Structures and Electrical Properties of β- and θ-(BTM-TTP)$_2$SbF$_6$

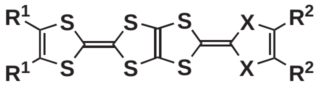
Manami Noda,[1,2] Misaki Yasuda,[1] Yoshiaki Nakano,[2] Akihiro Ito,[2,3] Hiroyuki Fueno,[2,3] Kazuyoshi Tanaka,[2,3]
Hideki Fujiwara,[3,4] Toyonari Sugimoto,[3,4] and Yohji Misaki*[1]
[1]*Department of Applied Chemistry, Graduate School of Science and Engineering, Ehime University,*
3 Bunkyo-cho, Matsuyama 790-8577
[2]*Department of Molecular Engineering, Graduate School of Engineering, Kyoto University,*
Nishikyo-ku, Kyoto 615-8510
[3]*JST-CREST*
[4]*Department of Chemistry, Graduate School of Science, Osaka Prefecture University,*
Gakuen-cho, Sakai, Osaka 599-8570

(Received December 17, 2007; CL-071398; E-mail: misaki@eng.ehime-u.ac.jp)

Two kinds of (BTM-TTP)$_2$SbF$_6$ salts, where BTM-TTP is 2-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene, have been prepared. X-ray structure analyses have revealed that needle-like and plate-like crystals have the so-called β- and θ-type arrays of the donors, respectively. The β-type salt exhibits metallic conducting behavior down to 5 K, while the θ-type salt is a semiconductor even at room temperature.

A bis-fused TTF donor, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP) has played an important role to explore novel molecular conductors.[1] BDT-TTP and its derivatives have actually yielded a large number of molecular complexes retaining their metallic conductivity down to liquid helium temperature.[2] X-ray structure analyses of various BDT-TTP salts have revealed that BDT-TTP has tendency to form a uniform β-type molecular packing.[2,3] On the other hand, the other molecular packing patterns have been observed when appropriate substituents are introduced on BDT-TTP framework. For example, fusion with a cyclohexene ring results in the formation of a non-stacked κ-type molecular packing.[4] In contrast, TMEO-ST-TTP has yielded various radical cation salts with a strongly dimerized β-type molecular packing,[5] while EO-TTP has afforded β-type salts with uniform stacks.[6] In this connection, the elucidation of substitution effect of methylthio groups on the molecular packing of TTP conductors is of interest. Although the synthesis of bis(methylthio)-TTP (BTM-TTP) has been reported in 1993,[7] there has been only two examples of BTM-TTP conductors whose crystal structures have been determined.[8,9] In this letter, we report herewith structures and electrical properties of two kinds of (BTM-TTP)$_2$SbF$_6$ salts (Chart 1).

Two kinds of single crystals (needles and plates) of BTM-TTP salts were obtained by an electrocrystallization technique at a controlled current method[10] from 0.2 to 1.0 µA in the presence of PPN•SbF$_6$, where PPN is bis(triphenylphosphoranylidene)ammonium, as the electrolyte in chlorobenzene at room temperature. The needle salt crystallizes in a triclinic system, while the plate one in monoclinic one. X-ray structure analyses indicate both salts have the same stoichiometry of (BTM-TTP)$_2$SbF$_6$.[11,12] Among them, the needle salt is isostructural with the reported (BTM-TTP)$_2$TaF$_6$ salt.[9] The packing pattern of the donors is classified with the so-called β-type as shown in Figure 1a. Thus, the donors form face-to-face stacks along the (*a*–*b*) direction with interplanar distances of 3.48 (*p*1) and 3.51 (*p*2) Å, respectively. The donors are overlapped in a head-to-tail manner in the stack (Figure 1b). Both the slip distances along the



$R^1 = R^2 = H$, X = S, BDT-TTP
$R^1 = H$, $2R^2 = OCH_2CH_2O$, X = S, EO-TTP
$2R^1 = OCH_2CH_2O$, $R^2 = SMe$, X = Se, TMEO-ST-TTP
$R^1 = H$, $R^2 = SMe$, X = S, BTM-TTP
$2R^1 = SCH_2CH_2S$, $R^2 = SMe$, X = S, TMET-TTP

Chart 1.

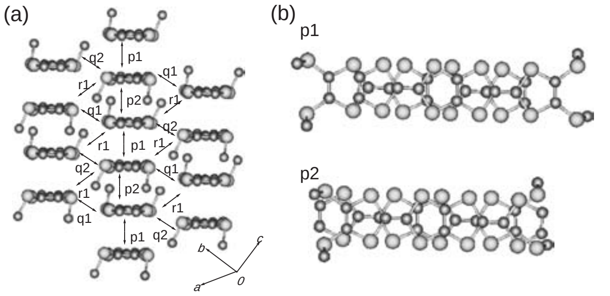


Figure 1. (a) Donor sheet structure of β-(BTM-TTP)$_2$SbF$_6$ viewed along the donor long axis, and (b) overlap mode in the stack. The intermolecular overlaps between HOMOs are $p1 = 22.7$, $p2 = 25.5$, $q1 = -3.5$, $q2 = -3.2$, $r1 = -6.7 \times 10^{-3}$.

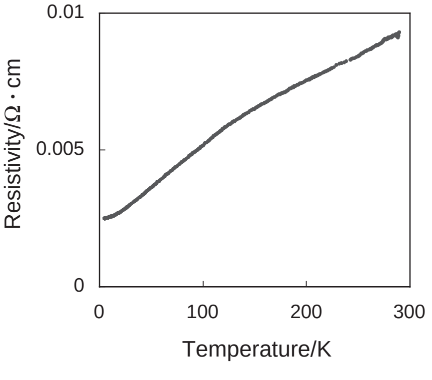


Figure 2. Conducting behavior of β-(BTM-TTP)$_2$SbF$_6$.

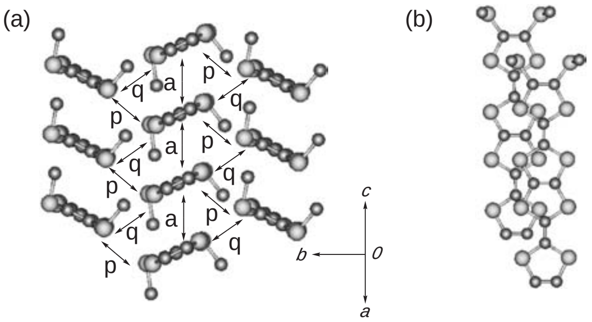


Figure 3. (a) Conducting sheet structure of θ-(BTM-TTP)$_2$SbF$_6$ viewed along the donor long axis. The intermolecular overlaps between HOMOs are $a = 7.7$, $p = 6.5$, $q = 3.6 \times 10^{-3}$, and (b) the overlap mode of the donors in the stack.

donor long axis ($p1$ and $p2$) are about a half (1.6 Å) of the length of a 1,3-dithiole ring. It is noted that BTM-TTP molecules form a nearly uniform column in spite of the presence of bulky methylthio groups. The calculation of overlap integrals[13,14] indicates that the donors are slightly dimerized in the stack. On the other hand, the interstack overlap integrals are 14–26% of the larger intrastack one ($p2$). A tight binding calculation showed that the width of the conduction band is relatively large (1.1 eV). The calculated Fermi surface is open, being characteristic of quasi one-dimensionality.[12] This salt showed a high conductivity of $\sigma_{\rm rt} = 120\,{\rm S\,cm^{-1}}$ and exhibited metallic temperature dependence of resistivity down to 5 K (Figure 2).

On the other hand, the plate-like crystal adopts the so-called θ-type arrangement of the donors as shown in Figure 3a. The donors are uniformly stacked along the a axis with an interplanar distance of 3.44 Å. The donors slip along both the donor short and long axes (Figure 3b), in contrast to θ-BEDT-TTF salts,[15] in which only the slip along the donor short axis is observed. A similar phenomenon has been also observed in θ-TMET-TTP salts.[16] The dihedral angle of the donors between the neighboring columns is a large value of 130.7°, indicating smaller overlap integrals compared with those of the θ-salts with smaller dihedral angles.[17] The calculated bandwidth (0.57 eV) is about half of that of β-(BTM-TTP)$_2$SbF$_6$ (1.1 eV). The calculated Fermi surface is closed characteristic of two-dimensional metal.[12] However, this salt exhibited a relatively low conductivity of $\sigma_{\rm rt} = 0.8\,{\rm S\,cm^{-1}}$ and showed semiconductive temperature dependence with $E_{\rm a} = 0.13\,{\rm eV}$. Semiconductive behavior in spite of the calculated two-dimensional Fermi surface is probably dueto narrow bandwidth and resultant large electron correlation in the quarter-filled band system, because the band calculation used here contains no electron correlation.[13] The static magnetic susceptibility of θ-(BTM-TTP)$_2$SbF$_6$ at 300 K after the correction of diamagnetic contribution is $8.3 \times 10^{-4}\,{\rm emu\,mol^{-1}}$, suggesting a highly correlated electronic state. It exhibits the Curie–Weiss temperature dependence with a weak antiferromagnetic interaction of $\theta = -6\,{\rm K}$ and a Curie constant of $C = 0.23\,{\rm emu\,K\,mol^{-1}}$.[12] The fact that the observed magnetic susceptibility is smaller than the theoretical value of isolated $S = 1/2$ spin suggests that the electrons are weakly (or not completely) localized. The similar phenomena are also reported in θ-(BEDT-TTF)$_2$(Rb$_{1-x}$Cs$_x$)Zn(SCN)$_4$[18] and β''-(DODHT)$_2$PF$_6$.[19,20] This is consistent with the semiconducting behavior of θ-(BTM-TTP)$_2$SbF$_6$.

In summary, two kinds of molecular conductors have been obtained from BTM-TTP with the SbF$_6{}^-$ anion. The results obtained from this work indicate that BTM-TTP shows no self-aggregating property in contrast to a number of TTP donors. The further investigations, in particular, correlation between molecular structures and molecular packing patterns by means of theoretical calculation are actively in progress.

We are grateful to Dr. Hengbo Cui, Dr. Kazuyuki Takahashi, and Prof. Hayao Kobayashi (Institute for Molecular Science, Japan) for X-ray structure analyses by use of a Rigaku AFC-8 MERCURY CCD system. 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, by Japan Society for the Promotion of Science, and by Ehime University COE incubation program.

References and Notes

1 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, H. Fujiwara, T. Yamabe, T. Mori, H. Mori, S. Tanaka, *Chem. Lett.* **1994**, 1653.
3 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.
4 Y. Misaki, T. Miura, M. Taniguchi, H. Fujiwara, T. Yamabe, T. Mori, H. Mori, S. Tanaka, *Adv. Mater.* **1997**, *9*, 714.
5 Y. Misaki, M. Taniguchi, K. Tanaka, K. Takimiya, A. Morikami, T. Otsubo, T. Mori, *J. Solid State Chem.* **2002**, *168*, 608.
6 Y. Misaki, K. Tanaka, M. Taniguchi, T. Yamabe, T. Kawamoto, T. Mori, *Chem. Lett.* **1999**, 1249.
7 Y. Misaki, H. Nishikawa, T. Yamabe, T. Mori, H. Inokuchi, H. Mori, S. Tanaka, *Chem. Lett.* **1993**, 729.
8 T. Mori, K. Murata, Y. Misaki, K. Tanaka, *Chem. Lett.* **1998**, 435.
9 M. Noda, Y. Misaki, K. Tanaka, *Curr. Appl. Phys.* **2006**, *6*, 943.
10 H. Anzai, J. M. Delrieu, S. Takasaki, S. Nakatsuji, J. Yamada, *J. Cryst. Growth* **1995**, *154*, 145.
11 Crystal data for β-(BTM-TTP)$_2$SbF$_6$: triclinic, space group $P\bar{1}$, $a = 7.294(3)$, $b = 7.551(4)$, $c = 20.158(12)$ Å, $\alpha = 91.86(3)$, $\beta = 98.96(3)$, $\gamma = 62.64(2)°$, $V = 973.0(9)$ Å^3, $Z = 1$, $R = 0.058$, $R_w = 0.080$ for 2924 ($I \geq 3\sigma(I)$) observed reflections from 8055 unique data; θ-(BTM-TTP)$_2$SbF$_6$: space group $P2_1/n$, $a = 4.9683(2)$, $b = 10.9242(5)$, $c = 36.092(1)$ Å, $\beta = 90.080(1)°$, $V = 1958.9(1)$ Å^3, $Z = 2$, $R = 0.090$, $R_w = 0.10$ for 1878 ($I \geq 2\sigma(I)$) observed reflections from 3968 unique data.
12 Supporting Information is electronically available on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
13 T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, H. Inokuchi, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 627.
14 The sulfur 3d atomic orbitals are included in the calculation.
15 H. Kobayashi, R. Kato, A. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita, W. Sasaki, *Chem. Lett.* **1987**, 459.
16 T. Mori, H. Inokuchi, Y. Misaki, H. Nishikawa, T. Yamabe, H. Mori, S. Tanaka, *Chem. Lett.* **1993**, 733; T. Mori, M. Ashizawa, M. Aragaki, K. Murata, Y. Misaki, K. Tanaka, *Chem. Lett.* **1998**, 253; M. Aragaki, H. Hoshino, T. Mori, Y. Misaki, K. Tanaka, H. Mori, S. Tanaka, *Adv. Mater.* **2000**, *12*, 983.
17 H. Mori, S. Tanaka, T. Mori, *Phys. Rev. B* **1998**, *57*, 12023.
18 H. Mori, T. Okano, S. Tanaka, M. Tamura, Y. Nishio, K. Kajita, T. Mori, *J. Phys. Soc. Jpn.* **2000**, *69*, 1751.
19 H. Nishikawa, Y. Sato, K. Kikuchi, T. Kodama, I. Ikemoto, J. Yamada, H. Oshio, R. Kondo, S. Kagoshima, *Phys. Rev. B* **2005**, *72*, 052510.
20 DODHT is (1,4-dioxane-2,3-diyldithio)dihydrotetrathiafulvalene.

Published on the web (Advance View) March 1, 2008; doi:10.1246/cl.2008.396