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Structures and Electrical Properties of $(BTM\text{-}TS\text{-}TTP)_4PF_6$

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$(BTM\text{-}TS\text{-}TTP)_4PF_6$, where BTM-TS-TTP is 2-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-5-(1,3-diselenol-2-ylidene)-1,3,4,6-tetrathiapentalene, has been prepared. An X-ray structure analysis reveals that it has a λ-type array of the donors. It exhibited metallic conducting behavior down to 5 K.

Considerable effort has been devoted to explore molecular materials exhibiting exotic electronic properties such as electrical, magnetic, and optical properties. In particular, the construction of molecular metals with multidimensional electronic structures is of significant interest to realize metallic conductivity down to low temperature.[1,2] We have reported that a bis-fused TTF donor, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP) (Chart 1) and its derivatives have produced a large number of molecular complexes exhibiting metallic conducting behavior down to liquid helium temperature.[3–16] Although BDT-TTP itself has a strong tendency to form a uniform β-type molecular packing,[5–9] the introduction of appropriate substituents on the BDT-TTP framework results in the adoption of the other molecular packings.[10–15] We have recently reported that bis(methylthio)-TTP (BTM-TTP) has afforded two types of the SbF_6^- salts with β- and θ-type molecular packings.[16] In usual TTP conductors, the exchange of sulfur atoms with selenium atoms does not affect their molecular packing.[7,8,15] In contrast, we have found that BTM-TS-TTP, a selenium analog of BTM-TTP, affords a radical cation salt with molecular packing different from those of BTM-TTP salts. In this paper, we report the structures and electrical properties of a new molecular metal, $(BTM\text{-}TS\text{-}TTP)_4PF_6$.

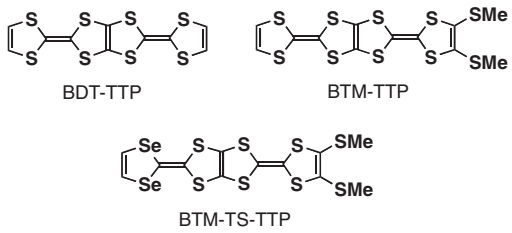

Chart 1.

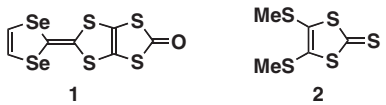

Chart 2.

Synthesis of BTM-TS-TTP was carried out by $P(OMe)_3$-mediated coupling reaction between the 1,3-dithiol-2-one derivative **1**[8] fused with diselenadithiafulvalene and 4,5-bis(methylthio)-1,3-dithiole-2-thione (**2**) in refluxing toluene (28% yield) (Chart 2). Cyclic voltammogram of BTM-TS-TTP measured in benzonitrile consisted of four pairs of redox waves at 0.05, 0.28, 0.59, and 0.73 V (vs. Fc/Fc^+, at 25 °C). An electrocrystallization of BTM-TS-TTP using $^nBu_4N\cdot PF_6$ as the electrolyte in 1,2-dichloroethane at room temperature gave slender rectangular plate-like single crystals.

An X-ray structure analysis[17] of the present salt reveals that two BTM-TS-TTP molecules (A and B) are crystallographically independent. Two methylthio groups in the molecule B are orientationally disordered, while those in the molecule A are ordered. On the other hand, one PF_6^- anion is located on a center of inversion. Thus, the stoichiometry of the present salt can be determined as $(BTM\text{-}TS\text{-}TTP)_4PF_6$. The crystal structure of $(BTM\text{-}TS\text{-}TTP)_4PF_6$ is shown in Figure 1. The donors form conducting sheets in the *ab* plane. The anions exist between the donor layers, but there are small HOMO–HOMO interactions between the donor layers through the space of anion layers. The calculated interlayer overlap integrals between HOMOs are $c1 = 0.08 \times 10^{-3}$, $c2 = 0.20 \times 10^{-3}$. The packing pattern of the donors is λ-type (Figure 2).[18] Two crystallograpically independent molecules A and B form a stack with a fourfolded period as the pattern of A′–A–B–B′.[19] The interplanar distances are 3.59, 3.53, and 3.57 Å for A–A′, B–B′, and A–B, respectively (Figure 3a). The unsymmetrical donor molecules overlap in a head-to-tail manner for A–A′ and B–B′, and in a

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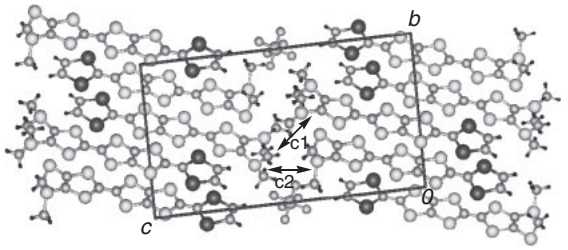

Figure 1. Crystal structure of $(BTM\text{-}TS\text{-}TTP)_4PF_6$ projected onto the *bc* plane. The calculated overlap integrals are $c1 = 0.08 \times 10^{-3}$, $c2 = 0.20 \times 10^{-3}$.

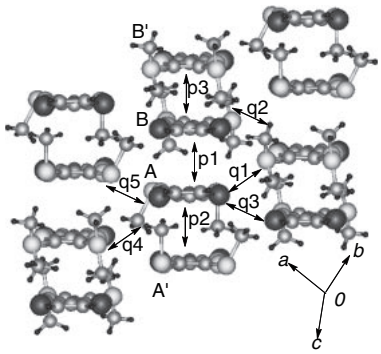

Figure 2. Donor sheet structure of $(BTM\text{-}TS\text{-}TTP)_4PF_6$ viewed along the molecular long axis. The calculated overlap integrals are $p1 = 24.3 \times 10^{-3}$, $p2 = 35.5 \times 10^{-3}$, $p3 = 27.5 \times 10^{-3}$, $q1 = -5.5 \times 10^{-3}$, $q2 = 0.8 \times 10^{-3}$, $q3 = 0.4 \times 10^{-3}$, $q4 = -9.6 \times 10^{-3}$, $q5 = 2.9 \times 10^{-3}$.

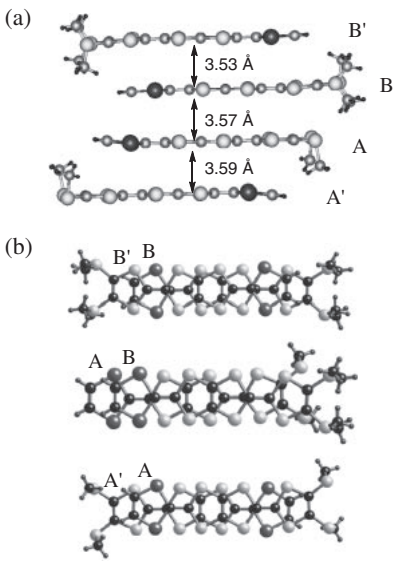

Figure 3. (a) Stacking structure of $(BTM\text{-}TS\text{-}TTP)_4PF_6$ viewed along the molecular short axis, and (b) overlap modes in the stack.

head-to-head manner for A–B (Figure 3b). The slip distances along the donor long axis are about a half-length of a 1,3-dithiole ring (1.6–1.7 Å) for all the overlaps. The calculated overlap integrals between the HOMOs in the stack are 24.3×10^{-3}–35.5×10^{-3}. On the other hand, the largest side-by-side interaction ($q4 = -9.6 \times 10^{-3}$) is 27–40% of the intrastack interactions. The calculated Fermi surface[20] is closed

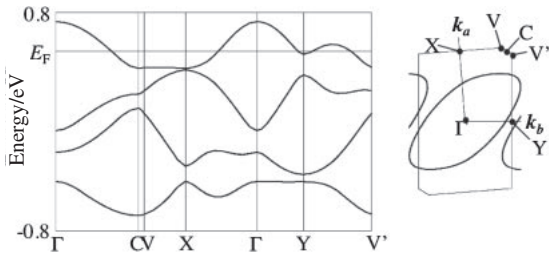

Figure 4. The calculated energy dispersion and Fermi surface of $(BTM\text{-}TS\text{-}TTP)_4PF_6$.

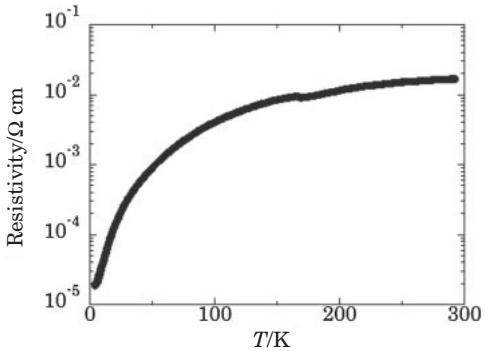

Figure 5. Conducting behavior of $(BTM\text{-}TS\text{-}TTP)_4PF_6$.

and is characteristic of two-dimensional metals as shown in Figure 4.

The electrical conductivity of the present salt was measured on a single crystal using a four-probe technique. Figure 5 shows temperature dependence of electrical resistivity. The room-temperature conductivity was a high value of $\sigma_{rt} = 60\ S\ cm^{-1}$. This salt exhibited metallic temperature dependence of resistivity down to 5 K. It is noted that the ratio of the resistivity at room temperature to that at 5 K ($R_{rt}/R_{5K} = 880$) is very large, suggesting the quite stable metallic state of this salt.

In summary, we have developed a new molecular metal stable down to low temperature. Crystal growth of BTM-TS-TTP conductors with other counter anions is actively in progress.

Experimental

General. Trimethyl phosphite was dried over sodium and then distilled under argon. Toluene was dried over calcium hydride and then distilled. 1,2-Dichloroethane was purified with concentrated hydrogen sulfate, and then washed with distilled water, followed by distillation under argon. Melting point was determined with a Yanaco MP-J3 micro melting point apparatus and not corrected. Elemental microanalysis was performed at Integrated Center for Sciences, Ehime University. NMR spectrum was recorded on a JEOL FT-NMR Model NM-SCM270 (270 MHz for ^1H) spectrometer, and chemical shift values are given in parts per million (ppm) relative to internal tetramethylsilane. IR spectrum was recorded on JASCO FT/IR-4200 spectrometer.

Synthesis of BTM-TS-TTP. To a suspension of 2-(1,3-diselenol-2-ylidene)-1,3,4,6-tetrathiapentalen-5-one (**1**) (200 mg, 0.515 mmol) and 4,5-bis(methylthio)-1,3-dithiole-2-thione (**2**) (174 mg, 0.770 mmol) in toluene (10 mL) was added trimethyl phosphite (10 mL). The reaction mixture was stirred for 2 h at refluxing temperature, and then cooled down to room temperature. The resultant reddish brown precipitate was filtered, washed with *n*-hexane, and then dried in vacuo. The residue was column chro-

matographed on silica gel with CS_2 as the eluent to afford BTM-TS-TTP (82 mg, 0.14 mmol) as dark red crystals in 28% yield. Mp 199–201 °C (dec.); IR (KBr): 2918, 1638, 1422, 1385 cm^{-1}; ^1H NMR (CS_2–C_6D_6): δ 7.09 (s, 2H), 2.40 (s, 6H); Anal. Calcd for $C_{12}H_8S_8Se_2$: C, 25.44; H, 1.42%. Found: C, 25.38; H, 1.51%.

Preparation of Radical Cation Salt. Black plate-like crystals were electrochemically grown at 50 °C in 1,2-dichloroethane (17 mL) containing ethanol (1 mL, ca. 5%) in the presence of the donor (5 mg) and tetra-*n*-butylammonium hexafluorophosphate (33 mg) using an H-type glass cell fitted with two platinum electrodes. The current was changed stepwise from 0.2 to 0.7 μA during electrocrystallization (1–2 weeks).[21]

Electrochemical Measurement. The cyclic voltammetry system used in this experiment was composed of an ALS/chi 617B Electrochemical Analyzer. The measurement was performed in benzonitrile containing a donor molecule (0.3 mM) and tetra-*n*-butylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte by use of platinum working and counter electrodes and Ag/Ag^+ reference electrode (scan rate: 50 mV s^{-1}). The redox potentials were calculated using the redox potential of ferrocene as the standard potential measured under identical conditions.

X-ray Structure Analysis. A black plate crystal was used for X-ray measurements at 296 K on a Rigaku AFC-8 Mercury CCD diffractometer with a confocal X-ray mirror system (Mo Kα radiation; $\lambda = 0.7107$ Å). The structure was solved by a direct method (*SIR92*),[22] expanded by *DIRDIF94*,[23] and refined on F^2 with full-matrix least-squares analysis. Calculated positions of the H atoms [d(C–H) = 0.95 Å] were included but not refined in the final calculations. All of the calculations were performed using the *CrystalStructure* crystallographic software package of the Molecular Structure Corp.[24] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-795549. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Band Calculation. The tight-binding band structure was calculated on the basis of the extended Hückel approximation, according to which the transfer integrals are assumed to be proportional to the intermolecular overlap integrals of frontier molecular orbitals. The basis set consisted of Slater-type orbital single-ζ quality for Se 4s, 4p, and 4d; S 3s, 3p, and 3d; C 2s and 2p; and H 1s orbitals.

Slater type atomic orbitals were used for the calculation of molecular orbitals. The exponent ζ and the ionization potential (eV) are: Se 4s, 2.112, −1.470; Se 4p, 1.827, −0.808; Se 4d, 1.500, −0.500; S 3s, 2.122, −1.470; S 3p, 1.827, −0.808; S 3d, 1.500, −0.400; C 2s, 1.625, −1.573; 2p, 1.625, −0.838; H 1s, 1.0–1.000.

Electrical Conductivity Measurement. The electrical conductivity was measured by four-probe technique with low-frequency alternating current using a Huso Electro Chemical System HECS 994 Multichannel 4-terminal conductometer. Electrical contacts were achieved with gold paste.

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17 Crystal data for $(BTM\text{-}TS\text{-}TTP)_4PF_6$: triclinic, space group $P\bar{1}$, $a = 7.8384(11)$, $b = 11.815(2)$, $c = 20.990(3)$ Å, $\alpha = 91.908(10)$, $\beta = 99.889(9)$, $\gamma = 85.459(10)°$, $V = 1908.5(5)$ $Å^3$, $Z = 2$, $R1 = 0.0415$, $wR_2 = 0.0858$ for 4059 observed reflections ($I > 2.00\sigma(I)$).

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