V-J Synthesis and Physical Properties of Novel Molecular Metals

Development of organic materials which exhibit interesting electrical properties such as metallic conductivity and superconductivity has received considerable attention. A bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6tetrathiapentalene (TTP) is a promising π -electron framework for preparation of stable metals down to low temperatures, because it has a ladder-like array of sulfur atoms indispensable for constructing two-dimensional network of the donors. In fact, we have found that the unsubstituted TTP has a strong tendency to afford highly conducting radical cation salts retaining metallic conductivity down to ≤ 1.2 K regardless of shape and size of counter anions. In the present study, we have developed several organic metals by means of comprehensive modification of TTP, namely i) introduction of substituents, ii) exchange of sulfur atoms in the TTP framework with selenium, iii) synthesis of TTP analogs possessing non-TTF donor unit.

V-J-1 Preparation, Structures and Physical Properties of Selenium Analogues of DTEDT as Promising Donors for Organic Metals

FUJIWARA, Hideki^{1,2}; MISAKI, Yohji^{1,2}; YAMABE, Tokio¹; MORI, Takehiko^{2,3}; MORI, Hatsumi⁴; TANAKA, Shoji⁴

(¹Kyoto Univ.; ²IMS; ³Tokyo Inst. Tech.; ⁴ISTEC)

[J. Mater. Chem. 10, 1565 (2000)]

Three selenium analogues of DTEDT [2-(1,3dithiol-2-ylidene)-5-(2-ethanediylidene-1,3-dithiole)-1,3,4,6-tetrathiapentalene] have been synthesized. They showed four pairs of single-electron redox waves. The E_1 values are a little higher by 0.02–0.05 V than that of DTEDT. On the other hand, the E_2 - E_1 values are almost equal to that of DTEDT. TCNQ complex and cation radical salts of them show fairly high electrical conductivities and several salts exhibit metallic conductivities. Especially the ReO₄⁻ and Au(CN)₂⁻ salts of DTEDS and the SbF₆⁻, TaF₆⁻ and I_3 ⁻ salts of DSEDS exhibited stable metallic behaviour down to 1.5–4.2 K. An X-ray crystal structure analysis of the metallic salt (DSEDS)₃TaF₆ reveals that this salt has twodimensional β -type packing motif of donor molecules similar to the superconducting (DTEDT)₃Au(CN)₂. The calculated Fermi surface of (DSEDS)₃TaF₆ is a twodimensional closed ellipsoid.





Figure 1. Crystal structures of $(DSEDS)_3TaF_6$ viewed (a) along the *c*-axis and (b) along the molecular long axis.

V-J-2 Preparation and Properties of Gold Complexes with TTF Dithiolato Ligands

MISAKI, Yohji^{1,2,3}; TANI, Yoshihiro¹; TANIGUCHI, Masateru¹; MAITANI, Tatsuyuki; TANAKA, Kazuyoshi; BECHGAARD, Klaus³ (¹Kyoto Univ.; ²IMS; ³Risø National Lab.)

[Mol. Cryst. Liq. Cryst. 343, 59 (2000)]

Several gold(III) complexes with TTF dithiolato ligands have been prepared as the tetrahexylammonium salts. The cyclic voltammograms in DMF showed two or three pairs of redox waves. X-Ray structure analysis of Ph₄P·Au(eodt)₂·(DMF)₂ reveals that the Au(eodt)₂ anion takes a significantly folded chair conformation. Charge-transfer salts of Au(dt)₂ derivatives with TCNQ showed high conductivity ($\sigma_{rt} = 10^0 - 10^1$ S cm⁻¹ on a compressed pellet).





Figure 1. Crystal structure of $Ph_4P \cdot Au(eodt)_2 \cdot (DMF)_2$ viewed onto the *bc* plane.

V-J-3 New TTP Donors Containing Chalcogenopyran-4-ylidene: Preparation, Structures, and Electrical Properties

TAKAHASHI, Kazuyuki¹; NAKAYASHIKI, Takashi¹; MISAKI, Yohji^{1,2}; TANAKA, Kazuyoshi¹ (¹Kyoto Univ.; ²IMS)

Several selenium analogues of TM-PDT-TTP (2-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-5-(pyran-4ylidene)-1,3,4,6-tetrathiapentalene), SM-PDT, SM-TPST, SM-SPDT, and TM-SPDT have been prepared. Among them, SM-PDT affords relatively high conducting 1:1 radical cation salt, (SM-PDT)AsF₆·H₂O ($\sigma_{rt} = 8.3 \text{ S cm}^{-1}$, $E_a = 0.045 \text{ eV}$). X-Ray structure analysis of (SM-PDT)AsF₆·H₂O revealed that the sideby-side interactions are inhibited owing to existence of the anions on the side of the donor columns. Instead, the donors form two-dimensional sheets thanks to significant interaction along the donor long axis as well as stacking structure (Figure 1).



X = O, Y = Se, SM-PDT X = S, Y = Se, SM-TPDT X = Se, Y = Se, SM-SPDTX = Se, Y = S, TM-SPDT





Figure 1. Donor sheet structure of (SM-PDT)AsF $_6$ ·H₂O.

V-J-4 Structures and Properties of CHEO-TTP Salts

TANIGUCHI, Masateru¹; MIURA, Takeshi¹; MISAKI, Yohji^{1,2}; TANAKA, Kazuyoshi¹; YAMABE, Tokio¹; MORI, Takehiko^{2,3} (¹Kyoto Univ.; ²IMS; ³Tokyo Inst. Tech.)

Radical cation salts of CHEO-TTP, where CHEO-TTP is 2-(4,5-cyclohexeno-1,3-dithiol-2-ylidene)-5-(4,5-ethylenedioxy-1,3-dithiol-2-ylidene)-1,3,4,6tetrathiapentalene showed metallic temperature dependence down to liquid helium temperature. An Xray crystal structure analysis of CHEO-TTP(ReO₄)_{0.35} reveals that the arrangement of the donors is the socalled κ -type. The band structure calculated based on a tight-binding approximation suggests the present salt has a two-dimensional Fermi surface similar to those of the superconducting κ -type salts.



Figure 1. Donor sheet structure of CHEO-TTP(ReO₄)_{0.35}.

V-J-5 Structures and Physical Properties of (CHTM-TTP)₂TCNQ

TANIGUCHI, Masateru¹; MISAKI, Yohji^{1,2}; TANAKA, Kazuyoshi¹; MORI, Takehiko^{2,3}; NAKAMURA, Toshikazu

(¹Kyoto Univ.; ²IMS; ³Tokyo Inst. Tech.)

X-Ray structure analysis of the title compound revealed that the donors form a two-dimensional conducting sheets of the so-called β -type, while no significant interaction was observed in the TCNQ sheets. The frequency of CN stretching obtained by IR spectroscopy suggested the degree of charge-transfer in TCNQ is about -1. A tight binding band calculation indicates the present complex has a quasi onedimensional Fermi surface closed to the stacking direction. It exhibited metal-like temperature dependence of resistivity down to $T_{\rm MI} = 30$ K though the resisitivity increased one around 220 K.



Figure 1. Conducting behaviour of (CHTM-TTP)₂TCNQ.