Toyoki Kunitake

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へそ曲り壁登り来て京都賞

By climbing o'er walls
With unswerving quest for truth
Kyoto Laureate is honored

夏嵐ナノの不可思議漸くに

Nano mysteries
emerged like a summer storm
finally, at last

This issue is a tribute to Dr. Toyoki Kunitake, a pioneer in the chemistry of molecular self-assembly, a topic of great interest to the *Langmuir* readership.

Dr. Kunitake was born in Kurume City in Fukuoka Prefecture, Kyushu, Japan on February 26, 1936. Following a high school education, he entered the Department of Applied Chemistry, Faculty of Engineering, Kyushu University in 1958. He graduated with B.Sc. (1962) and MSc. (1964) degrees, with a focus on polymer synthesis. His B.Sc. and MSc. supervisors were Prof. Saburo Akiyoshi and Prof. Chuji Aso, professors of synthetic chemistry. Dr. Kunitake then moved to work under Prof. C. C. Price at the University of Pennsylvania, where he obtained his Ph.D. in 1962. A post-doctoral year (bioorganic chemistry and enzyme reactions) followed with Prof. C. G. Nieman in theDepartment of Chemistry, California Institute of Technology.

In 1963, he returned to the Department of Synthetic Chemistry, Kyushu University as an associate professor under the guidance of Prof. Chuji Aso. He initiated a study on mechanistic aspects of cationic polymerization, focusing, among other, on the phenomenon of stereoregularity and how to control it. After his promotion to full professor in 1974, his research interests changed to the design of polymer catalysts for use in aqueous media, based on the model of enzymatic hydrolysis. He prepared several vinyl polymers having a hydrophobic site acting as the substrate binding pocket and a functional group, such as an imidazole, acting as a nucleophile. They represent the first examples of synthetic polymer catalysts showing a substrate binding process. He went on to prepare other bifunctional polymer catalysts and contributed to the development of enzymatic models for catalysis in micellar and macromolecular systems. This body of work had a significant impact on bioorganic chemistry, polymer catalysis, and colloid and surface science.

In 1977, Dr. Kunitake discovered that synthetic organic molecules could spontaneously form a bilayer membrane, the basic structure common to the biological membranes of living cells. His first report of a "Totally Synthetic Bilayer Membrane" became a landmark article that has been cited more than 320 times. His subsequent research established the formation of bilayer membranes as a universal phenomenon, observed not only in water but also in organic solvents, for synthetic amphiphilic compounds with various precisely designed molecular structures. His group synthesized hundreds of amphiphilic molecules, including cationic, anionic, nonionic, and zwitterionic hydrophilic headgroups in combination with two, three, and four alkyl or perfluoroalkyl chains. He systematized the mechanism of synthetic bilayer membrane formation through his unique organic chemistry-based research methodology combined with various physicochemical characterization techniques. He also developed methods to immobilize bilayer membranes and to produce various self-assembling materials. Through these approaches, he opened up a new and promising academic field of chemistry based on molecular self-assembly. In 1982, Dr. Kunitake reported the fabrication of immobilized bilayer films in which synthetic bilayer membranes were fixed with polymers by casting from organic solutions. This was the first example of self-standing molecular self-assembled films. He extended this idea to lipid–inorganic composite films prepared from alkoxysilane or silica gels.

Dr. Kunitake'sapproach to synthetic bilayer membranes was revolutionary, overturning the previously held assumption that ordered molecular self-organized structures such as biological membranes could be formed only by biolipids in nature. His research made it possible, for the first time, to gain a molecular design-based understanding of how molecularly organizational structures and physical properties, which are created in a hierarchical manner through self-assembly, correlate with the molecular structures of components. While extending the formation of molecular self-assembly from aqueous to organic solvents, he generalized the conventional image of hydrophilic and hydrophobic portions of amphiphilic molecules. Dr. Kunitake also showed that specific interactions among functional groups derived from advanced ordered structures appear in bilayer membranes, thereby establishing the fundamental concept of chemistry based on self-assembly where interactions on the molecular level lead to collective functions that are controlled according to molecular orientation and distribution. He converted this fundamental understanding to innovations in materials science as a director of the ERATO molecular architecture project (JST, 1987–1992), the ICORP supramolecular project (1992–1997), and the Group Director of the RIKEN Frontier Research System (1999–2007).

Dr. Kunitake's major achievements toward innovation include the following: (1) the development of various methods for bilayer membrane immobilization, thereby enabling the creation of precisely organized membranes; bilayer membranes immobilized in this way are used to produce superlaminated solid molecular-oriented film electrodes in fully automated electrolyte analyzers for medical use and in vitro diagnostic testing; (2) the development of a molecular self-assembly-based synthetic methodology for two-dimensional polymers and two-dimensional ultrathin silica films by using organic molecular assemblies as templates; their microstructures follow the morphologies used as templates; (3) the discovery of a technique for manufacturing large, free-standing nanostructured thin films, the giant nanomembrane, which possesses notable strength as well as extreme flexibility. These characteristics had long been sought in the field of functional membranes, and at present, there are high expectations for their wide-ranging applications, including fuel cells and gas and water separation, which can contribute to solutions for environmental problems.

Through these achievements, Dr. Kunitake has converted the concept of molecular self-assembly-based chemistry into one of the most useful methodologies in advanced functional materials design and has reached a new frontier in the field of materials science using self-assembly techniques. At the same time, he has trained a large number of highly accomplished researchers in these academic fields as well as industry and has made an invaluable contribution to international academic exchange.

Dr. Kunitake also served as the Dean of the Faculty of Engineering, Kyushu University for 1992–1994; Professor and Vice President, University of Kitakyushu for 1999–2008; and President of the Kitakyushu Foundation for the Advancement of Industry, Science and Technology, for 2009–2016. Dr. Kunitake is currently a University Professor of Kyushu University. He has received numerous honors, including the Medal with Purple Ribbon, Order of Culture, Japan in 1999; the Japan Academy Prize in 2001; an H. C. Brown Lectureship, Purdue University in 2000; Alexander Memorial Lecturer, University of Sydney, 2001; and Order of Culture, Japan in 2014.

This special issue of *Langmuir* is dedicated to the Kyoto Prize he received in 2015 and his 80th birthday. We thank all of the authors who contributed to this special issue.