# Self-Assembling Molecular Systems Based on Coordination Chemistry

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**Professional Employment**
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1999 Professor, Nagoya University
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**Awards**
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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
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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)
2018 Wolf Prize in Chemistry
2019 The Imperial Prize and the Japan Academy Prize
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2020 Clarivate Citation Laureates (Chemistry)
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Our research is based on the design of new self-assembled molecular systems using coordination chemistry. We not only create the new self-assembled molecular systems but also try to utilize the created system for various purpose. One example is a molecular system called crystalline sponge (CS).

The CS is a porous crystal of a coordination network, into which various kinds of small molecules could be introduced. Notably, we can know structures of the small molecules accommodated in the pore of the CS by X-ray crystallography, because the CS has the accommodated small molecules periodically aligned. Thus, the CS can be utilized for the structure analysis, and this technique is called the CS method. This method has some advantages; i) only nanogram to microgram scale of analytes is required, ii) the absolute stereochemistry can be determined, iii) even oily substances can be analyzed by X-ray crystallography. Because of these fascinating features, the CS method attracts the interests of many people not only in academia but also in industry.

Currently, we are improving the CS method in various ways. At the same time, we also try to apply the CS method to other field of science. For example, we use the CS method for the studies on natural product chemistry.

## 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, N. Mizuno, T. Kumasaka and M. Fujita, “Self-Assembly of Tetravalent Goldberg Polyhedra from 144 Small Components,” *Nature* **540**, 563–566 (2016).

Here, we show our recent attempts to improve the performance of the CS method and deepen understanding of this method. These studies would broaden the range of compounds, which can be analyzed by the CS method, and provide information helpful for people who want to try this method. We hope these studies encourage many people who needs to analyze the structure of small molecules to use the CS method for their own works and studies.

## 1. Solvent Effect in the Crystallin Sponge Method[1)]

Recently, we found that a choice of a solvent used in the CS method is important, especially when we want to heighten the quality of data obtained by this method. Before the analytes are introduced into the CS, the pore of the CS is filled with solvents. When the analytes come into the CS, the solvents go out, but a part of the solvents still remain in the pore. Previously, non-polar solvents are frequently used in the CS method, because the non-polar solvents exhibit only limited interactions with the CS, and are easily replaced with analytes. However, in this study, we tried to use various kinds of polar solvents. As a result, we found that the polar solvents are sometimes better than the non-polar solvents. Since the polar solvents remained in the pore show stronger interactions with both analyte and the CS, it can mediate the interaction between the analytes and the CS (Figure 1). It would result in an inhibition of disorder of analyte in the pore of the CS and an improvement of the quality of data.

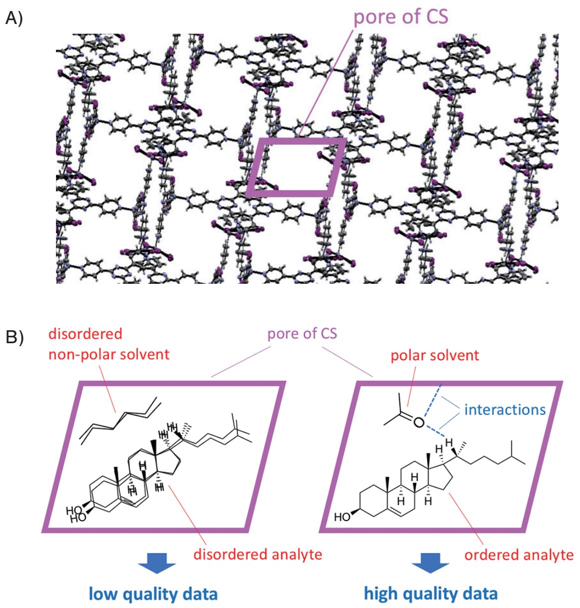


**Figure 1.** A) Structure of the CS. B) Image of the solvent effect in the CS method.

## 2. Crystalline Sponge Method Is Suitable for the Structure Analysis of Halogenated Compounds[2)]

The CS method could be used for the structure analysis of a broad range of small molecules. However, it is worth knowing which kinds of analytes is suitable for the analysis using the CS method. We recently found that the halogenated compounds are easily analyzed by the CS method in many cases. For example, we successfully analyzed a series of halogenated compounds classified as persistent organic pollutants (POPs), which are important compounds from the point view of environmental problem. The analysis of the POPs using the CS method revealed that halogen atoms of the analytes effectively interact with the CS (Figure 2). We consider that these interactions help the alignment of the halogenated compounds inside the pore of the CS.

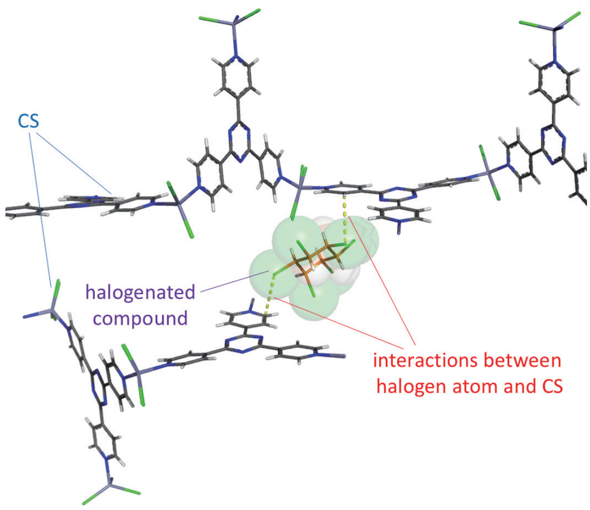


**Figure 2.** One example of interaction between the CS and a halogenated compound.

### References

1) N. Wada, K. Kageyama, Y. Jung, T. Mitsuhashi and M. Fujita, *Org. Lett.* **23**, 9288–9291 (2021).

2) J. Chen, T. Kikuchi, K. Takagi, H. Kiyota, K. Adachi, T. Mitsuhashi and M. Fujita, *Chem. Lett.* **51**, 85–87 (2022).

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