Japan Academy Prize to:

Susumu KITAGAWA
Director, Institute for Integrated Cell-Material Sciences, Kyoto University
Professor, Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University

for "Studies on Creation and Application of Porous Coordination Polymers"

Outline of the work:

Looking back on the advent of synthetic materials, one can realize that the development of new materials faced a difficult path. Until 1997, it was believed that crystalline compounds with a regular porous structure based on organic molecules were different from inorganic zeolites and they collapsed without guest filling. Prof. Susumu Kitagawa challenged this notion and successfully synthesized robust crystalline porous materials from organic molecules. He became the first person in the world to synthesize a porous metal complex material, called porous coordination polymer (PCP) (or metal-organic framework (MOF)), which is sufficiently robust for storing gases such as carbon dioxide (CO_2) and methane (CH_4). This discovery marked an epoch in material science and technology. Further, he discovered self-assemblies of metal ions, which act as coordination centers, link various organic bridging ligands under mild conditions to yield tailored nanoporous host materials. His major achievements are described below.

(1) Safe storage of the explosive acetylene gas

Because acetylene gas reacts explosively when pressurized to two atmospheres or higher at normal temperature, materials or techniques that can store pure acetylene gas at two atmospheres or more were lacking. Prof. Kitagawa demonstrated that a PCP can easily and safely store acetylene at high density. This finding has significantly impacted researchers not only in academia but also in industries worldwide.

(2) Separation materials for exhaust gas and biogas (e.g., separation of CH_4, CO_2, and CO)

If a useful gas could be separated from an exhaust gas or a by-product gas and stored efficiently, the reduction of CO_2, which is a global challenge, could be resolved. Using conventional porous materials, a gas is separated by utilizing the difference in molecular sizes. Note that the pore size plays an important role because the composition, concentration, pressure, and scale of the components in the air and by-product gases (e.g., exhaust gas) depend on the source. Consequently, it is difficult to selectively recover CO_2. Prof. Kitagawa developed a new concept based on soft, porous PCP materials. He developed a practical PCP that can separate CO_2, O_2, acetylene, and CO with high selectivity and high efficiency without losing pore regularity and stability of the skeleton structure.

(3) Development of proton conductive materials

From the viewpoint of improving the energy efficiency and durability of fuel cells, solid electrolytes operating at a 0% humidity level and a temperature ranging from 100°C to 300°C are some of the most needed materials. Prior to Prof. Kitagawa's report on this subject, an efficient proton conductor did not exist for this environment. Prof. Kitagawa demonstrated that filling the pores of PCP with organic molecules (e.g., imidazole) creates a novel but efficient material for solid electrolytes. Unlike conventional solid polymer proton conductors, his novel material has high proton conductivity and works steadily at mild temperatures without humidification.

Prof. Kitagawa is a visionary who has shown exceptional creativity in the development of innovative chemistry to create a new class of functional materials. The social contribution of Prof. Kitagawa to science and technology is related to easy separation and storage of gases. His efforts have not only enhanced the industrial value of PCP but also opened pathways to store and separate key gas substances that will provide solutions for key issues in the energy, environment, natural chemical resources and health care sectors.

List of Publications

(1) M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka and S. Kitagawa, Three-Dimensional Framework with Channeling Cavities for Small Molecules: $\{[M_2(4,4'\text{-bpy})_3(NO_3)_4]\cdot xH_2O\}_n$ (M = Co, Ni, Zn), *Angew. Chem. Int. Ed. Engl.*, **36**, 1725–1727 (1997).

(2) M. Kondo, T. Okubo, A. Asami, S. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka and K. Seki, Rational Synthesis of Stable Channel-Like Cavities with Methane Gas Adsorption Properties: $[\{Cu_2(pzdc)_2(L)\}_n]$ (pzdc=pyrazine-2, 3-dicarboxylate; L=a Pillar Ligand), *Angew. Chem. Int. Ed. Engl.*, **38**, 140–143 (1999).

(3) S. Noro, S. Kitagawa, M. Kondo and K. Seki, A New Methane Adsorbent, Porous Coordination Polymer $[\{CuSiF_6\ (4,4'\text{-bipyridine})_2\}_n]$, *Angew. Chem. Int. Ed.*, **39**, 2081–2084 (2000).

(4) R. Kitaura, K. Fujimoto, S. Noro, M. Kondo and S. Kitagawa, A Pillared-Layer Coordination Polymer Network Displaying Hysteretic Sorption: $[Cu_2(pzdc)_2(dpyg)]_n$ (pzdc=Pyrazine-2, 3-dicarboxylate; dpyg=1, 2-Di(4-pyridyl)-glycol), *Angew. Chem. Int. Ed.*, **41**, 133–135 (2002).

(5) R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, K. Kindo, Y. Mita, A. Matsuo, M. Kobayashi, H. Chang, T. Ozawa, M. Suzuki, M. Sakata and M. Takata, Formation of a One-Dimensional Array of Oxygen in a Microporous Metal-Organic Solid, *Science*, **298**, 2358–2361 (2002).

(6) R. Kitaura, K. Seki, G. Akiyama and S. Kitagawa, Porous Coordination-Polymer Crystals with Gated Channels Specific for Supercritical Gases, *Angew. Chem. Int. Ed.*, **42**, 428–431 (2003).

(7) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, S. Horike and M. Takata, Guest Shape-Responsive Fitting of Porous Coordination Polymer with Shrinkable Framework, *J. Am. Chem. Soc.*, **126**, 14063–14070 (2004).

(8) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe and Y. Mita, Highly Controlled Acetylene Accommodation in a Metal-Organic Microporous Material, *Nature*, **436**, 238–241 (2005).

(9) T. K. Maji, R. Matsuda and S. Kitagawa, A Flexible Interpenetrating Coordination Framework with a Bimodal Porous Functionality, *Nature Materials*, **6**, 142–148 (2007).

(10) S. Bureekaew, S. Horike, M. Higuchi, M. Mizuno, T. Kawamura, D. Tanaka, N. Yanai and S. Kitagawa, One-Dimensional Imidazole Aggregate in Aluminum Porous Coordination Polymers with High Proton Conductivity, *Nature Materials*, **8**, 831–836 (2009).

(11) S. Shimomura, M. Higuchi, R. Matsuda, K. Yoneda, Y. Hijikata, Y. Kubota, Y. Mita, J. Kim, M. Takata and S. Kitagawa, Selective Sorption of Oxygen and Nitric Oxide by an Electron-Donating Flexible Porous Coordination Polymer, *Nature Chemistry*, **2**, 633–637 (2010).

(12) H. Sato, R. Matsuda, K. Sugimoto, M. Takata and S. Kitagawa, Photoactivation of a Nanoporous Crystal for On-Demand Guest Trapping and Conversion, *Nature Materials*, **9**, 661–666 (2010).
(13) N. Yanai, K. Kitayama, Y. Hijikata, H. Sato, R. Matsuda, Y. Kubota, M. Takata, M. Mizuno, T. Uemura and S. Kitagawa, Gas Detection by Structural Variations of Fluorescent Guest Molecules in a Flexible Porous Coordination Polymer, *Nature Materials*, **10**, 787–793 (2011).
(14) J. Reboul, S. Furukawa, N. Horike, M. Tsotsalas, K. Hirai, H. Uehara, M. Kondo, N. Louvain, O. Sakata and S. Kitagawa, Mesoscopic Architectures of Porous Coordination Polymers Fabricated by Pseudomorphic Replication, *Nature Materials*, **11**, 717–723 (2012).
(15) Y. Sakata, S. Furukawa, M. Kondo, K. Hirai, N. Horike, Y. Takashima, H. Uehara, N. Louvain, M. Meilikhov, T. Tsuruoka, S. Isoda, W. Kosaka, O. Sakata and S. Kitagawa, Shape-Memory Nanopores Induced in Coordination Frameworks by Crystal Downsizing, *Science*, **339**, 193–196 (2013).
(16) D. Umeyama, S. Horike, M. Inukai and S. Kitagawa, Integration of Intrinsic Proton Conduction and Guest-Accessible Nanospace into a Coordination Polymer, *J. Am. Chem. Soc.*, **135**, 11345–11350 (2013).
(17) H. Sato, W. Kosaka, R. Matsuda, A. Hori, Y. Hijikata, R. V. Belosludov, S. Sakaki, M. Takata and S. Kitagawa, Self-Accelerating CO Sorption in a Soft Nanoporous Crystal, *Science*, **343**, 167–170 (2014).

Reviews

(1) S. Kitagawa and M. Kondo, Functional Micropore Chemistry of Crystalline Metal Complex-Assembled Compounds, *Bull. Chem. Soc. Jpn.*, **71**, 1739–1753 (1998).
(2) S. Kitagawa, R. Kitaura and S. Noro, Functional Porous Coordination Polymers, *Angew. Chem. Int. Ed.*, **43**, 2334–2375 (2004).
(3) S. Horike, S. Shimomura and S. Kitagawa, Soft Porous Crystals, *Nature Chemistry*, **1**, 695–704 (2009).
(4) S. Horike, D. Umeyama and S. Kitagawa, Ion Conductivity and Transport by Porous Coordination Polymers and Metal-Organic Frameworks, *Acc. Chem. Res.*, **46**, 2376–2384 (2013).