Novel tellurium containing fulvalene-type electron donors, triselenatellurafulvalene (TSTeF) and diselenaditellurafulvalene (DSDTeF); synthesis, conductivities and crystal structures of their TCNQ complexes†

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Novel tellurium containing fulvalene-type electron donors, triselenatellurafulvalene (TSTeF) and diselenaditellurafulvalene (DSDTeF) are synthesized by an efficient two- or three-stage procedure. They behave as superior electron donors to give highly conductive charge-transfer (CT) complexes with TCNQ. TSTeF–TCNQ shows a high conductivity of 2000 S cm^{-1} at room temperature and is metallic down to 85 K, where a metal–insulator (MI) transition takes place. In contrast, the conductivity of DSDTeF–TCNQ is 1400 S cm^{-1} at room temperature and monotonously increases down to 4.2 K without any MI transition. An X-ray structural analysis shows that TSTeF–TCNQ is crystallographically isostructural with TTF–TCNQ comprising typical one-dimensional donor and acceptor columns. On the other hand, the crystal structure of DSDTeF–TCNQ is characterized by quasi one-dimensional donor stacks with side-by-side intercolumnar interactions through Te–Se contacts, which stabilize the metallic state at low temperature.

Introduction

Since the discovery of the first organic metal, tetrathia-fulvalene–tetracyanoquinodimethane (TTF–TCNQ),[1] metallic molecular conductors have attracted considerable interest. In order to develop novel molecular conductors, structural modifications of the TTF framework have been extensively carried out.[2,3] One of the successful modifications is to replace the skeletal sulfur atoms by selenium or tellurium atoms with larger polalizability.[4] The TCNQ complexes of tetraselena-fulvalene (TSF)[5] and tetratellurafulvalene (TTeF)[6] showed much higher room temperature conductivities of 800 and 2200 S cm^{-1}, respectively, than TTF–TCNQ (500 S cm^{-1}). Besides the extraordinarily high conductivity, it should be noted that the TTeF–TCNQ complex remains metallic down to 2 K, in contrast to TTF–TCNQ and TSF–TCNQ which demonstrate a MI transition (Peierls transition) at 59 K and 40 K, respectively.[1,5] This drastic change of conductive behavior observed for TTeF–TCNQ can be rationalized by the existence of stronger intermolecular interactions through the tellurium atoms, which induce a different crystal structure in TTeF–TCNQ from those of TTF–TCNQ and TSF–TCNQ.[6d]

A question may be then posed: how many tellurium atoms in the fulvalene skeleton are essential for suppressing the MI transition of the TCNQ complexes? In this context, hybrid tetrachalcogenofulvalenes containing fewer tellurium atoms than TTeF would provide useful information on the contribution of tellurium atoms in the design of organic metals. In this paper, we describe the simple two- or three-stage synthesis of triselenatellurafulvalene (TSTeF) and diselenaditellurafulvalene (DSDTeF)[7] together with the high conductivities and crystal structures of their TCNQ complexes.


X = S   TTF
X = Se TSF
X = Te TTeF

DSDTF

X = Se, Y = Te   TSTeF
X = Y = Te   DSDTeF
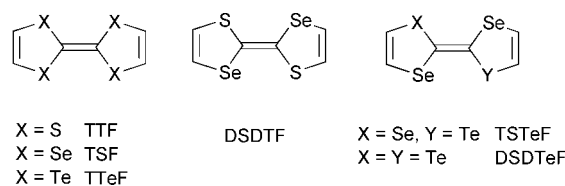
Results and discussion

### Synthesis and characterization of DSDTeF and TSTeF

We have recently established a facile procedure for the synthesis of 1,3-dithiole-2-thione and 1,3-diselenole-2-selone derivatives from readily available mono-substituted acety-lenes.[8] For the synthesis of a key intermediate of the present tellurium systems, 1,3-selenatellurole-2-selone **1**, we have examined this procedure using commercially available tri-methylsilylacetylene as the starting material. As shown in Scheme 1, trimethylsilylacetylene was metallated with *n*-butyl-lithium and subsequently reacted with tellurium powder and carbon diselenide to give **1** in 83% isolated yield. A conventional coupling reaction of **1** promoted by triethyl phosphite gave DSDTeF in 23% yield. The ^{1}H NMR spectrum of DSDTeF contains two sets of doublets in a ratio of 2:3, indicating the coexistence of *cis* and *trans* isomers.

The synthesis of TSTeF was not so straightforward and required a modification of the cross-coupling using the corresponding half precursors (Scheme 2). A simple coupling
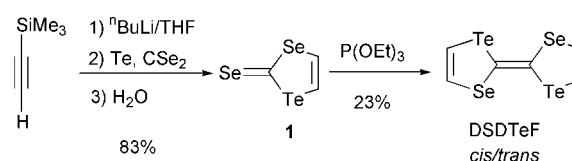
Scheme 1 Synthesis of DSDTeF.
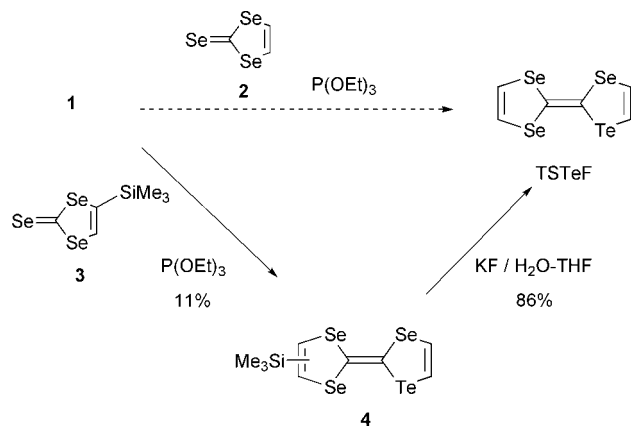
Scheme 2 Synthesis of TSTeF.

reaction of **1** and 1,3-diselenole-2-selone (**2**) under similar conditions gave a mixture of three expected products: one cross-coupling product, TSTeF, and two homo-coupling products, DSDTeF and TSF. Isolation of TSTeF from the mixture, however, could not be achieved by means of any conventional technique. Alternatively, the counterpart (**2**) of the cross-coupling was replaced with the trimethylsilyl (TMS) derivative of 1,3-diselenole-2-selone (**3**). In this case, all the expected products were easily separated by gel permeation chromatography with size-excluding type columns, thanks to the bulkiness of the TMS substituent, affording the desired triselenatellurafulvalene with a TMS group (**4**) in 11% isolated yield. The TMS group was then readily removed by the action of potassium fluoride in aqueous THF, giving TSTeF in 86% yield.

Redox properties and charge-transfer complexes with TCNQ

The electrochemical properties of the new tellurium-based donors were studied by cyclic voltammetry. As seen for many TTF-type electron donors, the present tellurium donors show two reversible one-electron redox couples, which correspond to the successive formation of the radical cation and the dication. Table 1 summarizes their first and second redox potentials together with those of the all-selenium analogue, TSF. The first potentials are lowered by the increasing number of tellurium atoms in the order of TSF, TSTeF and DSDTeF, as expected from the lower oxidation potential of TTeF compared to that of TSF.[6a]

Preparation of CT-complexes was carried out by slow cooling of a hot acetonitrile solution containing the donor and TCNQ. As shown in Table 1, their conductivities are of the highest class for organic conductors, similarly to the TTeF–TCNQ ($\sigma_{rt} = 2200$ S cm^{-1}).[6d,e] However, the temperature dependence of conductivities of TSTeF–TCNQ and DSDTeF–TCNQ are quite different: the former showed a MI transition at around 85 K as seen in TTF–TCNQ[1] and TSF–TCNQ,[5a] whereas the latter remains metallic down to liquid helium temperature without any significant transition (Fig. 1), being reminiscent of TTeF–TCNQ.[6d,e]

Table 1 Redox potentials[a] and conductivity[b] of TCNQ complexes[c]

Donor	$E(1)$/V	$E(2)$/V	ΔE/V	TCNQ complex σ_{rt}/S cm^{-1} (T_{MI}/K)
TSF	0.47	0.78	0.31	800 (40)[d]
TSTeF	0.45	0.75	0.30	2000 (85)
DSDTeF	0.42	0.71	0.29	1400 (<4.2)

[a]V *vs.* Ag/AgCl in PhCN. [b]Measured on a single crystal with a four probe method. [c]The ratio of donor : acceptor is 1 : 1 for all the complexes, based on microanalyses. See Experimental section. [d]Reference 5(a).
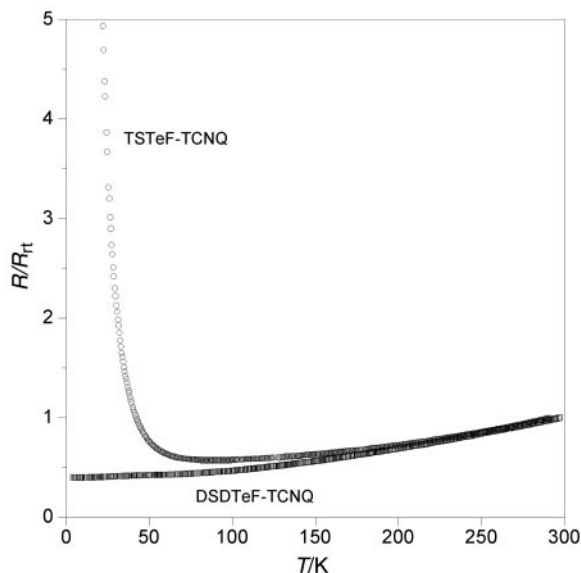
Fig. 1 Temperature dependence of the resistivity of TSTeF–TCNQ and DSDTeF–TCNQ.

It should be pointed out that one tellurium substitution on TSF–TCNQ is effective enough to enhance the room temperature conductivity but unable to suppress the MI transition, whereas two tellurium substitution brings about not only enhancement of the room temperature conductivity but also suppression of the MI transition.

Crystal structure of TCNQ complexes

The above striking difference between temperature dependence of conductivities for both TCNQ complexes has prompted us to clarify their crystal structures. The crystal structure of TSTeF–TCNQ is depicted in Fig. 2. As seen in its packing diagrams, it is obvious that TSTeF–TCNQ is isostructural with those of TTF–TCNQ[9] and TSF–TCNQ;[5a] the crystal structure is dominated by homogeneous stacks of segregated donors and acceptors parallel to the short *b*-axis. (Fig. 2(a)) The higher room temperature conductivity of TSTeF–TCNQ than those of TTF–TCNQ (500 S cm^{-1}) and TSF–TCNQ (800 S cm^{-1}) suggests that the introduced Te atom definitely plays an efficient role in enhancing the intra-columnar interaction through chalcogen atoms, resulting in a wide conduction band. On the other hand, the higher MI transition temperature of TSTeF–TCNQ can be ascribed to the positional disorder of Te atom; half of the TSTeF molecule is crystallographically independent, meaning that the position of the Te atom can not be determined, and the refinement of occupancy factors for the two chalcogen atoms indicates the positional disorder of the Te atom.[10]

The crystal structures of DSDTeF–TCNQ viewed along the *a*- and *b*-axis directions are shown in Fig. 3.[11] Donor columns with short Se–Se, Te–Te and Se–Te contacts as well as acceptor columns are observed (Fig. 3(a)) as seen for TSTeF–TCNQ. However, the relative position of the donor and acceptor columns is entirely different from that of TSTeF–TCNQ. Along the *a*-axis direction, each donor or acceptor is related to the lateral ones by a translational operation, resulting in belt-like arrays of donor and acceptor molecules, as shown in Fig. 3(b). Between the donor neighbors, there are two side-by-side Se–Te contacts (4.11 Å), and between the adjacent donor and acceptor, a short Te–N contact (3.04 Å) is observed. A similar packing mode has been reported for TTeF–TCNQ, where side-by-side Te–Te interactions between the donor columns play an essential role in suppressing the MI transition.[6d]
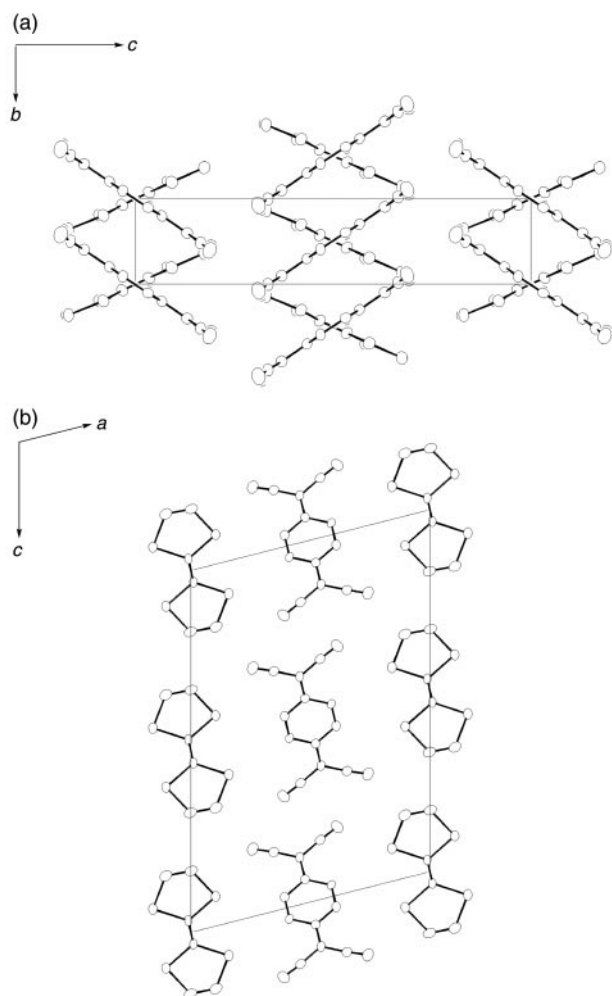
Fig. 2 Crystal structure of TSTeF–TCNQ: (a) *a*-axis projection and (b) *b*-axis projection

Fig. 3 Crystal structure of DSDTeF–TCNQ: (a) *a*-axis projection. The Te–Te and Se–Se contacts (solid lines) are 3.88 Å, and the short Te–Se contacts (dashed lines) are 4.02 Å. (b) *c*-axis projection. The Te–Se contact (dashed line) is 4.11 Å, and the Te–N contact (solid line) is 3.04 Å.

Band calculation

In order to understand the different electronic structures of these two TCNQ complexes, their band calculations based on the extended Hückel method using the tight-binding approximation were carried out.[12] The calculated overlap integrals for donor arrays are shown in Fig. 4(a) and 5(a). In the TSTeF–TCNQ complex, the overlap integral between the donor columns (designated by *c*) is negligible compared to that in the column (*b*) (Fig. 4(a)). Thus, the complex obviously has a one-dimensional electronic structure as indicated by its open Fermi surface (Fig. 4(b)). In contrast, the overlap integrals between DSDTeF columns (*a*1 and *a*2 in Fig. 5(a)) are approximately one tenth of that in the column (*c*), meaning that a substantial interaction in the transverse direction exists in this complex, which is well demonstrated by its quasi one-dimensional Fermi surface as shown in Fig. 5(b).

Conclusion

We have demonstrated that novel tellurium containing hybrid donors, TSTeF and DSDTeF, can be effectively synthesized by a simple two- or three-stage procedure. The TCNQ complex of TSTeF possessing only one tellurium atom evidently resembles TSF–TCNQ in terms of a MI transition at relatively high temperature, whereas the TCNQ complex of DSDTeF with two tellurium atoms behaves like TTeF–TCNQ without any MI transition down to liquid helium temperature. The stable metallic behavior of DSDTeF–TCNQ is rationalized by its crystal structure: the donor molecules have many intermolecular
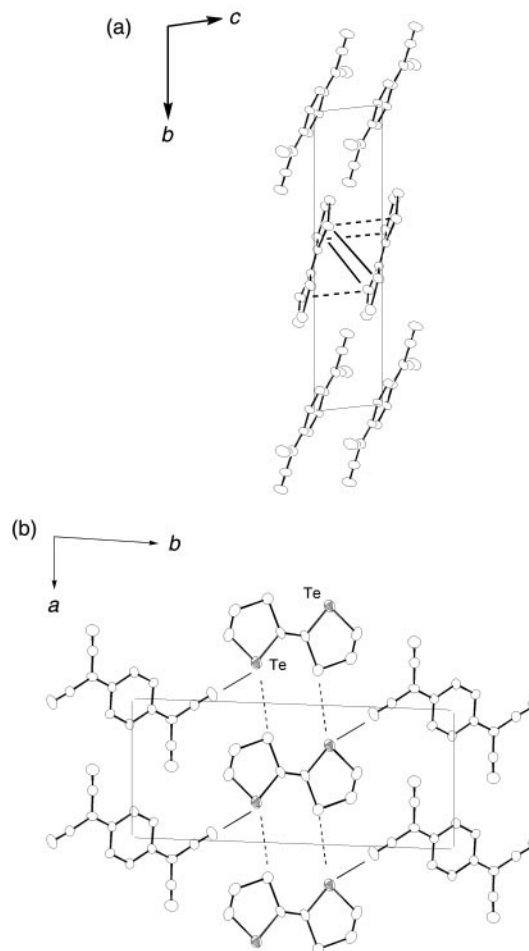
interactions through Se–Te, Se–Se, and Te–Te contacts not only in the stacking direction but also in the transverse direction, which results in a quasi one-dimensional electronic structure to suppress a MI transition characteristic of one-dimensional organic metals.

It is thus possible to categorize TCNQ complexes of tetrachalcogenofulvalene type donors into two classes; one consists of typical one-dimensional organic metals with a MI transition at low temperature, which TTF–TCNQ, TSF–TCNQ and the present TSTeF–TCNQ belong to. The other is grouped by quasi one-dimensional organic metals, such as TTeF–TCNQ and DSDTeF–TCNQ, which possess side-by-side heteroatomic interactions between donor columns and retain metallic behaviour down to low temperatures. It can be thus concluded that the number of Te atoms is crucial to the classification of these organic metals. Therefore, taking its easy access into consideration, the present DSDTeF is an electron donor of choice for studying tellurium-containing organic metals.

Experimental

General

All chemicals and solvents are of reagent grade and used without further purification unless otherwise noted. All reactions were carried out in a nitrogen atmosphere. Tellurium powder was purified according to the reported procedure.[6f] Carbon diselenide was synthesized according to the literature procedure.[13] Tetrahydrofuran was distilled from benzophenone–sodium
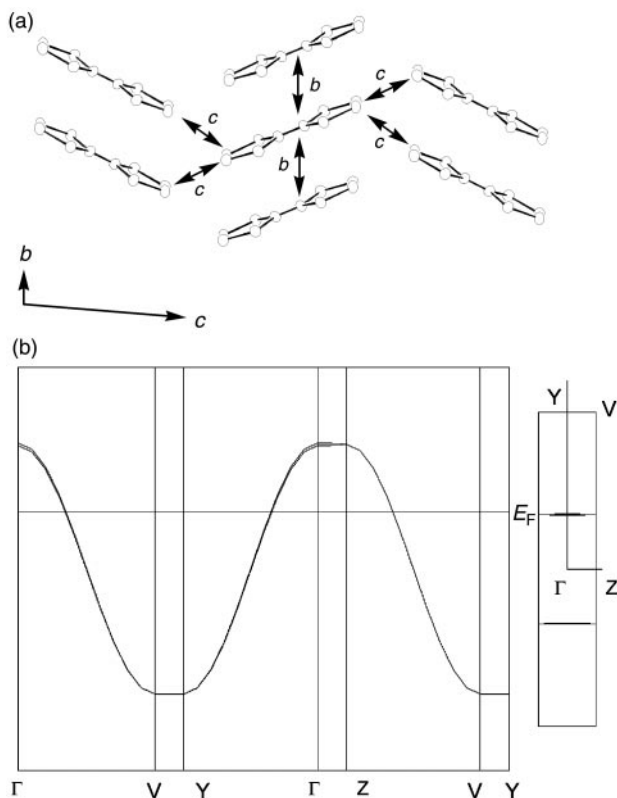
Fig. 4 Calculated overlap integrals (a) and band structure (b) of TSTeF–TCNQ: overlap integrals: $b = -15.64 \times 10^{-3}$, $c = 0.08 \times 10^{-3}$.
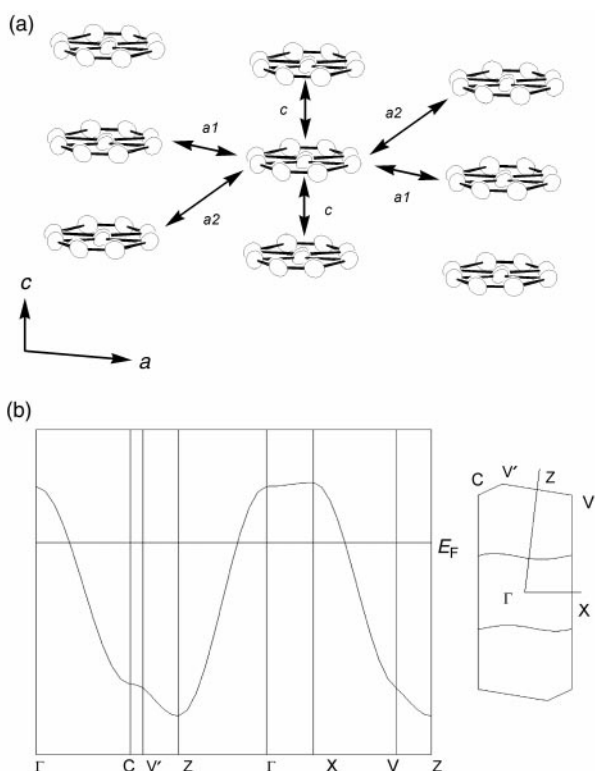

Fig. 5 Calculated overlap integrals (a) and band structure (b) of DSDTeF–TCNQ: overlap integrals: $c = -16.59 \times 10^{-3}$, $a1 = 1.38 \times 10^{-3}$, $a2 = 1.08 \times 10^{-3}$.

ketyl. Methanol was distilled from sodium. Toluene was distilled from calcium hydride. Melting points are uncorrected. Microanalyses were carried out by Mr Hideaki Iwatani, Microanalytical Laboratory in Department of Applied Chemistry, Faculty of Engineering, Hiroshima University.

NMR spectra were obtained in deuterated chloroform with a JEOL Lambda 400 spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C using tetramethylsilane as internal reference; chemical shifts (δ) are reported in parts per million. IR spectra were taken on a Shimadzu FTIR 8100 spectrophotometer with a KBr disk method. MS spectra were measured at 70 eV on a Shimadzu GCMS-QP 2000 spectrometer using a direct insertion technique. The molecular ion peaks of the selenium- and/or tellurium-containing compounds showed a typical isotopic pattern, and all the mass peaks are reported for [80]Se and [128]Te. Cyclic voltammograms were measured at room temperature using a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator. Preparative gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-908 equipped with a JAI-GEL 1H, 2H column assembly.

1,3-Selenatellurole-2-selone (1)

To a mixture of trimethylsilylacetylene (0.98 g, 10 mmol) and TMEDA (3.0 mL, 20 mmol) in dry THF (30 mL) cooled at $-78\,^{\circ}C$ was added a hexane solution of n-BuLi (1.6 M, 6.3 mL, 10 mmol), and the resulting solution was stirred for 30 min at the same temperature. To the resulting lithium acetylide solution, tellurium powder (1.28 g, 10 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature during a period of 2 h and stirred for a further 3 h at room temperature. To the clear telluride solution cooled to $-90\,^{\circ}C$, carbon diselenide (0.7 mL, 11 mmol) was added, and after 3 minutes the resulting mixture was quenched by the addition of water containing THF (1 : 1, v/v) (30 mL), and allowed to warm to room temperature. Water (50 mL) was then added, and the precipitate was collected by filtration and washed with MeOH (50 mL). Recrystallization from chlorobenzene gave **1** (2.68 g, 83%) as black plates.

Mp 128 °C (melt with decomposition). ^{1}H NMR δ 8.27 (d, $J = 8.5$ Hz, 1H, CH), 8.80 (d, $J = 8.5$ Hz, 1H, CH). IR v 845 cm^{-1} (C=Se). MS (EI) m/z 326 (M$^+$). Anal. Calcd for $C_3H_2Se_2Te_1$: C, 11.14; H, 0.62%. Found: C, 11.27; H, 0.60%.

4-Trimethylsilyl-1,3-diselenole-2-selone (3)

To a mixture of trimethylsilylacetylene (0.49 g, 5.0 mmol) and tetramethylethylenediamine (1.53 ml, 10 mmol) in dry THF (20 mL) cooled at $-78\,^{\circ}C$ was added a hexane solution of n-BuLi (1.6 M, 3.1 mL, 5 mmol), and the resulting solution was stirred for 30 min at the same temperature. To the resulting lithium acetylide solution, selenium (395 mg, 5 mmol) was added in one portion, and the reaction mixture was allowed to warm to 0 °C during a period of 2 h and stirred for an additional 2 h at 0 °C. Then the mixture was cooled again to $-90\,^{\circ}C$, and carbon diselenide (0.35 mL, 5.5 mmol) was added. The mixture was stirred for 3 min and then poured into aqueous HCl solution (2 M, 20 mL) at 0 °C. The resulting mixture was allowed to warm to room temperature and extracted with dichloromethane (40 mL × 3). The combined extracts were washed with water (120 mL) and dried over anhydrous MgSO$_4$. Evaporation of the solvent and subsequent column chromatography on silica gel eluted with carbon disulfide ($R_f = 0.4$) gave practically pure **3** (1.41 g, 81%). An analytical sample was obtained as red plates by recrystallization from chloroform–hexane.

Mp 70.0–72.0 °C. ^{1}H NMR δ 0.33 (s, 9H, TMS), 8.12 (s, 1H, CH). ^{13}C NMR δ −0.27, 143.53, 163.20, 211.52. IR v 914 cm^{-1} (C=Se). MS (EI) m/z 350 (M$^+$). Anal. Calcd for $C_6H_{10}Se_3Si_1$: C, 20.76; H, 2.9%. Found: C, 20.63; H, 2.87%.

Diselenaditellurafulvalene (DSDTeF)

A mixture of **1** (1.10 g, 3.41 mmol) and distilled triethyl phosphite (9.2 mL, 51 mmol) in toluene (45 mL) was refluxed

for 2 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The resulting residue was purified with column chromatography on silica gel eluted with carbon disulfide to afford DSDTeF ($R_f = 0.6$, 192 mg, 23%). ^{1}H NMR spectrum contained two sets of doublets assignable to two regioisomers with a ratio of 2:3. Recrystallization from benzene gave black prisms (mp 139.0–140.0 °C), which was determined as the *trans* isomer by means of an X-ray analysis.[14] However, its ^{1}H NMR spectrum was almost the same as before recrystallization, implying the occurrence of a quick isomerization in chloroform solution.

^{1}H NMR major isomer; δ 7.60 (d, $J = 8.2$ Hz, 2H, CH), 8.15 (d, $J = 8.2$ Hz, 2H, CH). minor isomer; δ 7.76 (d, $J = 8.2$ Hz, 2H, CH), 8.08 (d, $J = 8.2$ Hz, 2H, CH). MS (EI) m/z 492 (M^+). Anal. Calcd for $C_6H_4Se_2Te_2$: C, 14.73; H, 0.82%. Found: C, 14.96; H, 0.87%.

Trimethylsilyltriselenafulvalene (4)

A mixture of **1** (324 mg, 1.0 mmol), **3** (347 mg, 1.0 mmol) and distilled triethyl phosphite (2.5 mL, 10 mmol) in toluene (30 mL) was refluxed for 2 h. The mixture was cooled to room temperature and concentrated under reduced pressure. Column chromatography on silica gel eluted with carbon disulfide gave a mixture of bis(trimethylsilyl)TSF, DSDTeF and **4** ($R_f = 0.6$). Further purification of this fraction with GPC gave analytically pure **4** (52 mg, 11%, $V_R = 210$ mL) as red oil. ^{1}H NMR spectrum showed that compound **4** consisted of two isomers with respect to the position of the trimetylsilyl group, and the ratio of isomers was almost 1:1. ^{1}H NMR δ 0.24 × 2 (s, 9H, SiMe$_3$), 7.29 and 7.40 (s, 1H, CH), 7.65 (d, $J = 7.9$ Hz, 1H, CH), 7.66 (d, $J = 7.9$ Hz, 1H, CH), 8.06 (d, $J = 7.9$ Hz, 1H, CH), 8.07 (d, $J = 7.9$ Hz, 1H, CH). ^{13}C NMR δ −0.62, −0.66, 88.37, 88.41, 114.14, 117.84, 118.17, 123.07, 123.09, 128.49, 131.49, 144.83, 145.85. MS (EI) m/z 516 (M^+). Anal. Calcd for $C_9H_{12}Se_3Si_1Te_1$: C, 21.08; H, 2.36%. Found: C, 21.09; H, 2.37%.

Triselenatellurafulvalene (TSTeF)

To a solution of **4** (88 mg, 0.17 mmol) in THF (7 mL) was added an aqueous solution of potassium fluoride (1.7 M, 7 mL) at 0 °C, and the resulting solution was stirred for 6 h at 0 °C. Then the reaction mixture was extracted with dichloromethane (10 mL × 3), and the extract was washed with water (30 mL) and dried over anhydrous MgSO$_4$. Evaporation of the solvent and subsequent column chromatography on silica gel eluted with carbon disulfide gave TSTeF ($R_f = 0.6$, 64 mg, 86%). Recrystallization from benzene–hexane gave brown needles.

Mp 124.0–125.0 °C. ^{1}H NMR δ 7.19 (d, $J = 7.0$ Hz, 1H, CH), 7.29 (d, $J = 7.0$ Hz, 1H, CH), 7.66 (d, $J = 8.0$ Hz, 1H, CH), 8.08 (d, $J = 8.0$ Hz, 1H, CH). ^{13}C NMR δ 89.03, 89.07, 113.89, 123.27, 124.17, 131.22. MS (EI) m/z 444 (M^+). Anal. Calcd for $C_6H_4Se_3Te_1$: C, 16.36; H, 0.92%. Found: C, 16.39; H, 0.98%.

Charge-transfer complexes

The charge-transfer complexes of DSDTeF and TSTeF were prepared by slow cooling of a hot acetonitrile solution of the donor and the acceptor. The precipitated needle-like crystals were collected by filtration, washed with cold dichloromethane and dried. All the complexes were determined on the basis of microanalysis to have a 1:1 ratio of donor:acceptor as follows.

TSTeF–TCNQ

Calcd for $C_{18}H_8N_4Se_3Te_1$: C, 33.53; H, 1.25; N, 8.69%. Found: C, 33.63; H, 1.37; N, 8.53%. IR (KBr) ν_{CN} 2193 cm^{-1}.

Table 2 Crystal data of TCNQ complexes

	TSTeF–TCNQ	DSDTeF–TCNQ
Molecular formula	$C_{18}H_8N_4Se_3Te_1$	$C_{18}H_8N_4Se_2Te_2$
Formula weight	644.77	693.41
Crystal dimensions/mm^3	0.42 × 0.15 × 0.05	0.50 × 0.30 × 0.02
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	12.633 (3)	7.271 (3)
b/Å	3.901 (3)	16.735 (9)
c/Å	18.557 (2)	3.876 (2)
$\alpha/°$		96.38 (5)
$\beta/°$	104.24 (1)	98.17 (4)
$\gamma/°$		87.04 (4)
V/Å^3	886.4 (6)	463.6 (4)
Z	2	1
D_{calcd}/g cm^{-3}	2.417	2.483
N_{data}	1731 ($I > 2.0\sigma$ (I))	1726 ($I > 2.0\sigma$ (I))
R^a, $R_W{}^b$	0.024, 0.022	0.052, 0.052

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

DSDTeF–TCNQ

Calcd for $C_{18}H_8N_4Se_2Te_2$: C, 31.18; H, 1.16; N, 8.08%. Found: C, 30.90; H, 1.23; N, 7.97%. IR (KBr) ν_{CN} 2193 cm^{-1}.

Crystal structure determinations‡

A Rigaku AFC-7R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) was used and data collected at room temperature for all the crystals. Intensities were measured from continuous ω–2θ scans. All intensities were corrected for Lorenz polarization effects. The structures were solved by the direct methods or Patterson methods. Hydrogen atoms were located by calculation and not refined. All non-hydrogen atoms were refined by a full matrix least-squares technique with anisotropic temperature factors. Structure solution and refinement were carried out using the TEXSAN program package.[15] A summary of crystal data and structural refinement results are given in Table 2.

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15   TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992.