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## Phosphorus, Sulfur, and Silicon and the Related Elements

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# Special Issue of *Phosphorus, Sulfur, and Silicon and the Related Elements* Dedicated to Professor Naomichi Furukawa

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#### **EDITORIAL**

Special Issue of *Phosphorus, Sulfur, and Silicon* and the Related Elements Dedicated to Professor Naomichi Furukawa

#### Greetings!

It gives me immense pleasure to present this special issue of *Phosphorus*, *Sulfur*, *and Silicon and the Related Elements* that comprises 39 invited manuscripts dedicated to the achievements of Professor Naomichi Furukawa, now an Emeritus Professor of Chemistry at Tsukaba University. I would like to thank the many authors who have contributed excellent scientific manuscripts for publication and to my European Editor, Konstantin Karaghiosoff, for all of his work in getting the issue together through his editorial process. I would also like to thank Professors Jozef Drabowicz (Łodz, Poland) and Takeshi Akasaka (Tsukuba, Japan) for their organization as Guest Editors for this issue.

Below you will find an invited tribute to the lifetime of contributions to main group chemistry from Professor Furukawa that has been written by Professors Drabowicz and Akasaka. I hope it begins to reveal some of the marvelous chemistry we have been fortunate enough to read in the articles that have been published by his group.

With my best wishes, Martin D. Rudd Editor-in-Chief

#### Professor Naomichi Furukawa—A Tribute

Professor Naomichi Furukawa was born on March 21, 1937, in Osaka (Japan). After graduating from the Department of Agriculture (Agricultural Chemistry) at Kyoto University (Kyoto, Japan) in 1960, he immediately began his scientific career as a Senior Researcher at the Radiation Center of Osaka Prefecture, where he met Professor Shigeru Oae. They worked together until 1983. With his doctoral supervisor, Professor Oae, he moved to the Department of Applied Chemistry at Osaka City University in 1963, where, in 1968, he obtained his doctoral degree with a thesis entitled "Studies on the Reaction Mechanisms of the Alkaline Fusion of Benzene Sulfonic Acid and Related Sulfur Compounds by Using <sup>14</sup>C Labeled Compounds." From 1963 to 1973, he was appointed as a Research Associate and then Lecturer. In the meantime (from 1968 to 1970), Professor N. Furukawa moved to the United States as a post-doctoral fellow and worked at Brookhaven National Laboratory together with Professor Alfred P. Wolf on research related to <sup>11</sup>C hot atom chemistry. In 1974 he accepted an Associate Professor position at Tsukuba University (a completely new university aimed at the renewal of Japanese universities, which was

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founded in 1973). He was promoted to Professor in 1984 and remained in this position until his retirement in 2000 and his appointment as Emeritus Professor. During his 26 years of service to Tsukuba University, he held various positions of an academic and administrative nature: Director of the Isotope Center (1987–1988), Chairman of the Department of Chemistry (1988–1990, 1992–1994), Chairman of the Graduate Course of the Department of Chemistry (1990–1992), and Director of the Tsukuba Advanced Research Alliance Center (1998–2000).

Professor N. Furukawa started his scientific activity in the field of physical organic chemistry. His work concentrated particularly on nucleophilic substitution reactions of benzene sulfonic acid and related organic sulfur compounds using labeled compounds of various radioisotopes such as <sup>14</sup>C, <sup>35</sup>S, and <sup>37</sup>Cl and those of stable isotopes such as <sup>13</sup>C and <sup>2</sup>H. After finishing his doctoral thesis in 1968, he started his studies on mechanistic and synthetic aspects in the chemistry of trivalent organic sulfur compounds such as sulfoxides and sulfilimines. During the 1970–1983 period, he concentrated his efforts on the investigation of the chemistry sulfilimines and sulfoximines including many new synthetic methodologies. Among those works, the synthesis of N-unsubstituted diaryl sulfilimines and optically active derivatives became a standard method for the synthesis of so-called free sulfilimines, which were used as amino-group transfer agents. During that period, he also studied nucleophilic substitution reactions at the sulfinyl sulfur atom with other trivalent organic sulfur compounds, such as sulfoxides, sulfilimines, and S-ylides. He discovered that a ligand coupling reaction takes place between the benzyl and 2-pyridyl groups upon treatment of benzyl 2-pyridyl sulfoxide with Grignard reagents. This coupling gave 2-benzyl pyridine quantitatively. Furthermore, when an optically active  $\alpha$ -phenylethyl derivative was used in the reaction, the stereochemistry of the reaction was found proceed with retention of the configuration at a stereogenic carbon atom of the  $\alpha$ -phenylethyl group in the product, indicating that the reaction proceeds via a pentacoordinated sulfur intermediate (hypervalent sulfurane). This was a first discovery of a sulfurane having four carbon ligands around the sulfur atom, but the sulfurane remained a hypothetical compound. This result prompted Professor Furukawa to start experiments devoted to the synthesis and isolation of the stable C4 sulfuranes. He also extended this chemistry to other elements of group 16 of the periodic table (selenium and tellurium). After many trials, he succeeded in the first detection of sulfurane (2,2'-bis-biphenylilene diphenylsulfurane) using low temperature <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and finally he isolated "bis(2,2'-biphenylilene)sulfuranyl bis(tetrafluoroborate)" as a stable crystalline sulfurane. Its structure was determined using X-ray crystallography. The results were published, respectively, in *Tetrahedron Lett.* and J. Am. Chem. Soc. Aside from these sulfuranes, the corresponding selenuranes and telluranes were also isolated, and their structures were determined using X-ray crystallography and <sup>1</sup>H, <sup>13</sup>C, <sup>77</sup>Se, and <sup>125</sup>Te NMR spectroscopy.

During the same period, Professor Furukawa investigated other chemistry of chalcogen-containing compounds. One was the transannular interaction between two chalcogen atoms involving S–S, Se–Se, and Te–Te atoms, which gave new chalcogen—chalcogen dicationic species. If the counter anions were strongly electronegative species such as F<sup>-</sup> or <sup>-</sup>OR anions, then the chalcogen dications were converted to dichalcogenurane species, which constituted new target molecules. In the case of Te<sup>+</sup> derivatives, he found new molecules bonded linearly among tetra<sup>+</sup> and hexa<sup>+</sup> Te atoms, which might open a new field in heteroatom chemistry. The chemistry of these new compounds might open new possibilities for material science, such as a new memory molecule via hysteresis.

The scientific achievements of Prof. Furukawa are notable indeed. They comprise more than 330 original papers, published mainly in esteemed internationally recognized journals, such as *J. Am. Chem. Soc.*; *J. Org. Chem.*; *Organometallics*; *Angew. Chem.*; *J. Chem. Soc.*, *Perkin Trans.*; *Chem. Commun.*; *Tetrahedron*; *Tetrahedron. Lett.*; *Bull. Chem. Soc. Jpn.*; and others. In addition he is the coauthor of 20 review articles, 10 monographic chapters, and two books.

Professor N. Furukawa was a member of Editorial Boards of *Phosphorus, Sulfur, and Silicon and the Related Elements* (1994–2000) and *Heteroatom Chemistry*. He also served as the Chairman of the Organizing Committees of various international and domestic scientific conferences including the 17th International Symposium on the Organic Chemistry of Sulfur (ISOCS-17, Tsukuba, Japan as Vice-Chair), First International Conference on Heteroatom Chemistry (Tsukuba, Japan, 1989), and the First International Symposium on the Reactive Species of Chalcogen Compounds (Tsuchiura, Japan, 1998).

Professor N. Furukawa has been invited as a plenary (and section) lecturer at many international conferences on the chemistry of organic sulfur, selenium, and tellurium; the chemistry of heteroatoms; and physical organic chemistry.

He has been an invited lecturer to many universities outside Japan, including the Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences (Łodz, Poland), University of Marburg (Marburg, Germany), KAIST (Seoul, Korea), University of California (Davis, USA), and Univ. of Adelaide (Adelaide, Australia).

Jozef Drabowicz Takeshi Akasaka Guest Editors