Synthesis and Properties of Bis(ethyleneseleno)tetrathiafulvalene (BES-TTF) and Diselenolotetrathiafulvalene (DS-TTF) as Novel Electron Donors

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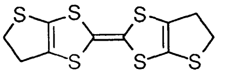
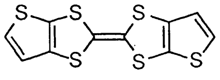
The title selenocycle-fused tetrathiafulvalene derivatives, BES-TTF and DS-TTF have been synthesized as novel electron donors, and their conductive charge-transfer complexes have been studied. All complexes of the BES-TTF compound with TCNQ, ClO_4, and PF_6 showed very high conductivities of the order of 10^2 S cm^{-1} as well as metallic temperature-dependent behavior.

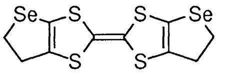
Since the discovery of numbers of superconductors based on bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), special interest has been placed on the development of heterocycle-fused TTF donors.[1] The fused heterocyclic rings play a considerably important role in intermolecular interactions between the TTF donors and accordingly in the solid state properties of the derived charge-transfer complexes. Bis(ethylenethio)tetrathiafulvalene (BET-TTF) and dithienotetrathiafulvalene (DT-TTF) are among the early developed heterocycle-fused TTF derivatives, but their complexes have been studied only with TCNQ.[2] Recently Rovira and coworkers revealed that BET-TTF can behave as a superior electron donor forming metallic radical cation salts.[3] Since one of the most general modifications of TTF-type donors is to replace the sulfur atoms with higher polarizable selenium,[4] the selenocyclic analogues of BET-TTF and DT-TTF are expected to be more potential electron donors.[5] Such selenium-containing donors can often make more conductive complexes with increased bandwidth and enhanced dimensionality. We now would like to report the synthesis and properties of bis(ethyleneseleno)tetrathiafulvalene (BES-TTF) and diselenolotetrathiafulvalene (DS-TTF) as novel electron donors.



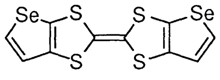
BET-TTF



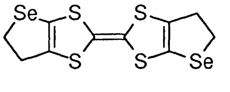
DT-TTF



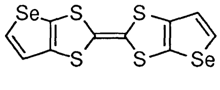
BES-TTF (*cis*)



DS-TTF (*cis*)

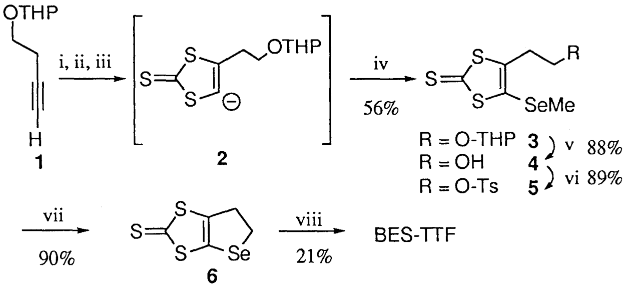


BES-TTF (*trans*)



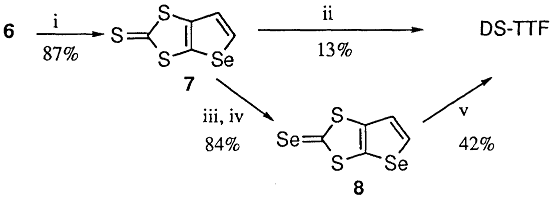
DS-TTF (*trans*)

Our approach to BES-TTF and DS-TTF required the efficient preparation of the key intermediates, 4,5-dihydroselenolo[2,3-*d*]-1,3-dithiole-2-thione (**6**) and selenolo[2,3-*d*]-1,3-dithiole-2-thione (**7**). Although the reported synthesis of similar sulfur intermediates for BET-TTF and DT-TTF involves the construction of the 1,3-dithiole-2-thione ring by conventional methods starting with thiolan-2-one[2] or thiolan-3-one,[3] these methods are not suitable for the synthesis of the present system, because the corresponding starting selenocyclic materials can not be readily prepared. Alternatively, we developed a convenient route which involves the initial synthesis of the 1,3-dithiole-2-thione ring via cyclization reaction of a terminal acetylene with sulfur and carbon disulfide,[6] followed by the construction of the additional selenocyclic ring as shown in Scheme 1. Thus commercially available THP-protected 3-butyn-1-ol (**1**) was treated with *n*-BuLi at -70 °C in THF to generate its lithium acetylide, which was successively reacted with elemental sulfur and carbon disulfide. The resulting vinyl anion (**2**) was then reacted with selenium and subsequently quenched by addition of methyl iodide to give THP-protected 4-(2-hydroxyethyl)-5-methylseleno-1,3-dithiole-2-thione (**3**) in 56% yield. After the THP protecting group was removed by treatment with dilute hydrochloric acid (88% yield), the resulting alcohol (**4**) was converted into the tosylate (**5**) in 89% yield. The second ring formation was achieved by unique transalkylation reaction on **5** via a hypervalent selenium intermediate promoted by sodium iodide in DMF, giving rise to the key intermediate (**6**) in high yield (90%). The conventional desulfurization coupling of **6** promoted by trimethylphosphite gave BES-TTF in 21% yield.[7]



Scheme 1. Reagents and conditions: i, *n*-BuLi, TMEDA, THF, -70 °C, 0.5 h; ii, S, 0 °C, 3 h; iii, CS_2, -90 °C, 3 min; iv, Se powder, then MeI, rt, 2 h; v, HCl aq., acetone-MeOH, rt, 12 h; vi, TsCl, pyridine, 0 °C, 12 h; vii, NaI, DMF, 80 °C, 0.5 h; viii, $P(OMe)_3$, reflux, 2 h.

The precursor of DS-TTF, selenolo[2,3-*d*]-1,3-dithiole-2-thione (**7**) was readily prepared in 87% yield by dehydrogenation of **6** with DDQ in refluxing toluene. A similar coupling reaction of **7** gave DS-TTF in 13% yield. Alternatively **7** was converted to the corresponding selone (**8**) by a well-established procedure



Scheme 2. Reagents and conditions: i, DDQ, toluene, reflux, 20 h; ii, $P(OMe)_3$, reflux, 2 h; iii, $(MeO)_2SO_2$, 80 °C, 0.5 h, then aq. HBF_4; iv, $NaBH_4$, Se, EtOH, rt, 0.5 h; v, $P(OMe)_3$, benzene, reflux, 1 h.

(84%),[8] and then coupled to give a better yield of DS-TTF (42%) (Scheme 2).

As seen in the case of the sulfur analogues,[2] two structural isomers with different symmetry, *i.e. cis* (C_{2v}) and *trans* (C_{2h}), can exist for BES-TTF and DS-TTF. This was confirmed by the observation of two kinds of A_2X_2 signals (1:1 integral ratio) with slightly different chemical shifts for the ethylene protons in the ^{1}H NMR spectrum of BES-TTF, but their separation with chromatographic and fractional crystallization techniques failed.

The cyclic voltammetry of BES-TTF and DS-TTF showed two reversible one-electron redox waves (Table 1). When compared to TTF, the half-wave oxidation potentials of BES-TTF are a little lower, and those of DS-TTF are a little higher, indicating their strong electron donor abilities. This is in sharp contrast to that the first oxidation potentials of both BET-TTF and DT-TTF are higher than that of TTF.[3]

Table 1. Half-wave oxidation potentials[a]

Donor	$E_{1/2}(1)$ / V	$E_{1/2}(2)$ / V	ΔE / V
BES-TTF	0.32	0.66	0.34
DS-TTF	0.38	0.71	0.33
TTF	0.34	0.71	0.37

[a]Vs. Ag/AgCl in PhCN containing 0.1M $^n\mathrm{Bu_4NClO_4}$; scan rate 400 mV / sec.

Upon equimolar mixing of BES-TTF and TCNQ in acetonitrile deposited a 1:1 charge-transfer complex as black needle-shape crystals. Its electrical conductivity measured on a single crystal showed a high conductivity of 150 S cm^{-1} at room temperature as well as a metallic temperature-dependent behavior (Table 2). At 110 K, it reached a maximum (270 S cm^{-1}), and then a metal-to-insulator transition occurred. Similarly, DS-TTF with TCNQ formed a 1:1 complex which, however, showed a room temperature conductivity of 0.20 S cm^{-1} and was semiconductive. This conductivity is much lower than the above BES-TTF's one, but higher by two orders of magnitude than the value of the (DT-TTF)•TCNQ complex (10^{-3} S cm^{-1}).[2] Furthermore, electrocrystallization of BES-TTF afforded plate-like crystals of radical cation salts with $\mathrm{ClO_4}$ and $\mathrm{PF_6}$, which also showed high conductivities of 280 and 200 S cm^{-1}, respectively, with a metallic temperature-dependent behavior. These results clearly support that BES-TTF is a potential electron donor forming metallic molecular complexes. Further detailed investigation on the crystal structures as well as molecular structures of the conductive molecular complexes by X-ray crystallographic analyses is now under way.

Table 2. Molecular complexes of BES-TTF and DS-TTF

Donor	Acceptor	Appearance	σ_{rt} / S cm^{-1} a	Remark
BES-TTF	TCNQ	Black needles	150	metallic ($T_{M\text{-}I}$ = 110 K)
DS-TTF	TCNQ	Black needles	2.0 x 10^{-1}	semiconductive (E_a = 0.064 eV)
BES-TTF	$\mathrm{PF_6}$	Black plates	200	metallic ($T_{M\text{-}I}$ = 240 K)
BES-TTF	$\mathrm{ClO_4}$	Black plates	280	metallic ($T_{M\text{-}I}$ = 110 K)

[a]Measured on a single crystal with a four-probe method.

References and Notes

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7 All new compounds were characterized by elemental analyses, NMR, and MS spectroscopy. Selected physical and spectral data. **6**: yellow needles from chloroform-hexane; mp 117.0-117.5 °C; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ 3.16 (t, J = 7.8 Hz, 2H) and 3.84 (t, J = 7.8 Hz, 2H); MS (EI, 70 eV) *m/z* 240 (M^+) with an isotopic pattern of one selenium atom; IR (KBr) 1053 cm^{-1} (C=S). Anal. Found: C, 25.34; H, 1.67%. Calcd for $\mathrm{C_5H_4S_3Se}$: C, 25.10; H, 1.69%. **7**: yellow prisms from chloroform-hexane; mp 150.0-150.5 °C; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ 7.30 (d, J = 5.8 Hz, 1H) and 8.29 (d, J = 5.8 Hz, 1H); MS (EI, 70 eV) *m/z* 238 (M^+) with an isotopic pattern of one selenium atom; IR (KBr) 1063 cm^{-1} (C=S). Anal. Found: C, 25.37; H, 0.84%. Calcd for $\mathrm{C_5H_2S_3Se}$: C, 25.32; H, 0.85%. **8**: orange needles from chloroform-hexane; mp 160.0-161.0 °C; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ 7.29 (d, J = 5.8 Hz, 1H) and 8.37 (d, J = 5.8 Hz, 1H); MS (EI, 70 eV) *m/z* 286 (M^+) with an isotopic pattern of two selenium atoms; IR (KBr) 932 cm^{-1} (C=Se). Anal. Found: C, 21.15 H, 0.72%. Calcd for $\mathrm{C_5H_2S_2Se_2}$: C, 21.14; H, 0.71%. BES-TTF: reddish orange needles from toluene; mp 209.0-210.0 °C (decomp.); ^{1}H NMR (400 MHz, $\mathrm{CS_2}$ - $\mathrm{CDCl_3}$) one isomer: δ 2.87 (t, J = 7.8 Hz, 4H) and 3.78 (t, J = 7.8 Hz, 2H); the other isomer: δ 2.86 (t, J = 7.8 Hz, 4H) and 3.78 (t, J = 7.8 Hz, 2H); MS (EI, 70 eV) *m/z* 414 (M^+) with an isotopic pattern of two selenium atoms. Anal. Found: C, 29.13; H, 1.99%. Calcd for $\mathrm{C_{10}H_8S_4Se_2}$: C, 28.99; H, 1.95%. DS-TTF: golden yellow leaflets from chloroform; mp 237.0-237.5 °C; ^{1}H NMR (400 MHz, $\mathrm{CS_2}$ - $\mathrm{CDCl_3}$) δ 7.00 (d, J = 5.7 Hz, 2H) and 7.86 (d, J = 5.7 Hz, 2H); MS (EI, 70 eV) *m/z* 412 (M^+) with an isotropic pattern of two selenium atoms. Anal. Found: C, 29.29; H, 0.96%. Calcd for $\mathrm{C_{10}H_4S_4Se_2}$: C, 29.27; H, 0.98%.

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