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## Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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## **Foreword**

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## **FOREWORD**

It is well known that saturated organic compounds are electrical insulators. Conjugated carbon-carbon double bonds, however, give rise to mobile electrons within the molecule, as typified by benzene. Aromatic compounds were found to exhibit unusual magnetic properties in the early 1900's, and graphite, a benzene network compound, was found to have the largest electrical conductivity among non-metallic materials.

In the 1940's when polycyclic aromatic compounds, phthalocyanines, and dyestuffs, such as cyanine dyes, were the major objects of study, the quantitative investigation of electrical conductivity of organic compounds was started and "Organic Semiconductors" was established as a new field of research.

Chemists, particularly organic chemists, have known for a long time that addition compounds are formed between two different organic compounds, or between organic and inorganic compounds. A typical example of this phenomenon is the range of colors observed when iodine interacts with benzene, alcohol or starch. In the beginning of the 1950's a remarkable conductivity due to mobile electrons was discovered in one of the addition compounds, a complex formed between an aromatic hydrocarbon and iodine or bromine.

The study of electrical conductivity in organic compounds started in these two groups of materials and developed into the study of organic semiconductors and organic conductors. The adoption of experimental and theoretical methods used in the study of inorganic semiconductors led to further developments. Great efforts were also made to find new materials with higher electrical conductivity.

Polymer semiconductors appeared in the late 1950's, and readily processable and plastic charge transfer type polymeric semiconductors were produced by iodine or alkali metal doping of polymers containing electron donating or accepting groups. Polyacetylene and other highly conjugated polymers were synthesized in an attempt to achieve high conductivity in the undoped material. Although polyacetylene was first studied in the early 1950's, it was not until the late 1960's that relatively stable polyacetylene films were synthesized, from which a succession of new conducting polymers were prepared.

Various solid state properties of these materials (carrier mobility, ionization potential, electron affinity, photoconductivity, pressure dependence of electrical conductivity, etc.) were investigated quantitatively, and established as a new field of scientific study.

In the 1950's, tetrathianaphthacene was found to show abnormal electrical conductivity. In the early 1970's tetrathiafulvalene (TTF) was synthesized, and by combining it with tetracyano-p-quinodimethane (TCNQ) an organic conductor was produced, whose conductivity shows the decrease of conductivity with increasing

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temperature characteristic of a metal. The appearance of the organic conductor—synthetic metal—promoted the research to a discovery of an organic superconductor.

In 1980 superconductivity was discovered in a charge transfer complex under applied pressure. BEDT-TTF was synthesized in the search for two-dimensional conducting complexes based on TTF, which led to the preparation of superconductors having transition temperatures above 10 K.

Organic semiconductors have already found practical applications. A charge transfer polymeric semiconductor has been used as a receptor in a dry-processing photocopier, by virtue of its high photoconductivity.

Research on organic semiconductors/conductors has been carried out for these forty years. We believe that reviewing the history of its development will contribute a great deal to our future research. Our symposium will be concerned with the past, present and future of organic semiconductors, and will focus on the following topics:

- 1. A review of the synthesis, structure and solid state properties of monomeric and single component organic semiconductors.
- 2. Pristine polyacetylene,  $(SN)_x$  and the history of the discovery of charge transfer organic conductors.

Scientists from various parts of the world have been invited to take part in the symposium so that our understanding of the history of research in this field will be extensive and well-balanced. The symposium is entitled, "THE OJI INTERNATIONAL SEMINAR," and is sponsored by the Fujihara Foundation of Science and the Japan Society for the Promotion of Science, to whom we wish to express our hearty thanks. We hope that it will be the new starting point for further development of organic semiconductor/conductor research.

This proceedings consists of three parts: a review of the studies of organic semiconductors for these forty years, materials and methods, and future projects and development. The generous contribution of Gordon and Breach, Science Publishers, Inc. is gratefully acknowledged.

> Mizuka Sano Hiroo Inokuchi