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A Novel Type of Organic Semiconductors. Molecular Fastener

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The electrical conductivity of alkylthio-substituted tetrathiafulvalene (TTC_n-TTF) single crystal has been measured in a vacuum of 10^{-4} Pa with the two probe method. The room temperature dark conductivity of TTC_{10}-TTF reaches 10^{-5} S cm^{-1}, a value that is extraordinarily high compared with those of other organic semiconductors constructed with a single component. The cause of this high conductivity is that the central tetrathiafulvalene skeleton has been fastened strongly with the four long alkyl chains.

Two major categories of organic solids are known to offer the prospect of high electrtical conductivity. The first kind consists of charge transfer complexes: The first report of conducting perylene-bromine complexes appeared in Nature in 1954.[1)] Subsequently measurements on a large number of donor-acceptor complexes have been carried out. The other kind comprises compounds of single component; typical examples of this group are polycyclic aromatic compounds[2,3)] and phthalocyanines.[4)] Generally speaking, their conductivities are not so good as those of the donor-acceptor kind.

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In this report, we will present a new strategy to fabricate molecular assemblies in a fashion that organic π-molecules can pile up one after another tightly so that the system can show a high conductivity even in a single component. Actually, we have found a novel type of single-component organic semiconductors, with a resistivity as small as 10^5 Ω cm, which is realized by introducing strong intermolecular interaction between adjacent molecules.

The molecular structure of an example of such organic semiconductors, namely decanylthio-substituted tetrathiafulvalene (hereafter refered to as TTC_{10}-TTF), is shown in Fig. 1. The whole series of alkythio-substituted tetrathiafulvalenes TTC_n-TTF, with the carbon number n in each alkyl chain ranging from 1 to 18, have been synthesized; the method of synthesis will be reported elsewhere.[5)]

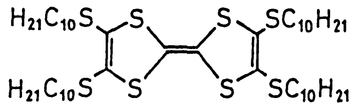

Fig. 1. Molecular formula of TTC_{10}-TTF.

The electrical conductivities of single crystals of this series have been measured in a vacuum of 10^{-4} Pa with the two probe method using silver or gold paste as electrodes. The results are summarized in Table 1.

Table 1. The electrical resistivity of alkylthio-substituted tetrathiafulvalene (TTC_n-TTF) single crystals

n	Electrical resistivity / Ω cm $a^{a)}$	$b^{a)}$	$c^{a)}$	S - S distance[b)] / Å	I_s[c)] / eV
1	2.9×10^{10}	2.7×10^{11}	1.7×10^{11}	3.80	5.0_5
2	1.2×10^{10}	1.4×10^{14}	1.2×10^{10}	3.80	5.1_5
9	5.0×10^{7}	2.9×10^{13}	1.2×10^{8}	3.57	4.6_5
10	2.7×10^{5}	—	—	3.57	4.7_0
11	5.6×10^{5}	—	—	—	—

a) Crystal axes of single crystal. The molecular packing along each axis is as follows: a; C_6S_8 moiety is stacked along this axis, b; C_6S_8 is separated distinctly by the alkyl side chains and c; there is considerable interaction between the neighbouring TTF moieties.

b) The nearest distance of S-atom between neighbouring C_6S_8 moieties in crystal.

c) Ionization threshold energy of TTC_n-TTF crystal.

The room-temperature dark conductivity reaches 10^{-5} S cm^{-1}, a value that is extraordinarily high compared with those of other organic semiconductors constructed with a single component. For example, as seen in Table 1, the conductivity of TTC_1-TTF is less than 10^{-10} S cm^{-1}, and that of violanthrene under high vacuum is 10^{-17} S cm^{-1}.[6)]

What is the cause of this high conductivity? We suggest the close packing of molecule in crystal. The central tetrathio-tetrathiafulvalene moiety (C_6S_8) is not in all cases planar; the central six atoms (the tetrathioethylene group) are coplanar, whereas the outer dithioethylene groups on each side form two other planes. The angle between the central plane and the outer planes decreases with increasing n. From the analysis of crystal structural data, the shortest distance between sulphur atoms of C_6S_8 skeleton in two adjacent molecules was found to be 3.57 Å for both TTC_9-TTF and TTC_{10}-TTF, which is considerably shorter than the sum of the van der Waals radius (3.70 Å). Corresponding value for TTC_1-TTF and TTC_2-TTF is 3.80 Å as shown in Fig. 2. The proximity in the TTC_9-TTF or TTC_{10}-TTF case is attributed to the strong interchain interaction between the two pairs of long nonyl or decanyl substitutent chains, and, in turn, is used to explain the high conductivity of TTC_n-TTF with n = 9, 10, and 11 (See Fig. 3); that is to say, the central skeleton

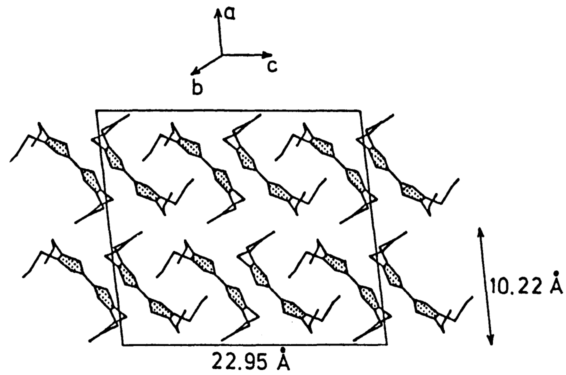

Fig. 2. Schematic diagram of molecular packing in TTC_2-TTF crystal.

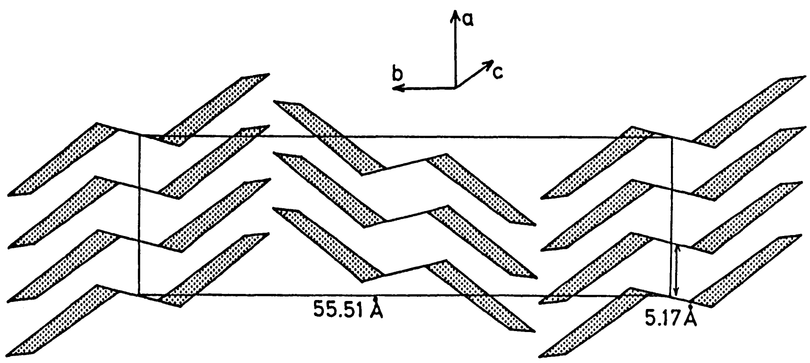

Fig. 3. Molecular packing in TTC_9-TTF crystal. It can be easily understood a-direction of TTC_9-TTF crystal shows a fairly high conductivity.

has been ´fastened´ strongly with the four long alkyl chains. We call this type of organic semiconductors by the name of molecular fasteners.

The ionization threshold energies of TTC_9-TTF and TTC_{10}-TTF determined with the photoelectron spectroscopical method are such low values as 4.6_5 and 4.7_0 eV, respectively. These values are comparable to that of graphite, 4.70 eV. In contrast, those of TTC_1-TTF and TTC_2-TTF are 5.15 and 5.0 eV, respectively. These small values are a good confirmation of the strong interaction of TTC_n-TTF molecules having long alkyl chains. The photoelectron spectroscopic study will be reported in detail elesewhere.[7]

We are extending this work to the search for more conducting single-component compounds by means of molecular fastening principle.

References

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