

## Professor Osamu Ishitani of the Graduate School of Science and Engineering, Tokyo Institute of Technology, Japan

We interviewed Professor Osamu Ishitani of the Graduate School of Science and Engineering, Tokyo Institute of Technology (Tokyo, Japan). His research is focused mainly on artificial photosynthesis. He and Shimadzu started a collaborative relationship in 2012, which resulted in the QYM-01 photoreaction quantum yield evaluation system\* that permits accurate and simple quantitation measurements of absorbed photons.

\* The QYM-01 system is not available in Europe and may not be available in some other countries. Please contact your local Shimadzu representative for availability.

**Dr. Ishitani, thank you very much for sparing time for this interview. First of all, could you explain the background to this collaborative research with Shimadzu? Why did you choose Shimadzu as your partner?**

I have conducted research into the photochemistry of metal complexes, and in particular into the development of artificial photosynthesis systems, for many years, and in recent years the number of researchers participating in this field of research has increased drastically. However, it worries me that upon attending the presentations of these researchers, it is not uncommon that many of them will not calculate quantum yield, and will not pose their arguments based on quantum yield results.

While quantum yield is the most important and fundamental quantitative value for research into photoreactions, it is not simple, experimentally, for a researcher that is researching photochemistry to measure the quantum yield of a photoreaction. One of the first things taught to students in classes on photochemistry is the first law of photochemistry. Simply put, this law states that light absorbed by a molecule gives rise to a photoreaction. Consequently, a measurement of quantum yield requires not a calculation of the quantity of light emitted, but a calculation of the number of photons absorbed by a substrate. Calculating this number requires the preparation of various experimental conditions and execution of a complicated procedure. In our laboratory, we prepare hand-made equipment and have summarized the research procedure in manual form so that all students are able to, without fail, measure quantum yield. Nevertheless, I believe a fair number of students find this research difficult to conduct, despite these preparations. Also, our equipment and methods have not always been totally satisfactory. For example, the equipment we developed could be used to calculate the number of photons entering the reaction vessel, but calculating the number of photons that pass through the vessel has not been easy. Consequently, experiments had to be performed under the assumption that almost all incident light was absorbed by the solution inside the reaction vessel. Furthermore, when a light source is emitting light continuously for an extended period of time, the light source gradually degrades and the quantity of emitted light decreases. We were unable to estimate this change. We needed to work together with engineers skilled at systemization of equipment as well as experts in spectroscopy to make the improvements to our equipment required for resolution of these problems.

When approached by Shimadzu regarding the joint research into development of equipment for photoreactions, two areas of equipment development occurred to me that I thought could be realized. One was to enable people who conducted research into photochemical reactions but were not specialists in photochemistry to perform accurate yet simple measurements, and the other was to enable measurements of quantum yield with smaller errors than previously possible while under diverse experimental conditions.



**Could you provide a summary of this research and tell us what discoveries and achievements have been made so far?**

Basically, this research aims to enhance the functionality of, and improve the operability of equipment used in photoreactions, where the equipment in question is unique and was created by us. The three main topics of this research are as follows.

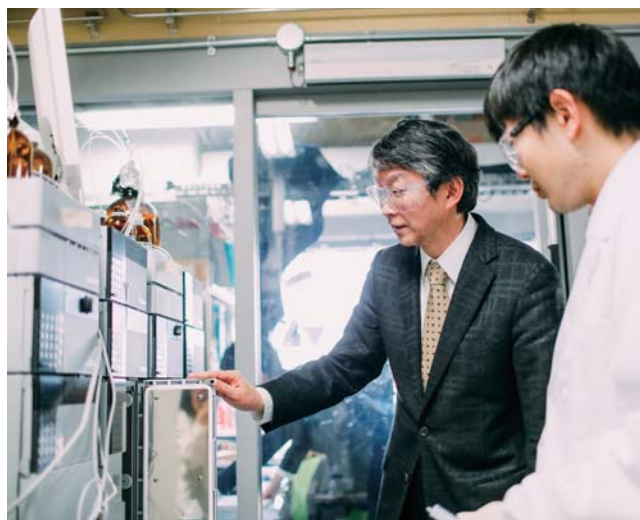
First is ease-of-operability of light quantity measurement and improvement of the precision. Two commonly used methods of measuring light quantity employ a chemical actinometer and a photoelectric transducer. Our equipment previously employed a method that used a chemical actinometer, but operation of this equipment was complex and required an experienced operator. This problem was resolved for us by Shimadzu. Second is measurement of the quantity of light transmitted through the reaction solution. Measuring the quantity of light transmitted through the reaction vessel requires an extremely complex procedure, a problem that was resolved by introducing a system that takes constant measurements of the quantity of illuminating light during the photoreaction. By utilizing this equipment, we can now change the substrate concentration (which affects the extent of absorbance by the reaction solution) at will and determine the quantum yield of the photoreaction. Third was the problem of canceling out error caused by degradation of the light source. This was resolved based on a proposal made by an engineer at Shimadzu. The mechanism devised introduces a beam splitter in front of the reaction vessel to take off part of the illuminating light, which is directed into another system that provides a constant measurement of the quantity of light. This allows us to perform measurements of quantum yield with good precision even during experiments using a light source for an extended period of time. A system that uses a photodiode detector to measure the absorption spectra of the solution was added to the light illumination system we developed, and placed at right angles to the illuminating light used for photoreactions. This system detects reaction intermediates that accumulate in solution during the actual photoreaction, and has been

found useful in tracing the degradation process of photocatalysts. This equipment was also integrated into Shimadzu's equipment. In this way, we can now use this equipment to perform accurate measurements of the quantum yield of photoreactions, while simultaneously tracing changes in the spectra of the reaction solution.

### Why are you interested in artificial photosynthesis? What is the goal of your research?

My entry into this field was probably influenced by my experience of the 1973 oil crisis. The family business was as a wholesaler of cosmetic and sanitary products. When the first oil crisis hit, nearly all stocks of these products were sold out, and for days on end we had no products to sell. I can still remember the frantic atmosphere in the family shop at the time. I felt first-hand how a lack of oil would result in an extremely dangerous situation for humanity. After that, I studied industrial chemistry at Kobe University, where I found myself moving into research into artificial photosynthesis. I then moved away from Kobe University, which had no laboratories performing research into this field at the time, to become a postgraduate at the Graduate School of Engineering of Osaka University, which was a mecca for photochemistry research then and since. It is there I came under the tutelage of Chyongjin Pac (currently a professor at Korea University), a world authority in photochemistry, which was a very positive experience for me.

Since then, I have been pursuing research focusing on fundamental research into the chemistry required for conversion of light energy into chemical energy. I am particularly interested in the utilization of sunlight for recycling carbon dioxide. The overall objective is quite obvious: to utilize sunlight to convert carbon dioxide into a high-energy substance. A real-world practical application of this idea would provide a method of resolving in one blow the problems of energy, dwindling carbon-based energy sources, and of global warming, which are, problems faced by all humanity that are likely to become more grave as time goes on.



### How are our instruments helping you?

It is essential to the advancement of photochemistry that the efficiency of photoreactions conducted by different research groups can be evaluated with high precision and without difficulty. I hope sincerely that Shimadzu instruments will be introduced in many other laboratories, allowing us to debate with them from the same standpoint. In that respect, I would like to see improvements made that reduce the price of these instruments so they can be introduced to all laboratories.

### What are Shimadzu's strengths compared to other vendors (not limited to the instruments)?

Shimadzu's strength is its comprehensive reach. Even this project was realized thanks to the involvement of a Shimadzu specialist in spectroscopy and a Shimadzu engineer skilled at system design and system structure.

### Finally, could you share any requests that you have with respect to analytical and measuring instrument vendors?

I am extremely grateful for the interest you have shown in the evaluation of photoreactions. Since research advances in parallel in all areas of the world, I would like you to make progress towards the launch of products on a worldwide scale.

**It was significant to know what you think of us and our collaboration. We will strive to meet your request more than ever. Thank you very much.**



Here are his recent publications:

1. H. Takeda, K. Ohashi, A. Sekine, O. Ishitani, Photocatalytic CO<sub>2</sub> Reduction Using Cu(I) Photosensitizers with a Fe(II) Catalyst, *J. Am. Chem. Soc.*, **2016** in press, DOI:10.1021/jacs.6b01970
2. R. Kuriki, H. Matsunaga, T. Nakashima, K. Wada, A. Yamakata, O. Ishitani, K. Maeda, A Nature-Inspired, Highly Durable CO<sub>2</sub> Reduction System Consisting of a Binuclear Ruthenium(II) Complex and an Organic Semiconductor Using Visible Light, *J. Am. Chem. Soc.*, **2016** in press, DOI:10.1021/jacs.6b01997
3. A. Nakada, T. Nakashima, K. Sekizawa, K. Maeda, O. Ishitani, Visible-light-driven CO<sub>2</sub> reduction on a hybrid photocatalyst consisting of a Ru(II) binuclear complex and a Ag-loaded TaON in aqueous solutions. *Chemical Science* **2016** in press, DOI: 10.1039/C6SC00586A.
4. G. Sahara, R. Abe, M. Higashi, T. Morikawa, K. Maeda, K. Ueda, O. Ishitani, Photoelectrochemical CO<sub>2</sub> reduction using a Ru(II)-Re(I) multinuclear metal complex on a p-type semiconducting NiO electrode *Chem. Commun.*, **2015**, accepted (DOI: 10.1039/C5CC02403J)
5. Y. Yamazaki, T. Morimoto, O. Ishitani, Synthesis of Novel Photofunctional Multinuclear Complexes Using a Coupling Reaction *Dalton Trans.* **2015**, accepted (DOI: 10.1039/C5DT01717C)
6. G. Sahara, O. Ishitani, Efficient Photocatalysts for CO<sub>2</sub> reduction *Inorg. Chem.* **2015**, 54, 5096-5104. (DOI: 10.1021/ic502675a)
7. E. Kato, H. Takeda, K. Koike, K. Ohkubo, O. Ishitani, Ru(II)-Re(I) Binuclear Photocatalysts Connected by -CH<sub>2</sub>XCH<sub>2</sub>- (X = O, S, CH<sub>2</sub>) for CO<sub>2</sub> Reduction *Chem. Sci.* **2015**, 6, 3003-3012, OnlineOpen (DOI: 10.1039/C4SC03710C)
8. A. Nakada, K. Koike, T. Nakashima, T. Morimoto, O. Ishitani, Photocatalytic CO<sub>2</sub> Reduction to Formic Acid using a Ru(II)-Re(I) Supramolecular Complex in an Aqueous Solution *Inorg. Chem.* **2015**, 54, 1800-1807. (DOI: 10.1021/ic502707t)
9. K. Maeda, G. Sahara, M. Eguchi, O. Ishitani, Hybrids of a Ruthenium(II) Polypyridyl Complex and a Metal Oxide Nanosheet for Dye-Sensitized Hydrogen Evolution with Visible Light: Effects of the Energy Structure on Photocatalytic Activity *ACS Catal.* **2015**, 5, 1700-1707. (DOI: 10.1021/acscatal.5b00040)
10. Y. Ueda, H. Takeda, T. Yui, K. Koike, Y. Goto, S. Inagaki, O. Ishitani, A Visible-Light Harvesting System for Efficient CO<sub>2</sub> Reduction Using a Supramolecular Ru(II)-Re(I) Photocatalyst Adsorbed in Periodic Mesoporous Organosilica *ChemSusChem.* **2015**, 8, 439-442. OnlineOpen (DOI: 10.1002/cssc.201403194)