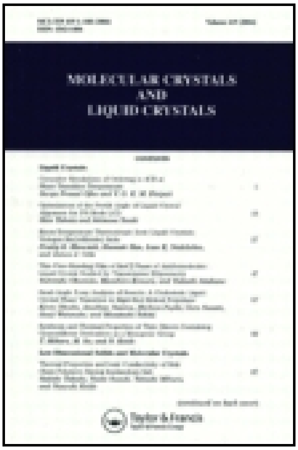

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A Vinylog of Bis-Fused TTF: Novel π-Electron Framework for Metallic and Superconducting Organic Solids

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A VINYLOG OF BIS-FUSED TTF: NOVEL π-ELECTRON FRAMEWORK FOR METALLIC AND SUPERCONDUCTING ORGANIC SOLIDS

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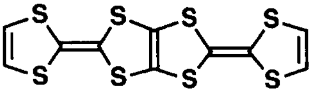
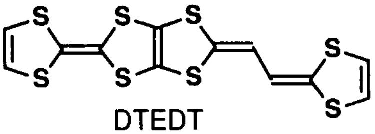
Abstract The first vinylog of bis-fused tetrathiafulvalene (DTEDT) has been synthesized as a new donor component for organic conductors. Many cation radical salts of DTEDT showed metallic conducting behavior down to liquid helium temperature regardless of counter anions. Further, $(DTEDT)_3Au(CN)_2$ exhibited superconducting transition at 4 K under ambient pressure. X-Ray crystal structure analysis of $(DTEDT)_3Au(CN)_2$ reveals that this salt has a "uniform β-type" arrangement of donor molecules in the conducting sheet. The band calculation indicates it has a closed Fermi surface.

INTRODUCTION

In the past two decades, considerable attentions have been focused on organic superconductors.[1] Although more than fifty kinds of organic superconductors have been prepared so far, only three kinds of π-electron frameworks are known as conducting components, namely, tetrathiafulvalene (TTF) derivatives[1,2] $M(dmit)_2$ (M = Ni, Pd), where dmit is 4,5-dimercapto-1,3-dithiole-2-thione,[1,3] and C_{60}.[4] In this context, the development of new class of π-electron frameworks producing organic superconductors has been desirable. In order to stabilize metallic state down to low temperature and eventually to cause superconducting transition, realization of two-dimensional (2D) electronic structure has been regarded as the most available strategy, which has been usually attained by substitution of "capped" dichalcogeno groups on TTF represented as BEDT-TTF.[1,2] Recently we have developed bis-fused TTF donors, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalenes (BDT-TTPs),[5,6] and found that BDT-TTP tends to produce 2D metals without introduction of such substituents.[6] In this connection, investigation on bis-fused 1,3-dithiole donors other than BDT-TTP is of particular interest in elucidation of scope and limitation of utilizing bis-fused donors for development of 2D metals. In particular, current attention on extended TTFs[7] encouraged us to develop extended BDT-TTP, in other words, bis-fused donors containing extended TTF moieties. Firstly we noted a TTF vinylog, 2,2'-ethanediylidenebis(1,3-dithiole) (**1**)[8] which is the most simply extended TTF analog. In the present proceedings, we report the synthesis and properties of the first vinylogous BDT-TTP, 2-(1,3-dithiol-2-ylidene)-5-(2-ethanediylidene-1,3-dithiole)-1,3,4,6-tetrathiapentalene (DTEDT) in which one molecule of **1** is involved. In the course of this study, we have found that its $Au(CN)_2$ salt, $(DTEDT)_3Au(CN)_2$ shows superconductivity.[9] We also describe its structures and physical properties.

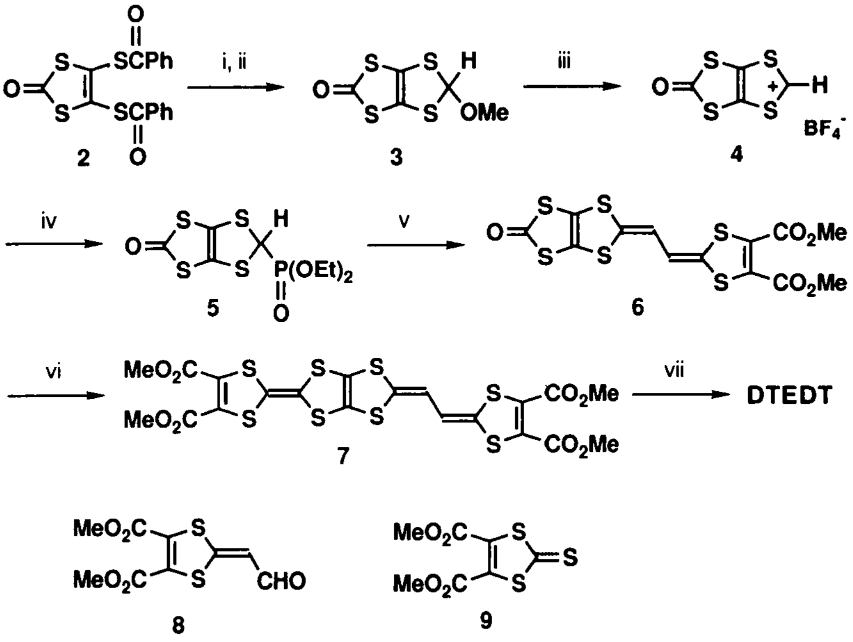

BDT-TTP


DTEDT

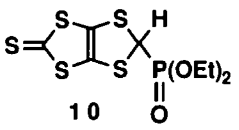
RESULTS AND DISCUSSION

Synthesis and Characterization of DTEDT

Construction of DTEDT skeleton has been achived by two sequential introductions of outer 1,3-dithiole rings to the central tetrathiapentalene moiety by application of well established unsymmetrical synthetic strategies for both TTF and vinylogous TTF (Scheme I). The compound **5** is an important precursor considering the other materials for introduction of the outer 1,3-dithioles (**8** and **9**) can be commercially available, or easily prepared according to literature.[8] The key reaction for the synthesis of **5** is basic cleavage of benzoylthio groups of **2** followed by treatment of α,α-dichloromethyl methyl ether, and the resultant product **3** can be easily converted to **5** by way of a 1,3-dithiolium salt **4**, using well-known procedures. Because **5** is slightly unstable, we have also examined to use the thione analog of **5** (**10**) which has been already developed in our laboratory.[10] In this case, however, the resultant vinylogous TTF fused with 1,3-dithiole-2-thione (**11**) could not be converted to **6** by use of mercury(II) acetate owing to low solubility of both **11** and **6** in the solvents used for the reaction. The synthetic route shown in Scheme I can be also applicable to the preparation of various DTEDT derivatives and its selenium analogues.[11]



SCHEME I i, NaOMe (2 equiv), CH_2Cl_2-acetone (1:1, v/v), room temp., 40 m; ii, Cl_2CHOMe (2 equiv), acetone, 1 h (52%), iii, 42% aqueous HBF_4 (2 equiv), CH_2Cl_2-acetic anhydride (4:1, v/v), 0 °C, 1 h (92%); iv, $P(OEt)_3$ (2 equiv), NaI (2 equiv), acetone, room temp., 12 h (83%); v, Compound **8** (1 equiv), 0.5 M LDA (1 equiv), THF, -70 °C, 30 m (57%); vi, Compound **9** (2 equiv), $P(OMe)_3$ (100 equiv), toluene, 110 °C, 2 h (70%); vii, LiBr·H_2O (20 equiv), HMPA, 90 °C, 1h, 130 °C, 45 m (88%).



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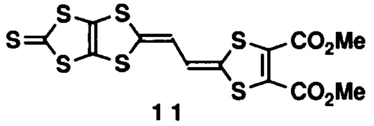

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The cyclic voltammogram of DTEDT exhibits four pairs of single-electron redox waves. Table I summarizes its redox potentials along with the related donors measured under the identical conditions. The E_1 value of DTEDT is lower by 0.07 V than that of BDT-TTP (+0.44 V). However, it is higher by 0.08 V compared with that of **1** (+0.29 V) and is comparable to TTF (+0.35 V), indicating the donor ability becomes rather weaker by fusion of two donor units. This is a common feature in bis-fused donors. On the other hand, E_2-E_1 value (0.13 V) is smaller than those of BDT-TTP (0.18 V), TTF (0.42 V) and **1** (0.20 V), suggesting decrease of on-site Coulomb repulsion in the dication.

Figure 1 shows the highest occupied molecular orbital (HOMO) of DTEDT calculated based on a semiempirical MNDO method. The geometry was fully optimized

TABLE I Redox potentials of DTEDT and its related compounds[a]

Compound	E_1	E_2	E_3	E_4	E_2-E_1
DTEDT	+0.37	+0.50	+0.81	+1.05[b]	0.13
BDT-TTP	+0.44	+0.62	+1.05 [a]	+1.13[b]	0.18
TTF	+0.35	+0.77			0.42
1	+0.29	+0.49			0.20

[a]0.1 M *n*-Bu_4NClO_4 in PhCN, V vs. SCE, Pt electrode, 25 °C. [b]Irreversible step. Anodic peak potentials.

supposing a C_s symmetry. Thus, the HOMO of DTEDT is composed of those of TTF and **1** which are interacted in phase to each other. Namely, π-orbital of sulfur atoms at the terminal of the vinylogous 1,3-dithiole ring in DTEDT are out of phase with those of the other sulfur atoms in HOMO. Considering this result along with the crooked structure of DTEDT, it is anticipated to cause both sterically and electronically less effective transverse intermolecular interaction in the charge-transfer salts than strip-like BDT-TTP in which all sulfur atoms have the same phase.

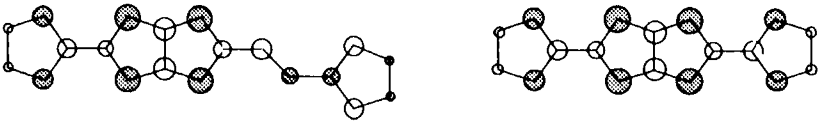


FIGURE 1 The highest occupied molecular orbitals of DTEDT (left) and BDT-TTP (right). The radii of circles are approximately proportional to the LCAO coefficients.

Preparation and Conducting Properties of DTEDT Salts.

Cation radical salts of DTEDT were prepared by electrochemical oxidation in the presence of the corresponding tetra-*n*-butylammonium salts under a constant current of 0.3-1 μA/cm^2 in chlorobenzene or 1,1,2-trichloroethane at 50 °C. The I_3 salt was obtained using the diffusion technique with *n*-Bu_4NI_3 in chlorobenzene at 50 °C. Table II shows their electrical properties measured by four-probe technique on single crystals. DTEDT affords single crystals of various cation radical salts, all of which display very high conductivity of 10^1-10^2 S cm^{-1} at room temperature. It is noteworthy that all the DTEDT salts except TCNQ complex measured on a compressed pellet show metallic conducting behavior down to low temperature (1.4-4.2 K) regardless of both shape and size of counter anions, although resistivity of several salts slightly increase at low temperature. This indicates that DTEDT has a strong tendency to stabilize metallic state in spite of unfavorable molecular and electronic structures.

TABLE II Composition and electrical conductivity of DTEDT salts (DTEDT·A_x).

Anion	Form	x[a]	σ_{rt} / S cm^{-1} [b]	Conducting behavior[c]
TCNQ	–	1.0(Anal.)	8[d]	$E_a = 0.029$ eV
ClO_4	Needle	0.67(Cl)	830	M[e]
BF_4	Flake	– [f]	540	M[e]
ReO_4	Needle	0.39(Re)	900	M down to 1.4 K
$GaCl_4$	Needle	0.48(Ga)	50	M down to 1.4 K
PF_6	Needle	0.39(P)	170	M down to 4.2 K
AsF_6	Needle	0.54(As)	90	M down to 1.4 K
SbF_6	Plate	0.57(Sb), 0.33(X)	80	M down to 1.4 K
TaF_6	Plate	0.48(Ta)[g]	150	M down to 1.4 K
I_3	Flake	0.34(I)	670	M down to 1.4 K
$AuBr_2$	–	0.31(Br)	13[d]	M down to 4.2 K
$Au(CN)_2$	Plate	0.39 (Au), 0.33(X)	15	$T_c = 4$ K[h]

[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 elementary analysis and X-ray structure analysis, respectively. [b] Room temperature conductivity measured by four-probe technique on a single crystal. [c] M designates metallic behavior. [d] Measured on a compressed pellet. [e] The resistivity increases a little at low temperatures, but is essentially metallic down to 1.4 K. [f] The contents of light elements such as B and N were not reliably determined by EDS. [g] Containing a solvent $(PhCl)_{0.3}$. [h] T_c designates critical temperature of superconducting transition.

Physical Properties and Structures of Superconducting $(DTEDT)_3Au(CN)_2$.

Figure 2 shows conducting behavior of the $Au(CN)_2$ salt. The room temperature conductivity (15 S cm^{-1}) is lower by about one order compared to the other metallic DTEDT salts. It shows metallic behavior down to liquid helium temperature, although the temperature dependence is somewhat weak (ρ_{rt}/ρ_{min} = 3–4) and the resistivity slightly increase below ca. 20 K. An abrupt drop of resistivity which characteristic of superconducting transition was observed at onset of 4 K. However, the resistivity gently decreased and remained non-zero even at 2 K probably owing to existence of non-superconducting domains in the crystal. The superconductivity was also confirmed by magnetic susceptibility measurement using a SQUID susceptometer (Figure 3). Both zero-field cooled data (ZFC) and field cooled data (FC) start to decrease at 4 K, therefore the critical temperature (T_c) was determined to be 4 K because it could not be determined from resistivity measurement owing to non-zero resistivity after transition.

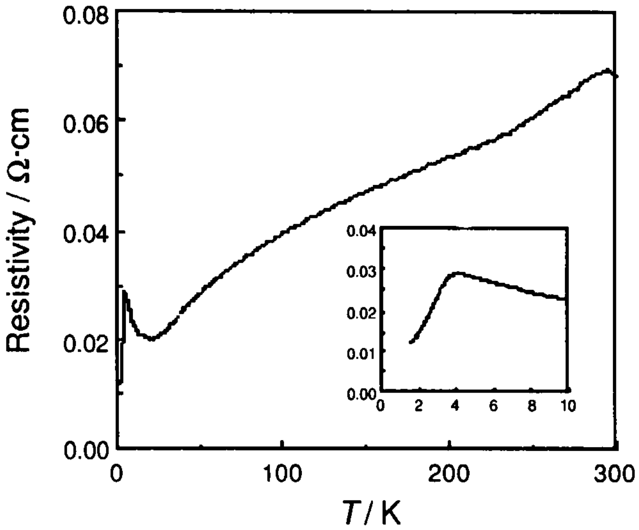


FIGURE 2 Temperature dependence of resistivity of $(DTEDT)_3Au(CN)_2$. The inset shows the resistivity in the range of 1.4 - 10 K.

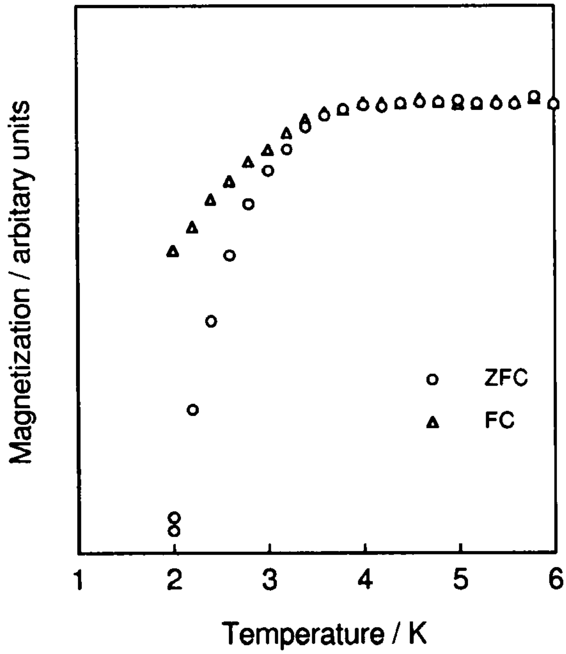


FIGURE 3 Temperature dependence of magnetization at an applied magnetic field of 2 mT.

The crystal structure of the new organic superconductor was investigated by X-ray structure analysis.[12] As shown in Figure 4, the donors form conducting sheets parallel to the *ac* plane, and the linear anion, $Au(CN)_2$, is aligned along the *c* axis. At first, every other anion site was considered to be occupied in the probability of 80% because the population analysis indicated that the ratio of DTEDT and $Au(CN)_2$ is 1 : 0.4. The length of the doubled c axis: 2c = 2 x 3.857 Å = 7.714 Å is, however, too short for an $Au(CN)_2$ anion to be included because the length of $Au(CN)_2$ anion is about 9.4 Å. An oscillation photograph along the crystallographic c axis showed clear three-fold satellite reflections even at room temperature. Then the reflection data of the three-fold structure were collected by a four-circle diffractometer, and usual structure analysis was carried out.[13] By assuming the anion population is to be 1.0, the analysis has been successful ($R = 0.0946$). Therefore we should regard that every third anion site of the average structure is occupied, and the correct composition is $(DTEDT)_3Au(CN)_2$, or $x = 0.33$ in $(DTEDT)[Au(CN)_2]_x$. It is not surprising that the energy dispersion spectroscopy gave $x = 0.39$, and the population analysis of the X-ray analysis of the average structure gave $x = 0.40$, because the estimations of these measurements are not so accurate. We will, however, hereafter describe the crystal structure by using the results of the average structure analysis as far as we will not specially mention, because three-fold structure analysis is not accurate enough to discuss the detail of the donor modulation. We consider that the three-fold structure analysis is only meaningful in confirming the composition and the anion periodicity.

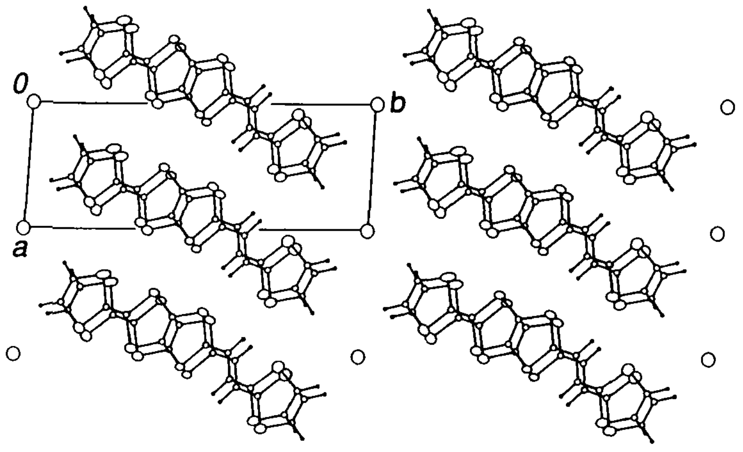


FIGURE 4 Crystal structure of $(DTEDT)_3Au(CN)_2$ projection onto the *ab* plane.

The donors are stacked in a face-to-face manner, and the overlap mode is so-called ring-over-bond type (Figure 5). Interestingly, they are arranged making both the stacking and transverse directions parallel, while unsymmetrical donors such as DMET[14] and MDT-TTF[15] are usually stacked alternately. Because DTEDT has a crooked structure and the HOMO in which π-orbital of sulfur atoms at the outer vinylogous 1,3-dithiole ring are out of phase with those of the others, such a parallel arrangement causes both sterically and electronically most effective intermolecular interaction. The arrangement of donors resembles that of β-(BEDT-TTF)$_2$X (X = I$_3$, IBr$_2$, AuI$_2$)[2] and (EDT-TTF)$_2$X (X = ReO$_4$, ClO$_4$, BF$_4$) as shown in Figure 6[16] However, the donors form completely uniform stacks in the present salt with the interplanar distance of 3.51 Å, while they are dimerized in usual β-type salts mentioned above. Such a "uniform β-type" arrangement of donors is also observed in (BDT-TTP)$_2$X (X = ClO$_4$, SbF$_6$),[6] and (DTEDT)$_3$SbF$_6$.[17] The fact that both the SbF$_6$ and Au(CN)$_2$ salts

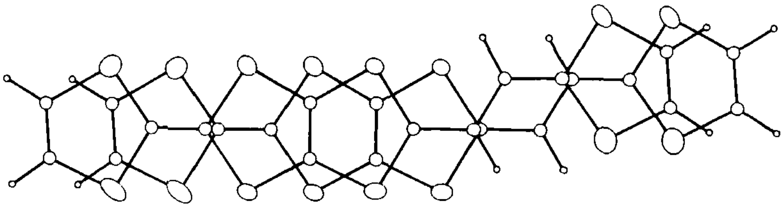


FIGURE 5 Overlap mode of donors in (DTEDT)$_3$Au(CN)$_2$ projection onto the donor molecular plane.

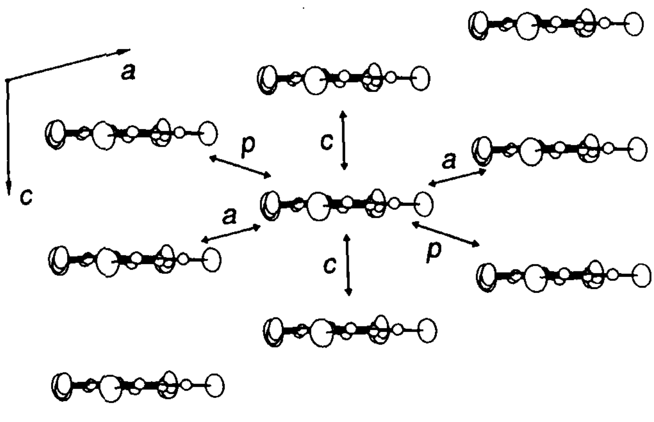


FIGURE 6 Donor sheet structure of (DTEDT)$_3$Au(CN)$_2$.

have isostructural two-dimensional array of donors regardless of the shape of counter anions indicates that DTEDT has a strong tendency to form two-dimensional β-type array in spite of its unfavorably unsymmetrical and crooked structure at first glance.

The band structure calculated by the tight binding method is shown in Figure 7. Although the transfer integral along the stack is fairly large ($c = -18.3 \times 10^{-3}$), the interstack overlap is about one third of the intrastack interaction. Such a comparatively large interstack interaction and a large band filling (5/6 filled) gives a closed Fermi surface, although one-dimensional character along the stacking direction is dominant. The closed Fermi surface is 16.7% of the first Brillouin zone. By considering the three-fold structure, the first Brillouin zone is folded so that the periodicity along the k_c direction is one third of the average structure. Then the new ZV zone boundary may touch the Fermi surface, and the Fermi surface may be separated on this boundary, making open one and a small one. The modulation of the donors are, however, not very large. It is interesting whether experiments will be consistent with this latter small Fermi surface or with the large one from the average structure (or both).

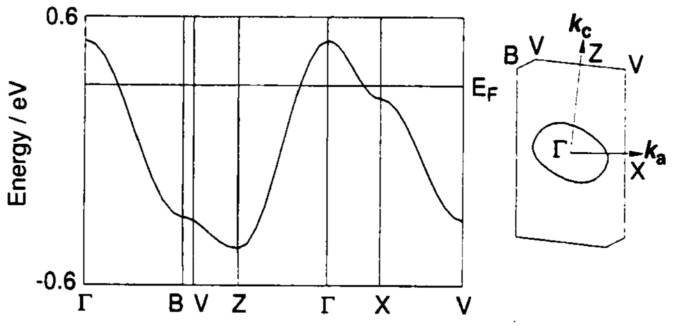


FIGURE 7 Energy band structure and Fermi surface of $(DTEDT)_3Au(CN)_2$. The intermolecular overlap integrals are $a = -1.5$, $c = -18.3$, $p = -5.0 \times 10^{-3}$.

Figure 8 shows the thermoelectric power (Seebeck coefficient) of $(DTEDT)_3Au(CN)_2$. The thermoelectric power is positive and T-linear in the whole temperature range. This is in agreement with a simple metal and with conduction electrons derived from donors. Because crystal and band structures indicate that this salt has a closed Fermi surface, we could not estimate the bandwidth assuming a tight-binding one-dimensional band. However, the thermoelectric power at room temperature (30 μV/K) is relatively large, suggesting a little narrow bandwidth, in other words, a little strong electron correlation.

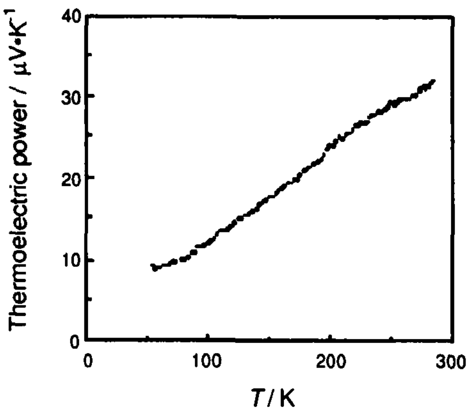


FIGURE 8 The thermoelectric power of $(DTEDT)_3Au(CN)_2$.

Conducting Behavior of Cation Radical Salts Based on the Other DTEDT Derivatives

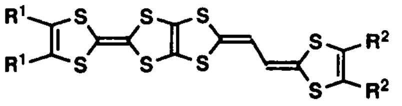
Table III summarizes conducting properties of cation radical salts based on the other DTEDT derivatives measured on a single crystal. The dimethyl derivative (**15**) affords metallic cation radical salts with octahedral anions (AsF_6, SbF_6 and TaF_6) down to T_{MI} = 150-260 K, whereas PF_6 salt is semiconductor with low conductivity ($\sigma_{rt} = 10^{-3}$ S cm^{-1}). The PF_6 and AsF_6 salts of **16** are also metallic, and show metal to semiconductor transition around 50 K, indicating their metallic state are more stabilized

TABLE III Electrical properties of cation radical salts of DTEDT derivatives

Donor	Anion	Form	x[a]	σ_{rt} / Scm^{-1} [b]	Conducting behavior
15	PF_6	Needle	0.40(P)	5.0×10^{-3}	- [d]
	AsF_6	Plate	0.52(As)	34	$T_{MI} \approx 260$ K
	SbF_6	Plate	0.41(Sb)	32	$T_{MI} \approx 250$ K
	TaF_6	Plate	0.40(Ta)	13	$T_{MI} \approx 150$ K
	$Au(CN)_2$	Needle	1.0(Au)	1.7×10^{-3}	- [d]
	$Au(CN)_2$[c]	Plate	0.44(Au)	8.5×10^{-3}	$E_a = 0.16$ eV
16	PF_6	Polycrystal	0.44(P)	7.7	$T_{MI} \approx 50$ K
	AsF_6	Polycrystal	0.35(As)	8.7	$T_{MI} \approx 50$ K
	$Au(CN)_2$	Needle	1.3(Au)	9.8×10^{-2}	- [d]
17	PF_6	Needle	0.89(P)	7.7×10^{-2}	$E_a = 0.11$ eV
	AsF_6	Needle	1.1(As)	1.3×10^{-1}	$E_a = 0.18$ eV

[a] Determined by the energy dispersion spectroscopy (EDS) from the ratio of sulfur and the elements designated in the parentheses. [b] Room temperature conductivity measured by a four-probe technique on a single crystal. [c] Containing a solvent $(PhCl)_{0.6}$. [d] The E_a value could not be estimated because of very large raw resistivity.

than the salts of **15**. On the other hand, single crystals of PF_6 and AsF_6 salts based on **17** are low conducting (σ_{rt} = 10^{-2}-10^{-1} S cm^{-1}) semiconductors with large E_a values (10^{-1} eV), while the corresponding BDT-TTP derivative produces metallic cation radical salts with the same anions.[18]



15 R^1 = H, R^2 = Me
16 R^1 = H, $2R^2$ = $-(CH_2)_3-$
17 R^1 = SMe, $2R^2$ = $-(CH_2)_3-$

CONCLUSION

In summary, DTEDT has a strong tendency to form stable metals in spite of its apparently unfavorable molecular and electronic structures compared to BDT-TTP. This should bring an expectation that fusion of two 1,3-dithiole donors is a reliable guiding principle for stabilization of metallic state in organic charge-transfer salts. Further, we have also found a new organic superconductor, $(DTEDT)_3Au(CN)_2$. The present superconductor has several unique points. Thus, DTEDT is the first π-electron donating framework for organic superconductors other than TTF as well as the first vinylogous component. This is only the second example of organic superconductors having 3:1 (D:A) composition . The symmetry of DTEDT (C_s) is quite low compared with the other conducting component for organic superconductors; D_{2h} for symmetrical TTF (TSF) and $M(dmit)_2$ derivatives, C_{2v} for unsymmetrical TTF (TSF and STF) ones and I_h for C_{60}. Unfortunately, the role of vinylogous TTF moiety for superconductivity is not clear at the present time. The further investigations on physical properties of the present salt are in progress.

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13. Crystal data of the three-fold structure (DTEDT)$_3$Au(CN)$_2$: triclinic, space group $P1$, a = 6.322(1), b = 17.166(4), c = 11.559(6) Å, α = 93.72(2), β = 95.56(3), γ = 93.72(2)°, V = 1240.3(7) Å^3, Z = 1, D_c = 1.97 cm^{-3}.
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