

Tetrachalcogenafulvalenes with outer chalcogeno substituents. Precursors of organic metals, superconductors, LB films, etc.

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Abstract - An overview of a series of tetrachalcogenafulvalene derivatives and their charge transfer complexes is presented in connection with the molecular designing of molecular conductors of single-component (molecular fastener and chalcogen-chalcogen chain compound), two-dimensional organic metals, organic superconductors, LB films, etc.

INTRODUCTION

Many aspects of organic solid state chemistry and physics have been developed since the discovery of tetrathiafulvalene (TTF) by F. Wudl (ref. 1). Among them are molecular conductors including organic metals and organic superconductors. Organic metals such as TTF·TCNQ are low-dimensional in nature due to the electrical conduction only along the face-to-face stacking columns and inevitably sustain metal-insulator instabilities at low temperatures. If these instabilities were suppressed somehow, one might have high possibility of getting organic superconductors. One of such methods of the suppression is a chemical modification to increase the dimensionality of molecular conductors (ref. 2). Chalcogen atoms have been known to form intermolecular chalcogen-chalcogen atomic contacts, and hence, in order to increase the dimensionality of charge transfer (CT) complexes replacement of sulfur atoms of TTF with other chalcogen atoms with bigger van der Waals (vdW) radius is effective. These intermolecular chalcogen-chalcogen atomic contacts may enable electrons to transport not only along the face-to-face stacking columns but also perpendicular to the columns. This idea was successfully adopted in the first organic superconductor (TMTSF)₂PF₆ by Bechgaard and Jerome et al. (ref. 3) which is quasi two-dimensional due to the intercolumn Se..Se contacts. The extension of the idea is to use tellurium atoms whose vdW radius (2.06 Å) is 14% and 8% bigger than those of sulfur (1.80 Å) and selenium (1.90 Å), respectively (ref. 4). But heavy molecules have disadvantages to lower the superconducting critical temperature T_c supposing that the superconduction is BCS type and the lattice motion produces the attractive forces for Cooper pairs since T_c ~ 1/(molecular weight)^{1/2}. Therefore an alternative idea was to prepare CT complexes with sufficiently high dimensionality by employing molecules which contain lighter atoms than selenium. It was found by us that a complex of BEDT-TTF, which has an extended skeleton of TTF with four sulfur atoms, can provide two-dimensionality to suppress the metal-insulator transitions (ref. 2). Extension of the works on the complexes of this capped alkythio substituted TTF revealed several superconductors by several groups.

In the BEDT-TTF complexes, the characteristic properties of the metallic behaviors and dimensionality are to a large extent ascribed to the large number of intermolecular interactions to which sulfur atoms contribute significantly. Two-dimensional S..S networks have been observed along the molecular short axis in many BEDT-TTF complexes. Therefore the C₆S₈ group (Fig. 1) is the basic segment which is responsible for the electronic and structural properties above mentioned.

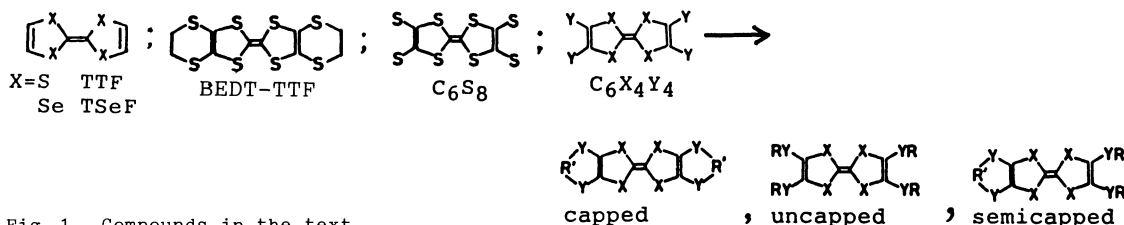


Fig. 1. Compounds in the text

Heavy hetero atoms such as chalcogenides and halogens in a molecule are known to increase molecular polarizability and reduce on-site Coulomb repulsive energy. These heavy-atom effects are preferable factors for electric conduction in a crystal. The electric conductivity σ is represented by $\sigma = n e \mu$, and in the case of semiconductors as $\sigma = \sigma_0 \exp(-E_g/2kT)$. Where n is the density of carrier (electron and/or hole), e is the unit charge of an electron, μ is the mobility of the carrier, E_g is band gap and k is Boltzmann constant. Heavy atoms in a molecule are supposed to increase the mobility through the formation of intermolecular atomic contacts and/or to increase the density of the carrier through the reduction of band gap.

For example, tetrathiatetracene and tetraselenatetracene exhibit the electrical conductivities of 10^{-8} and 10^{-7} Scm^{-1} , respectively, under vacuum. These are the most conductive ones among the molecular crystals of one component (excluding co-ordination compound with metal ions), though there have been several arguments against the results because of the possibility of impurity conduction. The application of pressure to a crystal will enforce the intermolecular interactions and hence increase the conductivity. Tetraselenatetracene has a conductivity of 10 Scm^{-1} at 200 kbar and p-iodanil becomes more conductive (20 Scm^{-1}) at 500 kbar though the latter material is a good insulator at ambient pressure (10^{-12} Scm^{-1}). Therefore $\text{C}_6\text{X}_4\text{Y}_4$ compounds (Fig. 1) are good candidates for the conductive materials of single-component as well as of CT complexes. In this paper we present a few new phenomena on the electrical conduction and structural features of these $\text{C}_6\text{X}_4\text{Y}_4$ compounds, especially single-component conductors in detail. These $\text{C}_6\text{X}_4\text{Y}_4$ molecules are classified into three groups (Fig. 1) where the substituents are restricted to alkyl groups in this work.

EXPERIMENTAL

Fig. 2 illustrates the synthetic schemes which are simple and composed of known procedures. A series of C_6S_8 compounds with normal alkyl groups; tetrakis(n-alkylthio)-TTF, $\text{TTC}_n\text{-TTF}$, $n=1-18$, was synthesized according to the Scheme 1 and 2. The yield of $\text{TTC}_n\text{-TTF}$ decreased with increasing the length of the alkyl chain in the last coupling reaction in Scheme 1 (C_1 90, C_8 52%). Scheme 2 surpasses Scheme 1 in the total yield though the yield also decreased with increasing n in the last step (C_3 96, C_{10} 72, C_{17} 63%). The other alkylchalcogeno derivatives of TTF ($\text{X}=\text{S}, \text{Y}=\text{Se}, \text{Te}$) were prepared on the basis of the method developed by Aharon-Shalom et al. for $\text{TTeC}_n\text{-TTF}$ ($n=1,2$) (ref. 5) (Scheme 3). The yield of $\text{TYC}_n\text{-TTF}$ ($\text{Y}=\text{Se}, \text{Te}, n=1-18$) is fairly high which did not depend on the length of the alkyl chain but on the purification process. A series of $\text{X}=\text{Se}$ compounds ($\text{Y}=\text{S}, \text{Se}, \text{Te}, n=1$) was also prepared by the same method as $\text{TYC}_n\text{-TTF}$ ($\text{Y}=\text{Se}, \text{Te}$) above mentioned (Scheme 4). In these cases the yield was lower than those of the TTF derivatives maybe due to the lower reactivity of $\text{C}_6\text{Se}_4\text{Y}_4^{4-}$ than that of $\text{C}_6\text{S}_4\text{Y}_4^{4-}$ to alkylhalides. An alternative route to prepare $\text{TYC}_1\text{-TSeF}$ is to treat tetralithio derivative of TSeF with dimethyldichalcogenide and this method gave higher yield than that by Scheme 4. The capped C_6S_8 compounds were prepared by the same procedures as in Scheme 1 & 2. In this case Scheme 1 surpasses Scheme 2 where polymerization process by the intermolecular cross linkage of $\text{C}_6\text{S}_8^{4-}$ by alkyl dihalide easily occurs even by dilution method. A semicapped compound ($n'=2, n=7$) was prepared by cross coupling of the corresponding ketones and the compound was isolated from the capped (BEDT-TTF) and uncapped ($\text{TTC}_7\text{-TTF}$) compounds. All the materials were purified by repeated recrystallization and column chromatography.

The melting points were measured using Yanagimoto MP-S3 (uncorrected) and/or Seiko DSC-10, SSC/580. Redox potentials were determined using cyclic voltammetry (Yanagimoto p-1100) in a standard three-electrode cell (Pt electrodes, vs SCE) in anhydrous 1,2-dichloroethane with 0.1 M Bu_4NBF_4 under N_2 with scan rate of 100 mV/s. X-ray data were collected on a Rigaku four-circle diffractometer with Cu K α radiation. The electrical conductivities of single crystals and compacted samples were measured by a two-probe method under a vacuum of ca. 10^{-4} Pa with gold paste for single-component materials.

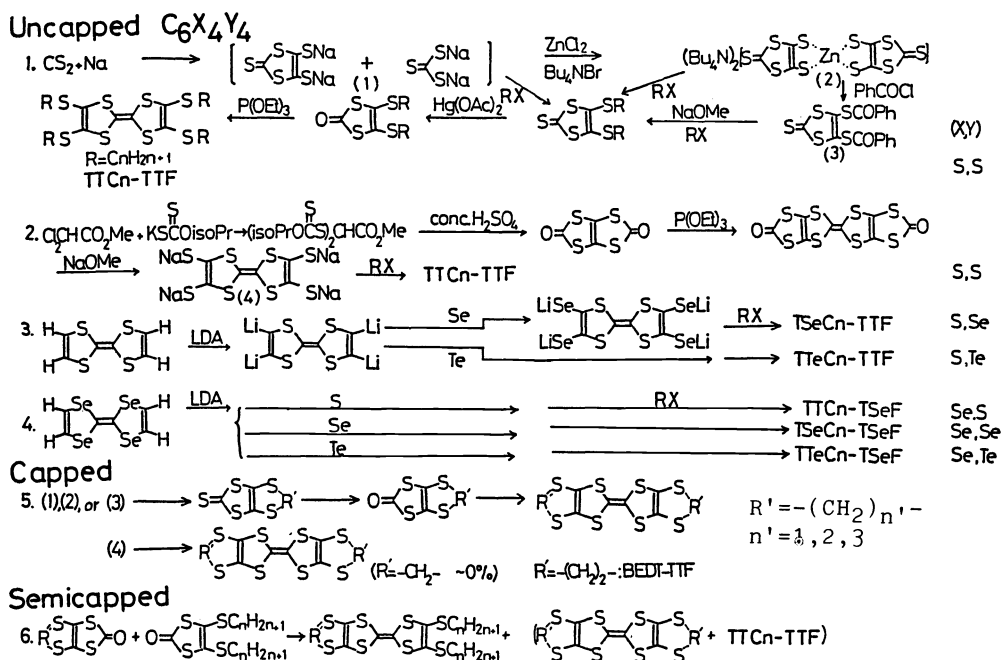


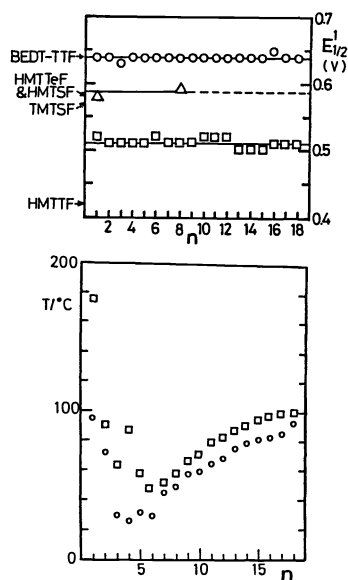
Fig. 2. Synthetic scheme of $\text{C}_6\text{X}_4\text{Y}_4$ compounds

TTC_n-TTF AND FASTENER EFFECT (ref. 6)

Judging from the first half wave redox potentials ($E_{1/2}^1 = (E_{\text{ox}}^1 + E_{\text{red}}^1)/2$) of a series of TTC_n-TTF (Fig. 3), the electronic energies of the highest occupied molecular orbitals (HOMO) of the alkyl substituted C₆S₈ molecules are almost independent on the size of the substituents. In addition to that, the capped (n'=1,2,3 in Scheme 5, Fig. 2) and semicapped (n'=2, n=7 in Scheme 6, Fig. 2) molecules show almost the same oxidation potentials indicating that the HOMO energies are also independent on the shape of the substituents. However, the features are quite different in the solid state where the size and shape dependence of the solid state ionization potentials are clearly observed. BEDT-TTF (4.78 eV) has a significantly smaller threshold potential than TTC₁- (5.05 eV) and TTC₂-TTF (5.15 eV), while TTC_n-TTF's with large n have even smaller values (4.80, 4.65, 4.60, 4.70 eV for n=8,9,10,14, respectively) than both of them. The melting points of C₆S₈ compounds also show the size and shape dependence. The melting points of uncapped TTC_n-TTF are relatively low compared with those of the capped ones (191, 243, 265 °C for n'=1,2,3, respectively) and they decrease rapidly with increasing the length of the alkyl chains up to n=4 then increase gradually with n (Fig. 4). The semicapped compound has even lower melting point and is liquid at room temperature. By cooling the compound rapidly to liq. N₂ temperature no crystals but a glassy state appeared. While keeping the oil below -20 °C for one week made it crystallize with a melting point of 12 °C. These peculiar dependences of the ionization potentials and melting points on the size and shape of the substituents are understandable on the basis of the conformation and stacking/packing manner of the molecules in the crystals.

The C₆S₈ moieties of TTC_n-TTF (n=1,2) and BEDT-TTF are not planar but show boat-like form (Fig. 5). A number of short S...S atomic contacts are observed in the crystals of TTC₁-, TTC₂-TTF and BEDT-TTF, but the modes of the contacts are different between the uncapped and capped ones. In the latter the specific S...S contacts (3.48-3.69 Å) are along the molecular short axis as mentioned before, while along the molecular long axis are observed very short contacts (3.48-3.66 Å) in TTC₁- and TTC₂-TTF crystals. Furthermore both of the outer and inner sulfur atoms construct the S...S networks of BEDT-TTF, but only outer sulfur atoms contribute to the contacts of TTC_n-TTF (n=1,2) (Fig. 5). Since the atomic population of inner sulfur atoms is fairly larger than that of outer sulfur atoms of the capped and uncapped C₆S₈ molecules, the mode of the contacts of the capped compound is significantly superior to that of the uncapped compounds in order to form stable molecular crystals. This may be one of the reasons of the high melting points of the capped compound. From the stacking and packing patterns of the molecules of TTC_n-TTF (n=1,2) and BEDT-TTF, it is said that π-electrons are relatively localized in the crystals due to dimerization, as a consequence, they show poor conductivities.

The central C₆S₈ moiety becomes flat with increasing n (>4). At the same time, the molecular conformation changes from boat- to chair-like structure as is depicted for TTC₁₀-TTF (Fig. 5). With increasing n, a bundle of long alkyl chains of TTC_n-TTF assembles C₆S₈ moieties in a fashion that the flat π-electron systems (C₆S₈ moieties) can pile up one after the



Figs. 3 and 4. Redox potentials (Fig. 3) and melting points (Fig. 4) of TTC_n-TTF (○), TSeC_n-TTF (△), TTeC_n-TTF (□), and TTF derivatives.

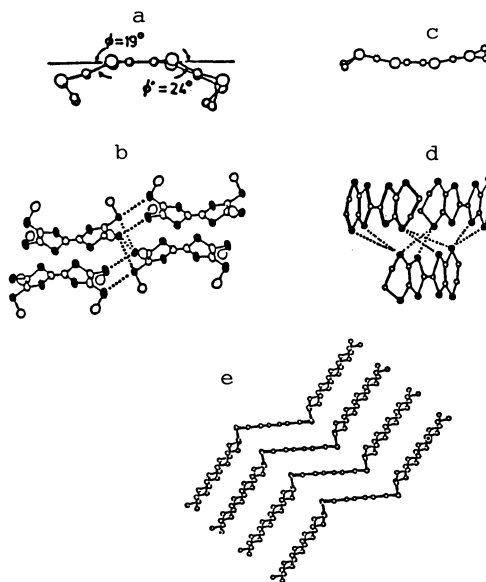


Fig. 5. Schematic view of molecular and crystal structures. a: TTC₁-TTF, b: S...S atomic contacts of TTC₁-TTF (●:S), c: BEDT-TTF, d: S...S contacts of β-(BEDT-TTF)₂I₃ (●:S), e: molecular fastener TTC₁₀-TTF

other very tightly. The C_6S_8 planes form one-dimensional face-to-face regular stacks with short S..S contacts (3.57 Å for $n=9,10$) as if they were subjected to a pressure. As a result, TTC_n -TTF molecules were forced to have big intermolecular interactions which gave small ionization potentials in solid, low resistivities ($2\sim 3 \times 10^{-6} \text{ Scm}^{-1}$ for $n=10,11$), small band gaps (0.26~0.34 for $n=10,11$, cf. 0.58~0.76 eV for $n=1,2$), and high mobilities ($9\sim 20 \text{ cm}^2/\text{V sec}$). This phenomenon, named as a Fastener Effect, may be a concerted one between the vdW interactions of the long alkyl chains (fastening part) and the resonance interactions of the π -electron moieties and this sort of molecular crystals is named as molecular fastener.

$TTeC_n$ -TTF AND $Te..Te..Te$ CHAIN COMPOUND (ref. 7)

One of a systematic investigation of the Fastener Effect is to replace sulfur atoms of the C_6S_8 moiety with other chalcogen atoms. Considering the intermolecular C..C contacts (3.99-4.35 Å for TTC_9 -TTF) of the side alkyl chains between two neighboring TTC_n -TTF molecules along the stack, the Fastener Effect may be expected to increase by such replacement. Since uncapped TTC_1 -TTF molecules tend to form the S..S contacts only with outer sulfur atoms, the effects of Y of $C_6X_4Y_4$ compounds were elucidated at first. The molecular ionization potentials of TYC_n -TTF (Y=Se,Te) were found to be independent on n similar to that observed in TTC_n -TTF, but dependent on only Y within a series of $C_6S_4Y_4$ compounds (Fig. 3). By changing Y (S \rightarrow Se \rightarrow Te), TYC_n -TTF molecule becomes stronger electron donor by 0.06 eV monotonically.

The size and shape dependences of solid state physical properties on the length of the alkyl chain were observed too. The melting points of TYC_n -TTF (Y=Se,Te) showed similar n dependences as that of Y=S (Fig. 4). $TTeC_n$ - and $TSeC_n$ -TTF have higher melting points by 10-20 and 0-7 °C with a few exceptions than the corresponding TTC_n -TTF, respectively. Among the exceptions, $TTeC_1$ -TTF has considerably higher melting point (175-176 °C) than TTC_1 -TTF (95-96 °C) suggesting strong intermolecular interactions of $TTeC_1$ -TTF molecules in solid. The electrical conductivities of TYC_n -TTF are higher by one to two orders of magnitude than those of the corresponding sulfur analogues (Y=Se, 5.6×10^{-10} , 1.5×10^{-9} , 1.3×10^{-6} ; Y=Te, 4.3×10^{-10} , 4.0×10^{-8} , 5.8×10^{-7} vs Y=S, 8.3×10^{-11} , 1.0×10^{-10} , and $1.4 \times 10^{-8} \text{ Scm}^{-1}$ for $n=2, 3, 8$, respectively) maybe due to the heavy atom effect mainly. These results also confirm that the Fastener Effect operates in the crystals of TYC_n -TTF (Y=Se,Te) with large n.

On the other hand, the electrical conductivity of $TTeC_1$ -TTF was noticeably high although alkyl chains are too short to attain the Fastener Effect. The conductivity was $1.4 \times 10^{-5} \text{ Scm}^{-1}$ at room temperature which is five orders of magnitude higher than that of TTC_1 -TTF and even higher than those of molecular fasteners above mentioned. The carrier mobility determined by a standard time-of-flight method was obtained as; $\mu_h = 28.5 \pm 0.5$ and $\mu_e = 18.6 \pm 0.4 \text{ cm}^2/\text{V.s}$ which are one order of magnitude larger than those of usual organic semiconductors ($\sim 1 \text{ cm}^2/\text{V.s}$) and comparable to that of cuppor ($35 \text{ cm}^2/\text{V.s}$). These exceptionally large conductivity and mobilities are not explained by the Fastener Effect as mentioned above. X-ray crystallographic study revealed unique packing and stacking manners of $TTeC_1$ -TTF molecules in the crystal (Fig. 6). Contrary to the bent molecular structure of TTC_1 -TTF, the π -electron system of $TTeC_1$ -TTF ($C_6S_4Te_4$ moiety) is planar completely and forms one-dimensional regular stacks along the b-axis. A relatively large interplanar spacing of 3.76 Å was found between the neighboring $C_6S_4Te_4$ groups and the $Te..Te$ distances within the stack were more than 5.48 Å indicating that the direct π -electron face-to-face interactions are not responsible for the high conductivity and mobilities of this compound. Between the neighboring columns were found very short $Te..Te$ contacts (3.644 Å) which forms a number of zigzag chains of ($..Te..Te..Te..$) through the crystal along the b-axis. On the basis of these structural features the novel transport of $TTeC_1$ -TTF is most likely associated with the conductive $Te..Te..Te$ chains cooperated with the highly polarizable TTF segments which mediate the chains.

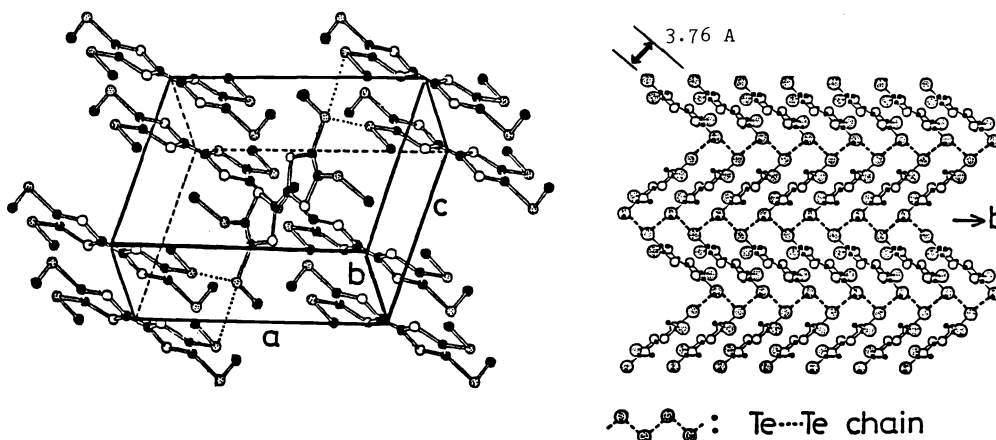


Fig. 6. Crystal structure of $TTeC_1$ -TTF and its schematic representation

TSeC₁-TTF shows rather high conductivity of $1.0 \times 10^{-6} \text{ Scm}^{-1}$ which may suggest some strong intermolecular interactions in a solid though the melting point of which (93-94 °C) is lower than that of TTC₁-TTF (other polymorphic isomer of TSeC₁-TTF has $\sigma_{RT} = 3.7 \times 10^{-9} \text{ Scm}^{-1}$ with melting point = 105 °C). Precise structural studies and physical measurements of TSeC_n-TTF and other systems, TYC₁-TSeF, are underway.

The conductivities and mobilities of TYC_n-TTF (large n) and TTeC₁-TTF are to a large extent ascribed to the characteristic strong intermolecular interactions, which give rise to wide band widths of valence and conduction bands and hence reduce the effective carrier mass provided that a band model is applicable. For a one-dimensional system, a simple band theory gives electrical conductivity and mobility as; $\sigma = 2ne^2a^2t/\hbar^2$ and $\mu = 2a^2et/\hbar^2 = e\tau/m^*$, respectively, where a is interplanar or interatomic separation, t is transfer integral which is a measure of intermolecular interactions, τ is relaxation time, h is Plank constant, and m* is effective carrier mass. Therefore in order to obtain highly conductive material, it is indispensable to increase both n and t. t is associated with band width (=4t for one-dimensional compound) and obviously dependent on the stacking and packing manners of molecules in a crystal as has been observed in TYC_n-TTF system. n is correlated with band gap, E_g, as expressed in INTRODUCTION and E_g can be reduced by using a system of big band widths. But the more fundamental requirement to reduce E_g is that a component of molecular crystal should have small energy difference between HOMO and LUMO (lowest unoccupied molecular orbital). Since TYC_n-TXF does not satisfy this fundamental requirement, TYC_n-TXF is relatively poor conductor compared to CT complexes. No organic metals nor semimetals of single-component molecular crystals have been prepared yet since density of carrier is too small. Modification of the T-electron systems of TYC_n-TXF and using the construction method of molecular assemblies such as Fastener Effect or Chalcogen..Chalcogen Chain above mentioned will improve the transport properties of single-component molecular crystals.

BEDT-TTF AND SUPERCONDUCTIVITY (ref. 8)

BEDT-TTF was introduced by us as a promising organic component of organic superconductor since BEDT-TTF has high ability to produce two-dimensional organic metal of CT type. The most important character of BEDT-TTF complexes is the correlation between the face-to-face and side-by-side interactions of BEDT-TTF molecules. The sulfur atoms are tend to form S..S network along the molecular short axis, hence conductivity can be achieved along this direction as well as along the stacking axis due to the face-to-face interactions where nonplanarity of the outer ethylene groups (C₆S₈ moiety of BEDT-TTF becomes flat on the formation of CT complex) prevents good face-to-face overlap. As a result, the balance between the face-to-face and side-by-side interactions and flexibility of the outer ethylene groups yield a variety of polymorphic complexes depending on the solvents, counter anions, and other experimental conditions of crystal growth. One of the most investigated BEDT-TTF superconductors is β -(BEDT-TTF)₂I₃ which was found by Yagubskii et al. (ref. 9) with T_c of ca.1.5K at ambient pressure. We and the Russian group have found, independently, a rapid increase of T_c to ca.7.5K under a moderate pressure of ca.1.5kbar. By releasing the pressuer to 1bar, the high T_c phase (T_c 8K) was found to coexist with the low T_c phase (Fig. 7). The appearance of the high T_c phase was found to correlate to the dynamical motion of one of the outer ethylene groups (Williams, ref. 10). The Fermi surface of β -(BEDT-TTF)₂I₃ is closed and the coherence lengths of superconductivity are $\xi_a(0)=633$, $\xi_{b'}(0)=608$, $\xi_c^*(0)=29$ Å in the low T_c phase and the critical magnetic fields are 9.4 KG(a), 9.3 KG(b'), 0.46 KG(c*) at 0.5K. The critical magnetic field increased drastically in the high T_c phase as 105 KG(b') at 1.5K. Up to now about ten BEDT-TTF superconductors were discovered by several groups out of more than one hundred BEDT-TTF complexes.

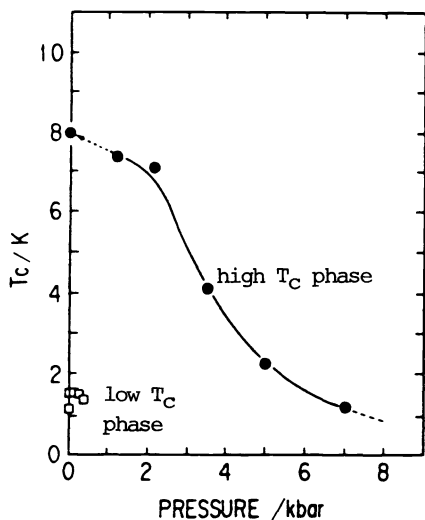


Fig. 7. Schematic phase diagram of T_c vs. pressure for β -(BEDT-TTF)₂I₃

SEMICAPPED C₆S₈ COMPOUND AND LB FILM

The most conductive LB film so far reported is composed of CT complex of tetramethyl-TTF (TMTTF) and octadecyl-TCNQ with $\sigma_{RT} = \text{ca. } 1 \text{ Scm}^{-1}$ as a monolayer (ref. 11). Temperature dependence of the conductivity of the monolayer or multilayers is semiconductive ($E_g = 0.16 \text{ eV}$) maybe due to the imperfection of the arrangement of the complex in the films. TMTTF (and octadecyl-TCNQ) molecules stack one-dimensionally in a segregated manner on the substrate, but accompanied with a variety of defects due to inhomogeneous island formation, dissociation of complex on subphase, etc. So the films show almost no anisotropy of conductivity within the lateral surface. In order to improve the conductivity of a LB film, it is necessary to overcome the above disadvantages. One of the ways is to use a single-component organic conductor, but no such compounds have been developed yet as has been mentioned. The other way is to use a CT complex with high dimensionality which may strengthen the complex formation on subphase and also the electron transport may be relatively insensitive to the imperfection of the lattice compared to that of the one-dimensional system. Furthermore it is essential to employ molecules with short or less bulky alkyl chains to improve the volume conductivity.

On the basis of these ideas, a series of semicapped C₆S₈ compounds is under examination whether they are suitable components of a LB films or not. A semicapped compound ($n'=2, n=7$) cannot form monolayer on pure water by itself judging from the surface pressure-area isotherms. However, a CT complex of the semicapped donor with tetrafluoro-TCNQ forms a monolayer with the extrapolated area per complex of 60 \AA^2 . Although the multilayers of this CT complex is insulator due to the complete electron transfer between the components, this result indicate that CT interaction assists the formation of monolayer and multilayer even though neither donor nor acceptor molecule can built up films individually.

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REFERENCES

1. F. Wudl, G.M. Smith, and E.J. Hufnagel, *J. C. S. Chem. Commun.*, **1970**, 1453-1454.
2. G. Saito, T. Enoki, K. Toriumi, and H. Inokuchi, *Solid State Commun.*, **42**, 557-560 (1982).
3. D. Jerome, A. Mazaud, M. Ribault and K. Bechgaard, *J. Phys. Lett.*, **41**, 95-98 (1980).
4. A. Bondi, *J. Phys. Chem.*, **68**, 441-451 (1964).
5. E. Aharon-Shalom, J.Y. Becker, J. Bernstein, S. Bittner and S. Shaik, *Tetrahedron Lett.*, **26**, 2783-2786 (1985).
6. P. Wu, G. Saito, K. Imaeda, Z. Shi, T. Mori, T. Enoki and H. Inokuchi, *Chem. Lett.*, **1986**, 441-444, H. Inokuchi, G. Saito, P. Wu, K. Seki, T. Tang, T. Mori, K. Imaeda, T. Enoki, Y. Higuchi, K. Inaka and N. Yasuoka, *ibid*, **1986**, 1263-1266, K. Seki, T.B. Tang, T. Mori, W. Pei Ji, G. Saito and H. Inokuchi, *J. C. S. Faraday Trans. 2*, **82**, 1067-1075 (1986), G. Saito, *Physica* **143B**, 296-300 (1986), and G. Saito, H. Kumagai, C. Katayama, C. Tanaka, J. Tanaka, P. Wu, T. Mori, K. Imaeda, T. Enoki, H. Inokuchi, Y. Higuchi and N. Yasuoka, *Israel J. Chem.*, in press.
7. N. Okada, H. Yamochi, F. Shinozaki, K. Oshima and G. Saito, *Chem. Lett.*, **1986**, 1861-1864, H. Inokuchi, K. Imaeda, T. Enoki, T. Mori, Y. Maruyama, G. Saito, H. Yamochi, N. Okada, K. Seki, Y. Higuchi and N. Yasuoka, unpublished.
8. G. Saito, T. Enoki, M. Kobayashi, K. Imaeda, N. Sato and H. Inokuchi, *Mol. Cryst. Liq. Cryst.*, **119**, 393-400 (1985), K. Murata, M. Tokumoto, H. Anzai, H. Bando, G. Saito, K. Kajimura and T. Ishiguro, *J. Phys. Soc. Jpn.*, **54**, 2084-2087 (1985), M. Tokumoto, H. Bando, K. Murata, H. Anzai, N. Kinoshita, K. Kajimura, T. Ishiguro and G. Saito, *Synth. Metals*, **13**, 9-20 (1986), and ref. 2.
9. E.B. Yagubskii, I.F. Schchegolev, V.N. Laukhin and L.I. Buravov, *Pis'ma Zh. Eksp. Teor. Fiz.*, **39**, 12-15 (1984).
10. P.C.W. Leung, T.J. Emge, M.A. Beno, H.H. Wang and J.M. Williams, *J. Am. Chem. Soc.*, **106**, 7644-7645 (1984), P. C. W. Leung, T.J. Emge, M.A. Beno, H.H. Wang, J.M. Williams, V. Petricek and P. Coppens, *ibid*, **107**, 6184-6191 (1985), and A.J. Schultz, H. H. Wang, J.M. Williams and A. Filhol, *Physica* **143B**, 354-356 (1986).
11. T. Nakamura, F. Takei, M. Tanaka, M. Matsumoto, T. Sekiguchi, E. Manda, Y. Kawabata and G. Saito, *Chem. Lett.*, **1986**, 323-324, Y. Kawabata, T. Nakamura, M. Matsumoto, M. Tanaka, T. Sekiguchi, H. Komizu, E. Manda and G. Saito, *Synth. Metals*, **19**, 663-668 (1986) and K. Ikegami, S. Kuroda, M. Sugi, M. Saito, S. Iizima, T. Nakamura, M. Matsumoto, Y. Kawabata and G. Saito, *ibid*, **19**, 669-674 (1986).