© 2001 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 74, 59–65 (2001)

Tetrathiapentalene Derivatives with Long Alkyl Chains

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(Received August 11, 2000)

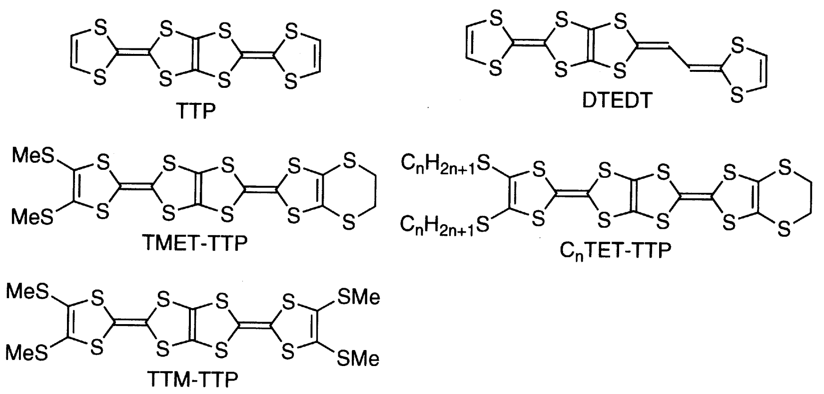
Bis-fused π-electron donors having alkylthio chains, C_nTET-TTP (2-[4,5-bis(alkylthio)-1,3-dithiol-2-ylidene]-5-(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene; $n = 2$–4) have been synthesized. C_2TET-TTP (**1a**) forms radical-cation salts with BF_4^- and ClO_4^-, which are metallic ($\sigma_{rt} = 900$–2500 S cm^{-1}) down to helium temperatures. The I_3 salts of C_3TET-TTP (**1b**) and C_4TET-TTP (**1c**) are semiconductive from room temperature ($\sigma_{rt} = 0.041$ and 0.025 S cm^{-1}, respectively). (C_2TET-TTP)$_2ClO_4$ has uniform stacks of the donors, and has an elliptical Fermi surface characteristic of two-dimensional metals. (C_4TET-TTP)I_3 is dimeric, and can be regarded as a band insulator. These crystal structures demonstrate the tendency that the long alkyl chains increase the anion content, and stabilize the usual stacking structure as well as the dimerization.

Since the first organic metals were reported early in the 1970s,[1] a variety of organic donors have been synthesized. Examples of organic donors include derivatives of tetrathiafulvalene (TTF),[2] tetrathiatetracene (TTT),[3] phthalocyanines (pc),[4] and porphyrins.[5] In particular, many TTF derivatives have been synthesized. Among them, tetramethyl-tetraselenafuluvalene (TMTSF)[6] and bis(ethylenedithio)-TTF (BEDT-TTF)[6] have received remarkable attention because some of their salts show superconductivity.

To develop the extended π-electron systems derived from TTF, fusion of 1,3-dithiole donors, namely, insertion of a tetrathiapentalene moiety, is a promising strategy.[7] Actually, a bis-fused TTF donor, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (TTP, Scheme 1), has produced many metallic cation radical salts stable down to helium temperatures, owing to their two-dimensional conduction networks and the small on-site Coulomb repulsion U. However, the stabilization of the metallic behavior seems to also inhibit the transition to superconducting phases. There is no superconductor derived from the usual TTP-type donors except for the vinylogous analog 2-(1,3-dithiol-2-ylidene)-5-[2-(1,3-dithiol-2-ylidene)ethylidene]-1,3,4,6-tetrathiapentalene (DTEDT, Scheme 1), which has been found to form a superconductive salt, (DTEDT)$_3$Au(CN)$_2$ ($T_c = 4$ K).[8]

This superconductor and many other salts of TTP donors tend to have small anion content, and the positive charge on the donors is comparatively small.[9] Most of conventional organic superconductors like BEDT-TTF salts have 2 : 1 composition or larger anion content,[10] and the control of the filling is obviously important for superconductivity. However, there is practically no strategy to control the donor : acceptor composition.

We have chosen TMET-TTP (= C_1TET-TTP, bis(methylthio) ethylenedithio–TTP, Scheme 1) as the starting donor for our synthetic modification. This donor forms 4 : 1 radical cation salts with AuI_2^-, PF_6^-, ReO_4^-, IO_4^-, and ClO_4^-.[9] In order to increase the ratio of anion, we have attempted to replace the methylthio chains with longer alkylthio chains. The flexible alkyl chains are expected to increase the free space available to



Scheme 1.

the counter anions, and to increase the anion ratio. Since the donors to both of whose sides four alkyl chains are attached, for example TTM-TTP (tetrakis(methylthio)–TTP, Scheme 1), are known to inhibit transverse intermolecular interactions resulting in highly one-dimensional conductors that undergo the Peierls transitions at low temperatures,[11] one side of the donor is fixed to have an ethylendithio moiety, and the two alkyl chains of the other side are replaced. In this article we describe synthesis, structures, and physical properties of charge-transfer salts of TMET-TTP derivatives with C_n-alkyl chains ranging from $n = 2$ to 4 (C_nTET-TTP). Particular attention has been paid to two radical-cation salts whose crystal structures have been analyzed: $(C_2TET\text{-}TTP)_2ClO_4$, which is metallic down to helium temperatures, and $(C_4TET\text{-}TTP)I_3$, which is an insulator from room temperature. Although the examples are few, these crystal structures well represent the character of the donors, and the effects of the alkyl-chain substitution.

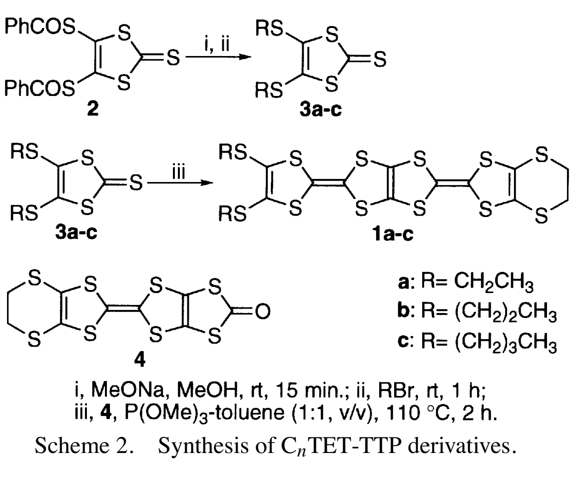
Synthesis

The synthesis of C_nTET-TTP (**1a–c**) was achieved as shown in Scheme 2. 5-(4,5-Ethylenedithio-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalen-2-one (**4**) was prepared via 2,3-bis(cyanoethylthio)-6,7-ethylenedithio-tetrathiafulvalene by the previously reported method.[9,12]

4,5-bis(alkylthio)-1,3-dithiole-2-thione derivatives (**3a–c**) were obtained in 44–96% yields by the deprotection of 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (**2**) and the following alkylation by the addition of alkyl bromide at room temperature.[13] The compounds **3a–c** and **4** were cross-coupled in trimethyl phosphite–toluene (1 : 1, v/v) at 110 °C to give the corresponding C_nTET-TTP derivatives (**1a–c**) in 10–19% yields.

Electrochemical Properties

The electrochemical properties of newly synthesized donors C_nTET-TTP were investigated by cyclic voltammetry in benzonitrile in the presence of $n\text{-}Bu_4NPF_6$ as a supporting electrolyte using Pt working and counter electrodes and an $Ag^+/AgCl$ reference electrode at 25 °C. The donors displayed four pairs of redox waves corresponding to one-electron transfer processes. The redox potentials are summarized in Table 1.



i, MeONa, MeOH, rt, 15 min.; ii, RBr, rt, 1 h;
iii, **4**, $P(OMe)_3$-toluene (1:1, v/v), 110 °C, 2 h.

Scheme 2. Synthesis of C_nTET-TTP derivatives.

Table 1. Redox Potentials of C_nTET-TTP Derivatives (V)

Compound	E_1	E_2	E_3	E_4	$E_2 - E_1$
1a	+0.44	+0.68	+0.94	+1.18	0.24
1b	+0.46	+0.67	+0.86	+0.99	0.21
1c	+0.46	+0.67	+0.84	+0.99	0.21
TMET-TTP	+0.44	+0.68	+0.90	+1.05	0.24

The comparison of the first redox potentials reveals that the oxidation potentials of C_nTET-TTP derivatives are almost the same as that of TMET-TTP. The E_2–E_1 values of C_nTET-TTP derivatives, which are a measure of the on-site Coulomb repulsion, are similar to that of TMET-TTP. This suggests that the replacement of methylthio groups with long alkylthio groups does not change the electron donating ability of TMET-TTP.

Preparation and Electrical Properties of Charge Transfer Complexes

The donor molecules, C_nTET-TTP, are much more soluble in organic solvents than TMET-TTP. All charge transfer complexes were prepared by electrochemical oxidation in 1,1,2-trichloroethane, 1,2-dichloroethane, or chlorobenzene at 25–28 °C in the presence of tetrabutylammonium salts of various anions. The temperature-dependent resistivity values of some salts are shown in Fig. 1(a).

The ethylthio derivative, C_2TET-TTP (**1a**), form complexes with BF_4^- and ClO_4^- in the form of black needles. The composition of the ClO_4 salt is found to be 2 : 1 by EDS and the X-ray structure analysis. From the comparison of the lattice constants, the ClO_4 and BF_4 salts are isostructual. These salts exhibit high electrical conductivities at room temperature: 900 S cm^{-1} for the ClO_4 salt and 2500 S cm^{-1} for the BF_4 salt. These values are among the highest in molecular conductors. These salts show metallic conductivity down to 0.5 K.

Thermoelectric power values of $(C_2TET\text{-}TTP)_2ClO_4$ and $(C_2TET\text{-}TTP)_2\,BF_4$ are shown in Fig. 1(b). The thermoelectric power follows T-linear dependence, characteristic of the metallic nature.

Figure 1(c) shows the temperature dependence of the magnetic susceptibility and linewidth of $(C_2TET\text{-}TTP)_2ClO_4$ measured by ESR. The linewidth changes linearly to T. The spin susceptibility is almost constant, showing the Pauli-like spin susceptibility. These results also indicate the metallic nature of $(C_2TET\text{-}TTP)_2ClO_4$.

The propylthio and butylthio derivatives, C_3TET-TTP (**1b**) and C_4TET-TTP (**1c**), yielded I_3 salts in the form of black plates. Both of them are found to be 1 : 1 complexes from EDS, and show semiconductive behavior from room temperature ($\sigma_{rt} = 0.041$ and 0.025 S cm^{-1}, respectively). From the temperature-dependence, the activation energies E_a are 0.13 and 0.23 eV, respectively.

Crystal and Electronic Structures of $(C_2TET\text{-}TTP)_2ClO_4$ and $(C_4TET\text{-}TTP)I_3$

X-Ray single crystal structure analysis was carried out for $(C_2TET\text{-}TTP)_2ClO_4$ and $(C_4TET\text{-}TTP)I_3$. The data collection was performed at room temperature for $(C_2TET\text{-}TTP)_2ClO_4$

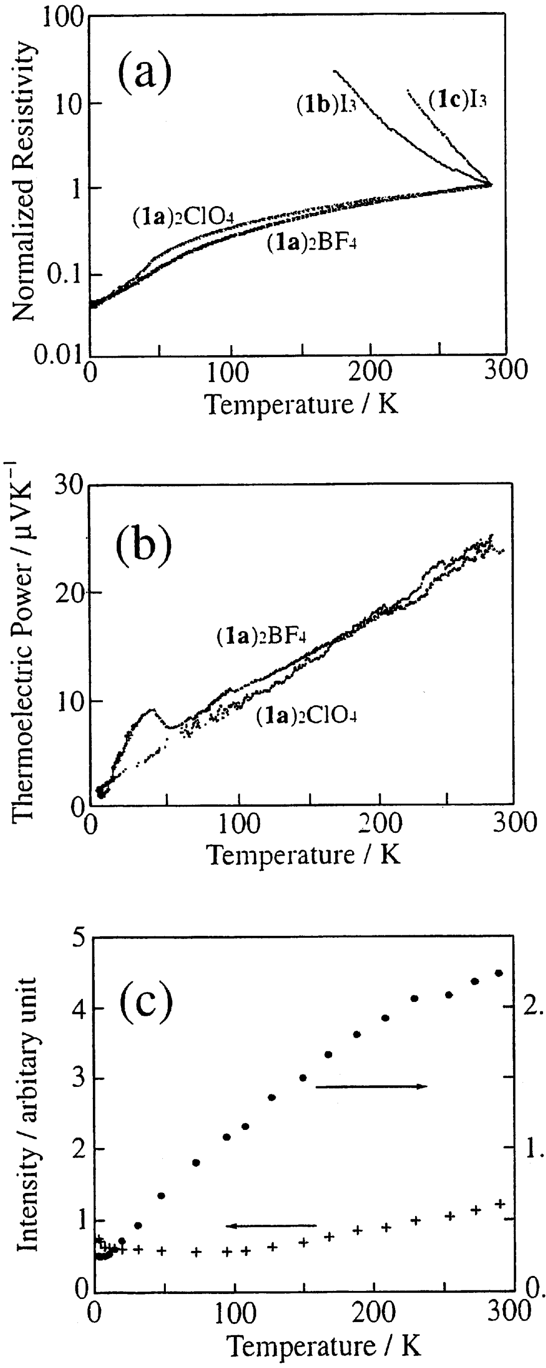


Fig. 1. (a) Temperature dependence of the resistivities of C_nTET-TTP salts (heating process, normalized to the values at room temperature), (b) thermoelectric power of C_2TET-TTP salts (heating process), and (c) temperature dependence of the ESR intensity and peak-to-peak line width of $(C_2\text{TET-TTP})_2ClO_4$ (*H*//b).

and at 200 K for $(C_4\text{TET-TTP})I_3$, as the butyl chains of **1c** were too movable at room temperature to be determined exactly. The crystal data are summarized in Table 2.

The atomic numbering scheme is shown in Fig. 2. Figure 3 shows the crystal structure of $(C_2\text{TET-TTP})_2ClO_4$. One crystallographically independent donor molecule is located on a

Table 2. Crystallographic Data

	$(C_2\text{TET-TTP})_2ClO_4$	$(C_4\text{TET-TTP})I_3$
Chemical formula	$C_{32}H_{28}ClO_4S_{24}$	$C_{20}H_{22}I_3S_{12}$
Formula weight	1281.46	1027.83
Shape	black needle	black plate
Space group	$C2/c$	$P\bar{1}$
a/Å	25.31(5)	9.801(8)
b/Å	5.842(4)	23.71(2)
c/Å	32.67(6)	8.677(4)
α/°	90.0	102.57(1)
β/°	97.94(9)	124.42(4)
γ/°	90.0	90.19(6)
V/Å^3	4784(11)	1603(2)
Z	4	2
D_{calc}/g cm^{-3}	1.779	2.071
λ/Å	0.71070	0.71070
T/K	298	200
$R^{a)}$	0.069	0.099
$R_w^{b)}$	0.084	0.111
Reflections used	1943	2763

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, b) $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

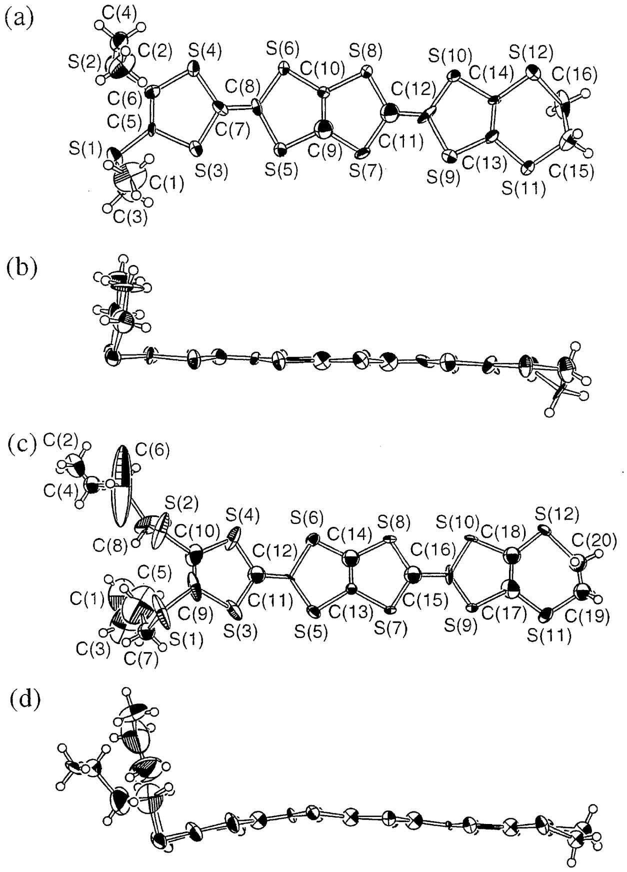


Fig. 2. (a) ORTEP drawing and atomic numbering scheme and (b) side view of the donor molecule of $(C_2\text{TET-TTP})_2ClO_4$. (c) ORTEP drawing and atomic numbering scheme and (d) side view of the donor molecule of $(C_4\text{TET-TTP})I_3$.

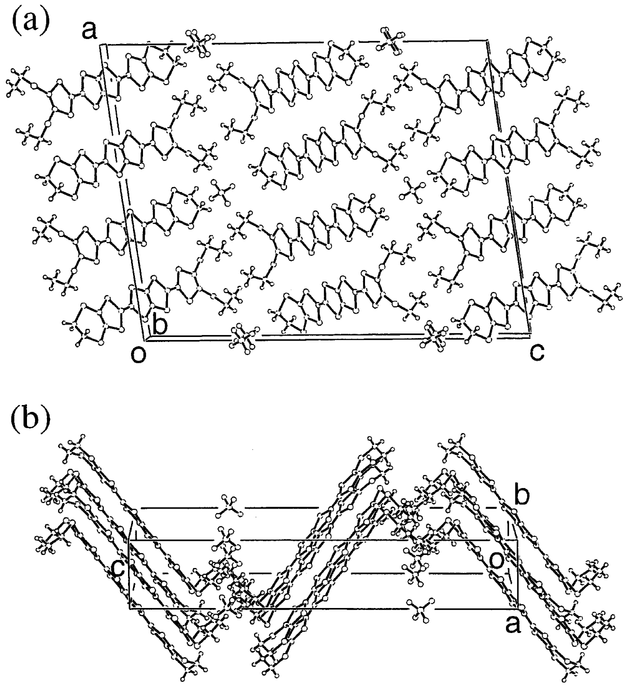


Fig. 3. Crystal structure of (C$_2$TET-TTP)$_2$ClO$_4$, (a) projected along the b axis and (b) projected along the molecular short axis.

general position and one ClO$_4$ anion on a two-fold axis. In consequence the composition is 2:1. As shown in Fig. 2(b), the TTP moiety of (C$_2$TET-TTP)$_2$ClO$_4$ is almost flat, and the ethylthio chains extend nearly perpendicular to the TTP skeleton. This is usual for quarter-filled donors.[11] The donors form conducting sheets along the *ab* plane, and the anions, separating each conducting sheet, are located in pockets surrounded by the ethylthio chains and the ethylenedithio rings. The donors form a uniform chain along the *b* axis; all interactions (designated b in Fig. 4) in a chain are equivalent. This is also obvious from the short lattice constant (b = 5.842 Å) along the chain axis. In this chain the donors are stacked in a head-to-head manner (Fig. 5(a)). The overlap mode is the so-called ring-over-bond type; the interplane distance is 3.47 Å and the slip distance along the donor long axis is 4.72 Å. As shown in Fig. 3(a), the donors in the neighboring chains are arranged in a head-to-tail manner.

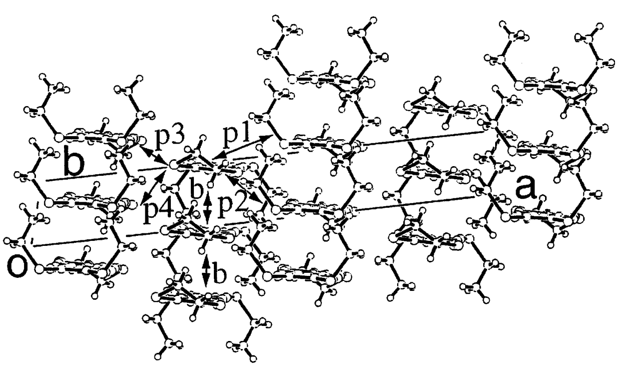


Fig. 4. Donor arrangement of (C$_2$TET-TTP)$_2$ClO$_4$. The overlap integrals are b = −20.2, $p1$ = 7.0, $p2$ = 2.1, $p3$ = −0.9, and $p4$ = 9.6 × 10^{-3}.

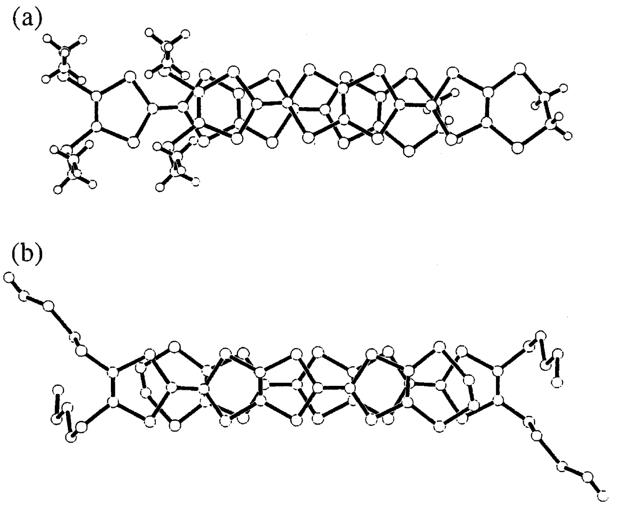


Fig. 5. Overlap mode of (a) (C$_2$TET-TTP)$_2$ClO$_4$ and (b) (C$_4$TET-TTP)I$_3$.

In the case of the methylthio analog, TMET-TTP, the charge-transfer complexes with AuI$_2^-$, PF$_6^-$, ReO$_4^-$, IO$_4^-$, and ClO$_4^-$ are semiconductive below 200 K.[9] The compositions are nearly 4:1, and the array of the donors is θ-type.[14] On the contrary, the present salt, (C$_2$TET-TTP)$_2$ClO$_4$, has β-type structure.[15] Therefore, the replacement of the methylthio groups by the ethylthio groups results not only in increasing the ratio of anions, but also in changing the donor arrangement. In general, β-type BEDT-TTF salts have strong dimerization, but the present salt has uniform stacks. From this viewpoint, the present structure bears a close resemblance to (BETS)$_2$-(Cl$_2$TCNQ),[16] which is a superconductor below 1.3 ± 0.3 K (3.5 kbar).

As the donor chains of (C$_2$TET-TTP)$_2$ClO$_4$ interact each other by shorter S···S contacts than the sum of the van der Waals radii (3.70 Å), the electronic structure is two-dimensional. The overlap integrals calculated from the overlap of HOMO are b = –20.2, $p1$ = 7.0, $p2$ = 2.1, $p3$ = –0.9, and $p4$ = 9.6 × 10^{-3} (Fig. 4). The interchain overlaps (the p interactions) are about half of the intrachain overlap (the b interaction), indicating the two-dimensionality. As shown in Fig. 6, the Fermi surface based on the tight-binding band structure calculated by using these over-

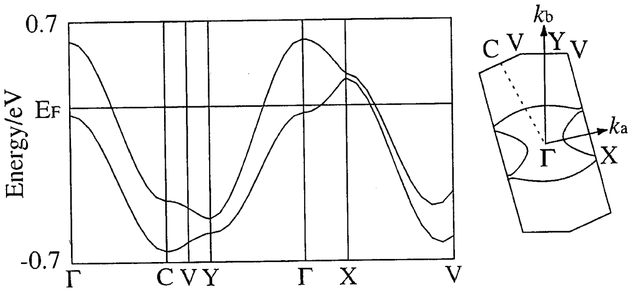


Fig. 6. Energy band structure and Fermi surface of (C$_2$TET-TTP)$_2$ClO$_4$.

lap integrals has an elliptic shape.

(C_4TET-TTP)I_3 displays a quite different structure compared to (C_2TET-TTP)$_2$$ClO_4$. One crystallographically independent donor molecule and one I_3 molecule are located on general positions, so the composition is 1 : 1 and the donor has +1 charge. In this structure, the TTP moiety of **1c** is almost flat, and the butylthio chains are standing (Fig. 2d). These out-of-plane terminal chains are rather an exception for a donor maintaining a charge of +1;[11] this is probably due to the steric hindrance of the butylthio chains.

As shown in Fig. 7, this salt has a dimeric structure. The overlap mode in the dimer of (C_4TET-TTP)I_3 is the so-called ring-over-bond type; the interplana distance is 3.35 Å and the slip distance along the donor long axis is 3.81 Å (Fig. 5b). The interplanar distance and slip distance are shorter than that of the uniform stack of (C_2TET-TTP)$_2$$ClO_4$. This indicates that the intradimer interaction of (C_4TET-TTP)I_3 becomes far stronger. The dimeric pairs are separated by I_3 anions; this causes the semiconductive property of this complex, and a uniform stacking structure is broken. Overlap integrals of HOMO depicted in Fig. 8 are calculated to be $c = -16.6$, $p1 = -0.6$, and $p2 = 0.03 \times 10^{-3}$. Compared with the intradimer overlap (the c interactions), the interdimer overlaps are very small. As a consequence, the energy band calculated from these overlaps is a band insulator. The activation energy (E_a) estimated from the energy band is 0.30 eV, which is in the same order as that determined by temperature dependence of the resistivity (0.23 eV). Although full structure analysis of (C_3TET-TTP)I_3 has not been successful, similar lattice constants suggest that (C_3TET-TTP)I_3 has a similar dimeric structure.

Since it is relatively difficult in TTP-series donors to obtain good crystals suitable for structure analysis, the number of crystals whose structure analyses have been successful is small. Nonetheless TTP-series donors have strong tendency to realize the same donor arrangement irrespective of the counter anions, as all TMET-TTP salts take the θ-type arrangement. Then the two examples reported here represent well the effect of alkyl chain substitution.

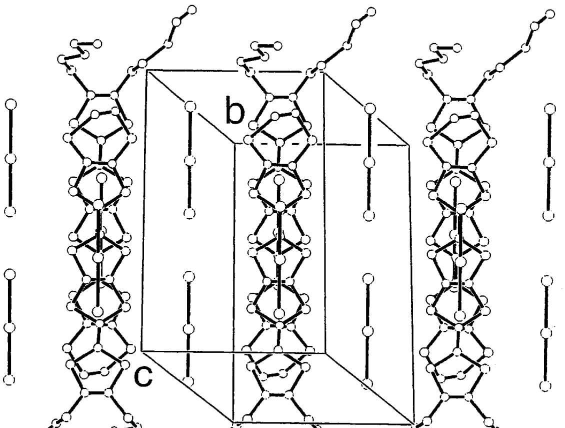


Fig. 7. Crystal structure of (C_4TET-TTP)I_3, projected in the stacking direction.

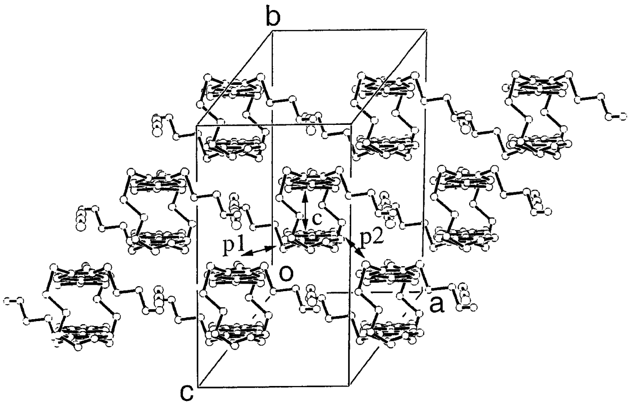


Fig. 8. Donor arrangement of (C_4TET-TTP)I_3. The overlap integrals are $c = -16.6$, $p1 = -0.6$, and $p2 = 0.03 \times 10^{-3}$.

In the first place, with increasing the carbon number, the anion content increases from 4 : 1 for TMET-TTP,[9] to 2 : 1 for C_2TET-TTP, to 1 : 1 for C_3TET-TTP and C_4TET-TTP. This is interpreted as an increase of the free space available for anions surrounded by the alkyl chains. This rightly follows our first expectation, and the substitution with longer alkyl chains is concluded to be a powerful strategy to increase the anion content.

In the second place, the donor arrangement changes from θ-type in TMET-TTP, to β-type uniform stack in C_2TET-TTP, and to dimeric in C_3TET-TTP and C_4TET-TTP. This is attributed to the increasing tendency to face-to-face overlap. The θ-type arrangement is composed of ring-over-atom overlap, so-called in Ref. 14, where the donors are slid not only along the molecular long axis in a usual manner, but along the molecular short axis. This kind of overlap is preferred by such organic donors as BO (bis(ethylenedioxy)tetrathiafulvalene), and is regarded as having the least tendency to form a stacked (or dimerized) structure (see Fig. 17 in Ref. 14). This is mediated in C_2TET-TTP, which results in uniform chains; the tendency to the face-to-face overlap is moderate; it realizes usual stacks, but no dimerization is introduced. If the tendency to form strong face-to-face overlaps is further increased, the donors construct an independent dimer structure like C_3TET-TTP and C_4TET-TTP. Therefore the structure change from θ-type to β-type and then to dimeric is considered to be the consequence of an increasing preference for the face-to-face overlap.

In BEDT-TTF, the flexibility of the ethylenedithio parts plays an important role in realizing the variety of donor arrangements. In TTP-series donors, the rigid core skeleton is expanded, so that two ethylene parts (or similarly four flexible carbon atoms as in TMET-TTP) seem to be insufficient to afford the flexible anion space. The present study suggests that six carbon atoms like C_2TET-TTP seem to be appropriate in TTP donors, but more than eight atoms in C_3TET-TTP bring about too strong dimerization. It should be noted that in TTF-series donors even TTC_2-TTF (tetrakis(ethylthio)tetrathiafulvalene) leads to exceeding dimerization.[17] Although the structure changes too sensitively as a function of the carbon number, the substitution of longer alkyl chains seems to be a powerful tool to control the anion content and preference for the stacking structure.

Experimental

General Data. THF was freshly distilled under argon over sodium and benzophenone. Trimethyl phosphite was distilled under argon by fractional distillation. Methanol was distilled under argon over magnesium. Acetone was used after the storage over 4A molecular sieves. Melting points were determined with a Yanaco MP micro melting point apparatus. NMR spectra were obtained with a JEOL JNM-AL300 spectrometer and ESR spectra were taken with a JEOL JES-TE100 spectrometer. CV spectra were measured on a Yanaco VMA-010 spectrometer. Microanalyses were performed at Microanalytical Laboratory, Tokyo Institute of Technology. IR spectra were recorded on a SHIMADZU FTIR-8000 spectrometer, and mass spectra on a SHIMADZU QP-5000 spectrometer.

4,5-Bis(ethylthio)-1,3-dithiole-2-thione (3a). To a suspension of sodium methoxide (1.06 g, 19.6 mmol) in methanol (12 cm^3), 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (1.98 g, 4.86 mmol) was added; the mixture was stirred under argon for 30 min at room temperature. The reaction mixture was treated with ethyl bromide (2 ml, 26.8 mmol) and stirred for 2 h. After the solvent was evaporated in vacuo the residue was suspended in carbon disulfide and filtered through Celite. The organic solvent was evaporated in vacuo to yield a red oil, which was purified by column chromatography (silica gel/CS$_2$) to afford **3a** (835 mg, 67.3%) as a red oil. ^{1}H NMR (CDCl$_3$) δ 1.36 (6H, t, J = 7.3 Hz), 2.91 (4H, q, J = 7.3 Hz); ^{13}C NMR (CDCl$_3$) δ 14.9, 30.9, 136, 211; Anal. Calcd for $C_7H_{10}S_5$: C, 33.04; H, 3.96; S, 63.00%. Found: C, 33.12; H, 3.99; S, 63.90%; MS *m*/*z* 254 (M$^+$). Compounds **3b** and **3c** were prepared similarly.

4,5-Bis(propylthio)-1,3-dithiole-2-thione (3b). 70.1% yield; red oil; ^{1}H NMR(CDCl$_3$) δ 1.04 (6H, t, J = 7.4 Hz), 1.70 (4H, dd, J = 7.2, 7.4 Hz), 2.86 (4H, t, J = 7.2 Hz); ^{13}C NMR (CDCl$_3$) δ 13.1, 23.0, 38.6, 136, 211; Anal. Calcd for $C_9H_{14}S_5$: C, 38.26; H, 4.99; S, 56.74%. Found: C, 38.38; H, 4.83; S, 57.21%; MS *m*/*z* 282 (M$^+$).

4,5-Bis(butylthio)-1,3-dithiole-2-thione (3c). 83.5% yield; red oil; ^{1}H NMR (CDCl$_3$) δ 0.93 (6H, t, J = 7.2 Hz), 1.44 (4H, m, J = 7.2, 7.0 Hz), 1.64 (4H, m, J = 7.0, 7.4 Hz), 2.88 (4H, t, J = 7.2 Hz); ^{13}C NMR (CDCl$_3$) δ 13.5, 21.7, 31.6, 36.4, 136, 211; Anal. Calcd for $C_{11}H_{18}S_5 \cdot CS_2$: C, 37.26; H, 4.69; S, 58.04%. Found: C, 37.68; H, 4.76; S, 54.96%; MS *m*/*z* 310 (M$^+$).

C$_2$TET-TTP (1a). Compound **4** (354 mg, 0.919 mmol) and **3a** (661 mg, 2.60 mmol) in toluene (16 cm^3) were refluxed with a large excess of trimethyl phosphite (16 cm^3) under argon for 2 h. The mixture was cooled to room temperature and the resulting precipitate was filtered and washed with small portions of methanol and hexane. The solid was purified by column chromatography (silica gel/CS$_2$) to afford **1a** (101 mg, 18.6%) as an orange solid. mp 193 °C; IR (KBr) 2961, 2923, 2365, 1730, 1516, 1377, 1283, 1125, 1073, 961, 884, 766 cm^{-1}; ^{1}H NMR (CS$_2$–CDCl$_3$) δ 1.31 (6H, t, J = 7.4 Hz), 2.84 (4H, q, J = 7.4 Hz), 3.29 (4H, s); Anal. Calcd for $C_{16}H_{14}S_{12} \cdot 0.3\ CS_2$: C, 31.89; H, 2.30; S, 65.82%. Found: C, 31.89; H, 2.10; S, 66.08%. Compounds **1b** and **1c** were prepared similarly

C$_3$TET-TTP (1b). 17.0% yield; mp 181 °C; IR (KBr) 2957, 2924, 2363, 1456, 1416, 1377, 1235, 959, 889, 767 cm^{-1}; ^{1}H NMR (CS$_2$–CDCl$_3$) δ 1.02 (6H, t, J = 7.4), 1.64 (4H, m, J = 7.1, 7.4 Hz), 2.76 (4H, t, J = 7.1), 3.28 (4H, s); Anal. Calcd for $C_{18}H_{18}S_{12}$: C, 34.92; H, 2.93; S, 62.15%. Found: C, 34.64; H, 2.80; S, 62.60%.

C$_4$TET-TTP (1c). 9.98% yield; mp 173 °C; IR (KBr) 2958, 2923, 2363, 1455, 1379, 1281, 965, 885, 766 cm^{-1}; ^{1}H NMR (CS$_2$–CDCl$_3$) δ 0.93 (6H, t, J = 7.4 Hz), 1.42 (4H, m, J = 6.7, 7.4 Hz), 1.59 (4H, m, J = 6.7, 7.2 Hz), 2.77 (4H, t, J = 7.2), 3.28 (4H, s); Anal. Calcd for $C_{20}H_{22}S_{12}$: C, 37.12; H, 3.43; S, 59.45%. Found: C, 37.03; H, 3.21; S, 59.20%.

X-ray Diffractional Analysis. Crystal data: Intensity data were collected by a Rigaku Raxis II area detector with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71070 Å). The crystal structures were solved by the direct method, SHELX86.[18] The structures were refined by the full-matrix least-squares refinement. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC 150512 and 150513. The data are also deposited as Document No. 74002 at the Office of the Editor of Bull. Chem. Soc. Japan.

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