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Synthesis, crystal structure and electrochemical properties of bis(ethylenedioxy)tetraselenafulvalene (BEDO-TSeF)

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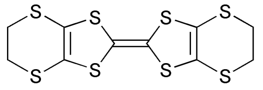
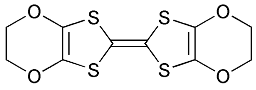
Bis(ethylenedioxy)tetraselenafulvalene (BEDO-TSeF) has been synthesized using elemental selenium as the only source of the selenium atoms, and its crystal structure and electrochemical properties are examined and compared with its sulfur analogues.

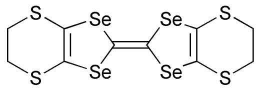
Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET)[1] is the most successful π-donor derived from TTF and its tetraselenafulvalene (TSeF) analogue, *i.e.* bis(ethylenedithio)tetraselenafulvalene (BETS),[2] also provides a several organic superconductors.[3] On the other hand, bis(ethylenedioxy)tetrathiafulvalene (BO),[4] which is an ethylenedioxy analogue of BEDT-TTF has supplied a large number of stable organic metals with various inorganic or organic counter anions including two superconducting salts.[5] Striking features of the BO molecule is its high solubility towards most organic solvents and ability to construct CH···O hydrogen bonding. These features are in contrast to the other BEDT-TTF analogues and are essentially impossible without a favour of the oxygen atoms. Taking into account the synthetic difficulties and instability of the tetratellurafulvalene (TTeF)[6] and tetraoxafulvalen (TOF)[7] skeletons, the title compound is practically the last promising analogue of BEDT-TTF, and its synthesis has long been awaited. It is expected that BEDO-TSeF unites the best qualities of BO and BETS and its physical properties including information on stability of the molecule have attracted much attention in TTF chemistry. We report here the first synthesis of BEDO-TSeF together with its crystal structure and basic electrochemical properties.



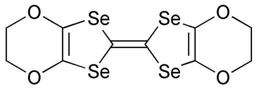
BEDT-TTF (ET)



BO

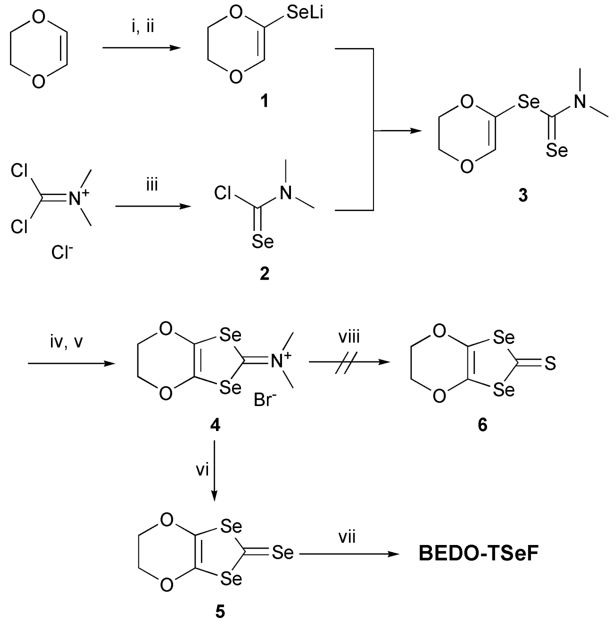


BETS



BEDO-TSeF

It is always difficult to synthesize TSeF analogues without the use of highly toxic reagents, such as CSe_2 or H_2Se gas. Furthermore, the synthesis of the title compound has an additional problem in that many of the synthesis routes known for TSeFs are not available because of the higher reactivity of the 1,4-dioxene ring compared with its sulfur analogue. There are two strategic points in our synthetic route to BEDO-TSeF: the one is the selection of the starting materials for the diselenocarbamate **3**, and the other one is the reaction condition of the last coupling step to construct the TSeF skeleton. Usually, the diselenocarbamate anion itself is used for the synthesis of diselenocarbamate esters including compound **3**, however, the highly toxic reagent CSe_2 or H_2Se gas is normally used for the synthesis of the *N*,*N*-dimethyldiselenocarbamate anion[8] and we have searched for a more practical and safer route. The key-intermediate **3** was synthesized by the reaction between the selenol anion **1**[9] and *N*,*N*-dimethylselenocarbamoyl chloride **2**.[10] Both materials **1** and **2** could be prepared from elemental selenium powder and conventional reagents. The typical procedure is as follows: to a THF solution of **2** (21 mmol in 70 ml THF) was added a THF solution of **1** (23 mmol, prepared in 30 ml THF) at 0 °C under argon atmosphere using tube-transfer technique and the mixture was warmed to room temperature over night. After the filtration of the inorganic salts and evaporation of the solvent, crude **3** was obtained and it was roughly purified by short silica-gel chromatography using Et_2O as eluent (ochre powder, 1.94 g, 33%). The diselenocarbamate **3** is moisture and air sensitive and it was used for the next step without further purification. The diselenocarbamate **3** could be transformed to the iminium salt **4** quantitatively according to the usual manner in the BO synthesis;[4] however, we could not obtain the thione **6** using the conventional NaSH–AcOH method.[11] On the other hand, we obtained the selone **5** using a NaSeH–AcOH method[8] (12% based on **4**). The selone **5** is stable in air for several months at room temperature and could be purified by column chromatography (SiO_2/CH_2Cl_2). Use of the dry H_2Se gas generated from Al_2Se_3 and concentrated H_2SO_4 lowered the yield of the selone to less than 2%. Synthesis of the title compound was accomplished by the coupling reaction under a very mild condition: to a benzene solution of the selone **5** (396 mg, 1.2 mmol in 50 ml benzene) was added 0.44 ml of hexamethylphosphorous triamide (HMPT, 2.4 mmol) at room temperature and the solution was stirred for 3.5 hours under argon atmosphere. After the removal of the solvent under vacuum, the crude products were purified by column chromatography ($SiO_2/CS_2–CH_2Cl_2$) and the target BEDO-TSeF was isolated as purple pink micro crystals which had a good solubility towards usual organic solvents (90 mg, 30%).† Trials of the coupling reactions using the more popular conditions, *i.e.* $P(OEt)_3$-solvents with heating, did not give good results and only a trace amount of BEDO-TSeF could be obtained. The lowering of the yield of the coupling reaction is a trend in the



Scheme 1 *Reagents and conditions*: i. *n*-BuLi–hexane, −10 °C, ii. Se, THF, −40 °C, iii. Se, $LiAlH_4$–THF, iv. Br_2, CH_2Cl_2, 0 °C, v. Δ, 110 °C, 10 torr, vi. NaSeH–AcOH, EtOH, −20 °C, vii. HMPT–benzene, rt, viii. NaSH–AcOH, EtOH.

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selenium substitution of the inner sulfur of the BO molecule as shown in the synthesis of bis(ethylenedixoy)diselenadithiafulvalene (BEDO-STF).[9] This would be due to the weakness of the C–Se bonds attached to the electron-donating dioxene ring rather than those of the sulfur analogues. De-selenation of the diselenole ring proceeds before the desired coupling reaction.

A single crystal of the BEDO-TSeF was harvested from a CS_2–hexane solution evaporated at room temperature and X-ray structure analysis was performed.‡ Fig. 1 shows the crystal structure of BEDO-TSeF together with a view of the unit cell. BEDO-TSeF crystallizes in the orthorhombic system, space group $P2_12_12_1$ and the packing motif is isostructural with the parent BO. The inner TSeF skeleton of BEDO-TSeF is held in a boat conformation and the folding angles are 13.2° and 25.8° respectively. There exist five short CH···O intermolecular contacts less than 3.0 Å and the strong ability to construct hydrogen bondings is successfully inherited from the parent BO molecule.

Table 1 summarizes the half-wave potentials of BEDO-TSeF and related BEDT-TTF analogues measured under the same condition. BEDO-TSeF shows two reversible waves and the first half-wave potential of BEDO-TSeF is comparable with that of BEDT-TTF and the difference between the first and second half-wave potentials ($\Delta E = E^2{}_{1/2} - E^1{}_{1/2}$) is almost equal to that of BETS. Usually, the introduction of selenium atoms lowers the donor ability and caused the $E^1{}_{1/2}$ value of BETS to be in a higher region as an organic π-donor. Thanks to the electron-donating ethylenedioxy group, BEDO-TSeF has kept the $E^1{}_{1/2}$ values in the lower region and this is an advantage over BETS for the synthesis of charge transfer complexes with organic π-acceptors.

In summary, we have achieved the first synthesis of BEDO-TSeF without the use of irritating reagents and its basic properties have been disclosed. The new donor has enough solubility towards conventional organic solvents and ability to construct CH···O hydrogen bonding. Its electrochemical properties are also desirable for the preparation of novel organic metals including superconductors. Research on conducting charge transfer salts is currently in progress in our laboratory.

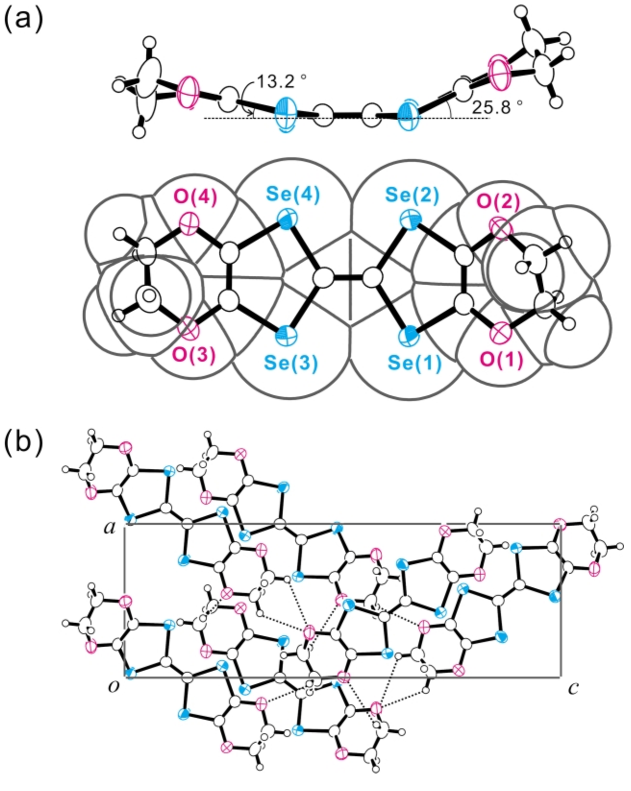

Fig. 1 Crystal structure of BEDO-TSeF: (a) molecular structure (b) packing diagram viewed along the crystallographic *b*-axis. Dotted lines indicate short CH···O contacts less than 3.0 Å.

Table 1 Half-wave potentials of BEDO-TSeF and related analogues[a]

Donor	$E^1{}_{1/2}$/V	$E^2{}_{1/2}$/V	$\Delta E = E^2{}_{1/2} - E^1{}_{1/2}$
BEDO-TSeF	0.08	0.34	0.26
BEDO-STF[b]	0.01	0.30	0.29
BO	−0.05	0.27	0.32
BEDT-TTF	0.06	0.38	0.32
BETS	0.23	0.48	0.25

[a] *vs.* $Cp_2Fe–Cp_2Fe^+$ couple, in PhCN with 0.1 M *n*-Bu_4NBF_4, grassy carbon working electrode, 100 mVs^{-1}, r.t. [b] *cis–trans* mixture

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Notes and references

† *Selected data for new compounds* **BEDO-TSeF**: purple pink micro crystals, mp 193 °C (decomp.); δ_H ($CDCl_3$, 270 MHz) 4.28 (s, 4H); δ_C (CD_2Cl_2, 125 MHz) 67.11, 99.28, 125.68; *m/z* (EI, 70 eV): 510 (M^+ with an expected isotopic pattern); Calcd for $C_{10}H_8O_4Se_4$: C, 23.36; H, 1.57. Found: C, 23.64, H, 1.59 %; **3**: ochre powder; δ_H ($CDCl_3$, 300 MHz) 3.35 (s, 3H), 3.65 (s, 3H), 4.24 (m, 2H), 4.36 (m, 2H), 6.55 (s, 1H); δ_C ($CDCl_3$, 67.8 MHz) 44.81, 49.78, 64.49, 67.09, 129.74, 138.03, 195.40; *m/z* (EI, 70 eV) 301 (M^+ with an expected isotopic pattern); **5**: deep red crystals, mp 184 °C (decomp.); δ_H ($CDCl_3$, 270 MHz) 4.38 (s, 4H); δ_C ($CDCl_3$, 67.8 MHz) 66.90, 139.34, 191.41; *m/z* (EI, 70 eV): 334 (M^+ with an expected isotopic pattern); Calcd for $C_5H_4O_2Se_3$: C, 18.04; H, 1.21. Found: C, 17.88, H, 1.24%.

‡ *Crystal data for* **BEDO-TSeF**: purple red plate (0.60 × 0.10 × 0.06 mm), $C_{10}H_8O_4Se_4$, MW = 508.01, orthorhombic, space group $P2_12_12_1$ (#19), $a = 7.7348(4)$, $b = 7.8387(5)$, $c = 21.9084(13)$ Å, $V = 1328.32(13)$ Å^3, $T = 293$ K, $\mu = 11.049$ mm^{-1}, $Z = 4$, 10056 reflections measured, 3311 unique (Rint = 0.0244). Final R indices [$I > 2\sigma(I)$]: $R1 = 0.0372$, $wR2 = 0.0943$. *R* indices (all data): $R1 = 0.0444$, $wR2 = 0.0979$. CCDC 233921 See http://www.rsc.org/suppdata/cc/b4/b403559c/ for crystallographic data in .cif or other electronic format.

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