Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Y. Misaki, K. Kawakami, H. Fujiwara, T. Miura, T. Kochi, M. Taniguchi, T. Yamabe, T. Mori, H. Mori & S. Tanaka (1997): Synthesis, Structures And Properties Of Cyclopenteno Annelated Bis-Fused TTF Donors And Their Molecular Complexes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 296:1, 77-95

To link to this article: http://dx.doi.org/10.1080/10587259708032315

Mol. Cryst. Liq. Cryst., 1997, Vol. 296, pp. 77–95
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SYNTHESIS, STRUCTURES AND PROPERTIES OF CYCLOPENTENO ANNELATED BIS-FUSED TTF DONORS AND THEIR MOLECULAR COMPLEXES

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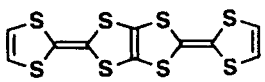
(Received 28 August 1996; In final form 5 November 1996)

Abstract A series of cyclopenteno annelated bis-fused TTF derivatives (CP-TTP **1a**-**d**) have been synthesized. The present donors have produced many molecular complexes showing high conductivity. In particular, several cation radical salts based on the bis(methylthio)- (CPTM-TTP **1c**) and ethylenedithio (CPET-TTP, **1d**) derivatives are metallic down to liquid helium temperature, though resistivity of CPTM-TTP salts increases a little at low temperature. Among metallic salts, $(CPTM\text{-}TTP)_4X$ ($X = PF_6^-$, AsF_6^- and SbF_6^-) are isostructural and have two-dimensional "β-type" arrangement of donor molecules. The band calculations of these salts indicate they have eclipsed Fermi surfaces characteristic of two-dimensional metals.

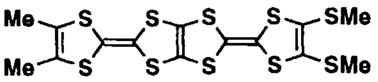
Keywords: Organic metal, tetrathiafulvalene, electrical conductivity, X-ray structure analysis, band structure

INTRODUCTION

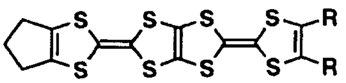
In the search for metallic organic materials, realization of two-dimensional (2D) electronic structure has been the most available strategy to stabilize metallic state down to low temperatures.[1-3] A bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP or simply TTP),[4,5] is a promising π-electron framework to prepare 2D metals because it has a "ladder-like" array of sulfur atoms similar to bis(ethylenedithio)-TTF (BEDT-TTF), which has yielded numerous 2D metals and superconductors.[2,3] In fact, many TTP donors including the parent one have produced a great number of cation radical salts, in which the donors are arranged in 2D fashions, retaining metallic conductivity down to low temperatures.[5] Because TTP itself has a strong tendency to form 2D arrangement, its derivatives having substituents such as alkyl, benzo and/or methylthio groups are also available to develop 2D metals, while the corresponding TTF derivatives usually give one-dimensional conductors.[6] In fact, we have recently found several cation radical salts based on DMTM- and CPTM-TTP, where DMTM- and CPTM-TTP are 4,5-dimethyl-4',5'-bis(methylthio)- and 4,5-cyclopenteno-4',5'-bis(methylthio)-TTP, show metallic conducting behavior down to liquid helium temperature.[7] In this article, we describe the synthesis of a series of TTP donors annelated with cyclopentene ring (**1a**-**d**), and structures and conducting properties of their molecular complexes.[8]



BDT-TTP



DMTM-TTP

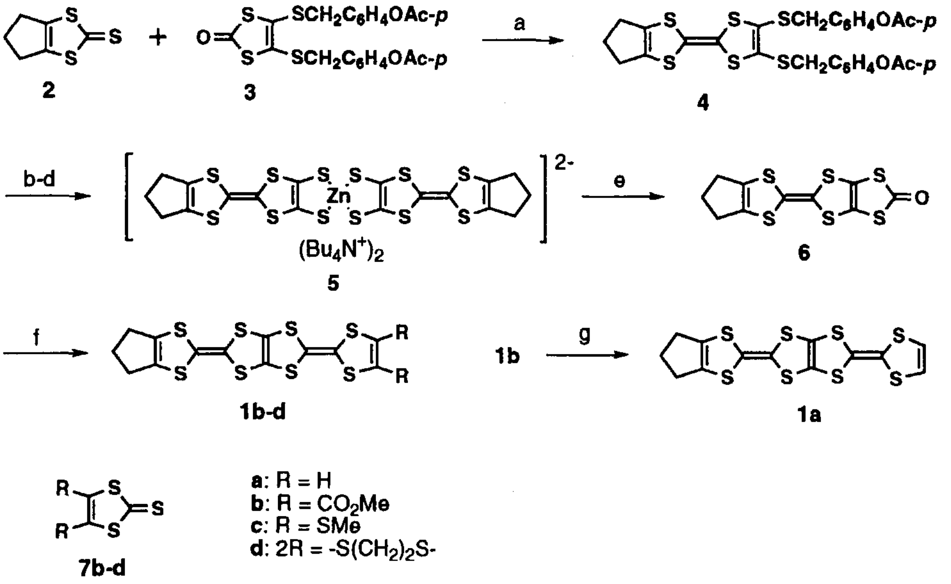


1a: R = H, CP-TTP
1b: R = CO_2Me
1c: R = SMe, CPTM-TTP
1d: 2R = $-S(CH_2)_2S-$, CPET-TTP

RESULTS AND DISCUSSION

Synthesis

The synthesis of CP-TTP derivatives **1a**-**d** was achieved by a procedure similar to that for methyl substituted TTP derivatives as shown in Scheme I.[4c] 4,5-Cyclopenteno-1,3-dithiole-2-thione (**2**) and 4,5-bis(*p*-acetoxybenzylthio)-1,3-dithiol-2-one (**3**)[4a,9] were cross-coupled in neat triethylphosphite at 110 °C to afford 4,5-cyclopenteno-4',5'-bis(*p*-acetoxybenzylthio)-TTF (**4**) in 45% yield. The acetoxybenzyl groups on **4** were removed by treatment with excess (8 equiv. mol) sodium methoxide in dichloromethane-methanol (1 : 3, v/v) at room temperature, followed by treatment with zinc chloride and tetrabutylammonium bromide. The resultant zinc TTF dithiolato complex (**5**)[9] formed *in situ* was reacted with an excess of triphosgen in THF at -78 °C to afford TTF fused with 1,3-dithiol-2-one (**6**, 60% yield). By the cross-coupling reaction between **6** and appropriate 1,3-dithiole-2-thiones (**7b**-**d**, 2 equiv.) with a

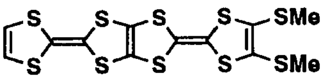


SCHEME I a) $P(OEt)_3$, 110 °C, 2 h (45%); b) NaOMe (8 equiv.), CH_2Cl_2-MeOH (1:4, v/v), room temp., 1 h; c) $ZnCl_2$, 30 min; d) Bu_4NBr, 30 min; e) $(Cl_3CO)_2CO$, THF, -78 °C - room temp., 1 h (60% based on **4**); f) Compound **7b-d** (2 equiv), $P(OMe)_3$ (100 equiv), toluene, 110 °C, 2 h (45-91%); g) $LiBr \cdot H_2O$ (20 equiv.), HMPA, 90 °C, 1h, 120 °C, 30 m (70%).

TABLE I Redox potentials of **1a-d** and related compounds.[a]

Compound	E_1	E_2	E_3	E_4[b]	E_2-E_1
1a	+0.43	+0.67	+1.01	+1.30	0.24
1b[c]	+0.68	+0.91	+1.20	+1.68	0.23
1c	+0.46	+0.69	+0.98	+1.13	0.23
1d	+0.46	+0.65	+0.90	+1.32	0.19
BDT-TTP	+0.44	+0.62	+1.05[b]	+1.13	0.18
8	+0.49	+0.71	+0.99	+1.13	0.22

[a] 0.1 mol dm^{-3} Bu_4NClO_4 in benzonitrile, Pt electrode, 25 °C, scan rate 50 mV s^{-1}, V *vs.* saturated calomel electrode (SCE). [b] Irreversible steps. Anodic peak potentials. [c] Measured in benzonitrile-carbon disulfide (1:1, v/v) using Bu_4NBF_4 as an electrolyte.



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large excess of trimethylphosphite in refluxing toluene were obtained the target **1b-d** in 45-91% yields. The unsubstituted derivative (**1a**) was obtained by heating of diester **1b** with an excess of lithium bromide monohydlate in hexamethylphosphoric triamide (HMPA) at 90-120 °C in 70% yield.

The cyclic voltammograms of all the new donors **1** show four pairs of single-electron redox waves as summarized in Table I. The first redox potentials of **1a** and **1c** are slightly lower by 0.01-0.03 V than those of BDT-TTP and 4,5-bis(methylthio)-TTP (**8**),[10] respectively, suggesting the donor ability is a little enhanced by substitution of an electron-donating trimethylene group.

Preparation and Electrical Conductivity of Molecular Complexes Based on CP-TTP Donors

All the CP-TTP donors except bis(methoxycarbonyl) derivative **1b** reacted with tetracyano-*p*-quinodimethane (TCNQ) and tetra-*n*-butylammonium triiodide to afford the corresponding TCNQ complexes and I_3^- salts. The other cation radical salts were prepared by an electrochemical oxidation method at a constant current in the presence of the corresponding tetra-*n*-butylammonium salts as electrolytes. The ratio of donor and acceptor was determined by elemental analysis, energy dispersion spectroscopy (EDS)[11] or X-ray structure analysis. The electrical conductivity of the obtained salts was measured by using a four-probe technique with gold paste contacts. As shown in Table II, most of salts showed high conductivity of 10^0-10^2 S cm^{-1} at room temperature. Temperature dependence of resistivity of CP-TTP·TCNQ and (CP-TTP)$_3$I$_3$ was semiconductive, however, their activation energies (E_a) had very small values of 0.010 and 0.008 eV, respectively. Therefore they are expected to show metallic conductive behavior if the measurement is carried out on a single crystal.

The TCNQ complex of CPTM-TTP **1c** also displayed high conductivity of σ_{rt} = 20 S cm^{-1} on a compressed pellet and semiconductive behavior with small E_a value of 0.022 eV similar to CP-TTP·TCNQ. In contrast, CPTM-TTP salts with various inorganic anions were obtained as single crystals. Among them, cation radical salts with some octahedral (PF_6^-, AsF_6^- and SbF_6^-) and linear ($Au(CN)_2^-$) anions are metallic, though the NbF_6^- and TaF_6^- salts are low conducting (σ_{rt} = 10^{-1}-10^{-3} S cm^{-1}) semiconductors. On the other hand, the tetrahedral anions (ClO_4^-, BF_4^- and $GaCl_4^-$) afforded semiconductive salts showing relatively high conductivity (σ_{rt}= 10^0 S cm^{-1}) with activation energy of 0.031-0.061 eV. Figure 1 shows conducting behavior of metallic CPTM-TTP salts. All the metallic salts except the SbF_6^- salt exhibited tricky temperature dependence of resistivity. The resistivity decreased monotonically down

TABLE II Composition and electrical conductivity of TCNQ complexes and cation radical salts based on CP-TTP derivatives (Donor·A_x).

Donor	Acceptor	Solvent	Form	x[a]	σ_{rt}/Scm^{-1} [b]	Conducting Behavior
1a	TCNQ	PhCl	-[c]	1.0(Anal.)	40[d]	E_a = 0.010 eV
	I_3^-	PhCl	-[c]	0.33(Anal.)	5[d]	E_a = 0.008 eV
1c	TCNQ	PhCl	-[c]	1.0(Anal.)	20[d]	E_a = 0.022 eV
	ClO_4^-	PhCl	N	0.52(Cl)	2	E_a = 0.031 eV
	BF_4^-	PhCl	N	-[e]	4	E_a = 0.038 eV
	$GaCl_4^-$	PhCl	P	1.5(Ga)	4	E_a = 0.061 eV
	PF_6^-	PhCl	P	0.25(X)	110	M[f]
	AsF_6^-	PhCl	P	0.25(X)	70	M[f]
	SbF_6^-	DCE[g]	N	0.25(X)	7	T_{MI} = 50 K
	NbF_6^-	PhCl	P	1.3(Nb)	5×10^{-1}	E_a =0.058 eV
	TaF_6^- [h]	PhCl	N	0.90(Ta)	6×10^{-3}	E_a = 0.14 eV
	I_3^-	PhCl	P	0.59(I)	11	E_a = 0.017 eV
	$Au(CN)_2^-$	PhCl	N	0.68(Au)	40	M[f]
1d	TCNQ	PhCl	-[c]	1.0(Anal.)	50	σ_{max} = 170 K
	ClO_4^-	PhCl	P	0.54(Cl)	100	T_{MI} = 220 K
	ReO_4^-	PhCl	P	0.45(Re)	100	M[f] down to 4.2 K
	AsF_6^-	PhCl	-[c]	0.69(As)	8[d]	σ_{max} = 180 K
	I_3^-	PhCl	-[c]	1.2(I)	2×10^{-1}	E_a = 0.04 eV
	$Au(CN)_2^-$	PhCl	F	0.50(Au)	30[d]	M[f] down to 4.2 K

[a] Determined by the energy dispersion spectroscopy (EDS) from the ratio of sulfur and the elements designated in the parentheses. Anal. and X designate the value determined from elemental and X-ray structure analysis, respectively. [b] Room temperature conductivity measured by four-probe technique on a single crystal. [c] Obtained as powder. [d] Measured on a compressed pellet. [e] The contents of light elements such as B and F were not reliably determined by EDS. [f] M designates metallic. [g] DCE = 1,2-dichloroethane. [h] Containing a solvent $(PhCl)_{0.4}$.

to 100-200 K in the cooling run, and then it increased about one order as large as the room temperature value with several minor jumps in the low temperature region. However, the temperature dependence of resistivity was not semiconductive around liquid helium temperature. In the heating process, the PF_6^- and AsF_6^- salts are metallic in the low temperature region, and a huge hump of resistivity was observed around 80 K (Figure 1). On the other hand, resistivity of the $Au(CN)_2^-$ salt decreased as the temperature increased, though its temperature dependence was very weak and not semiconductive. Therefore, we believe these salts are essentially metallic down to liquid helium temperature. This anomalous conducting behavior is probably owing to formation of microcrack during the cooling and/or to an intrinsic phase transition from metal to the other metallic (or semimetallic) state.[12] Such conducting behavior is often observed in TTP systems such as (BDT-TTP)$_2$X (X = ClO$_4^-$, BF$_4^-$ and ReO$_4^-$)[5b] and (TMEO-TTP)$_2$Au(CN)$_2$,[4d] where TMEO-TTP is 4,5-bis(methylthio)-4',5'-ethylenedioxy-TTP. On the contrary, the SbF$_6^-$ salt showed very weak temperature dependence of resistivity and underwent a metal to semiconductor transition around

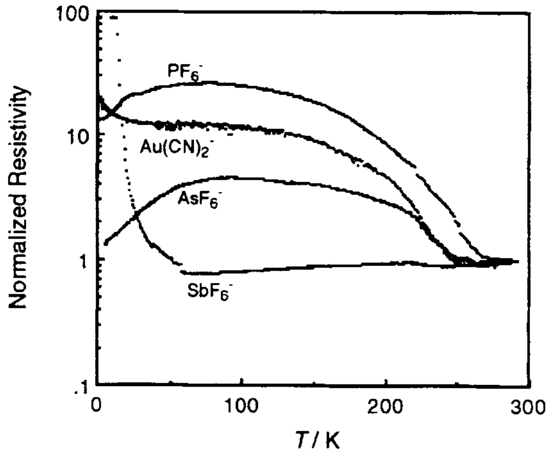

FIGURE 1 Conducting behavior of metallic CPTM-TTP salts.

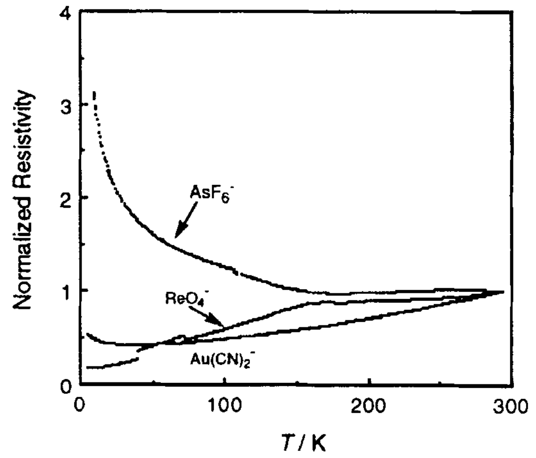

FIGURE 2 Conducting behavior of metallic CPET-TTP salts.

50 K (see also Figure 1). However, no hysteresis was observed in this case.

In contrast with CPTM-TTP salts, single crystals of the ReO_4^- and $Au(CN)_2^-$ salts of CPET-TTP **1d** exhibited rather "simple" metallic behavior. Their resistivity decreased as the temperature decreased (Figure 2), though the degree of temperature dependence is weak ($\rho_{min}/\rho_{rt} \approx 0.2\text{-}0.4$). On the other hand, its TCNQ complex and AsF_6^- salt also showed metallic temperature dependence around room temperature, and then the resistivity increased a little ($\rho_{4.2K}/\rho_{rt} \approx 3\text{-}10$) in lower temperature region. Considering that the conductivity measurement was carried out on compressed pellets, these two salts are essentially metallic and expected to show more simple metallic temperature dependence on single crystals.

Crystal and Electronic Structures of (CPTM-TTP)$_4$X (X = PF_6^-, AsF_6^- and SbF_6^-)

Among the conducting salts obtained, single crystals of metallic CPTM-TTP salts with octahedral anions (PF_6^-, AsF_6^- and SbF_6^-) were suitable for an X-ray structure

TABLE III Crystallographic data of (CPTM-TTP)$_4$X (X = PF_6^-, AsF_6^-, SbF_6^-)

Compound	(CPTM-TTP)$_4$PF$_6$	(CPTM-TTP)$_4$AsF$_6$	(CPTM-TTP)$_4$SbF$_6$
Molecular Formula	$C_{60}H_{48}S_{40}PF_6$	$C_{60}H_{48}S_{40}AsF_6$	$C_{60}H_{48}S_{40}SbF_6$
Formula Weight	1098.20	1120.18	1143.9
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a /Å	11.796(6)	11.799(4)	11.818(4)
b /Å	21.151(4)	21.210(7)	21.334(6)
c /Å	8.388(5)	8.410(3)	8.430(2)
α /°	92.52(3)	92.41(3)	92.38(3)
β /°	100.70(5)	100.78(3)	100.67(2)
γ /°	91.11(3)	91.28(3)	91.37(3)
V /Å^3	2053(1)	2065(1)	2085(1)
Z	1	1	1
D_c /gcm^{-3}	1.776	1.811	1.821
μ(Mo Kα) /cm^{-1}	11.06	14.86	13.86
R	0.076	0.045	0.063
R_w	0.086	0.044	0.056
Reflections measured	12516	12571	10650
Reflections used	2210 ($I>3\sigma(I)$)	3858 ($I>3\sigma(I)$)	1770 ($I>3\sigma(I)$)

analysis. All of them are isostructural with each other as summarized in Table III. A unit cell contains two crystallographically independent donor molecules (molecules A and B), whereas the anion lies on a center of inversion. Thus, the ratio of donor and anion was determined to be 4:1. Figures 3 and 4 show the donor structures in (CPTM-TTP)$_4$SbF$_6$. The two donors A and B have a little different structure each other. In the TTP skeleton of the molecule A, the outer 1,3-dithiole ring substituted with methylthio groups has an envelop conformation slightly folded at the sulfur atoms,

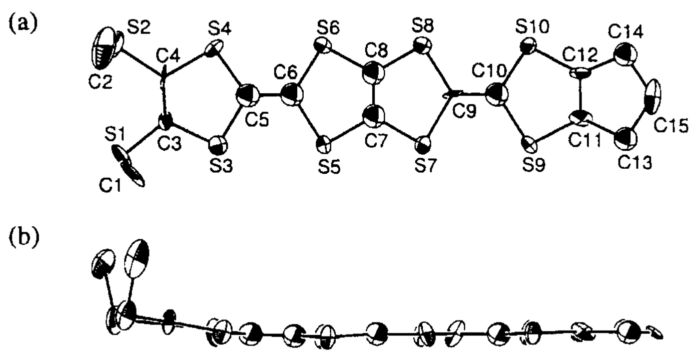

FIGURE 3 (a) ORTEP drawing and atomic numbering scheme of the molecule A, and (b) side view of (CPTM-TTP)$_4$SbF$_6$.

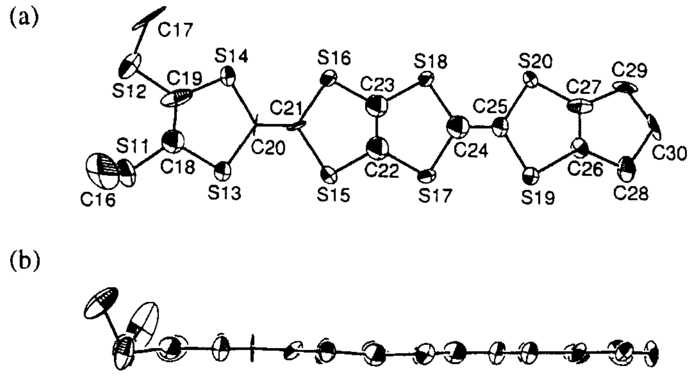

FIGURE 4 (a) ORTEP drawing and atomic numbering scheme of the molecule B, and (b) side view of (CPTM-TTP)$_4$SbF$_6$.

TABLE IV Selected bond lengths of (CPTM-TTP)$_4$AsF$_6$ and neutral DMTM-TTP.

	(CPTM-TTP)$_4$AsF$_6$		DMTM-TTP
	Molecule A	Molecule B	
C5-C6 (C20-C21)	1.355(8)	1.349(8)	1.341(6)
C9-C10 (C24-C25)	1.356(7)	1.353(8)	1.347(6)
Average	1.356(8)	1.351(8)	1.344(6)
S3-C5 (S13-C20)	1.750(7)	1.747(6)	1.751(4)
S4-C5 (S14-C20)	1.754(6)	1.743(7)	1.754(4)
S9-C10 (S19-C25)	1.758(6)	1.742(7)	1.746(4)
S10-C10 (S20-C25)	1.750(7)	1.760(6)	1.752(4)
Average	1.753(7)	1.748(7)	1.751(4)
S5-C6 (S15-C21)	1.759(6)	1.754(7)	1.761(4)
S6-C6 (S16-C21)	1.754(7)	1.765(7)	1.771(4)
S7-C9 (S17-C24)	1.755(7)	1.753(6)	1.768(4)
S8-C9 (S18-C24)	1.759(6)	1.756(7)	1.768(4)
Average	1.757(7)	1.757(7)	1.767(4)
S3-C3 (S13-C18)	1.770(7)	1.751(7)	1.757(4)
S4-C4 (S14-C19)	1.746(7)	1.736(7)	1.753(4)
S9-C11 (S19-C26)	1.727(7)	1.734(7)	1.752(4)
S10-C12 (S20-C27)	1.747(7)	1.727(7)	1.763(4)
Average	1.748(7)	1.737(7)	1.756(4)
S5-C7 (S15-C22)	1.717(6)	1.742(7)	1.754(4)
S6-C8 (S16-C23)	1.740(7)	1.716(6)	1.742(4)
S7-C7 (S17-C22)	1.744(7)	1.722(6)	1.736(4)
S8-C8 (S18-C23)	1.725(6)	1.733(7)	1.743(4)
Average	1.732(7)	1.728(7)	1.744(4)
C3-C4 (C18-C19)	1.326(8)	1.351(9)	1.340(6)
C11-C12 (C26-C27)	1.335(8)	1.388(8)	1.318(6)
C7-C8 (C22-C23)	1.342(8)	1.351(8)	1.324(6)
Average	1.334(8)	1.363(8)	1.327(6)

while TTP π-electron framework in the molecule B is almost planar. Both the methylthio groups in the molecule B are bent up almost perpendicularly to the molecular plane. On the other hand, one of the methyl groups in the molecule A overhangs from the molecular plane, and the other projects outside of the molecular long axis. Table IV shows intramolecular bond distances of molecules A and B in $(CPTM\text{-}TTP)_4AsF_6$ together with those of neutral DMTM-TTP. There is a tendency that the averaged C=C distances in the molecules A and B are about 0.01-0.04 Å longer than those in the neutral DMTM-TTP. In contrast, most C-S distances tend to be shorter by about 0.01-0.02 Å. In comparison of bond distances between molecules A and B, no large difference of the bond distances is observed. Therefore, we think that both crystallographycally independent donor molecules A and B are in partially oxidized states, and that there is no significant difference in the formal charge between these molecules although bond distances obtained are not enough accurate to estimate the exact formal charge of each donor.

The donors form conducting sheets along *ac* plane, which are separated by anion layers as shown in Figure 5. The array of donors resembles those of the β-type of BEDT-TTF salts (Figure 6).[13] The donors form a stack with a four-folded period as AABB. Therefore, there are three kinds of overlap modes of donor molecules stack as shown in Figure 7, namely A-A (p1), A-B (p2) and B-B (p3). The donors A-A and B-B are stacked in a head-to-tail manner, while the overlap for A-B is a head-to-head manner. In the case of $(CPTM\text{-}TTP)_4SbF_6$, the interplanar distances are 3.42, 3.61 and 3.58 Å for p1, p2 and p3, respectively. All the overlap modes are ring-over-bond

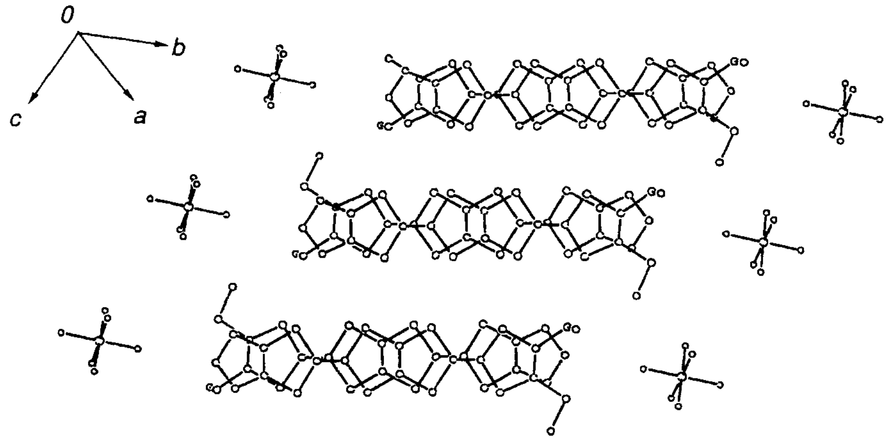

FIGURE 5 Crystal structure of $(CPTM\text{-}TTP)_4SbF_6$.

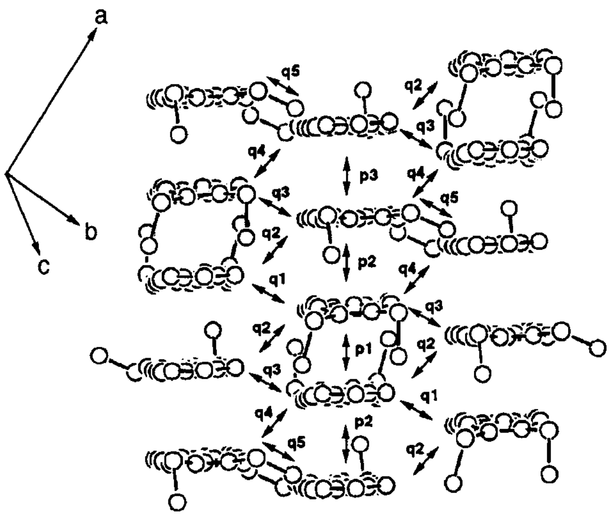

FIGURE 6 Donor sheet structure of $(CPTM\text{-}TTP)_4SbF_6$. Projection along the molecular long axis.

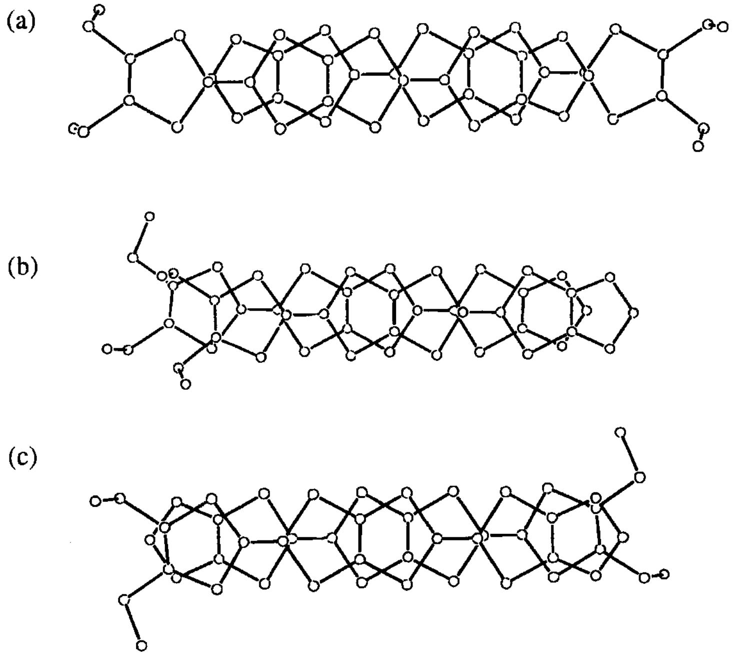

FIGURE 7 (a) Overlap modes of donor molecules A-A (p1), (b) A-B (p2) and (c) B-B (p3) in $(CPTM\text{-}TTP)_4SbF_6$. Projection onto the molecular planes.

type, though the slip distance D of p1 along the molecular long axis (4.76 Å) is more than twice as large as those of p2 (1.69 Å) and p3 (1.56 Å) as shown in Table V. For TTF systems, such a large D value usually makes an overlap considerably small. In contrast, π-electron framework of TTP is about twice longer than that of TTF, and the interplanar distance for p1 is about 0.2 Å shorter than the others. Therefore, such a large D value of p1 may be less sensitive to overlap integral very much in the present salts. In fact, the calculated overlap (see also Table V)[13] of p1 (18.3×10^{-3}) is only ca. 20% smaller than those of the other intrastack interactions. As a result of a weak tetramerization, the band widths of $(\text{CPTM-TTP})_4X$ correspond to a still large value of

TABLE V Intermolecular overlap integrals of the HOMO, S, and the parameters ϕ and D which define the orientation of adjacent molecules in $(\text{CPTM-TTP})_4\text{SbF}_6$

	$S / \times 10^{-3}$	$\phi / °$	D / Å
p1	18.3	88	4.76
p2	-21.2	87	1.69
p3	21.4	89	1.56
q1	-0.3	14	1.41
q2	6.1	19	3.10
q3	-0.2	12	1.66
q4	7.4	20	3.04
q5	1.5	13	4.67

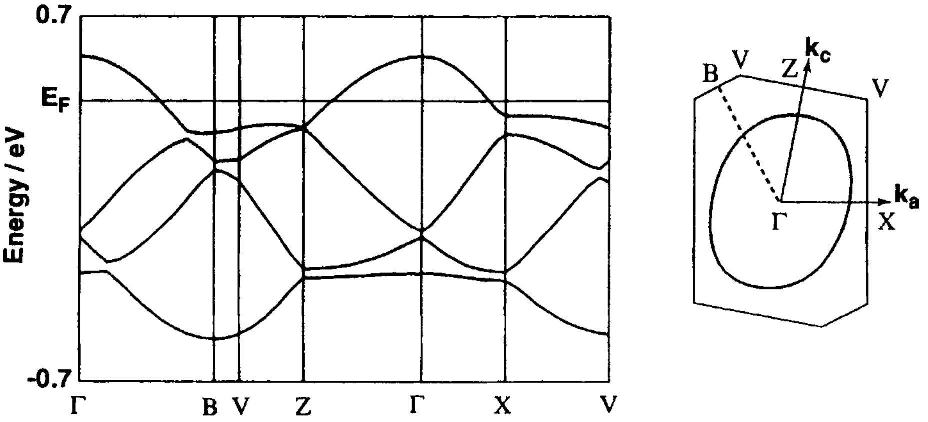

FIGURE 8 Energy band structure and Fermi surface of $(\text{CPTM-TTP})_4\text{SbF}_6$.

1.1 eV. On the other hand, interstack overlaps q2 and q4 are about one thirds of the intrastack interactions. Thanks to such comparatively large interstack interactions and a large band filling (7/8 filled), the Fermi surface of all the (CPTM-TTP)$_4$X calculated by a tight-binding method[14] has ecliptical cross sections characteristic of 2D metals as is observed in β-(BEDT-TTF)$_2$I$_3$ (Figure 8).[13b] The closed Fermi surface is 50% of the first Brillouin zone. Though these three CPTM-TTP salts have a same band structure with a closed Fermi surface, (CPTM-TTP)$_4$SbF$_6$ shows exceptionally metal to semiconductor transition around 50 K, while the others undergo metal to metal (or semimetal) transition. Considering that these metallic CPTM-TTP salts are isostructural with each other and that their calculated Fermi surfaces are closed, the formation of charge density wave for (CPTM-TTP)$_4$SbF$_6$ seems to be hard. On the other hand, the results obtained from band calculation suggest that the topmost band and the next one are energetically less overlapped each other. Among metallic (CPTM-TTP)$_4$X, the SbF$_6^-$ salt may have the narrowest bands because it has the largest anion. Therefore, we temporarily think the topmost band of (CPTM-TTP)$_4$SbF$_6$ is exactly half filled. In that case, it is plausible to show very weak temperature dependence of resistivity as is observed in (TTM-TTP)I$_3$, where TTM-TTP is tetrakis(methylthio)-TTP.[15] It is very close whether (CPTM-TTP)$_4$X show metallic behavior down to low temperature or metal to semiconductor transition.

CONCLUSION

In summary, we have synthesized a series of bis-fused TTF donors annelated with cyclopentene ring. Among them, CPTM-TTP and CPET-TTP have formed metallic cation radical salts which retain metallic conductivity down to liquid helium temperature. Organic metals (CPTM-TTP)$_4$X (X = PF$_6^-$, AsF$_6^-$ and SbF$_6^-$) are isostructural with each other and have 2D "β-type" array of donors. Tight-binding band calculations suggest the above salts have 2D closed Fermi surfaces though the SbF$_6^-$ salt exceptionally showed metal to semiconductor transition. Considering that the calculated topmost bands of these salts are almost half-filled, it is very close whether they are metallic down to low temperature or subject to a metal to semiconductor transition. In TTF system, substitution of alkyl and/or methylthio groups usually prevents formation of 2D electronic structure owing to their less electronic effect and steric hindrance. On the contrary, such modifications are available in TTP system without the reduction of 2D nature, because TTP itself has ability to form 2D structure thanks to ladder-like sulfur array and to longer π-electron framework than TTF.

DEDICATION

It is our pleasure to dedicate this paper to Professors Fumio Ogura and Yusei Maruyama on the occasion of their retirement from Hiroshima University, Higashi-Hiroshima and the Institute for Molecular Science, Okazaki, respectively.

ACKNOWLEDGMENT

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Area (No. 07232219), and Proposal-Based Advanced Industrial Technology R & D Program (No. A-1033).

EXPERIMENTAL

General

Melting points were determined with a Yanaco MP-J3 micro melting point apparatus and not corrected. Microanalyses were performed at the Microanalysis Center, Kyoto University. ^{1}H NMR spectra were recorded on a JEOL FT-NMR Model FX 90A (90 MHz) and a JNM GSX-270 FT-NMR (270 MHz) spectrometers, and chemical shift values are given in a parts per million (ppm) relative to internal tetramethylsilane. Mass spectra were obtained with a SHIMADZU QP-1000 EX spectrometer and IR spectra with a BIO-RAD FTS-30 FTIR spectrometers.

4,5-Bis(*p*-acetoxybenzylthio)-4',5'-cyclopentenotetrathiafulvalene (**4**)

4,5-Cyclopenteno-1,3-dithiole-2-thione (**2**) (2.61 g, 15.0 mmol) and 4,5-bis(*p*-acetoxybenzylthio)-1,3-dithiol-2-one (**3**) (4.78 g, 10.0 mmol) were heated in triethylphosphite (60 ml) at 110 °C under argon atmosphere for 2 hours. After triethylphosphite was evaporated *in vacuo*, the residue was chromatographed on silica gel firstly with dichloromethane-*n*-hexane 1:1 (v/v) and then with 4:1 (v/v) as the eluent. The crude product was purified by recrystallization from dichloromethane-methanol to afford **4** (2.69 g, 4.45 mmol) as orange microcrystals in 45% yield. mp 179.0-180.0 °C (recrystallized from dichloromethane-*n*-hexane); IR (KBr) ν (cm^{-1}) 1761 (s), 1506 (m), 1373 (m), 1219 (s), 1192 (s); ^{1}H-NMR (CDCl$_3$, 270 MHz) δ 7.26 (d, 4H, J 9.0Hz), 7.02 (d, 4H, J 8.9Hz), 3.84 (s, 4H), 2.50-2.31 (m, 6H), 2.28 (s, 6H); MS m/z 604 (M$^+$); Anal. Calcd. for $C_{27}H_{24}O_4S_6$: C, 53.62; H, 4.00; S, 31.80. Found: C, 53.56; H, 4.04; S, 31.58.

2-(4,5-Cyclopenteno-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalen-5-one (6)

To a solution of **4** (886 mg, 1.47 mmol) in 24 ml of dichloromethane-methanol (1:3, v/v) was added excess 28% sodium methoxide solution in methanol (2.27 g, 11.8 mmol) at room temperature, and the reaction mixture was stirred for 20 minutes under argon atmosphere. The reaction mixture was treated with zinc chloride (203 mg, 1.50 mmol) and stirred for 10 minuets, followed by treatment with tetra-*n*-butylammonium bromide (567 mg, 1.76 mmol) and stirring for additional 1 hour. After the reaction mixture was dried up *in vacuo*, the residue was suspended in dry THF (50 ml), and then an excess of triphosgen (1.17 g, 3.94 mmol) was added in one portion at -78 °C. The reaction mixture was warmed up to room temperature, and an excess methanol (6 ml) was added to decompose excess of triphosgen. After the reaction mixture was concentrated *in vacuo*, methanol was added, and the resultant precipitate was filtered off and washed successively with methanol, water and *n*-hexane. The dark brown solids were collected and column chromatographed on silica gel with carbon disulfide as an eluent to afford **6** (293 mg, 0.87 mmol) as red microcrystals in 60% yield. mp 184.0-185.0 °C (dec.) (recrystallized from chlorobenzene); IR (KBr) ν (cm^{-1}) 1676 (s), 1459 (m); ^{1}H-NMR (CS$_2$-C$_6$D$_6$, 270 MHz) δ 2.51-2.43 (m, 4H), 2.40-2.33 (m, 2H); MS m/z 334 (M$^+$); Anal. Calcd. for $C_{10}H_6OS_6$: C, 35.90; H, 1.81. Found: C, 35.85; H, 1.66.

2-(4,5-Cyclopenteno-1,3-dithiol-2-ylidene)-5-[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-1,3,4,6-tetrathiapentalene (1b)

A mixture of **6** (150 mg, 0.45 mmol) and 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione (**7b**) (338 mg, 1.35 mmol) in toluene (7 ml) was refluxed with a large excess of trimethylphosphite (7 ml) under argon atmosphere for 2 hours. After the reaction mixture was cooled to room temperature, methanol was added. The resultant black precipitate was filtered off, washed with *n*-hexane, and then dried *in vacuo*. Compound **1b** (219 mg, 0.41 mmol) was obtained as black luster crystals in 91% yield. mp 214.0-214.5 °C (dec.) (recrystallized from *o*-dichlorobenzene); IR (KBr) ν (cm^{-1}) 1720 (s), 1573 (m), 1434 (m), 1236 (s); ^{1}H-NMR (CS_2-C_6D_6, 270 MHz) δ 3.64 (s, 6H), 2.45-2.42 (m, 6H); MS m/z 542 (M$^+$); Anal. Calcd. for $C_{17}H_{18}O_4S_8$: C, 37.75; H, 2.41. Found: C, 38.04; H, 2.55.

Above synthetic method was applied to the preparation of **1c**, **d**.

1c: 48% yield; orange crystals; mp 204.5-205.0 °C (dec.) (recrystallized from *o*-dichlorobenzene); IR (KBr) ν (cm^{-1}) 1561 (w), 1540 (w), 1427 (m), 1421 (m), 1339 (m), 1311 (m), 1283 (w); ^{1}H-NMR (CS_2-C_6D_6, 270 MHz) δ 2.50-2.45 (m, 4H), 2.44-2.31 (m, 8H); Anal. Calcd. for $C_{15}H_{12}S_{10}$: C, 34.99; H, 2.11; S, 62.33. Found: C, 35,13; H, 2.34; S, 62,51.

1d: 45% yield; reddish brown powder; mp 218.0-219.5 °C (dec.) (recrystallized from *o*-dichlorobenzene); IR (KBr) ν (cm^{-1}) 1558 (w), 1541 (w), 1443 (m), 1405 (m), 1355 (m), 1310 (m), 1286 (m); ^{1}H-NMR (CS_2-C_6D_6, 270 MHz) δ 3.11 (s, 4H), 2.50-2.40 (m, 4H), 2.36-2.28 (m, 2H); Anal. Calcd. for $C_{15}H_{10}S_{10}$: C, 35.44; H, 1.88. Found: C, 35.27; H, 1.97.

2-(4,5-Cyclopenteno-1,3-dithiol-2-ylidene)-5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (1a)

A mixture of **1b** (80 mg, 0.15 mmol) and lithium bromide monohydrate (158 mg, 1.5 mmol) in hexamethylphosphoric triamide (20 ml) was vacuumed for 1 h to eliminate the trace of amines of solvent. The mixture was stirred for 1 hour at 90 °C and then for 30 minutes at 120 °C under bubbling argon gas. After cooled to room temperature, the reaction mixture was poured into distilled water. The resultant precipitate was washed with methanol, and then chromatographed on silica gel with carbon disulfide as an eluent to afford **1a** as brown powder (44 mg, 70%). The analytically pure sample (yellow orange microcrystals) was obtained by recrystallization from chlorobenzene. mp 201.0-201.5 °C (dec.); IR (KBr) ν (cm^{-1}) 1557 (w), 1537 (w), 1442 (m), 1312 (w), 1279 (w); ^{1}H-NMR (CS_2-C_6D_6, 270 MHz) δ 6.10 (s, 2H), 2.47-2.40 (m, 4H), 2.36-2.28 (m, 2H); MS m/z 420 (M$^+$); Anal. Calcd. for $C_{13}H_8S_8$: C, 37.12; H, 1.92. Found: C, 37.34; H, 2.02.

General Procedure for Preparation of TCNQ Complexes and I_3^- Salts.

The typical procedure for preparation of TCNQ complex and I_3^- salt is as follow. Hot solutions of donor molecule and TCNQ or tetra-*n*-butylammonium triiodide in chlorobenzene were mixed. After the reaction mixture was cooled to room temperature, the resultant precipitate was collected by filtration. TCNQ complex was washed successively with carbon disulfide and acetonitrile, and dried *in vacuo*. The I_3^- salt was washed successively with carbon disulfide and methanol, and dried *in vacuo*. The ratio of donor and TCNQ or I_3^- was determined by elemental analysis or energy dispersion spectroscopy (EDS) from the ratio of sulfur and the elements designated in the parentheses of Table II.

General Procedure for Preparation of Cation Radical Salts

Cation radical salts of **1c** and **d** were prepared by electrochemical oxidation in chlorobenzene or 1,2-dichloroethane containing ca. 5% absolute ethanol at a constant current of 0.1 - 0.5 μA in the presence of the corresponding tetra-*n*-butylammonium salts at 50 °C for 1-2 weeks. The crystals obtained were washed successively with ethanol and were air-dried at room temperature. The ratio of donor and anion was determined by EDS from the ratio of sulfur and the elements designated in the parentheses of Table II.

X-Ray Structure Analysis of (CPTM-TTP)$_4$X (X = PF_6^-, AsF_6^- and SbF_6^-)

A black plate crystal was used for X-ray measurement at 293 K on a Rigaku AFC7R diffractometer equipped with graphite monochromated MoKα radiation and a 12 kW rotating anode generator. Cell constants were determined from 25 carefully centered reflections in the range $6 < 2\theta < 25°$. Intensity data were collected to a maximum 2θ value of 60° by the ω-2θ scan technique. The structure was solved by a direct method (SHELXS86).[16] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The structure was refined by full-matrix least squares.

Electrochemical Measurement

The cyclic voltammetry system used in this experiment was composed of a Yanaco polarographic analyzer Model P-1100, a Graphtec X-Y recorder Model WX-1200. The measurement was performed in benzonitrile or benzonitrile-carbon disulfide (1:1, v/v) containing 0.1 M tetra-*n*-butylammonium perchlorate or tetrafluoroborate as a supporting electrolyte using platinum working and counter electrodes, and a Yanaco saturated calomel electrode (SCE) Model MR-P2A as a reference electrode (scan rate: 50 mV/sec).

Electrical Conductivity Measurement

Electrical conductivity measurement was carried out by four-probe technique using Huso Electro Chemical System HESS 994 Multi-channel 4-terminal conductometer. Electrical contacts were achieved with gold paste.

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