

nm-region to approximately 10  $\mu\text{m}$ , they can immediately be used as column packings.

In addition to these two geometrical strategies for the construction of complex  $\mu$ -networks, many other possibilities exist based on varying the chemical composition of  $\mu$ -gels. Just two of the most important should be mentioned. Burchard et al. have examined  $\mu$ -gels made of two incompatible polymers, where a cross-linked core of one polymer is surrounded by a shell of grafted linear chains of the other type.<sup>[15]</sup> Light scattering techniques can be used to determine the structures of these systems, which model inner surfaces in polymer blends. Another course is being followed by Obrecht, Seitz and Funke, who have examined<sup>[15]</sup> different possibilities for synthesizing "reactive" or functionalized  $\mu$ -gels. For instance, some properties of  $\mu$ -networks containing vinyl, sulfate or hydroxy groups have been described.

Although the strategies applied for  $\mu$ -network synthesis are still relatively crude (compared to nature), some possible goals of all these efforts are worth mentioning. The combination of a fixed, soluble structure of nanometer dimensions with a specific functionality is one possible starting point for the construction of tailor-made polymeric catalysts, mediators or phase transfer reagents. The term "artificial enzyme" in the context of this kind of research is certainly presumptuous, but functionalized  $\mu$ -gels are already used as catalysts in non-aqueous media and as sta-

bilizers in complex coatings, and that is just the beginning. Nature's concepts will increasingly be applied to synthetic materials. The development and examination of structured polymers is just one field where the patterns of nature are imitated;  $\mu$ -gels are one component within this strategy.

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# New Organic Superconductors

By Hiroo Inokuchi\*

BEDT-TTF Salts  
2D (Super)Conductors  
Charge-Transfer Complexes

## 1. Introduction

The first report of the discovery of an organic superconductor,  $(\text{TMTSF})_2\text{PF}_6$ , a tetramethyltetraselenafulvalenium cation radical salt, appeared in 1980.<sup>[1]</sup> Since then, thirty different types of charge transfer complexes have been reported as organic superconductors, as summarized in Table I.

Of the seven kinds of  $(\text{TMTSF})_2\text{X}$  superconductors, the so called Bechgaard salts, only the  $\text{ClO}_4^-$  salt becomes superconducting at ambient pressure. Though TMTSF contains selenium atoms, after the discovery of superconductivity in  $(\text{BEDT-TTF})_2\text{ReO}_4$ , the first sulfur-based organic

superconductor, a large part of the research into organic superconductors was devoted to the BEDT-TTF salts. The most important BEDT-TTF superconductor was  $\beta$ -(BEDT-TTF) $_2\text{I}_3$ .<sup>[23]</sup> It was the first ambient-pressure BEDT-TTF superconductor, in addition its  $T_c$  could be increased greatly to 8 K by the application of moderate pressure; this value was the highest  $T_c$  of organic superconductors before the discovery of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ . Following  $\beta$ -(BEDT-TTF) $_2\text{I}_3$ , several other BEDT-TTF iodine salts with different crystal structures, designated by the Greek letters  $\beta$ ,  $\gamma$ ,  $\theta$ , and  $\kappa$ , were found to be ambient-pressure superconductors. The  $\beta$ -(BEDT-TTF) $_2\text{I}_3$  salt also stimulated research into salts with other linear anions, from which it has been found that  $\text{IBr}_2^-$  and  $\text{AuI}_2^-$  salts<sup>[26,27]</sup> can become superconducting.

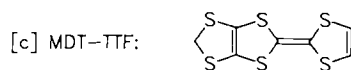
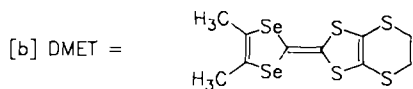
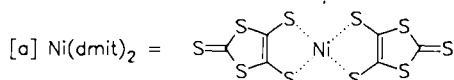
One should also mention the unique  $[\text{M}(\text{dmit})_2]$  series; these salts are the only acceptor-based organic supercon-

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ductors known so far. The asymmetric donor DMET, which is a hybrid of TMTSF and BEDT-TTF, has been found to generate superconductors. A superconductor based on another asymmetric donor, MDT-TTF, has also been discovered (Table 1).

Table 1. Organic Superconductors.

Compounds	$T_c$	Ref.
(TMTSF) <sub>2</sub> PF <sub>6</sub>	1.4 K (6.5 kbar)	[1, 16]
(TMTSF) <sub>2</sub> AsF <sub>6</sub>	1.4 K (9.5 kbar)	[17]
(TMTSF) <sub>2</sub> SbF <sub>6</sub>	0.38 K (10.5 kbar)	[18]
(TMTSF) <sub>2</sub> TaF <sub>6</sub>	1.35 K (11 kbar)	[18]
(TMTSF) <sub>2</sub> ClO <sub>4</sub>	1.4 K	[19]
(TMTSF) <sub>2</sub> ReO <sub>4</sub>	1.2 K (9.5 kbar)	[20]
(TMTSF) <sub>2</sub> FSO <sub>3</sub>	2.1 K (6.5 kbar)	[21]
(BEDT-TTF) <sub>2</sub> ReO <sub>4</sub>	2 K (4 kbar)	[22]
β-(BEDT-TTF) <sub>2</sub> I <sub>3</sub>	1.5 K	[23]
	8 K (1.3 kbar)	[24, 25]
β-(BEDT-TTF) <sub>2</sub> IBr <sub>2</sub>	2.5 K	[26]
β-(BEDT-TTF) <sub>2</sub> AuI <sub>2</sub>	3.8–5 K	[27]
γ-(BEDT-TTF) <sub>2</sub> (I <sub>3</sub> ) <sub>2</sub>	2.5 K	[28]
θ-(BEDT-TTF) <sub>2</sub> I <sub>3</sub>	3.6 K	[29]
κ-(BEDT-TTF) <sub>2</sub> I <sub>3</sub>	3.6 K	[30]
(BEDT-TTF) <sub>2</sub> Hg <sub>2</sub> Cl <sub>8</sub>	1.8 K (12 kbar)	[31]
(BEDT-TTF) <sub>2</sub> Hg <sub>2</sub> Br <sub>8</sub>	4.3 K	[32]
(BEDT-TTF) <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	2 K (16 kbar)	[3]
(BEDT-TTF) <sub>2</sub> Cu(NCS) <sub>2</sub>	10.4 K	[2]
TTF[Ni(dmit) <sub>2</sub> ] <sub>2</sub> [a]	1.6 K (7 kbar)	[33]
α-TTF[Pd(dmit) <sub>2</sub> ] <sub>2</sub> [a]	6 K (19 kbar)	[34]
[(CH <sub>3</sub> ) <sub>4</sub> Ni(dmit) <sub>2</sub> ] <sub>2</sub> [b]	5 K (7 kbar)	[35]
(DMET) <sub>2</sub> Au(CN) <sub>2</sub> [b]	0.8 K (5 kbar)	[36]
(DMET) <sub>2</sub> AuCl <sub>2</sub> [b]	0.83 K	[37]
(DMET) <sub>2</sub> AuI <sub>2</sub> [b]	0.55 K (5 kbar)	[37]
(DMET) <sub>2</sub> I <sub>3</sub> [b]	0.47 K	[38]
(DMET) <sub>2</sub> IBr <sub>2</sub> [b]	0.59 K	[38]
(DMET) <sub>2</sub> AuBr <sub>2</sub> [b]	1 K (1.5 kbar)	[39]
(MDT-TTF) <sub>2</sub> AuI <sub>2</sub> [c]	3.5 K	[40]

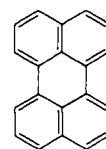


Recently, Urayama et al. of the Institute for Solid State Physics, University of Tokyo, discovered an ambient pressure superconductor, (BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>. BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene, with a transition temperature  $T_c$  above 10 K.<sup>[2]</sup> Mori and the present author, of the Institute for Molecular Science, Okazaki, have reported a novel organic superconductor, (BEDT-TTF)<sub>3</sub>Cl<sub>2</sub>·2H<sub>2</sub>O, with an unusual molecular structure,<sup>[3]</sup> with  $T_c$  = 2 K at a pressure of 16 kbar.

In this article we shall review these two organic superconductors with their historical background.

## 2. Historical Background

Between 1925 and 1940, two groups worked on “perylene addition compounds”. Clar et al. reported on perylene polyhalides under the title of “unpaired halides” or “anomalous halides”. Their first paper<sup>[4]</sup> described the formation of dark brownish black needles by the addition of bromine to a saturated benzene solution of perylene; the needles were found to have the composition of perylene tribromide, C<sub>20</sub>H<sub>12</sub>Br<sub>3</sub>.



perylene, C<sub>20</sub>H<sub>20</sub>

Zinke et al. published a large series of papers entitled “Studies on Perylene and its Derivatives”. They reported that pulverized perylene absorbed bromine quickly and produced a greenish-black product. This product, with assigned formula C<sub>20</sub>H<sub>12</sub>Br<sub>4</sub>, was not stable and liberated hydrogen bromide.<sup>[5]</sup>

These results were very interesting in the light of considering perylene as a fragment of graphite, and the reported electrical conductivity of graphite-lamellar compounds, now known to be graphite-intercalation compounds.<sup>[6]</sup>

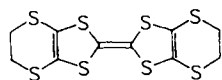
In 1954 we prepared a perylene-bromine complex by Zinke’s method and measured its magnetic susceptibility and electrical resistivity.<sup>[7]</sup> The pressed pellets of the complex were found to have a resistivity of 8 Ωcm. The magnetic susceptibility,  $-61 \times 10^{-6}$ , was smaller than that estimated by the additivity rule,  $-286 \times 10^{-6}$ . This was the first report of the electrical conductivity of charge transfer complexes.

Since this discovery an enormous amount of research has been carried out to obtain novel conducting organic compounds—the so-called “conductive charge transfer complexes”—and the research field of organic semiconductors/conductors has been developed.

## 3. Two-dimensional conductors: BEDT-TTF complexes

The charge transfer complexes, (TMTSF)<sub>2</sub>X (X = PF<sub>6</sub> or AsF<sub>6</sub>) have a metal-to-semiconductor transition at 19 and 15 K respectively at ambient pressure, while under moderate pressure these salts remain metallic, with the onset of superconductivity at 0.9 and 1.3 K, respectively. From this consideration it seemed desirable to synthesize organic metals, in which the metal-to-semiconductor transition is suppressed, so as to make new type organic superconductors and to lead to a better understanding of the requirements for them.

The alkylthio substituted tetrathiafulvalene (TTF), BEDT-TTF **1**, a  $\pi$  donor, was therefore made in the hope that the chemical modification by extending the TTF moiety, with an increased polarizability, would increase the conduction band width and reduce the on-site Coulomb repulsion, resulting in a considerable enhancement of the metallic character.<sup>[8]</sup>

BEDT-TTF, **1**

This character was confirmed by resistivity measurements on  $(\text{BEDT-TTF})_2\text{ClO}_4 \cdot \text{Cl}_2\text{HCCCH}_2\text{Cl}$  in comparison with  $(\text{TMTTF})_2\text{ClO}_4$  ( $\text{TMTTF}$  = tetramethyl-TTF), as shown in Figure 1. As listed in Table 1, two-thirds of organic superconductors are BEDT-TTF derivatives; at present, BEDT-TTF is the most appropriate  $\pi$ -donor to produce organic superconductors.

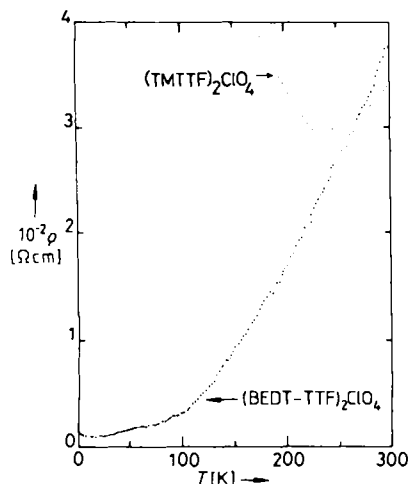


Fig. 1. Electrical resistivity  $\rho$  vs. temperature  $T$  along the elongated axis of a  $(\text{BEDT-TTF})_2\text{ClO}_4 \cdot 0.5$  1,1,2-trichloroethane single crystal compared with that of  $(\text{TMTTF})_2\text{ClO}_4$ .

#### 4. $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ <sup>[\*]</sup>

$(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  is the first organic superconductor with a  $T_c$  higher than 10 K under ambient pressure.<sup>[2]</sup> The preparation and crystal growth of this charge-transfer complex was carried out as follows: 30 mg of highly purified BEDT-TTF and 250 mg of purified  $\text{K}(\text{18-crown-6 ether})\text{Cu}(\text{NCS})_2$  were placed in the anode side of an H-type reaction cell (total volume about 20 mL), and 50 mg of  $\text{K}(\text{18-crown-6 ether})\text{Cu}(\text{NCS})_2$  were placed in the cathode side. The cell was evacuated and then filled with nitrogen. 100 mL of dried 1,1,2-trichloroethane was added,

and it was stirred 15 h under inert gas. The electrolysis, using platinum wires (1–2 mm diameter), was carried out at a constant current (1 to 5  $\mu\text{A}$ ). Crystal growth (typical dimensions  $3 \times 2 \times 0.05 \text{ mm}^3$ ) proceeded for 5 to 14 days and the harvested crystals were washed with 1,1,2-trichloroethane, methanol and tetrahydrofuran and dried under vacuum. The crystals were stable against air and moisture.

The crystal structure of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  is analogous to that of  $\kappa\text{-(BEDT-TTF)}_2\text{I}_3$ . However, the superconducting transition temperature  $T_c$  was different. In the crystal two BEDT-TTF molecules form a dimerized pair and the pairs are linked to each other by short  $\text{S} \cdots \text{S}$  contacts almost perpendicularly, forming two-dimensional conducting sheets in the  $bc$ -plane. Each conducting layer is sandwiched by the insulating layers of anions along the  $a$ -axis.

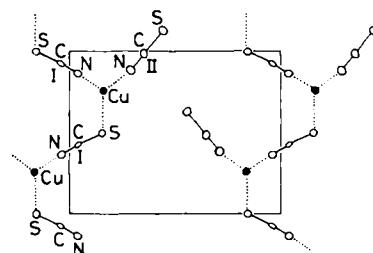
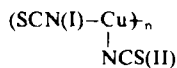


Fig. 2. Packing of  $\text{Cu}(\text{NCS})_2$  anions in  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ .

The anion  $\text{Cu}(\text{NCS})_2$  is neither symmetric nor linear, but asymmetrically bent like a boomerang. Two crystallographically independent NCS groups (I and II in Fig. 2) are almost linear. The boomerang units are arranged one after the other along the  $b$ -axis to form a zig-zag one-dimensional flat polymer. Three NCS groups (I, II, III) coordinate to a copper cation ( $\text{Cu}^{2+}$ ) with two nitrogen atoms and one sulfur atom. Thus the polymer is represented as



that is to say, two isomers, thiocyanate and isothiocyanate are coordinated to a copper cation. This structure suggests that the molecular force field in a complex strongly influences the formation of new types of chemical species.

The electrical resistivity of this superconductor as a function of temperature is shown in Figure 3. The room temperature resistivity along the crystal long axis (the  $b$ -axis) was 2 to  $7 \times 10^{-2} \Omega\text{cm}$ ; it is fairly high among the organic superconductors. In the  $bc$  plane the resistivity is almost isotropic, while along the  $a$  axis the resistivity is 600 to 1000 times greater than that in the  $bc$  plane. Down to 270 K weak metallic behavior was observed. Thereafter, the resistivity increases with diminishing temperature, and the maximum value at around 90 to 100 K is four to six times greater than that at room temperature. Below 90 K metallic behavior reappeared, followed by a superconduct-

[\*] With H. Urayama and G. Saito.

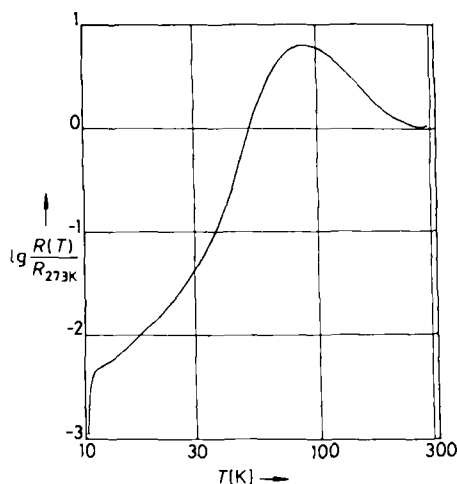


Fig. 3. Temperature dependence of electrical resistivity of (BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>.

ing transition at 10.4 K. The physicochemical properties, electronic structure,<sup>[9]</sup> XPS and ESR spectra,<sup>[10]</sup> thermoelectric power,<sup>[10]</sup> magnetic resistance,<sup>[9]</sup> magnetic susceptibility,<sup>[12]</sup> a.c. magnetic susceptibility, polarized reflectance spectra, anomalous NMR relaxation, tunneling spectroscopy,<sup>[13]</sup> and other properties, have already been measured. From the tunneling spectroscopy data the observed gap of 4 meV leads to a value of 4.5 for  $2\Delta/kT_c$ , (where  $2\Delta = 4$  meV and  $T_c = 10.4$  K), which is of the same order as the BCS ratio of 3.52.

## 5. (BEDT-TTF)<sub>3</sub>Cl<sub>2</sub>·2H<sub>2</sub>O<sup>[1]</sup>

The chlorine salt, (BEDT-TTF)<sub>3</sub>Cl<sub>2</sub>·2H<sub>2</sub>O, shows superconduction at 2 K under a pressure of 16 kbar.<sup>[3]</sup> An enormous number of charge-transfer complexes with halogens as acceptors have been prepared. However, no report of complex formation with chlorine has appeared so far as we know. In the case of graphite intercalation compounds, only the larger size halogens, Br<sub>2</sub>, I<sub>2</sub>, ICl and IBr can form intercalation compounds, and the fluorine molecule reacts directly with graphite to form insulating compounds involving F-substituted sp<sup>3</sup> carbon atoms.

In the structural chemistry of the BEDT-TTF salts, the discontinuity between iodine and bromine is related to the ability of iodine to form trimer anions such as I<sub>3</sub><sup>-</sup>. The halogen atoms Br and Cl are themselves too small to form charge-transfer complexes with BEDT-TTF, but the clusters solvated by H<sub>2</sub>O are included in the BEDT-TTF salts. The 3:2 BEDT-TTF salts occur when the counter-anions are relatively small, e.g. as with ClO<sub>4</sub><sup>-</sup> and ReO<sub>4</sub><sup>-</sup>. Because the Br and Cl salts have not only the same composition but also a similar donor arrangement to the salts of these tetrahedral anions, these complex anion clusters, Br<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> and Cl<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>, can be regarded as rather small anions.

The preparation of this intriguing complex, (BEDT-TTF)<sub>3</sub>Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, was also unusual: the complex was obtained by electrolysis using [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>CoCl<sub>4</sub> as electrolyte,<sup>[14]</sup> and by chlorine abstraction from the solvent CH<sub>2</sub>Cl<sub>2</sub>.<sup>[15]</sup> Recently the same complex was obtained by electrolysis in the presence of [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]Cl.

The structure of the anion, Cl<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>, in the salt is illustrated in Figure 4. Two Cl atoms are connected to two O atoms through hydrogen bonds to form a rectangle. This unit has a close resemblance to the Br<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> unit in (BEDT-TTF)<sub>3</sub>Br<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>. However, in the chlorine salts additional Cl and O atoms are attached to this unit by hydrogen bonding.

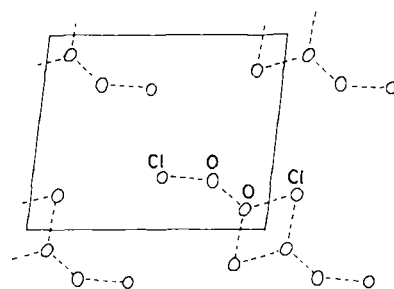


Fig. 4. Packing of [Cl<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>0-</sup> anions.

The bromine salt, (BEDT-TTF)<sub>3</sub>Br<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, exhibits metallic conduction at room temperature, and then undergoes a metal-to-insulator transition at 185 K. On the other hand, the chlorine salt, (BEDT-TTF)<sub>3</sub>Cl<sub>2</sub>·2H<sub>2</sub>O, has a high conductivity as a (BEDT-TTF) complex, 500 S cm<sup>-1</sup> at room temperature, and is metallic down to 100 K. Although this salt undergoes a metal-to-insulator transition around 100 K, superconductivity has been found at 2 K under a pressure of 16 kbar as mentioned above.

As can be seen from Table 1, all other organic superconductors except this chlorine salt have the 2:1 composition, irrespective of whether the conducting components are donors or acceptors, and their energy bands are quarter-filled. If the band structure is calculated by the extended Hückel approximation, the BEDT-TTF superconductors usually give comparatively simple two-dimensional metal bands. This chlorine superconductor, on the contrary, gives a semimetallic energy band.<sup>[14]</sup> This result demonstrates that neither the 2:1 composition nor a simple two-dimensional metal band is a necessary condition for organic superconductivity.

Schweitzer et al. have reviewed their excellent contributions to the field of BEDT-TTF molecular metals and superconductors.<sup>[41]</sup>

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## Research News

# Molecular Electronics: Silicon to Soliton and Other Trends

When the British Association for the Advancement of Science (BA) first met in Oxford some one hundred and fifty years ago, only a few scientists, apart from *Faraday*, were then engaged in the new task of assembling electrical circuits. In those days, long before the age of mass production, the diameter of conducting rods was of millimeter dimension. Nowadays, with world-wide interest in the pursuit of the ultramicro-miniature, there is intense activity in the design and construction of molecular electronic devices made up of organic semiconductors, organic metals and conducting polymers which are of either organic or inorganic provenance (such as polysulfur nitride). Into the lexicon of the molecular architect a new word has been

recently introduced, a "proconductor" which is the non-conducting form of a molecular entity that can also be made conducting by loss or gain of an electron by partial oxidation or reduction. Present day studies<sup>[1]</sup> which, inter alia, seek to arrive at favored molecules for memory, logic and amplification—with a view to constructing computers based, not on silicon or gallium arsenide, but on self-assembling molecules of the kind that abound in biology—focus on such problems as whether a  $\pi$ -conjugated molecule, a hundred Ångström or so in length, can serve as a proconductor or a conductor when placed between two metallic conductors. It is conceivable that the 'electronic wiring', which, it is thought, will be a characteristic of the