A Place in the "X-ray" Sun

On the Cutting Edge

Since the inception of the SPring-8 utilization in 1997, more than 100,000 users have visited SPring-8 and carried out experiments to uncover mysteries in science. Described here are a lineup of the nine pioneers in Life Science, Materials Science, Chemical Science, Earth & Planetary Science, and Light Source Technology from SPring-8.

1. A Scenario Writer of Interplay between Protein and Ion in Membrane Transport
Chikashi TOYOSHIMA

Noted for his distinguished achievements for the calcium ion pump (Sarco- (Endo-) plasmic reticulum Calcium ATPase 1, SERCA1) in structural biology, Chikashi Toyoshima has been one of the top international biophysicists in the highly competitive world of life science. He is a professor of Molecular and Cellular Biosciences at the University of Tokyo.

He started his scientific career as an electron microscopist and worked on muscle filaments and ion channels. Drawing on all of his expertise in the fields of mathematics, physics and biology, he has uncovered the atomic structures of biomolecular complexes that could never be studied before. From 1986-1988, he worked on the acetylcholine receptor and a motility assay for motor proteins as a Postdoctoral Fellow with Drs. Nigel Unwin and James Spudich at Stanford University, in the USA. He then moved to the MRC Laboratory of Molecular Biology in Cambridge in the UK to continue his work with Dr. Unwin on the electron crystallography of 2D and tubular crystals of membrane proteins. During this

Chikashi Toyoshima
Leading his research team even at midnight at SPring-8

period, he initiated collaboration on SERCA1a with Dr. David Stokes. Toyoshima was a major contributor to the development of cryo-electron microscopy and computer programs that permit 3D structures to be reconstructed from tubular crystals. He used these methods to obtain the first images of the nicotinic acetylcholine receptor in its native membrane and an 8 Å structure of SERCA1a.

After that, Toyoshima determined the structure of the calcium pump in different phases of the reaction cycle by X-ray crystallography. The work provided a magnificent result for the structural elucidation of the mechanism of the action of P-type ATPases: cation pumps that become phosphorylated during the reaction cycle and are responsible for maintaining cation gradients across membranes. The questions that he has successfully addressed using SERCA1a as a model are as follows: How are cation binding sites created and destroyed in the transmembrane domain following chemical events at the phosphorylation site 50 Å away? How is the chemical energy in ATP converted to transfer ions against a concentration gradient? What is the role of phosphorylation? Why is countertransport necessary, despite the fact that the countertransported ions return to the original side through ion channels? He has provided answers to these fundamental questions by combining X-ray crystallography, electron microscopy and molecular dynamics simulations and, therefore, "revolutionized how researchers are able to study the structure of proteins" (Hitchcock Lectures citation at the University of California, Berkeley, 2008). His research produced the first images of an ion pump at work in atomic detail and explained well the mechanism of the reaction scheme.

Toyoshima has also collaborated with Dr. MacLennan to provide an explanation at molecular and atomic levels for the mechanism of regulation of SERCA by phospholamban and sarcolipin in cardiac tissues. He showed thapsigargin (TG) and two other inhibitors prevent the movements of transmembrane helices in SERCA, and a complementary protein surface is enough to confer a picomolar dissociation constant for TG. These are the first studies for the structural elucidation of inhibitors that bind to a transmembrane region.

Cover Picture of Nature in 2000

On the basis of his crystal structures and proposals, a new generation of experimental studies, including mutagenesis, spectroscopy, and electrophysiology, and theoretical studies have been conducted. For instance, by analyzing his crystal structures, an even more potent derivative of TG was developed by an American/Danish group and its application to prostate cancer therapy is advancing. His work is thus widely influential and has been included in textbooks of biochemistry and even statistical physics. There is no doubt that SPring-8 has played a crucial role in his achievements in Structural Biology. His paper in this scientific highlights is shown on page 18 .

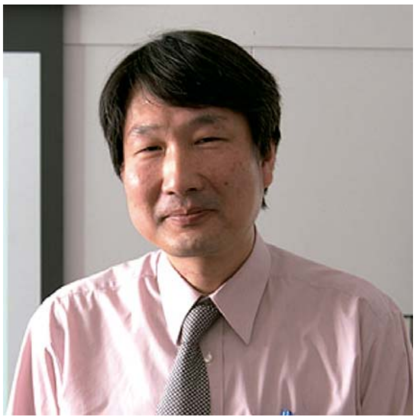
Toyoshima is always leading off his experiment

2. A Pathfinder in Materials Science of Correlated Electron System
Hidenori TAKAGI

Hidenori Takagi is a professor at the University of Tokyo and a chief scientist of RIKEN. He has been breaking ground on various advanced hard materials by discovering the self-organization of electrons, superconductivity thermoelectricity, and negative thermal expansion as well as with their applications. In his research, SPring-8 is one of the indispensable tools for unveiling a rich variety of exotic electronic materials.

So far, right after the discovery by Bednorz and Muller of high temperature superconductivity in La- Ba-Cu-O, Takagi verified for the first time the occurrence of superconductivity by magnetization measurement and subsequently identified the layered K_2NiF_4 structure responsible for high temperature superconductivity, by which "two-dimensionality" was recognized. He then discovered the electron-doped superconductor $(Nd,Ce)_2CuO_4$ and showed that high temperature superconductivity shows up symmetrically by both hole- and electron-doping. This has brought a drastic change in our understanding of high-T_c cuprate superconductors. He found the unusual charge transport (such as resistivity and Hall effect) in the normal state of cuprates, which led to the concept of the pseudo (normal state)-gap, one of the most important key ideas in cuprate physics nowadays. Since then, he has been addressing the mystery of the pseudo-gap phase. To understand the much-discussed hidden electronic order behind the pseudo-gap, he developed a new class of cuprate superconductors $(Ca,Na)_2CuO_2Cl_2$ as a playground, which led to the discovery of a self-organized state of electrons, often called a checkerboard or nanostripe.

He recognized the very rich physics in correlated electrons through those outstanding achievements in cuprate physics. In the mid-90s, he expanded his repertoire from cuprates to transition metal oxides in general. Since then, he has been pioneering work on the novel electronic phases of a variety of complex transition metal oxides, particularly exotic charges and spin liquids produced by geometrical frustration. His discoveries include a frustration-induced heavy fermion state in mixed-valent LiV_2O_4, magnetic-field-induced half-magnetization state in the strongly frustrated S=3/2 anti-ferromagnet $CdCr_2O_4$, three-dimensional quantum spin liquid state in $Na_4Ir_3O_8$ with hyper-kagome lattice, Jahn-Teller driven charge ordering in mixed-valent $LiRh_2O_4$, and spin-orbit complex state in a Mott insulator Sr_2IrO_4. Now, he is trying to open the door to the 5*d* metal magnetism using a newly developed magnetic scattering technique in SPring-8, whose details are described in the section of Materials Science, page 54. His recent discovery of a spin-orbital Mott state in Sr_2IrO_4 shall ignite intensive research on exotic 5*d* metal oxides.



Hidenori Takagi

3. Twosome Players in Fullerene Superconductivity Kosmas PRASSIDES & Matthew ROSSEINSKY

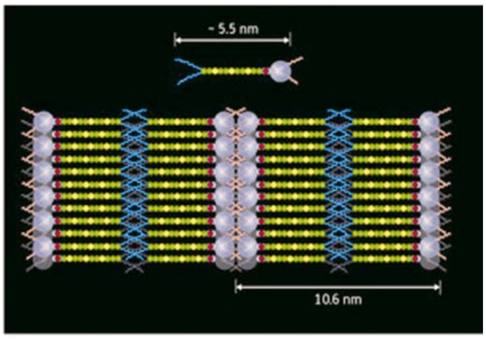
Kosmas Prassides is professor of Materials Chemistry at the Department of Chemistry, Durham University. Matthew Rosseinsky is professor of Inorganic Chemistry at the University of Liverpool and was elected a Fellow of the Royal Society (FRS) in 2008.

They share a common scientific origin to their careers since both obtained their D. Phil. degrees under the supervision of professor Peter Day FRS. Their research interests are multi-disciplinary and encompass a range of structural, magnetic and electronic problems in advanced materials, straddling the areas of condensed matter physics and chemistry. Their work has been spanning several fields, microporous materials science, mixed valency and transition metal oxide chemistry as well as fullerene science and they have extensive collaborations at SPring-8.

Kosmas Prassides

In the last two decades, Rosseinsky and Prassides have been leading the research on fullerene superconductivity since the discovery of alkali metal fullerides (*Nature* 352 (1991) 787). They have been using core chemical approaches to access unusual structures and electronic, conducting and magnetic ground states and probe the physics in key materials, especially metal fulleride solids. Rosseinsky has been developing synthesis techniques of novel functional materials in a chemically understandable manner. Prassides has unveiled their structure-property relationships. He is a frequent user himself of the SPring-8 facilities and his recent activities have been facilitated by utilization of the BL44B2 & BL10XU beamlines. In the last two years, Prassides and Rosseinsky have developed the metal fullerides into the best model systems for correlated electron high T_c superconductivity (*Nature Materials* 7 (2008) 367; *Science* 323 (2009) 1585; *Nature* 465 (2010) doi:10.1038/nature09120) and have supported their ideas by structural characterization using high pressure powder diffraction experiments at BL10XU (see page 58). Their work has advanced the understanding of molecular superconductivity and magnetism and the generic problem of the metal-Mott insulator transition to an unprecedentedly high level.

Matthew Rosseinsky



New liquid-crystal molecule (top) designed with fullerene (purple). The oligothiophene chains (yellow/green) self organize. Liquid crystal photovoltaic device (bottom) tailored using hydrophobic/hydrophilic tails represented by blue/red lines, respectively.

4. The Tailor of Superb Exotic Molecules Takuzo AIDA

Takuzo Aida, Professor; the University of Tokyo/RIKEN is known as one of the most imaginative and productive polymer chemists in the world. His energy and creativity have helped shape polymer chemistry for more than two decades. Aida has achieved seminal and creative chemistry demonstrating novel syntheses and functions of linear, dendritic, and supramolecular polymers as well as tailoring nanoscale functions through precision control of molecular interactions.

In recent years, he has used SPring-8 as a key tool to prove that the molecular structure is conclusively created as he designed it as well as to find a clue to more advanced designs of molecules. His first successful utilization of SPring-8 was the structure confirmation of a new type of nanotube that could also conduct electricity.

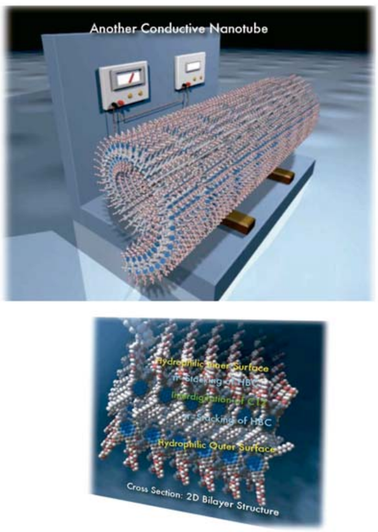
Several years ago, Aida aimed to create s new nanotube using a new type of graphene molecule by adding hydrophilic and hydrophobic moieties. The molecule "self-organization" combined to form nanotubes of 20 nm diameter with hydrophobic moieties inside.

Takuzo Aida

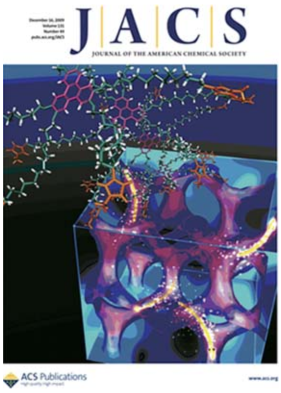
By the SR scattering experiment, he established solid evidence that graphene molecules bearing hydrophobic and hydrophilic moieties bond together at the hydrophobic moiety, forming molecular pairs that build up in a spiral pattern to creat a tube (*J. Am. Chem. Soc.*, 2008). Consequently, his discovery proved the feasibility of creating a new functional graphite nanotubes by changing the structural design of the original molecules.

Aida has also succeeded in designing liquid crystals phase that flows like a liquid but has a short-range order between molecules that spontaneously assemble to form a donor-acceptor array, which should lead to the development of high-efficiency organic photovoltaic devices (*J. Am. Chem. Soc.*, 2008).

This year, his discovery of "bicontinuous cubic liquid crystalline materials from discotic molecules" led to a photograph of the materials being the cover



Novel graphite nanotube created by Aida



Novel graphite nanotube

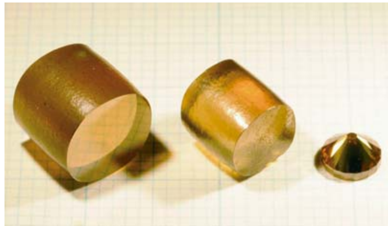
picture of the Journal of the American Chemical Society. The details will appear in the section of Chemical Science, page 60. Aida's quest for a new paradigm creation in Chemistry shall attract increasing attention via SPring-8.

5. An Expedition Cartographer in High Pressure Science
Tetsuo IRIFUNE

One of the pioneers in Earth Sciences, Tetsuo Irifune, is a professor at Ehime University. He has been leading synchrotron radiation experiments under high pressure using the Kawai-type multianvil apparatus (KMA) at BL04B1 since beamline construction started. He published the very first paper from SPring-8 in *Science* (1998) and has been keeping on top of world-class research activities. One of his representative works is "*Phase transitions in mantle and subducting plate materials*".

Irifune has been conducting systematic experiments on phase transitions and associated density changes in the subducting lithosphere (plate) as well as on surrounding mantle materials using the KMA, combined with synchrotron radiation in addition to SEM, XRD, TEM, etc. His research covers various materials of the Earth's interior, such as pyrolite, harzburgite, basalt, and granite compositions, as well as related minerals with simpler chemical compositions. In the past decade, Irifune's findings have led to new models on the dynamics and circulation of plate-related materials in the mantle. Some breakthroughs in the Earth Sciences began to arise from his discovery of new high-pressure phases, such as the calcium-ferrite type $MgAl_2O_4$, CAS phase,

Tetsuo Irifune



HIME-DIAs

K-hollandite II, and $MgCO_3$ magnesite II (*Nature*, 2004), in which SPring-8 played a major role.

His research and development at SPring-8 have also facilitated various innovations on a higher-pressure generation techniques, which have been applied in order to upgrade the measurement techniques, and allowing for the exploring of even deeper Earth mineralogy at SPring-8. One of his most important contributions is the development of an advanced cell (Ehime cell) for the KMA apparatus, which allows *in situ* X-ray observations of phase transitions under higher pressure and temperature. The first successful application was the precise determination of the spinel-postspinel transition boundary in Mg_2SiO_4 (*Science*, 1998). This high-performance cell has been opened for public use and has widely contributed to the Earth science community at SPring-8.

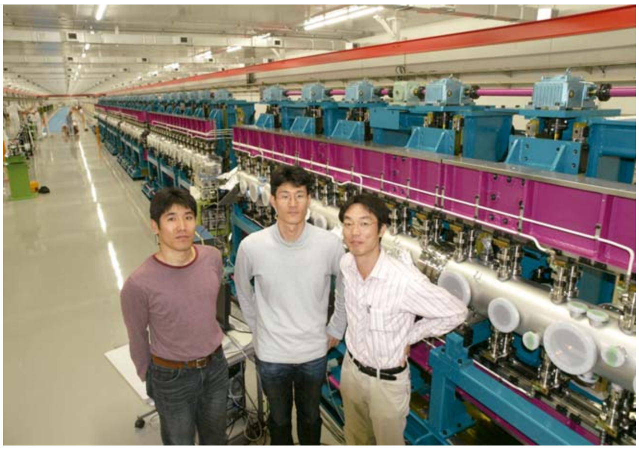
Very recently, an upgraded form of the Ehime cell generated pressures above 50 GPa and temperatures of ~2500 K. One outcome from such an advanced technique has been published in *Science* (2010) and is described in the section of Earth & Planetary Science in this scientific highlights (see page 114). In the meantime, he applied KMA technology to materials synthesis and succeeded in the first synthesis of a pure nano-polycrystalline diamond (NPD or HIME-DIA = Highly Incompressible and Mechanically Endurable DIAmond) under high pressure (*Nature*, 2003). Irifune is now applying the HIME-DIA for various purposes relevant to high-pressure Earth and Materials Sciences, including those for further higher pressure and temperature generation at SPring-8.

Irifune's Laboratory

6. Trinity Siblings at the Forefront of the XFEL Project

Takahiro Inagaki, Takashi Tanaka & Kazuaki Togawa

One of the three X-ray Free-Electron Laser (XFEL) facilities in the world is nearing completion at the SPring-8 campus. The others are the Linac Coherent Light Source (LCLS, Stanford University, USA) and the European XFEL (DESY, Germany (EU)). Among them, the XFEL in SPring-8 has a unique concept, i.e., SCSS (SPring-8 Compact SASE Source), which will achieve a high-performance XFEL in a compact size. This concept requires accomplishing three technical innovations: a low-emittance injector based on a 500-kV pulsed thermionic gun with a single-crystal cathode, a high-gradient C-band acceleration system, and a short-period in-vacuum undulator. The following three young scientists (RIKEN) have been tackling these challenging tasks.



Kazuaki Togawa is a thoughtful achiever, who made a breakthrough in the common assumption of low-emittance injector technology. When the discussion of the SCSS concept design started, most scientists thought that a photocathode RF gun would be the best choice for the XFEL. Thus, our choice, which is a thermionic-gun based system, was thought to be a high-risk challenge. However, his elaborate thermionic-gun system succeeded in achieving the homogeneous and stable low-emittance electron beams required for XFEL and disproved the prejudice. The original system based on a CeB_6 single crystal cathode produced by his deep technical insight and passion for the XFEL project is cornerstone of the achievements of the XFEL project as well as of the EUV FEL in utilization.

Takashi Tanaka is a task leader for the development of the short-period in-vacuum undulator. He has created a specific permanent-magnet formation optimized for the required short period toward the present design limit. He has also developed the world's first *in situ* field measurement system named "SAFALI" (Self Aligned Field Analyzer with Laser Instrumentation), to achieve the strict field quality specification for the XFEL. In addition, he constructed a three-dimensional FEL simulator, SIMPLEX (reverse order of X-ray fEL Practical SIMulator; abbreviation in reverse), which is a powerful tool for figuring out various technical problems, because gimmicks on the performance of the undulator train associated with alignment tolerance, an energy chirp by undulator resistive-wall impedance, and an orbit setting error, among other factors should be removed to achieve the full-power operation of the SASE XFEL. So far, SIMPLEX has provided feasible approaches to solve all the problems we had for the XFEL construction at the SPring-8 site.

Takahiro Inagaki is a key person in the development of the operational acceleration system based on the C-band optimized for the XFEL. Since this system provides a high gradient of 35~40 MV/m, which is twice as high as a conventional gradient of ~20 MV/m, the length of an electron linear accelerator, a main part of the facility, can be reduced by half. Also, he succeeded in developing an ultra-stable klystron modulator power supply to stabilize the RF acceleration phase, which is crucial for the stable operation of the XFEL. His painstaking work, the newly developed C-band system, has achieved the design performance of XFEL, i.e., 39 MV/m at a repetition rate of 60-pps, with the lowest fault rate satisfying a usable level.

by Masaki Takata and Hitoshi Tanaka