Synthesis and X-ray crystal structure of a selenophenoquinonoid-extended donor, BEDT–BDTS, affording highly conducting tetracyanoquinodimethane and I_3 complexes

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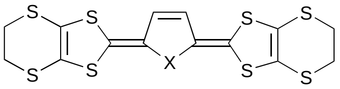
2,5-Bis(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-2,5-dihydroselenophene (BEDT–BDTS), a selenophenoquinonoid-extended analogue of bis(ethylenedithio)tetrathiafulvalenes (BEDT–TTF), has been synthesized as a promising candidate for an electron-donating component of high T_c organic superconductors. BEDT–BDTS is air-stable and has a significantly enhanced electron-donating ability compared with that of BEDT–TTF. The molecular and crystal structures of BEDT–BDTS have been determined by single crystal X-ray analysis in which short intermolecular $S\cdots S$ contacts have been found in the side-by-side directions of the donor arrangements. A 1 : 1 TCNQ complex and a 3 : 1 I_3^- radical cation salt of BEDT–BDTS have been obtained and proved to exhibit fairly high room temperature conductivities.

As a result of a great deal of investigation on organic conductors based on TTF (tetrathiafulvalene) and BEDT–TTF type donors, numerous criteria for the design of donor molecules have been proposed to afford organic conductors with high conducting properties and with two-dimensional character in the electronic structures of their conduction bands.[1] The incorporation of sulfur atoms at the periphery of TTF type molecules has been widely utilized to increase the dimensionality by taking into account relatively strong intermolecular $S\cdots S$ interactions.[2] An increase in dimensionality is essential in stabilizing the metallic state by suppressing the metal-to-insulator (MI) transition induced by charge- or spin-density wave localization at lower temperatures.[3] Indeed, bisethylenedithio–TTF (BEDT–TTF), with a strong ability to produce two-dimensional conducting layers, afforded many superconducting cation radical salts with high superconducting transition temperatures (T_c).[4] On the other hand, elongation of donor π-systems has been adopted as a molecular design strategy to decrease Coulombic repulsive energy which can participate in increasing the transfer integrals of electron wave functions.[5] So far, many elongated donors in which an sp^2 carbon chain or a benzoquinonoid ring as a π-linking bridge is inserted between the two 1,3-dithiole rings of TTF have been synthesized.[6] In these efforts, we proposed for the first time the incorporation of a sulfur atom in the π-linking bridge to stabilize the radical cation state.[7] More recently, however, it has been realized that such conjugation-elongated donors are expected to give high T_c organic superconductors since the T_c value of an organic superconductor is roughly proportional to the volume of the most effective space (V_{mes}) in which the carrier can distribute effectively and the V_{mes} can be increased with increasing thickness of the effective conducting donor layer.[8] Consequently, donor molecules with an elongated π-system and with outer chalcogen atoms to increase dimensionality have become interesting in obtaining high T_c organic superconductors. With this motivation, we have recently synthesized a thienoquinonoid-extended donor, 2,5-bis(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-2,5-dihydrothiophene (BEDT–BDTT) **1**[9] as well as related heterocycle-extended donors[10] and clarified that the 1 : 1 TCNQ complex of BEDT–BDTT **1** exhibits metallic properties with a metal-to-insulator (MI) transition temperature of *ca.* 150 K even on a compressed powder sample.



1 BEDT-BDTT: X = S

2 BEDT-BDTS: X = Se

However, the crystal structures of neither the neutral **1** nor its complex have been determined to date. Crystal growth and intermolecular chalcogen–chalcogen contacts would be much enhanced by replacing the sulfur atom(s) with selenium atom(s), since the diffuse *p*-orbitals of the selenium atom(s) may enhance the mutual intermolecular contacts.[1b] Here, we describe the synthesis of 2,5-bis(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-2,5-dihydroselenophene (BEDT–BDTS) **2**,[11] incorporating a central selenium atom, and the X-ray crystal structure of this new donor with short $S\cdots S$ contacts in the transverse direction, along with the conducting properties of its TCNQ complex and an I_3^- radical cation salt.

Results and Discussion

Synthesis and electrochemical properties

BEDT–BDTS **2** was synthesized according to Scheme 1. The key intermediates **5** and **6** were obtained in 25 and 18% yields, respectively, by the reaction of selenosuccinic anhydride **3**[12] with 2 equiv. of **4** in the presence of excess trimethyl phosphite in refluxing benzene. Further treatment of **5** with 3 equiv. of **4** under the same reaction conditions afforded the bis-capped product **6** in 18% yield. Dehydrogenation of **6** into BEDT–BDTS **2** was achieved in 76% by treatment with chloranil in xylene at refluxing temperature. BEDT–BDTS **2**, dark-red microcrystals, exhibits the longest-wavelength absorption maximum at 479 nm in THF (tetrahydrofuran) solution and is stable not only in the solid state but also in solution in common organic solvents. BEDT–BDTS displays two reversible, one-electron redox waves. The electrochemical parameters obtained by cyclic voltammetry are summarized in Table 1 along with those of reference compounds measured under the same conditions. The electron-donating ability of BEDT–BDTS is much higher than that of BEDT–TTF and rather close to that of TTF, since the first half-wave oxidation potential E_1^{ox} of BEDT–BDTS is lower by 0.22 and 0.07 V than those of BEDT–TTF and TTF, respectively. According

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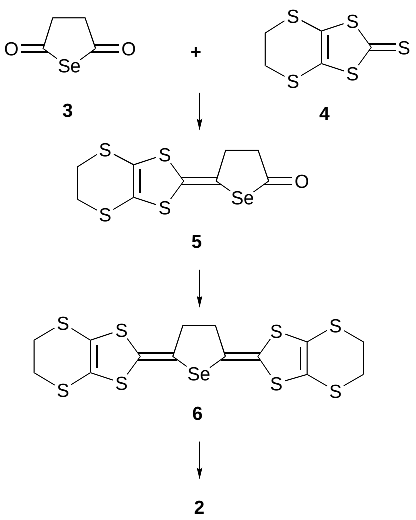

Scheme 1

Table 1 Electrochemical data of BEDT–BDTS and some reference compounds for comparison. Half-wave potentials[a] are given in V *versus* standard calomel electrode (SCE)

donor	E_1^{ox}/V	E_2^{ox}/V	ΔE^{ox}/V	log K_{sem}
BEDT–BDTS	+0.30	+0.45	0.15	2.55
BEDT–BDTT	+0.26	+0.43	0.17	2.88
BEDT–TTF	+0.52	+0.83	0.31	5.25
TTF	+0.37	+0.75	0.38	6.44

[a]Determined by CV, 1.0 mmol dm^{-3} solutions in PhCN with 0.1 mol dm^{-3} Bu$^n_4$NClO$_4$: 50 mV s^{-1}.

to our expectations, the on-site Coulombic repulsion is significantly decreased in the elongated donor, BEDT–BDTS as compared with BEDT–TTF, which is revealed by the much smaller ΔE^{ox} value of the former than the latter (Table 1). The electron-donating ability of BEDT–BDTS **2** is a little lower than that of BEDT–BDTT **1**,[9] because the E_1^{ox} of **2** is higher by 0.04 V than that of **1**. The second half-wave oxidation potential, E_2^{ox} of **2** is also higher than that of **1**, but the difference is not large. The ΔE^{ox} value is a little smaller in **2** than in **1**. The small ΔE^{ox} value for **2** can be ascribed to the degree of the conjugative interaction between the terminal dithiole rings which may be relatively weak in **2** with a C—Se—C bond as compared with **1** with a C—S—C bond on consideration of sulfur bonding orbital interactions[13] and/or the reduced aromatic stabilization energy of the selenophene ring relative to the thiophene ring in the radical cation state.

X-Ray crystallographic analysis

Single crystals of BEDT–BDTS **2** were obtained by recrystallization from benzene. The crystal belongs to the triclinic system and the space group is $P\bar{1}$. The crystal data are listed in Table 2. The unit cell contains six donor molecules stacking along the *a*-axis in a face-to-face manner but with displacement in a direction parallel to the donor long axis, namely along the *b*-axis (Fig. 1). The six donors are constructed with a pair of trimers which consist of three crystallographically independent donor molecules designated as A, B and C. There is a centre of symmetry between the trimers. Consequently, the stacking arrangement of the donors along the *a*-axis is CABBAC. The molecular structures of A, B and C are given in Fig. 2. The bond distances in the molecule A are listed in Table 3. The mean values of C=C (1.337 Å) and C—S (1.757 Å) bond lengths in the 4,5-ethylenedithio-1,3-dithiole units of A, B and C are not significantly different from the mean values of the C=C (1.327 Å) and C—S (1.751 Å) distances in BEDT–TTF.[14] Mean values of the bond angles in A, B and C are also not significantly different from the corresponding values of BEDT–TTF. For the molecules A and B, fairly good planar geometries are formed in the portion of the central selenophenoquinonoid ring with the 1,3-dithiole rings, and the two sulfur atoms attached to one dithiole ring, while both of the terminal ethylene carbon atoms and the second six-membered ring sulfur atoms are displaced from the plane. The deviation of the second dithiole ring is small. The conformation of C is less planar than those of A and B, with both of the 1,3-dithiole rings and both of the six-membered rings having non-planar conformations. However, drastic deviations from the molecular plane for the carbon and sulfur atoms of the conjugated portions were not observed in these three donor molecules.

Table 2 Crystal data for BEDT–BDTS **2**

molecular formula	$[C_{14}H_{10}S_8Se]_3[C_6H_6]_3$
molecular mass	1775.36
crystal color, habit	dark red, prism
crystal size/mm	0.20 × 0.25 × 0.25
crystal system	triclinic
space group	$P\bar{1}$
a/Å	12.844(6)
b/Å	44.320(14)
c/Å	6.305(1)
α(°)	93.53(2)
β(°)	98.52(3)
γ(°)	92.37(3)
Z	2
V/Å^3	3538.2(4.4)
D_c/g cm^{-3}	1.67
μ (Mo-Kα)/cm^{-1}	22.63
$2\theta_{max}$(°)	43.0
unique data	5977
data observed	5136
$R1$, $wR2$	0.084, 0.095
$\Delta\rho$max, $\Delta\rho$min/eÅ^{-3}	0.62, −0.80

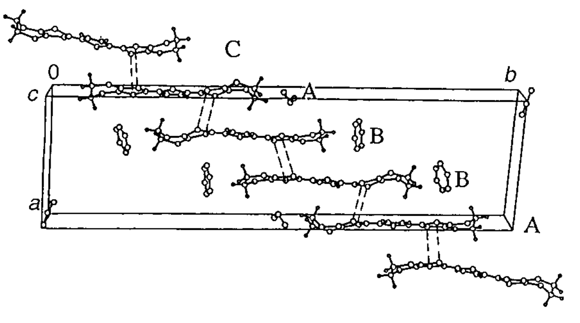

Fig. 1 Crystal structure of BEDT–BDTS viewed along the *c*-axis. Short intermolecular S···S distances (<3.85 Å) along the stacking direction (*a*-axis) are shown in dotted lines. Molecules A, B and C indicate three crystallographically independent BEDT–BDTS molecules. Symmetry operations are carried out for molecule C.

The overlapping modes for the donor molecules A, B and C are very similar to the so-called ring-over-bond-type; however, the donors overlap only three of their five rings as shown in Fig. 1. The intermolecular S···S distances along the stacking *a*-axis which are shorter than 3.85 Å are given in Table 4 and shown in dotted lines in Fig. 1. The short S···S distances are observed mainly between the sulfur atoms of the 1,3-dithiole rings. Most of these S···S distances are almost equal to the sum of the van der Waals radii of the sulfur atom as given by Pauling (3.70 Å).[15] The reason why there is no intrastack intermolecular S···S contact shorter than the sum of the van der Waals radii of the sulfur atom may be ascribed to the thermal motion of the ethylenic carbon atoms resulting from the non-planar conformations of the six-membered rings. The conjugated portions of the donor molecules may become more planar with an increase in charge on formation of charge-

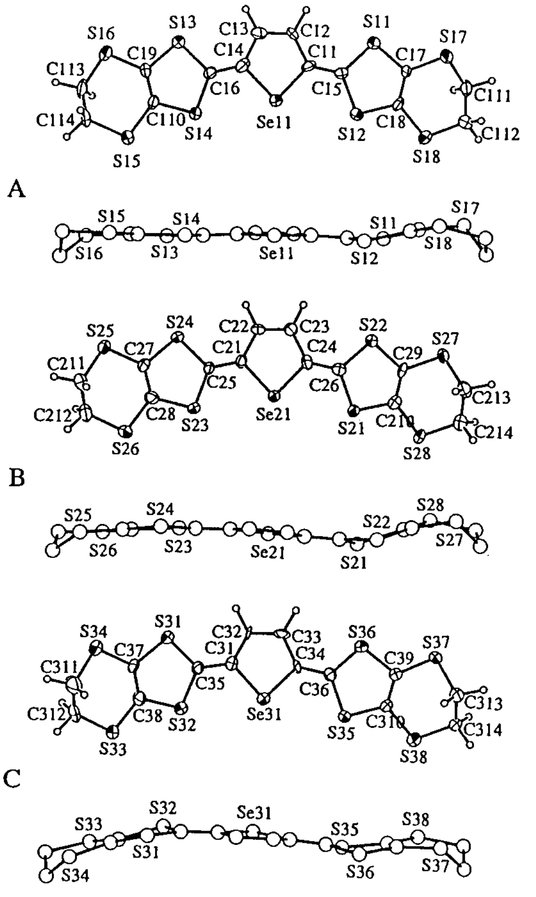

Fig. 2 Molecular structures (overviews and side views) of three crystallographically independent molecules A, B and C in the single crystal of BEDT–BDTS

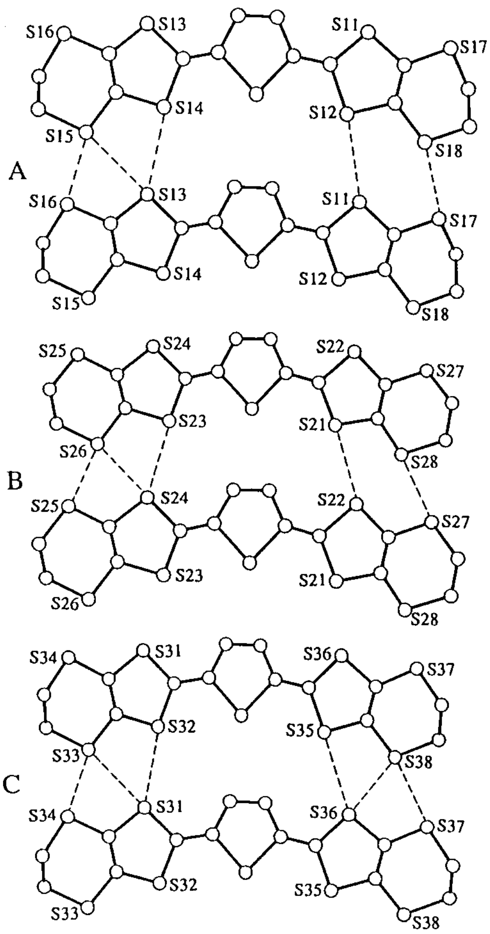

Fig. 3 Side-by-side molecular arrangements of A, B and C, viewed along the a-axis. Short intermolecular S···S distances (<3.9 Å) along the side-by-side directions are shown in dotted lines.

Table 3 Bond distances in the molecule A of BEDT–BDTS

	d/Å		d/Å
Se11–C11	1.907(19)	S17–C17	1.738 (22)
Se11–C14	1.925(20)	S17–C111	1.803 (25)
S11–C15	1.768 (21)	S18–C18	1.739 (20)
S11–C17	1.741 (21)	S18–C112	1.816 (28)
S12–C15	1.755 (21)	C11–C12	1.428 (28)
S12–C18	1.729 (20)	C11–C15	1.344 (27)
S13–C16	1.766 (20)	C12–C13	1.355 (29)
S13–C19	1.745 (21)	C13–C14	1.440 (29)
S14–C16	1.730 (20)	C14–C16	1.339 (28)
S14–C110	1.742 (20)	C17–C18	1.362 (28)
S15–C110	1.769 (20)	C19–C110	1.314 (27)
S15–C114	1.822 (28)	C111–C112	1.493 (36)
S16–C19	1.754 (21)	C113–C114	1.470 (37)
S16–C113	1.816 (26)		

Table 4 Short intermolecular S···S distances to 3.85 Å

along the a-axis	d/Å	along the c-axis	d/Å
S13–S32	3.77	S17–S18	3.56
S14–S31	3.77	S21–S22	3.79
S11–S21	3.70	S23–S24	3.82
S12–S22	3.73	S24–S26	3.61
S23–S24	3.82	S25–S26	3.48
along c-axis	d/Å	S27–S28	3.62
		S31–S32	3.85
S11–S12	3.79	S31–S33	3.57
S13–S15	3.75	S33–S34	3.57
S13–S14	3.85	S36–S38	3.85
S15–S16	3.55	S37–S38	3.64

transfer salts. Therefore, much shorter S···S contacts along the stacking a-axis will be observed on complexation.

In contrast to the stacking direction, there are short S···S contacts along the molecular short axis in A, B and C, forming three kinds of molecular arrays along the c-axis (Fig. 3), although each array is separated by solvent molecules along the b-axis as shown in Fig. 1. The ladder-like arrangements of the sulfur atoms of the 4,5-ethylenedithio-1,3-dithiole units play a central role for the formation of the characteristic side-by-side S···S interactions between the neighbouring molecules, since all of the A, B and C molecules are arranged so as to direct the central selenium atom to the same side of the molecule along the c-axis (Fig. 3). Interestingly, there are many side-by-side S···S contacts which are shorter than the sum of the van der Waals radii of the sulfur atom and shorter than the S···S distances along the stacking a-axis. The magnified crystal structure of BEDT–BDTS viewed along the c-axis is shown in Fig. 4. Indeed, side-by-side S···S contacts found in the insulating neutral BEDT–TTF crystal are also found in the conducting charge-transfer BEDT–TTF salts as their basic crystal structural features inducing characteristic two-dimensional band structures.[1,2] Therefore, it is suggested that BEDT–BDTS may have a strong tendency to form conducting donor layers with two-dimensional character and a large V_{mes} in its radical cation salts.

TCNQ complex and I_3^- salt

BEDT–BDTS **2** formed a 1 : 1 CT complex with tetracyanoquinodimethane (TCNQ), [BEDT–BDTS][TCNQ], and a radical cation salt, $[\text{BEDT–BDTS}]_3[I_3^-]$, on conventional electrochemical oxidation in chlorobenzene containing 50%

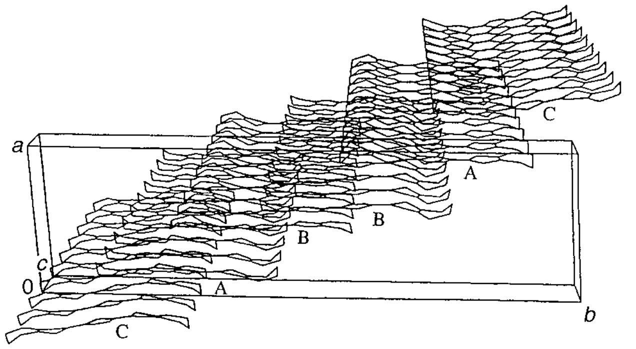

Fig. 4 Magnified crystal structure of BEDT–BDTS viewed along the *c*-axis

Table 5 Conductivities and related physical properties of TCNQ and I_3 salts of BEDT–BDTS

acceptor	D:A[a]	σ^b/S cm^{-1}	$\nu_{CT}{}^c$/cm^{-1}	$E_a{}^d$/eV
TCNQ	1:1	13	3000 (br)	—
I_3^-	1:3	5.6	2500 (br)	0.030

[a]Determined by elemental analysis. [b]Four-probe method on a compaction pellet measured at room temp. [c]Measured with FTIR using KBr disk. [d]Temperature range of 250–130 K

(v/v) of ethanol in the presence of tetra-*n*-butylammonium triiodide under a constant current of 1 μA. The conductivities measured on compressed samples as well as ν_{CN} and ν_{CT} bands of the complexes are summarized in Table 5. Both [BEDT–BDTS][TCNQ] and [BEDT–BDTS]$_3$[I_3^-] showed an extremely broad and characteristic intrastack ν_{CT} absorption band[16] at a very low energy region, revealing that both of these complexes have a segregated stacking mode in a partial CT state. The ν_{CN} band of [BEDT–BDTS][TCNQ] appeared at 2195 cm^{-1} which is lower by 25 cm^{-1} than that of neutral TCNQ. According to the 3:1 stoichiometry, the I_3^- salt may have a 5/6 filled band assuming a uniform stack. Unfortunately, we could not obtain a single crystal of the TCNQ complex at this time. The single crystals of the I_3^- salt obtained by the electrochemical oxidation are too small to attach silver or carbon wires for a standard four-probe conductivity measurement or to perform X-ray crystal structure analysis. The conductivities of both the TCNQ complex and the I_3^- salt are very high considering the measurement was carried out on a compressed powder sample. The temperature dependence of the resistivity on a compressed pellet of the I_3^- salt revealed that this pellet is a semiconductor in the temperature region 333–100 K. However, the activation energy in the temperature region of 250–130 K, $E_a = 0.030$ eV, is very small. Thus, if we could measure the conductivity of a single crystal, the I_3^- salt would undoubtedly show metallic behaviour. Electrocrystallization for obtaining single crystals of the I_3^- salt and other cation radical salts suitable for X-ray crystal analysis is now in progress.

Conclusions

The first synthesis of a selenophenoquinonoid-extended analogue of BEDT–TTF, namely BEDT–BDTS **2**, has been performed. The new donor, BEDT–BDTS, has a higher electron-donating ability and a decreased on-site Coulombic repulsion compared with BEDT–TTF. There are many short intermolecular S···S contacts in the side-by-side directions which are shorter than those of the stacking axis in the X-ray crystal structure. From this evidence it is suggested that the heterocycle-extended BEDT–TTF type donors may have a strong tendency to afford organic conductors with two-dimensional character. We have also succeeded in obtaining a 1:1 TCNQ complex and a 3:1 I_3^- salt of BEDT–BDTS exhibiting fairly high conductivities. Although we cannot observe any intermolecular short Se···S or Se···Se contacts in the crystal structure of BEDT–BDTS, the central selenium atom appears to play an important role for the growth of single crystals, since we have not yet succeeded in obtaining single crystals of BEDT–BDTT, **1**.

Experimental

Preparation of 2-(4,5-ethylenedithio-1,3-dithiol-2-ylidene)tetrahydroselenophen-5-one (5) and 2,5-bis(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-2,3,4,5-tetrahydroselenophene (6)

Selenosuccinic anhydride (**3**)[12] (500 mg, 3.07 mmol) and 4,5-(ethylenedithio)-1,3-dithiole-2-thione (**4**) (1.38 g, 6.14 mmol) were dissolved in dry benzene (17 ml) under an argon atmosphere at room temp. To this was added trimethyl phosphite (7.24 ml, 61.4 mmol) and the resulting mixture was heated at reflux for 6 h. After completion of the reaction, the solvent was evaporated *in vacuo* and the residue was chromatographed on silica gel with carbon disulfide as eluent to give a yellow powder of crude **6**; elution with benzene–hexane 2:1 gave light brown crystals of crude **5**. Recrystallization of the crude **5** from benzene afforded pure **5** (260 mg, 0.767 mmol, 25%) as yellowish green flakes, mp 184–185 °C (decomp.) (Calc. for $C_9H_8OS_4Se$: C, 31.85; H, 2.38; S, 37.79. Found: C, 31.59; H, 2.30; S, 37.68%); *m/z* (EI, 70 eV) 342 ($M^+ + 2$, 20%), 341 ($M^+ + 1$, 16%), 340 (M^+, 100%) δ_H($CDCl_3$, 200 MHz) 2.73 (4H, AA′BB′ type, multiplet centre, H-3′, 4′), 3.31 (4H, s, SCH_2CH_2S); ν_{max}/cm^{-1} (KBr) 2968, 2924, 2895, 1701, 1429, 1414, 1396, 1290, 1267, 1043, 1001, 985, 924, 910, 883, 771. Recrystallization of the crude **6** from benzene afforded pure **6** (285 mg, 0.553 mmol, 18%) as a yellow powder, mp 212–213 °C (decomp.) (Calc. for $C_{14}H_{12}S_8Se$: C, 32.61; H, 2.35; S, 49.74. Found: C, 32.44; H, 2.37; S, 49.58%); *m/z* (EI, 70 eV) 516 (M^+, 5%), 468 (12%), 436 (38%), 150 (100%) (HRMS: Calc. for $C_{14}H_{12}S_8Se$, 515.7869. Found, 515.7827); δ_H($CDCl_3$, 200 MHz) 2.64 (4H, s, H-3′, 4′), 3.29 (8H, s, SCH_2CH_2S); ν_{max}/cm^{-1} (KBr) 3060, 3030, 3012, 2972, 2951, 2914, 2900, 2819, 1581, 1508, 1400, 1286, 1255, 1213, 1145, 1126, 1084, 1007, 989, 931, 899, 847, 768, 744, 708, 677.

Preparation of compound 6 starting with compound 5

To a solution of ketone **5** (100 mg, 0.29 mmol) in benzene (9 ml) were added **4** (132 mg, 0.59 mmol) and trimethyl phosphite (1.1 ml, 8.8 mmol) under an argon atmosphere and the resulting suspension was heated at reflux. To this were added the second portion of **4** (33 mg, 0.15 mmol) after refluxing for 5 h and the third portion of **4** (33 mg, 0.15 mmol) after refluxing for 10 h. The reaction mixture was refluxed for 18 h in total, whereupon the reaction mixture was a dark red solution. The solution was allowed to cool to room temperature and then cooled in an ice bath. A powdery product which separated on cooling was collected by filtration, washed sequentially with methanol and hexane, and chromatographed on silica gel (carbon disulfide) to afford **6** (27.1 mg, 18%) as a yellow powder.

Preparation of 2,5-bis(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-2,5-dihydroselenophene (2: BEDT–BDTS)

A suspension of **6** (77.0 mg, 0.150 mmol) in dry xylene (20 ml) was heated at reflux at 160 °C under an argon atmosphere, whereupon the suspension became a clear solution. To this refluxing solution was added dropwise a solution of chloranil (55.3 mg, 0.225 mmol) in dry xylene (3 ml) over a period of 2 h. After the addition, the reflux was continued for further 2 h. The solvent was evaporated *in vacuo*. The residue was triturated with hot carbon disulfide and the insoluble matter was filtered off. The filtrate was evaporated *in vacuo* and the residual brown powder was washed with hot anhydrous methanol affording **2** (58.9 mg, 0.115 mmol, 76%) as a reddish brown powder, mp 209–209.5 °C (decomp.) (Calc. for $C_{14}H_{10}S_8Se$: C, 32.73; H, 1.96; S, 49.94. Found: C, 32.94; H, 2.02; S, 49.69%); *m/z* (EI, 70 eV) 516 ($M^+ + 2$, 19%), 514 (M^+, 12%), 486 (21%), 148 (100%) (HRMS: Calc. for $C_{14}H_{10}S_8Se$, 513.7713. Found, 513.7697); δ_H(CS_2–$CDCl_3$, 200 MHz) 3.32 (8H, s, SCH_2CH_2S), 6.28 (2H, s, H-3′, 4′); ν_{max}/cm^{-1} (KBr) 2924, 1639, 1545, 1508, 1450, 1408, 1346, 1286, 1263, 1176, 1147, 1128, 1080, 920, 901, 881, 823, 752, 679, 625; λ_{max}/nm (THF) (log ε) 479 (4.35), 447 (4.28), 278 (4.15).

Preparation of the [BEDT–BDTS][TCNQ] complex

Compound **2** (20.0 mg, 0.0389 mmol) was dissolved in dry carbon disulfide (40 ml) by heating. TCNQ (7.9 mg, 0.039 mmol) was dissolved in dry carbon disulfide (60 ml) by heating. Both solutions were separately filtered while hot to remove the small amount of undissolved matter. Then the two hot solutions were combined and concentrated to 2 ml by heating. Crystals that separated out on slow cooling were collected by filtration and washed successively with carbon disulfide and acetonitrile to afford [BEDT–BDTS][TCNQ] (7.4 mg) as a black powder, mp >300 °C (Calc. for $C_{26}H_{14}N_4S_8Se$: C, 43.50; H, 1.97; N, 7.80. Found: C, 42.99; H, 2.32; N, 7.63%); ν_{max}/cm^{-1} (KBr) 3000 (v br.), 2195, 2152, 1657, 1637, 1556, 1512, 1448, 1414, 1304, 1281, 1171, 1126, 1066, 947, 881, 835, 690, 600.

Preparation of [BEDT–BDTS]$_3$[I_3^-]

BEDT–BDTS **2** (5 mg, 0.0097 mmol) was dissolved in dry chlorobenzene (7 ml) and the resulting solution was placed in the anode compartment of a 15 ml H-shaped electrocrystallization cell. In the cathode compartment, separated from the anode compartment by a porous glass frit, was placed a solution of tetra-*n*-butylammonium triiodide ($TBAI_3$) (121 mg, 0.19 mmol) in absolute ethanol (7 ml). A constant current of 1 μA was passed through the cell for 7 d. Dark green silky needles of complex [BEDT–BDTS]$_3$[I_3^-] were harvested from the anode and were also collected from the walls of the anode compartment, mp 225.5–227 °C (decomp.) (Calc. for $C_{42}H_{30}S_{24}Se_3I_3$: C, 26.25; H, 1.57. Found: C, 26.31; H, 1.75%); ν_{max}/cm^{-1} (KBr) 2500 (v br.), 1441, 1408, 1371, 1336, 1306, 1275, 1254, 1230, 1173, 1149, 1128, 1070, 1047, 1004, 964, 922, 879, 839, 829, 781, 746, 704, 681.

X-Ray crystallography

The three-dimensional X-ray data of the single-crystal of BEDT–BDTS were collected by use of graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) on a Rigaku AFC5R automatic four-circle diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares analysis against F^2 of all data, using the TEXSAN crystallographic package on a Microvax computer. Crystal data and experimental details are listed in Table 2; atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1997, Issue 1. Any request to the CCDC for the material should quote the full literature citation and the reference number 1145/51.

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