# The 2007 Kyoto Prize Workshop in Advanced Technology

## Symposium

# "New Developments in Organic Semiconductors and Conductors"

Laureate: Dr. Hiroo Inokuchi

[Professor Emeritus, The University of Tokyo and Institute for Molecular Science, National Institutes of Natural Sciences]

November 12, 2007 (Mon.), 13:00 pm - 17:10 pm,
Kyoto International Conference Center

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# Program

**Coordinator**

Tisato Kajiyama

(Chairman, Kyoto Prize Committee; President, Kyushu University)

**Coordinator and Moderator**

Kazuhiko Seki

(Professor, Graduate School of Science, Nagoya University)

13:00 pm **Opening Address**

Hiroyuki Sakaki (Chairman, Kyoto Prize Selection Committee; Vice President, Toyota Technological Institute)

**Introduction to Laureate**

Hiroyuki Sakaki

**Laureate Lecture**

Hiroo Inokuchi (the Laureate in Advanced Technology)

"My 60 Years with Oraganic Semiconductors - From Basic Science to Advanced Technology"

**Intermission**

**Session Ⅰ**

Chairperson: Yasuhiko Shirota (Professor, Fukui University of Technology)

**Lecture A**

Yoshiya Harada (Professor, Faculty of Humanities, Seitoku University)

"Photoelectron Spectroscopy of Organic Semiconductors"

**Lecture B**

Tetsuo Tsutsui (Professor, Institute for Materials Chemistry and Engineering, Kyushu University)

"Advances in Organic Semiconductor Devices"

**Intermission**

**Session Ⅱ**

Chairperson: Takehiko Ishiguro (Fellow, Office for Research Initiative and Developments, Doshisha University)

**Lecture C**

Gunzi Saito (Professor, Graduate School of Science, Kyoto University)

"The World of Organic Conductors and Superconductors"

**Lecture D**

Susumu Yoshimura (Director/Specially Appointed Professor, Nagasaki Institute of Applied Science)

"Impact and Influences of Organic Electronic Materials on Industry"

**Closing Remarks**

Kazuhiko Seki

"Future Studies of Organic Semiconductors and Conductors"

17:10 pm **Closing**

# Abstract of the Laureate Lecture


## Dr. Hiroo Inokuchi

Professor Emeritus, The University of Tokyo and Institute for Molecular Science, National Institutes of Natural Sciences


## My 60 Years with Oraganic Semiconductors
## - From Basic Science to Advanced Technology

In 1947, I knocked on the door of Physical Chemistry Laboratory 1, headed by Professor Jitsusaburo Sameshima in the Department of Chemistry of the Faculty of Science at the University of Tokyo. The purpose of my study was to establish a method to measure the electrical resistance of carbon blacks. From Professor Sameshima and my senior colleagues, I learned how to build an experiment setup enabling quantitative measurement for complex systems. I then switched to studying a model compound, namely violanthrone ($C_{34}H_{16}O_2$), because of its structural similarity to carbon blacks. After repeated rigorous refining, I succeeded in measuring its electrical resistance in 1948. To disprove the idea that organic materials are insulators, I measured the photoconductivity of the model compound and carried out high-pressure experiments to test its semiconductivity, thereby showing that organic solids are semiconductors. I called such materials "organic semiconductors" (1954). The subsequent buildup of a solid foundation of experimental data due to the increase in research groups and advances in measurement technology enabled us to get the idea of organic semiconductors firmly established in the 1960s.

In 1954, my research on two-component (perylene-halogen) organic semiconductors, which I conducted with Dr. Yoshio Matsunaga in the laboratory of Professor Hideo Akamatu, proceeded to the study of organic conductors and opened up a huge field of science by spawning organic superconductors. I would like to leave the details in this area for the discussion in this workshop.

I embarked on research of photoelectronic spectroscopy under the reasoning that the elucidation of electron behavior in organic solids (molecular crystals) composed of independent molecules would provide the basis for understanding the essence of organic semiconductors. This reasoning sprang from a report I came across by Suhrmann (1935), which was quoted in a review article published in the 1940s on metal photo-emission, about an increase in electron emission efficiency due to the addition of naphthalene and anthrasene to alkali metals.

Focusing on these additives, Dr. Yoshiya Harada and I moved forward with a study on the external photoelectric effect of violanthrene-Cs compounds (1963), starting with extreme ultraviolet spectroscopy. We built up an impressive stock of results from a lot of research on photoelectronic spectroscopy with molecular organic solids. As we have been involved in the field of basic scientific fields, we are delighted that these results have made a contribution to the advanced technology behind all sorts of organic molecular electronics.

However, object of those who major chemistry is search of the substance which has new physical properties. Changes in physical properties due to irradiation with light from tetrabenzopentacene ($C_{34}H_{18}$, synthesized by Junji Aoki et al. in 1977) suggested the possibility of molecular devices. Synthesis of tetrathiafulvalene (TTF) with paraffin chains as its substitution groups in 1986 aimed for creation of new conductor.

There are nearly 100 million types of molecules on the face of the earth, some of which I believe are bound to hold the marvels of our dreams.

# Abstracts

## Yoshiya Harada
Professor, Faculty of Humanities, Seitoku University

### Photoelectron Spectroscopy of Organic Semiconductors

Photoelectron spectroscopy is the experimental technique that measures the kinetic energy distribution of electrons emitted from a material when it is irradiated with monochromatic light. The application of photoelectron spectroscopy to organic semiconductors enables us to obtain information on their electronic structures and molecular orientations. Using the information, we can interpret the electrical and optical properties of organic semiconductors and also can explore the possibility of their application to devices. As the light source for photoelectron spectroscopy, ultraviolet light, x-ray, or synchrotron orbital radiation (SOR), which includes the light of wide wavelength range from visible to X-ray region, is used. There are other electron spectroscopies, in which electrons, metastable atoms, etc. are used as irradiation sources instead of photons. In this talk, the electron spectroscopy of organic semiconductors using ultraviolet light and SOR together with that using metastable atoms will be described on the basis of the results obtained by Professor Hiroo Inokuchi and his collaborators.

## Tetsuo Tsutsui
Professor, Institute for Materials Chemistry and Engineering, Kyushu University

### Advances in Organic Semiconductor Devices

In an excellent textbook “Organic Semiconductors” published in 1964, Dr. Hiroo Inokuchi used a phrase “electric current flows in organic crystals” in a head of both the introduction and concluding remarks, for a brief and clear explanation of “organic semiconductors”. In addition, he left his perspective for the applications of organic semiconductors in future in the concluding remarks. “The words, organic semiconductors, give us a feeling that scientific research on organic semiconductors are readily connected with tomorrow success in applications. We know, however, that approaches towards real applications may face many quite hard difficulties. I dare to say it is not “impossible”, even though.” After 40 year, we are happy to know that the applications of organic semiconductor devices turned from dream to reality. Organic light-emitting devices are commercially available, and the research and development of organic semiconductor devices, such as organic thin-film transistors, organic solar cell and so on, are in progress.

As the topics related with charge-transfer complexes and doped organic semiconductor systems will be dealt in the latter sessions, I will focus on the progress in the development of organic semiconductor devices, in which charge carriers introduced by photo-irradiation or charge injection from electrodes play a major role.

## Gunzi Saito
Professor, Graduate School of Science, Kyoto University

### The World of Organic Conductors and Superconductors

The first organic conductor prepared by Akamatu, Inokuchi, and Matsunaga in 1954 has stimulated the developments of highly conductive organic compounds in the 60s, organic metals and conductive polymers in the 70s, and organic superconductors in the 80s. These breakthroughs in the basic science eventually had a large impact on the applied researchers and resulted in the practical use of organic electronics such as electrophotographs, batteries, condensers, and electroluminescences, and the extensive studies of solar cells and field-effect transistors. Physical and chemical parameters to be taken into account in the development of functional materials largely depend on the desired functions. As for the search of (super)conductors and phase transition systems, physical parameters such as ionicity, bandwidth, band-filling, dimensionality, and on-site Coulomb repulsion are of primarily importance, and the conversion them into chemical parameters such as molecular characteristics (size, symmetry, redox behavior, polarizability, and chemical stability) and crystal characteristics (molecular arrangement and interplanar spacing) is indispensable to create new conducting materials. In my lecture, the attraction of the interdisciplinary area between chemistry and physics will be presented focusing on transport properties, through (1) history of organic conductors, (2) search for low-dimensional metals, (3) expansion into two-dimensional metals, (4) development of superconductors, and (5) ultra-fast and gigantic response system.

**Susumu Yoshimura**
Director/Specially Appointed Professor, Nagasaki Institute of Applied Science

## Impact and Influences of Organic Electronic Materials on Industry

There is a long history of research on new electrically conductive materials aiming at new technologies which might follow the fully matured silicon technology. Just after the Second World War, Professor Inokuchi’s group at the University of Tokyo proposed the concept of “organic semiconductor” from its study on electrical conductivity of various hydrocarbons and their derivatives, and also synthesized highly conductive charge transfer complexes of aromatic hydrocarbons. Studies on the photoconductivity of organic semiconductors in early 1960’s have become profitable as a big business of organic photoconductors (OPCs) adopted in copying machines and laser-beam printers. The next generation of research in this field was on metallic behaviors of ion-radical salts of tetracyanoquinodimethane (TCNQ), which also encouraged the development of new electronic components. The basic concept of “enhanced electrical conductivity by the aid of the charge-transfer interaction (or electronic doping)” was further applied to organic polymers and carbonaceous materials including graphite. This instigated extensive and interdisciplinary research worldwide and resulted in novel ‘synthetic metals.’ This research was rewarded with good fruits of solid electrolytic components like ‘lithium-ion batteries’ and ‘specialty-polymer capacitors’ which are now vital to almost all digital electronic devices. Recent development of organic electroluminescent (EL) devices shows promise for their major role in the flat-panel display technology.