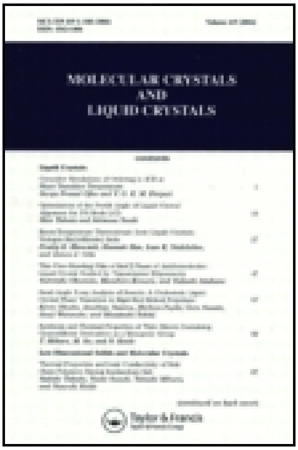

Molecular Crystals and Liquid Crystals

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New organic metal containing mixed donors: (ET)(MT) 2 (BF 4)(THF)

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NEW ORGANIC METAL CONTAINING MIXED DONORS: $(ET)(MT)_2(BF_4)(THF)$

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Single crystals of new organic metal, $(ET)(MT)_2(BF_4)(THF)$, were electrochemically grown in an H-type cell. In the X-ray crystal structure, ET and MT donors together form a layer in ac-plane, which is stacking along b-axis alternatively with the layer formed by BF_4^- and THF. Within the mixed-donor layer, MT molecules (stacking along a-axis) and ET molecules (arranged side-by-side) are almost perpendicular each other with their long in-plane molecular axes being along b-axis. ET and MT molecules within a layer are closely connected by short S...S interactions (3.226 ~ 3.694 Å) and achieve the 2D S...S network. Band electronic structure calculations on this complex show that it is a 2D metal at r.t. Bands are more dispersive along the a-axis which means that electrical conductivity is possibly better along this direction. However, the Fermi surface nesting which arises in many low dimensional metals, was not found.

Keywords: organic metal; mixed-donor; two-dimensional metal

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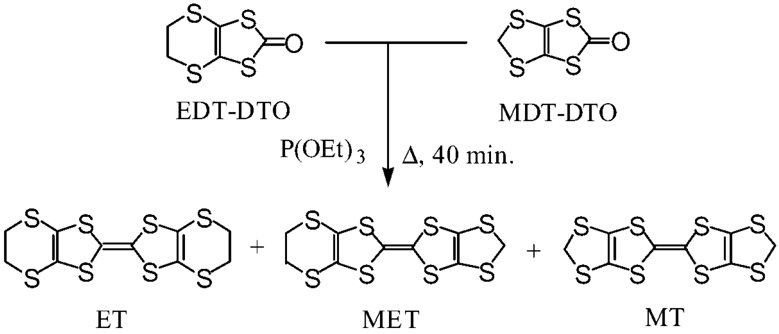
INTRODUCTION

Since the discovery of superconductivity in ET_2ReO_4 (ET: $C_{10}H_8S_8$: bis(ethylenedithio)tetrathiafulvalene) [1], ET has been one of the most promising donor molecule for an organic superconductor (OS). The development of new ET-based OS has been accompanied with the efforts to prepare more prominent donor molecules and their charge-transfer (CT) salt of a higher T_c. However, donor molecules better than ET do not seem to be synthesized yet. We developed an entirely new and facile way to prepare the ET-based CT salt which is expected to exhibit metallic conductivity and superconductivity. That is to make a CT salt containing mixed donors such as ET and MT (MT: $C_8H_4S_8$: bis(methylenedithio)-tetrathiafulvalene). Here, we describe the synthesis, X-ray crystal structure and electronic band calculation of $(ET)(MT)_2(BF_4)(THF)$.

EXPERIMENTAL

Synthesis of Donor Mixture

The mixture of MET, ET and MT was obtained by a cross-coupling reaction of equimolar EDT-DTO (1.455 g, 7.5 mmol) and MDT-DTO (1.545 g, 7.5 mmol) in freshly distilled $P(OEt)_3$ (Scheme 1). The red product was filtered, washed with methanol and dried under vacuum. Yield 73%. FABMS (M^+, %): 383.7980 (ET^+, 28.85), 369.7838 (MET^+, 27.16), 355.7834 (MT^+, 14.82). ^1H NMR ($CDCl_3$, δ): 4.958 (S-CH_2-S, s), 4.950 (S-CH_2-S, s), 3.301 (-CH_2-CH_2-, s). FT-IR (KBr, cm^{-1}): 2990, 2923 (CH_2 st), 1630 (C=C), 1408 (CH_2 def), 1284 (CH_2 weg), 765 (CH_2 oop). UV-vis (CH_3CN, nm): 224 s 322 m 344sh.



SCHEME 1.

Synthesis of $(ET)(MT)_2(BF_4)(THF)$

This complex was obtained by the typical electrochemical technique for crystal growing: The donor-mixture (20 mg) and n-$Bu_4N{\cdot}BF_4$ (52 mg 1.58×10^{-4} mol) were dissolved in freshly distilled THF (15 mL), respectively, and charged in an H-type cell. Thin plate crystals were collected from the anode after applying 2 μA for two weeks. Anal. Calcd for $C_{30}H_{24}BF_4OS_{24}$ C 28.67, H 1.92, S 61.23. Found C 28.10, H 1.84, S 62.15. FT-IR (KBr, cm^{-1}) 2974 (CH_2 st), 1336 (C=C), 1083 (BF_4 st), 764 (CH_2 oop). UV-vis (CH_2Cl_2, nm) 228 st, 320 m 462 m 558 vw.

X-ray Structure Analysis

X-ray diffraction data were collected on an Enraf-Nonius CAD-4 automatic diffractometer equipped with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The structure analysis shows that $(ET)(MT)_2$ $(BF_4)(THF)$ crystallizes in the monoclinic system with space group $P2_1/m$, $a = 7.599(2)$, $b = 32.572(7)$, $c = 10.157(2)$ Å, $\beta = 111.64(2)°$, $V = 2336.8(9)$ Å^3, $Z = 4$ and $R_1 = 0.0766$ $[I > 2\sigma(I)]$.

RESULTS AND DISCUSSION

The high-resolution FABMS analysis of the donor mixture exhibits that the intensity ratio of MET, ET and MT is close to 2 : 2 : 1. This composition could be accepted as the result of a semi-quantitative analysis based on the assumption that MET, ET and MT molecules have a nearly similar ionization potential due to their structural similarity.

Many attempts to obtain a CT salt of the mixed-donor were made by using n-$Bu_4N{\cdot}X$ (X = BF_4, ClO_4, PF_6, I_3, etc) as an electrolyte in an appropriate solvent such as nitrobenzene and THF charged in an H-type electrochemical cell. Among these, single crystals suitable for X-ray crystallography were obtained when n-$Bu_4N{\cdot}BF_4$ was used in THF. The composition of the crystal was verified as $(ET)(MT)_2(BF_4)(THF)$. It is interesting to see that the ratio of ET to MT in the crystal is 1 : 2 even though that in the pristine donor mixture is 2 : 1. Moreover, MET is not incorporated in the crystal.

The molecular structure is shown in Figure 1. The bond distances of C2-C3 and C4-C5 are 1.357(18) and 1.366(18) Å, respectively, which are longer than those of neutral MT (1.334 and 1.327 Å, respectively) [2]. On the contrary, the corresponding bond distances of ET do not deviate significantly from those of neutral ET. It is indicative of the charge separation of $(ET^0)(MT^{+0.5})_2$-$(BF_4^-)(THF)$ as observed in $(MT^0)(MT^{+0.5})_2(PF_6^-)$

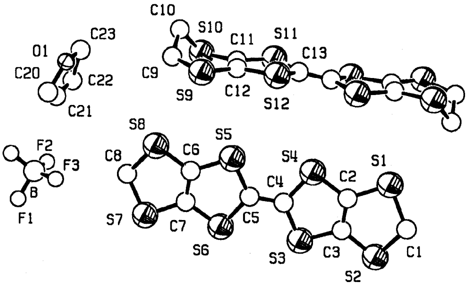


FIGURE 1 Molecular structure.

(DCE) [3]. In the crystal structure (Figure 2) MT molecules are stacking along the *a*-axis while ET molecules are arranged by the side-by-side mode. These two molecular arrays are incorporated each other in the *ab*-plane with ET and MT nearly perpendicular each other. The intermolecular network within the *ab*-plane is demonstrated in Figure 3, in which the short S...S contacts (3.226 – 3.694 Å) shorter than the sum of van der Waals radii (3.7 Å) [4] are indicated by dotted lines. These S...S networks are separated from each other by BF_4^- and THF. This is isostructural with $(MT)_3(PF_6)(DCE)$ [3] and α-$(MT)_3(BF_4)(TCE)$ [5].

Figure 4 shows the dispersion relation curve of the highest occupied band calculated for a donor layer of $(ET)(MT)_2(BF_4)$ on the basis of its r.t. crystal structure. In our tight-binding band calculations based upon the extended Hückel method, we employed double-ζ Slater-type orbitals for the *s* and *p* orbitals of carbon and sulfur to better represent the interstack S...S interactions between adjacent donor molecules. Since there are three donor molecules in a unit cell three highest bands are shown. The highest band represents the HOMO of MT molecule and is cut by the Fermi energy. It is similarly dispersive along the a^*- and c^*-directions which

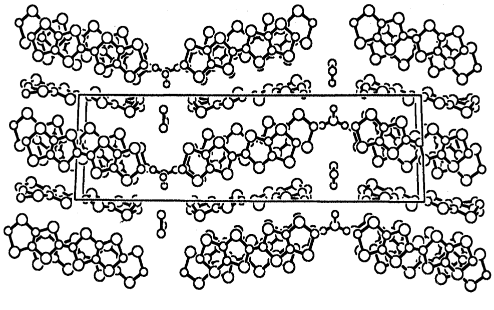


FIGURE 2 Crystal structure normal to (100) plane.

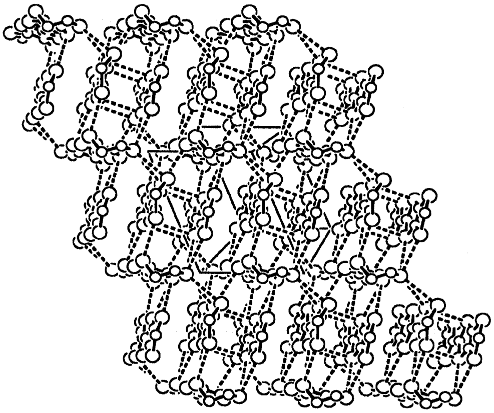


FIGURE 3 Intermolecular S…S network in the *ab* plane.

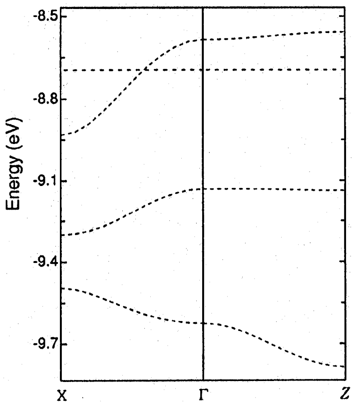


FIGURE 4 Band dispersion.

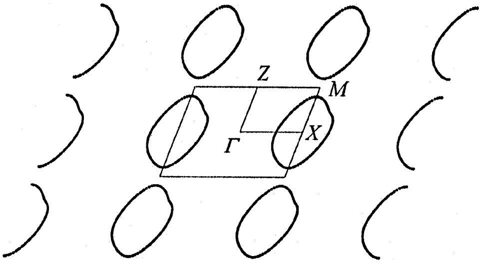


FIGURE 5 Extended Fermi surface.

means the compound is 2D metal. The Fermi surface associated with the highest band of Figure 4 is shown in Figure 5. The Fermi surface is distorted potato shape, so that the compound is 2D metal which is essentially similar to many layered organic conductors composed of donors and anions.

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