CRYSTAL AND ELECTRONIC STRUCTURES OF MOLECULAR CONDUCTORS BASED ON THE MULTI-SULFUR π-DONOR MOLECULES

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ABSTRACT

The electronic structures and electrical resistivities of molecular conductors based on multi-sulfur π-donor molecules such as BEDT-TTF(ET) and BMDT-TTF(MT) are examined. A new charge distribution rule due to the necessity of the reduction of Coulomb repulsion appears in two-dimensional (2D) conductors. The β"-ET₂(AuBr₂)₁₋ₓ(A)(A=IBr₂, I₃) is a new molecular metal with the 1D and 2D Fermi surfaces. The stepwise drops of the resistivity were observed in β-ET₂(AuI₂)₁₋ₓ(I₃)ₓ (x=0.1), indicating the existence of the high-Tc and low-Tc states. A new layered molecular superconductor, 0-ET₂(I₃)₁₋ₓ(AuI₂)ₓ (x<0.02) is also presented. Tc is 3.6 K. The system has an ideally 2D electronic structure.

INTRODUCTION

Since the electron conduction path in the organic molecular conductor is formed by the intermolecular overlapping of the frontier orbitals with π-character, the one-dimensionality has been long believed to be essential to the organic conductors. However, many two-dimensional (2D) conductors based on multi-sulfur π-donor molecules such as BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene, abbreviated hereafter as ET) and BMDT-TTF(MT) have been recently prepared.
RESULTS

Charge separation rule in 2D molecular conductor

The molecular structure and the charge distribution of the highest occupied molecular orbital (HOMO) suggest that the 2D property of MT is strongest in the ET analogs [1,2]. Figure 1 shows examples of the 2D molecular arrays of MT. At first sight, these 2D structures seem to have an instability, because the close contacts of the same molecules imply the enhancement of the electron-electron Coulomb repulsion. One possible way to avoid such an instability is to decrease the charge density. This may be the reason why MT compounds with 2D structures have large donor/anion ratio of 3. In addition, the charge distribution tends to be inhomogeneous. The examination of the bond lengths of the crystallographically independent molecules A and B (Fig. 1) suggests that the positive charges in \((\text{MT})_3(\text{PF}_6)(\text{DCE})(\text{DCE}=\text{1,2-dichloroethane})\) are distributed only on molecules A \((A^+1/2B^+1/2^0)(\text{PF}_6^-)(\text{DCE}^0))\) (Fig. 1). The neighbouring stacks of the charged molecules are separated by the neutral molecules. Thus, 2D system is reduced to 1D one, which is consistent with the large anisotropy of the resistivity [3].

Another characteristic charge distribution can be found in \((\text{MT})_3(\text{ClO}_4)(\text{DCE})\). The positive charges are distributed only on the molecule A \(((A^+B^0B^0)(\text{ClO}_4^-)(\text{DCE}^0))\). Each molecule A is surrounded by six neutral molecules B to form a "Wigner lattice". These facts suggest the existence of a charge distribution rule in 2D molecular conductors.

Electronic structures of ET compounds with linear anions

We have examined various molecular conductors of multisulfur \(\pi\)-donor molecules (Table 1). There are many compounds with linear anions. Despite the

![Fig. 1. Molecular arrangement of MT in \((\text{MT})_3(\text{PF}_6)(\text{DCE})\) (a) and that of \((\text{MT})_3(\text{ClO}_4)(\text{DCE})\) (b).](image)
semiconductive properties of $\beta'$-ET$_2$ICl$_2$, its structure closely resembles that of the well known superconducting $\beta$-ET$_2$I$_3$ [4]. Since two independent molecules are arranged alternately along the direction of the strongest intermolecular interaction (Fig. 2), the energy bands of $\beta'$-ET$_2$ICl$_2$ are separated into upper and lower bands. The upper band will behave as if it is a narrow half-filled band, so that the electrons will tend to be localized. This may be the reason why the system is semiconductive, in spite of the Fermi surface obtained by the simple tight-binding band calculation. The transverse interaction (c) (see Fig. 2) is very weak. The magnitude of the transverse interaction (c) is very sensitive to the intermolecular arrangement. If we can modify slightly the ET arrangement, a 2D closed Fermi surface will be obtained. When the anion size becomes large, the crystal structure transforms from $\beta'$-type structure to $\beta$-type one. In $\beta$-type structure, the interactions c and p2 become large. This is the origin of the 2D Fermi surface. It should be noted that the 2D electronic structure of $\beta$-ET$_2$I$_3$ is not so stable against the structural modification.

Fig. 2. Molecular arrangements, intermolecular overlap integrals (S), tight-binding band structures and Fermi surfaces. (a) $\beta$-ET$_2$I$_3$ (b) $\beta'$-ET$_2$ICl$_2$ (c) $\beta''$-ET$_2$(AuBr$_2$)$_{1-x}$(IBr$_2$)$_x$ (x=0.1).
TABLE 1

Molecular conductors of multi-sulfur \(\pi\)-donor molecules examined in this work

<table>
<thead>
<tr>
<th>BEDT-TTF COMPOUNDS</th>
<th>Monoclinic</th>
<th>P2(_1)/c pair of BEDT-TTF</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) BEDT-TTF molecule</td>
<td>P2(_1)/c side-by-side contact</td>
<td></td>
</tr>
<tr>
<td>(2) (BEDT-TTF)(_2)(CIO(_4))(TCE)</td>
<td>4:2:1 Triclinic</td>
<td>P1 2D conductor 20 Scm(^{-1})</td>
</tr>
<tr>
<td>(3) (BEDT-TTF)(_3)(CIO(_4)) (Dioxane)</td>
<td>3:2 Triclinic</td>
<td>P1 1D conductor 50</td>
</tr>
<tr>
<td>(4) α-(BEDT-TTF)(_2)PF(_6)</td>
<td>2:1 Triclinic</td>
<td>P1 semicond. 1</td>
</tr>
<tr>
<td>(5) β-(BEDT-TTF)(_2)BF(_4)</td>
<td>1:1 Monoclinic</td>
<td>P2(_1)/cm isostructural to (3)</td>
</tr>
<tr>
<td>(6) (BEDT-TTF)(_2)BrICl</td>
<td>1:1 Triclinic</td>
<td>P1 2D semicond. 1</td>
</tr>
<tr>
<td>(7) (BEDT-TTF)(_2)AsF(_6)</td>
<td>1:1 Triclinic</td>
<td>P1 3D contacts 10</td>
</tr>
<tr>
<td>(8) (BEDT-TTF)(_2)(TCNQ)</td>
<td>1:1 Triclinic</td>
<td>P1 1D metal 10</td>
</tr>
</tbody>
</table>

BPD-TTF COMPOUNDS

| (1) (BPD-TTF)\(_2\)PF\(_6\) | 3:2 Monoclinic | P2\(_1\)/m 1D conductor 0.3 Scm\(^{-1}\) |
| (2) (BPD-TTF)\(_2\)I\(_3\) | 2:1 Triclinic | P1 isomorphous to 2 |

Beside the β- and β'-structures, another modification has been recently discovered by Mori [5] and independently by us. We have prepared a series of β"-ET\(_2\)(AuBr\(_2\))\(_{1-x}\)(A)\(_x\)(A=IBr\(_2\), I\(_3\)). The structure resembles those of β- and β'-salts (Fig. 3). However, there is a striking difference in their electronic structures. Unlike β- and β'-salts, the largest interaction in β"-salt is that along c (Fig. 2). This is essential. The molecules are arranged regularly along c. The two energy branches originated from two crystallographically independent molecules are not separated by the energy gap. The 1D and 2D Fermi surfaces coexist, suggesting the β"-salt to be a new molecular metal with the intermediate dimensionality. In fact, the metallic state of β"-ET\(_2\)AuBr\(_2\) is stable down to 1.5 K (Fig. 4) and β"ET\(_2\)(AuBr\(_2\))\(_{1-x}\)(A)\(_x\)(A=IBr\(_2\), I\(_3\)) shows a resistivity minimum around 10 K.

It is well-known that there are high- and low-Tc states in β-ET\(_2\)I\(_3\) [6]. We have found that the high-Tc and low-Tc states exist in β-ET\(_2\)(AuBr\(_2\))\(_{0.9}\)(I\(_3\))\(_{0.1}\) (Fig. 5). Similar phenomena have been observed also in β-ET\(_2\)(I\(_3\))\(_{1-x}\)(I\(_2\)Br\(_x\))(x=0).
Recently we have prepared a new superconductor, $\theta$-ET$_2$($I_3$)$_{1-x}$($AuI_2$)$_x$ ($x<0.02$) with $T_c=3.6$ K (Fig. 6) [7]. In addition, $\theta$-ET$_2$($I_3$)$_{1-x}$($I_2Br$)$_x$ ($x<0.01$) and $\theta$-ET$_2$($I_3$)$_{1-x}$($AuI_2$)$_x$ ($x=0.03$) showed the partially

![Molecular arrangement (a), Fermi surface (b) and Superconducting transition (c) of $\theta$-ET$_2$($I_3$)$_{1-x}$($AuI_2$)$_x$ ($x<0.02$). Sa and Sc are two independent intermolecular interactions.](image-url)
superconducting behavior at 4 K [8]. The most characteristic feature of this new
superconducting system is in its ideally 2D properties. By neglecting the weak
reflections, the average structure was easily deduced (Fig. 6). The tight-
binding band calculation gave an ideally isotropic round Fermi surface, which can
be fairly reproducible by the nearly free electron model \((m^* = 2.5 m_e)\). Each ET
molecule is surrounded by six neighbouring molecules. This is the origin of the
ideally 2D metallic band. Thus, the crystals are composed of the metal layers
and anion sheets stacked alternately. This reminds us of the possibility of the
design of so-called "Ginzburg superconductor model."

By the appearance of the \(\theta\)-ET\(_{2}(I_3)_{1-x}(A)\) salts, the dimensionality of the
molecular conductors has been expanded greatly. Much progress will be expected
in the enlarged field of the multi-dimensional synthetic metals.

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of \(\theta\)-ET\(_{2}(I_3)_{1-x}(AuI_2)\).

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