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Newly modified TTF and DSDTF donors for developing molecular-based organic metals

Jun-ichi Yamada,*[a] Hiroyuki Nishikawa[b] and Koichi Kikuchi[b]

[a]*Department of Material Science, Faculty of Science, Himeji Institute of Technology,*
1475–2 Kanaji, Kamigori-cho, Ako-gun, Hyogo 678–1297, Japan.
E-mail: yamada@sci.himeji-tech.ac.jp
[b]*Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192–0397, Japan*

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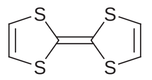
The development of organic metals based on newly modified TTF (tetrathiafulvalene) and DSDTF (diselenadithiafulvalene) donors *via* the Lewis acid-promoted reactions of organotin compounds with electrophiles is described. The Me_3Al-promoted reaction is versatile for construction of 1,3-dichalcogenol-2-ylidene moieties, and the BF_3-promoted reaction is utilized to prepare the 1,3-dithiole-2-chalcogenone derivatives condensed with a bis-fused six-membered heterocycle. The use of these reactions enables us to synthesize DHTTF (dihydrotetrathiafulvalene) donors, DHTTF-fused donors, DSDTF donors incorporating the vinylenedithio end group, and TTF donors with an extended periphery by addition of aliphatic heterocycles. The crystal structures of radical-cation salts derived from these π-electron donors, including some new κ-type salts with a 2 : 1 (donor : anion) stoichiometry, are also disclosed.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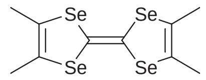
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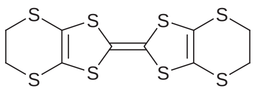
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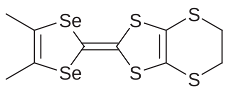
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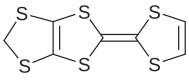
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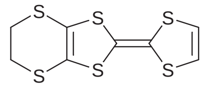
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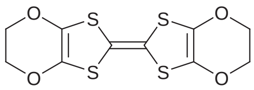
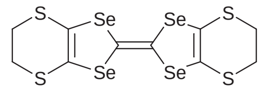
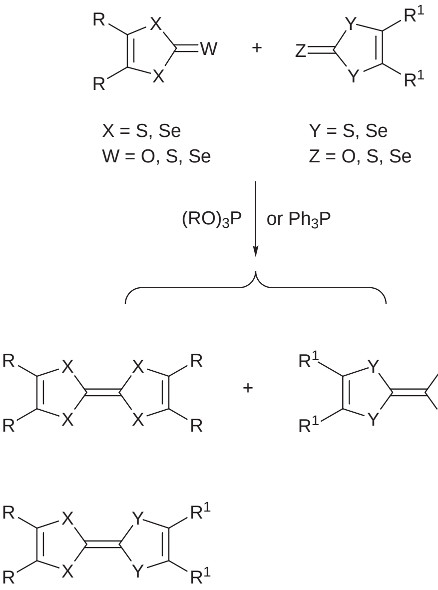

BEDO-TTF **7**


BETS **8**

Research on the development of molecular-based organic metals, which was initiated by the first finding that the charge-transfer (CT) complex composed of TTF (tetrathiafulvalene, **1**) and TCNQ (tetracyanoquinodimethane) exhibited metallic conducting behaviour,[1] has been increasingly accelerated by the discovery of superconductivity in the CT salts containing TMTSF (tetramethyltetraselenafulvalene, **2**) or BEDT-TTF (or simply, ET) [bis(ethylenedithio)tetrathiafulvalene, **3**] as a donor component,[2] followed by the salts of unsymmetrical donors DMET [dimethyl(ethylenedithio)diselenadithiafulvalene, **4**][3] and MDT-TTF (methylenedithiotetrathiafulvalene, **5**),[4] as well as the $Ni(dmit)_2$ (dmit = 4,5-dimercapto-1,3-dithiole-2-thione) complex with EDT-TTF (ethylenedithiotetrathiafulvalene, **6**).[5] Simultaneously, continuous interest in this field has been sustained by synthetic organic chemists resulting in the production of a good number of TTF derivatives and their analogs.[6] The rational designs of new TTF-based π-electron donors over the past several years have evolved mainly from (i) the realization of increased dimensionality of the conduction pathway in conducting materials, which was shown by the structural features of the superconducting ET salts with approximately isotropic conductivity in the donor sheet including the intermolecular S···S network [two-dimensional (2D) character], (ii) the expectation of a decrease in the on-site Coulombic repulsion involved in the formation of a dicationic species [an increase in delocalization of the generating positive charge(s)], and (iii) the novel suggestions for the donor packing motif in the CT complexes and/or salts. Thus, major attempts to modify the TTF skeleton have been directed towards (i) introduction of the extended π-conjugation unit as a spacer group in place of the central C=C bond of the TTF core, (ii) linkage of more than two TTF units (dimeric and oligomeric TTFs) through the σ-bond, including single atoms such as chalcogen and phosphorus, the π-conjugation spacer group, and the fused fashion, and (iii) functionalization by the substituent bearing -OH and/or -NRH groups that would enable intermolecular hydrogen bonding, and by halogen directly attaching to the TTF molecule. The resulting extended or functionalized TTF-type donor molecules have been surveyed in some excellent reviews[7] and conference proceedings[8] published in recent years. In addition, replacing sulfur atom(s) with the lighter oxygen or with the larger and more polarizable selenium or tellurium[9] has still been a promising simple modification of the skeleton for the prototype sulfur-based TTF derivatives. For example, ET was transformed, by substitution of the outer ring sulfur atoms with oxygen atoms, into BEDO-TTF [bis(ethylenedioxy)tetrathiafulvalene, **7**], which has yielded superconducting salts,[10] and the TSF (tetraselenafulvalene)-analog of ET [BETS, bis(ethylenedithio)tetraselenafulvalene, **8**] has also provided organic superconductors.[11]

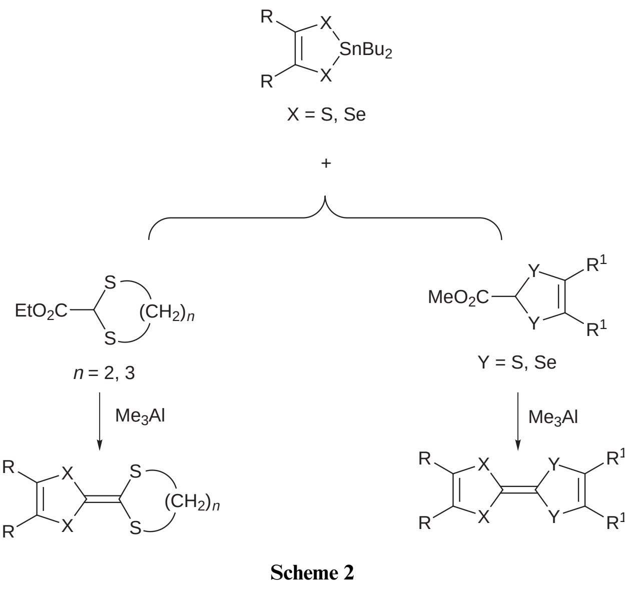
With such modifications of the TTF skeleton, the development of new methodology for the efficient synthesis of the desired TTF-type donors has been the major focus of attention of synthetic chemists. From a synthetic point of view, the coupling reaction of 1,3-dichalcogenole-2-chalcogenones using trivalent phosphorus reagents, *e.g.* trialkyl phosphites and triphenylphosphine, is a most powerful tool for the construction of tetrachalcogenafulvalene derivatives and π-electron donors incorporating 1,3-dichalcogenol-2-ylidene moieties. In addition, a variety of derivatives of 1,3-dithiole-2-thione, which are utilizable for this coupling reaction as building blocks leading to new donors, have been recently reviewed.[12] However, when this coupling reaction is applied to synthesis of the unsymmetrical TTFs and TSFs, as well as DSDTFs (diselenadithiafulvalenes), two symmetrical deriva-



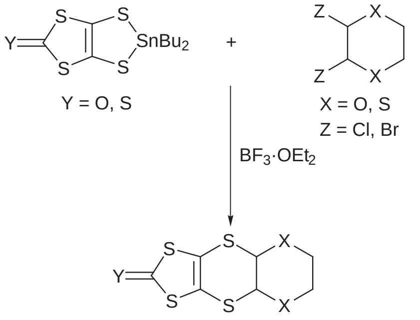
Scheme 1

tives as self-coupling products are, in principle, formed along with the unsymmetrical derivative as a cross-coupling product (Scheme 1).[13] Therefore, alternative methodology is required for the exclusive formation of unsymmetrical derivatives.

We ourselves have introduced the synthetic concept based on the stabilization–activation procedure[14] *via* Lewis acid-promoted reactions of organotin compounds with electrophiles into the TTF synthesis area,[15] and succeeded in developing the Me_3Al-promoted reaction to form 1,3-dichalcogenol-2-ylidene moieties (Scheme 2)[16] and the BF_3-promoted reaction to prepare 1,3-dithiole-2-chalcogenone derivatives condensed with a bis-fused six-membered heterocycle (Scheme 3) as building blocks for construction of a new TTF family.[17] The present review concentrates on our recent research to explore organic metals containing newly modified TTF and DSDTF donors by means of these synthetic methods. Our effort will be described in four parts: 1) studies on the annulated DHTTF (dihydrotetrathiafulvalene) derivatives, 2) studies on DHTTF-fused donors, 3) studies on the vinylenedithio-substituted DSDTF derivatives, and 4) studies on TTF donors with extended peripheral substituents by addition of heterocycles.



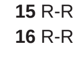
Scheme 2



Scheme 3

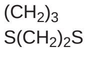
Heterocycle-annulated DHTTF donors and their analogs

The synthesis and electrochemical properties of the parent DHTTF **9** was first investigated by Coffen and co-workers,[18] and some synthetic studies involving its disubstituted derivatives as π-electron donors have been made.[19] On the other hand, to our knowledge, there has been no report on the systematic synthesis of aliphatic and aromatic heterocycle-annulated DHTTFs, in striking contrast with the broad synthetic study of the corresponding annulated TTFs. This is presumably due to the prediction that the partial reduction of the π-electronic system of the TTF core would adversely affect the electron-donating ability and the on-site Coulombic repulsion and, consequentially, would be deemed crucial in forming the segregated stacking of donor molecules in CT complexes or salts. However, it has been recognized that the 1,3-dithiol-2-ylidene moiety of DHTTF is oxidized to generate the 1,3-dithiolium cation which is stabilized by the aromatic 6π electron system,[18] and further, the additional chalcogen atoms by annulation of heterocycles might cause an enhancement in the intermolecular chalcogen···chalcogen interactions in the oxidation state, as can be found in the superconducting salts of the bis(heterocycle)- and heterocycle-annulated TTF derivatives such as ET and MDT-TTF. Thus, we investigated the systematic synthesis of new annulated DHTTFs, including their dithiane and selenium-containing analogs, and the preparation of their CT complexes and salts.[16a–c,f]

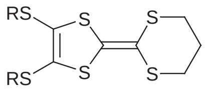


DHTTF **9**

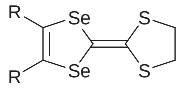
10 R-R = $(CH_2)_2$
11 R-R = CH=CH
12 R-R = CH_2 (MDHT)



13



14 R-R = $(CH_2)_2$
15 R-R = CH=CH
16 R-R = CH_2



17 R = R = Me
18 R-R = $(CH_2)_3$
19 R-R = $S(CH_2)_2S$

Synthesis of our target molecules **10**–**19** was attained by the Me_3Al-promoted reaction of the corresponding tin-masked dithiolates or diselenolates with 2-ethoxycarbonyl-1,3-dithiolane ($n = 2$ in Scheme 2) or 2-ethoxycarbonyl-1,3-dithiane ($n = 3$ in Scheme 2) in the following yields: **10**, 57%; **11**, 36%; **12**, 26%; **13**, 67%; **14**, 61%; **15**, 22%; **16**, 12%; **17**, 83%; **18**, 33%; **19**, 42%.[16a–c,f] On comparing the values of oxidation potentials for MDHT [methylenedithio(dihydro)tetrathiafulvalene, **12**] with those for MDT-TTF **5** [**12**; $E_1 = +0.60$ V, $E_2 = +1.00$ V, $E_3 = +1.14$ V (irreversible), ΔE $(E_2 - E_1) = 0.40$ V. **5**; $E_1 = +0.49$ V, $E_2 = +0.78$ V, ΔE $(E_2 - E_1) = 0.29$ V (V *vs.* SCE)], the first oxidation potential (E_1) of **12** is shifted to a more positive value relative to that of **5**, and the ΔE value of **12** is

Table 1 Conducting behaviour of the AuX_2 salts of MDHT **12**

X	Solvent[a]	D:A[b]	σ_{rt}/S cm^{-1}[c]
CN	CH_3CN	3:2	32[d] (E_a = 20 meV)[e]
Cl	TCE[f]	2:1[g]	250[h] (E_a = 6 meV)[e]
Br	CH_3CN	2:1	6.9[d] (E_a = 17 meV)[e]
I	CH_3CN	2:1	60[h] (metallic ⩾1.4 K)

[a] Used for controlled-current electrocrystallization. [b] Determined by elemental analysis unless otherwise noted. [c] Room temperature conductivity measured by a four-probe technique. [d] Measured on a compressed pellet. [e] Unpublished results. [f] 1,1,2-Trichloroethane. [g] Determined by X-ray diffraction analysis. [h] Measured on a single crystal.

larger than that of **5**, suggesting both a decrease in the donating ability and an increase in the on-site Coulombic repulsion, as expected. Nevertheless, DHTTF donors **10**–**13** and the seleno-containing derivatives **17** and **18** reacted with TCNQ to give the CT complexes, indicating that their donating abilities would be sufficient to form organic conductors. However, the room temperature conductivities of the resulting TCNQ complexes were all fairly low ($\sigma_{rt} < 10^{-6}$ S cm^{-1}). We then attempted to prepare the radical-cation salts of **10**–**12** and **17**–**19** by the controlled-current electrocrystallization method.[20] Among their salts so far obtained, the AuX_2 (X = CN, Cl, Br, and I) salts of MDHT exhibited high or relatively high room temperature conductivities for single crystals or compressed pellets (Table 1). Particularly, the $(MDHT)_2AuI_2$ salt remained metallic all the way down to a very low temperature (1.4 K),[16b] though the π-electronic system of MDHT is less extended than that of TTF.

While the refinement for X-ray diffraction data of the metallic $(MDHT)_2AuI_2$ salt is currently underway, the crystal structure of the semiconductive $(MDHT)_2AuCl_2$ salt was determined by X-ray diffraction (Fig. 1).[21] The MDHT molecules are stacked along the *b* axis to form a column. Although there exist intermolecular S···S contacts shorter than the van der Waals distance between columns, the dimerization of donor molecules within the column is fairly large, which may be responsible for the semiconductive behaviour of this salt.

In marked contrast to MDHT, its dithiane analog **16** has afforded no radical-cation salt under similar electrocrystallization conditions.[16f]

DHTTF-Fused donors

One attractive donor, formed by extending the π-electronic system as well as containing multi-chalcogen atoms, is the bis-fused TTF molecule [BDT-TTP (2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene), **20**], which was initially proposed by Schumaker.[22] Through the synthetic study of this compound and its related donors by Misaki,[23] production of a variety of TTF-fused donors has become feasible, and many of their radical-cation salts have exhibited metallic conducting behaviour down to low temperatures. Further, a vinylogous bis-fused TTF [DTEDT (2-(1,3-dithiol-2-ylidene)-5-(1,3-dithiol-2-ylideneethylidene)-1,3,4,6-tetrathiapentalene), **21**] has produced a superconductor $(DTEDT)_3Au(CN)_2$ with T_c = 4 K.[24] These results suggest that the insertion of a tetrathiapentalene (TTP) unit into the central C=C bond of the TTF core or its vinylog is a most promising molecular design for new π-electron donors leading to organic metals stable down to low temperatures. Therefore, it is interesting to clarify whether this molecular design is also applicable to the DHTTF core or not. In this section, we describe the short synthesis of DHTTF-TTF fused donors **22**–**26**, incorporating a TTP unit into the central C=C bonds of DHTTF and its derivatives, *via* the Me_3Al-promoted coupling reaction,[16c,e,25] a synthetic route to the bis-fused DHTTF donor BDH-TTP [2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene, **27**],[26] and crystal structures of the κ-type salts based on EDDH-TTP [2-(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-5-(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene, **24**][25] and BDH-TTP **27**.[26]

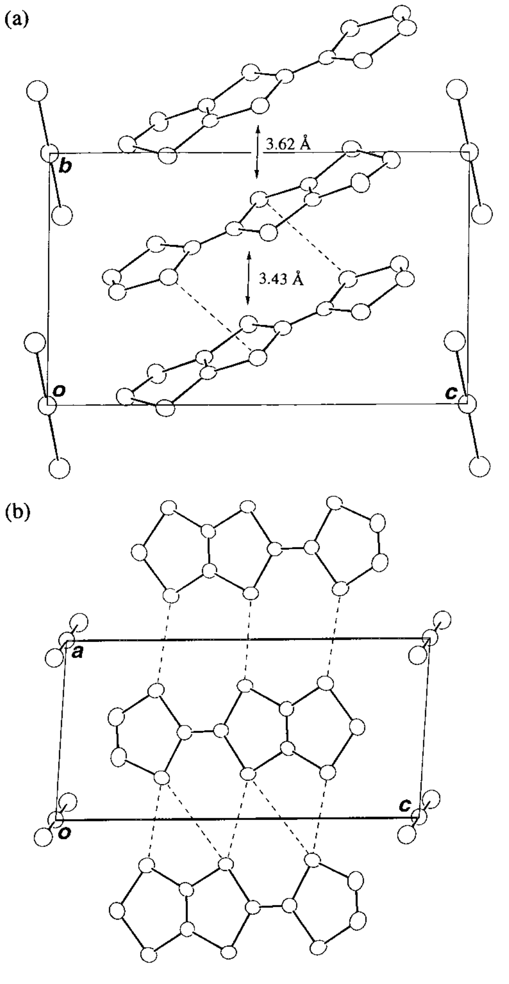
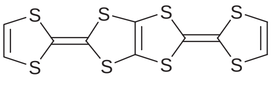
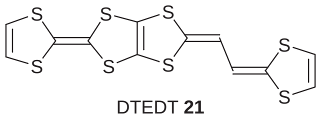


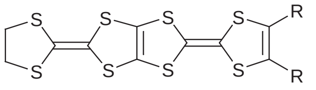
Fig. 1 Crystal structure of $(MDHT)_2AuCl_2$ viewed along the *a* axis (a) and the *b* axis (b). Intermolecular S···S contacts (<3.70 Å) are indicated by the dotted lines.



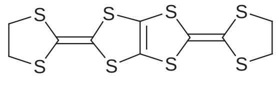
BDT-TTP **20**



DTEDT **21**

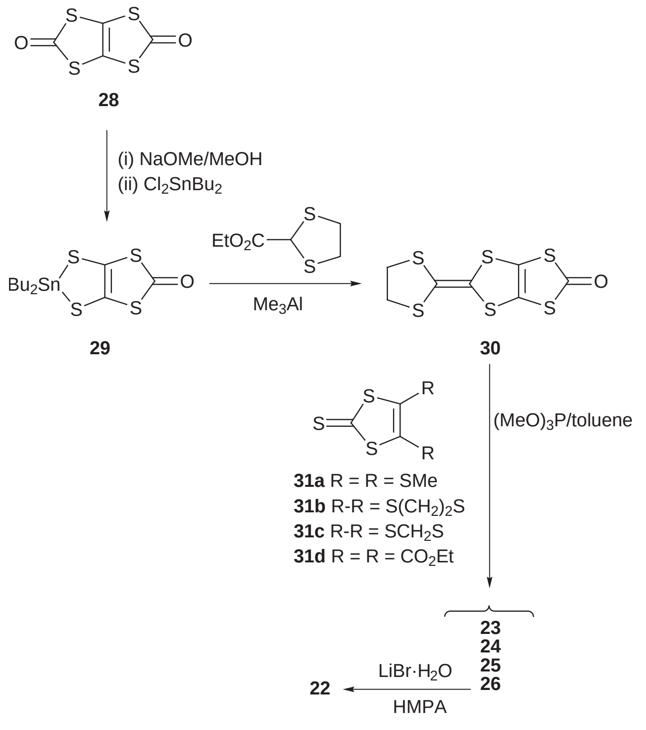


22 R = R = H
23 R = R = SMe
24 R-R = $S(CH_2)_2S$ (EDDH-TTP)
25 R-R = SCH_2S
26 R = R = CO_2Me



BDH-TTP **27**

The synthetic sequence for construction of **22**–**26** is outlined in Scheme 4. Treatment of thiapentalenedione **28**[22] with NaOMe in MeOH[27] followed by trapping with Cl_2SnBu_2 gave the tin-masked dithiolate **29** in 96% yield. Reaction of **29** with 2-ethoxycarbonyl-1,3-dithiolane in the presence of Me_3Al furnished the DHTTF-fused ketone **30** in 72% yield.[15] Our attempt to synthesize DHTTF-TTF fused donors from the resulting ketone **30** *via* the Me_3Al-promoted reaction was unsuccessful, because **30** was insoluble in the appropriate solvents used for conversion into the corresponding tin dithiolate. Accordingly, for obtaining **23**–**26**, solubility problems forced us to carry out the cross-coupling reaction between



Scheme 4

ketone **30** and thiones **31a–d** in $(MeO)_3P$ and boiling toluene (v/v = 1/1) for 2 h (**23**, 47%; **24**, 80%; **25**, 28%; **26**, 82%).[16c] Upon heating with an excess of $LiBr\cdot H_2O$ in HMPA at 90 °C for 1 h, and then at 130 °C for 1 h, the bis(methoxycarbonyl) derivative **26** underwent demethoxycarbonylation, affording the parent DHTTF-TTF fused donor **22** in 56% yield.[25] Eventually, we achieved the three- or four-step synthesis of DHTTF-TTF fused donors **22–26** *via* the Me_3Al-promoted coupling reaction.

The ethylenedithio-substituted DHTTF-TTF fused donor, EDDH-TTP **24**, produced metallic salts with linear anions [I_3^- ($\sigma_{rt} = 83\ S\ cm^{-1}$),[28] $Au(CN)_2^-$ ($\sigma_{rt} = 60\ S\ cm^{-1}$),[28] and AuI_2^- ($\sigma_{rt} = 14\ S\ cm^{-1}$)] and octahedral anions [PF_6^- ($\sigma_{rt} = 58\ S\ cm^{-1}$), AsF_6^- ($\sigma_{rt} = 170\ S\ cm^{-1}$),[28] and SbF_6^- ($\sigma_{rt} = 39\ S\ cm^{-1}$)[28]], all of which retained the metallic state down to liquid He temperatures. Among them, the crystal structure of $(EDDH\text{-}TTP)_2AuI_2$ was determined by X-ray diffraction.[25] The structure consists of κ-type sheets of EDDH-TTP donor molecules and sheets of AuI_2 anions, as illustrated in Fig. 2. The interplanar distance between pairs of donor molecules is 3.41 Å and the dihedral angle of the molecular planes between pairs is 80.72°. These values are almost the same as those (3.38 Å, 88°) in $\kappa\text{-}(ET)_2Cu(NCS)_2$.[29] In $(EDDH\text{-}TTP)_2AuI_2$, each donor molecule is also linked by several S···S contacts shorter than the sum of the van der Waals radii in the sheet, as shown in Fig. 3, which is responsible for metallic behaviour of this salt down to a low temperature. In addition, X-ray diffraction analysis of $(EDDH\text{-}TTP)_2AsF_6$ revealed that this salt also consists of κ-type sheets of EDDH-TTP donor molecules (Fig. 4).[28] In contrast to the AuI_2 salt, there are two κ-sheets in the unit cell of the AsF_6 salt, but the packing patterns of donor molecules are very similar to each other. It is significant that EDDH-TTP is the first TTF-fused donor providing κ-type 2 : 1 salts with both linear and octahedral anions;[30] note that many organic superconductors are of this structure.[2]

From our results that the DHTTF donor MDHT **12** provides a metallic AuI_2 salt stable down to 1.4 K and many radical-cation salts remaining metallic down to low temperatures are obtainable from the DHTTF-TTF fused donors, including EDDH-TTP **24**,[25] we anticipated that the bis-fused DHTTF molecule, BDH-TTP **27**, which is a structural isomer of ET, would produce the organic metals retaining the metallic state down to low temperatures, even though this compound contains no TTF molecule. Our synthetic route to BDH-TTP began with the dithiolane-added ketone **32**[31] (preparation of which will be described in the last section), as outlined in Scheme 5. Reaction of **32** with MeMgBr followed by trapping with Cl_2SnBu_2 gave tin dithiolate **33**, which was subsequently coupled with 2-ethoxycarbonyl-1,3-dithiolane by using Me_3Al as the promoter to afford the dithiolane-added MDHT **34** in 52% overall yield from **32**. Oxidation of the C–C bond between two *S*,*S*-acetals of **34** was effected by treatment with DDQ in refluxing toluene, giving BDT-TTP **27** in 89% yield.[26]

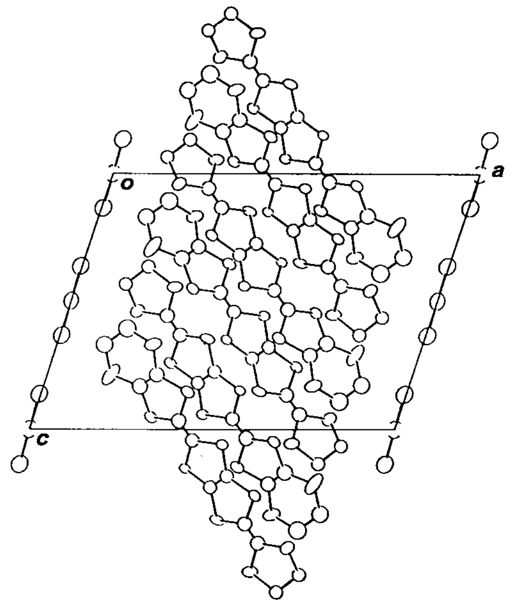


Fig. 2 Crystal structure of $(EDDH\text{-}TTP)_2AuI_2$ viewed down the *b* axis (Reprinted with permission from ref. 25).

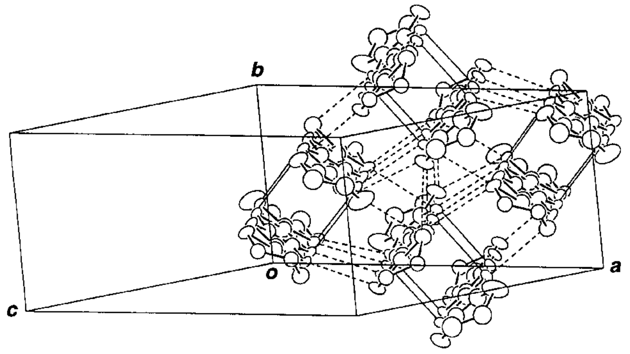


Fig. 3 Structure of the donor sheet in $(EDDH\text{-}TTP)_2AuI_2$; intrapair short S···S contacts (<3.70 Å) are indicated by lines, and interpair short S···S contacts are indicated by dotted lines (Reprinted with permission from ref. 25).

While TCNQ and $TCNQF_4$ complexes with BDH-TTP were semiconductors, a series of the BDH-TTP salts with the anions, I_3^- ($\sigma_{rt} = 230\ S\ cm^{-1}$), AuI_2^- ($\sigma_{rt} = 49\ S\ cm^{-1}$), BF_4^- ($\sigma_{rt} = 33\ S\ cm^{-1}$), ClO_4^- ($\sigma_{rt} = 106\ S\ cm^{-1}$), PF_6^- ($\sigma_{rt} = 102\ S\ cm^{-1}$), and AsF_6^- ($\sigma_{rt} = 49\ S\ cm^{-1}$), essentially retained the metallic conductivity down to around 2.0 K. Moreover, with decreasing temperature, their similar resistive behaviour could be observed independent of the structure and volume of the used anions. By X-ray diffraction analysis, the structure of $(BDH\text{-}TTP)_2PF_6$ was ascertained to consist of κ-type sheets of BDH-TTP donor molecules and sheets of PF_6 anions (Fig. 5).[26] The interplanar distance between pairs of donor molecules is 3.53 Å and the dihedral angle of the molecular

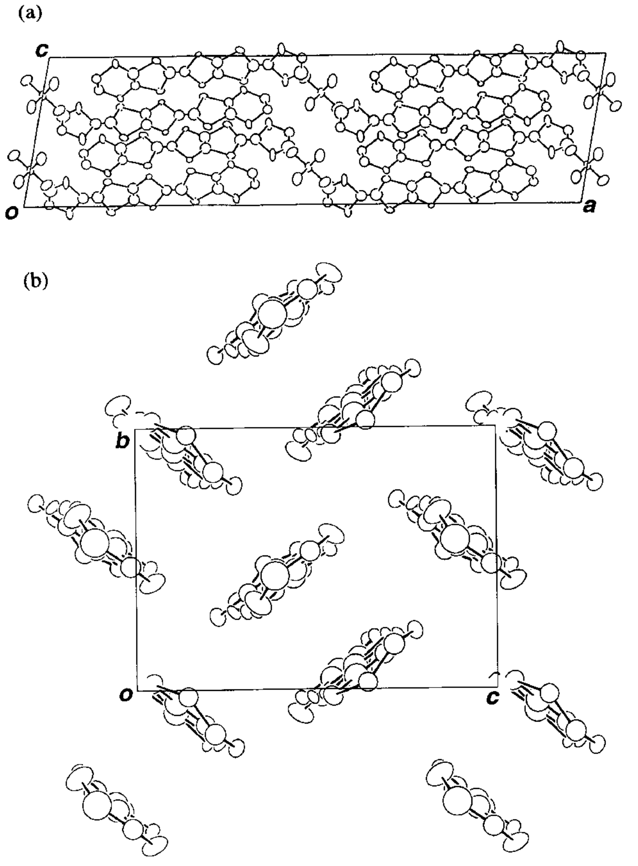
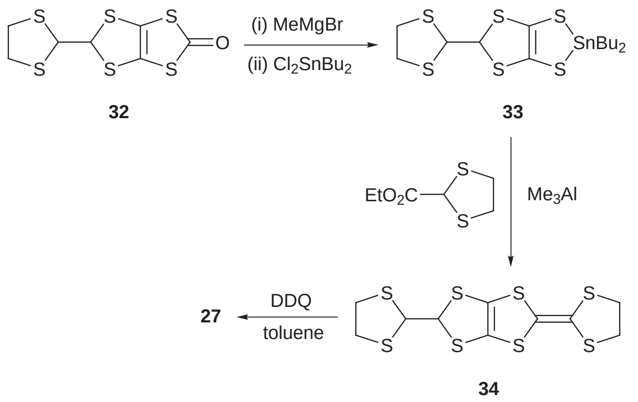


Fig. 4 Crystal structure of (EDDH-TTP)$_2$AsF$_6$ viewed down the *b* axis (a) and structure of the donor sheet in (EDDH-TTP)$_2$AsF$_6$ (b).



Scheme 5

planes between pairs is 82°. In the donor sheet, each molecule is linked by several S···S contacts shorter than the sum of the van der Waals radii, as depicted in Fig. 6. The large intermolecular overlap integrals are also calculated not only within a pair of donor molecules but also between pairs, which form 2D interaction in the *bc* plane. This 2D electronic structure is responsible for the metallic behaviour down to low temperatures.

Fig. 7 shows the distribution of the highest occupied molecular orbital (HOMO) of the BDH-TTP molecule calculated by the extended Hückel method, together with those of the MDHT **12** and EDDH-TTP **24** molecules. The common feature of each molecule is that the atomic orbital (2pπ) coefficients of two carbon atoms on the central double bond in the DHTTF backbone are largely different from each other. The difference between these two coefficients in the BDH-TTP molecule is comparable to that in the MDHT molecule, whereas, in the EDDH-TTP molecule, a very small coefficient

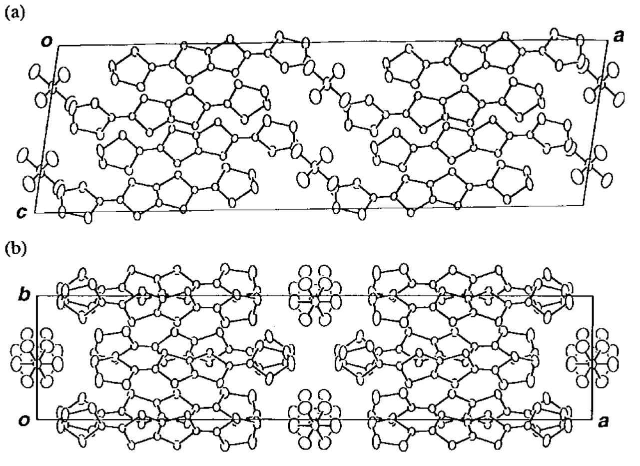


Fig. 5 Crystal structure of (BDH-TTP)$_2$PF$_6$ viewed along the *b* axis (a) and the *c* axis (b) (Reprinted with permission from ref. 26).

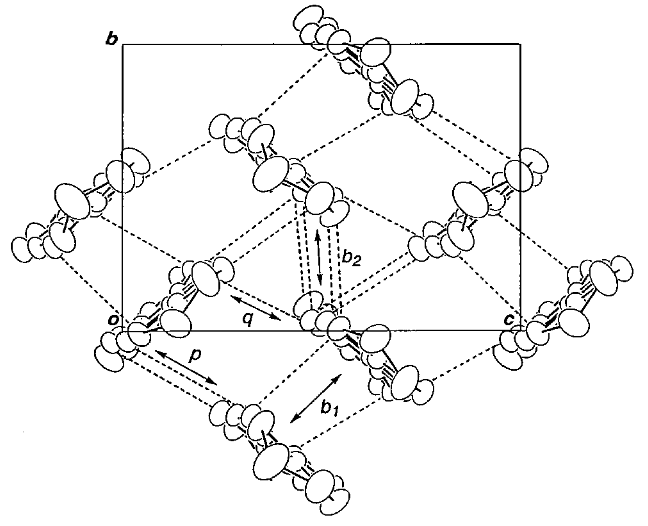


Fig. 6 Donor arrangement of (BDH-TTP)$_2$PF$_6$. Intermolecular S···S contacts (<3.70 Å) are indicated by the dotted lines. The values of intermolecular overlap integrals are $b_1=20.7$, $b_2=19.6$, $p=5.9$, and $q=-7.5$ ($\times 10^{-3}$) (Reprinted with permission from ref. 26).

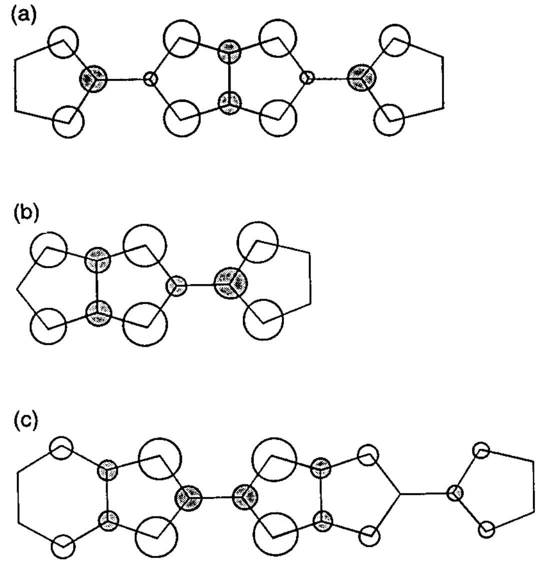


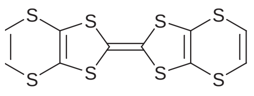
Fig. 7 The highest occupied molecular orbitals (HOMOs) of BDH-TTP **27** (a) (Reprinted with permission from ref. 26), MDHT **12** (b), and EDDH-TTP **24** (c). The geometries are taken from those in (BDH-TTP)$_2$PF$_6$, (MDHT)$_2$AuCl$_2$, and (EDDH-TTP)$_2$AuI$_2$, respectively.

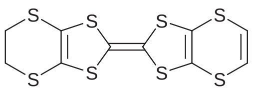
is observed for the carbon atom between two sulfur atoms situated in the 1,3-dithiole ring of the DHTTF moiety.

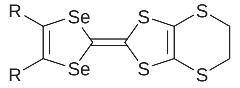
In addition to the κ-(EDDH-TTP)$_2$AuI$_2$ and κ-(EDDH-TTP)$_2$AsF$_6$ salts, BDH-TTP is also proved to produce a metallic 2D salt, κ-(BDH-TTP)$_2$PF$_6$. One synthetic target in this area of chemistry is to construct the non-TTF-based donor which tends to stack with 2D interactions,[32] so we believe that our studies on the BDH-TTP donor present a step forwards in that direction.

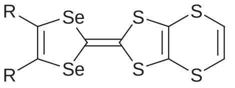
Vinylenedithio-substituted DSDTF donors

For ET-based superconductors, it has been proposed that the π-electronic system of the conducting component should be extended to its periphery to increase the T_c (superconducting transition temperature).[33] One synthetic strategy to extend the π-system in the ET molecule might be the replacement of the ethylene groups with vinylene groups, but investigation on the conducting behaviour and structural analysis of (VT)$_2$PF$_6$ [VT = bis(vinylenedithio)tetrathiafulvalene, **35**] has revealed that this salt undergoes an MI (metal-to-insulator) transition near 180 K due to its 1D character.[34] In addition, the unsymmetrical donor EVT [ethylenedithio(vinylenedithio)tetrathiafulvalene, **36**], which is a hybrid between ET and VT, has produced no metallic radical-cation salt.[35] Meanwhile, we have already found that an efficient synthesis of the ethylenedithio-substituted DSDTFs, such as DMET **4** and TMET-STF [trimethylene(ethylenedithio)diselenadithiafulvalene, **37**],[36] was accomplished by the Me$_3$Al-promoted reaction of the corresponding tin dithiolate or diselenolate with esters.[16a,c] In this context, the question of whether introduction of the vinylene end group instead of the ethylene end group into DMET, TMET-STF, and STF [bis(ethylenedithio)diselenadithiafulvalene, **38**][37] is recognized as a favoured strategy for the development of π-electron donors which lead to organic metals arose quite naturally. Thus, our investigation on the synthesis of the vinylenedithio-substituted DSDTF derivatives **39**–**41** was undertaken to solve this question.[16d]

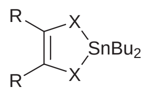

VT **35**

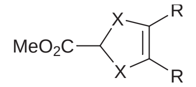

EVT **36**


37 R-R = $(CH_2)_3$ (TMET-STF)
38 R-R = $S(CH_2)_2S$ (STF)


39 R = R = Me (DMVT)
40 R-R = $(CH_2)_3$ (TMVT)
41 R-R = $S(CH_2)_2S$ (EDVT)

Our synthesis of **39**–**41** employed the Me$_3$Al-promoted reaction of the tin-masked diselenolates **42**–**44** with ester **46** (**39**, 40%; **40**, 28%; **41**, 13%). Also, TMVT [trimethylene(vinylenedithio)diselenadithiafulvalene, **40**] was obtained by the Me$_3$Al-promoted coupling between tin dithiolate **45** and ester **47** in 25% yield. While the DMVT [dimethyl(vinylenedithio)diselenadithiafulvalene, **39**] salts with the AuCl$_2^-$, AuI$_2^-$, I$_3^-$, ClO$_4^-$, and PF$_6^-$ anions exhibited semiconducting behaviour, metallic radical-cation salts were obtained from TMVT and EDVT [ethylenedithio(vinylenedithio)diselenadithiafulvalene, **41**].[16d]


42 X = Se, R = R = Me
43 X = Se, R-R = $(CH_2)_3$
44 X = Se, R-R = $S(CH_2)_2S$
45 X = S, R-R = S(CH=CH)S


46 X = S, R-R = S(CH=CH)S
47 X = Se, R-R = $(CH_2)_3$

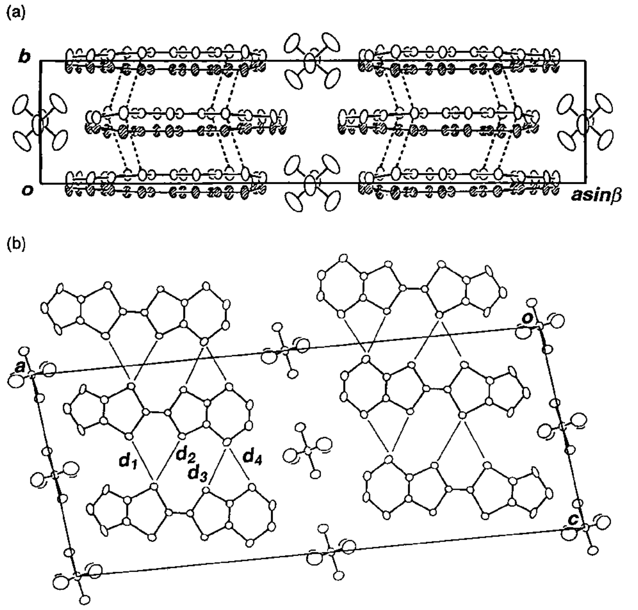


Fig. 8 Crystal structure of (TMVT)$_2$PF$_6$, viewed along the *c* axis (a) and the *b* axis (b); (a) intrastack shorter Se···S contacts (<3.85 Å) between the front molecules, which are drawn by open circles, shown by the dotted lines, (b) interstack shorter Se···Se contact (<4.00 Å): d_1 = 3.7022(9) Å, Se···S contact (<3.85 Å): d_2 = 3.787(2) Å, S···S contacts (<3.70 Å): d_3 = 3.506(2) Å, d_4 = 3.457(2) Å [Reprinted with permission from ref. 16(*d*)].

The crystal structure of the (TMVT)$_2$PF$_6$ salt (σ_{rt} = 620 S cm^{-1}, metallic down to 4.2 K) was determined by X-ray diffraction.[16d] The TMVT molecules stack head-to-tail along the *b*-axis, as shown in Fig. 8(a). The interplanar distance [3.5869(3) Å] is exactly equal to *b*/2 due to the symmetry restriction, so there is no dimerization within a stack. As illustrated in Fig. 8(b), there exist also several chalcogen···chalcogen contacts shorter than the sum of the van der Waals radii between stacks. In addition, the metallic (TMVT)$_2$AsF$_6$ (σ_{rt} = 125 S cm^{-1} in the *bc* plane) and (TMVT)$_2$ClO$_4$ (σ_{rt} = 135 S cm^{-1} in the *bc* plane) salts crystallized in the monoclinic space group *C*2/*c* with comparable unit cell volumes and axial lengths to those of the PF$_6$ salt.[38] Crystal data for the PF$_6$, AsF$_6$, and ClO$_4$ salts of TMVT are summarized in Table 2. The AsF$_6$ salt is isostructural with the PF$_6$ salt. While the difference in the ClO$_4$ and PF$_6$ (or AsF$_6$) salts can be discerned in the position of anions, the packing patterns of donor molecules are very similar. As depicted in Fig. 9, intermolecular chalcogen···chalcogen contacts located in intra- and inter-stacks, such as found in the PF$_6$ salt, are also observed in the ClO$_4$ salt. In these three TMVT salts, the structures of TMVT molecules are all approximately planar, in contrast to the fact that the two vinylene end groups of VT in (VT)$_2$PF$_6$ are far out of the molecular plane.[34]

TTF Donors with the periphery extended by addition of heterocycles

The donor ET, needless to say, produces the largest number of superconducting salts, and it is now well-known that the additional sulfur atoms, accompanied by fusion of a 1,4-dithiane ring onto both sides of the prototype TTF molecule, play an important part in the formation of 2D S···S sheets in the ET-based superconductors.[2] Therefore, one synthetic method for the construction of new TTF donors leading to conducting materials with enhanced dimensionality might be the addition of another heterocycle onto the existing one or

Table 2 Crystal data for the TMVT-based salts

	$(TMVT)_2PF_6$	$(TMVT)_2AsF_6$	$(TMVT)_2ClO_4$
Empirical formula	$C_{22}H_{16}S_8Se_4PF_6$	$C_{22}H_{16}S_8Se_4AsF_6$	$C_{22}H_{16}S_8Se_4ClO_4$
Formula weight	997.69	1041.64	952.23
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$C2/c$
Unit cell parameters	$a=32.119(6)$ Å $b=7.174(1)$ Å $c=13.084(2)$ Å $\beta=97.30(1)°$	$a=32.384(7)$ Å $b=7.207(2)$ Å $c=13.102(3)$ Å $\beta=97.18(2)°$	$a=32.720(12)$ Å $b=7.127(4)$ Å $c=13.045(6)$ Å $\beta=106.22(3)°$
Volume	2990.4(8) Å^3	3033.9(12) Å^3	2921.1(22) Å^3
Z	4	4	4
Reflections collected	4353	3015	4850
Independent reflections	2805	2485	3595
R, R_w	0.066, 0.082	0.070, 0.075	0.061, 0.065

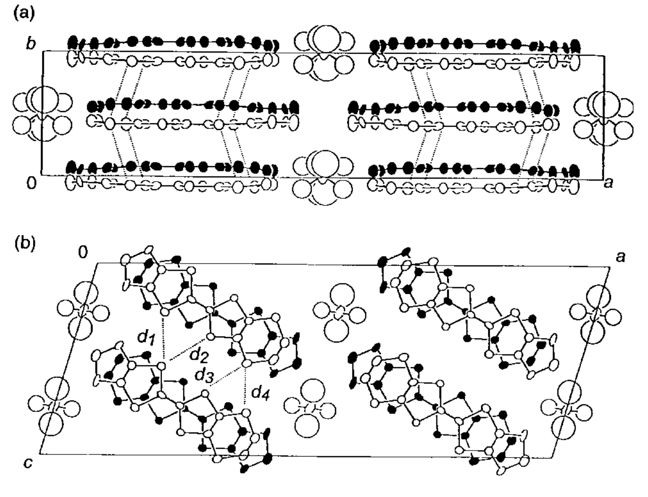
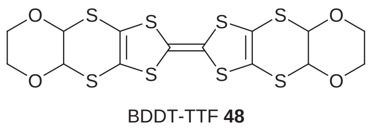
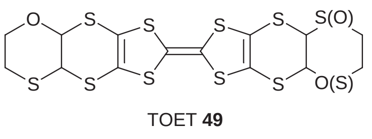


Fig. 9 Crystal structure of $(TMVT)_2ClO_4$; (a) intrastack shorter Se···S contacts (<3.85 Å) between the front molecules drawn by open circles, (b) interstack shorter Se···Se contact (<4.00 Å): $d_1=3.705(2)$ Å, Se···S contact (<3.85 Å): $d_2=3.803(3)$ Å, S···S contacts (<3.70 Å): $d_3=3.519(4)$ Å, $d_4=3.434(5)$ Å (Reprinted with permission from ref. 38). For the sake of clarity, the hydrogen atoms are omitted.

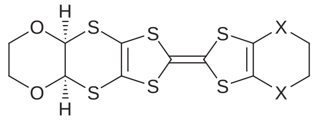
both outer rings in the known heterocycle- or bis(heterocycle)-fused TTF derivatives, and to this end, the bis(dioxane)- and bis(oxathiane)-fused ET donors, BDDT-TTF [bis(1,4-dioxanediyl-2,3-dithio)tetrathiafulvalene, **48**][39] and TOET



BDDT-TTF **48**



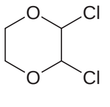
TOET **49**



50 X = S (DOET)
51 X = Se (DOES)

[bis(1,4-oxathianediyl-2,3-dithio)tetrathiafulvalene, **49**],[40] have been already synthesized. Further appearance of such π-donors would be of interest in preparation of new molecular-based conductors. In order to establish a synthetic route to a new TTF family with an extended periphery by addition of several heterocycles, we realized, at the outset, that we needed to develop a synthetic method for preparation of the 1,3-dithiole-2-chalcogenone derivatives condensed with a bis-fused heterocycle as building blocks. Our method was based on the BF_3-promoted reaction of the tin-masked dithiolates with 1,2-dihaloheterocycles (Scheme 3), and this synthetic method has enabled the syntheses of new bis(heterocycle)-fused ET donors and the heterocycle-fused ET, MET [methylenedithio(ethylenedithio)tetrathiafulvalene], and EDT-TTF donors.[17] From among this TTF family, we describe herein the studies on the dioxane-fused ET, DOET [(1,4-dioxanediyl-2,3-dithio)ethylenedithiotetrathiafulvalene, **50**],[17,41] and its selenium analog, DOES [(1,4-dioxanediyl-2,3-dithio)ethylenediselenotetrathiafulvalene, **51**].[42]

The tin-masked dithiolate **29** (see Scheme 4) reacted with *trans*-2,3-dichloro-1,4-dioxane **52** in the presence of 2 equiv. of $BF_3{\cdot}OEt_2$ to give the dioxane-fused ketone **53** as a single stereoisomer in 91% yield. The *cis* stereochemistry for two methine protons of **53** was confirmed by X-ray crystallography.[17] Synthesis of DOET[17] and DOES[42] was carried out by the cross-coupling reaction between ketone **53** and 2 equiv. of thiones **31b** (see Scheme 4) and **54** in the presence of $(MeO)_3P$ (DOET, 35%; DOES, 27%). X-Ray crystallographic analyses of DOET[17b] and DOES[43] confirmed that the dioxane rings of these molecules are fused *cis*- (Fig. 10). The DOET



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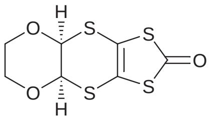

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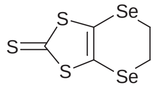

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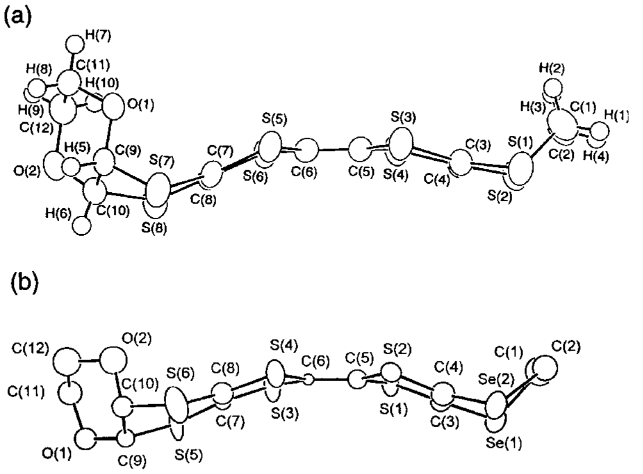


Fig. 10 Side views of molecular structures of DOET **50** (a) [Reprinted with permission from ref. 17(*b*)] and DOES **51** (b). In (b), the hydrogen atoms are omitted due to their large thermal motions.

Table 3 Crystal data for DOET **43** and DOES **44**

	DOET	DOES
Empirical formula	$C_{12}H_{10}O_2S_8$	$C_{12}H_{10}O_2S_6Se_2$
Formula weight	442.72	536.53
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1nb$
Unit cell parameters	$a=12.005(3)$ Å $b=21.532(7)$ Å $c=6.571(2)$ Å $\beta=96.93(3)°$	$a=15.098(4)$ Å $b=30.233(7)$ Å $c=7.653(2)$ Å
Volume	1686.1(9) Å^3	3493.3(5) Å^3
Z	4	8
R, R_w	0.043, 0.049	0.051, 0.068

molecule has a nonplanar structure [Fig. 10(a)], wherein the dioxane ring is forced to incline towards the outer ethylene group linking two sulfur atoms. Obviously, the whole molecular structure of DOET is bulkier than that of ET, but the dioxane ring added to the ET skeleton does not result in further deformation of the molecular structure of ET itself.[44] The structure of the DOES molecule [Fig. 10(b)] resembles that of DOET, though the crystallographic data for the former differ from those for the latter (Table 3).

The dioxane-fused donor DOET provided the metallic salts with $Au(CN)_2^-$ ($\sigma_{rt}=13$ S cm^{-1}) and BF_4^- ($\sigma_{rt}=27$ S cm^{-1}), which underwent MI transitions as shown in Fig. 11,[45] and its seleno-analog DOES also produced the metallic I_3 ($\sigma_{rt}=60$ S cm^{-1}) and AuI_2 ($\sigma_{rt}=1.4$ S cm^{-1}) salts with MI transitions (Fig. 12). Though the resistivity of the I_3 salt of DOES increases slightly around room temperature with decreasing temperature, its temperature dependence is very small and a clear MI transition occurs at 250 K. This transition temperature was estimated by the derivative of the Arrhenius plot for the resistivity of the I_3 salt. X-Ray diffraction analyses of $(DOET)_2BF_4$[41] and $(DOES)_2(AuI_2)_{0.75}$[42] revealed that these salts have β-type crystal structures (Fig. 13 and 14), in which each mode of the donor molecular overlap is very similar to that in a superconductor β-$(ET)_2I_3$. In both DOET and DOES salts, donor molecules are stacked face-to-face to form columns along the individual [110] direction, and the bulky dioxane ring of each donor exists within a hollow space of the donor stack, so as to avoid the steric hindrance. In the β-structure, molecular dimerization is usually observed in a stack. In the case of $(DOET)_2BF_4$, the dimerization is rather smaller than that in β-$(ET)_2I_3$ [the overlap ratios of p_1 to p_2 are 1.6 and 2.1 in $(DOET)_2BF_4$ (Fig. 13(b)) and β-$(ET)_2I_3$, respectively]. Although, in $(DOES)_2(AuI_2)_{0.75}$, a shorter intradimer distance [3.47 Å, Fig. 14(a)] and a slightly longer interdimer distance (3.78 Å) relative to those in $(DOET)_2BF_4$ (intradimer: 3.50 Å; interdimer: 3.77 Å) are observed, the overlap ratio of p_1 to p_2 [Fig. 14(b)] is 0.94, which is relatively closer to 1.0 in comparison with that of $(DOET)_2BF_4$, suggesting that the donor stack is more uniform. In $(DOET)_2BF_4$, instead of no intermolecular S···S contact shorter than the van der Waals distance (3.70 Å) within a stack, there are many short S···S contacts

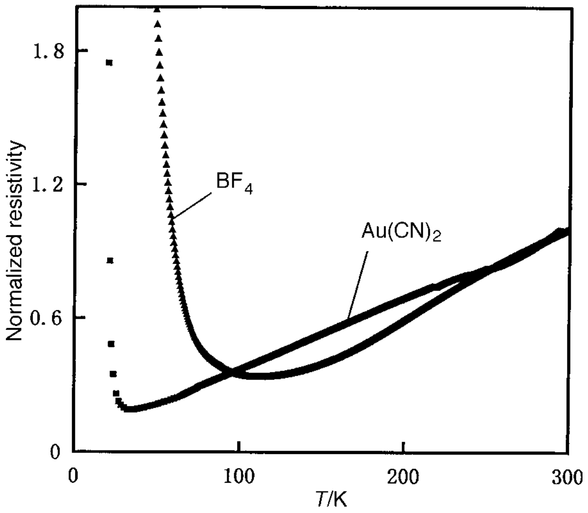


Fig. 11 Temperature dependence of normalized resistivity of the metallic DOET **50** salts.

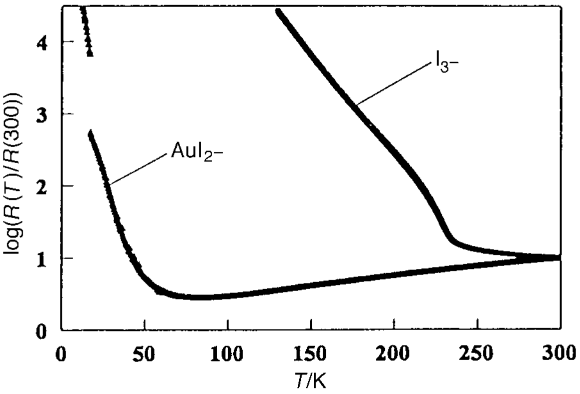


Fig. 12 Temperature dependence of relative resistivity of the metallic DOES **51** salts (Reprinted with permission from ref. 42).

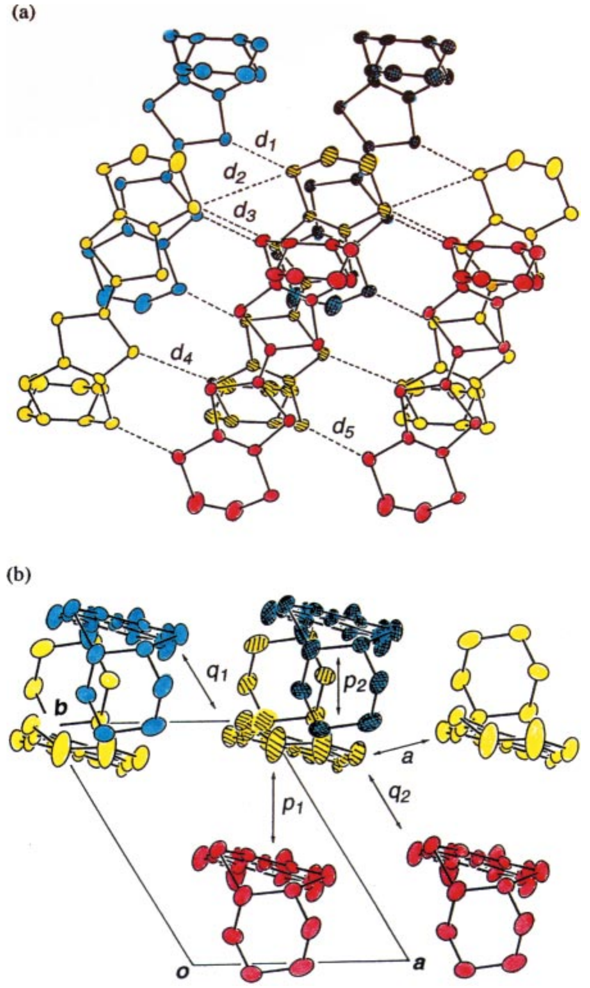


Fig. 13 Donor arrangement of $(DOET)_2BF_4$; (a) Intermolecular S···S contacts (<3.70 Å) are indicated by dotted lines: $d_1=3.543(3)$ Å, $d_2=3.695(3)$ Å, $d_3=3.486(3)$ Å, $d_4=3.455(3)$ Å, $d_5=3.654(3)$ Å. (b) Intermolecular overlap integrals ($\times 10^{-3}$) a, p_1, p_2, q_1, and q_2 are −4.66, 23.81, 15.17, 7.05 and 5.34, respectively (Reprinted with permission from ref. 41).

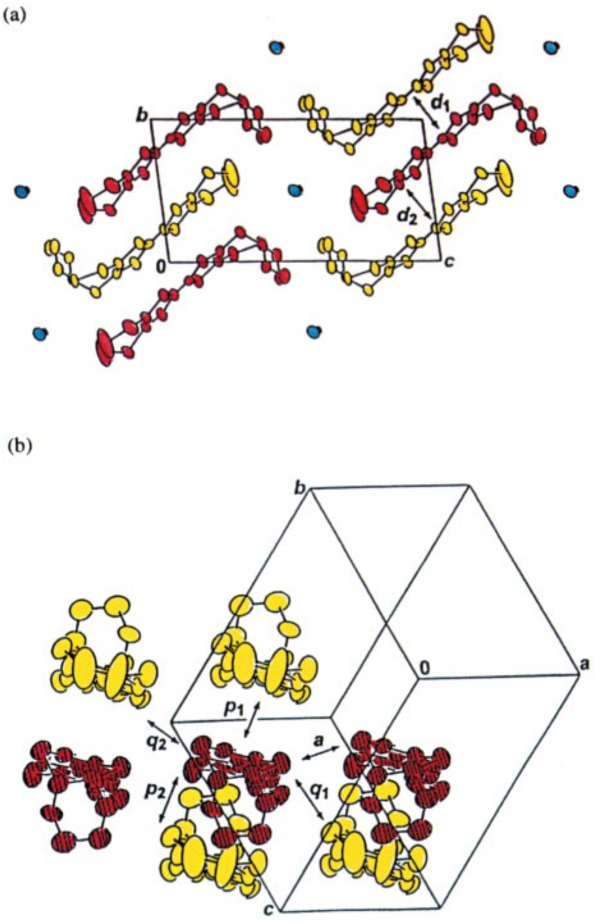


Fig. 14 Crystal structure of $(DOES)_2(AuI_2)_{0.75}$; (a) intermolecular face-to-face distances: $d_1 = 3.47$ Å, $d_2 = 3.78$ Å; (b) intermolecular overlap integrals ($\times 10^{-3}$) p_1, p_2, q_1, q_2 and a are 21.31, 22.72, 7.51, 8.51 and −3.15, respectively (Reprinted with permission from ref. 42).

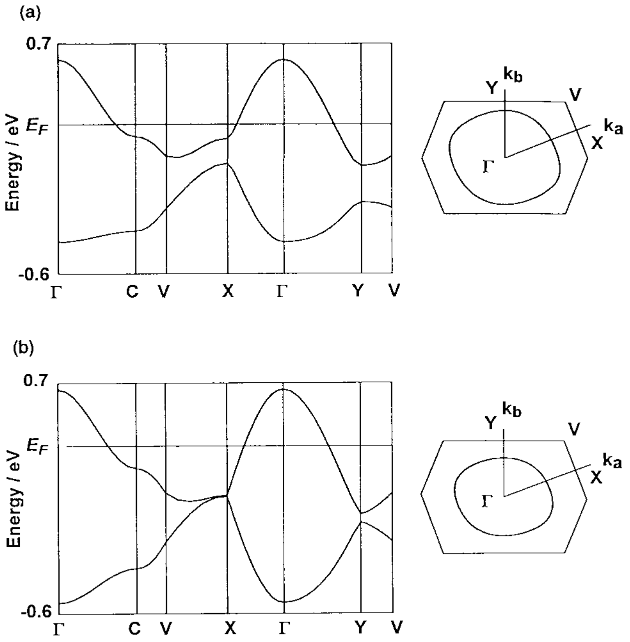
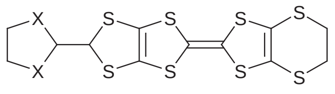


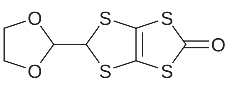
Fig. 15 Energy band structures and Fermi surfaces of $(DOET)_2BF_4$ (a) (Reprinted with permission from ref. 41) and $(DOES)_2(AuI_2)_{0.75}$ (b) (Reprinted with permission from ref. 42).

between stacks [Fig. 13(a)]; the same can be said for the mode of chalcogen···chalcogen contacts in $(DOES)_2(AuI_2)_{0.75}$. Therefore, these salts have 2D band structures with nearly isotropic closed Fermi surfaces (Fig. 15). Nevertheless, the $(DOET)_2BF_4$ salt becomes semiconductive around 100 K. According to the X-ray analysis, the orientation of BF_4 anions is completely disordered, so this random potential of BF_4 anion layers might disturb the electron conduction and make this salt semiconductive at a low temperature. In addition, the conduction band of $(DOET)_2BF_4$ is 3/4 filled, whereas the band filling of $(DOES)_2(AuI_2)_{0.75}$ increases by 8.3% compared with that of $(DOET)_2BF_4$. In consequence, the area of the Fermi surface of the $(DOES)_2(AuI_2)_{0.75}$ salt is smaller than that of the $(DOET)_2BF_4$ salt.

Finally, we describe the synthesis and molecular structures of the dioxolane and dithiolane derivatives of MET, DO-MET [((1,3-dioxolan-2-yl)methylenedithio)ethylenedithiotetrathiafulvalene, **55**] and DT-MET [((1,3-dithiolan-2-yl)methylenedithio)ethylenedithiotetrathiafulvalene, **56**], as well as the conducting behaviour of their CT complexes and salts.[16g,17b,31]

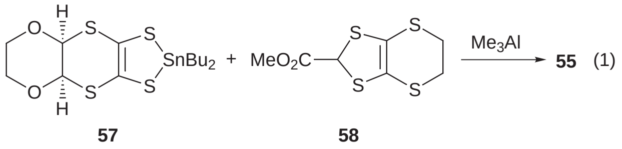


55 X = O (DO-MET)
56 X = S (DT-MET)



59

Our first synthesis of DO-MET **55** employed the Me$_3$Al-promoted reaction of tin dithiolate **57** with ester **58** accompanying the rearrangement of the existing two *O*,*S*-acetals in the bis-fused six-membered heterocycle to the five-membered cyclic *O*,*O*- and *S*,*S*-acetals [eqn. (1)], but its yield was relatively low (16%).[16g,17b] In addition, DT-MET could not be obtained by the Me$_3$Al-promoted reaction of the corresponding tin dithiolate with ester **58**, since the analogous rearrangement as can be found in the synthesis of DO-MET did not take place.[17] So, an alternative synthetic method to improve the yield of DO-MET and a synthetic approach to the construction of DT-MET were developed. Treatment of the dioxane-fused ketone **53** with an excess of $BF_3{\cdot}OEt_2$ (10 equiv.) induced isomerization of the bis-fused six-membered heterocycle to the five-membered biheterocycle, affording the dioxolane-appended ketone **59** in 80% yield together with trace amounts of **53**. The pure ketone **59** was obtained by recrystallization. Further, the addition of ethane-1,2-dithiol in this reaction gave the dithiolane-added ketone **32** (see Scheme 5) in 95% yield. Synthesis of DO-MET and DT-MET was carried out by cross-coupling of the resulting ketones **59** and **32** with 2 equiv. of thione **31b** (see Scheme 4) using $(MeO)_3P$ as a phosphite reagent (DO-MET, 80%; DT-MET, 94%).[31] The molecular structures of these two MET derivatives were determined by X-ray crystallography (Fig. 16).[16g,17b,31] The DO-MET molecule has a nonplanar structure, in which the dioxolane ring is attached perpendicularly to MET, and the MET framework itself is curved towards the dioxane ring. Accordingly, the dioxolane ring appended to MET makes it much bulkier than MET itself.[46] On the other hand, DT-MET has a distorted skeleton, wherein the plane formed by two sulfur atoms and one carbon atom linking them in the dithiolane ring is roughly parallel to the central tetrathioethylene middle plane of MET. The conformation of the dithiolane ring added to MET obviously makes it nonplanar, but the



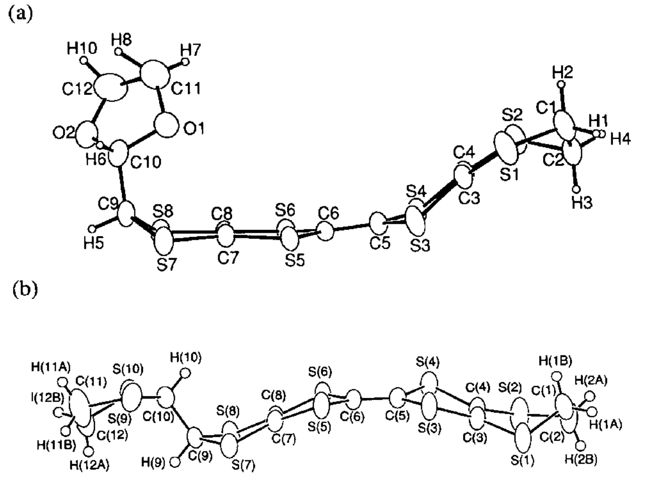


Fig. 16 Side views of molecular structures of DO-MET **55** (a) [Reprinted with permissions from refs. 16(*g*) and 17(*b*)] and DT-MET **56** (b) (Reprinted with permission from ref. 31).

whole molecular structure of DT-MET is less bulky than that of DO-MET.

Despite the presence of the bulky dioxolane ring, DO-MET reacted with TCNQ to yield a metallic CT complex ($\sigma_{\mathrm{rt}} = 12\ \mathrm{S\ cm^{-1}}$ for a compressed pellet) with MI transitions in cooling and warming processes (Fig. 17).[16g] In addition, we have found that some metallic radical-cation salts were obtained from DO-MET.[47] While the room temperature conductivity of the TCNQ complex with DT-MET was very low ($\sigma_{\mathrm{rt}} < 10^{-7}\ \mathrm{S\ cm^{-1}}$) for a single crystal, the temperature dependence of resistance of the DT-MET salts with $\mathrm{AuI_2}^-$ ($\sigma_{\mathrm{rt}} = 13\ \mathrm{S\ cm^{-1}}$), $\mathrm{BF_4}^-$ ($\sigma_{\mathrm{rt}} = 7.0\ \mathrm{S\ cm^{-1}}$), and $\mathrm{AsF_6}^-$ ($\sigma_{\mathrm{rt}} = 19\ \mathrm{S\ cm^{-1}}$) exhibited metallic conducting behaviour with MI transitions, as shown in Fig. 18.[31] At present, X-ray diffraction analyses of the metallic DO-MET and DT-MET salts are actively in progress.

Conclusions

In our research described in this review, the studies on the development of organic metals composed of the DHTTF-based donors, excluding the DHTTF-TTF fused donor system, are directed towards the post-TTF era, and their results indicate that the 1,3-dithiol-2-ylidene unit serves as an important moiety of donor components for developing organic metals. From MDHT **12**, containing only one of this unit, a stable metallic salt could be obtained, and BDH-TTP **27**, in which two of these units are contained in a different pattern from those in the isomeric ET molecule, yielded more metallic salts. Therefore, it can be anticipated that, on the molecular design of new π-donors, there is a good possibility of obtaining organic metals by increasing the number of these units contained in the designed molecules. However, the solubility problem of the designed donor molecules should be considered, and also, the difficulty in synthesizing them, *e.g.* a long-step synthesis or a troublesome separation of the desired product must be avoided. An approach to the solubility problem is the introduction of the σ-bond framework into donor molecules. The solubility of our new TTF family with a fused or appended heterocycle is, in general, enhanced in comparison with that of the prototype TTF derivatives.[48] Further, the extended TTF derivatives by the σ-bond framework may provide novel offerings for the molecular packing mode in the conducting materials. Such an investigation has begun in our laboratory, and will lead to a topic of future interest. In addition, the Lewis acid-promoted reactions, described herein, represent alternative approaches to the synthesis of the TTF-based donor molecules, and further modifications of the TTF skeleton should be possible by the use of the analogous Lewis acid-mediated reactions. Our effort to synthesize new π-electron donors producing materials with interesting and exciting solid-state properties, including superconductivity, currently continues.

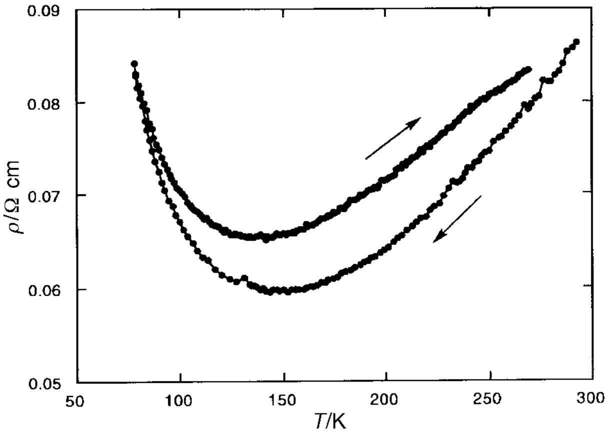


Fig. 17 Temperature dependence of resistivity of the metallic TCNQ complex with DO-MET **55**, measured on a compressed pellet [Reprinted with permission from ref. 16(*g*)].

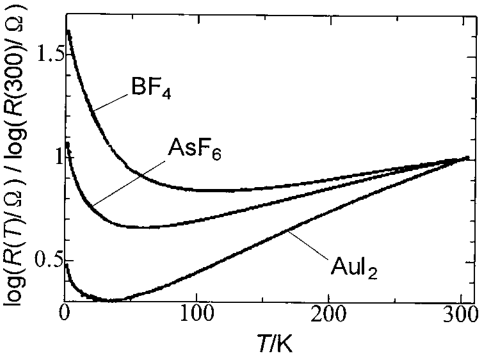


Fig. 18 Temperature dependence of relative resistance of the metallic DT-MET **56** salts (Reprinted with permission from ref. 31).

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