



RESEARCH ACTIVITIES

Division of Advanced Molecular Science

World-class researchers leading the frontiers of molecular science are invited as “distinguished professors.” The environment to devote themselves to research will be provided. We support top-level research in the field of molecular science.

Self-Assembling Molecular Systems Based on Coordination Chemistry

Division of Advanced Molecular Science



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Education

1980 B.S. Chiba University
1982 M.S. Chiba University
1987 Ph.D. Tokyo Institute of Technology

Professional Employment

1982 Researcher, Sagami Chemical Research Center
1988 Assistant Professor, Chiba University
1994 Associate Professor, Chiba University
1997 Associate Professor, Institute for Molecular Science
1999 Professor, Nagoya University
2002 Professor, The University of Tokyo
2018 Distinguished Professor, Institute for Molecular Science

Awards

1994 Progress Award in Synthetic Organic Chemistry, Japan
2000 Division Award of Chemical Society of Japan (Organic Chemistry)
2001 Tokyo Techno Forum 21 Gold Medal
2001 Japan IBM Award
2003 Nagoya Silver Medal
2004 Izatt-Christensen Award
2006 G. W. Wheland Award (Chicago University Lectureship Award)
2010 The Reona Esaki Award
2010 The JSCC Award
2011 3M Lectureship Award (University of British Columbia)
2012 Thomson Reuters Research Front Award 2012
2013 The Chemical Society of Japan (CSJ) Award
2013 Arthur C. Cope Scholar Award (ACS National Award)
2013 Merck-Karl Pfister Visiting Professorship (MIT Lectureship Award)
2014 ISNSCE 2014 Nanoprize
2014 Medal with Purple Ribbon
2014 Fred Basolo Medal (Northwestern University)
2015 John Osborn Lecturer (Strasbourg University)
2016 Merit Award of The Naito Foundation
2018 Wolf Prize in Chemistry

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Secretary
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Keywords

Self-Assembly, Nano-Space, Coordination Chemistry

Our laboratory is exploring the construction of new molecular materials through metal-directed self-assembly. By using coordination bonds with appropriate bond energy and well-defined geometries as the driving force of self-assembly, a variety of three-dimensional architectures have been constructed at will. Among these nanostructures, we are particularly interested in hollow frameworks with a large inner space, where new properties and functions are developed. Recent outstanding results include the self-assembly of gigantic $M_{30}L_{60}$ and $M_{48}L_{96}$ spherical complexes. We are also interested in reproducing solution reactions within the pore of self-assembled porous complexes. In due course, we have recently developed a new X-ray technique that does not require the crystallization of target compounds (crystalline sponge method). This innovative analysis method is attracting considerable interests of not only academia but also industries such as pharmaceuticals and foods companies.

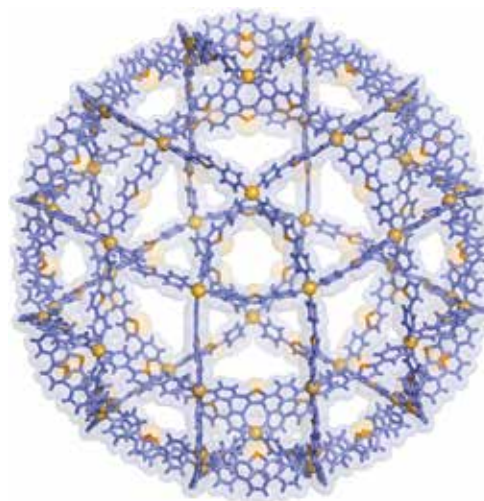


Figure 1. X-ray structure of $M_{48}L_{96}$ complex.

Selected Publications

- Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen and M. Fujita, "X-Ray Analysis on the Nanogram to Microgram Scale Using Porous Complexes," *Nature* **495**, 461–466 (2013).
- D. Fujita, Y. Ueda, S. Sato, H. Yokoyama, N. Mizuno, T. Kumasaka and M. Fujita, "Self-Assembly of $M_{30}L_{60}$ Icosidodecahedron," *Chem* **1**, 91–101 (2016).
- D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka and M. Fujita, "Self-Assembly of Tetravalent Goldberg Polyhedra from 144 Small Components," *Nature* **540**, 563–566 (2016).

1. Self-Assembly of Molecular Polyhedra

Rational control of the self-assembly of large structures is one of the key challenges in chemistry, and is believed to become increasingly difficult and ultimately impossible as the number of components involved increases. We have achieved in the self-assembly of a series of large spherical structures which belong to Platonic or Archimedean polyhedra containing up to 30 palladium ions coordinated by up to 60 bent organic bidentate ligands by considering their geometries and topologies.^{1,2)} We have also found the functionality in the large inner spaces of these structures such as protein encapsulation,³⁾ size-regulated synthesis of nanoclusters and so on.

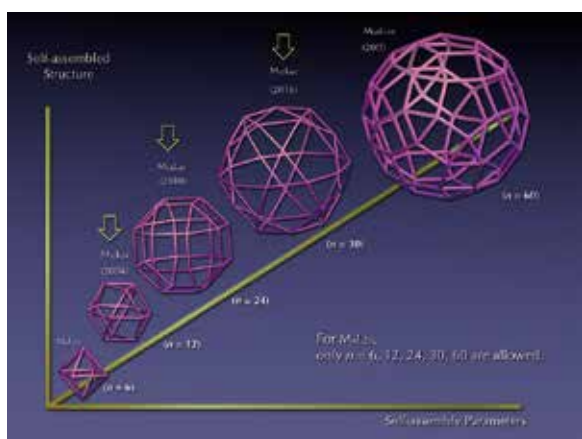


Figure 2. Series of large polyhedral structures.

Recently we serendipitously obtained the self-assembly of a spherical structure⁴⁾ that contains 30 palladium ions and 60 bent ligands, but belongs to a shape family that has not previously been observed experimentally (Figure 1). The new structure consists of a combination of 8 triangles and 24 squares, and has the symmetry of a tetravalent Goldberg polyhedron. Tetravalent Goldberg polyhedra have not previously been reported at the molecular level, although their topologies have been predicted using graph theory. We use graph theory to predict the self-assembly of even larger tetravalent Goldberg polyhedra, which should be more stable, enabling another member of this polyhedron family to be assembled from 144 components: 48 palladium ions and 96 bent ligands.

2. Crystalline Sponge Method

X-ray single crystal diffraction (SCD) analysis is one of the most effective methods for the structure determination and is the only one practical way to determine the absolute structure of molecules. However, it has the intrinsic limitation that

the target molecules must be obtained as single crystals. We have reported a new protocol for SCD analysis that does not require the crystallization of samples.⁵⁾ In our method, tiny crystals of porous complexes are soaked in a solution of a target, where the complexes can absorb and orient the target molecules in the pores. The crystallographic analysis clearly determines the absorbed guest structures along with the host frameworks. As the SCD analysis is carried out with only one tiny crystal, the required sample amount is of the nano-to-microgram order. This method can be applied to many varieties of molecules including oily materials which never crystallize in principle. With chiral guests, the space group of the crystal turned into chiral, enabling the determination of absolute configuration of the guests by anomalous scattering effect from the host heavy atoms (Zn and I).

This method has been applied to natural product chemistry, synthetic chemistry, and pharmaceutical research so far. For example, the absolute configurations of elatényne, first isolated in 1986, was reliably determined by the crystalline sponge method after 30 years. It had not been unequivocally confirmed because of its almost achiral meso-formed core structure that results in nearly zero $[\alpha]_D$ specific rotation. This faint chirality, defined only by the slight difference in the two alkyl side-chains, was precisely discriminated by crystalline sponge method. The total amount required for the experiments was only ~100 μg and the majority of this (95 μg) could be recovered after the experiments. Here, our group will widen and deepen this method more scientifically in close coordination with Nanotechnology Platform which started from 2018 at IMS.



Figure 3. Schematic representation of crystalline sponge method.

References

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- 2) D. Fujita, Y. Ueda, S. Sato, H. Yokoyama, N. Mizuno, T. Kumasaka and M. Fujita, *Chem* **1**, 91–101 (2016).
- 3) D. Fujita, K. Suzuki, S. Sato, M. Yagi-Utsumi, Y. Yamaguchi, N. Mizuno, T. Kumasaka, M. Takata, M. Noda, S. Uchiyama, K. Kato and M. Fujita, *Nat. Commun.* **3**, 1093 (2012).
- 4) D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka and M. Fujita, *Nature* **540**, 563–566 (2016).
- 5) Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen and M. Fujita, *Nature* **495**, 461–466 (2013).

Award

FUJITA, Makoto; Wolf Prize in Chemistry (2018).