TOPICAL REVIEW

Tetrathiapentalene-based organic conductors

Yohji Misaki

Department of Applied Chemistry, Graduate School of Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama 790-8577, Japan
E-mail: misaki@eng.ehime-u.ac.jp

Received 14 January 2009
Accepted for publication 17 March 2009
Published 6 July 2009
Online at stacks.iop.org/STAM/10/024301

Abstract
The synthesis, structure and properties of tetrathiapentalene-based (TTP) organic conductors are reviewed. Among various TTP-type donors, bis-fused tetrathiafulvalene, 2,5-bis(1,3-dithiol-2-ylidine)-1,3,4,6-tetrathiapentalene (BDT-TTP) and its derivatives afford many metallic radical cation salts stable down to low temperatures, regardless of the size and shape of the counter anions. Most BDT-TTP conductors have a $\beta$-type donor arrangement with almost uniform stacks. Introduction of appropriate substituents results in molecular packing that differs from the $\beta$-type. A vinylogous TTP, 2-(1,3-dithiol-2-ylidene)-5-(2-ethanediylidene-1,3-dithiole)-1,3,4,6-tetrathiapentalene (DTEDT) has yielded an organic superconductor (DTEDT)$_2$Au(CN)$_2$ as well as metallic radical cation salts, regardless of the counter anions. (Thio)pyran analogs of TTP, namely (T)PDT-TTP and its derivatives produce molecular conductors with novel molecular arrangements. A TTP analog with reduced $\pi$-electron system 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene (BDA-TTP) has afforded several organic superconductors. Highly conducting molecular metals with unusual oxidation states (+1, +5/3 and neutral) have been developed on the basis of 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP) derivatives and analogous metal derivatives $M$(dt)$_2$ ($M$ = Ni, Au).

Keywords: molecular conductor, tetrathiapentalene, cyclic voltammetry, x-ray structure analysis, band calculation

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the publication of the report on the metallic conductivity in a tetrathiafulvalene-tetracyanoquinodimethane (TTF·TCNQ) complex [1] and the subsequent discovery of the first organic superconductor (TMTSF)$_2$PF$_6$ (TMTSF = tetramethyltetraselenafulvalene) [2], TTF and its derivatives have played a leading role in the development of new molecular metals and superconductors [3–5]. To explore molecular organic superconductors, it is important to stabilize the metallic state down to low temperatures (≤4.2 K) by enhancing the dimensionality of electrical conductivity. In this way, the Peierls transition, which is observed in conventional one-dimensional (1D) conductors represented by TTF·TCNQ, can be suppressed. Since the discovery of 2D bis(ethylenedithio)-TTF (BEDT-TTF) metals and superconductors, substitution of ‘capped’ alkyl-dichalcogeno groups on TTF has been regarded as the most promising strategy for preparation of 2D metals [6, 7]. However, ‘capped’ alkyl-dichalcogeno groups on $\pi$-electron
frameworks other than TTF must be introduced. This limits the search for novel conducting components of metals stable down to low temperatures (scheme 1).

In this context, a new \( \pi \)-electron framework, having the ability to produce multidimensional metals without any substituent, is of significant interest. Thus, the introduction of substituent alkyl, benzo and/or methylthio groups, as well as unsubstitution, may also be effective in preparing 2D (or at least quasi-1D) metals for such \( \pi \)-electron systems, whereas the corresponding TTF derivatives usually yield completely 1D conductors. We have noticed a bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (abbreviated as BDT-TTP or simply TTP) as a promising candidate for the construction of 2D metals. This molecule can also be designed by insertion of the 1,3,4,6-tetrathiapentalene moiety between two 1,3-dithiole rings of TTF. Because BDT-TTP has the so-called ladder-like array of sulfur atoms, as in BEDT-TTF, its cation radical salts are expected to form 2D conducting sheets thanks to the lateral intermolecular interactions based on sulfur-sulfur contacts incorporated in the BDT-TTP framework (scheme 2). This article reviews the synthesis, structure and electrochemical properties of TTP donors, and the structure and properties of molecular conductors based on these TTP donors.

2. Synthesis, structure and properties of TTP molecules

2.1. Synthesis

The first synthesis of BDT-TTP derivatives (1) (scheme 3) was reported in 1980 [8]. Schumaker and co-workers synthesized BDT-TTP derivatives with strongly electron-withdrawing substituents such as cyano, methoxycarbonyl or trifluoromethyl groups by means of a phosphite-mediated cross-coupling reaction between 1,3,4,6-tetrathiapentalene-2,5-dione (2) and corresponding 1,3-dithiole-2-thiones (3) (scheme 3). However, this methodology has not been applied to the synthesis of the other BDT-TTP derivatives, probably because of difficulties in optimizing the reaction conditions for cross-coupling using 2. Furthermore, the details of the structure and properties of the products have not been reported, particularly the crystal structure, redox behavior and formation of conducting salts. The author and co-workers developed a versatile route for the synthesis of BDT-TTP derivatives early in 1990 as shown in scheme 4 [9, 10]. First, an unsymmetrical TTF moiety is constructed with protection groups for dithiolate. Then, the fused 1,3-dithiole ring is formed by deprotection of TTF dithiolate and successive reaction with triphosgene. Finally, the tritylphosphite-mediated cross-coupling reaction between the resultant 1,3-dithiol-2-one fused with TTF (5) and 1,3-dithiole-2-thione derivatives afford the desired BDT-TTP derivatives. Unfortunately, the cross-coupling reaction in
the final step does not proceed at all when unsubstituted or alkyl-substituted 3 is used. Thus, the unsubstituted derivative has been synthesized by demethoxycarbonylation of the bis(methoxycarbonyl) derivative using lithium bromide monohydrate in hexamethylphosphoric triamide (HMPA). In contrast, the tetramethyl derivative has not been synthesized to date [9–41]. Yamada et al. developed another synthetic strategy for 5 (scheme 6) [42]. One of the TTF frameworks is constructed via the Me3Al-promoted reaction (Me = methyl) of organotin compound 9 prepared from 2 with ester 10 in this procedure. However, P(OEt)3-mediated cross coupling is still required because of the extremely low solubility of 5 and 11 in common solvents.

### 2.2. Structure and electrochemical properties of BDT-TTP derivatives

Figure 1 shows the molecular structure of neutral BDT-TTP determined by x-ray structure analysis [10]. The BDT-TTP molecule adopts a chair conformation, in which the molecule is folded at the four sulfur atoms in the central tetrathiapentalene moiety. The dihedral angle is 27.17° (27.33°) between the two planes composed of S1–S2–C1–C2–S3–S4 (S5–S6–C7–C8–S7–S8) and S3–S4–C5–C6–S5–S6.

Table 1 summarizes the redox potentials of BDT-TTP derivatives measured by cyclic voltammetry. The cyclic voltammograms of most BDT-TTP derivatives exhibit four pairs of redox waves because they have four redox-active 1,3-dithiole rings. The first redox potential of BDT-TTP, $E_1 = +0.44$ V versus saturated calomel electrode (SCE) in benzonitrile, is higher than that of TTF (+0.35 V) by about 0.1 V in spite of the extension of π-conjugation. Instead, the $E_1$ value of BDT-TTP is comparable to those of 4, 5-bis(methylthio)-TTF (I2, +0.44 V) and 2-isopropylidene-1,3-dithio[4,5-d]-TTF (I3, 0.45 V) [43] measured under identical conditions. In contrast, the tetrakis(methylthio) derivative (TTM-TTP) has an $E_1$ value (+0.53 V) similar to the corresponding TTF TTM-TTF (+0.51 V). These results indicate that the positive charge formed by the first oxidation mainly distributes on one TTF moiety, while the other acts as a sulfur-based substituent. The $\Delta E (= E_2 - E_1)$ values

### Table 1. Redox potentials \( a \) of BDT-TTP derivatives and the related compounds (scheme 7).

| Donor     | $E_1$ | $E_2$ | $E_3$ | $E_4$ | $\Delta E (= E_2 - E_1)$ |
|-----------|-------|-------|-------|-------|--------------------------|
| BDT-TTP   | 0.44  | 0.62  | 1.05  | 1.13  | 0.18                     |
| TTM-TTP   | 0.53  | 0.72  | 0.99  | 1.11  | 0.19                     |
| I2        | 0.44  | 0.77  |       |       | 0.33                     |
| I3        | 0.45  | 0.76  | 1.14  |       | 0.31                     |
| TTM-TTF   | 0.51  | 0.78  |       |       | 0.27                     |

\( a \) versus SCE in benzonitrile containing 0.1 M Bu4NCIO4.  
\( b \) Irreversible step (an anodic peak potential).
of BDT-TTP (0.18 V) and TTM-TTP (0.19 V) are smaller by 0.24 and 0.08 V compared with those of TTF (0.42 V) and TTM-TTF (0.27 V), respectively. Because such a small \( \Delta E \) corresponds to a reduction of on-site Coulomb repulsion in the dicationic state of TTP derivatives, TTP conductors may be expected to show high conductivity.

### 3. Structures and conducting properties of TTP conductors

Numerous molecular conductors based on TTP donors have been synthesized (see scheme 8). Table 2 summarizes the molecular packing patterns and conducting properties of TTP-type conductors whose crystal structures have been determined. In this section, representative materials based on BDT-TTP derivatives are reported.

#### 3.1. (BDT-TTP)\( A_{x} \) and (ST-TTP)\( A_{2} \)

Several radical cation salts with various anions have been synthesized on the basis of BDT-TTP and its selenium analog ST-TTP. Most of these salts exhibit high room-temperature electrical conductivity \( \sigma_{\text{rt}} = 1-1000 \text{ S cm}^{-1} \) and show metal-like conducting behavior down to low temperatures (0.6–4.2 K) regardless of the size and shape of the counter anions [11, 12, 44–51]. Figure 2 shows the crystal structure of (BDT-TTP)\( _{2} \)SbF\(_{6} \), BDT-TTP molecules form 2D conducting sheets, each of which is divided by an insulating layer composed of the anions, as expected. The packing pattern of the donors is classified as the \( \beta \)-type in BEDT-TTF conductors (figure 3). The donors form a face-to-face stack with interplanar distances of 3.46 and 3.47 Å. The overlap mode of the donor molecules in the stack is the so-called ring-over-bond type. The slip distance is 1.6 Å along the long molecular axis in the stack. A similar molecular arrangement has also been found in most molecular conductors based on BDT-TTP and its selenium analogs ST-TTP and BDS-TTP with various anions (ClO\(_{4} \), BF\(_{4} \), ReO\(_{4} \), PF\(_{6} \), AsF\(_{6} \), SbF\(_{6} \), Re\(_{6}\)S\(_{8}\)Cl\(_{12}^{2-}\), Mo\(_{6}\)Cl\(_{14}^{2-}\), etc.). Therefore, BDT-TTP is regarded as having the strong self-aggregating property of \( \beta \)-type molecular packaging with little dimerization. This contrasts to the behavior of the array of donors in BEDT-TTF conductors,
Table 2. Molecular packing patterns and electrical properties of salts based on BDT-TTP derivatives (scheme 8); $\sigma_a$ refers to room-temperature conductivity.

| Material | Donor packing | $\sigma_a$ (S cm$^{-1}$) | Conducting behavior $^a$ | Ref |
|----------|---------------|--------------------------|--------------------------|-----|
| (BDT-TTP)$_2$A$_x$ | Uniform $\beta$-type | 160–400 | M$'$ | [44] |
| (A = ClO$_4$, Re$_x$O$_{2y}$, BF$_4$) | | | | |
| (BDT-TTP)$_2$SbF$_6$ | $\beta$-type | 48 | M | [45] |
| (BDT-TTP)$_2$A(TCE)$_2$ | $\beta$-type | 83–285 | M | [46,47] |
| (A = Mo$_x$Cl$_{6y}$, Re$_x$S$_y$Cl$_z$) | | | | |
| (BDT-TTP)$_2$(TCE)$_2$ | $\beta$-type | 180–800 | M | [47] |
| (A = Mo$_x$Cl$_{6y}$, Re$_x$S$_y$Cl$_z$) | | | | |
| (BDT-TTP)$_2$(Re$_x$S$_y$Cl$_z$)$_2$ | $\beta$-type | 200–1400 | M | [47] |
| (x $\approx$ 3) | | | | |
| (BDT-TTP)$_2$[(Ce(NO$_3$)$_6$]$_3$)(C$_2$H$_5$OH)] | $\beta$-type | 200 | M | [48,49] |
| (M = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) | | | | |
| (BDT-TTP)$_2$I | $\beta$-type | 206 | M | [50] |
| (M = Co, Mn, Zn, x $\approx$ 1.0) | | | | |
| (ST-TTP)$_2$AsF$_6$ | $\beta$-type | 200 | M$'$ | [11] |
| (ST-TTP)$_2$Re$_x$S$_y$Cl$_z$ | $\beta$-type | 600 | M | [47] |
| (BDS-TTP)$_2$AsF$_6$ | $\beta$-type | 70 | M | [12] |
| (CH-TTP)$_3$ | $\kappa$-type | 38 | M | [52] |
| (CHEO-TTP)(ReO$_4$)$_{0.38}$ | $\kappa$-type | 11 | M | [25] |
| (CHET-TS-TTP)(SbF$_6$)$_{0.36}$ | $\kappa$-type | – | – | [26] |
| (DM-TS-TTP)$_2$PF$_6$ | $\beta$-type | 55 | M | [23] |
| (EO-TTP)$_2$AsF$_6$ | $\beta$-type | 600 | M | [53] |
| (CFEO-TTP)(SbF$_6$)$_{0.40}$ | $\kappa$-type | 60 | M | [22] |
| (EOET-TTP)$_2$AsF$_6$ | $\kappa$-type | 60 | M | [14] |
| (BTM-TTP)$_2$A | $\beta$-type | 73–120 | M | [34,54] |
| (A = SbF$_6$, TaF$_x$) | | | | |
| (ST-TTP)$_2$(TCNQ)(TCE) | $\theta$-type | 0.8 | S | [54] |
| (M = SbF$_6$, TaF$_x$) | | | | |
| (SME-TS-TTP)$_2$ClO$_4$(DCE)$_6$ | $\beta$-type | 0.07 | S | [24] |
| (M = SbF$_6$, TaF$_x$) | | | | |
| (SME-TS-TTP)$_2$(TCNQ)(PhCl) | D-A stack | 5.3 $\times$ 10$^{-5}$ | S | [24] |
| (M = SbF$_6$, TaF$_x$) | | | | |
| (SME-TS-TTP)$_2$PF$_6$ | $\beta$-type | 9 | M | [27] |
| (M = SbF$_6$, TaF$_x$) | | | | |
| (BEDT-TTP)$_2$I | $\beta$-type | 900 | M | [61] |
| (M = SbF$_6$, TaF$_x$) | | | | |
| (EPT-TTP)$_2$Au(CN)$_2$ | $\beta$-type | 400 | M | [62] |
| (M = SbF$_6$, TaF$_x$) | | | | |
| (TMET-TTDA)$_2$A | $\theta$-type | 9–45 | T$_{MI}$ = 200 K | [63] |
| (A = PdF$_6$, ClO$_4$, ReO$_4$, IO$_4$, x = 0.13–0.34) | | | | |
| (TMES-TTP)$_2$I | $\theta$-type | 13 | S | [19] |
| (M = SbF$_6$, TaF$_x$) | | | | |
| (SMET-TS-TTP)$_2$TCNQ | $\theta$-type | 1–10 | T$_{MI}$ = 120 K | [20] |
| (A = PdF$_6$, ClO$_4$, BF$_4$) | | | | |
| (SMET-SBD-TTP)$_2$SbF$_6$ | $\theta$-type | 6 | S | [35] |
| (A = PdF$_6$, ClO$_4$, BF$_4$) | | | | |
| (SMET-DDT)$_2$A | $\theta$-type | 11 | S | [35] |
| (A = PdF$_6$, ClO$_4$, BF$_4$) | | | | |
| (SMET-DDT)$_2$A | $\theta$-type | 13–45 | S | [36] |
| (A = PdF$_6$, ClO$_4$, BF$_4$) | | | | |
| (C$_2$TET-TTP)$_2$I | Uniform $\beta$-type | 12–55 | M | [28] |
| (C$_2$TET-TTDA)$_2$A | Uniform $\beta$-type | 15–55 | M | [29] |
| (A = SbF$_6$, TaF$_x$, x = 0.30–0.33) | | | | |
| (C$_2$TET-TTP)$_2$I | Uniform $\beta$-type | 500 | M | [37] |
| (A = SbF$_6$, TaF$_x$, x = 0.30–0.33) | | | | |
| (C$_2$TET-TTP)$_2$I | Uniform $\beta$-type | 500 | M | [37] |
| (A = SbF$_6$, TaF$_x$, x = 0.30–0.33) | | | | |
| (C$_2$TET-TTP)$_2$I | Uniform $\beta$-type | 2.5 $\times$ 10$^{-2}$ | S | [28] |
| (A = SbF$_6$, TaF$_x$, x = 0.30–0.33) | | | | |
which strongly depends on both the shape and the size of the counter anions.

The overlap integrals of BDT-TTP salts were calculated by a molecular orbital method based on the extended Hückel approximation. The calculated intrastack overlap integrals between the highest occupied molecular orbitals (HOMOs) of (BDT-TTP)$_2$SbF$_6$ are almost identical ($a_1 = 25.1$, $a_2 = 25.3 \times 10^{-3}$), which is consistent with the interplanar distances and the slip distances along the long molecular axis. Thus, the donors form an almost uniform stack in this salt, while $\beta$-BEDT-TTF salts have a strongly dimerized stack. On the other hand, the calculated lateral overlaps ($S_l$) are relatively large compared with the stacking ones ($S_s$). The ratio of the largest intrastack overlap to the largest lateral one ($S_s/S_l$) is 2.9, which corresponds to an intermediate value between a typical 2D metal, $\beta$-(BEDT-TTF)$_2$I$_3$ ($S_s/S_l = 1.9$) [72] and a typical quasi-1D metal, (TMTTF)$_2$Br ($S_s/S_l = 6.6$) [73]. Thanks to such relatively large interstack interactions, the calculated Fermi surface is closed in the conducting layer (figure 4(a)). On the other hand, the Fermi surface, as deduced from the experimental reflection spectrum, is open in the $k_z$ direction, as shown in figure 4(b) [74]. When the theoretical calculation is performed by excluding 3d orbitals of sulfur

### Table 2. Continued.

| Material | Donor packing       | $\sigma_\ell$ (S cm$^{-1}$) | Conducting behavior | Ref       |
|----------|---------------------|-----------------------------|---------------------|-----------|
| (TMT-TTP)$_2$I$_3$ | Trimerized stack  | 0.03  | S | [64]  |
| (TMT-TTP)$_1$I  | Uniform $\beta$-type | 700  | $T_{MI} = 160$ K | [64]  |
| (TMT-TTP)$_2$$(X = Br, I)$ | Uniform 1D stack  | 200  | $T_{MI} = 20$ K | [54]  |
| (TMT-TTP)$_2$$(X = Br, I)$ | Dimerized 1D stack | 10–40 | S | [66]  |
| (TMT-TTP)$_2$Au(PhCl)$_{0.5}$SbF$_6$ | Dimerized 1D stack | 0.01–0.07 | S | [67, 68]  |
| (A = FeCl$_3$, FeBr$_3$, GaCl$_3$, GaBr$_3$) | | | | |
| (TMT-TTP)$_2$FeBr$_3$C$_{12}$ | Uniform 1D stack  | 1000  | $T_{MI} = 160$ K | [67]  |
| (TMT-TTP)$_2$(PF$_6$)$_{0.2}$THF$_{0.6}$ | Pentamerized stack | $3 \times 10^{-3}$  | S | [69]  |
| (TSM-TTP)$_2$I$_3$ | Uniform 1D stack  | 200  | $T_{MI} = 20$ K | [21]  |
| (TSM-TTP)$_2$I$_3$ | Trimerized stack  | 2.3  | S | [38]  |
| (TMT-DSDTP)$_2$I | Uniform 1D stack  | 280  | $T_{MI} = 60$ K | [38]  |
| (DTM-DSM-TS-TTP)$(X = Br)$ | Uniform 1D stack | 520  | $T_{MI} = 25$ K | [38]  |
| (TTM-BDS-TTP)$_2$I$_3$ | Uniform 1D stack | 630  | M | [38]  |
| (CPTM-TTP)$_2$I | $\lambda$-type | 7–110 | $M' (A = PF$_6$, AsF$_6$, SbF$_6$) | [17]  |
| (A = PF$_6$, AsF$_6$, SbF$_6$) | | | | |
| (ChETT-TTP)$_2$I | $\beta$-type | 20–150 | $T_{MI} = 100–150$ K | [18, 70]  |
| (A = AuBr$_3$, Au(CN)$_2$, GaCl$_3$) | | | | |
| (ChETT-TTP)$_2$ReO$_4$ | $\beta$-type | $8 \times 10^{-3}$  | S | [70]  |
| (Et$_2$BEDT-TTP)$_2$Hgl | Pseudo $\lambda$-type | 2  | S | [30]  |
| (TTP-PROXYL)$_2$MCl$_6$(M = Ga, Fe) | Uniform 1D stack | $1 \times 10^{-3}$ | S | [71]  |
| (CP-TTP-PROXYL)$_2$AsF$_6$ | Uniform 1D stack | 1  | S | [40]  |

$^a$ M: metallic down to low temperature ($\leq 4.2$ K), $M'$: increase of resistivity at low temperature, but no metal–insulator transition, $S$: semiconductor, $T_{MI}$: metal-insulator transition temperature.

$^b$ TCE = 1,1,2-trichloroethane, DCE = 1, 2-dichloroethane, cn = 1-chloronaphthalene.

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**Figure 2.** Crystal structure of (BDT-TTP)$_2$SbF$_6$ where dotted lines represent intermolecular S···S contacts. (Reprinted with permission from [45].)
atoms, the shape of the calculated Fermi surface approaches that of the Fermi surface obtained from the reflection spectrum. However, the overlap integrals are underestimated by about 30%.

Three exceptional molecular packing patterns that differ from uniform β-type packing have been identified for BDT-TTP conductors. (BDT-TTP)$_2$Cu(NCS)$_2$ adopts θ-type arrangement of the donors, and exhibits semiconducting temperature dependence of resistivity. Yakushi and co-workers reported that this salt shows a phase transition accompanied with a change in the activation energy at 250 K, below which the donors are in a charge-ordering state as is often observed in θ-phase conductors [75]. Kobayashi and co-workers reported that (BDT-TTP)$_3$I has a unique 3D donor packing with six crystallographically independent donor molecules, as shown in figure 5 [50]. This salt shows semiconducting behavior with a small activation energy of 0.014 eV due to charge disproportionation. Kobayashi and co-workers also developed BDT-TTP conductors with divalent anions [M$^{II}$Cl$_4$]$^{2−}$ (M = Co, Mn, Zn) [51]. Figure 6 shows the crystal structure of (BDT-TTP)$_3[M^{II}$Cl$_4$(EtOH)$_x$ (x ≈ 1.0). Three independent halves of BDT-TTP molecules (A, B, C) and half of a [M$^{II}$Cl$_4$]$^{2−}$ anion are crystallographically independent. Comparison of the bond lengths indicates that the formal charge of molecule C is nearly 0 and those of molecules A and B are +1. Donors A and B form a column along the c-axis with a ring-over-bond overlap mode. In contrast, donor C forms a unique 1D ‘BDT-TTP tape’ along the c-axis and the molecular plane of donor C is approximately perpendicular to the planes of donors A and B. These salts exhibit a relatively high conductivity of $σ_\parallel ≈ 5 \text{ S cm}^{-1}$ and weak metal like behavior down to about 150 K. At low temperature, the resistivity gradually increases with decreasing temperature, however, the conductivity is high even at 30 K. Magnetic susceptibility measurement reveals temperature-independent metal-like behavior in the [Zn$^{III}$Cl$_4$]$^{2−}$ salt.

3.2. κ-Type salts based on TTP donors

Molecular packing that differs from the β-type can be realized if appropriate substituents are introduced into the BDT-TTP framework. Construction of a κ-type structure is of significant interest because many κ-type radical cation salts based on TTF derivatives show superconducting transitions [4, 5, 7]. For TTF systems, the introduction of capped alkyl-dichalcogeno groups is indispensable for constructing κ-type conductors. The roles of the capped alkyl-dichalcogeno groups are as follows: (i) steric hindrance to avoid formation of stacking structure revealing in the formation of dimers and (ii) realization of 2D electronic structure through sulfur–sulfur lateral interaction. In fact, all TTF donors affording κ-type salts have one or two ethylenedithio, methylendithio or ethylenedioxy groups. In contrast, a ‘capped’ alkyl-dichalcogeno group is not needed for the BDT-TTP system, because it has enough sulfur atoms in the π-electron framework to realize lateral interactions. Thanks to the ability to form a 2D conduction layer, the introduction of a non-planar substituent such as a fused cyclohexene ring may be possible to construct a κ-type structure. In fact, 2-(4,5-cyclohexeno-1,3-dithiol-2-ylidene)-5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentanlene (CH-TTP) has afforded a κ-type salt with an I$_3^−$ anion (figure 7) [52]. This salt exhibits high conductivity of $σ_\parallel ≈ 38 \text{ S cm}^{-1}$ and metal-like temperature dependence down to 1.4 K. Superconductivity has not been observed in spite of the κ-type molecular packing, probably because the upper band of this salt is not half-filled due to a nearly 3:1 donor:acceptor composition. Whereas all the κ-type
superconductors discovered thus far have a 2 : 1 composition and a half-filled upper band as a result. The other BDT-TTP derivatives with a fused cyclohexene ring, CHEO-TTP [25] and CHET-TS-TTP [26], have also yielded \( \kappa \)-type conductors with ReO\(_4\) or SbF\(_6\) anion, both of which retain metallic conductivity down to 4.2 K.

In this regard, BDT-TTP derivatives fused with other six-membered rings are of interest to elucidate a correlation between molecular structure and the molecular array in the TTP conductors. BDT-TTP fused with dehydro-1,4-dioxane, in other words, ethylenedioxy-substituted BDT-TTP (EO-TTP), seems to afford the \( \kappa \)-type salts. However, x-ray structure analysis of (EO-TTP)\(_2\)AsF\(_6\) revealed a \( \beta \)-type packing pattern with little dimerized stacking as observed in (BDT-TTP)\(_2\)A [53]. The torsion angle around the ethylene bridge in (EO-TTP)\(_2\)AsF\(_6\) is 37°, which is about two-thirds of that in (CH-TTP)\(_2\)I\(_3\) (57°). Considering a smaller dihedral angle, as well as fewer hydrogen atoms in the dehydrondioxane ring (four hydrogen atoms) than in the cyclohexene rings (eight hydrogen atoms), steric hindrance between the donors in (EO-TTP)\(_2\)AsF\(_6\) should be smaller than that in (CH-TTP)\(_2\)I\(_3\). Smaller steric repulsion may favor the formation of the stacking \( \beta \)-type structure. A tight-binding band calculation indicates that this salt has a closed Fermi surface similar to (BDT-TTP)\(_2\)SbF\(_6\), although the 1D character is still strong owing to large overlaps in the stacking direction. EO-TTP salts with tetrahedral and octahedral anions including (EO-TTP)\(_2\)AsF\(_6\) exhibit very high conductivity of \( \sigma_\text{a} = 380–1300 \ \text{S cm}^{-1} \) with a simple metallic temperature dependence down to 1.5–4.2 K. On the other hand, CPEO-TTP [22] and EOET-TTP [14], which have the additional substitutent of an annelated cyclopentene ring or ethylenedithio group, have yielded \( \kappa \)-type salts with octahedral anions.

### 3.3. BDT-TTP conductors

The methylthio group seems to be more sterically hindered than the annelated cyclohexane group, being expected to afford \( \kappa \)-type or other type of packing of the donors. Bis(methylthio)-substituted TTP (BTM-TTP) has afforded two types of radical cation salts (needles and plates) with octahedral anions. x-ray structure analysis revealed that

![Figure 7. Donor-sheet structure of (CH-TTP)\(_2\)I\(_3\). The intermolecular overlap integrals are \( c = -4.32 \), \( p = 22.2 \), \( r = 7.61 \) and \( b = 12.0 \times 10^{-3} \). (Reprinted with permission from [52].)](image)

![Figure 8. (a) Conducting sheet structure of \( \theta \)-(BTM-TTP)\(_2\)SbF\(_6\) viewed along the donor long axis. The intermolecular overlaps between HOMOs are \( a = 7.7 \), \( p = 6.5 \) and \( q = 3.6 \times 10^{-3} \). (b) The overlap mode of the donors in the stack. (Reprinted with permission from [54].)](image)

...needle-like crystals of (BTM-TTP)\(_2\)A (A = SbF\(_6\), TaF\(_6\)) have the so-called \( \beta \)-type array of donors [34, 54]. BDT-TTP molecules form a nearly uniform column in spite of the presence of bulky methylthio groups. Namely, both the interplanar distances and the slip distances are almost the same (1.6 Å) along the donor long axis. Calculation of the overlap integrals indicates that the donors are slightly dimerized in the stack. On the other hand, the interstack overlap integrals are 14–30% larger than the intrastack ones. A tight-binding calculation suggests that the calculated Fermi surface is quasi-1D.

The plate-like crystal of (BTM-TTP)\(_2\)SbF\(_6\) adopts the so-called \( \theta \)-type array (figure 8(a)) [54]. The donors are uniformly stacked with an interplanar distance of 3.44 Å. The donors slip along both the short and long axes of the donor (figure 8(b)), in contrast to \( \theta \)-BDT-TTF salts, in which only slipping along the short axis is observed. The dihedral angle of the donors between the neighboring columns is large (130.7°), indicating smaller overlap integrals than those of the \( \theta \)-salts with smaller dihedral angles. The calculated bandwidth (0.57 eV) is about half of that in \( \beta \)-(BTM-TTP)\(_2\)SbF\(_6\). The calculated Fermi surface is closed, as is characteristic of a 2D metal.

The \( \beta \)-type salts exhibit relatively high conductivity of \( \sigma_\text{a} = 30–120 \ \text{S cm}^{-1} \) and metallic temperature dependence down to 5 K. In contrast, \( \theta \)-(BTM-TTP)\(_2\)SbF\(_6\) exhibits relatively low conductivity of \( \sigma_\text{a} = 0.8 \ \text{S cm}^{-1} \) and semiconducting temperature dependence with an activation energy of 0.13 eV, probably because of narrow bandwidth and resultant large electron correlation in the quarter-filled band system.

### 3.4. TMEO-TTP and TMEO-ST-TTP salts

The BDT-TTP derivative with ethylenedioxy and two methylthio groups TMEO-TTP affords many metallic radical cation salts with octahedral and linear anions down to low temperatures (0.6–4.2 K), whereas the salts with tetrahedral anions are semiconductors [14]. Among the metallic salts, the crystal structure of only (TMEO-TTP)\(_2\)Au(CN)\(_2\) has been determined [56]. This salt has the so-called \( \beta'' \)-type array of
Figure 9. Donor-sheet structure of (Tilde{TMEO-TTP})_2Au(CN)_2. The intermolecular overlap integrals are c = 4.2, a1 = 18.3, a2 = 7.3, p1 = −11.5 and p2 = −9.7 × 10^{-3}. (Reprinted with permission from [56].)

Figure 10. Electrical properties of (Tilde{TMEO-TTP})_2Au(CN)_2. (Reprinted with permission from [56].)

donors similar to (BEDT-TTF)_2ClO_4(TCE) [6] (see figure 9). It shows a resistivity maximum around 180 K (figure 10), while the other metallic TMOE-TTP salts exhibit simple metallic temperature dependence. The thermoelectric power and electron spin resonance (ESR) spectrum of this salt also exhibit anomalies around this temperature, indicating a metal-to-metal transition (see also figure 10).

On the other hand, a selenium analog TMOE-ST-TTP forms a 1 : 1 salt with an Au(CN)_2^{-2} anion [59]. The Au(CN)_2^{-2} anion is located in a cavity surrounded by four donor molecules in the ac-plane (see figure 11). Although the TMOE-ST-TTP molecules seem at first glance to form a 2D network in the ac-plane, there is no significant lateral interaction along either a- or c-axis. The donors are strongly dimerized in the column, because one of the overlaps makes a large slip along both the long and short axes of the donor, as shown in figure 12. Thus, a tight-binding band calculation indicates that this is a 1D band insulator. In contrast to the Au(CN)_2^{-2} anion, the octahedral anions (PF_6^{-}, AsF_6^{-} and TaF_6^{-}) have afforded conducting materials that retain metallic conductivity down to 4.2 K [59, 60]. X-ray structure analysis revealed that these materials have β-type donor packing with the composition of (TMOE-ST-TTP)_2A. In these salts, the overlap mode of the donors in the stack is the ring-over-bond type (figure 13). The slip distances along the long molecular axis are about half of the 1,3-dithiole ring for p1 (1.6–1.7 Å), and one-and-a-half for p2 (4.9–5.0 Å).

As a result, the donors are electronically dimerized along the stacking direction, although the interplanar distances are almost the same (3.50 and 3.52 Å for the PF_6^{-} salt). The ratio of the calculated overlap integrals (p1/p2) is 2.3 for the PF_6^{-} salt. A tight-binding band calculation suggests that the upper and lower bands are completely separated, which corresponds to strong dimerization along the stack, and results in the formation of an effectively half-filled band. The interstack overlaps are 10–20% of the larger intrastack overlap. Thus, the calculated Fermi surface is closed along the stacking direction, but open along the interstack direction as is observed in a quasi-1D system. However, the interstack interactions are sufficiently strong to suppress the metal-to-insulator transition at low temperature.

3.5. (BEDT-TTP)_2I_3 and (EP-TTP)_2Au(CN)_2

The title materials have the donor packing close to β-(BEDT-TTF)_2I_3 [61, 62]. However, the degree of dimerization in the stack is much smaller than for BEDT-TTF salts, because the longer π-electron framework of BDT-TTP is less sensitive to overlap integral than TTF systems. A tight-binding band calculation of (BEDT-TTP)_2I_3

Figure 11. Crystal structure of (TMOE-ST-TTP)Au(CN)_2. (Reprinted with permission from [59].)

Figure 12. Overlap modes of donor molecules in (TMOE-ST-TTP)Au(CN)_2. (Reprinted with permission from [59].)
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The Fermi surface of (BEDT-TTP) suggests the existence of a 2D Fermi surface as shown in figure 14. On the other hand, the calculated Fermi surface of (EP-TTP)Au(CN)2 is quasi-1D, because the lateral interaction is smaller than that of (BEDT-TTP)I3 owing to steric hindrance by the projected propylenedithio group along the lateral direction. Both the salts exhibit high conductivity of \( \sigma_{\text{ac}} = 600-900 \, \text{S cm}^{-1} \) and retain metallic conductivity down to 0.5–0.6 K. The temperature dependence of resistivity approximately obeys the \( T^2 \) law. Such simple metallic behavior indicates that the metallic states of these salts are significantly stabilized. As a result, they show no superconductivity in spite of being isostructural with the ambient-pressure superconductor \( \beta-(\text{BEDT-TTF})_2 \).

3.6. Conducting materials based on TMET-TTP and its analogs

A BDT-TTP derivative with both methylthio and ethynedithio groups TMET-TTP and its selenium analogs have afforded \( \theta \)-type salts regardless of the counter anions [19, 20, 35, 37, 63]. It is noteworthy that even TCNQ has yielded the \( \theta \)-type conductors [20]. In these materials, the donors make pseudo-stacks, in which they slip along both the short and long axes of the donor as observed for \( \theta-(\text{BTM-TTP})_2 \)SbF6 [54]. The dihedral angles between molecular planes of adjacent stacks are as large as 118–128°. Most of the \( \theta \)-type salts based on TMET-TTP-type donors have uniform stacks, whereas the donors form dimerized stacks in (TMES-TTP)I4. The calculated Fermi surface is 2D and is similar to that of \( \theta \)-type BEDT-TTF salts. These \( \theta \)-type salts show a metal-to-insulator transition at low temperatures or exhibit semiconducting behavior at and below room temperature. Destabilization of the metallic state in TMET-TTP conductors is probably due to the narrow bandwidth and resultant strong electron correlation derived from large dihedral angles between molecular planes, as pointed out in \( \theta \)-BEDT-TTF salts by H. Mori et al [77].

The BDT-TTP derivatives with long alkyl chains have been investigated by T. Mori and co-workers to change the ratio of donor to anion in TMET-TTP salts, most of which have the composition \( \text{(TMET-TTP)}_n \text{A} \). Among them, the crystal structures of \( (C_2\text{TET-TTP})_2 \)ClO4, \( (C_2\text{TET-TS-TTP})_2 \text{A} \) \((\text{A} = \text{PF}_6, \text{ClO}_4, \text{BF}_4)\) and \( (C_4\text{TET-TTP})_2 \text{I}_3 \) have been determined [28, 29]. The radical cation salts based on \( C_2 \text{TET-TTP} \) and \( C_4 \text{TET-TTS-TTP} \) are isostructural. They have \( \beta \)-type donor packing contrary to the initial expectation of the \( \theta \)-type array, although the ratio of the donor to anion (2:1) has indeed changed from 4:1. Surprisingly, the donors form a uniform stack in spite of the presence of sterically hindered ethynithio groups, whereas most donors with large substituents are dimerized to avoid steric hindrance as is observed in CH-TTP (\( \kappa \)-type) and TMEO-ST-TTP (dimerized \( \beta \)-type) salts, with the exception of TMET-TTP (\( \theta \)-type) and BTM-TTP (both \( \beta \)- and \( \theta \)-types).

In the \( C_2 \text{TET-TTP} \) salts (figure 15), large steric hindrance in the stack derived from the ethyl chain is reduced by a larger slip along the donor long axis (4.7 Å) than that of \( (\text{BDT-TTP})_2 \)ClO4 (1.6 Å), which also has a uniform \( \beta \)-type donor array. Whereas the donors form a pseudo stack so that steric hindrance is avoidable by a slip along the donor short axis in the \( \theta \)-type conductors. All the \( C_2 \text{TET-(TS)} \)-TTP salts with tetrahedral and octahedral anions exhibit metallic conductivity down to 1.5K owing to the uniform stacks of a relatively large bandwidth. On the other hand, two donor molecules and an anion are alternatively stacked in \( (C_4 \text{TET-TTP})_2 \text{I}_3 \), in which the donors are stacked in a head-to-tail manner (figure 16). The dimer is surrounded by four \( \Gamma_1 \) anions in the \( ac \)-plane, and the interdimer overlaps \( p1 \) and \( p2 \) are only \(-0.6 \) and \( 0.03 \times 10^{-3} \), respectively. Therefore, the bandwidth of this material is expected to be very small. It shows low conductivity of 0.025 S cm\(^{-1} \) at room temperature, and has a large activation energy of 0.23 V, which corresponds with a small bandwidth and a 1:1 composition.
3.7. \((TTM-TTP)\alpha_x\)

Tetrakis(thiomethyl) derivative TTM-TTP has afforded three types of \(I_5^-\) salts: \((TTM-TTP)_{2}I_3\), \((TTM-TTP)I_3\) and \((TTM-TTP)(I_3)_{3/3}\) [64, 65]. Among them, \((TTM-TTP)I_3\) is a low-conductive \((\sigma_{\parallel} = 0.03 \text{ S cm}^{-1})\) semiconductor with a tetramerized donor stack [64]. The crystal includes a neutral donor molecule in the anion layer. \((TTM-TTP)I_3\) exhibits very high conductivity of \(\sigma_{\parallel} = 700 \text{ S cm}^{-1}\), in spite of the fully oxidized +1 state of the donor. It shows metal-like temperature dependence down to \(T_M = 160\,\text{K}\) (figure 17) [64]. TTM-TTP molecules form uniform columns with a relatively short interplanar distance of 3.45 Å (figure 18). The arrangement of the donors may be classified as \(\beta\)-type. However, effective lateral interaction is inhibited, because the methylthio groups protrude from the long molecular axis. A tight-binding band calculation suggests that \((TTM-TTP)I_3\) has a large bandwidth of \(W = 1\,\text{eV}\). The nature of the insulating state of \((TTM-TTP)I_3\) has been investigated, but has not yet been elucidated [76–81]. On the other hand, \((TTM-TTP)(I_3)_{3/3}\) also has uniform donor stacks similar to \((TTM-TTP)I_3\), and it exhibits metallic conductivity down to \(T_M = 20\,\text{K}\) (see also figure 17). The donor molecule in this material has an anomalously large positive charge of +5/3. The metallic conductive behavior in spite of large positive charges of +1 and +5/3 in TTM-TTP conductors is due to the small on-site Coulomb energy as well as the large bandwidth derived from uniform stacks [65]. The AuI\(_5^-\) and \(M X^-\) \((M = \text{Fe, Ga, } X = \text{Cl, Br})\) anions also yield 1:1 salts; however, anions that are shorter than I\(_5^-\) make dimerized columns [66–68]. As a result, they exhibit the semiconducting behavior characteristic of band insulators. In contrast, \((TTM-TTP)\text{FeBr}_{1.4}\text{Cl}_{2.2}\) exhibits metallic behavior similar to \((TTM-TTP)I_3\), because it occasionally forms uniform donor columns [68].

3.8. \((CPTM-TTP)\alpha_xA(A = PF_6, AsF_6, SbF_6)\)

The title materials are isostructural and form molecular packing similar to \(\beta\)-type salts [17]. However, they have a tetramerized column in which two crystallographically independent donors A and B are stacked as AABB as shown in figure 19. Therefore, the donor sheet structure of these salts is closer to that of \(\lambda-(\text{BETS})\text{GaCl}_4\), an ambient-pressure superconductor with \(T_c = 8\,\text{K}\) [82], rather than to that of \(\beta\)-type BEDT-TTF salts. The donor molecules are stacked in a head-to-tail manner in A–A (p1) and B–B (p3), and in a head-to-head manner in A–B (p2). The interplanar distances are 3.58, 3.61 and 3.40 Å for p1, p2 and p3, respectively (for the AsF\(_6^-\) salt). All the overlap modes are the ring-over-bond type: however, the slip distance along the long molecular axis \((D)\) of p3 (4.73 Å) is much larger than those of p1 (1.55 Å) and p2 (1.68 Å). Such a large D value of p3 does not affect the overlap integral very much in this case, because
BDT-TTP is about twice as long as TTF. Thus, the overlap of \( p_3 \) (18.1 \( \times 10^{-3} \) for the \( \text{AsF}_6^- \) salt) is only about 20\% smaller than those of the other intrastack interactions. On the other hand, there are relatively large interstack interactions (\( q_2 \) and \( q_4 \)). As a result, the Fermi surface calculated by the tight-binding method is a typical eclipse characteristic of 2D metals. Among these salts, the \( \text{PF}_6^- \) and \( \text{AsF}_6^- \) salts exhibited metallic conductivity down to 4.2 K, although maximum resistivity was observed around 80 K. In contrast, an increase in resistivity below 50 K has been observed for the \( \text{SbF}_6^- \) salt. Although the low-temperature behavior of the \( \text{SbF}_6^- \) salt is not clear, it is plausible that the largest anion of \( \text{SbF}_6^- \) among those three salts induces a strong electron correlation.

4. TTP analogs including non-TTF moiety

Various TTP donors possessing non-TTF moieties have been synthesized (see scheme 9) [83–125]. Molecular packing patterns and electrical properties of molecular conductors based on these TTP analogs are summarized in table 3.

4.1. Radical cation salts based on vinylogous TTP donors, DTEDT and DSEDS

The BDT-TTP molecule has a stripe-like structure, and all sulfur atoms have the same phase in the HOMO (figure 20). On the contrary, vinylogous TTP donor 2-(1,3-dithiol-2-ylidene)-5-(2-ethanediylidene-1,3-dithiole)-1, 3,4,6-tetrathiapentalene (DTEDT) has a crooked structure, and the \( \pi \)-orbitals of sulfur atoms at the terminal of the vinylogous 1,3-dithiole ring in the HOMO are out of phase with those of the other sulfur atoms (see also figure 20). Thus, DTEDT conductors are expected to show both sterically and electronically less effective lateral interactions than BDT-TTP salts. However, similar to BDT-TTP, DTEDT has afforded many metallic radical cation salts regardless of the size and shape of the counter anions. Furthermore, (DTEDT)\(_3\)Au(CN)\(_2\) has exhibited a superconducting transition at 4 K under ambient pressure (figure 21) [83, 84]. The donors form conducting sheets parallel to the \( \alpha \)-plane as shown in figure 22. The array of the donors is close to that of most BDT-TTP salts of the \( \beta \)-type with an almost uniform stack (figure 23). In contrast to most \( \beta \)-type salts based on unsymmetrical donors, DTEDT molecules are arranged in such a way that the stacking and lateral directions are parallel in (DTEDT)\(_3\)Au(CN)\(_2\). Because DTEDT has a crooked structure and the phase of the sulfur atoms in the HOMO is reversed at the terminal vinylogous 1,3-dithiole ring, such a parallel array results in the most effective intermolecular interaction both sterically and electronically. On the other hand, a selenium analog of DTEDT, DSEDS, has afforded a metallic TaF\(_6^- \) salt, in which the array of donors is identical to...
Table 3. Molecular packing patterns and electrical properties of conducting salts based on TTP donors containing non-TTF moieties (scheme 10).

| Material                              | Donor packing | $\sigma_i$ (S cm$^{-1}$) | Conducting behavior$^a$ | Ref |
|---------------------------------------|---------------|---------------------------|-------------------------|-----|
| (DTEDT)$_2$Au(CN)$_2$                 | Uniform β-type | 15                        | SC, $T_c = 4$ K         | [83, 84] |
| (DSEDTS)TaF$_6$                       | Uniform β-type | 9                         | M                       | [86] |
| (ET-DTDT)$_2$PF$_6$(CN)$_b$          | λ-type        | 50                        | M                       | [89] |
| (TM-TPDS)$_2$AsF$_6$                 | Windmill type | 240                       | $T_M = 100$ K           | [92] |
| (SM-PDT)PF$_6$(PhCl)$_2$             | Pseudo β-type | 4.8                       | S                       | [93] |
| (SM-PDT)TCNQ(PhCl)                   | D-A stack     | $3.9 \times 10^{-3}$      | S                       | [126] |
| (BDH-TTP)$_2$PF$_6$                  | κ-type        | 102                       | M                       | [97] |
| (BDH-TTP)$_2$[Fe(NO)](CN)$_2$        | κ-type        |                           | M                       | [127] |
| (BDH-TTP)Br$_{55.88}$               | θ-type        | 98                        | M                       | [128] |
| (BDA-TTP)$_2$A                       | β-type        | 1.5–3.8                   | SC, $T_c = 4.4–5.9$ K  | [98] |
| (A = PF$_6$, AsF$_6$, SbF$_6$)       | 9.4–53        | SC, $T_c = 2–8$ K        | [129–131]               |
| (BDA-TTP)$_2$A                       | β-type        |                           |                         |     |
| (A = GaCl$_x$, FeCl$_x$, I$_x$)      | 8.1–39        | M                         | [99]                     |
| (A = PF$_6$, AsF$_6$)                | μ-type        |                           |                         |     |
| (DHDA-TTP)$_2$A                      | β-type        | 7.4                       | M                       | [99] |
| (A = PF$_6$, AsF$_6$)                | κ-type        | 14                        | M                       | [96] |
| (EDTH-TTP)$_2$A                      | κ-type        | 100                       | M                       | [132] |
| (Cr[phen](NCS)$_2$·2CH$_2$Cl)$_2$    | Uniform β-type | 200                      | M                       | [37] |
| (C$_7$TDA-TTP)$_2$PF$_6$             | DDA stack     | $<10^{-6}$                | S                       | [37] |
| (MeDTET)$_2$PF$_6$(TCE)$_4$          | κ-type        | 440                       | M                       | [134] |
| (CPDTE)-A$_4$                      | κ-type        | 4.2–27                    | M (A = AsF$_6$)          | [135] |
| (A = AsF$_6$, SbF$_6$, x = 0.72, 0.88) |              |                           | (A = SbF$_6$)            |     |
| (MeDTDM)$_2$AsF$_6$                  | β-type        | 94                        | M $\geq 20$ K           | [101] |
| (CPDT-STP)(TCNQ)                    | β-type        | 40                        | M                       | [102] |
| (MeDH-TTP)TCF$_5$                    | κ-type        | $T_M = 165–205$ K         | [103]                   |
| (MeDA-TTP)$_2$A                      | β-type        | 1.1–5.6                   | $T_M = 165–205$ K       | [104] |
| (A = PF$_6$, AsF$_6$, SbF$_6$)       |               |                           |                         |     |
| (MeDA-TTP)$_2$ClO$_4$                | β-type        | 1.2                       | S                       | [104] |
| Ni(pdt)$_2$                          | 3D            | 7                         | S                       | [138] |
| Ni(tmd)$_2$                          | 3D, β-type    | 400                       | M                       | [120] |
| Au(tmd)$_2$                          | 3D            | 3                         | S                       | [139] |
| Zn(tmd)$_2$                          | 3D            | 0.05                      | S                       | [140] |
| Cu(dmd)$_2$                          | 3D, β’-type   | 15                        | S                       | [141] |
| Co(dmd)$_2$                          | Dimeric structure | 0.012                    | S                       | [142] |
| Pd(dt)$_2$                           | Dimeric structure | 19                      | S                       | [144] |
| Pd(C3-tdt)$_2$                       | 10$^{-2}$     |                           |                         | [121] |

$^a$ M: metallic down to low temperature ($\leq 4.2$ K), M$: increase of resistivity at low temperature, but no metal-to-insulator transition; S: semiconductor; $T_{MI}$: metal-to-insulator transition temperature, SC: superconductor; $T_c$: superconducting transition temperature.
$^b$ cn = 1-chloronaphthalene, phen = 1, 10-phenanthroline.

4.2. Radical cation salts based on (thio)pyran analogs

Three-dimensional (3D) organic conductors are of significant interest from the viewpoint of the search for molecular superconductors with higher critical temperatures ($T_c$), because $M_2$C$_{60}$ ($M$ = alkali metal) in which C$_{60}$ molecules are arranged in a 3D fashion show superconductivity with the highest $T_c \sim 40$ K among molecular materials [144]. It has also been pointed out that an increase of 3D character through an insulating anion layer results in higher $T_c$ in BEDT-TTF superconductors [145, 146]. However, a 3D Fermi surface has not yet been observed in solids based exclusively on organic molecules, but it has been theoretically suggested by a tight-binding band calculation in a metal dithiolene system, Me$_x$H$_{4-x}$,N[Pd(dmise)$_2$]$_2$ ($x = 2, 3$) [147].

Figure 20. HOMO of DTEDT (left) and BDT-TTP (right).

the average structure of (DTEDT)$_2$Au(CN)$_2$ [86]. Therefore, DTEDT may have a strong tendency to form the β-type donor arrangement similar to BDT-TTP. A tight-binding band calculation suggests that (DTEDT)$_2$Au(CN)$_2$ has a closed Fermi surface, although the one-dimensional character along the stacking direction is stronger because the stacks are almost uniform.
TTP donors containing the pyran-4-ylidene moiety, 2-(1,3-dithiol-2-ylidene)-5-(pyran-4-yli
dene)-1,3,4,6-tetrathiapentalene (PDT-TTP) [89], and its thiopyran analog (TPDT-TTP) [90], are potentially interesting for the

preparation of 3D conductors, because a significant intermolecular overlap along the long molecular axis is expected through chalcogen atoms in the (thio)pyran ring, in addition to the π–π stacking and lateral chalcogen–chalcogen interactions.

The ethylenedithio derivative of PDT-TTP (ET-PDT) has yielded a 4:1 salt with the PF$_6$ anion (ET-PDT)$_4$PF$_6$(cn) (cn = 1-chloronaphthalene) [89]. The ET-PDT molecules form conducting sheets, each being divided by insulating layers composed of the anions and solvent molecules. The array of the donors is classified as the so-called λ-type (figure 24). Thus, two crystallographically independent ET-PDT molecules A and B form a face-to-face stack with a four-folded period AABB similar to (CPTM-TTP)$_4$A (A = PF$_6$, AsF$_6$, SbF$_6$) [17]. The molecules are stacked in a head-to-tail manner for molecules AA$'$ and BB$'$ and in a head-to-head manner for AB (figure 25). This salt has an almost uniform stack from the viewpoint of interplanar distances (3.60–3.62 Å). However, the head-to-tail overlap between the unsymmetrical π-electron frameworks of PDT-TTP prevents effective intrastack overlaps, because

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**Scheme 10.** Molecular structures of analogous TTP derivatives listed in table 3.

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**Figure 21.** Temperature dependence of resistivity of (DTEDT)$_3$Au(CN)$_2$. (Reprinted with permission from [83].)

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**Figure 22.** Crystal structure of (DTEDT)$_3$Au(CN)$_2$. (Reprinted with permission from [83].)
there is little consistency in the phases of the molecular coefficients between the outer 1,3-dithiole ring and the pyran ring. The calculated overlap integrals of the head-to-tail stack, $p1$ ($8.6 \times 10^{-3}$) and $p3$ ($4.9 \times 10^{-3}$), are only about 30–50% of the head-to-head overlap $p2$ ($-16.4 \times 10^{-3}$), indicating that the ET-PDT molecules are strongly tetramerized along the stacking direction. Such difference in the manner of overlap does not affect the overlap integrals in the (CPTM-TTP)$_4A$ ($19.7-21.3 \times 10^{-3}$ for $A = PF_6$), which has a symmetrical $\pi$-electron framework of BDT-TTP. On the other hand, relatively large interstack overlaps $a1$ ($4.4 \times 10^{-3}$) and $c2$ ($-4.5 \times 10^{-3}$) are coupled with the largest intrastack overlap integral $p2$ (figure 26). Thus, the overlap along the $c$-direction is much larger than that along the $a$-direction. As a result, the calculated Fermi surface is open along $k_a$.

Radical cation salts of bis(methylthio)-derivative TM-TPDS have quite a different donor packing from that of (ET-PDT)$_4PF_6(cn)$. The crystal structure of (TM-TPDS)$_2AsF_6$ is shown in figure 27. This salt does not form a 2D conducting sheet in contrast to the typical TTP conductors. Thus, the TM-TPDS molecules are arranged in a 'windmill' manner in the $bc$-plane, whereas they form a conduction column along the $a$-axis [92]. The anions are located in a cavity formed in the center of the windmill and are surrounded by hydrogen atoms of the methylthio groups and of the thiopyran rings in the donors. The unsymmetrical TM-TPDS molecules are stacked in a head-to-tail manner along the $a$-axis and are slightly dimerized. Several sulfur–sulfur contacts are shorter than the sum of van der Waals radii between the central tetrathiapentalene moiety and the thiopyran ring or methylthio groups. The calculated overlap integrals between the columns are as large as $\sim10\%$ of the intracolumnar overlaps, thanks to the relatively large molecular orbital coefficient of the sulfur atom in the thiopyran ring and to the short sulfur–sulfur contacts. However, the calculated Fermi surface is closed only along the $k_a$ direction because intrastack interactions are still dominant in this material. (TM-TPDS)$_2AsF_6$ has high conductivity of $\sigma_\eta = 240$ S cm$^{-1}$ and metal-like conducting behavior down to 100 K. At lower temperatures, the resistivity 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 has been observed below $T_{MI}$.

Exchange of sulfur (or oxygen) atoms with selenium atoms on tetrathiapentalene, methylthio and (thio)pyran-4-ylidene moieties is expected to form a windmill structure with a higher 3D character. For this reason,
bis(methylseleno) derivatives were investigated. SM-PDT has yielded single crystals of PF$_6^-$ and AsF$_6^-$ salts suitable for x-ray structure analysis and electrical conductivity measurement [93]. Unexpectedly, these salts adopt a fully oxidized state with a composition of (SM-PDT)A(PhCl)$_4$, (A = PF$_6$ and AsF$_6$), in which the arrangement of donors is quite different from that of (TM-TPDS)$_2$AsF$_6$. Thus, the donor columns are completely divided by the counter anions and by disordered solvent molecules along the $a$-axis (figure 28), indicating the absence of lateral interaction. Instead, the donor columns are bridged by short selenium–selenium contacts within the sum of the van der Waals radii to form a 2D sheet-like structure. The Se–Se contacts between selenomethyl groups may be more preferable in this salt than the edge-to-side interactions through the tetrathiapentalene moiety, as observed in (TM-TPDS)$_2$AsF$_6$. The donors are dimerized in the column with slip distances along the donor long axis of 1.4 and 4.7 Å. On the other hand, the interstack overlap integrals through the selenomethyl groups are $\sim 1/4$ of the intrastack ones (figure 29), and they are significantly larger than the longitudinal interaction. Calculation suggests that this salt is a band insulator because of its fully oxidized state and dimerized stack. However, it has relatively high conductivity of $\sigma_\alpha = 4.8$ S cm$^{-1}$. Considering the high conductivity (in spite of being a 1:1 salt) and the relatively large edge-to-edge interaction, the 2:1 salts with the same donor array are expected to exhibit metallic conductivity down to low temperature.

4.3. TTP donors with reduced $\pi$-electron system

TTP donors have yielded many molecular metals stable down to low temperatures, but only one superconductor. This is probably due to excessive stabilization of the metallic state by the large bandwidth as well as reduced on-site Coulomb repulsion [148].

Yamada et al have developed molecular conductors based on BDH-TTP and 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene (BDA-TTP) [97, 98]$^1$ whose $\pi$-electron systems have been reduced by the exchange of double bonds in the outer 1,3-dithiole rings of BDT-TTF with a saturated ethylene or propylene bridge. Cyclic voltammetry revealed that the $\Delta E$ value becomes larger than that in BDT-TTF, suggesting an increase of the on-site Coulomb repulsion by reduction of the $\pi$-electron system. Among the conducting materials based on BDH-TTP and BDA-TTP, most BDH-TTP conductors are metallic down to low temperatures. X-ray structure analysis of (BDH-TTP)$_2$PF$_6$ reveals that the donors adopt the $\kappa$-type arrangement [97]. In this material, intradimer overlap is much smaller than those of $\kappa$-type BEDT-TTF superconductors due to steric hindrance at the terminal sp$^3$ carbons. In contrast, interdimer interaction should be larger than in BEDT-TTF salts, because all the rings are five-membered. As a result, the split of the HOMO bands characteristic of $\kappa$-type conductors should not occur in this system. Thus, the metallic state of this material is stabilized considerably by the realization of a quarter-filled band instead of the half-filled one as observed in $\kappa$-type BEDT-TTF superconductors [5]. On the other hand, BDA-TTP conductors have a strong tendency to take $\beta$-type molecular packing. In these materials, intrastack interaction is smaller compared with that of typical $\beta$-type conductors and the degree of dimerization is very large.

$^1$ For a overview of the reduced TTP conductors see [136].
because the six-membered rings at the terminal of BDA-TTP largely protrude from the molecular plane as shown in figure 30. It is noteworthy that BDA-TTP affords several superconductors with various anions of octahedral (PF$_6^-$, AsF$_6^-$, SbF$_6^-$), tetrahedral (FeCl$_4^-$, GaCl$_4^-$) and linear (I$_3^-$) shapes (figure 31) [98, 129–131].

The author and co-workers have developed many reduced TTP derivatives, in which one of the 1,3-dithiolene rings is removed [43, 100–103]. An ethylenedithio derivative, MeDTET yields many metallic radical cation salts stable down to 0.6–1.5 K regardless of the counter anions. Among metallic MeDTET salts, x-ray structure analysis of the PF$_6^-$ salt revealed that this salt has the (MeDTET)$_2$PF$_6$(TCE)$_4$ composition as well as κ-type packing of donors [134]. No observation of superconductivity, even though it is a κ-type salt, is probably owing to reduced on-site Coulomb repulsion derived from a partially filled band rather than a half-filled band. A cyclopentane analog CPDTET also yields κ-type salts, (CPDT-TTF)$_2$(AsF$_6$)$_{0.72}$ and (CPDT-TTF)$_2$(SbF$_6$)$_{0.88}$ [135], in which two donor molecules are strongly dimerized with each other in a ‘head-to-head’ manner (figure 32). However, the transport properties are very different between these two salts. (CPDT-TTF)$_2$(AsF$_6$)$_{0.72}$ exhibits metallic temperature dependence down to 4.2 K. In contrast, (CPDT-TTF)$_2$(SbF$_6$)$_{0.88}$ shows a metal-to-semiconductor transition at 200 K, and it retains metallic behavior down to low temperatures under a high pressure of 5.6 kbar. The different transport properties are probably due to different occupancies of the anion sites. The band structure of the SbF$_6^-$ salt is very close to a half-filled band, leading to a metal–semiconductor transition due to strong electron correlation. In contrast, the band filling of the AsF$_6^-$ salt is far from half-filled because there are more anion defects than in the SbF$_6^-$ salt, which hampers the semiconducting transition. On the other hand, a selenium analog CPDST-STF forms a TCNQ complex with 2D β-type donor packing. (CPDT-STF)(TCNQ) exhibits metallic conductivity down to low temperatures [102]. A dimethyl-substituted derivative, MeDTDM, yields β-type salts. They show metallic conductivity down to 20 K, below which the resistivity increases [101].

Nishikawa et al. investigated TTP analogs, MeDH-TTP and MeDA-TTP, with more reduced π-conjugation [103, 104]. MeDA-TTP salts with octahedral and tetrahedral anions are isostructural and have β-type donor packing similar to that in BDA-TTP superconductors [104]. They exhibit metallic behavior down to 165–205 K, whereas the ClO$_4^-$ salt is a semiconductor with a small activation energy of 0.028 eV. (MeDH-TTP)$_2$AsF$_6$ crystallizes in a κ-type structure [103]. A tight-binding calculation suggests the dimerization gap in this salt is much smaller than in typical κ-type BEDT-TTF conductors, leading to an almost 3/4-filled band (figure 33). This salt shows semiconducting behavior below room temperature with a small activation energy of 0.032 eV. ESR measurements suggest an antiferromagnetic transition at 40 K [149]. A detailed study of the dependence of resistivity on T-P revealed simple metallic behavior above $P_c = 2.4$ GPa [150], which is much larger than the critical pressure for a typical Mott transition in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl ($P_c = 0.03$ GPa) [151] and is similar to that observed in the charge-ordered insulator (DIDCNQ)$_2$Ag ($P_c = 2.2$ GPa) [152]. Considering this salt has a quarter-filled band and a large $P_c$, the most plausible origin of the insulating state for (MeDH-TTP)$_2$AsF$_6$ is the charge-ordering state [150].

4.4. Higher homologs of TTP

The higher homologs of TTP donors are also of interest, not only as a promising component for molecular metals but also as a candidate for molecular electronics. A tris-fused TTF, 2,2′-bit(1′′, 3′-dithiol-2′-ylidene-1,3,4,6-tetrathiapentalene-5-ylidene)(BDT-TTPY, scheme 8), has been synthesized by the P(OE)$_3$-mediated coupling reaction of 1,3-dithiol-2-one fused with TTFs (5) [107, 108]. The cyclic voltammograms of BDT-TTPY derivatives measured in benzonitrile-carbon
disulfide are composed of three pairs of redox waves, each corresponding to a two-electron transfer [107]. The solubility of BDT-TTPYs in common organic solvents is extremely low compared with the corresponding BDT-TTF derivatives. Therefore, the usual electrochemical oxidation technique cannot be adopted for the preparation of conducting materials. Instead, chemical doping of the BDT-TTPY suspension with appropriate oxidants such as iodine or NO$_2$X (X = BF$_4$, SbF$_6$) has been carried out. Among the conducting materials obtained, several iodine complexes have high conductivity of $\sigma_n = 0.7$–16 S cm$^{-1}$ on compressed pellet samples [107, 108], and several have very small activation energies of 0.017–0.033 eV. Therefore, these materials are expected to exhibit metallic conductivity if conductivity measurements are performed on single crystals. A crystal of TTC$_3$-TTPY doped with iodine vapor exhibits metal-like conductivity down to 1.3 K, as shown in figure 34 [110].

Analogous TTPY donors containing a $\pi$-electron framework other than TTF have also been synthesized. In particular, extended TTPYs, in which an aromatic ring, such as benzene, thiophene or furan, is inserted into the central TTF moiety, exhibit higher solubility in common solvents [112]. As a result, CT complexes have been formed by the usual mixing technique in organic solvent. The TCNQF$_2$ complexes based on 14–16 exhibit relatively high conductivity of $\sigma_n = 10^{-1}$–10$^0$ S cm$^{-1}$ on compressed pellets. Higher homologues of TTPY possessing up to seven donor units have also been synthesized thanks to increased solubility using a thiophene-inserted TTF unit [113].

4.5. Analogous metal complexes of BDT-TTPY, $M(dt)_2$: highly conducting single-component molecular conductors

The derivatives of metal bis(TTF-dithiolato) ($M(dt)_2$), where dt is 2-(1,3-dithiol-2-ylidene)-1,3-dithiole-4,5-dithiolate, designed by exchange of the central double bond of BDT-TTPY with a metal ion, have received significant attention as candidates for single-component molecular metals, because both the donor (TTF) and acceptor (metal bis(dithiolato)) moieties are present in the molecule. Schmucker and Engler have reported, the synthesis of metal complexes with TTF-dithiolate ligands $M(dt)_2$ as analogs of BDT-TTPY [8]. Unfortunately, most anionic $M(dt)_2$ complexes are readily oxidized to insoluble neutral complexes due to the presence of strongly electron-donating TTF moieties. The first synthesis and characterization of anionic $M(dt)_2$ complexes have been reported independently by the groups of Underhill ($M = Hg$) and Matsubayashi ($M = Au$) [114, 115]. Several $M(dt)_2$ derivatives have been prepared since then: however, the synthesis of single crystals of neutral complexes remains difficult.

Kobayashi and co-workers have succeeded in growing single crystals of various $M(dt)_2$ derivatives using an electrocrystallization technique and have studied their structures and physical properties [119–123, 138–141]. Among them, Ni(tmdt)$_2$ exhibits very high conductivity of $\sigma_n = 400$ S cm$^{-1}$ on a single crystal. The temperature dependence of the resistivity and magnetic susceptibility reveals metallic conducting behavior down to 0.6 K [120]. Figure 35 shows the crystal structure of Ni(tmdt)$_2$. The packing pattern of the molecules viewed along the long molecular axis resembles the so-called $\beta'$-type as observed in BEDT-TTF conductors. On the other hand, half of the molecules are overlapped in the stack: namely, one molecule is stacked to extend over two molecules. A tight-binding band calculation, assuming a HOMO-LUMO (lowest unoccupied molecular orbital) gap of 0.1 eV, suggests that this material has a 3D Fermi surface. This result is consistent with the Fermi surface experimentally obtained by measuring the de Haas–van Alphen effect [151]. A gold complex, Au(tmdt)$_2$, is isostructural with Ni(tmdt)$_2$. The ESR, nuclear magnetic resonance, and magnetic susceptibility measurements revealed an antiferromagnetic transition at 110 K in this complex (figure 36) [139]. Electrical conductivity of single-crystal Au(tmdt)$_2$ revealed metallic behavior down to low temperatures, indicating coexistence of itinerant electrons and localized magnetically ordered spins. Thus, Au(tmdt)$_2$ is a new antiferromagnetic molecular metal with a critical temperature $T_N$ above 100 K.

2 For a overview of molecular conductors based on $M(dt)_2$ derivatives see [137].
The fusion of two (or more) donor units, in other words, the insertion of the tetrathiapentalene moiety into π-electron donors, is a reliable guiding principle to design stable molecular metals. However, the metallic state is too stabilized to cause superconducting transitions in many cases, with the exception of BDA-TTP systems. Furthermore, various chemical modifications of TTP molecules are important to control the bandwidth, band-filling and on-site Coulomb repulsion in their conducting materials and to develop new superconductors with higher $T_c$ and novel molecular metals with multifunctionality, such as magnetic molecular metals or photoinduced highly conducting materials.

Acknowledgments

The author is grateful to Dr T Shirahata and Professor H Nishikawa for valuable discussions. This work was partially supported by Grants-in-Aid for Scientific Research (Nos. 15073216, 18GS0208 and 20110006) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, from the Japan Society for the Promotion of Science, and from the Ehime University COE incubation program.

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