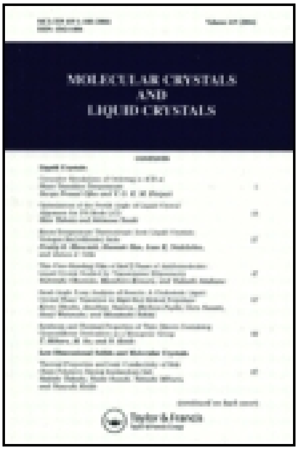

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An application of supramolecular chemistry to molecular conductors

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AN APPLICATION OF SUPRAMOLECULAR CHEMISTRY TO MOLECULAR CONDUCTORS

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From the viewpoint of "supramolecular chemistry", control of crystal and electronic structures of molecular conductors is described. We have developed a variety of cation and anion radical salts containing supramolecular assemblies. For the formation of the supramolecular structures, two types of supramolecular synthons, 1) iodine-based halogen bond $-I\cdots X-$ *(X = CN, Cl, Br, S), and 2) tellurium-based secondary bond* $Te\cdots S$*, have been examined. These compounds have indicated that supramolecular assemblies provide novel molecular packings and efficiently tune the donor or acceptor arrangement. We also found that the formal charge of conducting molecules can be controlled by the tuning of supramolecular assemblies.*

Keywords: molecular conductor; supramolecule; halogen bond; crystal structure; band calculation

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INTRODUCTION

Construction of higher dimensional electronic structures has been a matter of serious interest in the development of novel molecular metals and superconductors for the last twenty years [1]. In this process it has been revealed that the electronic state of the molecular conductor is sensitive to arrangement and orientation of component molecules. We have noticed that one molecule can exhibit a variety of arrangements and orientations depending on the counter part in crystal. Design of the *inter*-molecular interaction is indispensable in the rational development of molecular materials to still higher forms. As a possible solution to this problem, we are trying to introduce the concept of supramolecular assembly for the molecular conductor. This means that we change our viewpoint from the molecule to the ***supramolecular synthon*** [2]. We report here various molecular conductors containing supramolecular assemblies based on two types of supramolecular synthons, the iodine-based halogen bond and the tellurium-based secondary bond.

CATION RADICAL SALTS CONTAINING HALOGEN BONDS

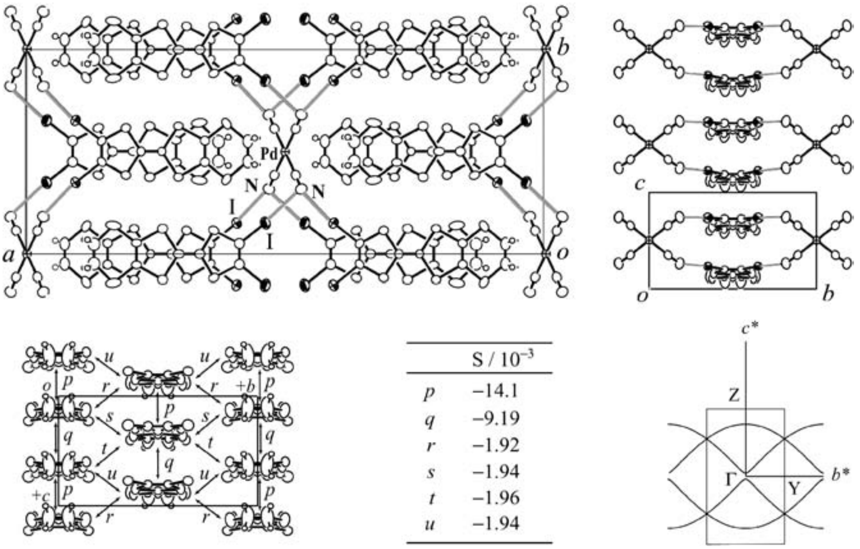
Carbon-bound iodine atoms are known to act as Lewis-acids and form short contacts with various species which can act as a Lewis-base (for example, $-$CN, $-$Cl, $-$Br, and $=$S). These non-covalent interactions that are classified into the halogen bond [3] can be strong and directional enough to control the assembly of molecules in crystal.

Iodine-containing Donor Molecules

An introduction of iodine atoms to TTF-type donor molecules has provided unique supramolecular assemblies. Since the electron negativity of iodine (2.2) is smaller than that of carbon (2.5), the introduction of iodine atoms does not depress the donor ability. In addition, a pπ orbital of the iodine atom contribute to HOMO of the donor molecule. The extension of HOMO toward iodine atoms is expected to reduce the on-site Coulomb interaction and enhance an interaction between conduction electrons and (functional) anions.

These iodine-containing donor molecules form a number of cation radical salts with various anions, including AuX_2^- ($X = Cl$, Br), $M(CN)_2^-$ ($M = Au$, Ag), $Au(CN)_4^-$, $M(CN)_4^{2-}$ ($M = Ni$, Pd, Pt), FeX_4^- ($X = Cl$, Br), and $Pd(dmit)_2^{n-}$. The halogen bonds between iodine atoms in the cation and $-$CN, $-$Cl, $-$Br, and $=$S segments in the anion form supramolecular assemblies which govern the donor arrangement within the conduction layer [4].

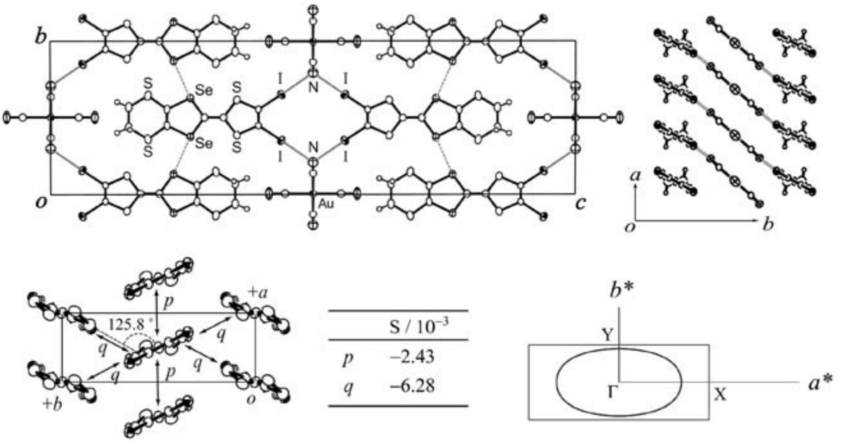
Among them, the cation radical salts of DIETS (diiodoethylenedithiodithiadiselenafulvalene) with square planar metal complex anions, $[PdCN_4]^{2-}$ and $[Au(CN)_4]^{-}$, are of special interest [5]. In the crystal of $(DIETS)_4[Pd(CN)_4]$, the $-I\cdots NC-$ network form the supramolecular cation$\cdots$anion assembly (Figure 1). All the four cyano groups in the anion are used to connect donor molecules and to form infinite cation$\cdots$anion chains along the *b* axis. Donor molecules are arranged in the head-to-head fashion along the *c* axis (stacking direction) and in the head-to-tail fashion along the *b* axis (side-by-side direction). The donor column is two-fold and there are many intra- and inter-column chalcogen$\cdots$chalcogen short contacts. Inter-molecular overlap integrals among HOMOs indicate that the donor molecules are dimerized within the column and the inter-column interactions are about 1/5 of the inter-dimer interaction. Tight-binding band calculation shows that this system has a pair of largely distorted open Fermi surface (Figure 1). Temperature-dependent resistivity of the $Pd(CN)_4$ salt shows a broad minimum around 80–90 K followed by a moderate upturn in the low-temperature region. This upturn is suppressed by an application of pressure up to 11 kbar. The higher pressure, however, induces a non-metallic behavior again.



	S / 10^{-3}
p	−14.1
q	−9.19
r	−1.92
s	−1.94
t	−1.96
u	−1.94

FIGURE 1 Crystal structure and calculated overlap integrals (S) and Fermi surface for $(DIETS)_4[Pd(CN)_4]$.

Replacement of the dianion $Pd(CN)_4^{2-}$ with the monoanion $Au(CN)_4^-$ largely affects the donor arrangement. In the $Au(CN)_4$ salt, the donor/anion ratio changes from 4:1 to 2:1. This compound also exhibits infinite cation⋯anion chains along the ***b*** axis (Figure 2). In contrast to the $Pd(CN)_4$ salt, the half of the four cyano groups in the anion is free from the supramolecular assembly and the $Au(CN)_4$ anions stack along the ***a*** axis with short Au⋯Au and Au⋯N contacts. The donor molecules are aligned uniformly in the head-to-head fashion along the ***a*** axis. The plane normal of the donor molecule is tilted from the ***a*** axis. Along the ***b*** axis (side-by-side direction), the donor molecules are arranged in the head-to-tail fashion and neighboring donors are tilted in opposite directions giving the dihedral angle of 125.8°. Therefore, the donor arrangement in the $Au(CN)_4$ salt is classified into the θ-type and the calculated Fermi surface is two-dimensional (Figure. 2). Resistivity of the $Au(CN)_4$ salt shows gradual increase down to 226 K at which a sharp transition to an insulating phase occurs, as is frequently observed in the θ-type salts. In contrast to the case of conventional θ-type salts, however, an application of pressure lowers the transition temperature. In the θ-type salts, the dihedral angle between neighboring donors is a key parameter for the electronic state. There seems to be no doubt that the strong inter-molecular I⋯N contacts make a difference in pressure dependence of the dihedral angle.



	S / 10^{-3}
p	−2.43
q	−6.28

FIGURE 2 Crystal structure and calculated overlap integrals (S) and Fermi surface for θ-$(DIETS)_2[Au(CN)_4]$.

In both salts, the DIETS molecules form the conduction layer and its formal charge remains +1/2. The plane normal of the square planar anion is inclined toward the conduction layer in the $Pd(CN)_4$ salt. On the other hand, in the $Au(CN)_4$ salt, the plane normal is parallel to the conduction layer and is inclined toward the side-by-side direction.

Unusual pressure effects in both salts indicate that rigid cation $\cdots$ anion connections would induce unique distortion of the donor arrangement under pressure. This is an important aspect of the supermolecular assembly in the molecular conductor.

Supramolecular Anions Based on Iodine-containing Neutral Molecules

The halogen bond can occur between Lewis-acidic iodine atoms in *neutral* molecules and Lewis-basic anions to form anionic supramolecules. These rigidly constructed anion networks accommodate cation radicals of organic donors and regulate their arrangement and orientation [6]. In addition, chemical modification of neutral molecules can tune the electronic state of the conduction part.

Neutral molecules with the $-C\equiv C-I$ group, DIA (diiodoacetylene), IIB (iodoethynylbenzene) and *p*BIB (*p*-bis(iodoethynyl)benzene), form one-dimensional chains with the halide anions (Cl^- and Br^-) in cation radical salts of BEDT-TTF (Bis(ethylenedithio)tetrathiafulvalene; ET). In these infinite chains, the neutral molecule and the halide anion are repeated alternately with short $-I\cdots X^-$ ($X=Cl$, Br) contacts. In every crystal, the donor arrangement retains basically the β-type. The most interesting point is that the unit length of the chain controls the donor/anion ratio and thus the formal charge of the BEDT-TTF molecule. The unit lengths are 11.64 Å for the DIA $\cdots$ Br chain, 16.07 Å for the IIB $\cdots$ Br chain, and 18.63 Å for the *p*BIB $\cdots$ Br chain. This means that negative charges on the chain are diluted with increasing the unit length. Considering that the donor/anion ratios in these salts are 2/1 for the DIA $\cdots$ Br chain, 5/2 for the IIB $\cdots$ Br chain, and 3/1 for the *p*BIB $\cdots$ Br chain, the formal charge of the donor molecule is reduced ($+0.5 \rightarrow +0.4 \rightarrow +0.33$) according to the decrease in density of the negative charge on the anion chain (Figure 3). Tight-binding band calculations indicate that all these salts have a two-dimensional Fermi surface. All of them are metallic down to 4.2 K.

In general, molecular conductors are classified into the ion radical salt where cation and anion govern the electronic state. We emphasize, however, that the neutral molecule can act as the *third* parameter by means of the supramolecular assembly. It should be noted that neutral molecules do not require a charge adjustment in designing the supramolecular framework and can accept a variety of functional substituents.

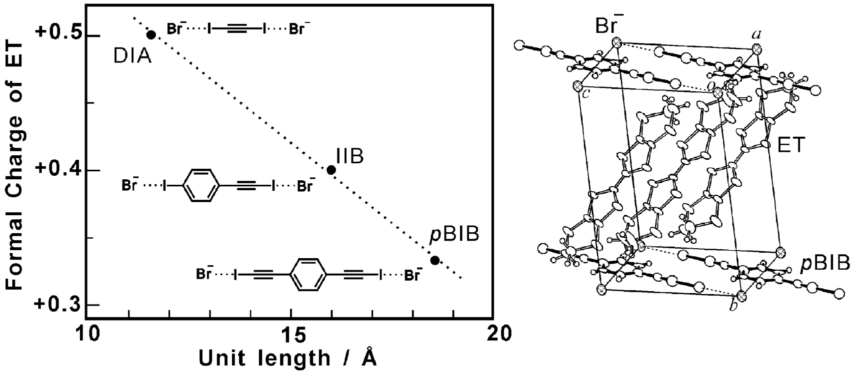


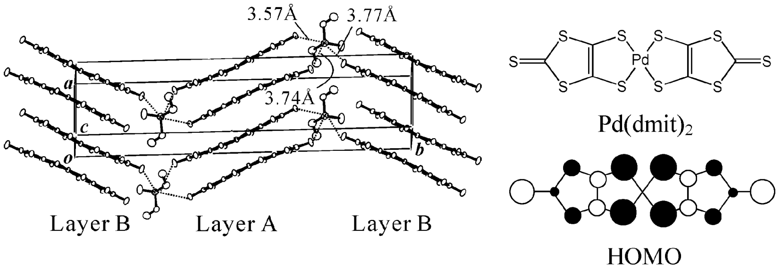
FIGURE 3 Crystal structure of $(ET)_3Br(pBIB)$ (right) and relation between the formal charge of ET and the unit length of the anionic supramolecular chain in $(ET)_2Br(DIA)$, $(ET)_5Br_2(IIB)$, and $(ET)_3Br(pBIB)$ (left).

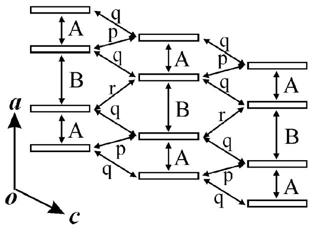
ANION RADICAL SALTS CONTAINING SECONDARY BONDS

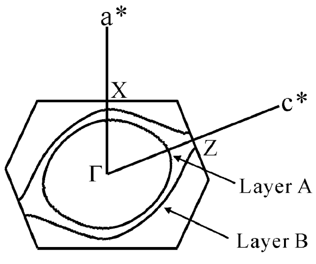
Tellurium has a strong tendency to form secondary bonds in crystalline compounds [7]. We have used the tellurium-based secondary bond as a supramolecular synthon in anion radical salts.

The electron acceptor molecule $Pd(dmit)_2$ (dmit = 2-thioxo-1,3-dithiol-4,5-dithiolate) is known to provide various anion radical salts including six high-pressure superconductors. Electronic structure and conducting properties of these $Pd(dmit)_2$ are full of variety depending on the counter cation and external pressure. The $Pd(dmit)_2$ salts are characterized by the face-to-face stacking of strongly dimerized $Pd(dmit)_2$ units. This strong dimerization and small energy difference between HOMO and LUMO induce a HOMO-LUMO band inversion in the band structure. At ambient pressure, the conduction band is formed by the HOMO band. Small changes of ***inter-dimer*** interactions within the conduction layer, induced by the shape and size effects of the cation, strongly affect anisotropy of the HOMO band and the electronic state under high pressure [8].

Recently, we have studied $Pd(dmit)_2$ salts with a series of pyramidal cations and found interesting supramolecular interactions in Me_3Te and Et_2MeTe salts. In this paper, we focus our attention on the Et_2MeTe salt. The unit cell contains two $Pd(dmit)_2$ columns, both of which are parallel to the *a* axis (Figure 4). These two columns of strongly dimerized $Pd(dmit)_2$ units are crystallographically independent and there are two different conduction layers (A and B) separated by Et_2MeTe^+ cations. The most prominent feature is an existence of very short Te···S contacts between







	S / 10^{-3} (among HOMOs)	
	Intra-column (A, B)	Inter-column (p, q, r)
Layer A	−44.76, −6.82	−1.60, −2.46, −3.84
Layer B	−46.60, −7.83	−1.71, −2.52, −3.48

FIGURE 4 Crystal structure and calculated overlap integrals (S) and Fermi surface for $Et_2MeTe[Pd(dmit)_2]_2$.

the cation and the terminal thioxo group of the $Pd(dmit)_2$ molecule. The Et_2MeTe cation contacts with two $Pd(dmit)_2$ molecules in the dimer within the layer A, whereas it contacts with only one $Pd(dmit)_2$ molecule within the layer B. This difference in pattern of the cation···anion interaction provides two types of Fermi surfaces associated with the layers A and B. In the layer A, the cations squeeze into the dimer. Competition between strong Pd···Pd and Te···S contacts bends the outer five-membered ring toward the terminal thioxo groups in adjacent dimers. In the HOMO of $Pd(dmit)_2$, thioxo sulfur atom p orbitals are out of phase with other sulfur atom p orbitals. These features reduce an inter-dimer HOMO···HOMO interaction within the column (designated B in Figure 4) and make an overall inter-dimer interaction (including B, p, q, r in Figure 4) more isotropic. Therefore, the calculated Fermi surface for the layer A is closed, whereas the one for the layer B is open (Figure 4). The Et_2MeTe salt shows a metallic behavior down to 30–40 K. Below this temperature, an upturn of the resistivity occurs. The system, however, remains moderately conductive even at 4.2 K.

The above example demonstrates that the supramolecular interaction provides the system where two different types of Fermi surfaces coexist within the ‘same’ crystal. This indicates that the tellurium-based secondary bond can be used for the tuning of the molecular arrangement and thus inter-molecular interactions in the anion radical salts.

CONCLUSION

We have demonstrated that supramolecular interactions have a significant influence on the electronic state of the molecular conductor. Further study will pave the way for a conceptual advance of material design in the field of the molecular conductor.

REFERENCES

[1] Kagoshima, S., Kato, R., Fukuyama, H., Seo, H., & Kino, H. (1999). In P. Bernier, S. Lefrant, & G. Bidan, (Eds.), *Advances in Synthetic Metals—Twenty Years of Progress in Science and Technology-*, Elsevier p. 262.

[2] Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.*, *34*, 2311.

[3] For example, Corradi, E., Meille, S. V., Messina, M. T., Metrangolo, P., & Resnati, G. (2000). *Angew. Chem. Int. Ed. Engl.*, *39*, 1782.

[4] Imakubo, T., Sawa, H., & Kato, R. (1995). *Synth. Met.*, *86*, 1847.

[5] Imakubo, T., Sawa, H., & Kato, R. (1995). *J. Chem. Soc., Chem. Commun.*, 1667; Imakubo, T., Miyake, A., Sawa, H., & Kato, R. *Synth. Met.*, (2001). *120*, 927.

[6] Yamamoto, H. M., Yamaura, J., & Kato, R. (1998). *J. Am. Chem. Soc.*, *120*, 5905.

[7] Alcock, N. W. (1972). *Adv. Inorg. Chem. Radiochem.*, *15*, 1.

[8] Kato, R., Liu, Y-L., Hosokoshi, Y., Aonuma, S., & Sawa, H. (1997). *Mol. Cryst. Liq. Cryst.*, *296*, 217. Kato, R., Yamamoto, K., Kashimura, Y., Okano, Y., & Aonuma, S. (1999). *Synth. Met.*, *103*, 2020.