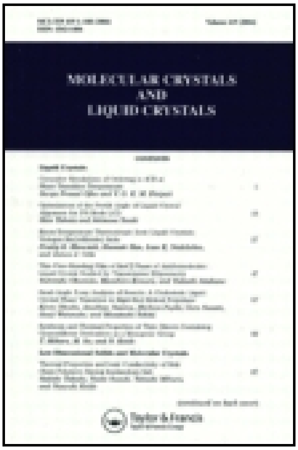

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New Organic Metals Based on Bis-Fused TTF Donors

Takehiko Mori [a], Tadashi Kawamoto [a], Yohji Misaki [b], Kazuya Kawakami [b], Hideki Fujiwara [b], Tokio Yamabe [b], Hatsumi Mori [c] & Shoji Tanaka [c]

[a] Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Tokyo, 152, Japan

[b] Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Yoshida, Kyoto, 606-01

[c] International Superconductivity Technology Center, Shinonome, Tokyo, 135, Japan

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NEW ORGANIC METALS BASED ON BIS-FUSED TTF DONORS

TAKEHIKO MORI AND TADASHI KAWAMOTO
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Tokyo 152, Japan

YOHJI MISAKI, KAZUYA KAWAKAMI, HIDEKI FUJIWARA, AND TOKIO YAMABE
Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Yoshida, Kyoto 606-01, Japan

HATSUMI MORI AND SHOJI TANAKA
International Superconductivity Technology Center, Shinonome, Tokyo 135, Japan

Abstract A large number of radical-cation salts that retain metallic conductivity down to low temperatures have been prepared on the basis of bis-fused tetrathiafulvalene (TTF) donors. The stable states are associated with inherent tendency of these extended molecules to form two-dimensional conducting sheets. Structural and conducting properties of various TTP salts so far obtained are summarized.

Radical cation salts of tetrathiafulvalene (TTF) derivatives have been attracted a great deal of attention because they show high electrical conductivity and sometimes superconductivity. A considerable amount of efforts have been exerted in order to extend the skeleton of TTF for developing new family of molecular conductors and superconductors. Among them the synthesis of bis-fused TTF, where two TTF molecules are directly connected by sharing two carbon atoms (Figure 1), have been attempted for many years.[1] Schumaker and Engler reported syntheses of bis-fused TTF with electron-withdrawing substituents, CN and CF_3, in as early as 1980,[2] but their method was not generally applicable; tetrathiapentalenedione cannot be cross-coupled with other ketones or thiones because the self-coupling reaction occurs immediately.

Their general synthetic routes were only recently designed by Misaki *et al.* They have discovered two independent routes to these extended donors. The key step of the first route is the use of dichloromethyl methyl ether, which enables preparation of the dithiolium salt derived from tetrathiapentalenedione.[3] This intermediate is used for

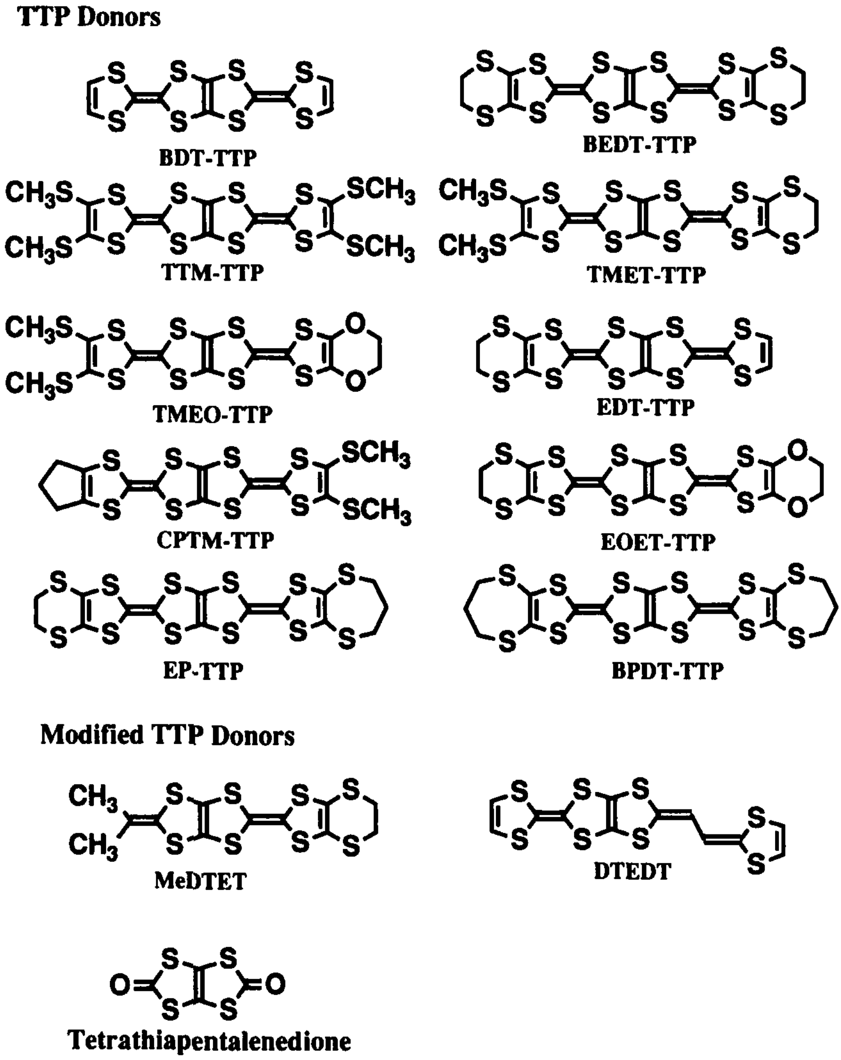


FIGURE 1 Representative TTP donors and modified TTP donors. Tetrathiapentalenedione does not have donor ability.

the preparation of MeDTET (2-isopropylidene-1,3-dithiolo[4,5-d]ethylenedithio-TTF) series and vinylogous DTEDT (2-(1,3-dithiol-2-ylidene)-5-(2-ethanediylidene-1,3-dithiole)-1,3,4,6-tetrathiapentalene) series donors (bottom in Figure 1), but the usual BDT-TTP derivatives are not prepared from this intermediate. The key steps of the second route are the use of acetoxybenzyl group as a protecting group, and successive deprotection after the first cross-coupling reaction.[4] Variously substituted BDT-TTP derivatives have been prepared from this route.

Since these bis-fused TTF donors have a structure where a tetrathiapentalene (TTP) unit (two five membered rings connected back to back with each other) is inserted into the central C=C bond of a TTF molecule (Figure 1), we usually call these donors as "TTP series" in contrast to the usual "TTF series." We will use an abbreviation system that a substituted BDT-TTP derivative is called by simply changing TTF to TTP in the abbreviation of the corresponding TTF; for example BEDT-TTP (bis(ehylenedithio)-TTP) from BEDT-TTF (Figure 1). As an exception, the parent unsubstituted donor will be called as BDT-TTP (2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene) instead of simply "TTP." On the other hand MeDTET and DTETD are regarded as "modified" TTP series; MeDTET is a "truncated" TTP and DTEDT is a vinyloeous TTP.

The first donor, whose radical-cation salts with various counter anions are extensively investigated, is TTM-TTP (tetrathiomethyl-TTP) (Figure 1),[4,5,6] where four hydrogen atoms of BDT-TTP are substituted by thiomethyl groups. Thanks to the flexibility of the thiomethyl groups, solubility of this donor in organic solvents is much improved; better than BEDT-TTF. The thiometyl groups of TTM-TTP, however, extend to the side of the molecule, inhibiting "side-by-side" intermolecular sulfur-to-sulfur contacts. Then the TTM-TTP salts exhibit highly one-dimensional properties, and actually many of them show semiconducting behavior even at room temperature.[5] This is the same situation already found in the corresponding TTM-TTF salts.[7]

The exception is its iodine salts. There have been found three different phases of the iodine salts: α-$(TTM\text{-}TTP)_2I_3$, β-$(TTM\text{-}TTP)_2I_3$ and $(TTM\text{-}TTP)I_3$.[6] The α-phase is a poorly conducting semiconductor, and its crystal structure is composed of

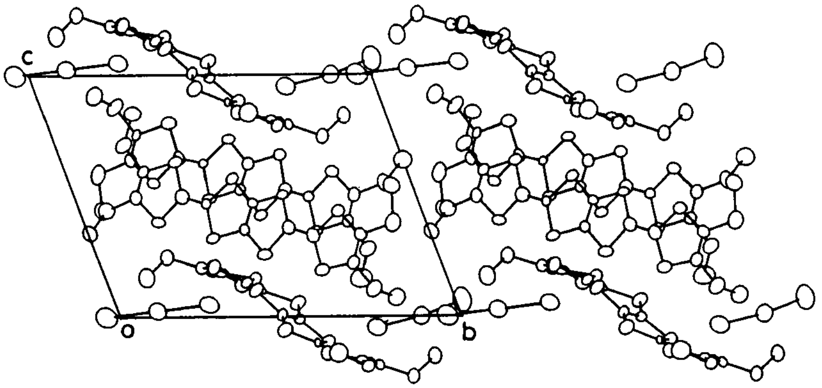


FIGURE 2 Crystal structure of α-$(TTM\text{-}TTP)_2I_3$, viewed along the stacking direction.

trimerized donor stacks and anion sheet incorporating donor molecules (Figure 2). The β-phase has a characteristic copper color, and undergoes a metal-insulator transition at 20 K, but its crystal structure is not known. In spite of the 1:1 composition (TTM-TTP)I_3 shows high conductivity 700 Scm^{-1} at room temperature and metal-like down to about 160 K, at which it exhibits a metal-insulator transition. This salt has a very simple uniform columnar structure. In general cation- or anion-radical salts with 1:1 composition are believed to be insulator, because they correspond to the half-filled case of the Mott-Hubbard model. The present compound is probably the first exception that violates this general rule.

Since a TTP series donor has four 1,3-dithiole units (five-membered rings), four successive oxidations up to D^{4+} are theoretically possible. Actually cyclic voltammogram of the TTP donor exhibits four reversible waves corresponding to four one-electron oxidations. Because the π-electrons are delocarized on the large molecule, the first oxidation E_1 from D^0 to D^+ and the second one E_2 from D^+ to D^{2+} appear comparatively close, and the difference $\Delta E=E_2-E_1$ is one-half to two thirds of those of the TTF series.[3] This difference ΔE is usually regarded as a measure of the on-site Coulomb repulsion U. The on-site Coulomb repulsion U has been also estimated from the optical measurement of (TTM-TTP)I_3 as 0.5 eV,[8] which is again considerably smaller than those of the TTF salts (0.6-1.2 eV). Undoubtedly small U is one of the most remarkable characteristic of the TTP donors, directly originating in the molecular structure. This point is clearly demonstrated by the occurrence of the 1:1 metallic salt, (TTM-TTP)I_3.

The second TTP donor whose salts are investigated in detail is TMET-TTP (dithiometylethylendithio-TTP) (Figure 1), where one side is substituted by two thiomethyl groups and another side by an ethylenedithio group.[9,10] The solubility of this donor is approximately comparable to BEDT-TTF. Irrespective of the counter anions, this donor forms basically isostructural salts with so-called θ-type donor arrangement (Figure 3). They are moderately conductive 10-30 Scm^{-1} at room temperature and undergo metal-insulator transitions around 200 K. (TMET-TTP)$_3$AsF_6 is an exception; it is metallic down to He3 temperatures, though its crystal structure is isostructural to the other TMET-TTP salts, by judging from its lattice constants.[11] These TMET-TTP salts have been investigated by scanning tunneling microscopy, where the molecular image and the thick conducting layers have been directly observed.[12]

It is worth noting that anion content of the TMET-TTP salts is relatively low, between x=0.20 and 0.40 in $D\bullet A_x$. The same tendency is generally observed in other

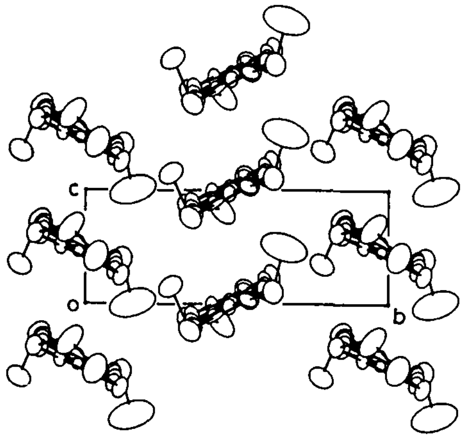


FIGURE 3 θ-type donor arrangement of (TMET-TTP)$_4$PF$_6$.

TTP donors; 3:1 and 4:1 compositions as well as the 2:1 composition are very common in the TTP salts. On the contrary 2:1 and 3:2 compositions are usual in the TTF salts. Since the TTP donors have two TTF units in a molecule and can be oxidized up to 4+ cations, high anion content and comparatively high oxidation states might be likely in the TTP series. What actually happens is the inverse of this naive consideration. The reason is still not clear, but it may be not related to the electronic origin but probably to the molecular size or packing.

The third family is donors having ethylenedioxy unit. In particular TMEO-TTP (dithiomethylethylenedioxy-TTP) (Figure 1), where the ethylenedithio group of TMET-TTP is substituted by the ethylenedioxy group, has a good solubility, better than BEDT-TTF. Its radical-cation salts with linear and octahedral anions show metallic conductivity down to He3 temperatures, whereas the salts with tetrahedral and monoatomic anions are semiconductive even at room temperature.[13,14] The tendency to make metallic salts regardless to the counter anions is similar to BO (bis(ethylenedioxy)-TTF). These TMEO-TTP salts are usually obtained as well-grown beautiful crystals, but their crystal structure analyses are ordinarily impossible. This is again similar to the BO salts; it is probably related to the strong "self-aggregation" of the donors owing to the hydrogen bonding of the ethylenedioxy parts, which tend to make the anion sheets seriously disordered.

As an exception, crystal structure of (TMEO-TTP)$_2$Au(CN)$_2$ has been investigated.[13] The donors form so-called ClO$_4$-type arrangement (Figure 4), which is again similar to the BO salts, because most BO salts make this donor arrangement.[15] Conducting behavior of this salt is not ordinary (Figure 5); it is metal-like down to 200

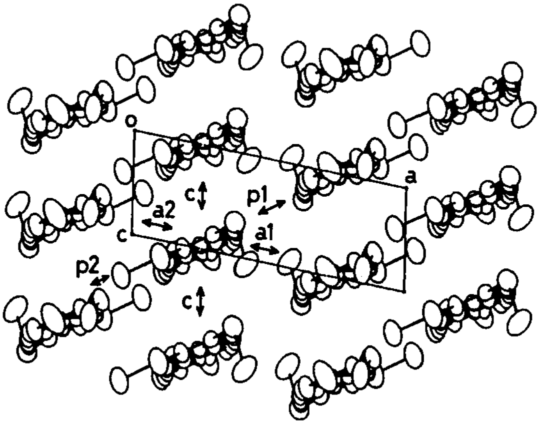


FIGURE 4 Donor arrangement of $(TMEO\text{-}TTP)_2Au(CN)_2$, viewed along the molecular long axis.[13]

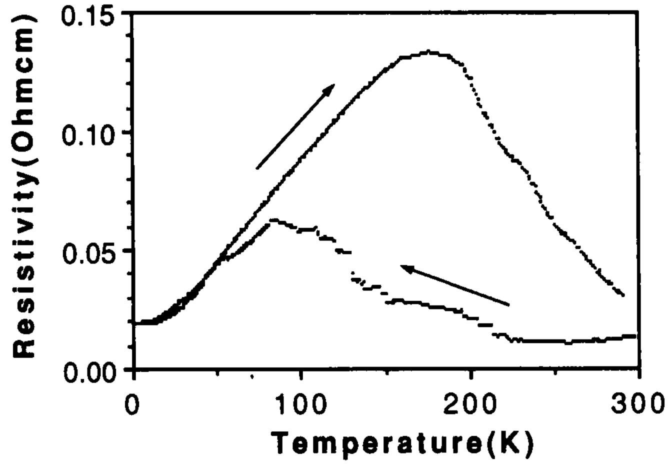
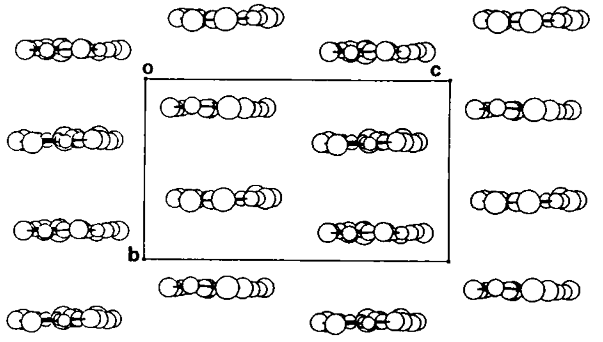


FIGURE 5 Electrical resistivity of $(TMEO\text{-}TTP)_2Au(CN)_2$.

K, below which the resistance jumps several times, but there again appears a steep metallic behavior below 100 K. In a heating run there is no hysteresis up to 100 K, but the resistivity makes a maximum at around 180 K, and decreases above this temperature, recovering the initial room-temperature value. Though this kind of behavior is usually attributed to crystal cracks, anomalies have been also found in ESR and the temperature dependence of the lattice constants. Therefore it is reasonable to believe that the anomalous conducting behavior is associated with some intrinsic "metal-to-semimetal" transition. Similar resistance jumps are frequently observed in other TTP salts: some BDT-TTP salts,[16] many EDT-TTP salts,[17] and some CPTM-TTP salts.[18] In particular, conducting behavior of (CPTM-TTP)$_4$PF$_6$, including its pressure and current direction dependence has been investigated in detail, and a phenomenological interpretation based on a kind of "metal-to-metal" transitions have been proposed.[18] It is especially characteristic of (CPTM-TTP)$_4$PF$_6$ that not only usual upward resistivity jumps but also *downward* resistivity jumps are frequently observed.

Another donor containing ethylenedioxy part is EOET-TTP (ethylenedioxy-ethylenethio-TTP) (Figure 1). Solubility of this donor is poorer than BEDT-TTF, but better than BEDT-TTP owing to its unsymmetrical structure. Its AsF$_6$ salt has κ-type donor arrangement, but its composition is 3:1, (EOET-TTP)$_3$AsF$_6$.[19] Similar 3:1 κ-phase has been also found in (MeDTET)$_3$PF$_6$TCE$_x$.[20] These salts are metallic but not superconducting down to He3 temperatures. Although the band structures of these salts are essentially similar to other κ-phase salts, the band-filling is different and the cross-section of the Fermi surface should be smaller. If good crystals of these salts are prepared, its Fermiology will be interesting.

It was a comparatively later stage of our research that we investigated the parent unsubstituted donor, BDT-TTP. Surprisingly this donor affords metallic salts regardless to the counter anions, including tetrahedral, octahedral, linear, and monoatomic anions.[21] Crystal structures of the BDT-TTP salts, so far solved, have almost uniform columns (Figure 6).[17] Since the magnitude of transverse transfer integrals are about one third to one fourth of the intracolumnar ones, the intercolumnar interactions are regarded as strong enough to suppress one-dimensional instabilities. This is associated with many short transverse sulfur-to-sulfur contacts, and is considered to be the direct result of the elongated molecular structure. It is easily convinced



FUGURE 6 Uniform columnar structure of (BDT-TTP)$_2$(ReO$_4$)$_{0.72}$, viewed along the molecular long axis.

that such a long molecule has to be packed parallel to each other in a crystal, and perpendicular packing like (TTF)$Cl_{0.77}$, which results in highly one-dimensional electronic structure, is unlikely.[22]

Greatest obstacle in the research of the TTP donors is their poor solubilities. In particular BEDT-TTP is practically insoluble even in carbon disulfide; such low solubility is a serious drawback both in the preparation (particularly in column chromatography) and in crystal growth. A lot of efforts have been done for overcoming this difficulty, and recently reasonably good crystals of some poorly soluble TTP donors have been obtained, and their crystal structures have been analyzed. First of them is $(EP\text{-}TTP)_2Au(CN)_2$ (EP-TTP: ethylenedithiotrimethylenedithio-TTP) (Figure 1).[23] Thanks both to the flexible trimethylene group and to the unsymmetrical structure, this donor shows a little better solubility than BEDT-TTP; it is reasonably soluble in carbon disulfide. This salt shows high conductivity 400 Scm^{-1} at room temperature, and metallic behavior following $\rho \propto T^2$ down to He3 temperatures, though superconductivity has not been found. Although the donor arrangement is essentially the same as β-$(BEDT\text{-}TTF)_2I_3$,[24] the calculated transfer integrals are rather one-dimensional; the intercolumnar transfer integrals are one fifth to sixth of the intracolumnar interaction. As a result, the calculated Fermi surface is composed of open sheets. This relatively one-dimensional nature reminds us one-dimensionality of $(BPDT\text{-}TTF)_2I_3$.[25] Though this salt is isostructural to β-$(BEDT\text{-}TTF)_2I_3$, it is highly one-dimensional and shows semiconducting property even at room temperature.

Another salt whose crystal structure has been analyzed is $(BEDT\text{-}TTP)_2I_3$.[26] Because of the poor solubility of BEDT-TTP, we first attempted "chemical doping" to this donor.[16] The donor was suspended in chloroform and treated with such oxidizing reagents as I_2, Br_2, $FeCl_3$, NO_2BF_4 and $Cu(ClO_4)_2$. The resulting black precipitate was filtered, dried, and the compressed pellets were prepared. These pellets showed high electrical conductivity, particularly in iodine-doped case, metallic conductivity down to He temperatures. It should be also mentioned that BPDT-TTP (Figure 1), after the same treatment, showed insulating properties. Therefore such a treatment is helpful to make a prediction as to the conducting properties of these salts.

Later we obtained crystals of the BEDT-TTP salts grown by means of the electrochemical crystallization at elevated temperatures, and these crystals exhibited metallic conductivity down to He temperatures almost irrespective of the counter anions. So far, however, only the crystal structure of $(BEDT\text{-}TTP)_2I_3$ has been investigated.[26] The conducting behavior of this salt is quite similar to $(EP\text{-}TTP)_2Au(CN)_2$; high conductivity 900 Scm^{-1} at room temperature, and metallic behavior following $\rho \propto T^2$ down to He3 temperatures (Figure 7), and superconductivity

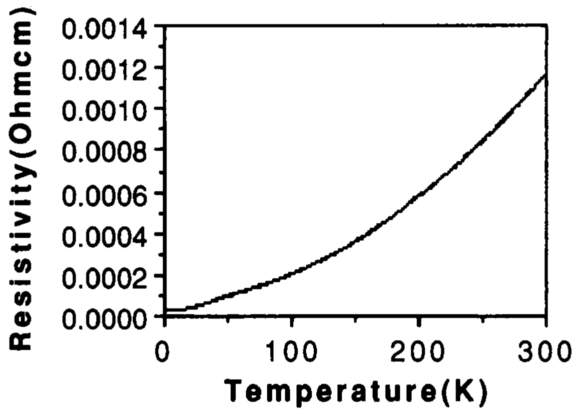


FIGURE 7 Electrical resistivity of $(BEDT\text{-}TTP)_2I_3$.

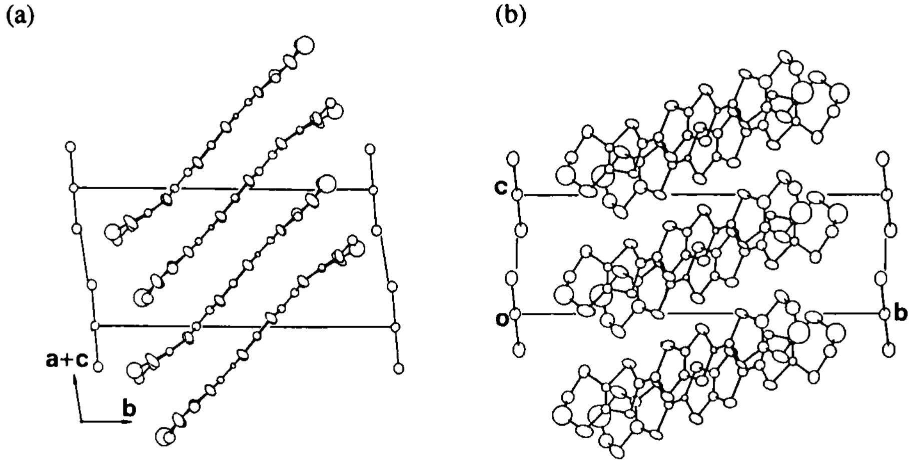


FIGURE 8 Crystal structure of $(BEDT\text{-}TTP)_2I_3$.

has not been found. This salt is again essentially isostructural to β-$(BEDT\text{-}TTF)_2I_3$ (Figure 8). The transfer integrals are rather similar to β-$(BEDT\text{-}TTF)_2I_3$ than $(EP\text{-}TTP)_2Au(CN)_2$, and the resulting Fermi surface is close like β-$(BEDT\text{-}TTF)_2I_3$.

Conducting behavior of these BEDT-TTP and EP-TTP salts conveys the impression that these donors make "too good metals" to realize superconductivity. Actually they are metallic irrespective of the counter anions, and room-temperature conductivities are very high. The $\rho \propto T^2$ behavior, which is attributable to the electron-electron interaction, indicates that these metals can be regarded as conventional Fermi liquid. In addition the thermoelectric power of these salts follows the usual T-linear behavior. On the contrary the thermoelectric power of BEDT-TTF salts show quite complicated temperature dependence and anisotropy.[27] This "simple" behavior of these metals is probably associated with the "small-*U*" character of these donors. As mentioned above, the on-site Coulomb repulsion *U* of the TTP donors is regarded as reduced in comparison with the TTF donors. On the other hand the calculation of transfer integrals has been shown that the bandwidths *W* of these TTP salts are comparable to those of the usual TTF salts (about 1 eV). Therefore the ratio U/W is reduced in the TTP salts, and the effect of correlation is relatively unimportant. This will increase the opportunity for obtaining metallic salts, but might reduce one for obtaining superconductors.

Though any superconductors have not been obtained among the usual TTP salts, recently $Au(CN)_2$ salt of the vinylogous analog, $(DTEDT)_3Au(CN)_2$ has been found to be superconducting below 4 K at ambient pressure.[27] Most other salts of this donor with different anions are also metallic down to He temperatures, but superconductivity has not been found in these cases. $(DTEDT)_3Au(CN)_2$ has uniform stack of donors. Owing both to the uniform structure and to the low anion content, the calculated Fermi surface is closed. It is worth noting that a 3:1 composition organic superconductor is quite rare.[29]

In the present paper we have summarized the present status of the research about the TTP series salts. These studies have clarified several characteristic features of the TTP salts: small on-site Coulomb repulsion *U*, small anion content, frequently observed metal-to-metal transitions, two-dimensional donor arrangements, and poor solubilities. Table I summarizes TTP salts whose crystal structures have been investigated. We have also described general tendency of each donor; whether each donor tends to form conducting salts or insulating salts, and whether each donor tends to form one-dimensional stacking or two-dimensional arrangement. We should, however, point out danger of excess generalization. If we generalize the properties of BEDT-TTF salts, it can be said that the general tendency of BEDT-TTF is forming semiconductors, because more than half of the reported BEDT-TTF salts are semiconductors even at room temperature, and about 20 % undergo metal-to-insulator transitions. Superconductors are only 10% of the so far reported BEDT-TTF salts.

It should also be pointed out that it is desirable to investigate each salt more carefully. In particular no experimental evidence of Fermi surface of TTP salts has been obtained. It is not obvious that the band calculation which has been agreeable with the experiments in BEDT-TTF salts is also realistic in the TTP salts. In order to carry out such experiments, improvement of crystal quality will be required. Some TTP salts are only obtained in the form of very thin plates, being mechanically weak,

TABLE I Structurally identified TTP salts.

Compound	Structure Type	Conductivity Scm^{-1}	a)	Ref.
α-(TTM-TTP)$_2$I$_3$	Trimerized Column	0.03	I	6
β-(TTM-TTP)$_2$I$_3$	Uniform Column?$^{b)}$	200	T_{MI}=20K	6
(TTM-TTP)I$_3$	Uniform Column	700	T_{MI}=160K	6
(TTM-TTP)(PF$_6$)$_{0.267}$(THF)$_{0.6}$	Pentamerized Column	0.003	I	5
(TMET-TTP)A$_x$ (A=AuI$_2$, PF$_6$, ReO$_4$, IO$_4$, ClO$_4$ x=0.13-0.34)	θ-type	9-45	T_{MI}=200K	10
(TMEO-TTP)$_2$Au(CN)$_2$	ClO$_4$-type	200	M'	13
(TMEO-TTP)$_3$SbF$_6$	Trimerized β'-type	9	I	14
(TMEO-TTP)AuBr$_2$THF	Dimerized Column	0.12	I	32
(EOET-TTP)$_3$AsF$_6$	κ-type	600	M	19
(BDT-TTP)A$_x$ (A=ClO$_4$, ReO$_4$, BF$_4$ x=0.36-0.50)	Uniform Column	160-400	M'	17
(BDT-TTP)$_2$SbF$_6$	β-type	48	M	21
(EP-TTP)$_2$Au(CN)$_2$	β-type	400	M	23
(BEDT-TTP)$_2$I$_3$	β-type	900	M	26
(MeDTET)$_3$PF$_6$TCE	κ-type	440	M	20
(DTEDT)$_3$Au(CN)$_2$	Uniform Column	15	SC (4K)	28

a) I: semiconductor at room temperature, M: metallic down to He3 temperatures, M': metal-to-metal transitions but metallic down to He3 temperatures, SC: superconducting.
b) Crystal structure of this salt is not solved, but its lattice constants strongly suggest the existence of uniform column.

and the residual resistivity ratio is not large. We hope that such experiments will open new features of chemistry and physics of these new materials.

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