V-L Synthesis and Physical Properties of Novel Molecular Metals

Development of organic materials which exhibit interesting electrical properties such as metallic conductivity and superconductivity has received considerable attention. A bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (TTP) is a promising π-electron framework for preparation of stable metals down to low temperatures, because it has a ladder-like array of sulfur atoms indispensable for constructing two-dimensional network of the donors. In fact, we have found that the unsubstituted TTP has a strong tendency to afford highly conducting radical cation salts retaining metallic conductivity down to ≤ 1.2 K regardless of shape and size of counter anions. In the present study, we have developed several organic metals by means of comprehensive modification of TTP, namely i) introduction of substituents, ii) exchange of sulfur atoms in the TTP framework with selenium, iii) synthesis of TTP analogs possessing non-TTF donor unit.

V-L-1 (CPDT-STF)(TCNQ): A New Charge-Transfer Complex Metallic Down to Low Temperature

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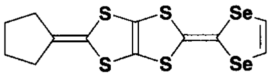
A new charge transfer complex (CPDT-STF)-(TCNQ) has been prepared. An X-ray crystal structure analysis revealed that this complex is composed of the donor and acceptor sheets orthogonally arranged to each other (Figure 1), which is similar to (ET)(TCNQ) and (ET)(TCNQF$_1$). The band calculations indicate that the CPDT-STF layer has significantly two-dimensional interaction, while the TCNQ one has one-dimensional Fermi surface. The electrical resistivity of the present complex showed metallic temperature dependence down to 0.6 K. The thermoelectric power was negative and changed from the positive to the negative gradient at 60 K. The static magnetic susceptibility and transport properties indicate coexistence of local and itinerant electrons in the present complex.



CPDT-STF

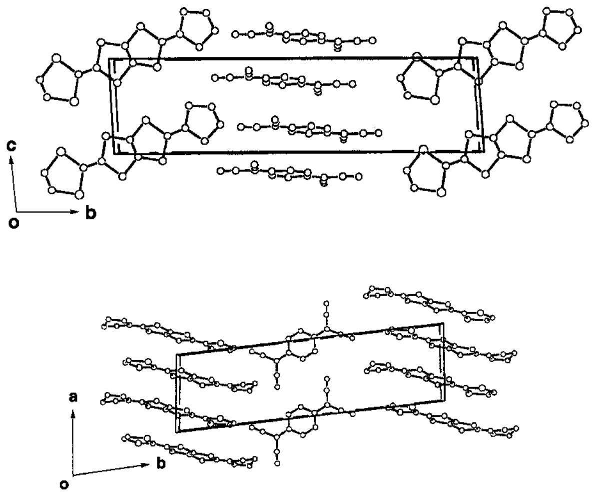


Figure 1. Crystal structure of (CPDT-STF)(TCNQ).

V-L-2 Structures and Electrical Properties of (EO-TTP)$_2$AsF$_6$

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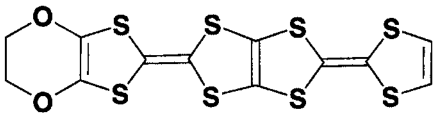
Tetrahedral and octahedral anions based on EO-TTP, where EO-TTP is 2-(4,5-ethylenedioxy-1,3-dithiol-2-ylidene)-5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene, afforded radical cation salts retaining metallic conductivity down to low temperature (1.5–4.2 K). X-Ray structure analysis of the AsF$_6$ salt (EO-TTP)$_2$AsF$_6$ reveals that it has the so-called b-type array of donors (Figure 1). A tight binding band calculation suggested that this salt has a two-dimensional closed Fermi surface.



EO-TTP

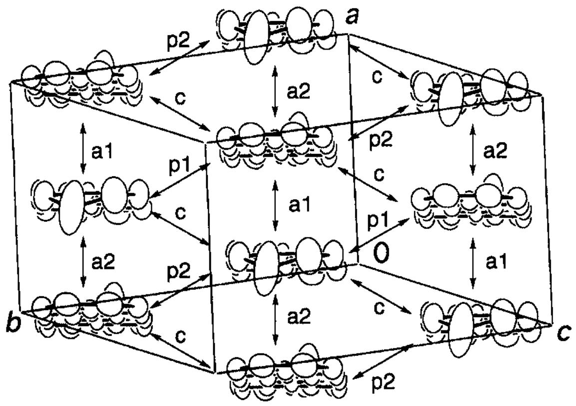


Figure 1. Donor sheet structure of (EO-TTP)$_2$AsF$_6$; The intermolecular overlap integrals are a1 = 26.9, a2 = 25.2, p1 = 0.47, p2 = 0.11, $c = -9.07 \times 10^{-3}$.

V-L-3 A Quasi Three-Dimensional Organic Conductor Based on a TTP Analogue Containing Thiopyran-4-ylidene

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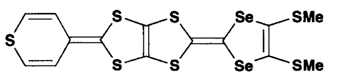
We have demonstrated that a bis-fused TTF, 2,5-bis-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (TTP) has afforded many metallic radical-cation salts stable down to liquid helium temperature regardless of shape and size of counter anions, in which the donors have a two-dimensional array. In contrast, (TM-TPDS)$_2$AsF$_6$, where TM-TPDS is 2-[4,5-bis(methlylthio)-1,3-diselenol-2-ylidene)-5-(thiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene has no two-dimensional conducting sheet in contrast to usual TTP conductors. The donors are arranged in a "windmill" manner in the *bc* plane (Figure 1). The anion is located on the center of "windmill," and are surrounded by methythio groups in the donors. The donors are alternately stacked along the *a* axis. There are many sulfur-sulfur contacts shorter than the sum of van der Waals radii (3.70 Å) between the central tetrathiapentalene moiety and the thiopyrane ring or methylthio groups. Thanks to a relatively large atomic coefficient of the sulfur atom in the thiopyrane ring, which is comparable to those of the others in the 1,3-dihiole rings, the calculated overlap integrals of the interclolumn interaction are comparatively large of about 10% of the intraclolumn one. As a result, the Fermi surface of the present salt is indeed one-dimensional, however, interactions in the *bc* plane is isotropical, namely this salt may be regarded to be a quasi three-dimensional metal. This salt showed high conductivity of 240 S cm^{-1} at room temperature, and exhibited metal-like temperature dependence down to 100 K. Below this temperature, the resisitivity gradually increased.



TM-TPDS

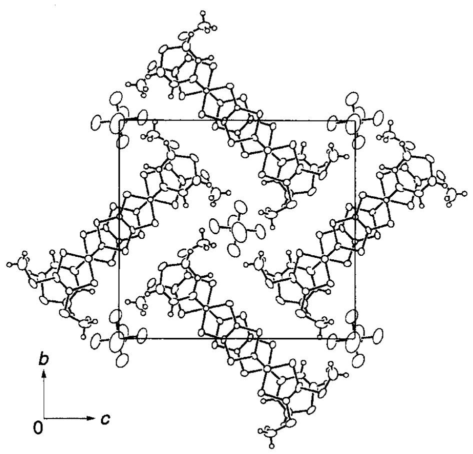


Figure 1. Crystal structure of (TM-TPDS)$_2$AsF$_6$.

V-L-4 Structures and Properties of Organic Metals Based on Dimethyl Substituted TTP Analogue

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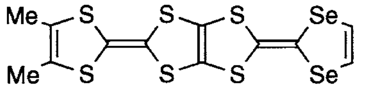
A selenium analogue of dimethyl substituted TTP (DM-TS-TTP) was prepared. (DM-TS-TTP)$_2$PF$_6$ showed metallic temperature dependence down to 4.2 K. X-Ray crystal structure analysis of this salt reveals that the donors form two-dimensional conducting sheets as is observed in most TTP type metals (Figure 1). The arrangement of donors is classified as the so-called β-type. The band structure calculated by a tight-binding method suggests that it has a quasi one-dimensional Fermi surface.



DM-TS-TTP

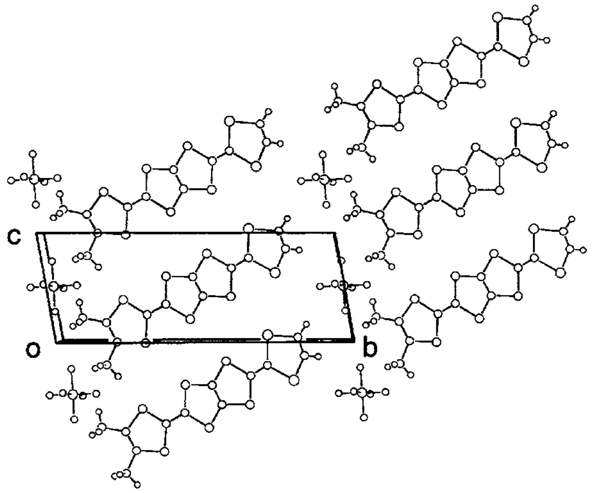


Figure 1. Crystal structure of (DM-TS-TTP)$_2$PF$_6$.

V-L-5 Synthesis and Properties of Methylthio Substituted ST-TTP Derivatives

MISAKI, Yohji[1,2]; KAIBUKI, Tadahiro[1]; MONOBE, Tae[1]; TANAKA, Koji[1]; TANIGUCHI, Masateru[1]; TANAKA, Kazuyoshi[1]; YAMABE, Tokio[1]; TAKIMIYA, Kazuo[3]; MORIKAMI, Atsushi[3]; OTSUBO, Tetsuo[3]; MORI, Takehiko[4]
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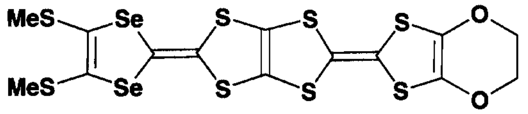
[*Synth. Met.* **102**, 1781 (1999)]

A new ST-TTP donor TMEO-ST-TTP, where TMEO-ST-TTP is 2-[4,5-bis(methylthio)-1,3-diselenol-2-ylidene)-5-(4,5-ethylendioxy-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene, has been prepared. It affords highly conducting PF$_6^-$ and AsF$_6^-$ salts retaining metallic conductivity down to 4.2 K, while the TCNQ complex and ClO_4^- salt are low conductive semiconductors. X-Ray structure analyses reveal that (TMEO-ST-TTP)(TCNQ)(PhCl) has a DA type mixed stack, and that the donor array of $(TMEO\text{-}ST\text{-}TTP)_2ClO_4(DCE)$ in the conducting sheet resembles β-BEDT-TTF salts (Figure 1).



TMEO-ST-TTP

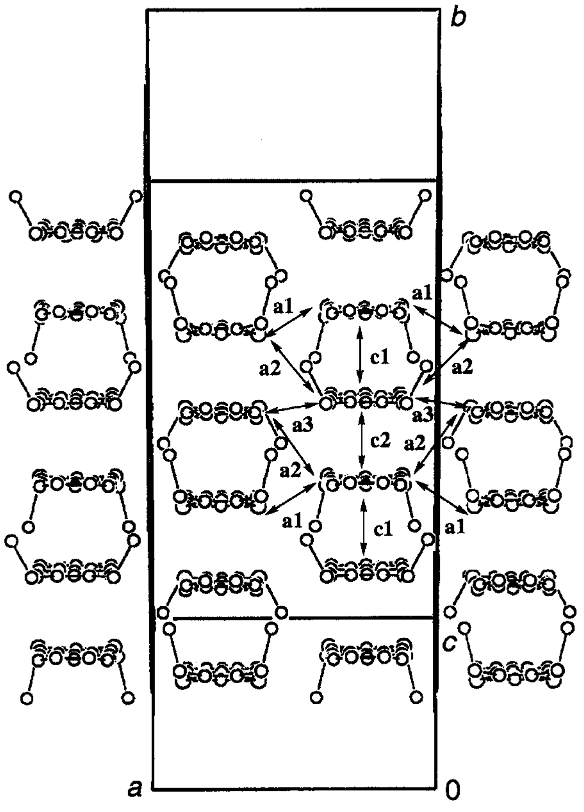


Figure 1. Donor sheet structure of $(TMEO\text{-}ST\text{-}TTP)_2ClO_4(DCE)$.