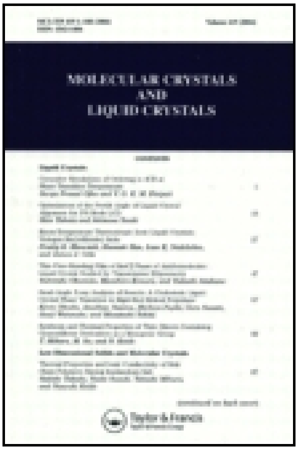

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ORGANIC SEMICONDUCTORS, PAST AND PRESENT

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Abstract Historical survey of organic semiconductors is presented. The peculiar character of two single component organic semiconductors, cytochrome c_3 and tetrabenzopentacene, is described.

HISTORICAL

During 1945 - 1950, three groups started to observe electron transport in organic solids. Photoelectric conduction in organic dyestuffs was measured in relation to the mechanism of the sensitization of photographic emulsions. A.T. Vartanyan made observations of photoconduction with thin films of dyes, tripaflavine and crystal violet, which were deposited onto quartz plate from alcohol solutions.[1] The phthalocyanine molecule is closely related to that of porphyrine. D. D. Eley investigated its electrical properties in connection with the contrubution of electron migration to biochemical catalysis.[2]

Electronic conduction in graphite and also carbons have already been known; their chemical structures are essentially aromatic. The possible existence of electronic conduction in simpler synthetic compounds of chemical structures is similar to that of graphite has been pointed out and investigated by H. Akamatu and H. Inokuchi.[3] These substances are polycyclic aromatic compounds which are situated on the series of chemical structures extending from benzene to graphite.

Since then, a number of investigations have been made in the observation of electrical conductions in organic solids when exposed to light, as well as in the dark. The experimental findings provided strong proof for the semiconductive characteristic of electronic conduction in organic solids. Through these findings, a number of substances which can be adequately called organic semiconductors have been found. The name of organic semiconductors was first used in an article published in 1954.[4]

The polycyclic aromatic compounds have a tendency to form molecular addition complexes with polar molecules. Almost thirty years ago, we employed two methods developed by Clar and Zinke respectively to prepare the aromatics-halogen molecular compounds. In Clar's method,[5] a known quantity of aromatic compound is dissolved or suspended in benzene, and an exess amount of bromine or iodine is added while the solution is boiled. After cooling of the solution, the black-color precipitates obtained are separated by filteration and washed with benzene. In Zinke's method,[6] a known quantity of the sample is put on a glass filter and brought in contact with a halogen vapor in a glass chamber. The formation of the complex is completed within about ten minutes.

The formation of the complex is recognized by a remarkable color change and an increment in weight. Among the complexes, perylene-bromine, violanthrene-bromine, perylene-iodine and pyranthrene-bromine complexes have been well investigated. In 1954, we found that these solid complexes possess high electrical conductivity.[7] It was surprising to find that such simple organic solids have electrical resistivities as low as 1 - $10^3 \Omega cm$, as summarized in Table I. These are also considered to be organic semiconductors.[8]

Table I SEMICONDUCTIVE DATA OF AROMATIC-HALOGEN COMPLEXES

Complex	Molar Ratio	$\rho_{15°C}$ Ωcm	ε eV
Perylene-Bromine	1:2	7.8	0.13
Perylene-Iodine	1:1.5	10	0.06
Pyranthrene-Iodine	1:2	17	0.09
Violanthrene-Bromine	1:2	66	0.20
Violanthrene-Iodine	1:2	45	0.15

PROGRESS IN ORGANIC SEMICONDUCTORS WORK

Since then, much works on organic semiconductors has been carried out at many places. Among them, several epoc-making pieces of work have been reported:

1960 Synthesis of TCNQ

1960 Electron mobility measurement in organic solids

1970 Synthesis of TTF

1973 Formation of organic metal

1980 Appearance of organic superconductors

Now, much efforts are devoted to finding appropriate components, donors and acceptors, to make a high-conductive and also, if possible, a high-T_c superconductive charge transfer complexes. Many reviews on charge-transfer complexes having high conductivities have been reported. Therefore, in this talk, we will focus our attention on a few examples of the single component organic semiconductors studied in out laboratory.

One of the example is the protein in biological systems.[9] In mitochrondrial respiratory electron-transfer systems, flavoproteins and cytochromes transfer electrons from organic substrates to the final electron acceptor, O_2. In nerve tissues, nervous impulses are transmitted by means of a charge-transfer system involving proteins such as acetylcholine acceptor. As mentioned above, one of the motivation of this work, namely the study of electronic-conduction in organic solids, was to analyse charge-transfer in biological systems. Eley and his school found the semiconductive behavior of proteins in solid state. In spite of these electron-transfer functions of proteins, isolated simple protein molecules are rather insulative.

However, we recently found a high electrical conductivity for the tetrahemoprotein electron carrier, cytochrome c3 at reduced state. A thin film of anhydrous cytochrome c3 containing a trace amount of hydrogenase was prepared on a quartz plate, and its electrical conductivity was measured under H_2 ambient gas. The change in electrical conductivity with temperature showed puzzling characteristics. The resistivity of the cytchrome c3 reached 56Ωcm when the H_2 pressure was kept at 102 KPa, and 8Ωcm at 200 KPa. Under high-pressure hydrogen at 1000 KPa, the minimum value was reached, near to $1 \times 10^{-3}\Omega$cm at 292 K.

Recently, the molecular structure was determined at 2.5 Å resolution with the x-ray diffraction method. The overall dimensions of cytochrome c_3 are approximately $33 \times 39 \times 34$ Å^3. It was found that four hemes are exposed to the surface of a molecule which might be the cause of intermolecular heme-heme interaction in the solid state.

The distance among the central iron atoms in hemes range from 11.3 to 18.1 Å. All heme groups find aromatic residues in proximity. These aromatic residues certainly intervene in the electron transfer: the transfer seems to occur through the π-electron system of aromatic residues around heme.

From the resistivity data described above, we would argue that "cytochrome c_3" is a good example of single component organic semiconductor and we expect to find more conductive substance in biological systems.

Another example of single component organic semiconductors is tetrabenzopentacene(TBPA). TBPA is a structural isomer of violanthrene A, one of the earliest found organic semiconductors. Among their several structural isomers, violanthrene A(VEA), violanthrene B (VEB), isoviolanthrene A (IsoVEA), isoviolanthrene B (IsoVEB), tetrabenzoperylene(TBP) and TBPA have their photoelectron spectra.[10] Table II shows the values of solid-state ionization potentials and also gas-phase adiabatic ionization potentials determined carefully with a graphical method.[11] In the table, I_s^{th} is the solid state ionization energies for the threshold and p_+, the polarization energy, is defined as $I_g^a - I_s^{th}$.

In Table II, we find the reduced polarization energies for TBP and TBPA. The reduction is interpreted as being caused by decreases both packing density and molecular polarizability, with each factor related to the molecular structure.

Table II IONIZATION ENERGIES OF THE SIX NANOCYCLIC AROMATIC COMPOUNDS

Compound	I_g^a(eV)	I_s^{th}(eV)	P_+(eV)	E_G(eV)
VEA	6.42	4.8_6	1.5_4	1.65
IsoVEA	6.36	4.9_2	1.4_4	1.8_3
VEB	6.36	4.8_2	1.5_4	1.6_3
IsoVEB	6.54	4.9_6	1.5_8	1.7_3
TBP	6.58	5.3_4	1.2_4	(2.4_5)
TBPA	6.13	4.9_8	1.1_5	(2.1_8)

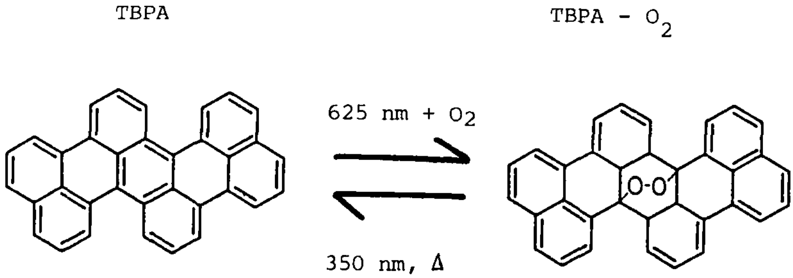
Futher, we also list the value of E_G, the gap energy between the highest occupied and the lowest unoccupied orbitals in the solid, obtained from the following relation:

$$E_G = I_s - A_g - P_+$$

The E_G-value for the four violanthrenes can be estimated to be ~1.7eV. This value is coincident with that obtained from the semiconductive character of VEA.[12] These findings suggest that ultraviolet photoelectron spectroscopy has come to be recognized as a powerful tool for studying the electronic structure of organic solids.

TBPA has a pecularity not only in its electronic structure, having the lowest ionization potential among the six compounds, but also in its electrical conductivity. The electrical resistivity (ρ) of TBPA at room temperature is $10^{12}\Omega$cm under high vacuum; this is the lowest ρ-value among the six homologs. A strong effect of oxygen on the resistivity was found: the value in air is about 10^5~10^6 cm.

Further, TBPA shows a peculiar photochemical reaction -- photooxygenation -- in the solution and also in the condensed phase. The dark blue color of TBPA disappears when it is exposed to 625 nm wavelength light. When the colorless compound is heated or kept in the dark, the original color recovers: TBPA shows photochromism. The mechamism of this phenomenon is illustrated as follows.



These simple photochromic behaviors may be applied to the build-up of molecular device.

We wish to thank our collaborators, without whom this work could not have been done.

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