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Emeritus Professor Akira Suzuki Nobel Prize Laureate in Chemistry Special Commemorative Issue

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Cover picture : Commemorative ceremony for the winner of the Nobel Prize in Chemistry (October 7, 2010, School of Engineering, Hokkaido University)



Hokkaido University Faculty of Engineering, Graduate School of Engineering http://www.eng.hokudai.ac.jp/faculty/

Revolutionary research in organic synthesis earns Hokkaido its first Nobel Prize

Emeritus Professor Akira Suzuki of Hokkaido University (formerly a professor at the School of Engineering) was awarded the compounds. Cross-coupling has applications in a wide range of fields (e.g., medicine, agricultural chemicals, liquid crystals used in IT equipment, and organic EL as a new generation of luminescent materials), and represents a major contribution to the development and commercial manufacture of products commonly seen in today's world.



- Graduate School of Science, Hokkaido University. 1961: Became an associate professor at the Department of Chemical
- 1963: Became a postdoctoral researcher at Purdue University (unti
- 1973: Became a professor at the Department of Applied Chemistry, Faculty of Engineering, Hokkaido University.
- University of Science, a professor at Kurashiki University of Science and the Arts, an invited professor at Purdue University (USA), an invited professor at National Taiwan University, and Emeritus Professor at Academia Sinica.
- 2006: Became Specially Appointed Professor at the Graduate School of Engineering, Hokkaido University.

Chemical Society of Japan Award ('89) Synthetic Organic Chemistry Japan Special Award ('04) Japan Academy Prize ('04) Order of the Sacred Treasure ('05) Paul Karrer Gold Medal ('09) Hokkaido Shimbun Cultural Award ('09) Order of Culture ('10)













zuki with the Dean of the Faculty of in Chemistry (October

Congratulatory Message | Professor Naoshi Baba, Dean of the Faculty of Engineering

Many congratulations to Professor Suzuki on being awarded both the Nobel Prize in Chemistry and the Order of Culture. On behalf of the School of Engineering, the Graduate School of Engineering, the Faculty of Engineering, and the School of Engineering Alumni Association, I would like to express my warmest compliments.

These awards represent the absolute pinnacle of accomplishment for the School of Engineering since its establishment in 1924, and are a source of great pride for everybody involved with the school.

Professor Suzuki rose from the position of instructor at the Department of Chemistry, Faculty of Science to become an associate professor at the newly established (April 1960) Department of Chemical Process Engineering, Faculty of Engineering in October 1961. From there, he became a professor at the Department of Applied Chemistry in April 1973, and went on making efforts to the School of Engineering with over 32 years of valuable service in both research and education until March 1994. The Nobel Prize in Chemistry was awarded in relation to a paper on Suzuki-Miyaura Coupling published in 1979, over a 14-year period

after Professor Suzuki returned from a spell of just under 2 years at Purdue University.

I believe it is highly significant that the research leading to the award of the Nobel Prize was carried out at the School of Engineering.

This provides great encouragement to all students and staff working both in education and research at the Faculty of Engineering, the School of Engineering, the Graduate School of Engineering, and the Graduate School of Chemical Science and Engineering.

In 2006, Professor Suzuki was given the ad vitam title of Specially Appointed Professor by the Graduate School of Engineering (now the Faculty of Engineering) in recognition of his achievements in winning the 2004 Japan Academy Prize and raising academic standards as well as for his significant contribution to the progress of academic research and expectations for research development. The School of Engineering, the Graduate School of Engineering, and the

Faculty of Engineering look forward to Professor Suzuki's continued leadership in the years to come.

Wisdom developed in Hokkaido: The effects of Suzuki Coupling on peoples' lives



Suzuki-Miyaura Coupling – a groundbreaking cross-coupling reaction

We asked Professor Miyaura, who engaged in around-the-clock research with Professor Suzuki, how he felt about the award of the prize and about Professor Suzuki's character.

Norio Miyaura Specially Appointed Professor Faculty of Engineering, Hokkaido University

Professor Miyaura graduated from the Department of Synthetic Chemical Engineering, Hokkaido University in 1969, and completed a postgraduate degree at the same university in 1971. He subsequently became an instructor in the same department and continued his research under Professor Suzuki before himself being promoted to the position of professor upon Professor Suzuki's retirement in 1994. Professor Miyaura retired in 2010. His work has been recognized with the Chemical Society of Japan Award ('08) and the Science and Technology Prize ('10). He was born in Iwamizawa City, Hokkaido.

Breakthrough after three years of struggling Gaining worldwide attention by developing the ultimate practicality

- First, how did you react to the good news of being awarded the Nobel Prize in Chemistry?

Miyaura : I was overcome by a sense of both elation and relief. In the 30 years since the 1979 announcement of Suzuki Coupling, how greatly it has changed the world! In Europe and the United States, the Suzuki Coupling achievement was called "the last great accomplishment of the 20th century," and the award of an accolade as distinguished as the Nobel Prize in Chemistry brought it worldwide recognition. At the press conference, Professor Suzuki's smiling face, as well as my own sentiments as somebody involved in the research, told me that we both felt a great weight had been lifted from our shoulders.

■The birth of the Suzuki Coupling reaction Reported in 1979, the first case involved diene synthesis employing vinyl-type boronic acid. R←→B(OH)₂ + Br→ Pd(PPh₃)₄ + R→→ R→→ Pd(PPh₃)₄ Tetrahedron Lett. 20, 3437 (1979) J. Am. Chem. Soc., 107, 972 (1985) Organic Syntheses, 68, 130 (1989) Chem. Rev. 95, 2457 (1995) R→→→ R→→ R→→ R→→ R→→ Pd(PPh₃)₄ trans-trans trans-cls cis-trans cis-cis

- When did you first meet Professor Suzuki?

Miyaura : When I was in my third year at the School of Engineering, Hokkaido University, I attended a lecture given by Professor Suzuki. I was drawn to his careful and clear explanations of organic chemistry from its theoretical concepts. I began paying visits to his office, and then went on to his laboratory. At that time, Professor Suzuki was an authority on research into organic boron compounds, and had just returned from working with Professor Herbert Brown at Purdue University. We pursued further research on the synthesis and utilization of organic boron compounds along with some other students.



▲Lecturing at the Department of Pharmaceutical Chemistry, Hokkaido University (1979)

- Many of the things around us are made of organic compounds, and the technology to realize the

Leaflets on

Suzuki Coupling reagents As Suzuki Coupling is used in a wide range of industrial applications and research projects, the necessary reagents are in high demand. As a result, a variety of them are sold by a large number of companies, and leaflets promoting them are also widely circulated.



coupling of different organic molecules is applied in a wide range of fields. What are the characteristics of Suzuki Coupling, which makes today's world so rich and varied?

Miyaura : First of all, the characteristic of Suzuki Coupling is the use of non-metallic elements in the form of boron compounds for cross-coupling. In past research on cross-coupling, metallic elements such as magnesium were involved in the reactant compounds, which are unstable even in air, and there were lots of factors that created a risk of toxic by-products. However, using organoboronic acids containing the non-metallic element boron makes the compounds stable in air and water, innocuous, and easy to handle. When considering practical application, user-friendliness is very important.



- The stability of organoboronic acids has become a new obstacle, hasn't it?

Miyaura : On one hand, organoboronic acids are stable and easy to handle. On the other hand, they are chemically inert, making synthesis reactions difficult. So, what can be done to bring about a reaction? The answer lies in the second characteristic of Suzuki Coupling - the use of a palladium catalyst in a basic aqueous solution. When this method was developed, the general consensus for cross-coupling was to use anhydrous conditions. I remember that we were hesitant about adding water. When we encountered this difficulty in initiating a reaction, we were at a loss about how to overcome it for three years. Everyone thought that we probed in the dark, but when we took the risk of putting a palladium catalyst in an aqueous base, it went quite smoothly. This was the breakthrough moment that finally brought us out of the darkness. After that, every day was a joy. We went from not even knowing whether we could create the desired chemical compound to developing a method with a near 100% yield. I couldn't wait to go to the laboratory every day, and was always thinking, "What conditions shall we try tomorrow?"

- In 1979, the reaction known as Suzuki Coupling was announced to the world. In this coupling, organoboronic acids react with organohalides in the presence of a palladium catalyst and a basic solution.

Miyaura : The buzz surrounding Suzuki Coupling started at the Max Planck Institute in Germany (a leading organization in the field of boronic acid research) and spread throughout Europe and to the United States, Eventually, it came to be highly evaluated by various academic societies related to synthetic organic chemistry and catalytic chemistry. Both the pharmaceutical and agricultural chemical fields now utilize Suzuki Coupling in their manufacturing methods for a range of products, including the hypertension drugs made by Merck & Co., Inc. in America, which outputs a ton of these drugs each year, and the vegetable bactericidal agents manufactured by BASF in Germany. The manufacture of the liquid crystals so commonly used in daily life is also supported by Suzuki Coupling. In addition, the reaction facilitates the development of organic EL materials - a luminescent element currently drawing attention as a next-generation technology.

Cultivation of mind and body on a green campus : an ideal environment for original research

- The research findings presented 30 years ago are being utilized this century as well as last. Did you imagine this would be the case at the time?

Miyaura: Professor Tamejiro Hiyama of Kyoto University, a researcher in the field of cross-coupling reactions, once said to me, "Suzuki Coupling is like a wine matured in a northern land." I remember it even today. It is difficult to cultivate such long-sustained research in a short period of time in a rushed environment. I am convinced that we were able to achieve this "maturing" thanks to Hokkaido University, where time seems to pass more slowly.

- Was Professor Suzuki also adept at taking a breather from academic life?

Miyaura : During research projects, things sometimes seem to be going badly for an awfully long time, and our work on Suzuki Coupling was no exception. Boron compounds, catalytic agents, solvents and bases, in addition to different combinations thereof and various factors such as reaction temperatures, were all intertwined in a web of trial and error. All we see in the laboratory is a clear liquid spinning in a transparent flask; we have no idea of what's actually going on inside it. I think



Genghis Khan barbecue party of the Laboratory of Synthetic Organic Chemistry, Department of Synthetic Chemical Engineering (around 1972)

Professor Suzuki was prepared for these times, which represent the true nature of an unremitting life of research. He also joined in with students' all-night parties. Professor Suzuki likes a drink, and students sitting near him would quickly tire of being kept their glass constantly topped up with sake served by him [laughs]. He would always find reasons – like the cherry blossoms blooming or alumni visiting – to have Genghis Khan barbecue parties, which helped us to relax.

- Professor Suzuki's research laboratory was quite uninhibited, wasn't it?

Miyaura: Yes, and there's one more thing worthy of special mention – Professor Suzuki's rich and varied international outlook. In the laboratory, we often had visitors from abroad, including students of Professor Brown, which created a real interdisciplinary atmosphere. I often saw Professor Suzuki take control of the situation while at the same time joking with the visitors. He has a very natural gentlemanly approach that could be seen in his mannerisms, like holding the door open for women. He has an open-minded and frank character, and is definitely capable of building strong relationships whether in Japan or abroad.



▲Professor Suzuki (right) in the Vienna Woods (1985)

- The achievement of receiving the Nobel Prize in Chemistry provides hope for Hokkaido researchers, particularly those of the future, doesn't it?

Mivaura : I think the perception that the research environment in Hokkaido University was at a disadvantage due to its distance from the center of Japan has been completely dispelled. Nowadays, information can be communicated via the Internet, so Hokkaido University's remoteness provides a contrast to environments characterized by an overabundance of information, where it can be difficult to implement highly creative, original research. It is an environment that allows the mind and body to breathe, which encourages good research results as seen with the great achievement recognized by the award of the Nobel Prize. Viewed in this light. Hokkaido University with its rich green campus provides the ideal environment for education and research. allowing students to devote themselves to work that they believe in. I hope this will give rise to further development from young researchers following in the footsteps of Professor Suzuki, who possesses the frontier spirit that Dr. Clark spoke of at the university's foundation.

SOME MEMORIES

An excerpt from Hokkoukai-shi (No. 58, March 1994)

One Saturday in 1962, I visited Maruzen Sapporo bookstore and found a chemistry textbook with a red and black binding that didn't look like any other academic publication. It was Hydroboration by Professor H. C. Brown (winner of the 1979 Nobel Prize in Chemistry). Out of idle curiosity, I picked it up and started reading. It was written in the professor's own unique style of expression, and it seemed interesting so I bought it and headed home. I remember even now that I started reading it after dinner and couldn't stop. It wasn't a very thick book, but it is one of the few academic books that have kept me up all night reading. At that time, I had just moved from the Faculty of Science to the Faculty of Engineering, so I was at a new workplace thinking about how I wanted to start research in a new field. Maybe this book was an inspiration for me.



 Working at Professor H. C. Brown's laboratory Purdue University (1964)



▲With Professor Brown and his wife in Red Square, Moscow (1993)

I learned many things from Professor Brown, including aspects of research philosophy, but something I remember vividly even now are his words, "Research the kind of thing that could appear in a school textbook." Although easier said than done, this has become the personal credo by which I work.

··· However, we received a report from Professor Brown's Laboratory saying that our method had been retested but there was no reaction. I remember a sentence from a letter that Professor Brown sent me:

"Chemistry should be international, why do we have such a big difference between two places, Sapporo, Japan and West Lafayette, USA?"

As Professor Brown's laboratory and ours were achieving inconsistent results, we examined the details and found something unexpected: a small amount of oxygen impurity in the nitrogen gas used in our system was accelerating the reaction.

► Hydroboration

A book about "the synthesis and reaction of organoboronic compounds" written by Professor H. C. Brown of Purdue University, who laid the foundations for organoboronic chemistry and was awarded the 1979 Nobel Prize in Chemistry



I think serendipity is something that any researcher can encounter. However, whether or not such opportunities can be seized may solely depend on the nature of the modesty and honesty in that researcher's heart as well as the kind of attentiveness that doesn't allow even a ray of light to be missed, a burning passion for research, and in addition to all these, good fortune. However, I can say one thing with conviction: If you never try, it will never happen.



▲Leaving Tokyo Haneda Airport for the US (1963)

At the congratulatory party for Nobel Prize winner Emeritus Professor Akira Suzuki (October 25)

This is the first time I've attended an event dedicated to building a sustainable society continued by Hokkaido University. Creating a society that has stability – in other words, going forth as a society that does not destroy the environment – is an urgent issue for everybody today, followed by that of our children and our grandchildren.

Even in my research field of chemistry, this issue has recently attracted much attention. The concept of eco-chemistry – or carrying out the work of chemistry without polluting the environment – is catching on, and research is actually starting to head in the same direction. In reality, achieving this goal may be very difficult, but I still think we should raise ourselves and strive to produce results in the near future. Of course, if this is the case, then I believe that each of us must bear this in mind and make constant efforts to address the related issues.

So, as I salute Hokkaido University for planning a well-timed project, I also hope that our society will evolve to become more sustainable in the future.



Creating a new age through application of the frontier spirit



The cross-coupling reaction developed by Professor Suzuki and his co-workers has been put to practical use in the fields of medicine, agricultural chemicals, liquid crystals used for IT devices, organic EL (electroluminescence) as next-generation luminescent materials, and more. Giving back to society through research findings is extremely important. We believe that it is the duty of the Faculty of Engineering, Hokkaido University to contribute to a better world.

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