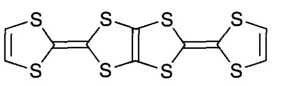
Synthesis and properties of the selenium analogue of DTEDT

Yohji Misaki,*[a] Hideki Fujiwara,[a] Tokio Yamabe,*[a] Takehiko Mori,*[b] Hatsumi Mori[c] and Shoji Tanaka[c]

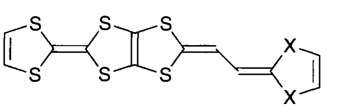
[a] *Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Yoshida, Kyoto 606-01, Japan*
[b] *Department of Organic and Polymeric Materials, Faculty of Engineering, Tokyo Institute of Technology, O-okayama, Tokyo 152, Japan*
[c] *International Superconductivity Technology Center, Shinonome, Tokyo 135, Japan*

Synthesis and electrochemical properties of the title donor are described; it gives a metallic TCNQ complex and radical-ation salts.

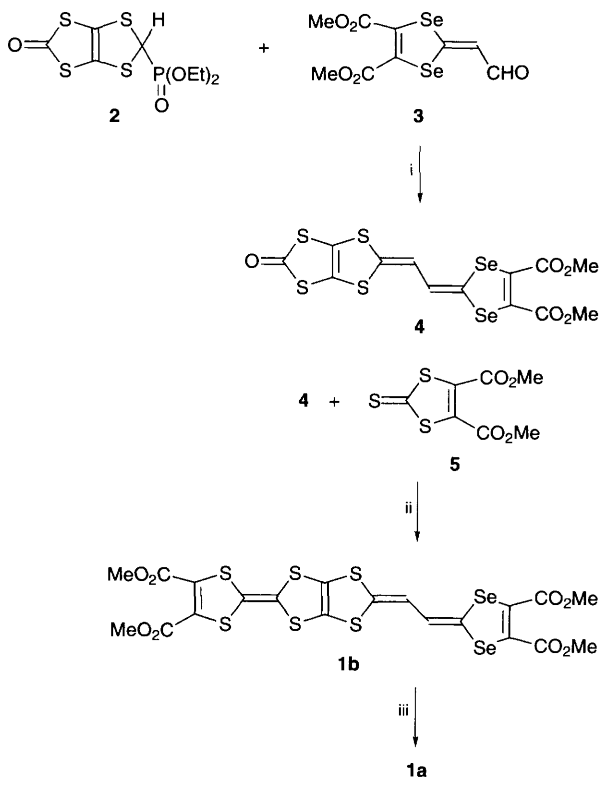
Recently, bis-TTF systems have received considerable interest as donor components for organic conductors.[1,2] We have synthesized various derivatives of bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP)[3] and its analogues,[4,5] several of which have produced metallic radical-cation salts down to liquid helium temperature.[3–6] Among them, a vinylogue of bis- fused TTF, 2-(1,3-dithiol-2-ylidene)-5-(2-ethanediylidene-1,3-dithiole)-1,3,4,6-tetrathiapentalene (DTEDT) is of particular interest because its $Au(CN)_2$ salt shows a superconducting transition at 4 K as well as many metallic radical-cation salts stable down to liquid helium temperature.[5a] In this context, modification of DTEDT is a subject of significant importance. We have very recently reported synthesis and properties of DTEDTs with various substituents.[5b] On the other hand, exchange of sulfur atoms with the other chalcogen atoms such as selenium and tellurium is also an attractive modification. We report herein the first synthesis of a selenium analogue of DTEDT, 2-(1,3-dithiol-2-ylidene)-5-[2-(1,3-diselenol-2-ylidene)ethylidene]-1,3,4,6-tetrathiapentalene (DTEDS, **1a**) in which the sulfur atoms of the terminal vinylogous 1,3-dithiole ring are exchanged by selenium atoms. Furthermore, conducting properties of its CT complex and radical-cation salts are also described.



BDT - TTP



X = S, DTEDT
X = Se, DTEDS, **1a**



Scheme 1 *Reagents and conditions*: i, 0.5 mol dm^{-3} LDA (1 equiv.), THF, −70 °C, 30 m; ii, $P(OMe)_3$ (100 equiv.), toluene, 110 °C, 2 h; iii, $LiBr{\cdot}H_2O$ (20 equiv.), HMPA, 90 °C, 1 h and 130 °C, 1 h

The synthesis of DTEDS was achieved by a similar method to DTEDT (Scheme 1). Thus, treatment of the phosphonate Wittig–Horner reagent **2** with lithium diisopropylamide (LDA) in the presence of 2-formylmethylidene-4,5-bis(methoxycarbonyl)-1,3-diselenole **3**[7] gave **4** in 48% yield. The trimethylphosphite-mediated cross coupling reaction between **4** and 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione **5** in refluxing toluene (1 : 1, *v*/*v*) afforded the tetrakis(methoxycarbonyl) derivative **1b** (52% yield). DTEDS **1a** was obtained in 62%

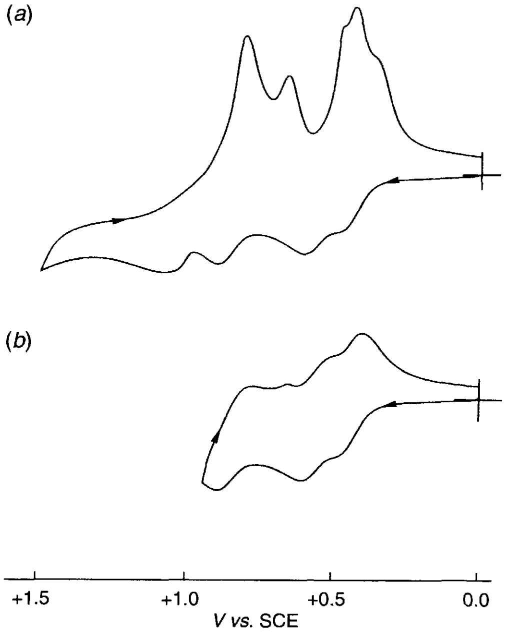


Fig. 1 Cyclic voltammogram of DTEDS in the potential range from 0.0 V to 1.5 V (*a*) and +0.94 (*b*). Unusual cathodic peaks in Fig. 1(*a*) are probably due to adsorption processes on the electrode surface or some chemical reactions after an electron transfer.

yield by demethoxycarbonylation of **1b** with an excess of LiBr·H_2O in HMPA at 90–130 °C, in the form of stable orange microcrystals.† DTEDS **1a** is less soluble in organic solvents than DTEDT.

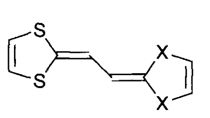
Both DTEDT derivatives **1a** and **b** show four pairs of single-electron redox waves; the first three redox processes are reversible, while the last ones are irreversible (Fig. 1). The first redox potential (E_1) of **1a** (+0.42 V) is higher by 0.05 V than that of DTEDT (+0.37 V)[5] measured under identical conditions (Table 1), indicating that donating ability becomes weaker by exchange of sulfur atoms with selenium. The positive shift of the E_1 value of **1a** compared with DTEDT is almost same as that of **6** relative to **7** (0.06 V). This result suggests that the positive charge in **1a**$^{+\bullet}$ mainly lies on the vinylogous diselenadithiafulvalene moiety, which is consistent with the substituent effect of DTEDT.[5b] On the other hand, the $E_2 - E_1$ value (0.12 V) is comparable to that of DTEDT (0.13 V).

DTEDS reacts with TCNQ in hot chlorobenzene to afford a 1 : 1 charge transfer (CT) complex. It shows high conductivity (σ_{rt} = 20 S cm^{-1}) on a compressed pellet. The temperature dependence of its resistivity revealed that it was metallic around room temperature, while the compressed pellet of DTEDT–TCNQ shows semiconductive temperature dependence. DTEDS also affords radical-cation salts with various anions, whose conductivities on single crystals were 10^{-1}–10^2 S cm^{-1} at room temperature (Table 2).‡ Among them, the $Au(CN)_2^-$ and ReO_4^- salts showed metallic temperature dependence down to 1.5 K, although several of them displayed semiconducting behaviour in contrast with DTEDT salts.[5] Further investigations, in particular the synthesis of other selenium analogues of DTEDT, are actively in progress.

Table 1 Redox potentials of **1** and related compounds[a]

Compound	E_1	E_2	E_3	E_4[b]	$E_2 - E_1$
1a	+0.42	+0.54	+0.81	+1.13	0.12
1b	+0.59	+0.73	+1.09	+1.32	0.14
DTEDT	+0.37	+0.50	+0.81	+1.05	0.13
TTF	+0.35	+0.77			0.42
6	+0.35	+0.50			0.15
7	+0.29	+0.49			0.20

[a] Bu_4NClO_4 0.1 mol dm^{-3} in PhCN, Pt electrode, 25 °C, scan rate 50 mV s^{-1}, V *vs.* saturated calomel electrode (SCE). [b] Irreversible steps. Anodic peak potentials.



6 X = Se
7 X = S

Table 2 Composition and electrical properties of DTEDS salts (DTEDS·A_x)

Acceptor	Form	x[a]	σ_{rt}/S cm^{-1}[b]	Conducting behaviour
TCNQ	—	1.0[c]	20[d]	T_{MI} = 260 K
BF_4	Needle	—[e]	10	E_a = 0.011 eV
ReO_4	Needle	0.43(Re)	180	Metallic down to 1.5 K
$GaCl_4$	Needle	1.3(Ga)	0.54	E_a = 0.11 eV
PF_6	Needle	0.63(P)	10	E_a = 0.010 eV
AsF_6	Needle	0.41(As)	13	T_{MI} = 200 K
I_3	Plate	0.56(I)	0.58	E_a = 0.023 eV
$Au(CN)_2$	Needle	0.47(Au)	26	Metallic down to 1.5 K

[a] Determined by the energy dispersion spectroscopy (EDS) from the ratio of sulfur and the elements designated in the parentheses. Unusual stoichiometries other than 0.5 are often observed in the radical-cation salts based on bis-fused donors, several of which have been also confirmed by X-ray structure analysis.[5a,6c,8] [b] Room temperature conductivity measured along the long axis on a single crystal using the four-probe technique. [c] Determined based on elemental analyses. [d] Measured on a compressed pellet. [e] The contents of light elements such as B and F are not reliably determined by the EDS.

This work is partially supported by Grant-in-Aid for Scientific Research No. 06243215, 07232219 and No. 00063275 from the Ministry of Education, Science, and Culture of Japan. One of the authors (H. F.) is indebted to the JSPS Research Fellowships for Young Scientists.

Footnotes

† *Selected data* for **1a**: orange microcrystals; mp 197 °C (decomp.) (Found: C, 29.00; H, 1.37. $C_{12}H_6S_6Se_2$ requires C, 28.80; H, 1.21%). ^{1}H NMR (270 MHz, CS_2–[$^2H_6$]benzene) δ 5.62 (1 H, d, *J* 11 Hz), 6.02 (2 H, s), 6.16 (1 H, d, *J* 11 Hz) and 6.90 (2 H, s); ν_{max}(KBr)/cm^{-1} 1538, 1506 (C=C) and 1273. For **1b**: dark brown powder; mp 198–199 °C (decomp.) (Found: C, 32.72; H, 2.04. $C_{20}H_{14}O_8S_6Se_2$ requires C, 32.79; H, 1.93%); ^{1}H NMR (270 MHz, CS_2–[$^2H_6$]benzene) δ 3.81 (s, 6 H), 3.85 (s, 6 H), 5.62 (1 H, d, *J* 11 Hz), 6.14 (1 H, d, *J* 11 Hz); ν_{max}(KBr)/cm^{-1} 1743, 1709 (C=O), 1575, 1558 (C=C), 1429, 1282 and 1235 (C–O).

‡ Radical-cation salts based on DTEDS were prepared by electrochemical oxidation in the presence of the corresponding tetrabutylammonium salts under a constant current of 0.2–0.3 μA in chlorobenzene or 1-chloronaphthalene–THF (1 : 1, *v*/*v*) containing *ca.* 5% absolute ethanol, except for I_3^- salt which was obtained by a diffusion technique (also containing 10% absolute ethanol).

References

1 M. Adam and K. Müllen, *Adv. Mater.*, 1994, **6**, 439.
2 H. Tatemitsu, E. Nishikawa, Y. Sakata and S. Misumi, *Synth. Met.*, 1987, **19**, 565; P. Wolf, H. Naarmann and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 288; M. Jørgensen, K. A. Lerstrup and K. Bechgaard, *J. Org. Chem.*, 1991, **56**, 5684; T. Tachikawa, A. Izuoka, R. Kumai, T. Sugawara and Y. Sugawara, *Solid State Commun.*, 1992, **82**, 19; T. Otsubo, Y. Kochi, A. Bitoh and F. Ogura, *Chem. Lett.*, 1994, 2047; E. Aqad, J. Y. Becker, J. Bernstein, A. Ellern, V. Khodorkovsky and L. Shapiro, *J. Chem. Soc., Chem. Commun.*, 1994, 2775.
3 Y. Misaki, H. Nishikawa, K. Kawakami, S. Koyanagi, T. Yamabe and M. Shiro, *Chem. Lett.*, 1992, 2321; Y. Misaki, H. Nishikawa, T. Yamabe, T. Mori, H. Inokuchi, H. Mori and S. Tanaka, *Chem. Lett.*, 1993, 729; Y. Misaki, T. Matsui, K. Kawakami, H. Nishikawa, T. Yamabe and M. Shiro, *Chem. Lett.*, 1993, 1337; Y. Misaki, H. Nishikawa, K. Kawakami, T. Yamabe, T. Mori, H. Inokuchi, H. Mori and S. Tanaka, *Chem. Lett.*, 1993, 2073; Y. Misaki, K. Kawakami, T. Matsui, T. Yamabe and M. Shiro, *J. Chem. Soc., Chem. Commun.*, 1994, 459.
4 Y. Misaki, H. Fujiwara and T. Yamabe, *J. Chem. Soc., Chem. Commun.*, 1993, 949.
5 (*a*) Y. Misaki, N. Higuchi, H. Fujiwara, T. Yamabe, T. Mori, H. Mori and S. Tanaka, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1222; (*b*) Y. Misaki, T. Ohta, N. Higuchi, H. Fujiwara, T. Yamabe, T. Mori, H. Mori and S. Tanaka, *J. Mater. Chem.*, 1995, **5**, 1571.
6 (*a*) T. Mori, H. Inokuchi, Y. Misaki, H. Nishikawa, T. Yamabe, H. Mori and S. Tanaka, *Chem. Lett.*, 1993, 2085; (*b*) Y. Misaki, H. Fujiwara, T. Yamabe, T. Mori, H. Mori and S. Tanaka, *Chem. Lett.*, 1994, 1653; (*c*) T. Mori, Y. Misaki, H. Fujiwara and T. Yamabe, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 2685; (*d*) T. Mori, Y. Misaki and T. Yamabe, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 3187; (*e*) T. Mori, Y. Misaki, T. Yamabe, H. Mori and S. Tanaka, *Chem. Lett.*, 1995, 549.
7 Z. Yoshida, H. Awaji and T. Sugimoto, *Tetrahedron Lett.*, 1984, **25**, 4227; T. Sugimoto, H. Awaji, I. Sugimoto, Y. Misaki, T. Kawase, S. Yoneda, Z. Yoshida, T. Kobayashi and H. Anzai, *Chem. Mater.*, 1989, **1**, 535.
8 T. Mori, H. Inokuchi, Y. Misaki, H. Nishikawa, T. Yamabe, H. Mori and S. Tanaka, *Chem. Lett.*, 1993, 733.

Received, 6th September 1995; Com. 5/05906B