

New ambient pressure organic superconductors κ_{H} - and κ_{L} -(DMEDO-TSeF) $_2$ [Au(CN) $_4$](THF) †

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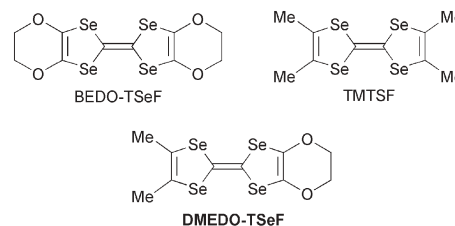
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We have developed two novel organic superconductors κ_{H} - and κ_{L} -(DMEDO-TSeF) $_2$ [Au(CN) $_4$](THF) (DMEDO-TSeF = dimethyl(ethylenedioxy)tetraselenafulvalene) with the onset transition temperatures of 4.8 K for the κ_{H} -phase and 3.0 K for the κ_{L} -phase at ambient pressure, where DMEDO-TSeF is the second example following tetramethyltetraselenafulvalene (TMTSF) after an interval of 25 years as a sulfur-free donor providing a bulk organic superconductor.

Organic electron donors containing the ethylenedioxy group possess excellent features such as high solubility towards organic solvents and the ability to construct the CH \cdots O hydrogen bond.¹ Bis(ethylenedioxy)tetrathiafulvalene (BO) has provided a large number of organic metals containing two organic superconductors² and the gigantic photoresponse of the PF $_6$ salt of ethylenedioxy-tetrathiafulvalene (EDO-TTF) has attracted much attention.³ On the other hand, there has long been a lack of reports on research on tetraselenafulvalene (TSeF) derivatives containing the ethylenedioxy group because of the difficulty in preparing the key synthetic intermediate. Recently, we achieved the synthesis of TSeF derivatives containing the ethylenedioxy group, bis(ethylenedioxy)tetraselenafulvalene (BEDO-TSeF)⁴ and DMEDO-TSeF,⁵ without the use of highly hazardous CSe $_2$. The PF $_6$, AsF $_6$ and SbF $_6$ salts of DMEDO-TSeF crystallized in the β -type structure and possessed a quasi-1D metallic nature, which is similar to that of the first organic superconductor (TMTSF) $_2$ PF $_6$.⁶ Unfortunately, these salts with octahedral anions did not show superconductivity and we explored other counter anions for the DMEDO-TSeF salts to obtain a new organic superconductor. The monovalent organometallic anions have provided unique organic superconductors, such as θ -(DIETS) $_2$ [Au(CN) $_4$] (DIETS = diiodo(ethylenedithio)diselenadithiafulvalene)⁷ and κ -(BEDT-TTF) $_2$ [M(CF $_3$) $_4$](TCE) (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene, M = Cu, Ag, Au, TCE = 1,1,2-trichloroethane).⁸ The former shows superconductivity under uniaxial strain applied along the I \cdots N iodine bond. The latter forms two superconducting phases (κ_{H} - and κ_{L} -phase) and the characteristic thickness of the anion layer (*ca.* 8.3 Å) is greater than that of regular organic superconductors. As these unique features are derived from the large and square planar shape of the organometallic anions, we decided to introduce

square planar anions into the DMEDO-TSeF system. In this study, we report the crystal structures and physical properties of new ambient pressure superconductors κ_{H} - and κ_{L} -(DMEDO-TSeF) $_2$ [Au(CN) $_4$](THF).



Black rhombic and hexagonal plate single crystals of (DMEDO-TSeF) $_2$ [Au(CN) $_4$](THF) were prepared by the galvanostatic oxidation (0.5 μ A, 2–3 days) of a THF solution (20 ml) containing DMEDO-TSeF (*ca.* 4 mg) and tetra-*n*-butylammonium tetracyanoaurate (*ca.* 20 mg) as a supporting electrolyte. Rhombic plate was the major product and it crystallizes in the monoclinic space group $P2_1/c$ (hereafter referred to as the κ_{H} -phase), while the crystal structure of the hexagonal plate could not be identified by its crystal morphology. We performed X-ray diffraction experiments on thirty hexagonal plates under random sampling; six plates crystallize in the orthorhombic space group $Pnma$ (hereafter referred to as the κ_{L} -phase) and the others are isostructural with the rhombic plates. The subscripts, H and L, are used to designate the higher- and lower- T_c phase, respectively, according to the precedent.⁸

Superconductivity was detected by resistivity and magnetic susceptibility measurements. Fig. 1 shows the temperature dependence of the resistivity for the κ_{H} - and κ_{L} -phases measured perpendicularly to the conducting plane down to 1.6 K. The resistivity for the κ_{H} -phase decreases monotonously with lowering temperature, and a superconducting transition occurred at $T_c = 4.8$ K (onset). On the other hand, temperature dependence of the resistivity for the κ_{L} -phase shows a broad maximum around 110 K, which resembles that of the κ -type BEDT-TTF salts,^{8,9} and a resistivity drop of the superconducting transition was observed at 3.0 K (onset). As shown in Fig. 2, superconductivity of these two salts was also confirmed by magnetic susceptibility measurements using randomly oriented samples of the κ_{H} -phase (0.10 mg) and the κ_{L} -phase (0.04 mg) in a polyethylene sample holder, respectively. The onset temperatures of diamagnetic transitions are 4.6 K for the κ_{H} -phase and 2.8 K for the κ_{L} -phase, which are slightly lower than those of the resistivity measurements. The calculated volume fractions of superconductivity at 1.9 K are *ca.* 90% and 20% of the perfect

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† Electronic supplementary information (ESI) available: Hydrogen bond tables, molecular packing of κ_{L} -phase and structures for the insulating layer of the κ_{H} - and κ_{L} -phase. See DOI: 10.1039/b516940b

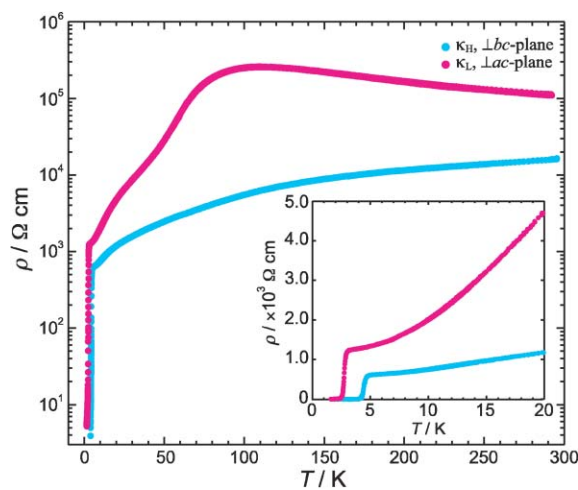


Fig. 1 Temperature dependence of the resistivities for κ_{H} - (light blue circles) and κ_{L} -phase (pink circles) measured perpendicularly to the conducting plane. The inset shows the resistivities in the low-temperature region.

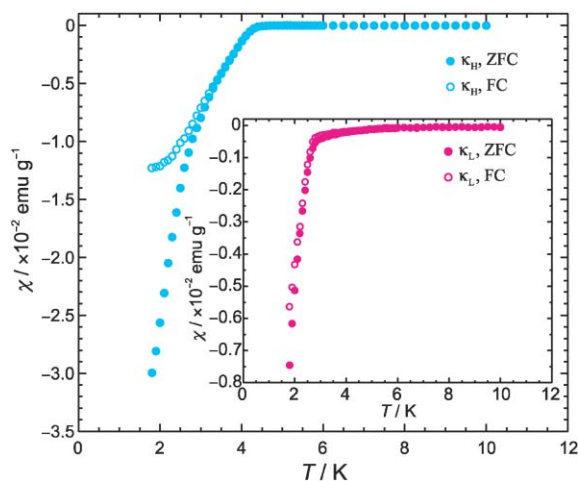


Fig. 2 Temperature dependence of ZFC (filled circle) and FC (open circle) DC magnetizations for κ_{H} - (light blue circles) and κ_{L} -phase (pink circles, inset) under an applied field of 10 Oe.

diamagnetism for the κ_{H} - and κ_{L} -phases, respectively, indicating that these two salts are bulk organic superconductors.

X-ray crystal structure analyses^{††} of the κ_{H} - and κ_{L} -phases were performed at 293 K. The molecular packing of the κ_{H} -phase, which crystallizes in the monoclinic space group $P2_1/c$, is shown in Fig. 3(a). The donor–anion–solvent ratio is 2 : 1 : 1 and two crystallographically independent donor molecules form conducting donor layers A and B. Terminal ethylene groups of the donor molecules show disorder due to flipping. The donor arrangements of layers A and B belong to the so-called κ -type structure and the head-to-tail-type dimers with an interplane distance of 3.51 Å and 3.49 Å are arranged orthogonally by the dihedral angle of 103.9° for layer A and 102.7° for layer B. The packing motifs of these two layers are solid crossing at an angle of 103.3° as shown in Fig. 3(b). The $\text{Au}(\text{CN})_4$ anions and THF molecules are located on $a \approx 0.25$ between the conducting donor layers. The AuC_4 -core of the anion is almost planar and the solvent molecules are taken in a cavity formed by the herringbone-type anion arrangement.

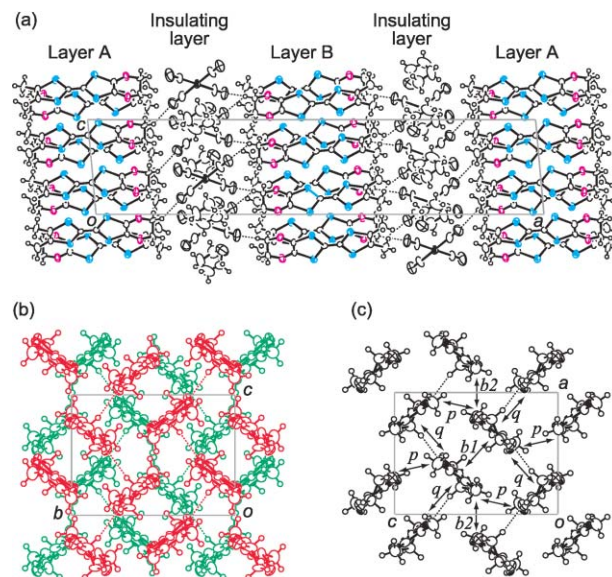


Fig. 3 Crystal structure for $(\text{DMEDO-TSeF})_2[\text{Au}(\text{CN})_4](\text{THF})$ at 293 K. Dotted lines indicate short $\text{CH}\cdots\text{N}$ contacts less than 2.75 Å and short $\text{CH}\cdots\text{O}$ contacts less than 2.72 Å. (a) Molecular packing of the κ_{H} -phase viewed along the crystallographic b -axis. (b) Donor arrangement of the κ_{H} -phase viewed along the crystallographic a -axis, where layers A and B are represented in red and green, respectively. (c) Donor arrangement of the κ_{L} -phase viewed along the crystallographic b -axis. The minor orientations of the disordered ethylene bridge of the donor molecule are omitted for clarity.

On the other hand, the κ_{L} -phase crystallizes in the orthorhombic space group $Pnma$ and the molecular arrangement resembles that of the κ_{H} -phase. The donor–anion–solvent ratio is 2 : 1 : 1 and one donor molecule with a disordered terminal ethylene bridge is crystallographically independent. As shown in Fig. 3(c), the κ -type donor arrangement is also formed and the head-to-tail-type dimers with an interplane distance of 3.49 Å are arranged orthogonally by the dihedral angle of 103.0°. The THF molecule is located in the general position around the mirror plane and extreme disorder of its orientation is observed. Crystallographic disorder can be detrimental to superconductivity as shown in the $(\text{TMTSF})_2\text{ClO}_4$ superconductor¹⁰ and it is consistent with the lower T_{c} of the κ_{L} -phase compared with that of the κ_{H} -phase with the ordered structure of the THF molecule. Moreover, there is a distinct difference in the relation of the two donor layers A and B between the κ_{H} - and κ_{L} -phases. As shown in the projection onto the ac -plane of the κ_{L} -phase (Fig. 3(c)), the two donor layers in the unit cell related by mirror symmetry overlap with each other almost completely, whereas the donor molecules of layers A and B for the κ_{H} -phase are solid crossing as mentioned above. These structural differences seem to affect their conducting properties including the T_{c} of the superconducting transition.

Interestingly, there exist not only the expected $\text{CH}\cdots\text{O}$ hydrogen bonds in the donor layers, but also many $\text{CH}\cdots\text{N}$ hydrogen bonds between the donor molecule and the counter anion in these two salts. The interlayer interaction through the characteristic $\text{CH}\cdots\text{N}$ hydrogen bonds is likely to play an important role in their superconductivity, because the conducting donor layers of these two salts are separated by the insulating layers (*ca.* 4.7 Å), which is the thickest for any organic

superconductor,[§] and electron transport through the anion layer must occur to achieve the superconducting state as the bulk property. It has already been reported that the weak donor–anion interactions sometimes influence the physical property in the classical TMTSF and BEDT-TTF salts.¹¹

Fig. 4 shows the calculated Fermi surfaces for the κ_{H} - and κ_{L} -phases based on the tight-binding approximation using the intermolecular overlap integrals calculated from the extended Hückel model.^{12,13} Unexpectedly, the calculated Fermi surfaces of the κ_{H} -phase are opened and anisotropy of the 2D Fermi surfaces of the κ_{L} -phase is large in spite of the κ -type crystal structure.¹⁴ The lowering of the electronic dimensionality is caused by the small p values of the overlap integrals, which are less than half of the $b2$ values in any layer. To explain the contradiction between the higher T_{c} and the lower dimensionality of the κ_{H} -phase compared with those of the κ_{L} -phase, the experimental information of the Fermi surfaces is anticipated, because the Hückel parameters of O and Se atoms for DMEDO-TSeF have not been optimized.¹⁵

In summary, we have succeeded in the development of new ambient pressure organic superconductors κ_{H} - and κ_{L} -(DMEDO-TSeF)₂[Au(CN)₄](THF) with T_{c} (onset) of 4.8 K and 3.0 K, respectively. In spite of the thickness of the insulating layers (*ca.* 4.7 Å) separating the conducting donor layers, the transition temperatures of these two salts are relatively high compared with the known κ -type superconductors based on unsymmetrical donors.¹⁶ These two salts are attractive for studies on low temperature physics from the perspectives of their crystal structures and the sulfur-free skeleton of the DMEDO-TSeF molecule. Recently, unconventional critical behavior was reported for the κ -type salts of BEDT-TTF¹⁷ and the present new superconductors based on the new donor molecule must have appeal to extend the materials map of the unique phenomena of the κ -type salts. Moreover, the DMEDO-TSeF molecule does not contain any sulfur atoms but does contain selenium atoms, which include an NMR active nucleus ⁷⁷Se, and this is advantageous to the direct observation of the electronic state at low temperature. Finally, it may be possible to tune the T_{c} values of the present system by modifying the counter anion and the solvent molecule in the insulating layer.

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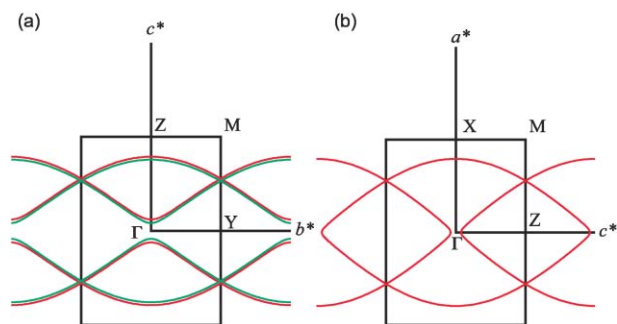


Fig. 4 (a) Calculated Fermi surfaces for the κ_{H} -phase. Red and green lines are associated with conducting donor layers A and B, respectively. Calculated overlap integrals ($\times 10^{-3}$) are $b1 = -20.91$, $b2 = -9.76$, $p = 4.34$, $q = 0.03$ for the layer A, $b1 = -19.96$, $b2 = -10.02$, $p = 4.10$, $q = 0.04$ for the layer B. (b) Calculated Fermi surfaces for the κ_{L} -phase. $b1 = -20.63$, $b2 = -9.32$, $p = 4.24$, $q = 0.21$. For the definition of the interactions $b1$, $b2$, p and q , see Fig. 3(c).

Notes and references

† Crystal data for κ_{H} -(DMEDO-TSeF)₂[Au(CN)₄](THF): C₂₈H₂₈AuN₄O₅Se₈, $FW = 1329.19$, $T = 293$ K, black rhombic block ($0.13 \times 0.12 \times 0.08$ mm³), monoclinic, $P2_1/c$ (#14), $a = 38.868(6)$, $b = 11.1527(16)$, $c = 8.2788(12)$ Å, $\beta = 95.033(3)^\circ$, $V = 3574.9(9)$ Å³, $Z = 4$, $D_{\text{c}} = 2.470$ g cm⁻³, $\mu = 12.304$ mm⁻¹, 72913 reflections measured, 9109 unique ($R_{\text{int}} = 0.1186$). Final R indices [$I > 2\sigma(I)$]: $R1 = 0.0490$, $wR2 = 0.1125$. $GOF = 0.938$.

‡ Crystal data for κ_{L} -(DMEDO-TSeF)₂[Au(CN)₄](THF): C₂₈H₂₈AuN₄O₅Se₈, $FW = 1329.19$, $T = 293$ K, black hexagonal plate ($0.30 \times 0.20 \times 0.04$ mm³), orthorhombic, $Pnma$ (#62), $a = 8.3269(13)$, $b = 38.638(6)$, $c = 11.1203(17)$ Å, $V = 3577.8(9)$ Å³, $Z = 4$, $D_{\text{c}} = 2.468$ g cm⁻³, $\mu = 12.294$ mm⁻¹, 67940 reflections measured, 4572 unique ($R_{\text{int}} = 0.1050$). Final R indices [$I > 2\sigma(I)$]: $R1 = 0.0492$, $wR2 = 0.1273$. $GOF = 0.967$.

CCDC 291264–291265. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516940b

§ The thickness of the insulating layer is based on the distance between the hydrogen edges of donor molecules and *ca.* 4.4 Å for κ_{L} -(BEDT-TTF)₂[Cu(CF₃)₄](TCE)⁸ is estimated using the same procedure.

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