Synthesis and Properties of New Tetrathiapentalene Donors Composed of Vinylogous TTFs

Shintaro Iwamoto,[1,†] Shunsuke Watanabe,[2] Hiroyuki Fueno,[2] Kazuyoshi Tanaka,[2] and Yohji Misaki*[1]
[1]*Department of Applied Chemistry, Graduate School of Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama 790-8577*
[2]*Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, and JST-CREST, Nishikyo-ku, Kyoto 615-8510*

(Received October 23, 2007; CL-071173; E-mail: misaki@eng.ehime-u.ac.jp)

A bis-fused donor composed of TTF vinylogues, 2,5-bis(2-ethanediylidene-1,3-dithiole)-1,3,4,6-tetrathiapentalene (BisEDT, **1a**) and its derivatives have been synthesized. Cyclic voltammograms of **1** consist of four-pairs of one-electron redox waves. X-ray structure analysis of tetrakis(methylthio)-**1** (**1b**) reveals the donor adopts almost planar structure. The $TCNQF_4$ complexes of **1** showed moderate conductivity of $\sigma_{rt} = 10^{-2}$ S cm^{-1} on a compressed pellet.

A bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP or simply TTP), is a promising π-electron framework for the development of organic metals stable down to low temperature, because it has yielded a large number of metallic radical cation salts retaining metallic conductivity down to liquid helium temperature.[1] Various TTP analogues with extended π-conjugation have been also synthesized,[2,3] and a vinylogous TTP analogue 2-(1,3-dithiol-2-ylidene)-5-(2-ethanediylidene-1,3-dithiole)-1,3,4,6-tetrathiapentalene (DTEDT) has afforded a superconducting $Au(CN)_2^-$ salt as well as stable metals with various counter anions.[2] In this context, a symmetrical TTP donor composed of two TTF vinylogues, 2,5-bis(2-ethanediylidene-1,3-dithiole)-1,3,4,6-tetrathiapentalene (BisEDT, **1a**) is of significant interest as a novel donor component for molecular metals, because it is expected to take two-dimensional (2D) molecular arrangement more effectively than DTEDT in the conducting materials. In this paper, we report synthesis and properties of BisEDT derivatives **1a**–**1c**, and their CT complexes (Chart 1).

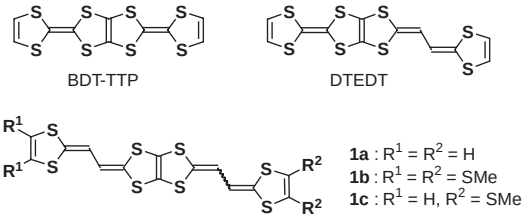
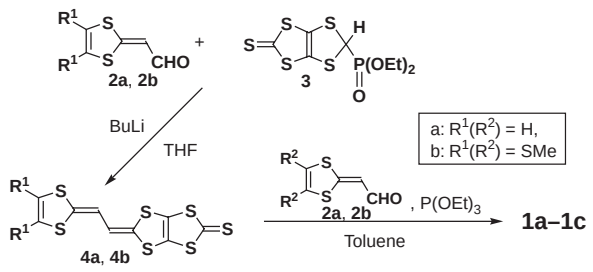


Chart 1.

Synthesis of BisEDT derivatives was carried out according to Scheme 1. The aldehydes **2a** and **2b**[4] were allowed to react with a 1,3-dithiole-2-thione with phosphonate ester **3**[5] in the presence of BuLi in THF at $-70\,^{\circ}$C. The triethylphosphite-mediated cross-coupling reaction between **4** and **2** in refluxing toluene gave the target molecules **1** in 48–59% yields.[6,7]

Electrochemical properties of **1a**–**1c** have been investigated by cyclic voltammetry. Cyclic voltammograms of all the derivatives consist of four pairs of one-electron redox waves, respectively in correspondence with the presence of four redox-active 1,3-dithiole rings. The first redox potential (E_1) of **1a** (-0.08 V vs. Fc/Fc^+ in PhCN) is negatively shifted by 0.06 V compared with that of BDT-TTP (-0.02 V) measured in the identical condition (Table 1). However, it is more positive by 0.09 V compared with that of **5a** in spite of extension of π-conjugation, and is comparable to those of DTEDT and **5c**. These results reveal that fusion of two vinylogous TTF units lowers the donating ability.[3,8] Furthermore, the E_1 values of **1a** and bis(methylthio) derivative **1c** are comparable to each other, while the tetrakis(methylthio) derivative **1b** has a more positive E_1 value (-0.03 V). On the basis of the results mentioned in this section, we think that a positive charge formed by the first one-electron oxidation mainly distributes on the one of the vinylogous TTF moiety, and the other unit of **5** acts as a sulfur-based substituent, as is observed in many TTP-type donors.



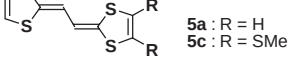
Scheme 1.

A single crystal of the tetrakis(methylthio) derivative **1b** was obtained by recrystallization from CS_2–THF, and the molecular structure was determined by X-ray diffraction analysis.[9] Figure 1 shows the molecular structure of **1b**. The molecule is located on a center of inversion, thus, configration of the two vinylogous TTF moieties adopts only a trans structure.[10] The π-electron framework of bisEDT is almost planar, while the four methyl groups orthogonally bent from the molecular plane. The molecules are uniformly stacked along the *c* axis (Figure 2a), and also form a sheet-like network along the *ac*

Table 1. Redox potentials of **1** and their related compounds (V vs. Fc/Fc^+, in PhCN containing 0.1 M Bu_4NPF_6)

Donor	E_1	E_2	E_3	E_4
1a	-0.08	0.08	0.23	0.46
1b	-0.03	0.09	0.30	0.49
1c	-0.07	0.07	0.28	0.51
BDT-TTP	-0.02	0.16	0.59[a]	0.67[a]
DTEDT	-0.09	0.04	0.35	0.59[a]
5a	-0.17	0.05		
5c	-0.09	0.07		

[a]Irreversible step. Anodic peak potentials.



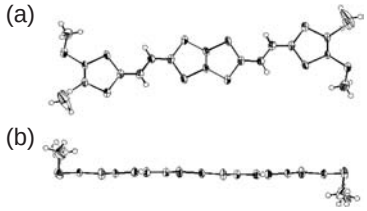


Figure 1. Molecular structure of **1b**, (a) projected onto the molecular plane and (b) viewed along the molecular short axis.

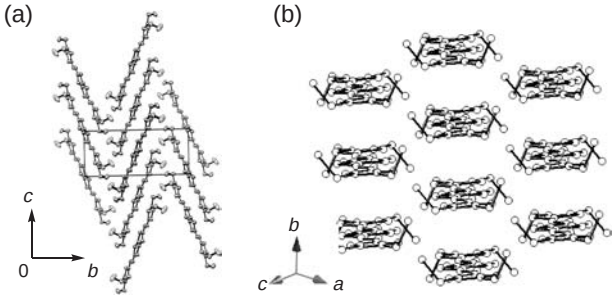


Figure 2. Crystal structure of **1b**, (a) viewed onto the *bc* plane and (b) viewed along the molecular long axis.

plane. The 2D packing pattern of **1b** molecules resembles to that of β-type molecular metals (Figure 2b). The half units of the molecules in the stack are effectively overlapped with each other, although the slip distance along the molecular long axis is quite large (10.4 Å). There are several short S···S contacts within the sum of van der Waals radii (3.70 Å) between the stacks, the shortest one being 3.504(2) Å. Thus, formation of 2D electronic structure in the conducting matrerials may be expected.

The molecular orbital calculation of the trans isomer of **1a** was carried out at the restricted Hartree–Fock theory with the 6-31G* basis set (RHF/6-31G*).[11] Figure 3 shows the highest occupied molecular orbital (HOMO) and the second HOMO (^{2nd}HOMO). The HOMO is composed of in-phase interaction between each HOMO of the TTF vinylogues. In contrast, ^{2nd}HOMO is constructed with out of phase interaction between HOMOs of each TTF vinylogue. Both the orbitals spread over the whole molecule. The larger molecular orbital coefficients at the sulfurs in the central tetrathiapentalene moiety are observed in the HOMO, while ^{2nd}HOMO has the larger molecular orbital coefficients at the sulfurs in the outer 1,3-dithiole rings. Considering the results that the HOMO has a_u symmetry, effective side-by-side interaction is expected in the conducting materials.

The $TCNQF_4$ complexes based on **1** were prepared by mixing of the donors with $TCNQF_4$ in hot chlorobenzene. Their electrical properties are summarized in Table 2. They showed moderate conductivity of $\sigma_{rt} = 10^{-2}\,S\,cm^{-1}$ on a compressed pellet. All the complexes exhibited semiconductive temperature

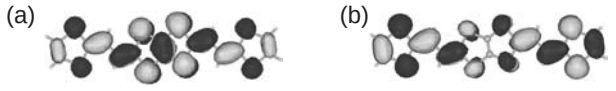


Figure 3. (a) HOMO and (b) 2nd HOMO of **1a**. The energy levels are −6.71 eV for HOMO and −7.18 eV for 2nd HOMO, respectively.

Table 2. Electrical properties of $TCNQF_4$ complexes of **1**

Donor	D:A[a]	σ_{rt}/S cm^{-1}[b]	E_a/V
1a	1:1	3.1×10^{-2}	0.14
1b	2:5	1.0×10^{-2}	0.15
1c	3:4	2.0×10^{-2}	0.18

[a]Determined by elemental analysis. [b]Measured on a compressed pellet by using four-probe technique.

dependence, and the activation energies were relatively high values of 0.14–0.18 eV. The further investigation, in particular, preparation of single crystals of molecular conductors based on BisEDT derivatives is actively in progress.

The calculation was carried out at Research Center for Computational Science. This work is partially supported by a Grant-in-Aid for Scientific Research (Nos. 15073216, 16350100, and 18GS0208) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and Japan Society for the Promotion of Science, and by Ehime University COE incubation program.

References and Notes

† Present address: Central Research Laboratories, Idemitsu Kosan Co., Ltd., Sodegaura, Chiba 299-0293.

1 Y. Misaki, H. Fujiwara, T. Yamabe, T. Mori, H. Mori, S. Tanaka, *Chem. Lett.* **1994**, 1653; T. Mori, Y. Misaki, H. Fujiwara, T. Yamabe, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2685; Y. Misaki, T. Kochi, T. Yamabe, T. Mori, *Adv. Mater.* **1998**, *10*, 588; A. Deluzet, P. Batail, Y. Misaki, P. Auban-Senzier, E. Canadell, *Adv. Mater.* **2000**, *12*, 436; Y. Misaki, in *TTF Chemistry-Fundamental and Applications of Tetrathiafulvalene*, ed. by J. Yamada, T. Sugimoto, Kodansha-Springer, **2004**, Chap. 10, pp. 225–257.

2 Y. Misaki, N. Higuchi, H. Fujiwara, T. Yamabe, T. Mori, H. Mori, S. Tanaka, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1222; Y. Misaki, N. Higuchi, T. Ohta, H. Fujiwara, T. Yamabe, T. Mori, H. Mori, S. Tanaka, *Mol. Cryst. Liq. Cryst.* **1996**, *284*, 27.

3 Y. Misaki, T. Sasaki, T. Ohta, H. Fujiwara, T. Yamabe, *Adv. Mater.* **1996**, *8*, 804; Y. Misaki, T. Kaibuki, K. Takahashi, H. Tanioka, K. Tanaka, *Mol. Cryst. Liq. Cryst.* **2002**, *380*, 151; Y. Misaki, Y. Natsume, K. Takahashi, H. Fueno, K. Tanaka, *Synth. Met.* **2003**, *135–136*, 671; K. Takahashi, H. Tanioka, H. Fueno, Y. Misaki, K. Tanaka, *Chem. Lett.* **2002**, 1002.

4 T. Sugimoto, H. Awaji, I. Sugimoto, Y. Misaki, T. Kawase, S. Yoneda, Z. Yoshida, T. Kobayashi, H. Anzai, *Chem. Mater.*, **1989**, *1*, 535; A. J. Moore, M. R. Bryce, *Tetrahedron Lett.* **1992**, *33*, 1373.

5 Y. Misaki, H. Nishikawa, K. Kawakami, T. Uehara, T. Yamabe, *Tetrahedron Lett.* **1992**, *33*, 4321.

6 T. Imakubo, T. Iijima, K. Kobayashi, R. Kato, *Synth. Met.* **2001**, *120*, 899.

7 **1a**: 57% yield; green-yellow powder; mp 215.0–215.5 °C (dec.); ^{1}H NMR (CS_2–C_6D_6) δ 6.07 (d, 2H), 6.03 (d, 2H), 5.89 (d, 2H), 5.70 (d, 2H); MS (EI, *m*/*z*) 432 (M^+). **1b**: 66% yield; green-yellow powder; mp 216.5–217.5 °C (dec.); ^{1}H NMR (CS_2–C_6D_6) δ 6.07 (d, 2H), 6.03 (d, 2H), 5.80–5.60 (m, 2H), 2.31 (s, 6H); HRMS (FAB, *m*/*z*) calcd. for $C_{16}H_{12}S_{10}$ (M^+) 523.8146, found 523.8141. **1c**: 71% yield; yellow-brown powder; mp 210.0–211.5 °C (dec.); ^{1}H NMR ($CDCl_3$) δ 5.81 (d, 2H), 5.62 (d, 2H), 2.22 (s, 12H); MS (EI, *m*/*z*) 616 (M^+).

8 Y. Misaki, T. Matsui, K. Kawakami, H. Nishikawa, T. Yamabe, M. Shiro, *Chem. Lett.* **1993**, 1337.

9 Crystal data of **1c**: monoclinic, space group $P2_1/c$, $a = 7.486(3)$, $b = 19.419(8)$, $c = 8.545(4)$ Å, $\beta = 94.541(2)^\circ$, $V = 1238.2(9)$ Å^3, $Z = 2$, $R = 0.048$, $R_w = 0.063$ for observed 4211 reflections ($I > 3\sigma(I)$). Supporting Information is electronically available on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

10 We think only the trans isomer crystalizes from cis/trans mixture so that an effective packing of the molecules can be achieved.

11 The molecular orbital calculation was carried out using the Gaussian 98 program. M. J. Frish et al., Gaussian 98, Gaussian, Inc., Pittsburgh, PA (1998).

Published on the web (Advance View) December 15, 2007; doi:10.1246/cl.2008.82