

Japan Academy Prize to:

Hisashi YAMAMOTO
 Arthur Holly Compton
 Distinguished Professor,
 The University of Chicago
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and

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for “Exploitation of Chemical and Physical Properties of Main-group Element Compounds based on Flexibility for High Coordination”

Outline of the work:

Drs. Hisashi Yamamoto and Kohei Tamao have made valuable contributions not only to basic science but also industrial technology by developing a number of synthetically useful chemical reactions and functional materials based on flexibility permitting high coordination among main-group element compounds.

Their work is based on the following common features of main-group element compounds. Organic compounds R_nE of certain main group elements, especially heavy elements of groups 13 and 14, have electron-accepting molecular orbitals and thus the central element E behaves as a Lewis acidic center to accept a ligand L to form hyper-coordinate species R_nEL , increasing both the nucleophilicity of the group R and the electrophilicity of the ligand L. The electronic states and steric environments around the central element E can be tuned by structural modification to the R and/or L.

Dr. Yamamoto is a pioneer in pointing out that well-designed molecular acid catalysts are extremely effective in the highly selective and practical synthesis of a variety of organic molecules, including both natural products and artificial materials. In particular, he has developed a number of molecular Lewis acid catalysts and molecular Lewis acid-Brønsted acid mixed catalysts, containing as central elements mainly boron, aluminum, tin, zirconium, and silver. In contrast to the conventional Brønsted acid and Lewis acid catalysts such as hydrochloric acid, sulfuric acid, aluminum chloride and boron trifluoride, Dr. Yamamoto’s molecular acid catalysts can be designed advantageously for asymmetric synthesis and for environment-friendly chemical transformations to solve various difficulties such as low yield and low selectivity, problems often encountered in traditional processes.

Yamamoto molecular acid catalysts can act just like natural enzymes to interact precisely with functional groups in the substrate to create a specifically designed reaction space. Also of great significance is the fact that Yamamoto catalysts consist of small molecules and are applicable to a wide range of substrates, as opposed to natural enzymes that have high molecular weights and act as catalysts only

for specific substrates.

He has successfully demonstrated a number of types of asymmetric carbon-carbon bond forming reactions, even among the most difficult chemical transformations, by developing well-designed chiral molecular Lewis acid catalysts with binaphthols, amino acids, and tartaric acid as chiral ligands. He has also extended his concept to develop several environmentally friendly catalytic reactions, as represented by an efficient esterification process between alcohols and carboxylic acids in quantitative yields at an extremely low catalyst concentration and low temperature.

A variety of molecular acid catalysts now commonly used worldwide originate from the pioneering work of Dr. Yamamoto. His guiding principle of molecular acid catalysis is widely appreciated as an important basis for many scientific and technological advancements.

Dr. Tamao is responsible for introducing a new concept in bond activation involving high coordination in modern synthetic organic chemistry, by developing a variety of bond cleavage reactions among hexacoordinate organosilicon compounds. Based on these developments, he discovered hydrogen peroxide oxidation of silicon-carbon bonds in ordinary tetracoordinate organosilicon compounds by introducing electronegative group(s) on silicon as essential substituents for the formation of activated hypercoordinate species. This oxidation reaction, now known as Tamao oxidation, represents the only existing general method for the synthesis of alcohols from organosilicon compounds, and has overturned the previously accepted wisdom among organic chemists that silicon-carbon bonds are fairly resistant to oxidative cleavage, greatly enhancing the synthetic utility of organosilicon compounds.

Another new chemical development in main-group element compounds developed by Dr. Tamao is the control of photophysical properties by coordination number change. A dramatic color change and a fluorescence change in boron and silicon compounds having three anthracene rings have been demonstrated through the addition of a fluoride ion which causes the coordination number change, further providing basic ideas for fluoride ion sensors.

He has also demonstrated that silole, a silicon-containing five-membered cyclic compound, is an electron-accepting molecule due to a unique orbital interaction involving a silicon atom. He developed a new general synthetic method for the introduction of silole rings into a variety of π -conjugated systems and applied, through collaboration with corporate interests, 2,5-dipyridyl-silole derivatives to electroluminescent (EL) devices as the most efficient electron-transporting materials, and which have achieved practical application in the production of small, full-color displays on commercial mobile telephones.

Dr. Tamao has consistently displayed leadership in the development of new fields of molecular and material science by blending a keen sense of modern synthetic organic chemistry with classic main-group element chemistry.