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# Stereochemically ordered donor columns in an organic conductor, $(Et_2BEDT\text{-}TTP)_2HgI_3$

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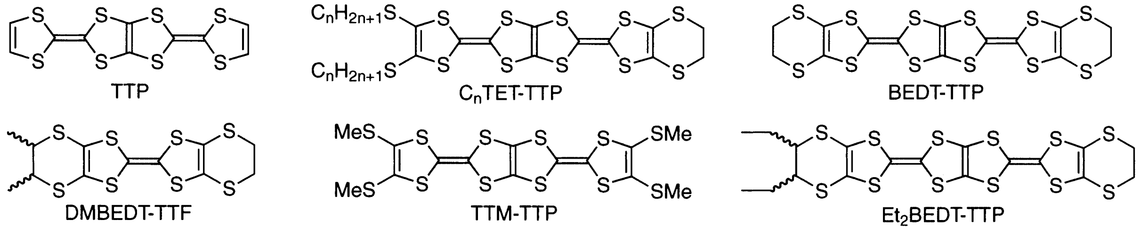
**Abstract**—A new diethyl-substituted organic donor, $Et_2$BEDT-TTP, has been synthesized. The radical-cation salt, $(Et_2BEDT\text{-}TTP)_2HgI_3$ has a unique crystal structure where the stereochemical *cis*- and *trans*-isomers are arranged regularly to make tetramerized columns. © 2001 Elsevier Science Ltd. All rights reserved.

Radical-cation salts of tetrathiapentalene (TTP, Scheme 1) based donors have been drawing considerable attention due to their stability of metal-like conductivity down to low temperatures.[1] Among them, we have reported alkylsubstituted TTP donors, $C_n$TET-TTP ($n=2$–4, Scheme 1), showing good solubility in organic solvents.[2] In particular, charge-transfer complexes of ethylthio-substituted donor, $(C_2TET\text{-}TTP)_2X$ ($X=BF_4$, $ClO_4$), have β-type uniform stacking structures and are metallic down to helium temperatures. From these results, we have concluded that the incorporation of $C_2$-alkyl chains is a promising strategy to improve solubility together with maintaining metallic stacking structures. A TTP analog of BEDT-TTF, BED-TTTP (Scheme 1) is an attractive donor, but very few charge-transfer complexes have been obtained due to its poor solubility.[3] Thus, we have chosen $C_2$-alkyl substituted BEDT-TTP as a synthetic target. Kini and co-workers have synthesized diethyl-substituted BEDT-TTF,[4] but they have reported only the *trans*-form. The molecular size of diethyl-substituted BEDT-TTP derivatives seems to be twice as large as DMBEDT-TTF (dimethyl-BEDT-TTF, Scheme 1), a *trans*-form of which is known to give a superconducting salt ((*S*,*S*)-DM-BEDT-$TTF)_2ClO_4$ ($T_c=3$ K, 5 kbar).[5]

This communication reports synthesis of a new type of diethyl-substituted BEDT-TTP ($Et_2$BEDT-TTP, Scheme 1) as well as crystal structure and physical properties of its salt $(Et_2BEDT\text{-}TTP)_2HgI_3$. For the sake of comparison, we present structural and physical properties of (TTM-TTP)$HgI_3$(TCE) (TTM-TTP: tetrakis(methylthio)-TTP, Scheme 1, TCE: 1,1,2-trichloroethane).

There are two possible stereoisomers of $Et_2$BEDT-TTP: *cis*- and *trans*-forms depending on the manner of substitution of the two ethyl chains. In order to prepare *cis*- and *trans*-$Et_2$BEDT-TTP separately, the synthesis was carried out according to Scheme 2.[6] Starting from commercially available *trans*-3-hexene (100% *trans*-



**Scheme 1.** Organic donors.

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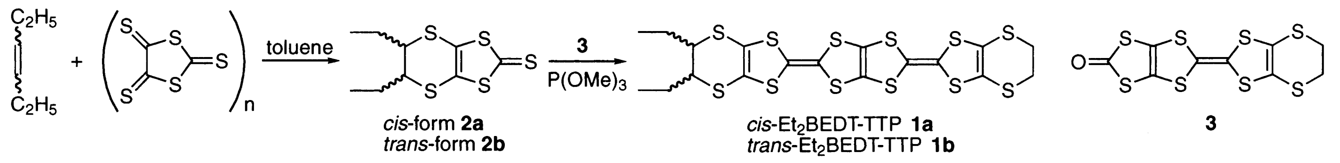


**Scheme 2.** The synthesis of $Et_2$BEDT-TTP.

form), we prepared stereochemically pure *trans*-form **2b**[4] by Diels–Alder reaction with oligomeric 4,5-dihydro-1,3-dithiole-2,4,5-trithione.[7] However, the Diels–Alder reaction, starting from commercially available *cis*-3-hexene (containing 4% *trans*-isomer) gave stereochemically mixed thione (23% yield, **2a**:**2b** = 85:15 according to the NMR spectra). The trimethylphosphite-mediated cross-coupling reaction between **2b** and 5-(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalen-2-one **3** afforded stereochemically pure *trans*-$Et_2$BEDT-TTP **1b** (25% yield). The same reaction between **1** and **3** gave a mixture of $Et_2$BEDT-TTP (20% yield, **1a**:**1b** = 85:15 according to the NMR spectra). These diastereomers can be distinguished easily by the chemical shifts of the methine protons; the signals of the *cis*- or *trans*-thione **2** located at 3.51 and 3.10 ppm, and those of $Et_2$BEDT-TTP at 3.39 and 2.99 ppm, respectively. The separation of the pure *cis*-isomer was neither successful for the thiones **2** nor donors **1** due to the near $R_f$ values, so the mixture of the donor **1a**+**1b** was used without further purification. It should be remarked that the *cis*-isomers are *meso*-type compounds, whereas the *trans*-isomers are racemic mixtures of *R*,*R* and *S*,*S* enantiomers. The cyclic voltammetry of the new donors **1** (versus Ag/AgCl in $Bu_4NPF_6$/PhCN) exhibited four reversible waves: $E_1 = 0.50$, $E_2 = 0.68$, $E_3 = 0.90$, $E_4 = 1.06$, and $E_2 - E_1 = 0.18$ V for the mixed-form (**1a**:**1b** = 85:15), and $E_1 = 0.48$, $E_2 = 0.66$, $E_3 = 0.88$, $E_4 = 1.13$, and $E_2 - E_1 = 0.18$ V for the *trans*-form.

Electrochemical crystallization of TTM-TTP and mixed-$Et_2$BEDT-TTP (**1a**:**1b** = 85:15) in 1,1,2-trichloroethane (TCE) or THF in the presence of a tetrabutyl-ammonium salt of $HgI_3^-$ gave black needle crystals or black plate crystals, respectively. The donor:acceptor ratios were determined to be 1:1 for the salt of TTM-TTP and 2:1 for $Et_2$BEDT-TTP by X-ray analysis.[8] Fig. 1 shows the crystal structure of (TTM-TTP)$HgI_3$(TCE). The donors form a one-dimensional column along the *c* axis. The anions form a dimeric unit $Hg_2I_6^{2-}$ with two bridging iodine atoms, the center of which locates on an inversion center. This type of square-shaped $Hg_2X_6^{2-}$ anion can be seen in (BEDT-TTF)$_4Hg_2Br_6$(TCE)[9] and (BEDT-TTF)$_4Hg_2I_6(I_8)$.[10] As shown in Fig. 2, two intrachain overlap modes are characterized by the slip along the molecular long axis, $D = 1.5$ Å for c1 and 4.4 Å for c2. The column structure is basically the same as (TTM-TTP)$AuI_2$ and (TTM-TTP)$AuBr_2$,[11] though these crystals are not strictly isostructural to the present salt owing to the different anion part. The TTP moiety is almost flat and four methylthio groups are on the TTP plane, in agreement with a TTP molecule with +1 charge.[12]

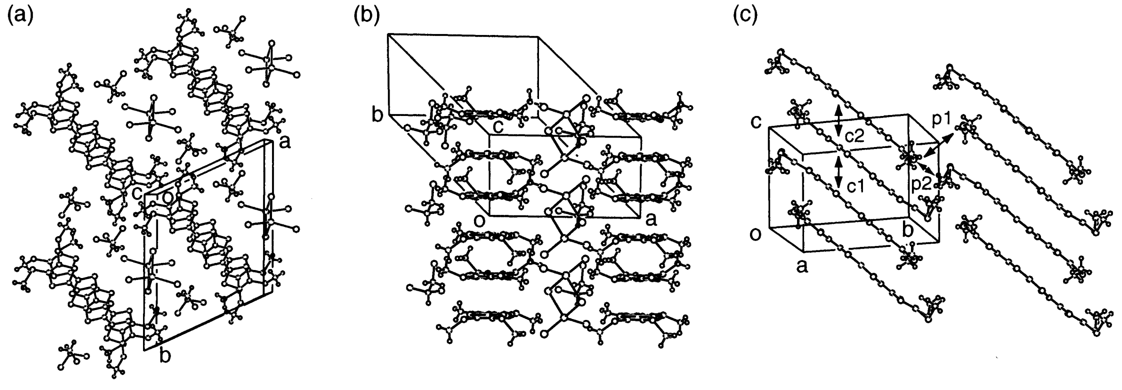


**Figure 1.** Crystal structure of (TTM-TTP)$HgI_3$(TCE) projected: (a) along the *c*-axis and (b) along the molecular long axis. (c) intermolecular overlaps in (TTM-TTP)$HgI_3$(TCE).

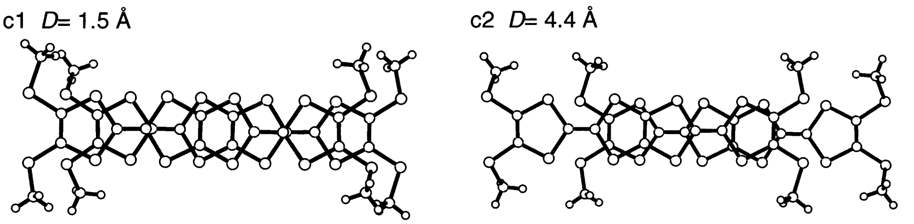


**Figure 2.** Overlap modes of (TTM-TTP)$HgI_3$(TCE).

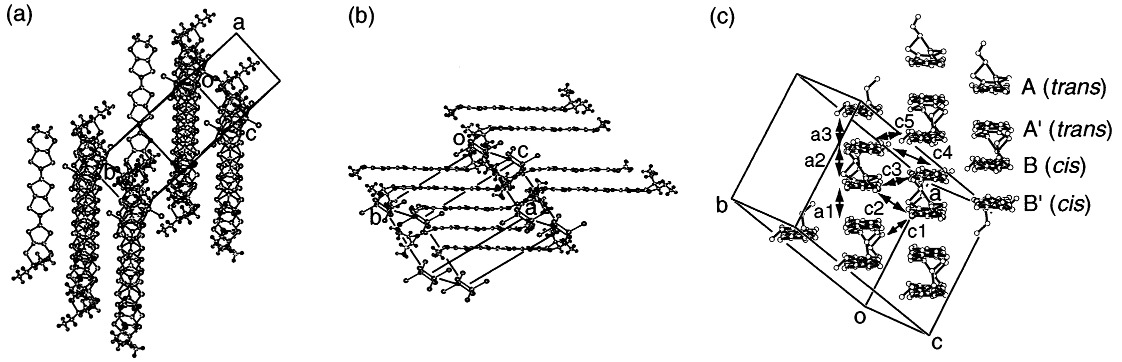
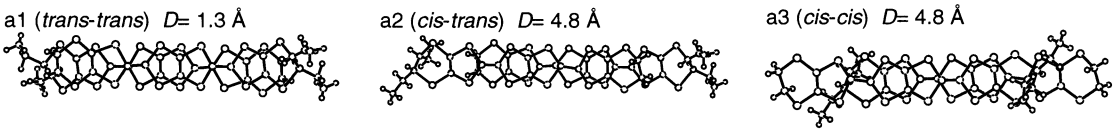


**Figure 3.** Crystal structure of $(Et_2BEDT\text{-}TTP)_2HgI_3$ projected: (a) in the stacking direction and (b) along the molecular short axis. (c) intermolecular overlaps in $(Et_2BEDT\text{-}TTP)_2HgI_3$.


a1 (*trans-trans*) $D$= 1.3 Å

a2 (*cis-trans*) $D$= 4.8 Å

a3 (*cis-cis*) $D$= 4.8 Å

**Figure 4.** Overlap modes of $(Et_2BEDT\text{-}TTP)_2HgI_3$.

The crystal structure of $(Et_2BEDT\text{-}TTP)_2HgI_3$ obtained from the mixed donor is shown in Fig. 3. Similarly to (TTM-TTP)$HgI_3$(TCE), the anions form a dimeric unit, $Hg_2I_6^{2-}$. In the stacks along the *a* axis, the donors form tetramers. At the center of the tetramer, an inversion center locates so that the donors are arranged as -*trans*(A)–*trans*(A′)–*cis*(B)–*cis*(B′)-, where a pair of two *trans*-isomers consist of a racemic couple. In this structure, the columns contain no disorder of the ethyl chains, so the content of the *trans*-form is 50%. When the 1:1 mixture of **1a** and **1b** was used in the electrocrystallization, the same crystal is obtained. On the other hand, the pure *trans*-product **1b** gave no crystal with $HgI_3$, indicating that the electrochemical oxidation does not change the stereochemistry. The ethyl chains are arranged alternately on the opposite ends of the donors in the column. These ethyl chains extend to the same side of the molecular planes even in the *trans*-donors as well as the *cis*-donors, and are oriented toward the *cis*–*trans* overlaps. The TTP skeleton of the *cis*-form is almost flat, but that of the *trans*-form is somewhat curved. This suggests charge separation, where the *cis*-form is more cationic than the *trans*-form. To confirm this, the comparison of the length of the ylidene double bonds in the TTP skeleton was attempted, but a clear difference was not detected owning to the limitation of the accuracy of the X-ray analysis. Fig. 4 shows three intrachain overlap modes; the slips along the molecular long axis are $D=1.3$ Å for a1 (*trans*–*trans*), 4.8 Å for a2 (*cis*–*trans*), and 4.8 Å for a3 (*cis*–*cis*). According to Ref. 13, this column structure is classified as $\beta_{43}$-type, in which three of the four overlap modes within the tetrameric periodicity have large $D$ values. This resembles but is different from the well-known $\lambda(\beta_{42})$-type structure.[14] This contrasts with (TTM-TTP)$HgI_3$(TCE) and $\beta$-$(BEDT\text{-}TTP)_2I_3$, which have simple dimeric ($\beta_{21}$) structures. The tetrameric structure of $(Et_2BEDT\text{-}TTP)_2HgI_3$ seems to be associated with the stereochemically ordered packing of the ethyl chains.

The room temperature conductivities of (TTM-TTP)$HgI_3$(TCE) and $(Et_2BEDT\text{-}TTP)_2HgI_3$ are about 5 and 2 S $cm^{-1}$, respectively. Both salts show semiconductive behavior; the activation energies are estimated to be 0.04 and 0.05 eV, respectively.

The overlap integrals calculated from the overlap of HOMO are $c1=24.4$, $c2=16.6$, $p1=0.05$ and $p2=0.03\times10^{-3}$ for (TTM-TTP)$HgI_3$(TCE), and $a1=17.2$, $a2=20.7$, $a3=16.1$, $c1=2.22$, $c2=-3.68$, $c3=-3.61$, $c4=-5.40$, and $c5=-0.24\times10^{-3}$ for $(Et_2BEDT\text{-}TTP)_2HgI_3$ (Figs. 1(c) and 3(c)). (TTM-TTP)$HgI_3$(TCE) is a 1:1 complex with strong dimerization, resulting in a band insulator. Similarly to other TTM-TTP salts, this salt is highly one-dimensional. $(Et_2BEDT\text{-}TTP)_2HgI_3$ has larger side-by-side interactions, but the Fermi energy lies between energy bands, so that it has no Fermi surface and is a band insulator. The energy gap is associated with the tetramerization in the donor stacks and the comparatively weak interchain interactions.

Other radical-cation salts of $Et_2BEDT$-TTP are currently under investigation in connection with packing patterns of stereochemically different donors.

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6. Mixed-Et$_2$BEDT-TTP: red solid; **1a**:**1b** = 85:15; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.09 (6H, t, $J$ = 7.4 Hz), 1.68 (4H, m), 2.99 (0.3H, m), 3.28 (4H, s), 3.39 (1.7H, m) ppm; anal. calcd for $C_{18}H_{16}S_{12}$: C, 35.04; H, 2.61; S, 62.35. Found: C, 35.18; H, 2.51; S, 62.45%.

   **1b**: red solid; mp 228–229°C (decomp.); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.05 (6H, t, $J$ = 7.4 Hz), 1.73 (4H, m), 2.99 (2H, m), 3.28 (4H, s) ppm; anal. calcd for $C_{18}H_{16}S_{12}$: C, 35.04; H, 2.61; S, 62.35. Found: C, 34.74; H, 2.44; S, 63.50%.

   Mixed-thione: dark-purple gummy-solid; **2a**:**2b** = 85:15; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.11 (6H, t, $J$ = 7.4 Hz), 1.74 (4H, m), 3.10 (0.3H, m), 3.51 (1.7H, m); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 11.9, 24.1, 49.1, 49.4, 121, 208 ppm; anal. calcd for $C_9H_{12}S_5$: C, 38.54; H, 4.31; S, 57.15. Found: C, 38.80; H, 4.02; S, 57.42%; MS $m/z$ 280 (M$^+$).
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8. Crystal data of (TTM-TTP)HgI$_3$(TCE): $C_{16}H_{15}S_{12}Cl_3I_3Hg$, $M$ = 1279.7, triclinic, space group $P$-1, $a$ = 13.328(8), $b$ = 15.835(4), $c$ = 9.148(2) Å, $\alpha$ = 87.89(2), $\beta$ = 98.33(3), $\gamma$ = 115.35(3)°, $V$ = 1726(1) Å$^3$, $Z$ = 2, $D_c$ = 2.463 g/cm$^3$, Mo K$\alpha$ radiation, $\lambda$ = 0.71070 Å, $\mu$ = 81.25 cm$^{-1}$, $F$(000) = 1186.00. The data were collected on a Rigaku Raxis II imaging plate area detector with graphite monochromated Mo K$\alpha$ radiation. The structure was solved by the direct method and refined by full-matrix least-squares analysis (anisotropic for non-hydrogen atoms) to $R$ = 0.057, $R_w$ = 0.063 for 3086 observed ($I$>5$\sigma$($I$)) reflections from 6167 data.

   (Et$_2$BEDT-TTP)$_2$HgI$_3$: $C_{36}H_{32}S_{24}I_3Hg$, $M$ = 1815.4, triclinic, space group $P$-1, $a$ = 14.797(4), $b$ = 21.253(7), $c$ = 9.152(4) Å, $\alpha$ = 97.43(3), $\beta$ = 103.04(2), $\gamma$ = 95.75(3)°, $V$ = 2755(2) Å$^3$, $Z$ = 2, $D_c$ = 2.188 g/cm$^3$ Mo K$\alpha$ radiation, $\lambda$ = 0.71070 Å, $\mu$ = 108.44 cm$^{-1}$, $F$(000) = 3484.00. The data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo K$\alpha$ radiation and a rotating anode generator using the $\omega$ scan technique to a maximum 2$\theta$ of 60°. The structure was solved by the direct method and refined by full-matrix least-squares analysis (anisotropic for non-hydrogen atoms) to $R$ = 0.072, $R_w$ = 0.084 for 2065 observed ($I$>3$\sigma$($I$)) reflections from 12732 unique data. All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center.
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