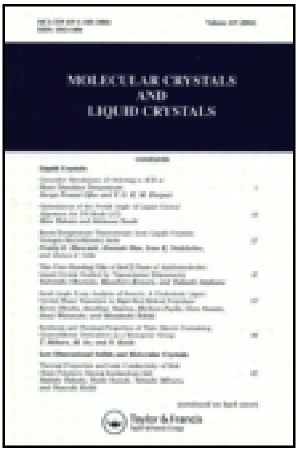

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A NEW TYPE OF ORGANIC SEMICONDUCTOR

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Abstract As one of the new type of organic semiconductors, we report the physico-chemical properties of BTQBT [(bis(1,2,5-thiadiazolo)-p-quinobis(1,3-dithiole)]; the electrical conduction, the ionization energy and the angle-resolved photoemission spectra.

TWO CATEGORIES OF ORGANIC SEMICONDUCTORS

Concerning the electrical conduction of organic solids, two major categories are known to offer the prospect of conduction. The first group consists of charge-transfer complexes. Since 1954, a large number of charge-transfer complexes have been studied from the viewpoint of their high electrical conduction. A historical survey of this research is illustrated in Fig. 1. The first report was of the electrical conduction of perylene-bromine addition compound.[1] In 1959, the electrical conduction of charge transfer complexes between two organic compounds, tetramethyl-p-phenylene diamine and chloranil, was reported.[2]

Since then a number of novel organic donors and acceptors have been synthesised, which have yielded new series of conductive charge transfer complexes; among them, TCNQ (1960)[3], TTF (1970)[4] and BEDT-TTF (1969,1982)[5] are representative compounds.

The first report of the discovery of the organic superconductor, tetramethyltetraselenafulvalenium cation radical salt, $(TMTSF)_2PF_6$, appeared in 1980.[6]

BEDT-TTF, the alkylthio-substituted TTF, was made in the hope that the chemical modification of extending the TTF moiety, with enhanced polarizability, would increase the conduction band width and reduce the on-site Coulomb repulsion, resulting in a considerable enhancement of the metallic character.

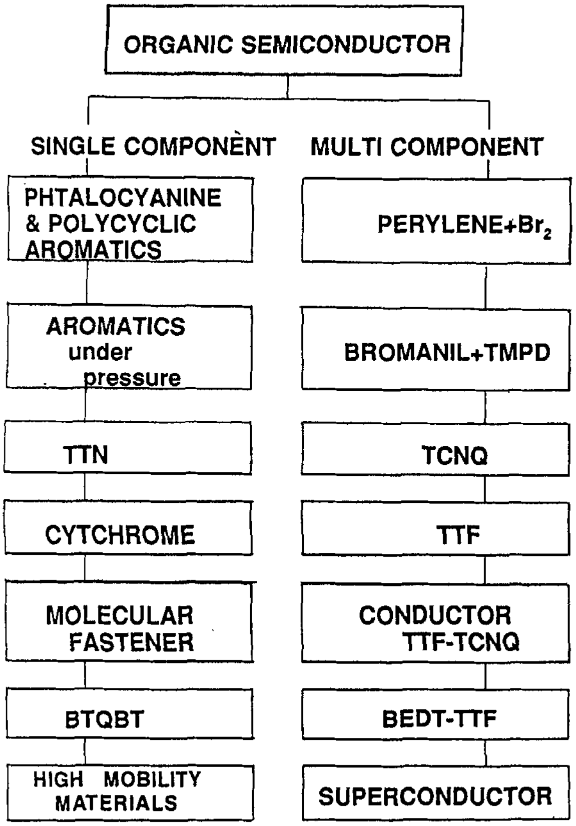


FIGURE 1 Research Progress on Organic Semiconductors.

Using this π-donor, organic cation radical salts were prepared by various methods. One of these salts, (BEDT-TTF)$_2$ClO$_4$(1,1,2-Trichloroethane)$_{0.5}$ showed two-dimensional metallic transport properties over the entire temperature range measured.[5] From these results of the two-dimensional character of the electrical, optical and also structural data[7], we have proposed practical molecular designs for organic metals with strong interchain interaction, which become organic superconductors of the (TMTSF)$_2$X type.

In 1983,⁸⁾ $(BEDT\text{-}TTF)_2ReO_4$ was reported as the first organic superconductor in the BEDT-TTF series. Already over 50 organic superconductors are known of which half are from the BEDT-TTF series; BEDT-TTF is the most appropriate donor to produce organic superconductors. A large number of researchers are working intensively to find new types of organic superconductors, especially those having higher transition temperatures.

The second group comprises single component materials. Examples of this group are polycyclic aromatics and phthalocyanines.⁹⁾¹⁰⁾ Generally speaking, their conductivities are not so good as those of the multi-component group, charge-transfer complexes. However we are employing the strategy of increasing the intermolecular overlap of π-electron charge clouds, and also introducing a degree of covalency to the intermolecular interaction. This is leading to several series of a new type of organic semiconductor having enhanced electrical conductivity.

It is known that the application of pressure to organic molecular solids decreases the intermolecular separation. We have observed an anomalous increase in the electrical conductivity of organic solids under compression, but of course the effect does not persist after the pressure is removed.¹¹⁾

At the first symposium on "Electrical conductivity in organic solids" in 1960, we reported results on sulphur compounds of aromatic hydrocarbons.¹²⁾ When aromatic hydrocarbons are heated with excess amount of sulphur in an evacuated tube up to 450°C, they react with sulphur liberating hydrogen sulphide. The resulting dark-coloured compounds are amorphous solids possessing semiconducting properties. The semiconductivity data of these solids shown in Table 1 are reproduced from this report. The proposed chemical structure of these compounds is illustrated in Fig. 2.

TABLE 1 Semiconduvtive data and and sulphur content of sulphur compounds of aromatic hydrocarbons.

Hydrocarbon	ρ_{15}, ohm-cm	ρ_{0}, ohm-cm	, eV	Sulphur content, number of sulphur atoms per hydrocarbon molecule
Anthracene	$1.0\text{x}10^{4}$	$2.7\text{x}10^{2}$	0.18	5.8
Naphthacene	$1.4\text{x}10^{4}$	$1.9\text{x}10^{2}$	0.15	7.1
Perylene	$2.0\text{x}10^{9}$	5.1x10	0.57	8.6
Pyranthrene	$5.0\text{x}10^{3}$	7.9x10	0.22	11.5
Violanthrene	$1.1\text{x}10^{4}$	$2.0\text{x}10^{2}$	0.19	9.7
Violanthrone	$4.0\text{x}10^{2}$	3.2x10	0.16	9.5

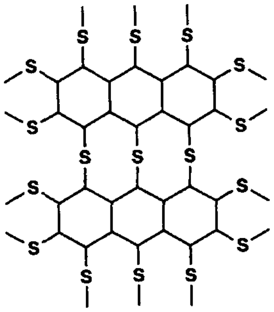


FIGURE 2 Proposed structure of aromatics sulphur compound.

In 1965, Matsunaga reported the synthesis of tetrathionaphthacene (TTN).[13] We reported its resistivity, as $10^{7}\Omega$cm; it is a quite low for single component compound.[14]

In 1986, we reported a new strategy for the fabrication of molecular assemblies in such a fashion that organic molecules can pile up one upon another so tightly that the system shows a high conductivity, even as a single component.[15] The molecular structure of these novel organic semiconductors, alkylthio-substituted tetra-thiafulvalenes,

(TTC_nTTF) is shown in Fig. 3. The electrical conductivity of single crystals of this series (n=1~11) have been measured in vacuo of 10^{-4}Pa with the two probe method using gold paste electrodes.

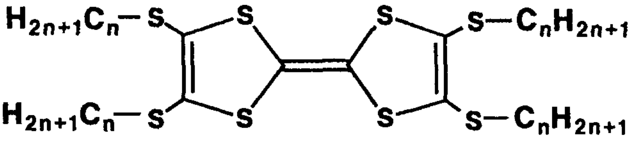


FIGURE 3 Molecular structure of TTC_nTTF.

Table 2 summarizes the electrical resistivity values, together with the melting point values. Among these compounds, we found the highest conductivity value to be $10^{-5}S^{-1}cm^{-1}$. The high conductivity can be rationalised in terms of the work function,[16] and the crystal structure with the close proximity of TTC_nTTF molecules (when n is greater than six) which is attributed to strong interaction between pairs of paraffin chains.[17] Thus central skeleton has been fastened together strongly by the four long alkyl chains. We call this type of organic semiconductor by the name molecular fastener.

Recently, we have been investigating the physico-chemical properties of BTQBT (bis(1,2,5-thiadiazolo)-p-quinobis(1,3-dithiole)). This is also a new type of single component organic semiconductor. We shall summarise the electronic properties of this series in this report.

BTQBT

A new type of single component organic semiconductor, bis(1,2,5-thiadiazolo-p-quinobis(1,3-dithiole)) (BTQBT), was synthesised, in which the electron withdrawing heterocycles are fused to the skeleton of a very strong electron donor, 2,2′-p-quinobis(1,3-dithiole).[18]

The crystal structure of the completely coplanar BTQBT indicates a strong intermolecular interaction : it should be noted that the distance between the S of the dithiol and the

TABLE 2 Electrical resistivity and melting point of TTC_nTTF. ρ values in parentheses are for compaction pellet specimens.

n	ρ(cm)	m.p. (°C)
1	2.9x10^{10}	96.5
2	1.2x10^{10}	70.6
3	9.6x10^{9}	30.4
4	6.2x10^{6}	24.6
5	6.4x10^{7}	32.2
6	3.0x10^{7}	28.6
7	3.8x10^{7}	44.0
8	7.0x10^{7}	47.6
9	5.0x10^{7}	56.8
10	3.7x10^{5}	59.4
11	5.6x10^{5}	63.6
12	(5.7x10^{7})	68.3
13	(2.3x10^{6})	72.7
14	(7.8x10^{7})	76.5
15	(2.9x10^{6})	79.3
16	(9.9x10^{6})	83.3
17	(1.6x10^{7})	84.1
18	(6.8x10^{9})	85.0

N of the thiadiazolo (2.78Å) is significantly shorter than the sum of the van der Waals distance (3.35Å), indicating the possibility of the delocalization of electrons through the S···N contacts. The coplanar molecules from a sheet-like network by S···S contacts as shown in Fig. 4. The S···S contact distance of 3.26Å is much shorter than the sum of their van der Waals radii (3.70Å).

We have also studied photoemission from BTQBT in the solid state and have obtained a value for the threshold ionisation energy of to be 4.5eV.[19]

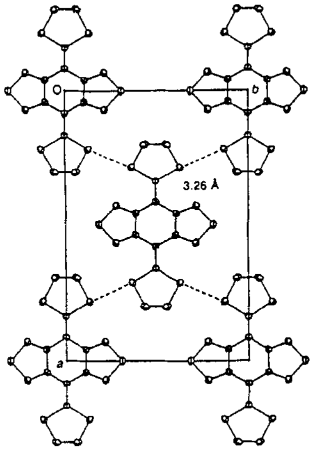
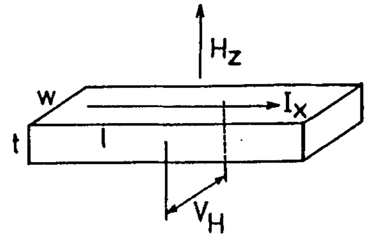


FIGURE 4 Molecular packing of BTQBT.

From these physical properties, we expect to find that carrier transport is facile in a BTQBT crystal. We have observed the temperature dependence of the resistivity along the long axis of a BTQBT crystal grown by sublimation ($1{\sim}2\times0.1\times0.1\,\mathrm{mm}^3$). The resistivity at room temperature (ρ_{RT}) was $2.7\times10^5\,\Omega$-cm with activation energy (E_a)=0.21eV; these values are remarkably low for a single-component organic compound.20)

We have also observed the anisotropy along the three directions of the crystal, ($\rho x(=\rho c)$, parallel to the long axis: ρy, perpendicular to the x-direction in the broad face of the crystal: ρz, perpendicular to the broad face of the crystal) was $\rho x:\rho y:\rho z=1:2:100$. The ratio ($\rho\perp/\rho_{//}$) of the resistivities along and between the intercolumns is very small (~2). This finding supports the existence of strong two-dimensional intermolecular interactions displayed in the crystal structure. These high electrical conductivities of the BTQBT crystal enabled us to measure a Hall mobility; the experimental result of Hall effect measurement is summarized in Table 3. The Hall mobility (μ_H) which is product of the Hall coefficient and the conductivity ($\mu_H=R_H\sigma$) was calculated to be $4\,\mathrm{cm}^2$/volt.sec.21)

TABLE 3 Hall effect measurement for BTQBT.



magnetic field	(H_z)	1.3T
applied voltage	(V_x)	10V
current	(I_x)	3.6μA
Hall voltage	(V_H)	0.25mV
sign of carriers		positive
Hall coefficient	(R_H)	$4\times10^3 cm^3 C^{-1}$
Hall mobility	(μ_H)	$4 cm^2 s^{-1} V^{-1}$

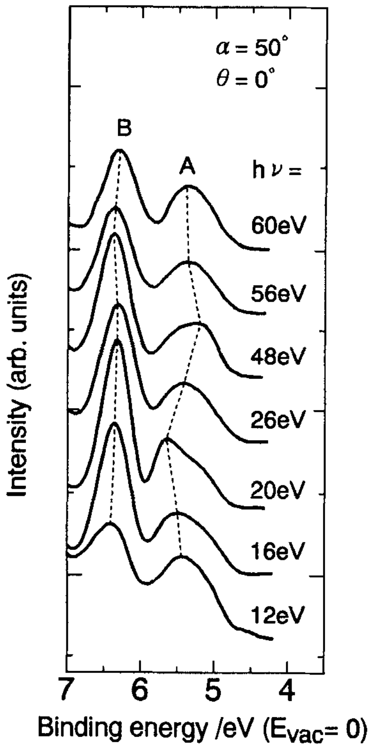


FIGURE 5 Photon energy dependence of photoelectron spectra at normal emission for BTQBT thin film. The binding energy region is 4~7eV. The HOMO and NHOMO bands are labeled A and B.

These results suggest that bandmodel is approprate for the electrical conduction in a BTQBT crystal. Using angle-resolved ultraviolet photoemission spectra with sychrotron radiation (12-60eV), we observed firstly the <u>inter</u>molecular dispersion in a single-component organic molecular crystal for an oriented thin film of BTQBT on HOPG graphite as illustred in Fig. 5. This demonstrates that the BTQBT molecules have a strong intermolecular interaction, which can be attributed to the introduction of a covalent interaction between S···S atoms in addition to the usual intermolecular interaction by van der Waals forces.[22)]

From this experimental research work, we believe more conductive single component organic solids having high mobility should be found in this second category of single component organic semiconductors.

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