# IV-J Development of New Molecular Conductors

Molecular conductors at the first stage were single component systems where only one degree of freedom governs transport properties. For example, the conduction band in KCP is a one-dimensional $d_{z^2}$ band. TTF-TCNQ has a HOMO band of TTF and a LUMO band of TCNQ, but both of them are one-dimensional pure π bands. Recently, however, increasing number of interesting systems which have “two” bands with different characters near the Fermi level, or where itinerant pπ electrons interact with localized *d* spins, have been reported: for example, the DCNQI-Cu salt with π and itinerant *d*, Pd(dmit)$_2$ salts with a two-dimensional HOMO band and a one-dimensional LUMO band, the organic superconductor (TMET-STF)$_2$BF$_4$ with a two-dimensional HOMO band and a one-dimensional HOMO band. On the other hand, in the BETS salt with FeCl$_4$, localized *d* spins on the Fe$^{3+}$ ions interact with itinerant π electrons. Such multi component systems exhibit interesting physical properties derived from the interplay of many degrees of freedom. The aim of this project is to forward further development of molecular-based conductors with many degrees of freedom.

Main subjects are;

(1) Supramolecular organic conductors: Design of the *inter*-molecular interaction is indispensable in the rational development of molecular materials to still higher forms. From this point of view, we are trying to introduce supramolecular chemistry into the molecular conductor. We have a great interest in an iodine-based *halogen bond* as a supramolecular synthon. 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). This non-covalent interaction (halogen bond) can be strong and directional, which would lead to 1) the reliable regulation of the molecular arrangement and orientation, 2) enhancement of an interaction between conduction electrons and functional molecules in the assembly of molecules.

(2) π-*f* system: 4*f* electrons in rare-earth ions exhibit very large anisotropic magnetic moments, as a result of the strong spin-orbit coupling and the high degeneracy due to strong correlation in a well-localized 4*f* orbital. This feature is never observed in 3*d* ions, organic π molecules nor other systems. We are trying to develop molecular conductors where 4*f* electrons are incorporated into a conduction π electron system. Using the heavy rare-earth complex anions [Ln(NCS)$_6$]$^{3-}$ (Ln = Ho, Er, Yb and Y) and organic donors BO and TTP, we have synthesized the first stable π-*f* metals that remain metallic down to very low temperature.

(3) Two-band system based on transition metal complexes: We have studied Pd(dmit)$_2$ salts with a series of pyramidal cations and found interesting supramolecular interactions through the tellurium-based secondary bond in Me$_3$Te and Et$_2$MeTe salts. These compounds demonstrate 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.

## IV-J-1 Synthesis and Properties of Novel Donor-Type Metal-Dithiolene Complexes Based on 5,6-dihydro-1,4-dioxin-2,3-dithiol (edo) Ligand

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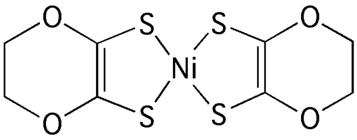
The donor-type metal-dithiolene complexes, where the central C=C bond in the TTF-based organic donor is replaced by the transition metal, are promising materials for the formation of molecular metals and superconductors. One drawback in the conventional donor-type metal-dithiolene complexes is their poor-solubility in usual organic solvents which gives a difficult obstacle in the preparation of the cation radical salt with high quality. We have successfully synthesized a novel donor-type metal-dithiolene complex, Ni(edo)$_2$ [edo = 5,6-dihydro-1,4-dioxin-2,3-dithiolate], and its mixed-ligand derivatives. The edo complex is an analog of the organic donor BEDO-TTF (BO) [bis(ethylenedioxo)-tetrathiafulvalene]. The BO molecule shows higher solubility in various organic solvents than other organic donors and is known to provide superconducting cation radical salts. The obtained edo-based complexes exhibit largely improved solubility and their donor abilities have been confirmed. The cation radical salts based on these newly synthesized metal complexes have exhibited novel donor arrangements including the trimer-based κ-type one. Notably the edo ligand shows a unique repulsive inter-ligand interaction and the face-to-face overlap of the edo ligands seems difficult to occur in the crystal, which frequently leads to the twisted and spanning overlap of the metal complexes. This is in contrast to the case of BO-based cation radical salts where the organic donor BO shows a strong tendency to aggregate into a two-dimensional layered structure by the aid of both inter-molecular C–H···O and side-by-side heteroatom contacts. In other words, the edo unit seems to have a strong tendency to restrict the mode of overlap, as the ethylenedioxo unit within BO but in the opposite way. An origin of this unique feature of the edo ligand remains an open question. We would make the most of what the edo ligand provides (improved solubility and unique molecular arrangement) in combination with the extended π-ligands derived from TTF. In such a largely elongated π molecule, its poor solubility is a serious problem and the spanning overlap mode plays an important role in the formation of the three-dimensional electronic structure. Further studies are in progress.



Ni(edo)$_2$

## IV-J-2 Structural and Physical Properties of Conducting Cation Radical Salts Containing Supramolecular Assemblies Based on *p*BIB Derivatives (*p*BIB = *p*-Bis(iodoethynyl)benzene)

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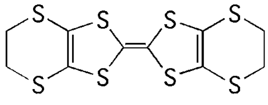
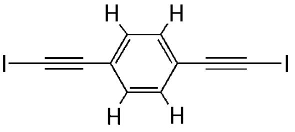
A cation radical salt $(\mathrm{ET})_3\mathrm{Cl}(p\mathrm{BIB})$ (ET = bis(ethylenedithio)tetrathiafulvalene, *p*BIB = *p*-bis(iodoethynyl)benzene) salt is a unique organic metal containing supramolecular assemblies based on the *p*BIB molecule and the Cl anion, $\cdots\mathrm{Cl}^{-}\cdots p\mathrm{BIB}\cdots\mathrm{Cl}^{-}\cdots$. We newly prepared chloride and bromide salts of ET with the use of di- and tetra-substituted *p*BIB derivatives: 1,4-difluoro-2,5-bis(iodoethynyl)benzene (DFBIB), 1,2,4,5-tetrafluoro-3,6-bis(iodoethynyl)benzene (TFBIB), 1,4-bis(iodoethynyl)-2,5-dimethylbenzene (BIDMB), and *p*-bis(iodoethynyl)benzene-$d_4$ ($p$BIB-$d_4$). The substitution effect has been studied by X-ray structure analyses, tight-binding band calculations, and resistivity measurements. The halide anion replacement ($\mathrm{Br}^{-} \rightarrow \mathrm{Cl}^{-}$) as well as the deuterium and difluoro-substitutions on the *p*BIB molecule do not change the fundamental crystal structure and the metallic behavior but change the $\mathrm{X}^{-}\cdots p\mathrm{BIB}\cdots\mathrm{X}^{-}$ period and the inter-chain distance. These systematic deformations of the anion framework act as *anisotropic chemical pressure* onto the donor layer and lead to a rotation of the donor molecule around the longitudinal molecular axis. The rotation of the donor molecules affects on the inter-molecular overlap integrals of HOMO and the tight-binding calculations indicate that the difluoro- and $\mathrm{Cl}^{-}$-substitutions increase the anisotropy of the Fermi surface. On the other hand, the tetrafluoro- and dimethyl-substitutions induce different donor arrangements that lead to semiconducting behaviors.



ET



*p*BIB