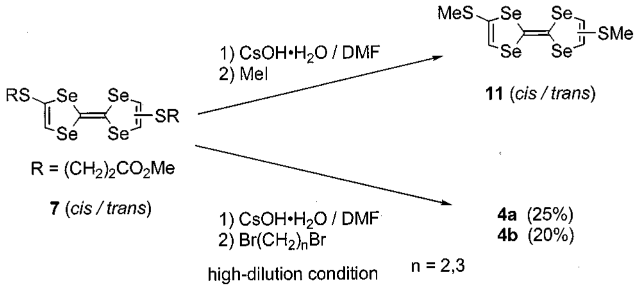
workers recently developed a synthetic methodology using a deprotection/realkylation sequence based on the protected TTF-tetrathiolate **6**, and this has been widely applied over the past several years to the synthesis of elaborate macrocycles incorporating TTF moieties.[6] Since this presents a great advantage for the in situ generation of unstable thiolate anions, we planned to use a similar technique for the generation of the TSF bisthiolate **5**. However, no protected TSF thiolate building block had then been reported. Thus, we first intended to develop 2,6(7)-bis(2-methoxycarbonylethylthio)tetraselenafulvalene (**7**) as a protected TSF bisthiolate.

The synthesis of **7** was readily achieved by utilizing a one-pot preparation of 1,3-diselenole-2-selones.[7,8] Thus, as shown in Scheme 2, the successive treatment of trimethylsilylacetylene (**8**) with *n*BuLi, selenium powder, carbon diselenide, and 3-thiocyanatopropionic acid methyl ester[9] gave a product mixture mainly consisting of 4-(2-methoxycarbonylethylthio)-5-trimethylsilyl-1,3-diselenole-2-selone (**9**). This mixture was directly desilylated using tetrabutylammonium fluoride (TBAF) in THF at −78 °C and then purified by column chromatography to afford the desired 1,3-diselenole-2-selone **10** as a dark red oil in 66% yield. The subsequent coupling reaction of **10**, promoted by trimethyl phosphite, gave the corresponding TSF derivative **7**, which exists as an equimolar mixture of the *cis* and *trans* forms, in 51% yield.



Scheme 2. Synthesis of TSF building block **7**

Prior to the TSF-phane synthesis, we examined a deprotection/realkylation of **7** as follows (Scheme 3). To a degassed DMF solution of **7** was added a methanol solution of a slight excess of cesium hydroxide monohydrate, and the resulting dark red solution was quenched by excess methyl iodide to give the desired bis(methylthio)-TSF (**11**) in 79% isolated yield. This result strongly supports the effectiveness of **7** as a protected TSF building block for in situ generation of the reactive TSF bisthiolate (**5**). In the TSF-phane synthesis, a DMF solution of the TSF bisthiolate (**5**), generated in situ, was treated with a solution of one equivalent of 1,2-dibromoethane in DMF under high dilution conditions, to give the desired TSF-phane (**4a**) in 25% yield. Additionally, when 1,3-dibromopropane was used as a reactant, the trimethylenedithio-bridged TSF-phane (**4b**) was also obtained, in 20% yield. The new approach, based on the deprotection/realkyation protocol of **7**, is apparently more advantageous than the original synthetic route to **4**



Scheme 3. Deprotection/realkylation of **7**

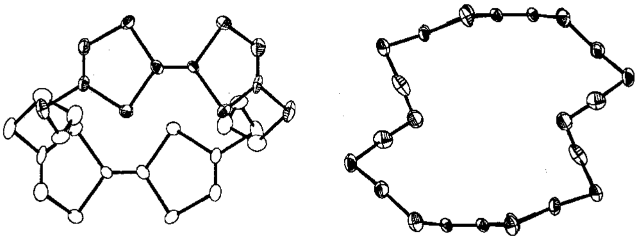
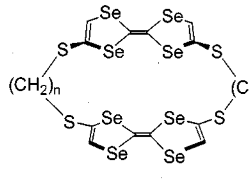


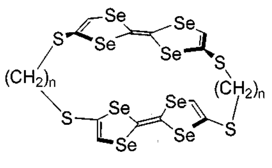
Figure 3. ORTEP drawings of **4b** (*cis-cis*): a top view (left) and a side view (right)

(Scheme 1), not only in terms of the total yield but also of its reproducibility.

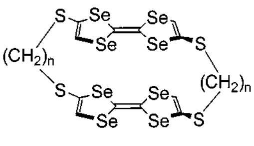
The obtained TSF-phanes **4** comprised three regioisomers; the result of the *cis* and *trans* substitution patterns of the alkylenedithio bridges on each TSF unit. When the mixture of **4a** was treated with a hot benzene/carbon disulfide solvent mixture, red columnar crystals and an insoluble orange powder were obtained. The red columnar crystals were fully characterized by ^{1}H NMR and X-ray analysis as the *cis-trans* isomer (Figure 1).



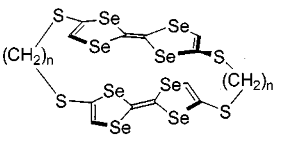
4 *cis-cis*



4 *cis-trans*



4 *trans-trans* (eclipse)



4 *trans-trans* (twist)

The insoluble orange powder was then similarly treated with hot chlorobenzene, to give pink, plate-like crystals and a further, extremely insoluble, orange powder. The pink, plate-like crystals were identified by X-ray analysis as the *trans-trans* (twist) isomer (Figure 2). The remaining insoluble powder was assigned as the *cis-cis* isomer by analogy with the case of TTF phane **3a**, in which the corresponding *cis-cis* isomer is the most insoluble.[4a] In the purification of the more soluble **4b**, recrystallization from carbon disulfide provided the *cis-cis* isomer exclusively, as characterized by X-ray analysis (Figure 3). There is no evidence of the existence of another possible isomer of the *trans-trans* (eclipse) type. These isomers are very stable in the crystalline states, but isomerize into one another relatively readily in solution. Consequently, during complexation in solution, rapid isomerization occurs, and the most stable isomer might be expected to predominate in the crystal structures of the molecular complexes. This is indeed the case: electrocrystallization of **4** gave radical cation salts containing only the *trans-trans* (eclipse) isomer (vide infra). This stereochemistry is reminiscent of that previously found for the double-bridged TTF phanes.

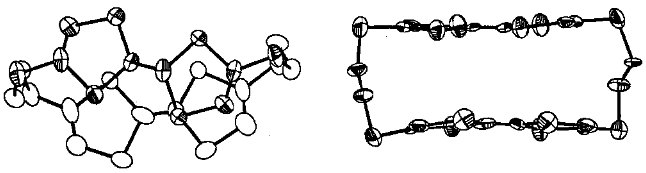


Figure 1. ORTEP drawings of **4a** (*cis-trans*): a top view (left) and a side view (right)

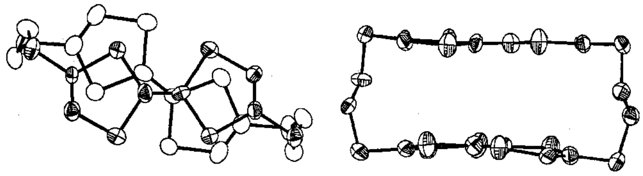


Figure 2. ORTEP drawings of **4a** (*trans-trans*): a top view (left) and a side view (right)

Radical Cation Salts

The facile synthesis of **4** enabled us to carry out an intensive study of their electrocrystallization. Table 1 summarizes the properties of the radical cation salts thus obtained. Their conductivities vary in the range of $10^{-3}-10^{0}$ S cm^{-1} at room temperature, with semiconductive temperature dependence. In addition, the composition ratios of the donor to the counter-anion are inconstant. Although the ethylenedithio-bridged TTF phane **3a** generally tends to give more highly conductive salts than does the trimethylenedithio-bridged **3b**,[4] the salts obtained from **4a** are not necessarily more conductive than those from **4b**. The Au(CN)$_2$ salt of **4a** is rather less conductive than either of the two salts of **4b** with the same Au(CN)$_2$ counter-ion.

The ClO$_4$ salt of **4a** (3.5 S cm^{-1}) is more conductive than the corresponding radical cation salt of the TTF phane **3a**

Table 1. Radical cation salts of TSF-phanes

Salt	Appearance	D:A(:solvent)[a]	σ_{rt} [S cm^{-1}][b]	E_{act} [eV]
4a•ClO$_4$	black needles	3:2	3.5	0.067
4a•BF$_4$	black plates	3:4[c]	0.04	0.114
4a•Au(CN)$_2$	black prisms	1:1:1[d]	2.8×10^{-3}	0.082
4b•AsF$_6$	black plates	2:3	1.3×10^{-3}	0.128
4b•Au(CN)$_2$	black plates	1:1[c]	0.2	0.057
4b•Au(CN)$_2$	black needles	1:1:1[c][e]	53	-

[a] Determined on the basis of elemental analysis unless otherwise stated. – [b] Measured on a single crystal with a four-probe method unless otherwise stated. – [c] Determined by X-ray crystallographic analysis. – [d] Chlorobenzene is included. – [e] 2-Propanol is included.

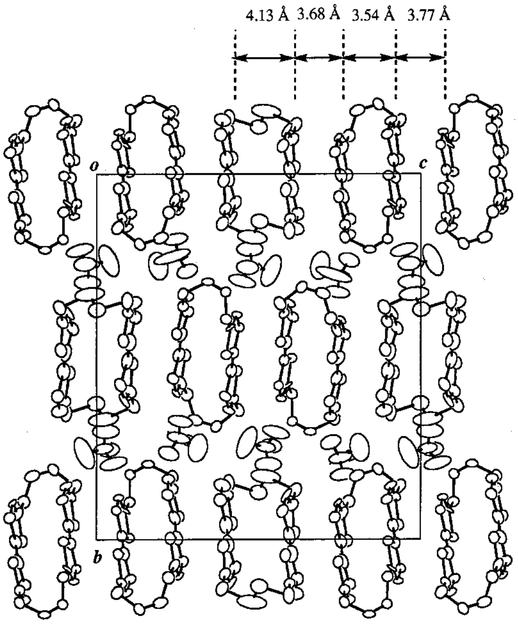


Figure 4. Crystal structure of **4a**·BF_4 viewed along *a*-axis

(0.16 S cm^{-1}),[4a] suggesting the effect of the selenium substitution. However, the BF_4^- salt of **4a** (0.04 S cm^{-1}) is less conductive than that of **3a** (1.5 S cm^{-1}). Figure 4 shows the crystal packing structure of the BF_4^- salt of **4a**, which contains two types of donor molecule, in a composition ratio of 2:1 in a stacking column. Both the molecules adopt the *trans-trans* (eclipse) form, which is not detected in the neutral state. The major component is monocationic and exhibits an interactive through-space distance of 3.54 A between the two TSF units. On the other hand, the minor component is dicationic and, because of the Coulombic repulsion, the corresponding distance is increased to 4.13 A, causing the two TSF units to be too far apart to interact. Presumably the conduction path along the column direction is interrupted at this site, resulting in the relatively low conductivity for this salt.

Electrocrystallization of **4b** in the presence of TBA·$Au(CN)_2$ (TBA = tetrabutylammonium) as a supporting electrolyte gave two morphoroic crystals, of plate and needle forms. Both revealed a 1: 1 (D:A) composition ratio, but the needle crystal included 2-propanol from the solvent. The plate form was semiconductive (0.2 S cm^{-1}), with a relatively small activation energy, whereas the needle form exhibited a very high conductivity of 53 S cm^{-1}. This value is much larger than that of any of the radical cation salts based on double-bridged TTF phanes **3**. As can be seen in Figure 5, the conductivity is almost constant down to 150 K, strikingly different from the semiconductive temperature dependence of the other salts.

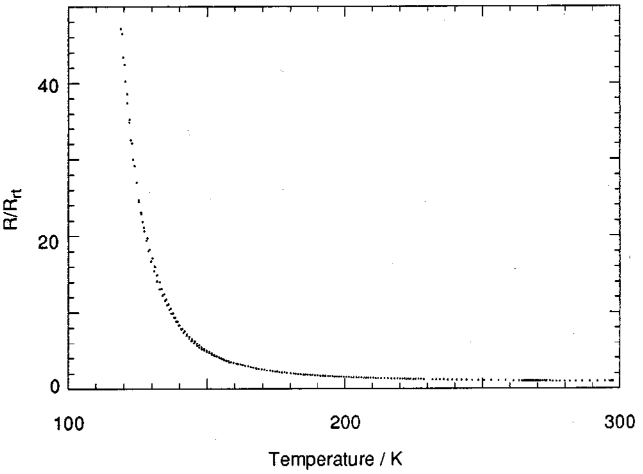


Figure 5. Temperature dependence of resistivity of **4b**·$Au(CN)_2$·(2-PrOH) (needle)

Figure 6 shows the crystal structure of the needle salt. The donor **4b** again takes the *trans-trans* (eclipse) form to give rise to a stacking column with other donors, with slight

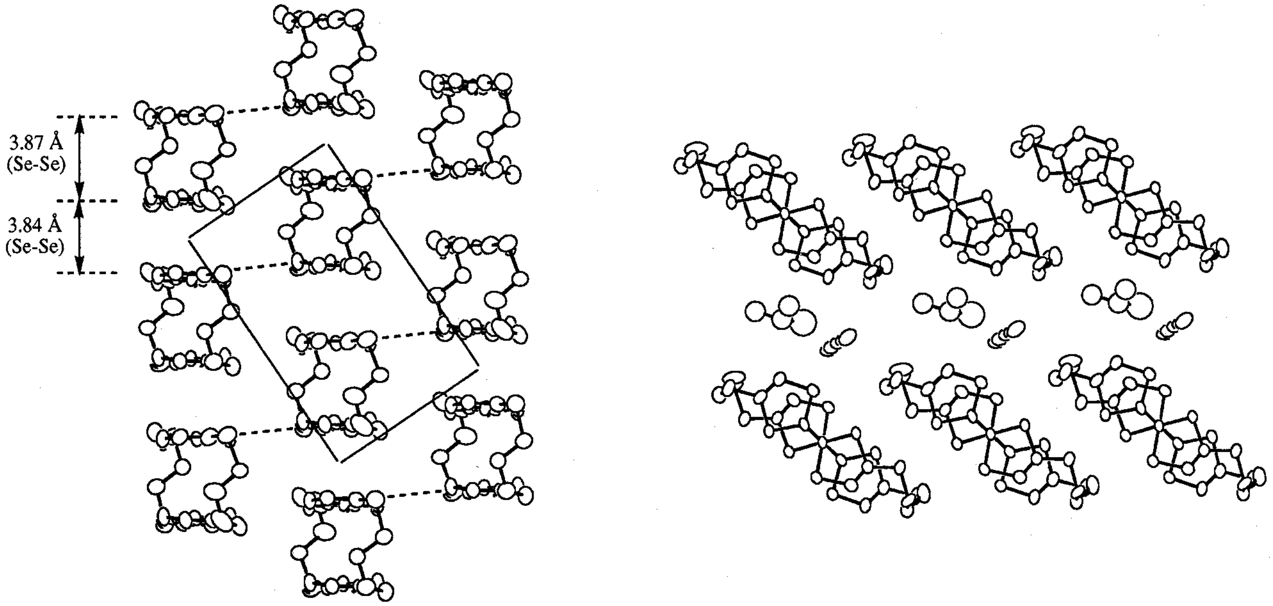


Figure 6. Crystal structure of **4b**·$Au(CN)_2$·(2-PrOH): a side view of the stacking columns; short Se−Se contacts (dashed lines) are 3.68 Å (left) and a projection along the stacking column (right)

sliding along the long axis direction of the molecule. Judging from the 1:1 (D:A) ratio, the formal oxidation state of **4b** is monocationic, meaning that each TSF formally carries half a positive charge, suitable for charge migration. The shortest intramolecular and intermolecular Se−Se contacts along the columnar direction are 3.87 Å and 3.84 Å, respectively, comparable to double the van der Waals radius (3.8 Å) of the selenium atom. In addition, there are close side-by-side Se−Se contacts (3.68 Å) between the neighboring donor columns, forming a sheet-like interaction. This sheet-like interaction array must contribute to the high conductivity of this salt.

Conclusion

We have demonstrated an improved synthesis of double-bridged TSF-phanes **4**, where the deprotection/realkylation protocol based on the protected TSF bisthiolate **7** is used at the crucial cyclization step. The use of **7**, analogously to that of the protected TTF-tetrathiolate **6**, would open ready access to a variety of macrocyclic systems incorporating TSF. Electrocrystallization of **4** gave several conductive radical cation salts. In particular, the **4b**·Au(CN)$_2$ salt showed a very high conductivity of 53 S cm^{-1} at room temperature; this can be explained not only by the half-oxidized state of the TSF moieties but also by the crystal structure of a sheet-like donor array possessing many intra- and intermolecular Se−Se contacts.

Experimental Section

General Remarks: All chemicals and solvents were of reagent grade and used without further purification unless otherwise noted. Tetrahydrofuran was distilled from benzophenone−sodium ketyl. Methanol was distilled from magnesium. Benzene and chlorobenzene was distilled from calcium hydride. DMF was dried by standing over 4-Å molecular sieves for at least 24 h. Melting points are uncorrected. − Microanalyses were carried out by Mr. Hideaki Iwatani, Microanalytical Laboratory of the Department of Applied Chemistry, Faculty of Engineering, Hiroshima University. − ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL Lambda 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz) using tetramethylsilane as an internal standard. − EI-MS spectra were measured at 70 eV on a Shimadzu GCMS-QP 2000 spectrometer using a direct insertion technique, and FAB-MS spectra were recorded on a JEOL JMS-SX 102A spectrometer using 3-nitrobenzyl alcohol as a matrix. − The electrical conductivities were measured by the conventional four-probe method, using gold paste as the electrical contacts. Carbon diselenide[10] was synthesized according to the literature procedures.

4-(2-Methoxycarbonylethylthio)-1,3-diselenole-2-selone (10): To a solution of trimethylsilylacetylene (196 mg, 2.0 mmol) in dry THF (10 mL) at −78 °C was added a hexane solution of *n*BuLi (1.6 M, 1.25 mL, 2.0 mmol), and the resulting solution was stirred for 30 min at the same temperature. To the resulting lithium acetylide solution, selenium powder (158 mg, 2.0 mmol) was added in one portion. The reaction mixture was allowed to warm to ice-bath temperature over a period of 2 h and stirred for further 3 h at room temperature. The clear selenolate solution was cooled to −90 °C, and methyl 3-thiocyanatopropionate (730 mg, 5.0 mmol) and carbon diselenide (0.14 mL, 2.2 mmol) were added. The resulting mixture was kept at −70 °C for 1 h. Then, aqueous THF (1:1, v/v) (20 mL) was added, and the mixture was allowed to warm to room temperature. The mixture was extracted with CH$_2$Cl$_2$ (3× 15 mL), and the extract was dried over MgSO$_4$. Evaporation of the solvent gave a mixture of 4-(2-methoxycarbonylethylthio)-5-trimethylsilyl-1,3-diselenole-2-selone (**9**) and 4-trimethylsilyl-1,3-diselenole-2-selone as a red, viscous oil, which was then treated with tetrabutylammonium fluoride solution (1.0 M in THF, 2.0 mL, 2.0 mmol) at −78 °C for 2 h, giving the desilylated **10** as the major product. Compound **10** was purified by column chromatography on silica gel eluted first with hexane/CH$_2$Cl$_2$ (1:1 v/v) and then with neat CH$_2$Cl$_2$. A red oil obtained (520 mg, 66%) was analytically pure and solidified upon cooling at −20 °C in a freezer. − ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 2.72 (t, ^3J = 7.1 Hz, 2 H, CH$_2$), 3.11 (t, ^3J = 7.1 Hz, 2 H, CH$_2$), 3.73 (s, 3 H, CH$_3$), 7.95 (s, 1 H, CH). − ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 31.6 (CH$_2$), 34.2 (CH$_2$), 52.0 (CH$_3$), 142.1 (C=C), 144.4 (C=C), 171.3 (C=O), 208.8 (C=Se). − MS (70 eV, EI); *m/z* (%): 394 (100) [M$^+$] with an isotropic pattern indicating three selenium atoms. − C$_7$H$_8$O$_2$SSe$_3$ (393.08): calcd. C 21.39, H 2.05; found C 21.36, H 1.90.

2,6(7)-Bis(2-methoxycarbonylethylthio)tetraselenafulvalene (7): A mixture of **10** (3.3 g, 8.4 mmol) and freshly distilled trimethyl phosphite (20 mL) in benzene (70 mL) was refluxed for 0.5 h under nitrogen. The reaction mixture was allowed to cool to room temperature and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel eluted with CH$_2$Cl$_2$ to afford **7** (R_f = 0.4, 1.35 g, 51%) as a red, viscous oil, which solidified in a freezer at −20 °C. − ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 2.685 and 2.688 (t, ^3J = 7.2 Hz, 4 H, CH$_2$), 3.001 and 3.004 (t, ^3J = 7.3 Hz, 4 H, CH$_2$), 3.707 (s, 6 H, CH$_3$), 7.271 and 7.274 (s, 2 H, fulvalenyl H) . − ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 31.5 (CH$_2$), 34.2 (CH$_2$), 51.9 (CH$_3$), 108.85 and 108.94 (central C=C), 127.4 and 127.6 (C=C), 129.1 and 129.3 (C=C), 171.6 (C=O). − MS (70 eV, EI); *m/z* (%): 630 (100) [M$^+$] with an isotropic pattern indicating four selenium atoms. − C$_{14}$H$_{16}$O$_4$S$_2$Se$_4$ (628.24): calcd. C 26.77, H 2.57; found C 26.74, H 2.43.

Deprotection of 7 and Realkylation of the Resulting TSF-Bisthiolate. − 2,6(7)-Bis(methylthio)tetraselenafulvalene (11): To a DMF solution (10 mL) of **7** (240 mg, 0.38 mmol) was added CsOH·H$_2$O (140 mg, 0.83 mmol) in methanol (5 mL) over 5 min, with stirring at room temperature. After the mixture had been stirred for a further 1 h, excess methyl iodide (ca. 1 mL) was added, and the mixture was again stirred for 1 h. The reaction mixture was concentrated under reduced pressure, and the residue was dissolved in CH$_2$Cl$_2$ (20 mL), washed with water (2 × 10 mL), and dried over MgSO$_4$. The concentrated organic phase was subjected to silica gel column chromatography. The desired product was eluted as a red oil (145 mg, 79%, R_f = 0.9) with CH$_2$Cl$_2$ as eluent. − ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 2.413 and 2.417 (s, 6 H, CH$_3$), 7.082 and 7.087 (s, 2 H, fulvalenyl H). − ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 20.4 (CH$_3$), 109.05 and 109.11 (central C=C), 121.9 and 122.0 (C=C), 129.1 (C=C), 132.06 and 132.12 (C=C). − MS (70 eV, EI); *m/z* (%): 486 (100) [M$^+$] with an isotropic pattern indicating four selenium atoms. − C$_8$H$_8$S$_2$Se$_4$ (484.11): calcd. C 19.85, H 1.67; found C 19.82, H 1.61.

Bis(ethylenedithio)-Bridged TSF-Phane (4a): To a solution of **7** (497 mg, 0.79 mmol) in DMF (20 mL) was added dropwise a solution of CsOH·H$_2$O (280 mg, 1.66 mmol) in methanol (10 mL) over

Table 2. Crystal data

	4a (*cis-trans*)	**4a** (*trans-trans*)	**4b** (*cis- cis*)	**4a**·BF_4	**4b**·$Au(CN)_2$·(2-PrOH)
Molecular formula	$C_{16}H_{12}S_4Se_8$	$C_{16}H_{12}S_4Se_8$	$C_{18}H_{16}S_4Se_8$	$C_{48}H_{36}S_{12}Se_{24}B_4F_{16}$	$C_{23}H_{24}S_4N_2Se_8AuO$
Formula weight	964.19	964.19	992.24	3239.79	1301.34
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/a$	$P2_1/a$	$P2_1/n$	$P1$
Color of crystals	reddish purple	pink	orange	black	black
a [Å]	8.304 (3)	17.283 (5)	10.378 (2)	7.992 (9)	12.910 (4)
b [Å]	22.611 (3)	8.071 (6)	13.198 (2)	23.86 (1)	13.859 (9)
c [A]	13.678 (2)	18.368 (4)	10.683 (2)	21.40 (1)	10.006 (6)
α [°]					102.88 (4)
β [°]	103.71 (2)	105.06 (2)	113.78 (1)	99.06 (8)	103.22 (4)
γ [°]					102.75 (4)
V [A]^3	2494.9 (8)	2476 (2)	1339.1 (4)	4031 (5)	1627 (1)
Z	4	4	2	2	2
R	0.060	0.047	0.059	0.078	0.059

5 min, with stirring at room temperature. The solution was stirred for a further 45 min. Then, this solution and a solution of 1,2-dibromoethane (148 mg, 0.79 mmol) in DMF (30 mL) were added simultaneously through dropping funnels to DMF (50 mL), over 3 h at room temperature. After completion of addition, the mixture was stirred overnight, and then concentrated in vacuo. The resulting residue was extracted with carbon disulfide (70 mL), and the extract was washed with water (2 × 30 mL) and dried over $MgSO_4$. Evaporation of the solvent and subsequent column chromatography (silica gel, carbon disulfide as eluent) gave **4a** (R_f = 0.2, 93 mg, 24%) as a reddish purple solid. − ^1H NMR (400 MHz, CS_2/[D_6]acetone, 25 °C, TMS): $\delta = 2.94-3.09$ (m, CH_2), 7.29, 7.30, 7.35, 7.37, 7.38 (each s, fulvalenyl H). − MS (positive ion FAB); *m/z*: 965 [M^+] with an isotropic pattern indicating eight selenium atoms. − $C_{16}H_{12}S_4Se_8$ (964.19): calcd. C 19.93, H 1.25; found C 19.96, H 1.19.

Recrystallization from benzene/CS_2 afforded red columnar crystals of the *cis-trans* isomer, which was characterized by X-ray crystallographic analysis. M.p. 184 °C (decomp.). − ^1H NMR (400 MHz, CS_2−[D_6]acetone, 25 °C, TMS): $\delta = 2.94-2.98$ (AA′BB′ m, 4 H, CH_2), 3.05−3.09 (AA′BB′ m, 4 H, CH_2), 7.30 (s, 2 H, fulvalenyl H), 7.38 (s, 2 H, fulvalenyl H). The powder insoluble in the hot benzene−CS_2 mixture was then recrystallized from chlorobenzene to give pink plates, which were identified as the *trans-trans* isomer by X-ray crystallographic analysis. M.p. 194 °C (decomp). − ^1H NMR (400 MHz, CS_2 /[D_6]acetone, 25 °C, TMS): $\delta = 2.94$ (s, 8 H, CH_2), 7.35 (s, 4 H, fulvalenyl H).

Bis(trimethylenedithio)-Bridged TSF-Phane (4b): Compound **4b** was synthesized in the same manner as described above, using 1,3-dibromopropane instead of 1,2-dibromoethane as the alkylation reagent. Yield 20%. M.p. 159 °C (decomp.). − ^1H NMR (400 MHz, CS_2−[D_6]acetone, 25 °C, TMS) of the isomeric mixture: δ = 2.03−2.15 (m, CH_2), 2.76−2.88 (m, CH_2), 7.285. 7.287, 7.31, 7.32, 7.37 (each s, fulvalenyl H). − MS (positive ion FAB); *m/z*: 993 [M^+] with an isotropic pattern indicating eight selenium atoms. − $C_{18}H_{16}S_4Se_8$ (992.24): calcd. C 21.79, H 1.63; found C 21.81, H 1.53. Recrystallization from CS_2 gave orange prisms of the *cis-cis* isomer, which was characterized by X-ray crystallographic analysis. M.p. 198 °C (decomp). − ^1H NMR (400 MHz, CS_2/[D_6]acetone, 25 °C, TMS): $\delta = 2.05$ (quint, $^3J = 7.6$ Hz, 4 H, CH_2), 2.83 (t, $^3J = 7.6$ Hz, 8H; CH_2), 7.31 (s, 4 H, fulvalenyl H).

Typical Electrocrystallization Procedure: Into a 20 mL, H-shaped glass cell, with a fine frit dividing the anolyte and catholyte compartments and equipped with platinum wire electrodes, were placed 15 mL of chlorobenzene and 3 mL of 2-propanol containing the appropriate tetrabutylammonium salt (50−150 mg). The donor (2−3 mg) was added into the anode compartment. The solution was degassed by passing a dry nitrogen stream through it, and electrolyzed under a constant current of 1−4 µA at 80 °C. Black crystals of radical cation salts gradually grew on the anode electrode over several days. The crystals were collected by filtration, washed with cold dichloromethane, and dried in vacuo. The ratios of donor to anion of following radical cation salts were determined by microanalysis.

Compound $(4a)_3$·$(ClO_4)_2$: $C_{48}H_{36}Cl_2O_8S_{12}Se_{24}$ (3091.48): calcd. C 18.65, H 1.17; found C 18.82, H 1.55.

Compound 4a·$Au(CN)_2$·(PhCl): $C_{24}H_{17}AuClN_2S_4Se_8$ (1325.76): calcd. C 21.74, H 1.29, N 2.11; found C 21.43, H 1.28, N 2.16.

Compound $(4b)_2$·$(AsF_6)_3$: $C_{36}H_{32}As_3F_{18}S_8Se_{16}$ (2551.23): calcd. C 16.95, H 1.26; found C 17.15, H 1.36.

X-ray Crystallographic Study:[11] A Rigaku AFC-6S diffractometer with graphite-monochromated Cu-K_α radiation ($\lambda = 1.5418$ A) or a Rigaku AFC-7R diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.7107$ A) was used and data were collected at 295 K for all the crystals. Periodic remeasurement of three standard reflections revealed no significant crystal decay. Intensities were measured by continuous $\omega-2\theta$ scans. All intensities were corrected for Lorenz polarization effects. The structures were solved by the direct method or Patterson method followed by subsequent Fourier-difference calculation and refined by full-matrix, least-square techniques with anisotropic temperature factors for the nonhydrogen atoms. Structure solution and refinement were carried out using the TEXSAN program package[11] for all the crystals.

A summary of crystal data and structural refinement results is given in Table 2. The crystallographic data for **4a** (*cis-trans)* and **4b** (*cis-cis*) were deposited as a part of a previous communication.[5] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100683 for **4a** (*cis-trans)* and **4b** (*cis-cis*) and no. CCDC-138172−CCDC-138174 for **4a** (*trans-trans)*, **4a**·BF_4 , and **4b**·$Au(CN)_2$·(2-PrOH). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@chemcrys.cam.ac.uk].

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