MOLECULAR DESIGN AND SOLID STATE PROPERTIES OF NEW SUPERCONDUCTORS AND MOLECULAR METALS WITH ORDERED SPIN STRUCTURES

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ABSTRACT

We have examined several new types of molecular metals including three new superconductors, θ-(BEDT-TTF)2I3, κ-(BEDT-TTF)2I3 and [(CH3)4N][Ni(dmit)2]2. According to our molecular designing analyses based on simple tight-binding band calculations, there are two ways to avoid the metal-insulator transition encountered in one-dimensional(1D) systems. They are to design (1) 2D metals and (2) "multi-Fermi surfaces systems". The 2D layered molecular superconductors, θ-and κ-(BEDT-TTF)2I3, Ni(dmit)2 superconductors and magnetic molecular metals, R1,R2-DCNQI2Cu(R1,R2=CH3,CH3O,Br,Cl) are described from the molecular designing point of view.

INTRODUCTION

Since the opening of the field of the organic molecular superconductors in 1980 [1], about 30 molecular superconductors have been reported. We have found three types of superconductors, θ-(BEDT-TTF)2I3 [2], κ-(BEDT-TTF)2I3 [3] and [(CH3)4N][Ni(dmit)2]2 (dmit=4,5-dimercapto-1,3-dithiole-2-thione) [4]. Although the knowledge on the architecture of molecular superconductors has been enriched by the recent systematic studies on the molecular conductors based on the multi-sulfur π-donor and/or π-acceptor molecules, almost nothing is known about the way to control the superconducting transition temperature(Tc). Almost all the molecular metals reported prior to 1980 are one-dimensional(1D) systems, which
transform into insulating states at low temperatures. This metal instability arises from the pπ character of the conduction molecular orbital (COMO). Considering the anisotropy of pπ orbital and the resultant 1D electronic structure, it is easily imagined that the molecular metals without 1D metal instability is hardly designed. It has been commonly recognized that the suppression of the metal-insulator (M-I) transition is the first barrier to be overcome to obtain the molecular superconductors. Since the metal instability is originated from the nesting of a pair of the plane Fermi surfaces, there may be two ways to avoid the metal instability: (1) design of quasi-2D metals where Fermi surface (FS) is not plane-like. (2) design of "multi-Fermi surfaces system" where single nesting vector cannot open the gap all over the FS.

When the crystal structures of (TMTSF)2PF6 [5] and Li0.8(H3O)0.2[Pt(mnt)2]2 1.7H2O (mnt=1,2-dicyanovinylene-1,2dithiolato, C4N2S22−) [6] were reported, the importance of the intermolecular short contacts between chalcogen atoms (Se...Se, S...S) along the directions parallel and perpendicular to the molecular stacks came to be noticed, because the amplitudes of COMOs are largest on the chalcogen atoms. Thus a possible route to design 2D molecular metal became clear. These new structure chemical features require us to estimate the degree of the multi-dimensionality of the molecular conductors. We considered that it may be appropriate to use the anisotropy of intermolecular overlap integrals (S) of COMO as a semi-quantitative measure of the dimensionality of the system because the intermolecular interaction is dependent not only on the compactness of the intermolecular contacts but also on the anisotropy of COMO. If we adopt the simple extended Hückel approximation (transfer integral t=S), we can visualize the dimensionality of the molecular conductor as a form of simple band structure. When COMO is composed of HOMO (the highest occupied molecular orbital) of donor molecule and/or LUMO (the lowest unoccupied molecular orbital) of acceptor molecule, the band calculation becomes extremely simple. Recent preliminary ab initio band calculation of β-(BEDT-TTF)2I3 by Kubler et al. [7] and the observation of its Shubnikov-de Haas oscillation by Murata et al. [8] have suggested that the simple extended Hückel band structure based on the single MO (HOMO of BEDT-TTF) is not sufficient for the physical discussions. However, we assume here that COMO is composed of HOMO and/or LUMO in order to obtain a simple but clear perspective on the relation between the structure chemical characteristics and the dimensionality of various types of the newly prepared molecular metals.

RESULTS

2D layered superconductors. β- and κ-(BEDT-TTF)2I3 [2,3,9]. We have examined a series of new molecular conductors based on the multi-sulfur(or selenium )
\( \pi \)-donor and/or \( \pi \)-acceptor molecules and pointed out that the molecular stacking, which was considered to be an essential requirement for the design of the molecular metals, is not inevitable [10]. Moreover, we have discovered the two-dimensionally isotropic association of the \( \pi \)-molecules and resultant ideally 2D metal systems. \( \theta \)-BEDT-TTF\(_2\)I\(_3\) is a layered superconductor with \( T_c=3.6 \) K and monoclinic unit cell (\( a=16.387 \), \( b=8.466 \), \( c=12.832 \) A and \( \beta=108.56^\circ \)). The metal layers composed of BEDT-TTF semications and the insulating layers of I\(_3^-\) anions are stacked alternately along [001]. In the metal layer, each BEDT-TTF is surrounded by six molecules nearly isotropically (Fig. 1). Every BEDT-TTF molecule is approximately equivalent. But strictly speaking, three BEDT-TTFs are crystallographically independent. The anisotropy of the intermolecular overlap integrals is very small, which is consistent with the results of optical reflection experiments [11]. The extended Hückel band examination gave four energy branches. An isotropic FS was obtained, which is nearly reproducible by the nearly free electron model (\( m^*/m_e=2.5 \)). Owing to the strong anisotropy of the planar \( \pi \)-molecules, the possibility of the design of such an ideally 2D layered molecular superconductor has been never imagined before the molecular designing analysis of \( \theta \)-BEDT-TTF\(_2\)I\(_3\).
κ-(BEDT-TTF)$_2$I$_3$ is another typical 2D layered metal, which transforms into superconducting state at 3.6 K. Similar to θ-(BEDT-TTF)$_2$I$_3$, the crystal has an alternate arrangement of the BEDT-TTF metal layers and the I$_3^-$ insulating layers. In the metal layer, two BEDT-TTF molecules form a dimer (Fig. 2). The orientation of the neighbouring dimers is almost perpendicular to each other. Each parallel dimer is surrounded by four perpendicular dimers. This mode of the molecular arrangement is completely different from that of the traditional molecular metals. Simple extended Hückel band structure analysis gave ideally 2D FS, consistent with the anisotropies of $Hc_2$ [9] and optical reflection [12]. Contrary to the 2D band structure of θ-(BEDT-TTF)$_2$I$_3$ obtained by the extended Hückel method, the 2D band structures of θ- and κ-type salts are stable against the small change of the intermolecular interactions [13]. A new molecular superconductor, (BEDT-TTF)$_2$Cu(NCS)$_2$ with $T_c$ of 10-11 K [14] has the κ-type molecular arrangement, whose Shubnikov-de Haas oscillation consistent with the extended Hückel band structure seems to show the validity of the extended Hückel band examination [15].

By the molecular designing analyses of the θ- and κ-type salts, the existence of the ideally 2D layered metal becomes clear. As was expected, these 2D metals are stable down to low temperature and transform to superconducting states at ambient pressure. Thus, the design of 2D metals provides the first route to obtain new superconducting systems.

Multi-Fermi surfaces system. The existence of the second way to avoid 1D metal instability came to be noticed recently through the molecular designing analyses of two Ni(dmit)$_2$ superconductors. (TTF)[Ni(dmit)$_2$]$_2$ is the first molecular superconductor containing π-acceptor molecules [16]. Cassoux et al. have reported that TTF and Ni(dmit)$_2$ are stacked face-to-face to form segregated columns, which are connected through close S...S networks indicating the existence of the 3D conduction pathways. But our molecular designing analysis suggests the strong 1D nature of the electronic structure, despite of the 3D close S...S networks [17]. The intermolecular overlap integrals (S) of COMOs (LUMO of Ni(dmit)$_2$ and HOMO of TTF) show a large 1D anisotropy ($S_{\perp}/S_{\parallel} > 20$). The transverse interaction cannot become large owing to the $b_2g$ symmetry of LUMO. The intracolumn overlap integrals in TTF and Ni(dmit)$_2$ columns are almost the same including the negative sign. This indicates that two types of band associated with donor and acceptor chains, respectively, are "parallel" and have almost equal width. Tight-binding band calculation gave, roughly speaking, one donor band and two acceptor bands, each of which is approximately doubly degenerated (Fig. 3). The energy difference between HOMO and LUMO is not known.
Nevertheless, it may be safely said that the system has three (approximately doubly degenerated) plane Fermi surfaces and three independent Fermi wave numbers \((k_1, k_2, k_3)\). Since there is no special relation between these wave numbers, no single periodical potential cannot open the gap all over the Fermi surfaces. A complete gap formation requires a complex perturbation potential, which is no longer so energetically favorable compared with the purely 1D case. We call such a system "multi-Fermi surfaces" system and proposed it as a second strategy for avoiding M-I transition [17]. If this is correct, we need not necessarily introduce strong 2D interaction to stabilize metal state. Recent study on \(^{1}H\) NMR of TTF of \((\text{TTF})\text{[Ni(dmit)]}_{2}\) has indicated that as far as TTF chains are concerned, the electronic properties are 1D like [18].

We have recently found the second Ni(dmit)$_2$ superconductor, which is regarded as another type of "multi-Fermi surface system" [19].

We consider \(R_1, R_2\)-DCNQI-Cu systems to have "multi-Fermi surface nature" (\(R_1, R_2\)-DCNQI= 2,5-substituted N, N'-dicynoquinonediimine). DMe-DCNQI$_2$Cu is a new molecular metal with stable metal state [20]. DCNQI molecules are stacked face-to-face to form columns along the tetragonal c axis. The Cu cation is coordinated in \(D_{2d}\) distorted tetrahedral (Td) fashion to the N atoms of DCNQI units, connecting the columns of DCNQI molecules (Fig. 4). At first sight, 3D constitution of the molecules and the stable metal state seem to suggest the 3D electronic structure. However, owing to the geometrical restriction, the transverse interaction cannot become large enough to produce a 3D metal band. Our discovery of the mixed valence state of Cu (Cu$^+$, Cu$^{2+}$) open the possibility of 3d (Cu) orbital mixing with \(p_{\pi}\) conduction bands [21]. The mixed-valence state will imply that the high-lying d orbitals of Cu cations are located near the
Fig. 4. Distorted Td coordination around Cu and schematic energy diagram of $R_1,R_2$-DCNQI$_2$Cu.

$\Delta \epsilon/\epsilon_F = 1/2$

Fig. 5. FS of $R_1,R_2$-DCNQI$_2$Cu (see Fig. 4).

Fig. 6. Correlation between $T_M$ and $\Delta \epsilon$. 

Fermi level of 1D $p_\pi$ band of DCNQI. The d–$p_\pi$ mixing turns the original 1D system into the "multi-Fermi surfaces" one. This will remove the 1D metal instability. We have prepared a series of related compounds, $R_1,R_2$–DCNQI$_2$Cu ($R_1$, $R_2$ = CH$_3$, CH$_3$O, Br, Cl). Besides DMe–DCNQI$_2$Cu, DMeO–DCNQI$_2$Cu is metallic down to 0.5 K [22]. The other systems exhibit sharp M–I transitions ($T_{M-I}$ = 150 – 230 K). However, there is little structure difference between DMe (or DMeO)–DCNQI$_2$Cu and the other systems. We have made a simple extended Hückel molecular designing analysis to make this point clear.

The intracolumn overlap integral is much larger than the d–$p_\pi$ overlap integrals, that is, the system is essentially 1D. In order to see the role of the d–$p_\pi$ interactions, we simply assumed that the high-lying $d_{xy}$ orbital is on the Fermi level. If the $D_{2d}$ distortion around Cu is small, the conduction bands are formed from LUMO of DCNQI and three d-orbitals of Cu ($d_{xy}$, $d_{xz}$, $d_{yz}$). The contribution of $d_{xz}$ and $d_{yz}$ will become small with increasing the distortion (i.e. crystal field splitting of d–levels). We calculated the band structure with varying the energy splitting between $d_{xy}$ and $d_{xz}$, $d_{yz}$ ($\Delta e$). When $\Delta e$ is small, the d–$p_\pi$ mixing turns the 1D $p_\pi$-metal band into the multi-Fermi surfaces one, where three complicated planar Fermi surfaces appear. The Fermi surfaces become simpler with increasing $\Delta e$. At the large $\Delta e$ limit, one doubly degenerated plane fermi surface and a slightly waved plane Fermi surface appear. Thus, it is easily imagined that the increase of the distortion reduces the "multi-Fermi surface nature" and make it possible to vanish the Fermi surfaces by single nesting vector (Fig. 5). In fact, $\Delta e$ calculated from the structure data obtained us has a good correlation with $T_{M-I}$ (Fig. 6) [23]. The periodical lattice distortion wave with the wave vector of $c^*/3$ and the $D_{2d}$ distortion develop at $T_{M-I}$. Because of the existence of Cu$^{2+}$, the $D_{2d}$ distortion is considered to have a character of Jahn-Teller distortion. These facts suggest that the M–I transition is not a simple CDW transition but a cooperative structural phase transition induced by the CDW and Jahn-Teller type lattice distortions.

The d–$p_\pi$ mixing will enhance the state density $N(E_F)$. The observed large constant paramagnetism of (R$_1$,R$_2$–DCNQI)$_2$Cu (5.3 x10$^{-4}$ emu/mole) is more than twice of the Pauli paramagnetism estimated by assuming a simple 1D tight-binding $p_\pi$-metal band along the DCNQI stacks.

Besides the novel structural phase transition, the DCNQI$_2$Cu system show salient magnetic transition. Below $T_{M-I}$, the 2$p_\pi$ conduction electron system transforms into non-magnetic state. But there remains spins on Cu$^{2+}$, which are antiferromagnetically coupled to each other. Then the system undergoes a antiferromagnetic phase transition at $T_N$ (≈10 K). In (DMe–DCNQI)$_2$Cu with stable metal state, evidences showing the coexistence of the 2$p_\pi$ conduction electrons and ordered spins located mainly on Cu$^{2+}$ have been obtained [24, 25].
In this report, on the basis of the molecular designing analyses, we proposed two ways to stabilize the metal state of the molecular system, which will provide a guideline to design new molecular superconductors.

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