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)-1,3,4,6-tetrathiapentalene (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

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Three selenium analogues of DTEDT [2-(1,3-dithiol-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<sub>1</sub> values are a little higher by 0.02–0.05 V than that of DTEDT. On the other hand, the E<sub>2</sub>–E<sub>1</sub> 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 ReO<sub>4</sub>– and Au(CN)<sub>2</sub>– salts of DTEDS and the SbF<sub>6</sub>–, TaF<sub>6</sub>– and I<sub>3</sub>– 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)<sub>3</sub>TaF<sub>6</sub> reveals that this salt has two-dimensional β-type packing motif of donor molecules similar to the superconducting (DTEDT)<sub>3</sub>Au(CN)<sub>2</sub>. The calculated Fermi surface of (DSEDS)<sub>3</sub>TaF<sub>6</sub> is a two-dimensional closed ellipsoid.

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

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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. The X-ray structure analysis of Ph<sub>4</sub>P·Au(eodt)<sub>2</sub>·(DMF)<sub>2</sub> reveals that this salt has two-dimensional β-type packing motif of donor molecules similar to the superconducting (DTEDT)<sub>3</sub>Au(CN)<sub>2</sub>. The calculated Fermi surface of (DSEDS)<sub>3</sub>TaF<sub>6</sub> is a two-dimensional closed ellipsoid.

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**Figure 1.** Crystal structures of (DSEDS)<sub>3</sub>TaF<sub>6</sub> viewed (a) along the c-axis and (b) along the molecular long axis.
V-J-3 New TTP Donors Containing Chalcogenopyran-4-yldiene: Preparation, Structures, and Electrical Properties

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Several selenium analogues of TM-PDT-TTP (2-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-5-(pyran-4-yldiene)-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 ($\sigma_{rt} = 8.3$ S cm$^{-1}$, $E_a = 0.045$ eV). X-Ray structure analysis of SM-PDT·AsF6·H2O revealed that the side-by-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).

Figure 1. Crystal structure of Ph3P·Au(eodt)2·(DMF)2 viewed onto the $bc$ plane.

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

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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)-1,3,4,6-tetrathiapentalene showed metallic temperature dependence down to liquid helium temperature. An X-ray crystal structure analysis of CHEO-TTP(ReO4)0.35 reveals that the arrangement of the donors is the so-called $\kappa$-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 $\kappa$-type salts.

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

V-J-5 Structures and Physical Properties of (CHTM-TTP)$_2$TCNQ

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X-Ray structure analysis of the title compound revealed that the donors form a two-dimensional conducting sheets of the so-called $\beta$-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 one-dimensional Fermi surface closed to the stacking direction. It exhibited metal-like temperature dependence of resistivity down to \(T_M = 30\) K though the resistivity increased one around 220 K.

Figure 1. Conducting behaviour of \((\text{CHTM-TTP})_2\text{TCNQ}\).