OCARINA通信

The OCU Advanced Research Institute for Natural Science and Technology

Special Project

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-The largest mystery solved in photosynthesis to which world attention is drawn-

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デザイン・イラスト

VOL.2

Special Project

Establishment of the Artificial Photosynthesis Research Center, a base for collaborative research with industry

–The largest mystery solved in photosynthesis to which world attention is drawn–

Beginning in the spring of 2013, the Artificial Photosynthesis Research Center at Osaka City University will begin in earnest. Building upon the results of photosynthesis research carried out at the OCU Advanced Research Institute for Natural Science and Technology (OCARINA), we are proceeding forward in an accelerated fashion with research that is aimed at outlets through collaboration with industry. Regarding that, here we present a roundtable discussion on the future prospects for photosynthesis and artificial photosynthesis research between OCU President NISHIZAWA; University Board Member YASUMOTO, who has devoted ceaseless efforts to establishing the Artificial Photosynthesis Research Center; Professor KINOSHITA, director of OCARINA; and Professor KAMIYA, who solved the greatest mystery of photosynthesis research.

Building on the results of photosynthesis research, towards research aimed at realizing artificial photosynthesis

Professor **KINOSHITA:** OCU's Advanced Research Institute for Natural Science and Technology (OCARINA) is made up of 9 people, 2 regular academic staff and 7 specially appointed researchers; has obtained funding from the Japan Science and Technology Agency (JST) as a Strategic Creative Research Promotion Project (CREST), from the Japan Society for the Promotion of Science (JSPS) as a funded project under Basic Research S, and research funding from many other sources; and is involved in groundbreaking research. Among our projects, one that has been cited as a major event is Professor Kamiya's research results in solving the greatest mystery of photosynthesis.

Prof. **KAMIYA:** Photosynthesis research is a rather well-established field, but there was still one obscured point that was not understood. Then, in 2011, working together with Professor Shen at Okayama University, we were able to clear that up. Through our research, the potential for realizing artificial photosynthesis has been heightened, and research is now accelerating around the world.

President **NISHIZAWA:** Professor Kamiya's research was listed by the journal Science as one of the top 10 world breakthroughs of the year 2011. It was chosen along with the solar rocket probe Hayabusa, which is a national project of the Japanese government. So I thought that our university should put even more effort into the project.

Prof. **KINOSHITA:** That's right. As one consequence of the great ripples in every direction caused by Professor Kamiya's research results, it turned into a current that I think led to the establishment now of this Artificial Photosynthesis Research Center. That is what has made it possible for the Artificial Photosynthesis Research Center and OCARINA to collaborate together and in the future develop photosynthesis and artificial photosynthesis research using the most advanced equipment.

Boar Member **YASUMOTO:** I believe this is the first research facility in Japan to be dedicated to Artificial Photosynthesis. Here at Osaka City University, we have not only Professor Kamiya, but also Professor Kinoshita and Professor Hashimoto, all specialists in photosynthesis research. Beyond that, you will taking up the challenge of artificial photosynthesis, which has been called the 'dream technology.'

Prof. **KAMIYA:** Often people tell us that our work is "really filled with dreams," but I think that already now artificial photosynthesis is not a 'dream' but has become a research theme that is something that "somehow we want to make it happen, we must make it happen." We will deepen the research through a 'Joint Research Course' with enterprises and the university working together closely as a tag team.

Board Member **YASUMOTO:** In the sense that it's a utilization of natural energy, I want us to start quickly and get at least one step closer to application. With that in mind, while we are still at the level of basic research, I've been proposing that we should move forward in collaboration with industry. As a result of that, we've been able to get the cooperation of the Osaka City government, and we've now reached the point where we've established the Artificial Photosynthesis Research Center.

Prof. KINOSHITA: We've held a lot of roundtable discussions and meetings with people in the Osaka City government, and yes, they have great expectations for artificial photosynthesis.

Board Member **YASUMOTO:** Usually, it's thought to be alright for basic research to be conducted at universities, but that's really not the case. Artificial photosynthesis is really an enormous technology and is a technology that in the future has the power to change the world, so it is important at an early stage to be involved in it in a collaboration between industry and academia. I myself come from a background in industry, and up until now I've had the impression that "there's no research done at the university that is aimed at outlets," and it was really not possible to realize an industry-academic collaboration in basic research. That's why now, in making it happen, I think there is a really important significance.

Prof. **KINOSHITA:** What has been called the 'holy grail' is something that we are now trying to grasp. On that point, I think the people in the world of industry as well have a lot to look forward to.

Prof. **KAMIYA:** We are doing basic research, so our job is to elucidate what it is that happens in photosynthesis that occurs in nature.

The results of that research, from the standpoint of artificial photosynthesis, become the 'blueprints.' And now, these blueprints have all been revealed. Therefore, we can work on them all together from now on, including the world of industry and the world of government.

Boar Member **YASUMOTO:** That's right. From now on, engineering professors will also have to get involved and work out plans for how to actually make this pay off. We will put together a joint research office at the university together with enterprises that have shown an interest in artificial photosynthesis, and researchers from those firms will be based there regularly together with regular staff researchers form the university. We will act to create such a "Joint Research Course." And we can expect that there will be wide requests from people in private industry to also use the large scale research equipment and facilities that we will be installing. Looking to the future, I would like to see us create an open research center that can also respond to requests from the private sector.

Prof. **KINOSHITA:** This kind of involvement is something that we researchers cannot start on our own. I think it's something where we need the active assistance of the university president and all of the board members. It needs to be an organization that can disseminate our work out the society, to Asia, and to the world as a whole.

President **NISHIZAWA:** Three years ago, when I became university president, I set out 3 important items on my agenda. Those were, first, to develop education and research in the field of urban science and strengthen our function as a think tank for the city of Osaka; second, to foster members of society with a high level of professional specialization; and third, to strengthen our international presence. Artificial photosynthesis fits in precisely with the first item, the field of urban science. From my first year serving as president, in conversations with the professors in OCARINA, I thought that this was probably something the university should promote more. I believe that strengthening the collaboration with industry, and carrying basic research disciplines forward into a form that can be utilized by society are also part of the university's job.

Prof. **KINOSHITA:** From April onwards, we will be entering a new phase. Even within the guidelines of OCARINA, there have been questions about "how do we get the word out to society?" but up until now we haven't moved away from an academic dissemination of information. At the Artificial Photosynthesis Research Center, we have to create an organization with the power to disseminate information, not only through academic channels, but with an awareness more of Asia's society as a whole. Right now, in the field of photosynthesis research, compared to even South Korea or China, our Japanese researchers, led by Professor Kamiya, are really out in front.

Prof. **KAMIYA:** In the basic research, I believe we are now the most advanced.

Prof. **KINOSHITA:** Japan has to have the backbone that comes from being the leader of the pack. Not being locally limited, but getting the word out from Osaka to Asia and further to the world. That perspective will be absolutely necessary.

President **NISHIZAWA:** That's quite true. This kind of research is something that can't be carried out by one lab or by one researcher. In order to put it into practical application, the power of enterprises will absolutely be necessary. I think this Artificial Photosynthesis Research Center has come about as the place that will connect them all together. Looking beyond that, since there are essentially parts of this that can be applied to the society, there will come a time when this will have to be dealt with even beyond the framework of this research center. Once it gets to a certain level, I think this research will spread out and speed up explosively. Up to that point, we are the ones that have to step up the process.

Proceeding with the research in cooperation with other universities, aiming towards practical implementation in the year 2030

Prof. **KINOSHITA:** Actually, we have proposed a road map for the Artificial Photosynthesis Research Center to the Osaka Municipal Assembly that aims at practical implementation by 2030. It's a road map in which research begins at maximum speed in 2015 and steps toward practical implementation begin in 2020. At present we have put

Special Project

profile
Yoshio YASUMOTO

Board of Directors Member, Osaka City University (in charge of industry collaboration, knowledge resources, and information) / Director, Industry-University Collaboration Promotion Headquarters / Director, New Industries Creation Research Center
B.S. and M.S. in Electrical Engineering, Kyoto University School of Engineering. Ph.D. in Engineering. Began working at Matsushita Electric (now Panasonic) Ltd. in 1977. Served as Director of Matsushita Electric's Overseas R&D Promotion Center, Board Member, R&D Area Supervisor, etc. In current position since 2010.

in place a system so that research can proceed quietly step by step in line with the road map, but we will first have to explode in 2015. That's coming very soon.

Prof. **KAMIYA:** Speaking honestly, I thought it was a road map that set the hurdles quite high, but research at OCARINA is proceeding substantially and the time is now here when the Artificial Photosynthesis Research Center can start to move, so I think that "this might work."

Board Member **YASUMOTO:** I too was quite surprised by the road map, but I certainly feel that we may be able to make it.

Prof. **KINOSHITA:** All kinds of economic evaluations have come out as to why 2030 is such an important year. The thing that will have the most effect is the fact that the balance between oil production and demand will collapse. People are putting their hopes in things like shale gas, but there are still a lot of problems, and so I think that will certainly be a problem in the year 2030. If we haven't found a way forward by that time, there will probably be a great deal of social unrest at the very least. Also, when spin-off research also appears, that was presented in the artificial photosynthesis forum, wasn't it?

Prof. **KAMIYA:** The breakdown reaction of water in photosynthesis that we are researching is a place where weed herbicide is at work. If the structure of that becomes clear, we will probably be able to make more effective herbicides. In the breakdown of water in artificial photosynthesis, if we can come to grips with the place where the oxygen producing reaction is, I think that will certainly give birth to other spin-off technologies and knowledge.

Board Member **YASUMOTO:** The Artificial Photosynthesis Forum which began in September 2012 is the venue for joint activities in disseminating information to the public by Osaka City University and the Osaka City Urban Industries Promotion Center public foundation. The other day we had talks by this university's Professor Umena and Professor Miyake from Osaka University. After that, time was provided for them to mix together with people from private industry and have an exchange of views, wasn't there?

Prof. **KINOSHITA:** After the research presentations at the venue for exchanges of views, there weren't just exchanges between us and the firms, but there was quite an active exchange of views between the various firms themselves, weren't there? Professor Miyake of Osaka University's Basic Engineering Department says that he will cooperate in every way with our research. Having opinions from a different perspective is extremely valuable, so we are quite gratified. I would also like to see us tie up fully with Osaka Prefectural University who are strong in general applied research.

President **NISHIZAWA:** That's right. I think we should advance joint research with an eye on the future.

Prof. **KINOSHITA:** We will proceed with the basic research here at OCU's OCARINA, and proceed with the applied research in cooperation with Osaka Prefectural University. Additionally, concerning practical application tied to the world of industry, we will be proceeding with that at the Artificial Photosynthesis Research Center.

profile
Isamu KINOSHITA

Director of Osaka City University's Advanced Research Institute for Natural Science and Technology (OCARINA) / Professor, Graduate School of Natural Sciences
B.S. in Chemistry, Tohoku University School of Natural Sciences. M.S., Graduate School of Natural Sciences, Nagoya University. Ph.D. in Natural Sciences. After serving as Assistant Professor, Lecturer, and Associate Professor at Osaka City University's School of natural Sciences, in current position since 2003.

profile
Yoshiki NISHIZAWA

President and Board Chairman, Osaka City University
Doctor of Internal Medicine, Osaka City University Medical School. Ph. D. in Medicine. Served as Assistant Professor, Lecturer, Associate Professor, and Professor at Osaka City University; Vice Director of OCU Hospital; Dean of Graduate School of Medicine and Chairman of Department of Medicine; Visiting Professor at Thomas Jefferson University, USA. In current position since 2010.

Making the Artificial Photosynthesis Research Center Flourish and Activating Young Researchers

Prof. **KINOSHITA:** The research that we are involved with, concretely speaking is hybrid artificial photosynthesis. Building on the fact that we are at the top level of natural photosynthesis in the world, we are involved in developing an artificial photosynthesis that combines both the natural and the artificial together. While there are some advantages to natural photosynthesis, there are also advantageous features in the artificial kind, and we are moving along well. Actually, in artificial photosynthesis, there is something called 'modularization.' Places where light is gathered, places where water is gathered, and places where CO2 is cycled, etc.– developing each of these to a high level, and finally combining them all– through doing that, I think that many kinds of spin-off technologies will emerge.

Board Member **YASUMOTO:** Speaking of industrial world, since there are many different kinds of industrial worlds, I think they should all be able to participate from their respective positions, whether it be as plant makers, oil companies, electrical appliance makers, etc. We still don't know in which of these practical application will happen the fastest. The direction that we take will have to be determined by the progress of the research and based on the views of the various participants.

President **NISHIZAWA:** If one thinks about returning the benefits to society, we have to make joint research with private firms and development of applied research flourish. Additionally, on the other hand, in order to cultivate the buds so that the flowers may flourish, we have to secure human resources in basic research that will become a firm foundation. At first glance, one might think that these two do not necessarily go together, but if the flowers can be made to bloom and flourish in one field, then young people will take an interest and gather, and I think that not only that field but research as a whole can become invigorated.

Prof. **KINOSHITA:** Professor Kamiya, since you were awarded with the Asahi Prize in 2012 for the work you did with Professor Shen Jian-ren of Okayama University on "Elucidating the Molecular Structure of Water Breakdown and Oxygen Production in Photosynthesis," I guess you're in the position of having to disseminate a lot of information, aren't you?

Prof. **KAMIYA:** A world in which artificial photosynthesis has actually been achieved will be a world in which the people living at that time will take artificial photosynthesis for granted. In order to bring that about, I think it is extremely important to keep putting out information that will energize young researchers at schools and at private firms. For that purpose, I think the role that the university plays, or the role that OCARINA plays, is extremely large. Already we have received all kinds of inquiries, and since we know that there are needs, we want to respond to them as much as we possibly can.

Prof. **KINOSHITA:** The world that we live in has been made through photosynthesis. If energy can no longer be supplied by oil and other fossil fuels that are the products of ancient photosynthesis, then we have no choice but to supply it by photosynthesis today. It is not just the energy problem– photosynthesis is a major key for understanding the world. Beginning this spring, the Advanced Research Institute for Natural Sciences and Technology and the Artificial Photosynthesis Research Center, cooperating together, will move forward developing research on photosynthesis and artificial photosynthesis.

profile
Nobuo KAMIYA

Professor, Advanced Research Institute for Natural Science and Technology and OCU Graduate School of Natural Sciences
B.S., M.S., and Ph.D., in Natural Sciences, Nagoya University. Served as Researcher and Chief Associate Researcher at the RIKEN Institute, and Director of the Office of Research Technology at RIKEN Harima Institute's Large Synchrotron Radiation Facility (SPring-8). In current position since 2005.
2012 Recipient of the Asahi Prize.

Introduction to Research

Emission of Excess Energy at the Photosynthetic Antennae of Purple Bacteria

profile
Daisuke KOSUMI
OCU Advanced Research Institute for Natural Science and Technology
Specially Appointed Associate Professor
B.S. in Physics, Aoyama Gakuin University Department of Science and Engineering, 2002.
M.S in Physics, Tohoku University Graduate School of Sciences, 2007.
Ph. D. in Natural Sciences. Served as Research fellows for the Japan Society for the Promotion of Sciences (2006–2011). In current position since April, 2011.
Figure: Outline diagram of energy transfer in the light-harvesting antennae of the photosynthetic purple bacteria.

The antennae of photosynthetic purple bacteria were bombarded with light from a femtosecond pulse laser which can discharge very strong energy in a very short time, and by recording the electron excitation state at 10 femtosecond intervals, it was discovered that of the total energy that is transmitted from the carotenoids to bacteriochlorophyll, 40% is returned to the carotenoids. The results of this research were published in the German academic journal Angewandte Chemie, International Edition (50, pp. 1097-1100, 2011).

• The Role of Photosynthetic Antennae

The photosynthetic antennae of plants and bacteria are composed of two kinds of pigment molecules, carotenoids and (bacterio-) chlorophyll, and the proteins that surround them. The spatial arrangement of these pigment molecules and proteins differs according to the plant or bacteria species, but it is known that the antennae of purple bacteria form a supermolecular aggregate in a ring shape. Since the (bacterio-) chlorophyll mainly absorb light at the near-ultraviolet and near-infrared parts of the spectrum, they cannot effectively utilize light from the visible spectrum in which the sun's rays are strongest. Because of that, the other photosynthetic pigments, the carotenoids, absorb visible light and transmit that energy to the (bacterio-) chlorophyll at ultra high speed and at high efficiency (light harvesting). This process of energy transmission is carried out between singlet states of electron excitation of the carotenoids and the (bacterio-) chlorophyll. The energy that is transmitted to the (bacterio-) chlorophyll moves between the antennae and ultimately is transported to the reaction centers where it is transformed into electrochemical energy that can be utilized by organic systems.

• Protective Action from Excess Light

When the photosynthetic body is exposed to excess light, a triplet state of electron excitation of the (bacterio-) chlorophyll is formed, and as a result the production of singlet oxygen is promoted which is harmful to the photosynthetic organism. In order to prevent the production of singlet oxygen, in the photosynthetic organ, energy from the electron excitation triplet state of the (bacterio-) chlorophyll is transmitted to the electron excitation triplet state of the carotenoids, and by doing this the organism is protected from excess light (photo protection). However, in antennae of the higher plants which live close to the earth's surface where the intensity of the sun's radiation is comparatively strong, before the singlet electron excitation state of the chlorophyll that is produced by light that is supplied in excess is transformed to a triplet excitation state, the energy is given off as heat to the outside (non-photochemical quenching, or NPQ). NPQ differs from the movement of energy through electron excitation triplet states as above, and loses the singlet excitation state through a non-radiative process so that energy can be dissipated efficiently from the organism to the outside. In this way, plants that live in environments where they are exposed to intense light have developed the function of protecting the organism from light more than that of collecting light.

• Reverse Energy Flow between Pigment Molecules in the Antennae of Purple Photosynthetic Bacteria

Between molecules of carotenoids and (bacterio-) chlorophyll in the singlet state of electron excitation, when the energy transport is carried out as below, we have discovered that there is not only one-way movement of energy from the carotenoids to the (bacterio-) chlorophyll, but as shown in the figure, reverse energy movement from the (bacterio-) chlorophyll to the carotenoids is also possible. For example, in the antennae of purple photosynthetic bacteria, it is possible for excited energy to move from the singlet electron excitation state Qx of bacteriochlotophyll to the singlet state S1 of the carotenoids. Focusing on this point, we attempted a search for the pathway of the reverse energy movement from the bacteriochlorophyll to the carotenoids using femtosecond time analysis measurement. As a result, as shown in the figure, on the S1 collector antenna of the purple bacterium Rhodospirillum rubrum, of the energy that the carotenoids absorb and transmit to the bacteriochlorophyll (43%), we found that 17% of that is returned back again to the carotenoids. We found that this reverse energy movement is carried out at the bacteriochlorophyll's Qx state and the carotenoid S1 state, and it is both a highly efficient (quantum efficiency of 40%) and extremely rapid (75 femtoseconds) movement of energy. There has been much research going back a number of years on energy transfer in the light collector antennae of the purple bacterium Rhodospirillum rubrum S1, and it is known that the energy movement efficiency of 30% from carotenoids to bacteriochlorophyll shows very low resistance. Nonetheless, the fact that 40% of the harvested energy is returned to the carotenoids means that the reverse energy movement in the light collector antennae of Rhodospirillum rubrum S1 is a protection mechanism from light that is similar in efficiency to the higher plants.

• Towards the Creation of Artificial Photosynthetic Antennae

The factor that determines the efficiency of energy transfer in photosynthetic antennae is the excited energy movement from carotenoids to (bacterio-) chlorophyll. The energy transfer efficiency (30~100%) and absorption wavelength spectrum (450~550 nm) of the antennae of purple bacteria depends on the combination of the carotenoids. If the low energy transport efficiency of the antennae which absorb light at long wavelengths (550 nm) as in the Rhodospirillum rubrum that was used in this research has its origin in the reverse energy movement from the bacteriochlorophyll to the carotenoids, by understanding the mechanism in detail and establishing technology to control it, the creation of artificial photosynthetic antennae that absorb a wider spectrum of light and are highly efficient will become possible.

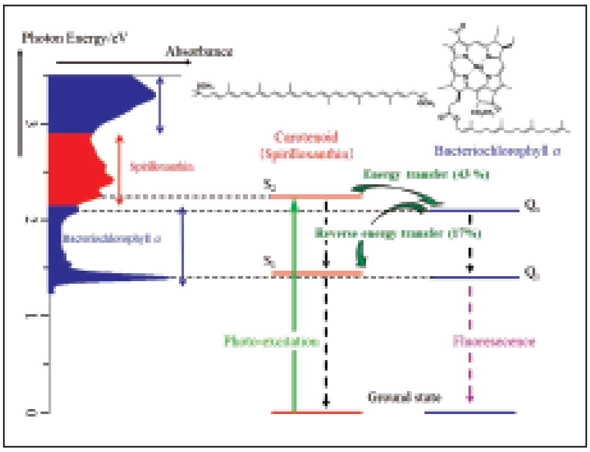


Figure: Outline diagram of energy transfer in the light collector antennae of the purple photosynthetic bacterium S1.

Inhibition Mechanism of the Oxygen-Evolving Reaction in Photosystem II Complex by Iodine Ions

profile
Keisuke KAWAKAMI
OCU Advanced Research Institute for Natural Science and Technology, Specially Appointed Researcher
2005. 3. B.S. in Biology, Okayama University Faculty of Science
2010. 3. Ph.D. in Bioscience, Okayama University Graduate School of Natural Science
2010. 4. Appointed as a Japan Society for the Promotion of Science Special Researcher in the Bioscience Laboratory of Osaka City University's Graduate School of Science
2011. 7. Began serving in current position
Field of Specialization: Plant physiology; X-ray crystallography of the Photosystem II complex

Iodine Ions inhibit the Oxygen-Evolving Reaction of Plants and Cyanobacteria

The Photosystem II (PSII) complex, along with converting the light energy of the sun into chemical energy that can be utilized by plants and cyanobacteria, is a membrane protein complex that catalyzes water splitting and produces oxygen molecule. The Mn_4CaO_5-cluster catalyzes this reaction, and there are many water molecules and a number of ions around the Mn_4CaO_5-cluster. They have the function of efficiently releasing the protons that are given off by the water-splitting reaction from the Mn_4CaO_5-cluster to the luminal bulk phase. The oxygen molecules that are formed by photosynthetic reaction of PSII are necessary for most of life on earth, however, the fact is that the mechanism of water splitting and oxygen evolution in PSII is not yet completely understood. Completely understanding this mechanism and applying those results to the development of artificial photosynthesis research is one of our missions as photosynthesis researchers. Previously studies have shown that chloride ion (Cl) is an essential cofactor for oxygen evolution of PSII, and that it is possible to replace Cl^- with bromide ion (Br^-) and iodine ion (I^-) which are homologous elements of Cl^-. The oxygen-evolving activity of PSII is not inhibited by substitution of Cl^- with Br^-, however, the activity is completely inhibited by substitution of Cl^- with I^-. Interestingly, the inhibition mechanism by I^- is a reversible reaction because the activity inhibited by I^- is recovered on re-substitution of I- by either Cl^- or Br^- (Figure 1).

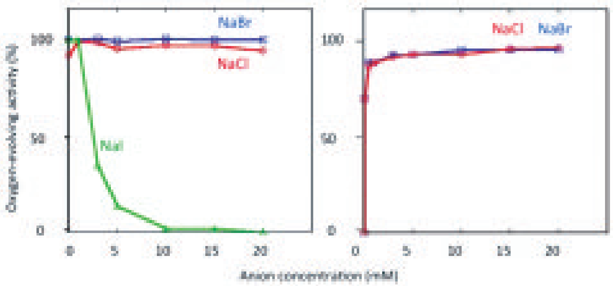


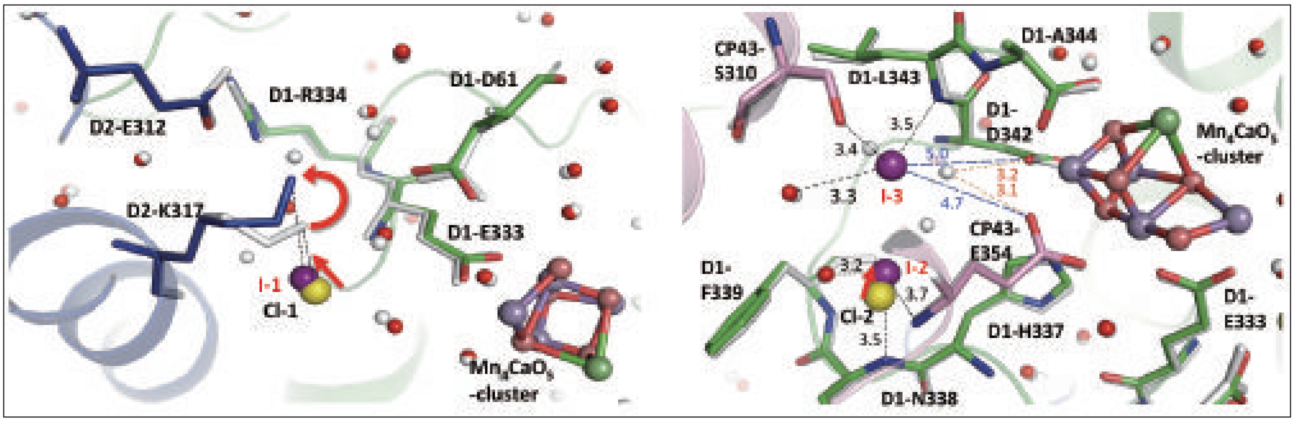
Figure 1: Effect on the oxygen-evolving activity in PSII at each anion concentration. Cl^- or Br^- does not inhibit the activity, however, I^- completely inhibits the activity at high concentration condition.

Conformational Changes in PSII are caused by Iodine Ions

X-ray crystallography is the most powerful method in order to determine the 3-dimensional structure of proteins, but its resolution greatly depends on the qualities of the obtained protein crystals. In particular, membrane protein complexes like PSII are very unstable, and it is almost impossible to obtain high quality crystals. Our research group has been involved with research for many years on improving the quality of PSII crystals, and we have succeeded in determining the conditions for obtaining high quality PSII crystals and elucidating the detailed structure of PSII (Umena et al., Nature, 2011). By utilizing these conditions to obtain PSII crystals in which I^- have been replaced and carrying out x-ray crystallography analysis, it has become possible to understand the fine conformational changes in PSII caused by I^-.

We have confirmed that the conformational change of the amino acid residue surrounding I^- (I-1) and the change of distributions of water molecules surrounding I-1 are induced. Moreover, newly I^- (I-3) is bonded surrounding Mn_4CaO_5-cluster, and we have actually confirmed the conformational changes in PSII caused by substitution with I^- (Figure 2).

By revealing the inhibition mechanism of the oxygen-evolving reaction in PSII, this will lead to an understanding of the reaction mechanism of the Mn_4CaO_5-cluster, and it can be expected that this result will contribute to research on artificial catalysis that mimics the structure of the Mn_4CaO_5-cluster.



A **B**

Figure 2: (A) Conformational changes near the binding site of Chloride ion (Cl-1) by substitution of Cl^- with I^-. Change in the arrangement of lysine residue (D2-Lys317) is confirmed, and the position of anion (I-1) has changed (red arrow). (B) Conformational changes near the binding site of Chloride ion (Cl-2) by substitution of Cl^- with I^-. The position of anion (I-2) has changed (red arrow) and also I^- (I-3) has binded. Unit numbers are in angstroms (Å).

Reports on Activities

OCARINA Seminar

At OCU's Advanced Research Institute for Natural Science and Technology(OCARINA), we invite scientists from Japan and overseas and put on open lectures on an occasional basis. From this year, a series of 'major seminar' of the DISCO Party (see note*) is also held as the OCARINA seminar.

DISCO Party : *Doctor course students' incorporated scientific communication party. This is a series of seminar run by the doctoral course students belongs to OCARINA, which is established this year to promote deep understanding among themselves across the boundaries of research fields. In addition to the weekly closed seminars for students only, the open seminars will be held with domestic/international invited lecturer(s) as the major seminer.

1st Meeting **[Oct. 27, 2010 Place: Bldg. No. 2, Room 220B]**
Guest: Tetsuya OGURA (Visiting Prof., OCARINA)
"Tequila, Inulin, and Agave Syrup Made from Agave Plants"

2nd Meeting **[Mar. 31, 2011 Place: Bldg. No. 2, Room 220B]**
Guest: Hitoshi WATARAI (Invited Prof., Nanoscience Education Research Center, Osaka Univ.)
"Liquid interface nanochemistry for the development of the next generation of green energy– new analytic principles using the outside and the creation of local analytic chemistry"

3rd Meeting **[Feb. 17, 2012 Place: 1F Cultural Exchange Room]**
Guest: Masahiro YAMASHITA (Prof., of Natural Science,Tohoku Univ.)
"Quantum molecular spintronics utilizing monomolecular quantum magnets– which is better, Nomo or Ichiro?"

4th Meeting **[April 28, 2012 Place: Bldg. No. 2, Room 220A]**
Guest: Jian-Ping ZHANG (Prof., Dept. of Chemistry, Renmin Univ. China)
"Morphological Effect on the Photogeneration of Charge Carriers in P3HT/PCBM Blend Films"
"Excitation Dynamics of the Light-Harvesting Complexes of Purple Bacterium Thermochromatium tepidum"

5th Meeting **(DISCO party Major Seminar #1)**
[July 3, 2012 Place: Bldg. No.2, Room 220B]
Guest: Noritake YASUOKA (Visiting Prof., OCARINA Protein Crystallography)
"Making medicines based on the 3-dimensional structure of proteins"
Student: Kiyokazu SANTO (D1, Molecular Design Laboratory)

6th Meeting **(DISCO party Major Seminar #2)**
[Aug. 30, 2012 Place: Bldg. No.2, Room 220B]
Guest: Yoshihito HAYASHI (Associate Prof., Kanazawa Univ. Metallic Oxides)
"The chemistry of metal oxide molecules"
Student: Chiasa URAGAMI (D1, Physics of Biological Materials and Crystal Growth Lab)

7th Meeting **[Oct. 19, 2012 Place: OCU Media Center 1F Cultural Exchange Room]**
Guest: Mitsuru FURUSAWA (Founder of Neo-Morgan, Inc. Research Lab)
"Theory of Imbalanced Evolution"

8th Meeting **[Oct. 23, 2012 Place: OCU Media Center 1F Cultural Exchange Room]**
Guest: Yutaka AMAO (Associate Prof., of Engineering, / JST-PRESTO Researcher)
"Creating an artificial photosynthesis system to produce solar fuel and matter"

9th Meeting **(DISCO party Major Seminar #3)**
[Nov. 19, 2012 place:Media Center 1F Cultural Exchange Room]
Guest: John T. KENNIS (Prof.,Vrije Univ. Time-resolved Spectroscopy)
"Carotenoids in Photosynthetic Light Harvesting and Photoprotection"
Guest: Anjali PANDIT (Researcher,Vrije Univ. Solid State NMR)
"In Shape for Photosynthesis"
Guest: Yoshio TEKI (Prof., OCU, ESR)
"Spin Alignment and Spin Dynamics in Photo-Excited States of π –Radicals"
Student: Satoko HORIBE (D3, Physics of Biological Materials and Crystal Growth Lab)
Student: Keisuke KAWAMOTO (D1, Molecular Design Lab)

10th Meeting **[Dec. 11, 2012 Place: OCU Media Center 1F Cultural Exchange Room]**
Guest: Ritsuko FUJII (Specially Appointed Associate Prof., OCARINA/ JST-PRESTO Researcher)
"Photosynthesis of marine seaweeds– revealing the mechanism of their efficient harvesting of sunlight and its application to artificial photosynthesis"

11th Meeting **(DISCO Party Major Seminar #4)**
[Jan. 24, 2013 Place: Bldg. No.2, Room 220B]
Guest: Masaru TATENO (Prof., Univ. of Hyogo, Theoretical Chemistry)
"Theoretical analysis of the biological mechanism that the movement of protons contributes to"
Guest: Yoshimasa FUKUSHIMA (Specially Appointed Assistant Prof., OCARINA, Low Temperature Spectroscopy)
"Analysis of the photoreaction intermediate by low temperature spectroscopy of the blue light photoreceptor TePixD"
Student: Yoshihiko FURUIKE (D1, Laboratory for Biological Structural Chemistry)

The 4th Annual meeting

Fiscal Year 2011 OCARINA Annual General Meeting

◆Date: March 5-6, 2012
◆Invited Lecturer
- Yasuo INOUE (Prof., Tokyo Metropolitan Univ. /Research Supervisor, JST-PRESTO)
- Nobuo KAMIYA (Prof., OCARINA)
- Hideki HASHIMOTO (Prof., OCARINA)
- Jin-Ren SHEN (Prof., Graduate School of Natural Sciences, Okayama Univ.)
- Miwa SUGIURA (Associate Prof., Cell Free Science and Technology Research Center, Ehime Univ.)
- Osamu ISHITANI (Prof., Graduate School of Science and Engineering, Tokyo Institute of Technology)
- Hideaki OGATA (Max Planck Institute)
- Yoshiki HIGUCHI (Prof., Graduate School of Life Science , Univ. of Hyogo)
- Masako KATO (Prof., Graduate School of Sciences, Hokkaido Univ.)
- Hiroshi TADAOKA (Institute for Molecular Science)
- Mikio HOSHINO (RIKEN)
- Shigemasa ARAI (Hill Research, Ltd. CEO)
- Yutaka AMAO (Associate Prof., Dept. of Applied Chemistry, Oita Univ.)

◆Symposium Outline

The 4th Annual Symposium was spurred on by the issue that the work of revealing of the oxidation center of PSII was selected by the journal science as one of the top 10 scientific breakthroughs of 2011. With a focus on the research topic of artificial photosynthesis and its related fields e.g., energy, resources, ecosystem, and all of humanity through the environment, a number of important researchers from all over Japan were invited to attend this meeting and high-spirited discussions were carried out. Additionally, a debrief meeting for the final year of the Strategic New Development for the Renewal of the Urban Environment project was also held in tandem, where the 3 Sub groups' activities over a four year period was reported.

Introduction to Facilities: ICP-MS

Tomomi SHIMONAKA

ICP-MS (Inductively Coupled Plasma Mass Spectrometry) is a skillful tool to analyze various isotopes with high sensitivity. ICP (Inductively Coupled Plasma) is the plasma that is produced by ionizing argon with induction current in a high frequency induction coil, and the ICP is used as ion source. Vaporized sample within argon plasma, is broken down into atoms, which are ionized with >90% efficiency. The ionized atoms are introduced into the mass spectrometer to determine the concentration of isobars.

ICP-MS has extremely outstanding features as an inorganic mass spectrometer; 1) it is extremely sensitive, and almost all elements can be measured in concentrations as low as parts per trillion (ppt) level; 2) dynamic range is large, and covering 9 orders of magnitude; 3) multiple elements can be analyzed at the same time; and 4) not only quantitative analysis but also qualitative (identification of elements and isotopes) and simultaneous semi-quantitative analyses can be available.

In the system installed in our institute (SPQ9700, Hitachi High-Tech Science Cooperation, formarly SII Nano Technology, Inc.), liquid samples are nebulized and introduced into the argon plasma. Thus, major and trace elements and their isotope of various types of samples can be analyzed if the sample is appropriately prepared as water solution; e.g., naturally environmental materials such as surface and ground waters, soils, rocks and minerals, organic materials such as foodstuffs, plants and animals, inorganic materials such as steel, precious metals and semiconductor alloy, highly purified pharmaceuticals, waste matters, and so on. The ICP-MS is one of the facilities as regulated methods to analyze environmentally controlled materials in waters and soils. ICP-MS is an indispensable facility for the trace element and isotope analyses in the wide range of field at present.

Elements in nature exist in numbers of different chemical states according to the environmental conditions. Metal and metalloid elements change those chemical states in association with redox condition. Bahaviors and toxicity of the elements also change with the chemical states. For example, arsenite (As^{III}) is more soluble and toxic than arsenate (As^{V}), and so does hexavalent chromate (Cr^{VI}) than tetravalent one (Cr^{IV}). Thus, the speciation of chemical state of elements is an important task to evaluate the behaviors and toxicity. Combined system of HPLC/ICP-MS is skillful for the speciation analysis. HPLC (High Performance Liquid Chromatography) can separate the different state of the elements, and ICP-MS is used as a detector of the separated elements. In our system, HPLC (SHIMADZU Corporation, LC-6A) is attached to the ICP-MS to analyze different states of arsenic.

Since installation of the ICP-MS in 2009, we have been analyzing arsenic in natural waters, soils and rocks, trace and rare earth elements in groundwaters, rocks and minerals, and lead and cupper in plant tissues.

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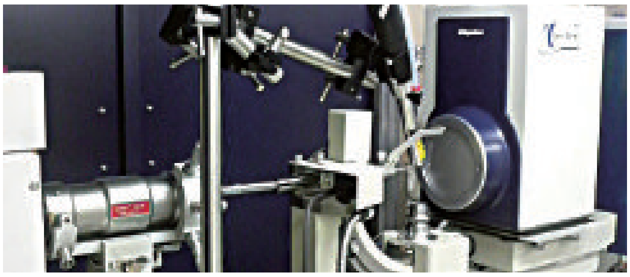
Advanced small molecule CCD crystallography system (VariMax with Saturn)

Ikuko MIYAHARA

Single crystal structural analysis by X-ray diffraction which determines directly the 3-D structure of molecules from the distribution of electron intensity is widely utilized from fields in chemistry that deal with organic compounds and organic metal complexes to fields in pharmacology that deal with chemical compounds that are pharmaceutical candidates, crystals in different states, and co-crystals. Since there are many cases where even a very small difference in the structure of molecules can have a determining influence on the molecule's physical properties or physiological activity, this method of analysis which makes determination of structures possible with a high level of reliability is an extremely powerful means of analysis. The equipment for single crystal structural analysis that we are now adopting is an X-ray diffraction machine that combines the world's highest standard high intensity X-ray beam and high sensitivity CCD camera, in which additionally the diameter of the beam and the length of the camera can be changed, making it possible to use it with very small crystals or crystals that have long lattices.

Microfocus rotating anode X-ray generator(RA-Micro7HFM)

Crystal rotating anode generator type with a maximum effective power of 1.2kW that uses a molybdenum (Mo) target to measure most of the diffraction points of small crystals with high precision.



Confocal X-ray optical assembly (Confocal Mirror 'VariMax Mo')

This is beam concentrating optical assembly using dual graded artificial multilayered membrane mirrors that are set at right angles and can concentrate the x-ray beam three dimensionally. These mirrors, the longest in the world, make it possible to obtain a very high intensity beam that is highly monochromatic.

Advanced 18-bit CCD detector technology (Saturn 724)

The large detection surface area (72 x 72 mm) makes data collection possible at high resolution even with samples that have large lattice constants, the camera length can be adjusted, and it has a high dynamic range (22 bits/pixel), and can be used to measure many different kinds of samples. Moreover, by achieving high sensitivity (180 electron/pixel/photon) and yet with super low noise (0.2 electron/pixel/sec), it is possible to detect the weak diffraction points of very small crystals with high precision. Additionally, by combining the high magnification CCD camera used for sample observation and absorption correction of the crystal's outward shape together with the ¼ χ-shape goniometer and the low temperature device for injection of samples, efficient and highly precise measurement is made possible.

We expect that from now on this equipment will be useful across a wide range of research fields in the development superconductors and molecular magnetism and new functional materials that realize organic EL, in the development of inorganic and organic catalysts, in creating pharmaceuticals based on leading compounds that include the basic structure of natural materials, and in the development of artificial photosynthesis that mimics natural photosynthetic systems.

Topics

profile

Hideki HASHIMOTO

OCU Advanced Research Institute for Natural Science and Technology Professor
M.S. and Ph.D., Kwansei Gakuin University Graduate School of Science. After serving as Assistant Professor in the Osaka City Univ. Dept. of Engineering and as Associate Professor in the Shizuoka Univ. Dept. of Engineering, became Full Professor in the OCU Graduate School of Science. Has served as a project leader at OCARINA since it was founded in 2008. Since 2010 has been a Specially Appointed Professor at OCARINA while still jointly serving in the Graduate School of Science.

Finishing the CREST Research

Our research project entitled “Functional Control of the Primary Process of Photosynthesis in nano-space” was adopted as a CREST project by the Japanese Science and Technology Agency for a 5 year term beginning in October, 2007. The final evaluation of the CREST research has been completed, and we received a very high evaluation. I would like to take this opportunity to sum up the results of the CREST research that we have been doing for the last 5 years.

In this research, we artificially fabricated photosynthetic membranes, and using a new spectroscopic method revealed the primary process of photosynthesis that accompanies the transport of excited energy, with the goal of verifying guidelines for its utilization as an efficient light-harvesting device. As a result, we firmly established the means for adjusting the artificial light-harvesting pigment protein complexes; succeeded in obtaining a high resolution atomic force microscopy (AFM) image of the artificial photosynthetic membranes; utilizing femtosecond-coherent spectroscopy, we clarified the dynamics of vibronic oscillation of photosynthetic pigments in a unified manner; and by doing this we completely revealed the transportation mechanism of excited energy between the carotenoids and bacteriochlorophylls that has an important role in the primary process of photosynthesis. Also, we firmly established a unified theory concerning the Stark absorption spectroscopy, which is extremely effective in revealing the structure and function of photosynthetic pigments.

In this way, in relation to revealing the operating mechanisms of the primary reaction in photosynthesis, by accumulating minute examinations from both experimental and theoretical aspects, we were able to produce numerous research results that now lead the world in this field. The research results have been reported in many papers published in the world’s top level academic journals (a total of 124 articles), and we have vigorously presented our findings to the outside world at both international conferences and conferences here in Japan. Moreover, since we have received numerous requests to give invited lectures at international conferences, our group of research presenters takes pride in the fact that we are leading the world in this field.

Revealing the function of the artificial pigment protein complexes in photosynthetic antennae and the design synthesis technology does not stop with understanding the functioning of the natural world, but also highlights highly valuable spin-off results in science and technology, such as the realization of super-photosynthesis that breaks through the limits of the natural photosynthesis, solar batteries with increased pigment sensitivity that adapts the technology of our device, and beyond that direct production of fuels. If these can be practically applied, without a doubt we expect that they will have great social impacts.

Based on this CREST research, the Artificial Photosynthesis Research Center will begin operating in the spring of 2013, and we intend to take up the development of solar fuels, the next-generation energy, in an industry-university collaboration.

profile

Nobuo KAMIYA

Advanced Research Institute for Natural Science and Technology Professor
Served as Researcher and Chief Associate Researcher at the RIKEN Institute, and Director of the Office of Research Technology at RIKEN Harima Institute’s Large Synchrotron Radiation Facility (SPring-8). Has been Professor in the OCU Graduate School of Science since 2005. Since 2010 has also been a Specially Appointed Professor at OCARINA.

Beginning ‘Basic S’ Research

The project funded under Scientific Research Funding Basic Research (S) for “Revealing the Oxygen Production Mechanism at Atomic Level Resolution in the Photosystem II Compound in Photosynthesis” for a 5 year term began in 2012, made up of these participants: Principal researcher: Professor Nobuo KAMIYA (OCARINA), Joint researcher: Professor Tomoyuki YATSUHASHI (OCU Graduate School of Science, Specializes in Molecular Physics, jointly serves at OCARINA), Collaborating researchers: Specially Appointed Assoc. Prof. Keisuke KAWAKAMI (OCARINA) and Specially Appointed Assoc. Prof. Yasushi UMENA (OCARINA).

Most of life on earth is alive due to photosynthesis, and photosynthesis is one of the most important processes for the realization of a sustainable society for human beings. The compound photosystem II (PSII) absorbs sunlight and breaks down water, and along with molecular oxygen it produces electrons and protons. In April 2011, Kamiya et al. announced that they had for the first time in the world succeeded in revealing the detailed chemical structure of the Mn4CaO5 cluster in PSII that produces oxygen from water at a resolution of 1.9 Å (Nature [2011] 473, pp. 55-60). This corresponds to the S1 state of the 5 intermediate states that explain the oxygen producing reaction (Kok cycle Si stages, i=0~4), but in this new Basic (S) research our goal is to go further and conduct X-ray crystal structure analysis of states S0 and S2, and provide the basic information that is necessary for developing catalysts for water reduction and oxygen production. In this research we will first of all conduct X-ray diffraction structural analysis of: 1) two kinds of ion substitutions for the chloride ions (Cl-) that contribute to the production of oxygen in PSII, bromide ions (Br-) and iodide ions (I-); 2) compounds with 5 varieties of phytocides which block movement of electrons that are connected to oxygen production; and 3) an altered state of PSII that lacks a subunit of small molecular mass (PsbM) due to genetic manipulation, for a total of 8 kinds of crystals for X-ray diffraction structure analysis. In each of these PSII varieties, it is possible

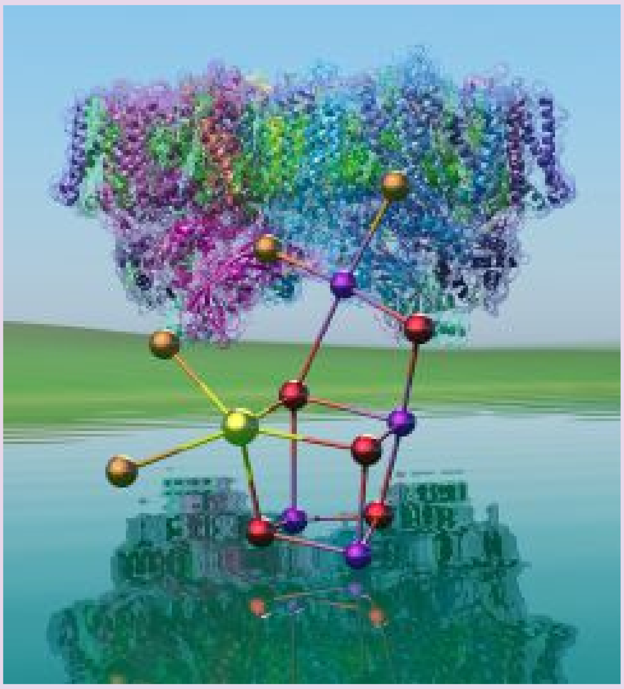
Introducing a New Staff

profile

Yoshimasa FUKUSHIMA

OCU Advanced Research Institute for Natural Science and Technology Specially Appointed Assistant Professor
B.S. in Physics, Nagoya University School of Science. M.S. and Ph. D., Nagoya Univ. Graduate School of Sciences. After serving as a researcher at the Nagoya Univ. Graduate School of Sciences and the same university’s Center for Gene Research, began serving in his current position in November, 2012.

that changes will be seen in electron transport activity, and it is possible the changes will also extend to the Mn4CaO5 clusters. Particularly in 1) in the iodide substitution, due to the reduction power of the iodine, there is a high possibility that the S0 state will be realized. On the other hand, in the Mn4CaO5 cluster, when light falls on PSII in state S1, one electron is emitted and it becomes state S2. The method for creating the S2 state when it comes to liquid samples of PSII has already been firmly established, but in crystal samples that are uses for X-ray diffraction structure analysis, peculiar circumstances arise. That is that because PSII contains a lot of chlorophyll and carotenoids that absorb visible light, crystals where PSII is condensed in high concentrations appear to be almost completely black. In other words, since almost no visible light can pass through the crystal, it is not easy to create an S2 state that is homogeneously spread throughout the crystal. At that point in this research, we will hand it over to Professor Yatsuhashi who has produced many results in research on the ionization of matter by multiple photons, and using infrared light that PSII does not absorb, and by using those two photons at the same time we will be able to create the S2 state. Also, by bringing in as a specially appointed assistant professor Dr. Yoshimasa FUKUSHIMA, who is a specialist in spectroscopy (see photo), we hope to succeed in fixing crystals with a homogeneous S2 state and analyzing their structure with X-ray diffraction analysis.



Professor Nobuo KAMIYA is Awarded the 2012 Asahi Prize!

The Advanced Research Institute for Natural Science and Technology's Professor Nobuo Kamiya has received the Asahi Prize for 2012 (joint recipient: Okayama University's Professor SHEN Jian-ren). This was due to the high esteem earned by the results of his research in revealing the molecular structure of the 'manganese cluster' which is the key to unlocking the mystery of photosynthesis.

The Asahi Prize was established in 1929 and is awarded to individuals or groups in a variety of fields in Japan who have produced the most outstanding work in the humanities or natural sciences and have made a considerable contribution to the development and improvement of culture and society. Many of the recipients of the Asahi Prize have gone on to win the Nobel Prize or other cultural medal awards in later years.

Additionally, Professor Kamiya's research results were posted in the online electronic edition of the British academic journal Nature in April, 2011, and were also chosen as one of the "Top Ten Breakthroughs in Science for 2011" by the American scientific journal Science.

I feel deeply honored to have been awarded this historic prize. When I look back on the course of my research on the X-ray crystallography of photosystem II (PSII) and photosynthesis, the faces of many people come floating up into my mind such as my mentor during my university student days, my seniors who started me out in PSII research, the people who have supported the research over a long period of time, the young people who have participated together in joint research with me, my colleagues and friends at my current workplace, and my family.

In natural science research, there are parts where it feels like a small child whimsically playing, and sometimes new discoveries are born in the midst of that. That needs to be carefully watched over with a long perspective, and in that sense, I feel once again that I've been lucky to have received many other people's assistance over such a long time.

From this point on, I would like to move forward doing research so that we can arrive as quickly as possible at the goal of completely understanding the water reduction and oxygen producing mechanism of PSII which will lead us to artificial photosynthesis.

Nobuo KAMIYA, Professor, Advanced Research Institute for Natural Science and Technology

Osaka City University Advanced Research Institute for Natural Science and Technology (OCARINA)

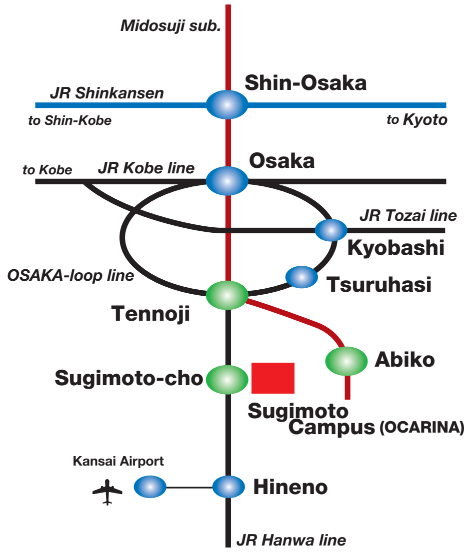
OCARINA, the OCU Advanced Research Institute for Natural Science and Technology, was established as a cross-disciplinary research organization that would strategically fuse together the knowledge and wisdom of this university to solve the top priority issues. This institute is meant to be the major player in project research to achieve the goals of "Through a project system, fusing together the most advanced science and technology across research disciplines, to deal with the foremost complex issues facing humanity of energy, resources, ecosystems, and the environment on a global scale, to speak out as scholars and members of society and to nurture human resources, and to effectively give back the findings that we obtain to the society and the local community."

In 2012 we began a new project for "Achieving the production of solar fuels through artificial photosynthesis." In the summer of 2012 the construction of a new building for complex of university science has been begun including many floor spaces for OCARINA. Additionally, the Artificial Photosynthesis Research Center (ReCAP) was in construction as a facility for the industry-university joint researches. It will open in 2013. In conjunction with that, two new full-time academic staffs will be joining us from April 2013, and we intend to make our research organization even more active.

With the desire to attempt to solve global scale problems as quickly as possible, a part of our facility has already been active moving on ahead, but the upgrading of all of our facilities is proceeding steadily, and we intend to keep moving forward making this research institute take on the role of base for disseminating world leading research from Osaka to the world.

大 阪 市 立 大 学
OSAKA CITY UNIVERSITY

Osaka City University Advanced Research Institute for Natural Science and Technology
3-3-138 Sugimoto, Sumiyoshi-ku
Osaka-shi, 558-8585 JAPAN
Tel: (+81) 06-6605-3634(changed)
Fax: (+81) 06-6605-3636



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