A Novel Organic Conductor with Three-Dimensional Molecular Array: $(TM\text{-}TPDS)_2AsF_6$

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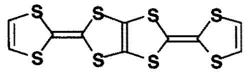
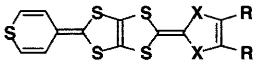
The title material, where TM-TPDS is 2-[4,5-bis(methylthio)-1,3-diselenol-2-ylidene]-5-(thiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene, has three-dimensional (3D) donor array, in which 1D donor columns are tetragonally arranged with each other. It shows metal-like conducting behavior down to T_{MI} = 100 K.

In the development of molecular conductors,[1] realization of three-dimensional (3D) electronic structure has received considerable attraction since discovery of C_{60} based superconductors.[2] The importance of increasing 3D character through insulating anion layer has also been pointed out for realization of higher T_c in BEDT-TTF superconductors.[3] However, examples of 3D molecular metals other than C_{60} salts are quite limited. Existence of 3D Fermi surface in molecular systems has been experimentally observed only in $Cu(DMDCNQI)_2$ (DMDCNQI: 2,5-dimethyl-1,4-dicyanoquinodiimine)[4] and θ-$(BEDT\text{-}TTF)_2I_3$,[5] in which the frontier orbitals of the inorganic counter ions also participate in their Fermi surfaces. On the other hand, 3D Fermi surface based on only organic molecule has not been observed yet, but been theoretically suggested by a band calculation in a metal dithiolene system, $Me_xH_{4-x}N[Pd(dmise)_2]_2$ (dmise: dimercapto-1,3-dithiole-2-selone).[6] We have reported that 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (TTP) derivatives and their analogs have afforded a large number of stable metals down to liquid helium temperature with 2D conducting sheets.[7] In this connection, 2-(1,3-dithiol-2-ylidene)-5-(thiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (TPDT-TTP)[8] is a promising π-electron framework to explore 3D conductors because the sulfur atom in the thiopyran ring could play a role for realizing considerable interaction along the donor long axis. We report herein structures and properties of a metallic radical cation salt having 3D molecular array based on a TPDT-TTP derivative, 2-[4,5-bis(methylthio)-1,3-diselenol-2-ylidene)-5-(thiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (TM-TPDS).[9]



TTP



X = S, R = H, TPDT-TTP
X = Se, R = SMe, TM-TPDS

Single crystals of $(TM\text{-}TPDS)_2AsF_6$ were grown by an electrochemical oxidation of TM-TPDS in the presence of tetrabutylammonium hexafluoroarsenate in 1,2-dichloroethane or chlorobenzene containing 5%(v/v) ethanol at 50 °C. Its crystal structure was determined by X-ray structure analysis.[10] The present salt does not form two-dimensional conducting sheet in contrast to usual TTP conductors as shown in Figure 1. Instead, the donors are arranged in a "windmill" manner in the *bc* plane, while they are stacked along the *a* axis. The anions are located on a cavity formed in the center of "windmill", and are surrounded by hydrogen atoms in the methylthio groups and thiopyran ring in the donors. The unsymmetrical TM-TPDS molecules are stacked alternately along the *a* axis, and are slightly dimerized with the interplanar distances of 3.52 and 3.64 Å, respectively. The both overlap modes in the stack are the so-called ring-over-bond type, and the slip distance along the molecular long axis is 1.8 and 0.9 Å, respectively. On the other hand, there are many sulfur–sulfur contacts shorter than the sum of van der Waals radii (3.60 Å) between the central tetrathiapentalene moiety and the thiopyran ring or methylthio groups. The shortest one is a quite small value of 3.42 Å (S1–S5, see Figure 1).

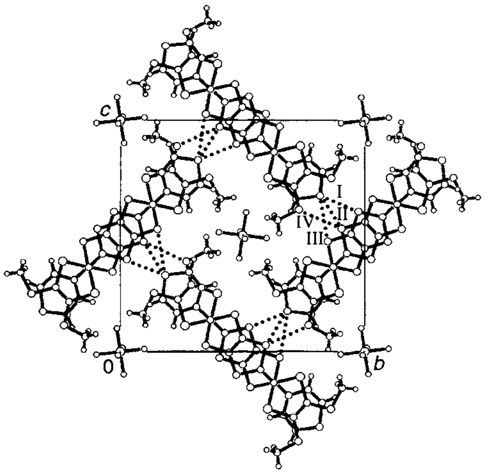


Figure 1. Crystal structure of $(TM\text{-}TPDS)_2AsF_6$ onto the *bc* plane showing intermolecular S-S contacts (≤3.60 Å) with dotted lines; I = 3.42 Å for S(1)-S(5), II = 3.57 Å for S(1)-S(4), III = 3.56 Å for S(1)-S(3), and IV = 3.57 Å for S(4)-S(7)

Similar windmill type array of donors has also been found in $TTF(A)_x$ (A = Cl, Br, I, x = 0.72–0.77)[11] and the ClO_4^- and PF_6^- salts of **1**.[12] However, the electronic structures of the above two systems should be completely 1D in spite of 3D array of the donors. Namely, there is little intercolumn π–π interaction owing to prevention from hydrogen atoms for the former, and to almost zero coefficient on the outer sulfur atoms in the HOMO of the donor for the latter. In contrast, molecular orbital coefficient of the sulfur in the thiopyran-4-ylidene moiety of TPDT-TTP is comparable to those in the 1,3-dithiole rings.[8] Thanks to such a large molecular orbital coefficient of the sulfur atom in the thiopyran ring as well as short sulfur–sulfur contacts, the calculated overlap integrals[13] between clolumns are as large as approx-

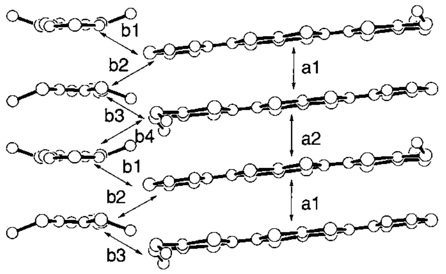
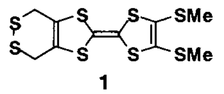


Figure 2. Donor column structure and definition of the overlap integrals of $(TM\text{-}TPDS)_2AsF_6$. The intermolecular overlap integrals are a1 = 20.8, a2 = 19.2, b1 = 0.9, b2 = 0.2, b3 = 2.2 b4 = 2.3 x 10^{-3}.



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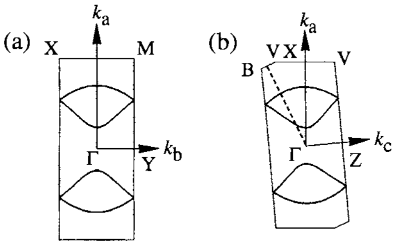

Figure 3. (a) Calculated Fermi surfaces of $(TM\text{-}TPDS)_2AsF_6$ in the k_a-k_b plane, and (b) in the k_a-k_c plane.

imately 10% of the intracolumn overlaps (Figure 2). However, the calculated Fermi surface is closed only along the k_a direction because intrastack interactions are still dominant in the present salt (Figure 3).[14]

The electrical conductivity of $(TM\text{-}TPDS)_2AsF_6$ was measured on a single crystal using a four-probe technique along the stacking direction. The conductivity at room temperature is very high value of 240 S cm^{-1}. It exhibited metal-like temperature dependence down to 100 K. Below this temperature, the resisitivity gradually increased (Figure 4). The critical temperature of metal to semiconductor transition decreased a little as the pressure increased, however, this transition could not be suppressed even at 11 kbar. This metal to semiconductor transition should not be a Peierls transition derived from highly 1D character because no obvious decrease of magnetic susceptibility was observed below T_{MI} (Figure 5).

The further investigations, elucidation of the nature of the insulating state as well as preparation of selenium rich analogues, are actively in progress.

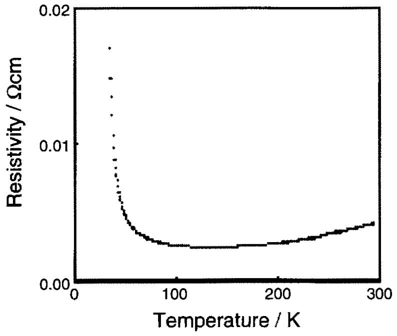

Figure 4. Conducting behavior of $(TM\text{-}TPDS)_2AsF_6$ in the heating run.

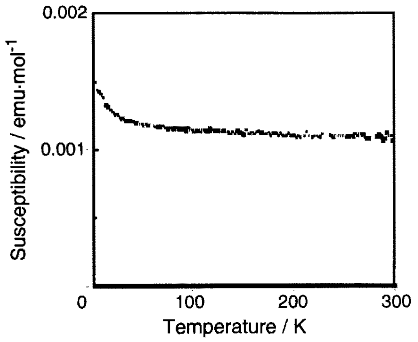

Figure 5. Magnetic susceptibility of $(TM\text{-}TPDS)_2AsF_6$.

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