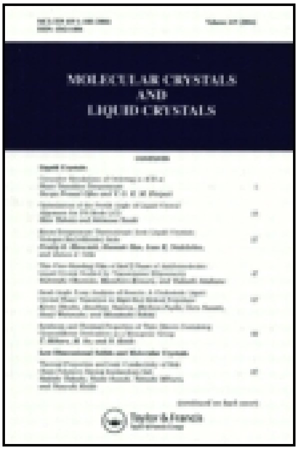

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Tetrathiapentalene type donors as promising π-electron frameworks for organic metals stable down to low temperatures

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TETRATHIAPENTALENE TYPE DONORS AS PROMISING π-ELECTRON FRAMEWORKS FOR ORGANIC METALS STABLE DOWN TO LOW TEMPERATURES

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A bis-fused TTF donor, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (TTP) and its derivatives affords many metallic salts stable down to low temperatures. X-Ray structure analysis reveals that most TTP salts have β-type conducting sheets regardless of counter anions. On the other hand, CH-TTP and TMET-TTP have a tendency to form κ-type and θ-type salts, respectively. A vinylogous TTP, DTEDT has afforded an organic superconductor (DTEDT)$_3$Au(CN)$_2$, and a TTP analog containing thiopyran ring TM-TPDS has yielded the AsF$_6$ salt with three-dimensional molecular array.

Keywords: organic metal; tetrathiapentalene; electrical conductivity; X-ray structure analysis; band calculation

INTRODUCTION

In the search for organic metals stable down to low temperature and superconductors, realization of two-dimensional (2D) electronic structure is needed [1]. For TIF system which has played a leading role for the recent quarter century, substitution of "capped" alkyl chalcogeno groups has been an indispensable requirement to introduce 2D character. In this

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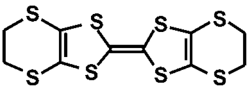
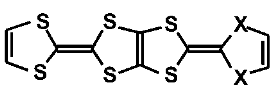
connection, synthesis of novel π-electron framework that has ability to produce 2D metals is of significant interest to explore novel stable metals. A bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP or simply TTP), is a promising π-electron framework because it has ladder array of sulfur atoms as is observed in BEDT-TTF. We have synthesized a number of TTP derivatives and analogous bis-fused donor systems, and have demonstrated how they are promising for the preparation of organic metals stable down to low temperature [2]. In these Proceedings, we overview synthesis of TTP type donors and structures and conducting property of their conducting materials.



BEDT-TTF

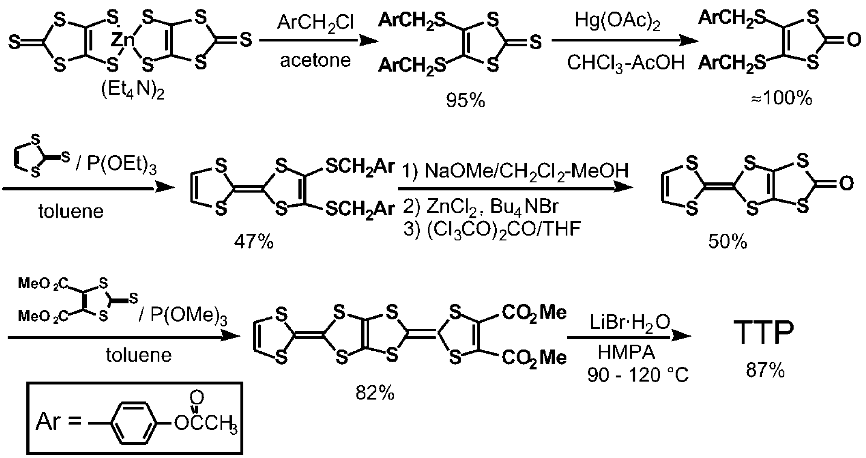


X = S, TTP
X = Se, ST-TTP

RESULTS AND DISCUSSION

Synthesis and Electrochemistry

We have established a general synthetic route to TTP derivatives as shown in Scheme 1 [3]. The cyclic voltammogram of TTP in benzonitrile shows four pairs of redox waves at +0.44, +0.62, +1.05 and +1.13 V (vs. SCE, 25°C). The E_1 value (+0.44 V) is higher by ca. 0.1 V than that of TTF (+0.35 V) in spite of extension of apparent π-conjugation. On the other



SCHEME 1.

hand, E_2–E_1 value was smaller by 0.24 V than that of TTF (0.42 V), suggesting significantly decreased on-site Coulomb repulsion in the dicationic state.

Structures and Conducting Property of Radical Cation Salts

Most of the salts based on TTP and its selenium analog ST-TTP show high electrical conductivity of $\sigma_{rt} = 10^1$–$10^3\,\mathrm{S\,cm^{-1}}$, and metal-like conductive behavior down to 0.6–4.2 K [4]. Figure 1 shows crystal structure of $(TTP)_2SbF_6$ [4a]. The donors form 2D conducting sheets, each of which is separated by insulating layer of anions. The molecular packing motif may be classified as the so-called β-type in BEDT-TTF conductors. The overlap mode of donor molecules is so called ring-over-bond type, and the slip distance along the molecular axis in the stack is 1.6 Å. The donors form an almost uniform stack with the interplanar distances of 3.46 and 3.47 Å, respectively, while they are dimerized in β-BEDT-TTF salts. As a result, the calculated overlap integrals in the stack are almost same with each other (a1 = 25.1, a2 = 25.3). On the other hand, side-by-side interactions are about one third compared to those along the stacking one. Such a relatively strong interstack interactions give a closed Fermi surface (Figure 2). The similar donor packing has been also found in $(TTP)_2X$ ($X = ClO_4$, BF_4, ReO_4) [4b], $(ST\text{-}TTP)_2AsF_6$ [4c], and $(TTP)_6X$ ($X = Re_6S_6Cl_8$, Mo_6Cl_{14}) [4d]. Therefore, TTP may be regarded to have strong self-aggregating property of uniform β-type packing.

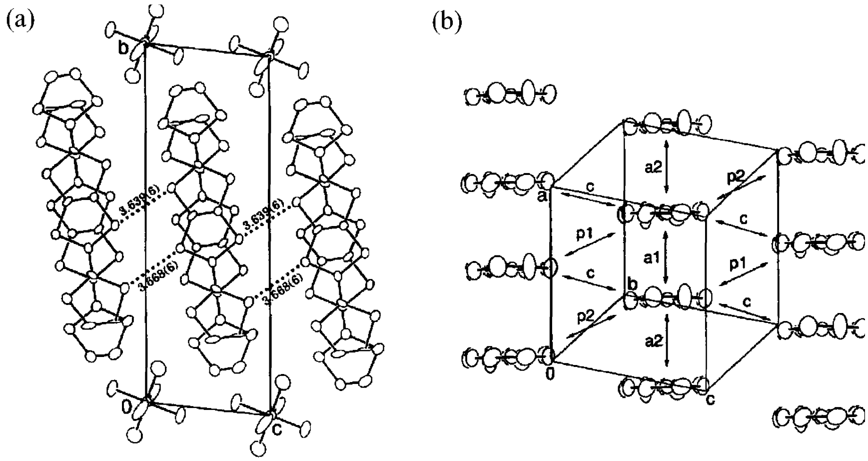


FIGURE 1 (a) Crystal structure of $(TTP)_2SbF_6$ viewed onto the bc plane, and (b) donor sheet structure viewed along donor long axis. The intermolecular overlap integral are a1 = 25.1, a2 = 25.3, p1 = 7.9, p2 = 8.6, c = 0.8 × 10^{-3}.

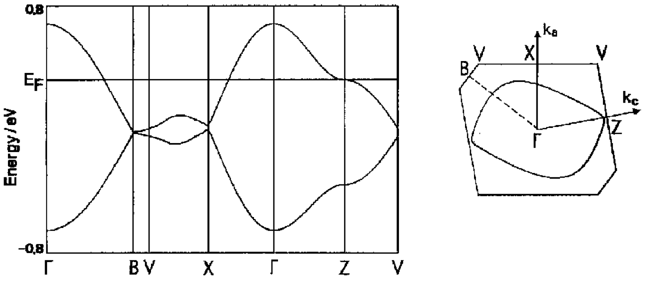
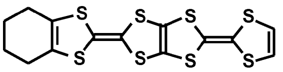
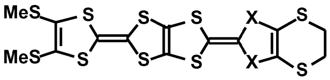


FIGURE 2 Energy dispersion and Fermi surface of $(TTP)_2SbF_6$.

In contrast, molecular packing other than β-type could be achieved if appropriate substituent is introduced on TTP framework. In fact, CH-TTP has afforded κ-type I_3- salt (Figure 3a) [5]. It is noteworthy that CH-TTP has no chalcogeno based substituent, while at least one "capped" alkyl-dichalcogeno group such as ethylenedithio group is necessary for TTF system. This salt exhibits high conductivity of $\sigma_{rt} = 38\,S\,cm^{-1}$, and metal-like temperature dependence down to 1.4 K. No observation of superconductivity in spite of the κ-type structure is presumably due to that the upper band of the present salt is not half-filled because of nearly 3:1 composition, while all the κ-type superconductors have 2:1 composition and the half-filled upper band. On the other hand, TMET-TTP and its



CH-TTP



X = S, TMET-TTP
X = Se, TMET-TS-TTP

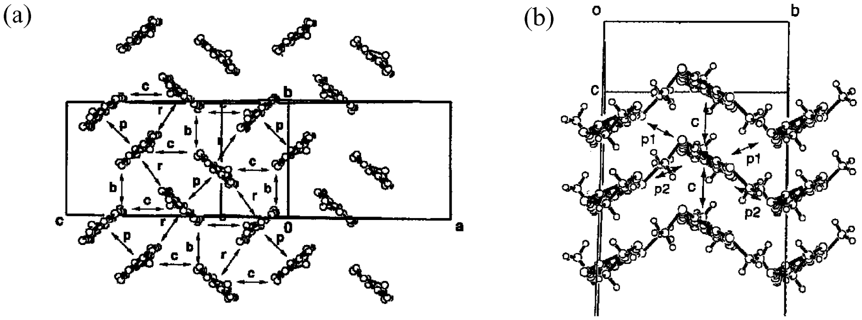
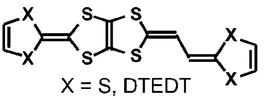


FIGURE 3 (a) Donor sheet structure of $(CH\text{-}TTP)(I_3)_{0.31}$, and (b) $(TMET\text{-}TS\text{-}TTP)_2$ TCNQ.

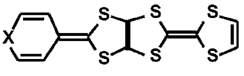
selenium analogs have yielded θ-type salts with various anions even with TCNQ (Figure 3b) [6]. Most of θ-type TMET-TTP salts exhibited metal to insulator transition at low temperature region, or semiconductors from room temperature due to large dihedral angles between molecular planes as pointed in θ-BEDT-TTF salts [7].

An Organic Superconductor: $(DTEDT)_3Au(CN)_2$

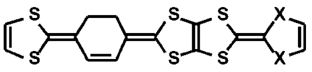
π-Electron frameworks modified TTP skeleton are of significant interest from the viewpoint of exploring novel conducting materials. We have synthesized various bis-fused donors possessing non-TTF π-systems and higher homologue of TTP [8–12]. Among them, DTEDT has a crocked structure and π-orbital of sulfur atoms at the terminal of the vinylogous 1,3-dithiole ring are out of phase with those of the other sulfur atoms in HOMO.



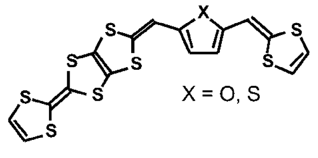
X = S, DTEDT
X = Se, DSEDS



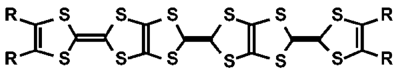
X = O, PDT-TTP
X - S, TPDT-TTP



X = S, Se



X = O, S



R = SMe, SEt, $SC_6H_{13}{}^n$

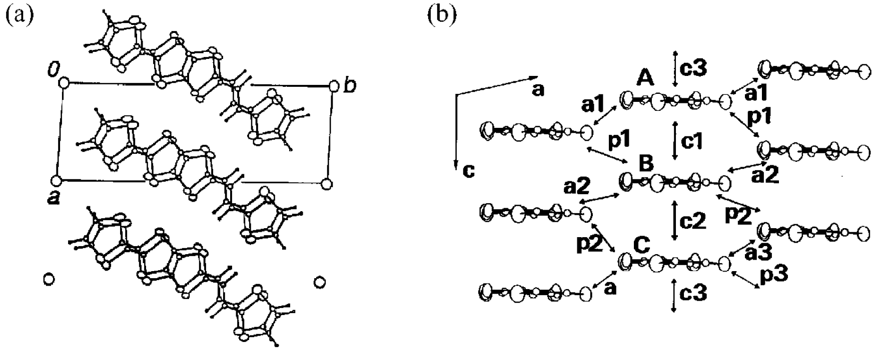


FIGURE 4 (a) Crystal structure of $(DTEDT)_3Au(CN)_2$ projection onto the *ab* plane, and (b) donor sheet structure. The intermolecular overlap integrals are c1 = −19.2, c2 = −19.9, c3 = −10.8, a1 = −1.5, a2 = −1.3, a3 = −0.7, p1 = −3.8, p2 = −3.4, p3 = -6.9×10^{-3}.

Therefore, it is anticipated to cause both sterically and electronically less effective side-by-side interaction in the charge-transfer salts compared with strip-like TTP in which all sulfur atoms have the same phase. However, DTEDT affords an organic superconductor $(DTEDT)_3Au(CN)_2$ ($T_c = 4\,K$ under ambient pressure) as well as many metallic radical cation salts regardless of size and shape of counter anions [8]. Figure 4 shows crystal structure of $(DTEDT)_3Au(CN)_2$. The donors form conducting sheets parallel to the *ac* plane, and the array of donors is classified as the β-type similar to TTP) salts [4]. In contrast to most β-type salts based on unsymmetrical donors, DTEDT molecules are arranged making both the stacking and transverse directions parallel in the present salt. Because DTEDT has a crooked structure and the phase of sulfur atoms in HOMO is reversed at the terminal vinylogous 1,3-dithiole, such a parallel arrangement results in most effective intermolecular interaction both sterically and electronically. On the other hand, a selenium analog of DTEDT, DSEDS affords TaF_6 salt, in which the donor array is identical with the averaged structure of $(DTEDT)_3Au(CN)_2$ [8b]. Therefore, we think DTEDT also has a strong tendency to form β-type molecular packing similar to TTP. The band structure calculated by a tight binding method suggests that $(DTEDT)_3Au(CN)_2$ has a closed Fermi surface, although one-dimensional character along the stacking direction is dominant (Figure 5).

A Novel Organic Conductor with 3D Molecular Array

TTP analogs containing (thio)pyran-4-ylidene moiety, (T)PDT-TTP are of interest as a promising component for preparation of 3D conductors because significant intermolecular overlap along the molecular long axis could be realized through chalcogen atoms in the (thio)pyran ring [10]. Figure 6a shows crystal structure of $(TM\text{-}TPDS)_2AsF_6$ [13]. The present salt does not form two-dimensional conducting sheet in contrast to usual TTP

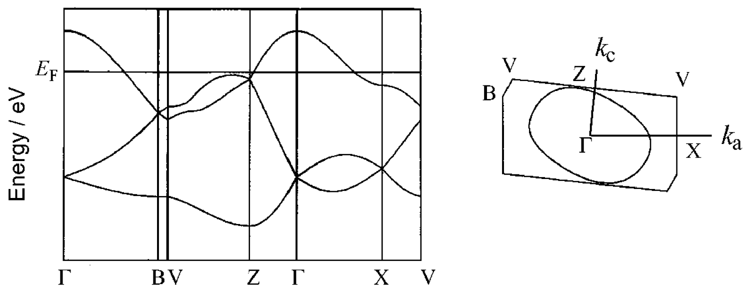


FIGURE 5 Energy band structure and Fermi surface of $(DTEDT)_3Au(CN)_2$.

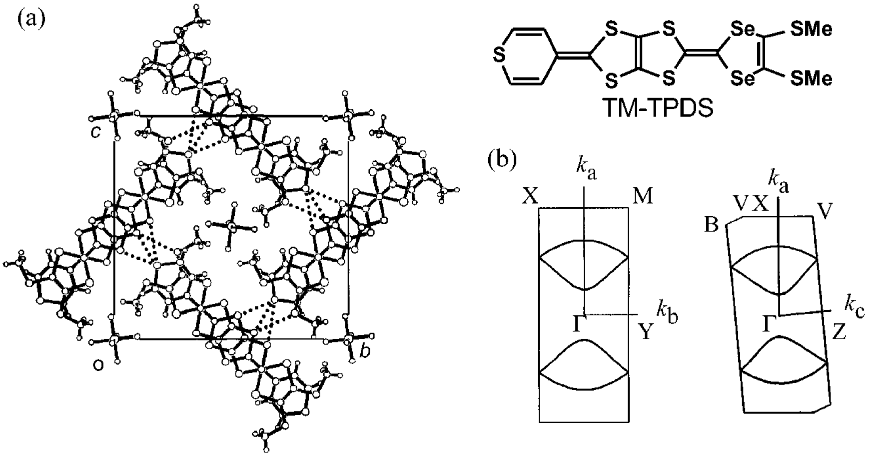


FIGURE 6 (a) Crystal structure of $(TM\text{-}TPDS)_2AsF_6$ onto the *bc* plane showing intermolecular S-S contacts (≤ 3.60 Å) with dotted lines, and (b) calculated Fermi surface.

conductors. Instead, the donors are arranged in a "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. 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. Thanks to relatively large molecular orbital coefficient of the sulfur atom in the thiopyran ring as well as short sulfur-sulfur contacts, the calculated overlap integrals between columns are as large as approximately 10% of the intracolumn overlaps. However, the calculated Fermi surface is unfortunately closed only along the k_a direction because intrastack interactions are still dominant in the present salt (Figure 6b). $(TM\text{-}TPDS)_2AsF_6$ showed high conductivity of $\sigma_{rt} = 240\,S\,cm^{-1}$, and exhibited metal-like temperature dependence down to 100 K. Below this temperature, the resisitivity gradually increased. 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}.

CONCLUSION

In summary, TTP and its derivatives have afforded many metallic radical cation salts due to side-by-side interaction through chalcogen atoms in the tetrathiaplentalene moiety as well as those in the outer 1,3-dithiole rings. Furthermore, a TTP vinylog DTEDT has yielded an organic superconductor though its half unit of vinylogous TTF itself has never yielded any metallic salt down to low temperature. The results mentioned here should bring much expectation that fusion of two 1,3-dithiole donors, in other words, insertion of tetrathiapentalene moiety in a π-electron donor, is a reliable guiding principle for stabilization of metallic state in conducting organic solids [14].

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