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A supramolecular superconductor θ-(DIETS)$_2$[Au(CN)$_4$]

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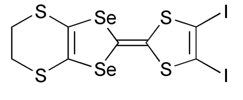
A supramolecular conductor θ-(DIETS)$_2$[Au(CN)$_4$] [DIETS = diiodo(ethylenedithio)diselenadithiafulvalene] has been revealed to be a new superconductor with T_c = 8.6 K (onset, 10 kbar) under uniaxial strain parallel to the crystallographic *c*-axis.

According to the research on organic conductors during the past two decades,[1] it is well recognized that the design of the molecular arrangement in a crystal is as important as the design of an independent donor or acceptor molecule for exploring interesting electronic properties, such as superconductivity. Nevertheless, there have been few attempts to develop an active method for the control of molecular arrangement of organic conductors.

We have noted the usefulness of the I···N strong intermolecular interaction[2] for the crystal design of organic conductors, and several unique crystals based on iodine-bonded unsymmetrical TTFs have been reported.[3] On the other hand, halogen-based intermolecular interactions have recently come to be called *halogen bonds* for any halogen element in the field of supramolecular chemistry;[4] however, the iodine atom has an intrinsic uniqueness. Unlike other halogen atoms, the electronegativity of the iodine atom is smaller than that of carbon. In addition, according to MO calculations, the σ-type LUMO is highly localized on the carbon(sp^2)–halogen bond in the case of the iodine atom. Therefore, the iodine-based intermolecular interaction mentioned above should be defined more specifically and we call it the *iodine bond*.

From the viewpoint of the anisotropic charactor of organic conducting crystals, some research groups have reported the application of uniaxial stress or strain to organic conductors instead of the usual hydrostatic pressure.[5] The most important aspect of the uniaxial pressure method is the selectivity of the intermolecular interaction to be enhanced, and the effect of the uniaxial pressure essentially depends upon the anisotropic character of the intermolecular interaction. Therefore, the supramolecular system tailored by the strong iodine bond mentioned above is one of the most suitable candidates to make best use of the uniaxial method, and it would be promising to find a new aspect of organic conductors. In this paper, we report a uniaxial strain-induced superconductivity of the title compound, which is a supramolecular conductor, tailored by the iodine bond.

DIETS [diiodo(ethylenedithio)diselenadithiafulvalene] is an unsymmetrical TTF analogue containing two iodine atoms on the edge of the skeleton.† Single crystals of the Au(CN)$_4$ salt were prepared by the electrochemical oxidation of a dichloromethane solution of DIETS in the presence of tetrabutylammonium tetracyanoaurate[6] as a supporting electrolyte. Black, elongated plates with a rhombus section (typical dimensions are: length, 0.8 mm; diagonal section, 0.3 × 0.1 mm) were obtained, and the relationship between the crystallographic axes and the crystal shape was confirmed by X-ray diffraction analysis.



DIETS

Fig. 1 shows the crystal structure of θ-(DIETS)$_2$[Au(CN)$_4$] containing alternating layers of the donor DIETS and the square planar tetracyanate anion.‡ The donor molecules are arranged uniformly along the *a*-axis, and the 'herring bone' packing within the donor layer belongs to the so-called θ-type. Each iodine atom on the donor molecule is connected to one Au(CN)$_4$ anion through the cyano group and the supramolecular network is constructed by the unique iodine bonds.

The strong iodine bond has an affect on the relationship between the crystallographic axes and the crystal shape. In the usual case of organic conductors based on TTFs, inter-layer direction between the donors and counter anions corresponds to the shortest dimension (*e.g.* thickness in the plate morphology). In the present case, the direction of the short diagonal of the rhombus section is the side-by-side direction (*b*-axis) within the donor layer, and the inter-layer axis (*c*-axis) corresponds to the long diagonal of the section (Fig. 2, left). This unique feature is derived from the iodine bond, which might be stronger than the side-by-side chalcogen···chalcogen contacts in this case.

The electronic band structure was calculated by performing

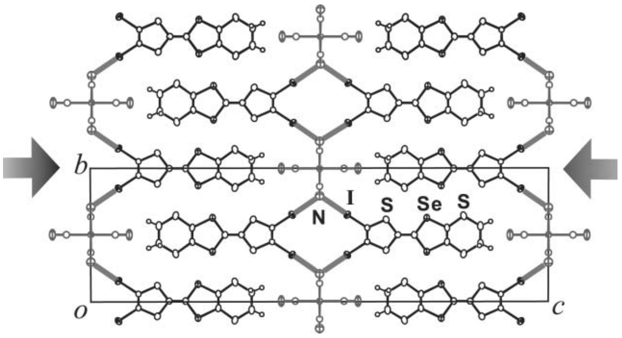


Fig. 1 Packing diagram of θ-(DIETS)$_2$[Au(CN)$_4$] viewed along the *a*-axis. The thick bonds indicate the short I···N interaction [3.018(7) Å] and the arrows indicate the direction of the uniaxial strain which induces superconductivity.

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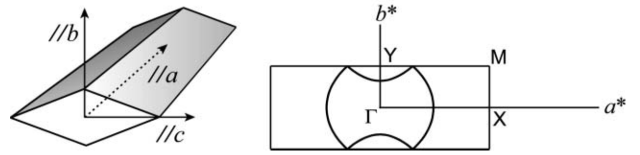

Fig. 2 Relationship between the crystallographic axes and the crystal shape (left) and the calculated Fermi surface (right). Calculated overlap integrals between HOMOs are -6.28×10^{-3} (intra-column) and -2.43×10^{-3} (inter-column).

the extended Hückel method based on the tight-binding approximation. The Fermi surface has a cross section of a distorted circle centred at Γ and folded at the boundary of the first Brillouin zone (Fig. 2, right). The band dispersion of the Au(CN)$_4$ salt is similar to those of the known θ-type salts.

The resistivity of the Au(CN)$_4$ salt was measured by the standard four-probe method. Under the hydrostatic pressure, a sharp (semi)metal–insulator transition around 226 K was gradually suppressed; however, it still remained under 18 kbar.[7] On the other hand, the conducting behaviour showed drastic change under the uniaxial strain. Uniaxial strain was applied using the epoxy-crystal method developed by Kagoshima *et al.*[5b,c] Fig. 3 shows the temperature dependence of the resistivity under the uniaxial strain parallel to the *c*-axis. The *c*-axis corresponds to the inter-layer direction, *i.e.* perpendicular to the donor layer. The (semi)metal–insulator transition around 226 K was mostly suppressed under a moderate pressure up to 5 kbar. At 10 kbar, a rapid decrease of the resistivity was observed at 8.6 K and it is characteristic of the onset of the superconducting transition. The small residual resistivity at lower temperature is probably due to the inhomogeneity of the uniaxial strain.

The existence of the superconductivity was confirmed by the recovery of resistance in a magnetic field (Fig. 4). To our knowledge, the superconducting transition temperature (T_c) of the known superconductors using unsymmetrical π-donors is lower than 5 K[8] and the T_c of the present salt (8.6 K) is currently the highest record. On the other hand, temperature dependence of the resistivity under the uniaxial strain parallel to the donor layer (along the *a*- or *b*-axis) resembles those under hydrostatic pressure and no superconductivity was observed up to 20 kbar.

According to the universal phase diagram proposed by Mori *et al.*[9] for the conventional θ-type salts with no supramolecular architecture, uniaxial strain towards the θ-type salt should work most effectively within the donor layer. In the present salt, however, the most effective direction of the uniaxial strain is perpendicular to the donor layer. The uniaxial pressure effect within the donor layer (*ab*-plane) does not show a distinct anisotropy and is not accompanied by superconductivity. Although the exact role of the iodine bond is not clear at the present time, the large anisotropy of the pressure effect upon the electrical conductivty at low temperature suggests some kind of relationship between the iodine bond and the electronic state at low temperature.

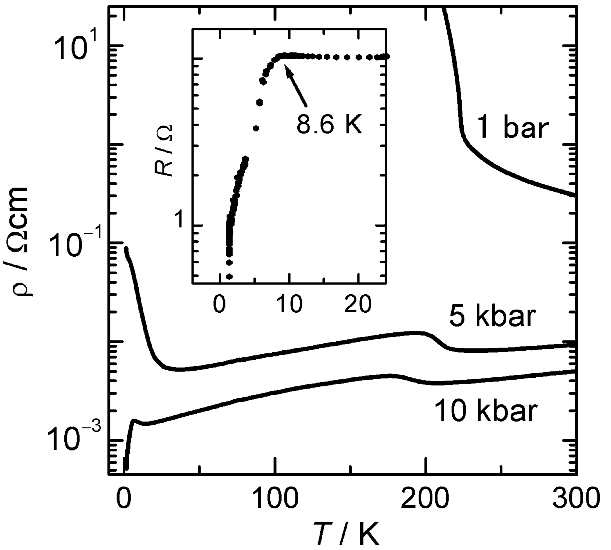

Fig. 3 Temperature dependence of the resistivity measured along the *a*-axis for θ-(DIETS)$_2$[Au(CN)$_4$] under uniaxial strain parallel to the *c*-axis. Inset shows the resistivity measured along the *c*-axis (P = 10 kbar // *c*).

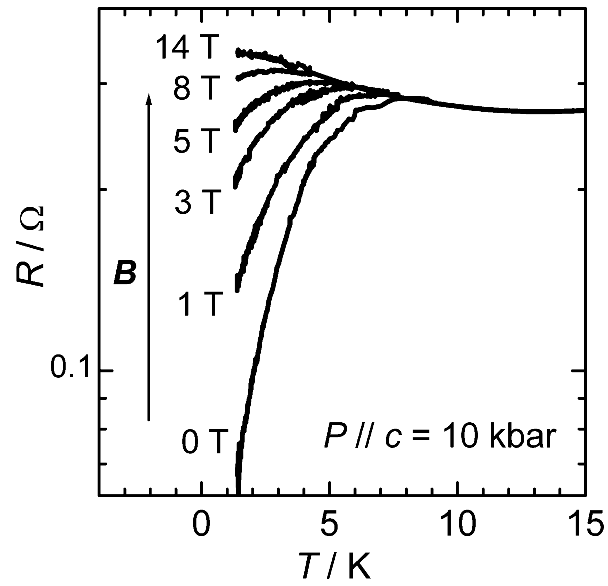

Fig. 4 Recovery of the resistance measured along the *a*-axis in a magnetic field parallel to the *c*-axis.

In summary, we have discovered superconductivity under uniaxial strain of a supramolecular conductor θ-(DIETS)$_2$[Au(CN)$_4$] which is tailored by characteristic *iodine bonds*. The onset temperature of the superconductivity is >8 K under a uniaxial strain of 10 kbar, and this is the highest record among the known organic superconductors based on unsymmetrical TTF derivatives. These findings will open up new architecture for the design of organic superconductors, possibly with higher transition temperature.

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Notes and references

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†Synthesis of DIETS was carried out according to the literature (T. Imakubo, H. Sawa and R. Kato, *Synth. Met.*, 1997, **86**, 1883). Reaction with a smaller amount of P(OEt)$_3$ (*ca.* 50 equiv.) and a shorter reaction time (30 min) improved the yield (46%) and avoided the de-iodination of the product. Selected data for DIETS: purplish-brown crystals; mp >170 °C (decomp.), δ_H (500 MHz, CDCl$_3$) 3.304 (s, 4H); *m*/*z* (EI, 70 eV): 642 (M$^+$ for C$_8$H$_4$I$_2$S$_4{}^{80}$Se$_2$); Elemental analysis: Calc. for C$_8$H$_4$I$_2$S$_4$Se$_2$: C, 15.01; H, 0.63. Found: C, 14.99; H, 0.75%.

‡X-Ray crystal structure of θ-(DIETS)$_2$[Au(CN)$_4$]: data were collected on a Rigaku AFC6S four-circle diffractometer (Mo-K$_\alpha$, λ = 0.71069 Å, graphite monochromator, T = 293 K, $2\theta_{max}$ = 60.0°). The structure was solved with a direct method (SAPI91) and refined by a full-matrix, least-square fit on $|F|$. All calculations were performed using the program package teXsan (Molecular Structure Corporation, 1985, 1999). Crystal data for θ-(DIETS)$_2$[Au(CN)$_4$]: C$_{20}$H$_8$N$_4$Au$_1$I$_4$S$_8$Se$_4$, M = 1581.21, black plate (0.5 × 0.2 × 0.1 mm), orthorhombic, space group *Pnnm* (no. 58), a = 4.274(2), b = 11.114(3), c = 37.426(4) Å,

$V = 1777.6(12)$ Å^3, $\mu = 122.16$ cm^{-1}, $D_c = 2.954$ g cm^{-3}, $Z = 2$, $R = 0.0329$, $wR = 0.0415$, GOF = 1.167 for 1905 observed reflections ($I \geqslant 3\sigma(I)$) out of 3091 unique reflections. CCDC reference number 167386. See http://www.rsc.org/suppdata/jm/b1/b110303b/ for crystallographic data in CIF or other electronic format.

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