AWARDS

Professor Inokuchi's Achievement

Professor Hiroo Inokuchi, Professor Emeritus of Institute for Molecular Science (IMS), received the Order of Culture in 2001 for his contribution to "Discovery and Development of Organic Semiconductor." He was a Faculty member of IMS (1975–1987), and acceded the Director-General of IMS (1987–1993) and President of Okazaki National Research Institutes (1993–1995). Professor Inokuchi opened a new scientific field "Organic Semiconductor." His academic achievements are summarized as follows.

1. *Discovery and Verification of Electronic Conduction in Conjugated π-Electron Molecular Solids.*
   Through physicochemical studies on carbon and graphite, Professor Hiroo Inokuchi initiated measurements of electrical conductivity in condensed polycyclic aromatic (π-electron) compounds such as violanthrone, isoviolanthrone and pyranthrone, and verified in a most convincing way that intermolecular electron transfer is mediated by intermolecular overlap of the π-electrons. The electronic conductivity was found to clearly increase by applying high pressure, and to decrease by removing the π-electrons through hydrogenation. He named these polycyclic π-electron compounds 'organic semiconductors' since their conductivities increase with temperature.
   Professor Inokuchi extended his π-electron materials to include charge-transfer complexes, and discovered extraordinarily high conductivity in a perylene-bromine complex. This was a great breakthrough from organic semiconductors to organic conductors, which finally lead to organic superconductors. Along this line, the first successful organic metal was TTF-TCNQ studied by Heeger *et al.*, but due to the 1-dimensional (1D) nature of this compound, the metal-insulator (M-1) transition at low temperatures presented a crucial obstacle for realizing a superconducting state in these materials. Professor Inokuchi tackled and overcame this difficulty by ingenious molecular design to elevate the dimensionality to 2-D to suppress the M-I transition. He measured confirmed a persistent metallic nature in $(BEDT\text{-}TTF)_2ClO_4$ for the first time, and finally succeeded in realizing superconductors based on BEDT-TTF salts which now comprise the largest family of organic superconductors.
   Professor Inokuchi was also influential in the area of single component molecular materials, where he proposed the idea of the 'molecular fastener effect,' which involves the enhancement of intermolecular interactions due to the additivity of van der Waals interactions between long hydrocarbon chains. This idea was successfully realized in various compounds.
2. *Catalytic Activity of Some Organic Materials.*
   Professor Inokuchi was also able to exploit π-electron functionality, to design molecular catalysts. He first observed that the *ortho-para* hydrogen conversion reaction proceeded very rapidly on polycyclic aromatic hydrocarbon-alkali metal charge-transfer complex, and reached the conclusion that the catalytic activity is mediated through charge transfer. In fact, this important discovery started an explosion of studies on the catalysis of charge-transfer complexes. Charge-transfer complexes, including graphite intercalation compounds, chloranil -alkali metal complexes, and cytochrome c_3-alkali metal complexes were investigated intensively. These studies established that reactivity is closely related to the electric and magnetic properties of the molecular catalyst such that, once again, the charge transfer plays a vital role. In particular, Professor Inokuchi observed high metallic conductivity of cytochrome c_3 thin film under a hydrogen atmosphere over a certain temperature range. This anomalous behavior suggests the possible superconductivity in the biological systems.
3. *U. V. Photoelectron Spectroscopy for Organic Solids.*
   Beginning in 1963, Professor Inokuchi developed U. V. photoelectron spectroscopy for organic thin films. By analyzing the kinetic energy of photoelectrons emitted from the films, he provided key information on the electronic structures of more than 100 organic compounds. Information such as the ionization potentials, the polarization energies, and the band gap energies provides a very useful powerful guide for the characterization of typical organic solids (including polymers) as well as enabling a systematic search for molecular functionality materials.
4. *Fundamental Aspects of Molecular Electronics.*
   Professor Inokuchi reached the concept of "molecular electronics" through the study of organic materials with π-electron functionality. He identified three important functions in molecular devices: transport, storage and regulation of electrons in molecular materials. Over the past 40 years, his studies on the electron transport properties of molecular conductors have set the standard for the field he largely created. In addition to this work, he also studied graphite intercalation compounds as a means for the storage of electrons and several photochromic as regulators of electrons. As mentioned above, Professor Inokuchi is the pioneer and the leader in the field of molecular electronics.
5. *Administrative Contributions to the Fields of Molecular Sciences and Solid State Chemistry.*
   Professor Inokuchi was a primary founding member of the Institute for Molecular Science, Okazaki, Japan, which has been one of the brightest centers of molecular science in the world. He also contributed to the development of the Institute as a faculty member and the Director-General for 17 years. His contribution to molecular science and solid-state chemistry through the activities in this Institute is enormous.

Professor Kitagawa's Scientific Achievements

Prof. Teizo Kitagawa of the Center for Integrative Bioscience received a Chemical Society of Japan Award in 2001 for his contributions to "The Elucidation of Structures and Dynamics of Heme Proteins by Time-resolved Resonance Raman Spectroscopy." By utilizing advantages of vibrational spectroscopy, Professor Kitagawa has studied molecular mechanisms of various hemoproteins including the allosteric effect of hemoglobin, molecular dynamics of myoglobin, and oxygen activation mechanisms of peroxidases and cytochrome oxidase. The followings are the summary of his scientific achievements related to the award.

1) Molecular structural studies on the allosteric effect of hemoglobin: hemoglobin, a tetramer protein consisting of two α and two β subunits, binds molecular oxygen with an allosteric effect. On the basis of the assignment and monitoring of the Fe(II)–Histidine stretching mode, Professor Kitagawa demonstrated how the binding affinity of molecular oxygen is controlled.
2) Studies on the molecular mechanism of cytochrome oxidase: the catalytic cycle of cytochrome oxidase consists of at least 6 intermediates and completes in 5 msec. Prof. Kitagawa successfully characterized all the intermediates including O=Fe(V) species, which had been considered to be Fe(III)–O–O–Cu(II) for more than 30 years.
3) Direct observation of cooling of heme upon photodissociation of carbonmonoxy myoglobin: the formation of vibrationally excited heme upon photodissociation of carbonmonoxy myoglobin and its subsequent vibrational energy relaxation were monitored by picosecond anti-Stokes resonance Raman spectroscopy. This direct monitoring of the cooling dynamics of the heme cofactor within the globin matrix allowed discussion on the thermal energy flow through the protein moiety and to the water bath.
4) Application of ultraviolet resonance Raman spectroscopy for higher order structural changes of proteins and their dynamics: a Raman spectrum of one specific amino acid residue such as tyrosine, tryptophan, phenylalanine, and histidine in a protein as large as 200,000 dalton was selectively observed by ultraviolet resonance Raman spectroscopy with the use of 200–240 nm Raman-excitation. The observation for a change of one particular amino acid enables us to understand a communication pathway between different subunits upon oxygen binding to a heme.

Associate Professor Taira's Scientific Achievements

Associate professor Takunori Taira of Laser Research Center for Molecular Science received the Technology Development Award of Japan Fine Ceramics Association in 2001 for his contribution to "Fabrication of extremely low-scattering-loss Nd:YAG ceramics and development of high-performance ceramic lasers." This award is given to the persons who invented new product or technology which made a big impact on the technology development for fine ceramics industries. He and his co-winner, Dr. Akio Ikesue of Japan Fine Ceramics Center and Professor Kunio Yoshida of Osaka Institute of Technology, developed quite a new technique to fabricate highly transparent Nd:YAG ceramics and succeeded in laser oscillation with much higher efficiency than using conventional Nd:YAG single crystals. YAG ceramics can be doped with much more Nd ions than YAG single crystals, which increases the absorption efficiency for the pump beam. This advantage is expected to realize high-power and highly efficient microchip (the thickness of laser medium is less than 1 mm) lasers which emit blue or green as well as 1 μm light. His achievements broke the preconception that ceramics are always opaque, opening the door to new applications of ceramics as "optical materials."

Associate Professor Kinoshita's Scientific Achievement

Prof. Masahiro Kinoshita at Kyoto University, a former visiting professor of our institute, has been awarded the "good paper prize" for 2001 from the Society of Chemical Engineers, Japan. The prize is awarded every year to about four distinguished papers that were published in the Japanese Journal of Chemical Engineering. Professor Kinoshita's paper to which the prize has been awarded is entitled "Statistical-Mechanical Analysis on Entropically Driven Formation of Ordered Structure" (*Kagaku Kogaku Ronbunshu* **Vol. 27**, No.6, pp. 683–689 (2001)). The paper was written during his stay at IMS as a visiting professor. Professor Kinoshita has been involved in a variety of collaborative projects in our institute. The outline of the paper is given below.

The paper sheds light on roles of the entropic excluded volumes in biological systems by a microscopic theory. It deals with the process that a surface and large particles immersed in small particles form ordered structure with the result of increase in the system entropy. More specific, major conclusions drawn for the entropically driven contact of large particles with a surface are as follows: Great specificity arises between the diameter of the large particle and the surface curvature, and high selectivity is provided for the lock and key steric interaction between macromolecules. It would be possible to control the motion of a large particle by adjustment of the surface geometry: the study could be extended to nano-technology such as control of particle arrays. Further development is described in the following: M. Kinoshita, "Spatial Distribution of a Depletion Potential between a Big Solute of

Arbitrary Geometry and a Big Sphere Immersed in Small Spheres," *J. Chem. Phys.* **116**(8), 3493–3501 (2002).

Research Associate Sato's Scientific Achievement

Dr. Hirofumi Sato in Kyoto University won the "The Chemical Society of Japan Award for Young Chemists for 2001."

Sato had been a research associate in our institute untill this April, and the prize is awarded to the research he has carried out in the institute.

Chemical reacion is not only a central issue in the material science, but also an essential problem to understand what going on in biological system. In the mean time, Chemical reactions in our real life is always taking place in some solvent environment, not in vacuo, which is true especially in our living systems. The prize is awarded to Sato for his contribution to establish a molecular theory with respect to the solvent effect on chemical reactions. Sato's accomplishments are classified roughly into two. The first is concerned with the methodological development of the RISM-SCF theory. The RISM-SCF theory is a theory first proposed by Tenno, Kato, and Hirata in 1993, which combines the statistical mechanics of molecular liquid (RISM) with the ab initio MO theory to determine the electronic structure of a solute molecule and solvent structure self-consistently. Sato has given an alternative formulation of the theory based on the variational principle, which at the same time has established a mthod of calculating the energy derivatives. The latter is of particular importance, for example, to optimize geometry of a molecule and to calculate the vibrational spectrum of a molecule in solution, and provides a new tool to explore chemical processes in solution. In fact, the theory of NMR chemical shift in solution, which has been developed by Dr. Yamazaki, is based on Sato's variational formalism and on the method of energy derivatives. With respect to methodological aspect, Sato has also made important contribution concerning coupling of the ab initio electronic structure theory with the 3D-RISM theory. The 3D-RISM theory has been developed by Dr. Kovalenko in our group during last few years, which provides detailed three dimensional structure of solvent around a solute. Sato has combined the theory with the ab initio method to study the electronic structure and solubility of a CO in water.

Dr. Sato's another contribution is to explore a wide variety of chemical reaction in solution, from inorganic to organic, by means of the RISM-SCF theory, and to give a microscopic explanation to reaction mechanisms which have long stayed in phenomenological levels. Among many interesting studies Sato has done, I would like to introduce just one example which concerns the acidity of hydrogen halides in water, a problem in high school text book. All the hydrogen halides except for hydrogen fluoride show strong acidity, while the fluoride exhibits weak acidity. The phenomena is paradoxical if one considers the fluoride has the largest electronegativity. The problem attracted attention from theoretical chemists including L. Pauling. The key to solve the puzzle is to take account for the solvent effect. In fact, Pauling has shown based on the experimental free energy of solvation that the non-dissociated form of HF has lower free energy than the dissociated form. However, Pauling could not answer the question why it happens, because his analysis was phenomenological. Based on the RISM-SCF method, Sato first has shown that HF is in fact a weak acid. Moreover, he could have successfully explain the reason. According to the explanation, HF makes two types of hydrogen-bonds with water molecules, ($H_2O\cdots H–F$) and ($FH\cdots H–O–H$), while all other hydrogen halides form only one type of hydrogen-bonds ($H_2O\cdots H–X$). The extra hydrogen-bond gives extra stability to the non-dissociated form of HF.

Research Associate Shoji's Achievements

Research Associate Dr. Ichiro Shoji of Laser Research Center for Molecular Science received "Young Scientist Award for the Presentation of an Excellent Paper," in 2002, from the Japan Society of Applied Physics ('JSAP) with the paper "Reduction of Depolarization Induced by Thermal Birefringence Using a (100)-cut YAG Crystal." This award was given to young scientists who have presented excellent papers at the JSAP annual meetings.

Dr. Shoji studied at the Tokyo University, there he investigated on the nonlinear optical phenomena and, together with Prof. Ito, he built the way to measure the absolute nonlinear constants. After moved to Taira group of the Institute for Molecular Science, and he becomes interested in the ceramic YAG lasers. The ceramic YAG is an attractive and strange material as the laser medium. He was bewildered by this new material and found the mistakes in the solid-state laser theory. In the Solid-State Laser field, many efforts were done toward the high-power and high-quality laser system by the compensation of thermally induced problems risen from the pump quantum defects. The solutions, which are complicated and not perfect are, based on (111)-cut YAG material. Every compensation method based on (111)-cut YAG because Drs. Koechner and Rice have built a beautiful theory about thermal effect in laser rod. Lately, Dr. Shoji found the mistakes in Koechner's theory by the experiments and built the new model. With detail measurement of thermally induced birefringence in Nd:YAG single crystal of (111), (100), and (110)-cut we discovered new way to reduce it drastically. This novel solution to reduce the thermal problems should apply to any solid-state optical devices.

His result makes it clear that, sometimes, we have to reconsider a problem from its basics in order to solve the complicated high technology and/or practical situations.

Mr. Hayashi's Scientific Achievements

Our Colleague Mr. Naoki Hayashi, Department of Molecular Structure, received the Award for young researcher of the Liquid Crystal Society of Japan in 2001 for his contribution to "Investigations of Molecular Orientational Ordering in Liquid Crystals by Polarized Raman Scattering." Since the discovery of V-shape switching of liquid crystals, the mechanism of the switching has been open to dispute. Especially a random switching mechanism has interested people, however, a clear evidence for the random switching mechanism has not been reported. Mr. Hayashi could give the experimental evidence proving the random switching mechanism of V-shape phenomena of liquid crystal by using the polarized Raman scattering measurement. Moreover, he has found the breaking out of the uniaxiality in the molecular orientational distribution in ferroelectronic phase of liquid crystal. His works have been published in the journals, *Phys. Rev. E*, *Phys. Rev. Lett.*, and *etc*.

Dr. Hisashi Tanaka's Scientific Achievement

Dr. Tanaka, a JSPS postdoctral fellow in Kobayashi Group at the department of Molecular Assemblies, received the first "Synthetic Metal Young Award" at the International Conference of Synthetic Metals held in Shanghai (ICSM2002)(June 29-July 5, 2002). This newly started award will be given every two years at ICSM meetings. The ICSM2002 had more than 2000 participants, from which four young participants (one student, two postdoctral fellows and one young independent researcher) were selected. Dr. Tanaka received the post-doc award for his contribution to the recent two remarkable achievements in the field of synthetic metals: (1) the development of single-component molecular metals and (2) the discovery of the field-induced superconductivity of organic conducting system.

Mr. Zhi-Hong Wang's Scientific Achievement

Mr. Zhi-Hong Wang in Urisu group, a third year Student of the Graduate University for Advanced Studies received the Award for Most Impressive Presentation in 2001 Microprocess and Nanotechnology Conference for his contribution "Hydrogen Diffusion and Chemical Reactivity with Water on Nearly Ideally H-terminated Si(100) Surface." He has observed the hydrogen atoms in the Si bulk spectroscopically for the first time by using BML-IRRAS (infrared reflection absorption spectroscopy using a buried metal layer substrate).