HETEROCYCLES, Vol. 54, No. 1, 2001, pp. 225 - 235, Received, 1st May, 2000

BIS(ETHYLENETHIO)TETRASELENAFULVALENE AND RELATED HYBRID DISELENADITHIAFULVALENES AS NOVEL ELECTRON DONORS FORMING HIGHLY CONDUCTIVE COMPLEXES WITH 7,7,8,8-TETRACYANOQUINODIMETHANE§

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

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan; E-mail otsubo@hiroshima-u.ac.jp

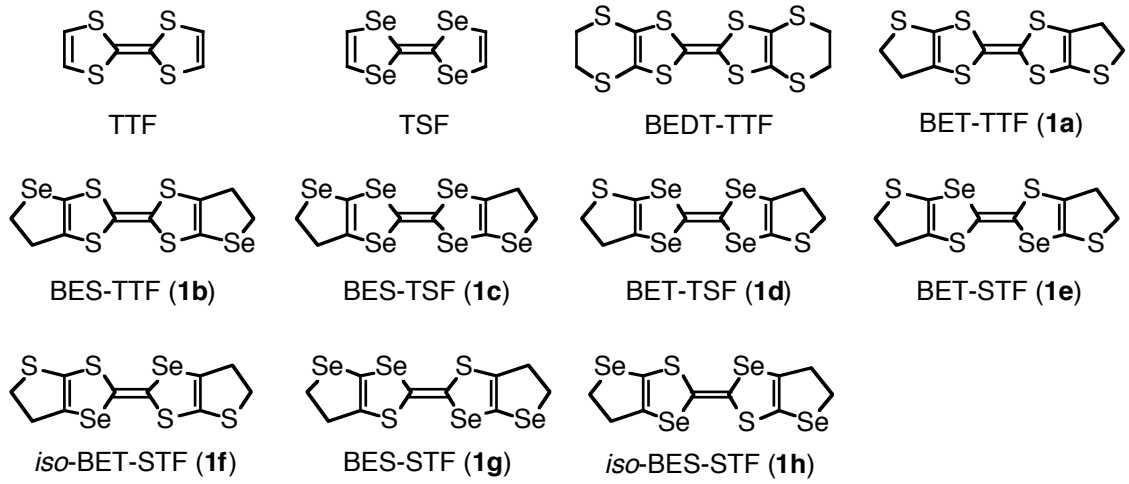
Abstract—The title tetraselenafulvalene (BET-TSF) and four related hybrid diselenadithiafulvalenes (STF) have been synthesized as a five-membered heterocycle-fused tetrathiafulvalene type of novel electron donors, which form highly conducting molecular complexes with 7,7,8,8-tetracyanoquinodimethane. In particular, the complex of BET-TSF shows a room-temperature conductivity of 2600 S cm^{-1}, which is of the highest class for a molecular complex.

INTRODUCTION

Since the discovery of numbers of superconductors based on bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF),[1] much attention has centered on the heterocycle-fused modifications of TTF and TSF electron donors for searching novel potential electron donors forming conductive molecular complexes.[2] A prototype of such electron donors is bis(ethylenethio)tetrathiafulvalene (BET-TTF, **1a**) fused with five-membered heterocycles, which has been long known, but currently has received a renaissance.[3] Since replacement of the sulfur atoms by selenium is well-known to be a promising modification of TTF-type electron donors,[4] we recently developed the selenocyclic analogues, bis(ethyleneseleno)tetrathiafulvalene (BES-TTF, **1b**) and bis(ethyleneseleno)tetraselenafulvalene (BES-TSF, **1c**), which gave metallic complexes with various electron acceptors.[5] In particular, it may be emphasized that the TCNQ complex of BES-TSF showed an extraordinarily high room-temperature conductivity of 2700 S cm^{-1}, which is of the highest class for a molecular complex. This high conductivity is in marked contrast to those of the TCNQ complexes of the TTF analogues: BET-TTF (30 S cm^{-1})[3a] and BES-TTF (150 S cm^{-1}).[5] This has prompted us to extensively study on all possible selenium-containing electron donors in this series. We now would like to report the synthesis and properties of heretofore unknown bis(ethylenethio)tetraselenafulvalene (BET-TSF) (**1d**) and four related

§ Dedicated to Professor Shô Itô on the occasion of his 77th birthday.

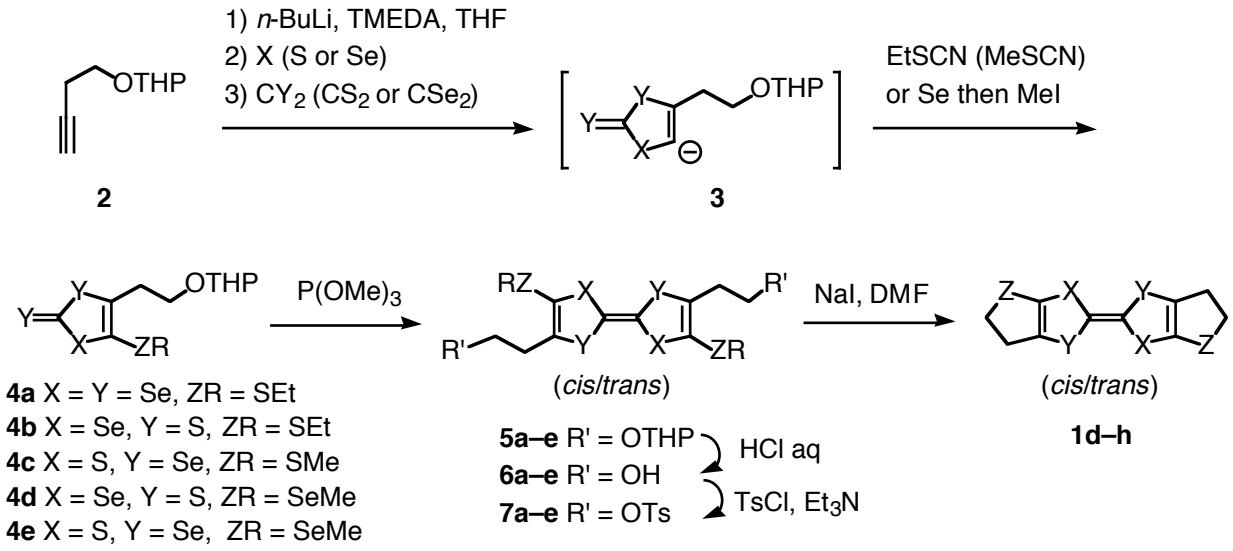
hybrid diselenadithiafulvalenes (**1e**–**h**).



RESULTS AND DISCUSSION

Synthesis. Compounds (**1d**–**h**) were synthesized according to a general synthetic route shown in Scheme 1, which first involves the formation of the 1,3-dichalcogenole-2-chalcogenone derivatives *via* the one-pot cyclization reaction of a terminal acetylene with chalcogen and carbon dichalcogenide,[6] secondly the formation of the inner fulvalenic ring system by conventional trimethyl phosphite-induced coupling, and finally the construction of the outer heterocyclic rings using a transalkylation reaction on the chalcogen atom. For the synthesis of BET-TSF (**1d**), commercially available tetrahydropyranyl (THP)-protected 3-butyn-1-ol (**2**) was treated with *n*-BuLi at –70 °C in THF to generate the lithium acetylide, which was successively reacted with elemental selenium at –70 – 0 °C and carbon diselenide at –90 °C. The resulting vinyl anion (**3**) was finally quenched by addition of ethyl thiocyanate to give 4-ethylthio-5-[2-(tetrahydropyran-2-yloxy)ethyl]-1,3-diselenole-2-selone (**4a**) in 80% yield. Subsequently the self-coupling of **4a** promoted by trimethyl phosphite under refluxing benzene gave the TSF derivative (**5a**) in 88% yield. After the THP protecting group was removed by treatment with dilute hydrochloric acid at room temperature (81% yield), the resulting alcohol (**6a**) was converted into the tosylate (**7a**) in 62% yield by treatment with tosyl chloride in dichloromethane including triethylamine. Heating **7a** with sodium iodide in DMF at 80 °C caused a substitution reaction of the tosyl groups to the iodo groups, and concurrently a transalkylation reaction on the outer sulfur atoms of the resulting iodide occurred, giving BET-TSF (**1d**) in high yield (77%). The driving force of the outer ring formation by the transalkylation reaction is release of the resulting ethyl iodide from the reaction mixture.

The above synthetic method was also found to be successfully applicable to the syntheses of the hybrid diselenadithiafulvalene derivatives (**1e**–**h**) by using combinations of the appropriate reagents. In the initial ring construction, thus, a successive one-pot treatment of the lithium acetylide with selenium, then carbon disulfide, and finally ethyl thiocyanate gave the hybrid 1,3-thiaselenole-2-thione (**4b**), which was similarly converted to the bis(ethylenethio)-fused diselenadithiafulvalene (BET-STF, **1e**). Similarly, a successive treatment with sulfur, carbon diselenide, and methyl thiocyanate afforded the 1,3-thiaselenole-2-selone (**4c**), which allowed the formation of the regioisomeric bis(ethylenethio)-fused



Scheme 1

diselenadithiafulvalene (*iso*-BET-STF, **1f**). When in the above initial ring construction the vinyl anion intermediates (**3**) were quenched with a combination of selenium and methyl iodide instead of alkyl thiocyanate, the methylseleno derivatives of 1,3-thiaselenole (**4d** and **4e**) were obtained, and successfully converted to the respective bis(ethyleneseleno)-fused diselenadithiafulvalenes (BES-STF, **1g** and *iso*-BES-STF, **1h**).

Molecular structures. The five-membered heterocycle-fused compounds, BET-TTF,[3a] BES-TTF, and BES-TSF[5] consist of a 1:1 mixture of two geometrical isomers with different symmetry, *i.e*. *cis* (C_{2v}) and *trans* (C_{2h}). These isomers are stable in the solid, but readily convertible into each other in solution.[7] The present compounds (**1d**–**h**) as well as the precursory TTF type intermediates are also expected to exist as such isomeric mixtures as drawn below for BET-TSF. This was confirmed by the observation of pairs of signals (nearly 1:1 integral ratio) with slightly different chemical shifts for some of the methylene protons in the ^{1}H NMR spectra and for some of the methylene carbons as well as the olefinic carbons in the ^{13}C NMR spectra (see the **EXPERIMENTAL**).

BET-TSF (*trans*) BET-TSF (*cis*)

Cyclic voltammetry. The cyclic voltammetry of BET-TSF (**1d**) and related hybrid diselenadithiafulvalenes (**1e–h**) showed two reversible one-electron redox waves. The half-wave oxidation potentials are summarized together with those of the related compounds in Table 1. Apparently the TSF type electron donors show higher first oxidation potentials (0.49 V) than the TTF type donors (0.32–0.36 V), and the hybrid STF type donors show intermediate oxidation potentials (0.40–0.41 V). Irrespective of any type, the fused heterocyclic rings have almost no influence on the first oxidation potentials. However, they induce a little lowering of the second oxidation potentials. These

Table 1. Half-wave oxidation potentials of hetrocycle-fused TTF type donors[a] and conductivities of their TCNQ complexes

Donor	$E_{1/2}(1)$ /V	$E_{1/2}(2)$ /V	ΔE /V	σ/S cm^{-1} crystal[b]	σ/S cm^{-1} pellet[c]	Remark
BET-TTF (**1a**)	0.36	0.68	0.32		30[d]	
BES-TTF (**1b**)	0.32	0.66	0.34	150[e]		Metallic down to 110 K
BES-TSF (**1c**)	0.49	0.76	0.27	2700[e]		Metallic down to 40 K
BET-TSF (**1d**)	0.49	0.73	0.24	2600	116	Metallic down to 60 K
BET-STF (**1e**)	0.41	0.68	0.27		66	
iso-BET-STF (**1f**)	0.41	0.71	0.30		66	
BES-STF (**1g**)	0.40	0.68	0.28		32	
iso-BES-STF (**1h**)	0.41	0.72	0.31		31	
TTF	0.34	0.71	0.37	500[f]		Metallic down to 59 K
TSF	0.49	0.78	0.29	800[f]		Metallic down to 40 K

[a]Cyclic voltammetry was carried out at a scan rate of 100 mV s^{-1} with Pt working and counter electrodes and an Ag/AgCl reference electrode in 10^{-3} mol dm^{-3} benzonitrile solution containing 10^{-1} mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte. [b]Conductivities were measured on a single crystal with a four-probe method. [c]Measured on a compacted pellet. [d]Ref. 3a. [e]Ref. 5b. [f]Ref. 8.

voltammetric data indicate that all the present compounds can behave as good electron donors to form molecular complexes.

TCNQ complexes. When a carbon disulfide solution of BET-TSF or the hybrid STFs was treated with an acetonitrile solution of TCNQ, molecular complexes were obtained as black needle crystals from an interface of both solutions. Most of these crystals were so fine that their conductivities were measured on compacted pellets. Only the crystals of BET-TSF•TCNQ complex were long enough to be also evaluated by a four-probe conductivity measurement on a single crystal. As shown in Table 1, all of the TCNQ complexes show high compacted pellet conductivities of the order of 10^1 to 10^2 S cm^{-1} at room temperature. The conductivities tend to increase in order of the donors, BET-TTF, BES-STF, BET-STF, and BET-TSF. Interestingly the complexes of the two kinds of STFs, irrespective of the regioisomeric donor species, show quite the same conductivities. The BET-TSF•TCNQ complex showing the highest compacted pellet conductivity (116 S cm^{-1}) marks 2600 S cm^{-1} for its single crystal conductivity, which is nearly comparable to that (2700 S cm^{-1}) of BES-TSF•TCNQ complexes and belongs to the most conductive class of molecular complexes. The extra high conductivities of the BET-TSF and BES-TSF complexes as compared to that (800 S cm^{-1}) of TSF•TCNQ complex are ascribable to the contribution of the heteroatoms of the fused heterocycles to side-by-side interactions in the transverse direction of the molecule. Furthermore, a variable temperature conductivity measurement of the BET-TSF complex demonstrated metallic behavior around room temperature and a typical metal-to-insulating (MI) transition at 60 K, characteristic of one-dimensional organic metals, as shown in Figure 1. A comparison with the MI temperature (40 K) of TSF•TCNQ indicates that the heteroatomic interactions are not sufficient to suppress the MI transition.

In summary, it can be concluded that all the five-membered heterocycle-fused TTF, TSF, and hybrid STF derivatives can behave as superior electron donors forming highly conducting molecular complexes with TCNQ. In particular, the complexes of BET-TSF and BES-TSF show extraordinarily high room-temperature conductivities, which are of the highest class for molecular complexes. Not only the inner heteroatoms but also outer heteroatoms of BET-TSF and BES-TSF evidently contribute to the high conductivities.

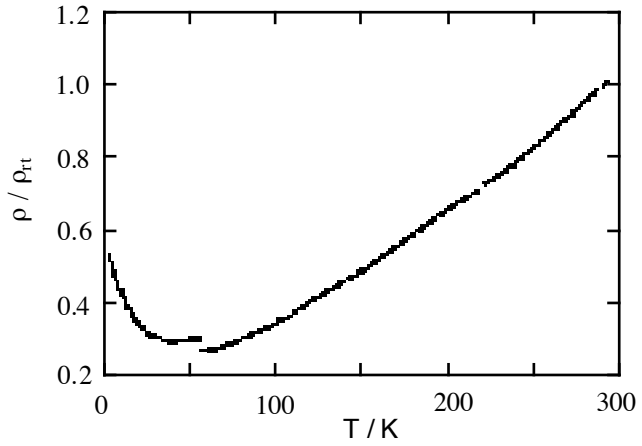


Figure 1. Normalized resistance vs. temperature plot for BET-TSF•TCNQ complex

ACKNOWLEDGMENT

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

EXPERIMENTAL

General. Melting points are uncorrected. NMR spectra were measured in deuteriochloroform 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. MS 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. IR 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 and were purified by conventional methods. All reactions were carried out under a nitrogen atmosphere with dry solvents. Column chromatography was performed with Daisogel IR-60 (63–210 μm). Preparative GPC was executed with JAIGEL-1H/2H columns using $CHCl_3$ as eluent. 2-(3-Butynyloxy)tetrahydro-2*H*-pyran (**2**) was purchased from Aldrich.

General synthetic method of 4: 4-Ethylthio-5-[2-(tetrahydropyran-2-yloxy)ethyl]-1,3-diselenole-2-selone (4a). To a solution of 2-(3-butynyloxy)tetrahydro-2*H*-pyran (**2**, 1.58 mL, 10 mmol) and TMEDA (3.0 mL, 40 mmol) in THF (80 mL) was added a solution of *n*-BuLi in hexane (1.61 M, 6.82 mL, 11 mmol) at –70 °C, and the solution was stirred at the same temperature for 30 min. After addition of

selenium powder (790 mg, 10 mmol), the mixture was warmed to 0 °C over a period of 2 h and stirred for 2 h at 0 °C. The solution was then cooled to –90 °C, and carbon diselenide (0.66 mL, 10 mmol) and ethyl thiocyanate (2.58 ml, 30 mmol) were successively added. The reaction mixture was warmed to 0 °C over a period of 2 h, and stirred at the temperature for 1 h. After water (100 mL) was added, the mixture was extracted with CH_2Cl_2 (100 ml x 3), and the extract was washed with brine and dried ($MgSO_4$). After concentration, column chromatography of the residue on silica gel with CH_2Cl_2 followed by purification with preparative GPC gave 3.73 g (80 %) of **4a** as a red oil, which was relatively unstable and slowly decomposed at ambient temperature: ^{1}H NMR δ 1.33 (t, J = 7.3 Hz, 3H, CH_3), 1.50-1.89 (br, 6H, CH_2), 2.83 (q, J = 7.3 Hz, 2H, SCH_2), 3.14–3.33 (m, 2H, CH_2), 3.45–3.94 (m, 4H, OCH_2), and 4.63-4.65 (br, 1H, CH); ^{13}C NMR δ 14.87, 19.18, 25.21, 30.36, 32.50, 33.34, 62.14, 65.83, 98.91, 138.59, 159.19, and 210.73; MS m/z 464 (M^+ based on ^{80}Se); IR (neat) 907 cm^{-1} (C=Se). Anal. Calcd for $C_{12}H_{18}O_2SSe_3$: C, 31.11; H, 3.92. Found: C, 31.79; H, 3.87.

Compound (**4b**) was synthesized with carbon disulfide instead of the carbon diselenide reagent, and **4c** with sulfur instead of the selenium reagent and methyl thiocyanate instead of the ethyl thiocyanate as the quencher. In the synthesis of **4d**, the same reactions as for **4b** were quenched with a combination of equivalent red selenium (2 h at 0 °C) and methyl iodide (0.5 h at rt).

In the synthesis of **4e**, the following modified procedure gave the best yield: the lithium acetylide solution of **2** (30 mmol) in tetrahydrofuran (150 mL) was treated with equimolar sulfur at 0 °C for 2–3 h, and cooled to –60 °C. Into the reaction mixture were successively added a small amount of methanol and equimolar red selenium. Then a solution of equimolar carbon diselenide in tetrahydrofuran (20 mL) was slowly added over a period of 1 h. The mixture was slowly warmed up to 0 °C (1.5 h), stirred at 0 °C for 1.5 h, and finally quenched with excess methyl iodide (91 mmol) for 0.5 h at rt. The usual work-up produced **4e** in 86% yield .

4-Ethylthio-5-[2-(tetrahydropyran-2-yloxy)ethyl]-1,3-thiaselenole-2-thione (4b). Yield 95%; a yellow oil; ^{1}H NMR δ 1.33 (t, J = 7.3 Hz, 3H, CH_3), 1.51–1.86 (br, 6H, CH_2), 2.83 (q, J = 7.3 Hz, 2H, SCH_2), 3.00–3.13 (m, 2H, CH_2), 3.49–3.93 (m, 4H, OCH_2), and 4.62–4.63 (br, 1H, CH); ^{13}C NMR δ 14.94, 19.21, 25.37, 30.42, 31.14, 32.50, 62.12, 65.84, 98.75, 133.61, 148.73, and 215.42; MS m/z 370 (M^+ based on ^{80}Se); IR (neat) 1051 cm^{-1} (C=S). Anal. Calcd for $C_{12}H_{18}O_2S_3Se$: C, 39.02; H, 4.91. Found: C, 39.04; H, 4.91.

5-Methylthio-4-[2-(tetrahydropyran-2-yloxy)ethyl]-1,3-thiaselenole-2-selone (4c). Yield 68%; a red oil; ^{1}H NMR δ 1.54–1.85 (br, 6H, CH_2), 2.43 (s, 3H, $SeCH_3$), 3.10–3.32 (m, 2H, CH_2), 3.45–3.96 (m, 4H, OCH_2), and 4.63–4.64 (br, 1H, CH); ^{13}C NMR δ 19.18, 20.69, 25.14, 30.31, 32.67, 62.20, 69.51, 98.95, 136.58, 156.17, and 208.43; MS m/z 404 (M^+ based on ^{80}Se); IR (neat) 936 cm^{-1} (C=Se). Anal. Calcd for $C_{11}H_{16}O_2S_2Se_2$: C, 32.84; H, 4.01. Found: C, 32.98; H, 4.03.

4-Methylseleno-5-[2-(tetrahydropyran-2-yloxy)ethyl]-1,3-thiaselenole-2-thione (4d). Yield 80%; a yellow oil; ^{1}H NMR δ 1.44–1.76 (br, 6H, CH_2), 2.77 (s, 3H, $SeCH_3$), 2.96–3.01 (m, 2H, CH_2), 3.43–3.86 (m, 4H, OCH_2), and 4.54–4.56 (br, 1H, CH); ^{13}C NMR δ 11.57, 19.02, 25.14, 29.36, 32.42, 61.89, 65.70, 98.53, 147.21, 174.82, and 217.03; MS m/z 404 (M^+ based on ^{80}Se); IR (neat) 1049.4 cm^{-1} (C=Se). Anal. Calcd for $C_{11}H_{16}O_2S_2Se_2$: C, 32.84; H, 4.01. Found: C, 32.78; H, 3.99.

5-Methylseleno-4-[2-(tetrahydropyran-2-yloxy)ethyl]-1,3-thiaselenole-2-selone (4e). Yield 63%; a red oil; ^{1}H NMR δ 1.54–1.85 (br, 6H, CH_2), 2.33 (s, 3H, $SeCH_3$), 3.13–3.31 (m, 2H, CH_2), 3.45–3.97 (m, 4H, OCH_2), and 4.63–4.64 (br, 1H, CH); ^{13}C NMR δ 11.19, 19.21, 25.19, 30.36, 34.38, 62.24, 65.69, 98.98, 126.27, 156.10, and 210.99; MS *m/z* 452 (M^+ based on ^{80}Se); IR (neat) 934 cm^{-1} (C=Se). Anal. Calcd for $C_{11}H_{16}O_2SSe_3$: C, 29.41; H, 3.59. Found: C, 29.30; H, 3.60.

General synthetic method of 5: 2,6(7)-Bis(ethylthio)-3,7(6)-bis[2-(tetrahydropyran-2-yloxy)ethyl]-1,4,5,8-tetraselenafulvalene (5a). A solution of **4a** (2.028 g, 4.37 mmol) and trimethyl phosphite (2.1 mL, 13.1 mmol) in benzene (25 mL) was refluxed for 2 h. After evaporation of the solvent under a reduced pressure, the residue was purified by column chromatography on silica gel with 4:1 CH_2Cl_2–ethyl acetate to give 1.48 g (88%) of **5a** as a red oil: ^{1}H NMR δ 1.28 (t, J = 7.4 Hz, 6H, CH_3), 1.52–1.90 (br, 12H, CH_2), 2.75 (q, J = 7.4 Hz, 4H, SCH_2), 2.89–3.05 (m, 4H, CH_2), 3.42–3.89 (m, 8H, OCH_2), and 4.62–4.64 (br, 2H, CH); ^{13}C NMR δ 14.94, 19.11, 25.34, 30.44, 31.41, 33.41 (isomer, 33.46), 61.89, 66.19, 105.20 (105.26), 123.41, and 142.55 (142.63); MS *m/z* 770 (M^+ based on ^{80}Se). Anal. Calcd for $C_{24}H_{36}O_4S_2Se_4$: C, 37.51; H, 4.72. Found: C, 37.36; H, 4.68.

2,6(7)-Bis(ethylthio)-3,7(6)-bis[2-(tetrahydropyran-2-yloxy)ethyl]-1,5(8)-diselena-4,8(5)-dithiafulvalene (5b). Yield 39%; a yellow oil: ^{1}H NMR δ 1.28 (t, J = 7.2 Hz, 6H, CH_3), 1.50–1.88 (br, 12H, CH_2), 2.73 (q, J = 7.3 Hz, 4H, SCH_2), 2.84–2.89 (m, 4H, CH_2), 3.47-3.88 (m, 8H, OCH_2), and 4.61–4.64 (br, 2H, CH); ^{13}C NMR δ 14.88 (isomer, 14.91); 19.10, 25.34, 30.40, 31.33, 31.51, 61.86, 65.70, 98.44 (98.47), 106.73 (107.38), 120.22 (120.63), and 139.85 (140.55); MS *m/z* 676 (M^+ based on ^{80}Se). Anal. Calcd for $C_{24}H_{36}O_4S_4Se_2$: C, 42.72; H, 5.38. Found: C, 42.72; H, 5.30.

2,6(7)-Bis(methylthio)-3,7(6)-bis[2-(tetrahydropyran-2-yloxy)ethyl]-4,8(5)-diselena-1,5(8)-dithiafulvalene (5c). Yield 71%; a yellow oil: ^{1}H NMR δ 1.52–1.90 (br, 12H, CH_2), 2.3346 (isomer 2.3444) (each s, 6H, SCH_3), 2.90–3.06 (m, 4H, CH_2), 3.41–3.88 (m, 8H, OCH_2), and 4.63–4.64 (br, 2H, CH); ^{13}C NMR δ 19.11 (isomer 19.15), 19.61 (19.64), 25.34, 30.45, 32.47 (32.61), 61.92 (61.94), 66.22, 98.70, 107.00 (107.59), 123.85 (124.63), and 136.61 (137.46); MS *m/z* 648 (M^+ based on ^{80}Se). Anal. Calcd for $C_{22}H_{32}O_4S_4Se_2$: C, 40.86; H, 4.99. Found: C, 40.74; H, 4.94.

2,6(7)-Bis(methylseleno)-3,7(6)-bis[2-(tetrahydropyran-2-yloxy)ethyl]-1,5(8)-diselena-4,8(5)-dithiafulvalene (5d). Yield 55%; a yellow oil: ^{1}H NMR δ 1.51–1.71 (br, 12H, CH_2), 2.2302 (isomer 2.2327) (each s, 6H, $SeCH_3$), 2.84–2.88 (m, 2H, CH_2), 3.47–3.87 (m, 8H, OCH_2), and 4.62–4.64 (br, 2H, CH); ^{13}C NMR (isomer) δ 10.84, 19.18, 25.40, 30.47, 32.78 (32.95), 61.95, 65.80, 98.54 (98.47), 108.35 (109.07), 111.25 (111.85), and 138.22 (139.11); MS *m/z* 744 (M^+ based on ^{80}Se). Anal. Calcd for $C_{22}H_{32}O_4S_2Se_4$: C, 35.69; H, 4.36. Found: C, 35.65; H, 4.38.

2,6(7)-Bis(methylseleno)-3,7(6)-bis[2-(tetrahydropyran-2-yloxy)ethyl]-4,8(5)-diselena-1,5(8)-dithiafulvalene (5e). Yield 86%; a yellow oil: ^{1}H NMR δ 1.52–1.88 (br, 12H, CH_2), 2.2467 (2.2577) (s, 6H, $SeCH_3$), 2.90–3.04 (m, 4H, CH_2), 3.43–4.64 (m, 8H, OCH_2), and 4.63–4.64 (br, 2H, CH); ^{13}C NMR δ 9.98, 19.08, 25.30, 30.40, 34.20 (isomer 34.04), 61.87, 66.23, 98.62 (98.68), 108.75 (109.31), 113.95 (114.67), and 135.57 (136.38); MS *m/z* 744 (M^+ based on ^{80}Se). Anal. Calcd for $C_{22}H_{32}O_4S_2Se_4$: C, 35.69; H, 4.36. Found: C, 35.53; H, 4.20.

General synthetic method of 6: 2,6(7)-Bis(ethylthio)-3,7(6)-bis(2-hydroxyethyl)-1,4,5,8-

tetraselenafulvalene (6a). A mixture of **5a** (1.13 g, 1.47 mmol), 1 *N* hydrochloric acid (27 mL), methanol (27 mL), and THF (54 mL) was stirred at rt overnight and then extracted with CH_2Cl_2. The extract was washed with brine, dried ($MgSO_4$), and then concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with 1:1 CH_2Cl_2–ethyl acetate to give 0.72 g (81%) of **6a** as a red oil: ^{1}H NMR δ 1.29 (t, J = 7.3 Hz, 6H, CH_3), 2.31 (br s, 2H, OH), 2.77 (q, J = 7.3 Hz, 4H, SCH_2), 2.92 (t, J = 6.1 Hz, 4H, CH_2), and 3.76 (t, J = 6.1 Hz, 4H, OCH_2); ^{13}C NMR δ 14.96 (isomer 14.98), 31.55, 35.98 (36.00), 61.98, 105.40, 124.16 (124.20), and 141.64 (141.67); MS *m/z* 602 (M^+ based on ^{80}Se); IR (neat) 3300 cm^{-1} (OH). Anal. Calcd for $C_{14}H_{20}O_2S_2Se_4$: C, 28.01; H, 3.36. Found: C, 27.90; H, 3.35.

2,6(7)-Bis(ethylthio)-3,7(6)-bis(2-hydroxyethyl)-1,5(8)-diselena-4,8(5)-dithiafulvalene (6b). Yield 99%; a red oil: ^{1}H NMR δ 1.29 (t, J = 7.4 Hz, 6H, CH_3), 1.96 (br s, 2H, OH), 2.75 (q, J = 7.4 Hz, 4H, SCH_2), 2.81–2.85 (m, 4H, CH_2), and 3.76–3.79 (m, 4H, OCH_2); ^{13}C NMR δ 14.95, 31.48 (isomer 31.51), 34.03 (34.24), 61.68, 106.91 (107.61), 121.02 (121.46), and 138.99 (139.71); MS *m/z* 508 (M^+ based on ^{80}Se); IR (neat) 3400 cm^{-1} (OH). Anal. Calcd for $C_{14}H_{20}O_2S_4Se_2$: C, 33.20; H, 3.98. Found: C, 33.26; H, 3.90.

2,6(7)-Bis(methylthio)-3,7(6)-bis(2-hydroxyethyl)-4,8(5)-diselena-1,5(8)-dithiafulvalene (6c). Yield 73%; an orange powder from dichloromethane–hexane; mp 102–104 °C; ^{1}H NMR δ 1.65 (br s, 2H, OH), 2.3492 (isomer 2.3602) (each s, 6H, SCH_3), 2.91–2.99 (m, 4H, CH_2), and 3.75–3.80 (m, 4H, OCH_2); ^{13}C NMR δ 19.75, 35.18, 62.15, 124.77, 125.77, and 136.52; MS *m/z* 480 (M^+ based on ^{80}Se); IR (KBr) 3500 cm^{-1} (OH). Anal. Calcd for $C_{12}H_{16}O_2S_4Se_2$: C, 30.13; H, 3.37. Found: C, 30.09; H, 3.27.

2,6(7)-Bis(methylseleno)-3,7(6)-bis(2-hydroxyethyl)-1,5(8)-diselena-4,8(5)-dithiafulvalene (6d). Yield 62%; a pale red powder from dichloromethane–hexane; mp 104–106 °C; ^{1}H NMR δ 1.57 (br s, 2H, OH), 2.25 (s, 6H, $SeCH_3$), 2.81–2.85 (m, 4H, CH_2), and 3.76–3.81 (m, 4H, OCH_2); ^{13}C NMR δ 11.00, 35.42 (isomer 35.60), 61.78, 112.56, 128.65, and 137.52 (139.71); MS *m/z* 576 (M^+ based on ^{80}Se); IR (neat) 3266 cm^{-1} (OH). Anal. Calcd for $C_{12}H_{16}O_2S_2Se_4$: C, 25.19; H, 2.82. Found: C, 25.43; H, 2.85.

2,6(7)-Bis(methylseleno)-3,7(6)-bis(2-hydroxyethyl)-4,8(5)-diselena-1,5(8)-dithiafulvalene (6e). Yield 70%; red needles from chloroform–hexane; mp 112–113 °C; ^{1}H NMR δ 1.58 (br, 2H, OH), 2.2644 (isomer 2.2760) (s, 6H, $SeCH_3$), 2.92–2.95 (m, 4H, CH_2), and 3.76–3.80 (m, 4H, OCH_2); ^{13}C NMR δ 10.13, 36.72 (36.78), 62.20, 114.83, 137.20, and 139.69; MS *m/z* 576 (M^+ based on ^{80}Se); IR (KBr) 3247 cm^{-1} (OH). Anal. Calcd for $C_{12}H_{16}O_2S_2Se_4$: C, 25.19; H, 2.82. Found: C, 25.10; H, 2.71.

General synthetic method of 7: 2,6(7)-Bis(ethylthio)-3,7(6)-bis[2-(tosyloxy)ethyl]-1,4,5,8-tetraselenafulvalene (7a). To a solution of **6a** (405 mg, 0.67 mmol) in dichloromethane (6.7 mL) including triethylamine (0.28 mL, 2.02 mmol) was added tosyl chloride (513 mg, 2.69 mmol) at 0 °C. The mixture was stirred at –10 – 0 °C for 2 h and then allowed to stand at 0 °C for 18 h. After 1 *N* hydrochloric acid (10 mL) ice-cooled was added, the resulting mixture was extracted with dichloromethane (50 mL). The extract was washed with brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with dichloromethane to give 379 mg (62%) of **7a**: violet needles from chloroform–hexane; mp 158 °C (decomp); ^{1}H NMR ($CDCl_3$) δ

1.24 (t, J = 7.3 Hz, 6H, CH_3), 2.45 (s, 4H, CH_3), 2.72 (q, J = 7.3 Hz, 4H, SCH_2), 2.97 (t, J = 6.4 Hz, 4H, CH_2), 4.10 (t, J = 6.4 Hz, 4H, OCH_2), 7.35 (d, J = 8.1 Hz, 4H, ArH), and 7.80 (d, J = 8.1 Hz, 4H, ArH); IR (KBr) 1356 and 1175 cm^{-1} (SO_2). Anal. Calcd for $C_{28}H_{32}O_6S_4Se_4$: C, 37.01; H, 3.55. Found: C, 37.09; H, 3.49.

2,6(7)-Bis(ethylthio)-3,7(6)-bis[2-(tosyloxy)ethyl]-1,5(8)-diselena-4,8(5)-dithiafulvalene (7b). Yield 61%; pink needles from chloroform–hexane: mp 158 °C (decomp); ^1H NMR δ 1.24 (t, J = 7.3 Hz, 6H, CH_3), 2.44 (s, 6H, CH_3), 2.70 (q, J = 7.3 Hz, 4H, SCH_2), 2.88–2.91 (m, 4H, CH_2), 4.11 (t, J = 6.5 Hz, 4H, OCH_2), 7.33 (d, J = 8.4 Hz, 4H, ArH), and 7.7725 (isomer 7.7838) (each d, J = 8.4 Hz, 4H, ArH); IR (KBr) 1356 and 1173 cm^{-1} (SO_2). Anal. Calcd for $C_{28}H_{32}O_6S_6Se_2$: C, 41.27; H, 3.96. Found: C, 41.55; H, 3.89.

2,6(7)-Bis(methylthio)-3,7(6)-bis[2-(tosyloxy)ethyl]-4,8(5)-diselena-1,5(8)-dithiafulvalene (7c). Yield 64%; pink needles from chloroform–hexane: mp 163 °C (decomp); ^1H NMR δ 2.3096 (isomer 2.3120) (each s, 6H, SCH_3), 2.44 (s, 6H, CH_3), 2.80–3.15 (m, 4H, CH_2), 4.10 (t, J = 6.3 Hz, 4H, OCH_2), 7.34 (d, J = 7.9 Hz, 4H, ArH), and 7.79 (d, J = 7.9 Hz, 4H, ArH); IR (KBr) 1350 and 1171 cm^{-1} (SO_2). Anal. Calcd for $C_{26}H_{28}O_6S_6Se_2$: C, 39.69; H, 3.59. Found: C, 39.66; H, 3.48.

2,6(7)-Bis(methylseleno)-3,7(6)-bis[2-(tosyloxy)ethyl]-1,5(8)-diselena-4,8(5)-dithiafulvalene (7d). Yield 82%; pink needles from chloroform–hexane: mp 153 °C (decomp); ^1H NMR δ 2.2070 (isomer 2.2083) (each s, 6H, $SeCH_3$), 2.43 (s, 6H, CH_3), 2.85–2.90 (m, 4H, CH_2), 4.07 (t, J = 6.4 Hz, 4H, OCH_2), 7.30 (d, J = 8.0 Hz, 4H, ArH), and 7.73 (d, J = 8.0 Hz, 4H, ArH); IR (KBr) 1352 and 1171 cm^{-1} (SO_2). Anal. Calcd for $C_{26}H_{28}O_6S_4Se_4$: C, 35.46; H, 3.20. Found: C, 35.43; H, 3.18.

2,6(7)-Bis(methylseleno)-3,7(6)-bis[2-(tosyloxy)ethyl]-4,8(5)-diselena-1,5(8)-dithiafulvalene (7e). Yield 98%; pink needles from chloroform-hexane: mp 146 °C (decomp); ^1H NMR δ 2.21 (s, 6H, $SeCH_3$), 2.43 (s, 6H, CH_3), 2.88–2.91 (br, 4H, CH_2), 4.12 (t, J = 6.4 Hz, 4H, OCH_2), 7.33 (d, J = 8.1 Hz, 4H, ArH), and 7.7658 (isomer 7.7553) (each d, J = 8.1 Hz, 4H, ArH); IR (KBr) 1350 and 1173cm^{-1} (SO_2). Anal. Calcd for $C_{26}H_{28}O_6S_4Se_4$: C, 35.46; H, 3.20. Found: C, 35.27; H, 3.10.

General synthetic method of 1: 2,3:6,7(7,6)-Bis(ethylenethio)-1,4,5,8-tetraselenafulvalene (BET-TSF, 1d). A mixture of **7a** (173 mg, 0.19 mmol) and NaI (86 mg, 0.57 mmol) in DMF (2 mL) was stirred at 80 °C for 0.5 h. Into the reaction mixture was added water (50 mL), and the resulting precipitate was collected by filtration and then purified by column chromatography on silica gel with carbon disulfide as eluent to give 36 mg (77%) of **1d**; red needles from carbon disulfide–hexane: mp 164 °C (decomp); ^1H NMRδ2.89 (t, J = 8.0 Hz, 4H, CH_2) and 3.69 (t, J = 8.0 Hz, 4H, SCH_2); MS m/z 510 (M^+ based on ^{80}Se). Anal. Calcd for $C_{10}H_8S_2Se_4$: C, 23.64; H, 1.59. Found: C, 23.65; H, 1.52.

2,3:6,7(7,6)-Bis(ethylenethio)-4,8(5)-diselena-1,5(8)-dithiafulvalene (BET-STF, 1e). Yield 82%; red needles from carbon disulfide–hexane; mp 174 °C (decomp); ^1H NMR δ 2.82 (t, J = 8.1 Hz, 4H, CH_2) and 3.69 (t, J = 8.1 Hz, 4H, SCH_2); MS m/z 416 (M^+ based on ^{80}Se). Anal. Calcd for $C_{10}H_8S_4Se_2$: C, 28.99; H, 1.95. Found: C, 28.98; H, 1.87.

2,3:6,7(7,6)-Bis(ethylenethio)-1,5(8)-diselena-4,8(5)-dithiafulvalene (*iso*-BET-STF, 1f). Yield 91%; red needles from carbon disulfide–hexane; mp 178 °C (decomp); ^1H NMR δ 2.90 (t, J = 8.1 Hz, 4H, CH_2) and 3.6914 (isomer 3.6975) (each t, J = 8.1 Hz, 4H, SCH_2); MS m/z 416 (M^+ based on ^{80}Se).

Anal. Calcd for $C_{10}H_8S_4Se_2$: C, 28.99; H, 1.95. Found: C, 28.85; H, 1.86.

2,3:6,7(7,6)-Bis(ethyleneseleno)-4,8(5)-diselena-1,5(8)-dithiafulvalene (BES-STF, 1g). Yield 77%; red needles from carbon disulfide–hexane; mp 226 °C (decomp); ^{1}H NMR δ 2.85 (t, J = 7.9 Hz, 4H, CH_2) and 3.74 (t, J = 7.7 Hz, 4H, $SeCH_2$); MS m/z 510 (M^+ based on ^{80}Se). Anal. Calcd for $C_{10}H_8S_2Se_4$: C, 23.64; H, 1.59. Found: C, 23.61; H, 1.60.

2,3:6,7(7,6)-Bis(ethyleneseleno)-1,5(8)-diselena-4,8(5)-dithiafulvalene (*iso*-BES-STF, 1h). Yield 80%; reddish brown needles from benzene–hexane; mp 190 °C (decomp); ^{1}H NMR δ 2.9205 (isomer 2.9175) (each t, J = 7.8 Hz, 4H, CH_2) and 3.7531 (3.7451) (each t, J = 7.8 Hz, 4H, $SeCH_2$); MS m/z 510 (M^+ based on ^{80}Se). Anal. Calcd for $C_{10}H_8S_2Se_4$: C, 23.64; H, 1.59. Found: C, 23.74; H, 1.60.

Complexation. All the TCNQ complexes of BET-TSF and hybrid STFs were prepared by gradual growth of black needle crystals from an interface between a carbon disulfide solution of the donor and an acetonitrile solution of TCNQ. Elemental analyses indicated that they comprise 1:1 composition ratio of donor and acceptor. Analytical data of **1a** (calculated data for 1:1 stoichiometry): C, 36.96 (37.10); H, 1.75 (1.70); N, 7.78 (7.87). **1b**: C, 42.56 (42.72); H, 1.90 (1.96); N, 8.81 (9.06). **1c**: C, 42.32 (42.72); H, 1.90 (1.96); N, 8.82 (9.06). **1d**: C, 36.19 (37.10); H, 1.23 (1.70); N, 8.31 (7.87). **1e**: C, 36.66 (37.10); H, 1.75 (1.70); N, 7.68 (7.87).

REFERENCES

1. For a comprehensive review 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, New Jersey, 1992.
2. For excellent reviews on the structural modifications of TTF, see: (a) G. Schukat, A. M. Richter, and E. Fanghänel, *Sulfur Rep*., 1987, **7**, 155. (b) G. Schukat and E. Fanghänel, *Sulfur Rep*., 1993, **14**, 245. (c) G. Schukat and E. Fanghänel, *Sulfur Rep*., 1996, **18**, 1.
3. (a) E. M. Engler, V. V. Patel, J. R. Andersen, R. R. Schumaker, and A. A. Fukushima, *J. Am. Chem. Soc*., 1978, **100**, 3769. (b) C. Rovira, J. Veciana, N. Santaló, J. Tarrés, J. Cirujeda, E. Molins, J. Llorca, and E. Espinosa, *J. Org. Chem*., 1994, **59**, 3307. (c) 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. (d) 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. (e) C. Rovira, J. Veciana, J. Tarrés, E. Molins, M. Mas, D. O. Cowan, and S. Yang, *Synth. Met*., 1995, **70**, 883. (f) E. Ribera, C. Rovira, J. Veciana, V. N. Laukhin, E. Canadell, J. Vidal-Gancedo, and E. Molins, *Synth. Met*., 1997, **86**, 1993. (g) 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. (h) A. Pérez-Benítez, J. Tarriés, E. Ribera, J. Veciana, and C. Rovia, *Synthesis*, 1999, 577. (i) 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, *Ad. Mater*., 2000, **12**, 54.
4. D. Cowan and A. Kini, 'The Chemistry of Organic Selenium and Tellurium,' ed. by S. Patai, John Wiley & Sons, New York, 1987, Vol. 2, Chapter 12.

5. (a) T. Jigami, K. Takimiya, Y. Aso, and T. Otsubo, *Chem. Lett.,* 1997, 1091. (b) T. Jigami, K. Takimiya, T. Otsubo, and Y. Aso, *J. Org. Chem.,* 1998, **63**, 8865.
6. K. Takimiya, A. Morikami, and T. Otsubo, *Synlett*, 1997, 319.
7. A. Souizi, A. Robert, P. Batail, and L. Ouahab, *J. Org. Chem.*, 1987, **52**, 1610.
8. D. O. Cowan, R. McCullough, A. Bailey, K. Lerstrup, D. Talham, D. Herr, and M. Mays, *Phos. Sul. Sil.,* 1992, **67**, 277.