METAL-ORGANIC FRAMEWORKS
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The field of metal-organic frameworks, or MOFs, is undergoing accelerated and sustained growth. I personally became acquainted with MOFs, or more generally coordination polymers, as an undergraduate research student while at Saint Mary’s University, Halifax, Nova Scotia, Canada, from 1991 to 1994. The process of mixing readily available metal precursors with organic linkers—many of which fell under the heading of being commercially available—to produce a wide array of extended frameworks clearly then, and now, captured the imagination of chemists and materials scientists worldwide.

From a fundamental standpoint, there is an important link between MOF chemistry and the field of inorganic chemistry. In many ways, MOF chemistry enables chemists to connect previously existing coordination complexes so as to make a conceptual link into the field of materials chemistry. This link has now evolved to afford applications ranging from catalysis to energy storage. Organic chemists are also able to contribute to the mix by crafting ligands with properties that one ultimately plans to express within the walls of MOFs. Solid-state chemists and X-ray crystallographers provide insights into the structures of MOFs so that the process of designing and synthesizing MOFs can be refined so as to ultimately control a targeted property and give rise to function.

My personal draw to MOFs was, in retrospect, also inspired by the field of supramolecular chemistry, particularly as it relates to the rational design of solids, or crystal engineering. The early 1990s witnessed supramolecular chemistry envelop the process of self-assembly, with a crystal being regarded as a supermolecule par excellence.¹ Metal–ligand bonding is reversible and, thus, fits within the realm of supramolecular chemistry. Self-assembly involves subunits of a larger superstructure
being repeated in zero-dimensional (0D), 1D, 2D, or 3D space, with the solid state being a perfect resting place for intermolecular forces to dominate. Today, many of the boundaries between these areas have become increasingly more difficult to distinguish, which can be expected as more is being uncovered and as more emphasis is placed on properties and function.

It is, thus, with great pleasure that I am able to assemble a multi-author monograph that includes authoritative contributions from leading research laboratories in the field of MOF chemistry. My goal is to provide insights into where the field of MOFs began to take root and provide an account of the fundamentals that define where the field has come and is able to go. Indeed, MOFs provide chemists a means to think about how to utilize coordination space to mimic the chemistry of zeolites with an added degree of organic function. These possibilities have become apparent in key developments and important advances that are outlined in the chapters that follow.

Fujita (Chapter 1) and Eddaoudi (Chapter 2), for example, document the first reports of MOFs, or coordination networks, particularly those that exhibit catalysis, the emergence of heteroaromatic ligands, and how carboxylates provided an important entry to increasingly robust solids. Batten (Chapter 3) demonstrates a role of symmetry in defining and understanding the simple and complex frameworks that result from the solid-state assembly process that affords a MOF. Next, Schroder (Chapter 4) addresses the design and synthesis of extended frameworks of increasingly structural complexity in the form of highly connected MOFs based on lanthanide ions. Kitagawa (Chapter 5) then shows how the internal structures of coordination networks can be rationally modified and tailored with organic groups while Lin (Chapter 6) documents some of the first systematic applications of MOFs as they relate to the generation of nonlinear optic materials. A great challenge facing mankind is making efficient use of energy. MOFs have emerged as potentially useful platforms for facing this challenge in the form of gas storage, separation, and conversion. Thus, Kim (Chapter 7) and Zhou (Chapter 8) address how MOFs interact with small gas molecules (e.g., H₂) and how these materials may be integrated into schemes for energy utilization. In a related topic, Friscic (Chapter 9) tackles the emerging issue of mechanochemical, or solvent-free, “green” preparation of MOFs while work by our group demonstrates how the walls of extended frameworks can be designed to serve as platforms for light-induced chemical reactions (Chapter 10). Finally, Snurr (Chapter 11) addresses how the field of computational chemistry can be used to understand, and ultimately, aide the design of MOFs, with targeted applications in separations, gas uptake, and materials characterization. Carefully chosen references serve to guide the reader through the extensive literature, which makes the field accessible to a wide and varied audience.

My initial interests in the chemistry of MOFs, and supramolecular chemistry and solid-state chemistry in general, stemmed from an experience as an undergraduate researcher. It is for this reason that I dedicate this monograph to the
undergraduate research experience and to all of those that support undergraduate research.

Leonard R. MacGillivray

Iowa City, IA
March 2010

REFERENCE

1 Dunitz, J. D. Pure Appl. Chem. 1991, 63, 177.
CONTRIBUTORS

Stuart R. Batten, School of Chemistry, Clayton Campus, Bldg. 19, Monash University, 3800 Australia

Neil R. Champness, School of Chemistry, The University of Nottingham, University Park, Nottingham, NG7 2RD, UK

Hyungphil Chun, Department of Applied Chemistry, College of Science and Technology, Hanyang University, 1271 Sadong, Ansan 426-791, Republic of Korea

David J. Collins, Department of Chemistry and Biochemistry, Miami University, Oxford, OH 45056, USA; Department of Chemistry, Texas A&M University, College Station, TX 77843, USA

David Dubbeldam, Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road E136, Evanston, IL 60208, USA

Saikat Dutta, Department of Chemistry, University of Iowa, Iowa City, IA 52242, USA

Mohamed Eddaoudi, Department of Chemistry, University of South Florida, 4202 East Fowler Avenue, CHE204, Tampa, FL 33620, USA

Jarrod F. Eubank, Department of Chemistry, University of South Florida, 4202 East Fowler Avenue, CHE204, Tampa, FL 33620, USA

Tomislav Friščič, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

Houston Frost, Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road E136, Evanston, IL 60208, USA
CONTRIBUTORS

Makoto Fujita, Department of Applied Chemistry, School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-8656, Japan

Ivan G. Georgiev, Department of Chemistry, University of Iowa, Iowa City, IA 52242, USA

Sujit K. Ghosh, Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan; Department of Chemistry, Indian Institute of Science Education and Research (IISER), Pune, India

Peter Hubberstey, School of Chemistry, The University of Nottingham, University Park, Nottingham, NG7 2RD, UK

Hyunuk Kim, National Creative Research Initiative Center for Smart Supramolecules, Department of Chemistry and Division of Advanced Materials Science, Pohang University of Science and Technology, Pohang, 790-784, Republic of Korea

Kimoong Kim, National Creative Research Initiative Center for Smart Supramolecules, Department of Chemistry and Division of Advanced Materials Science, Pohang University of Science and Technology, Pohang, 790-784, Republic of Korea

Susumu Kitagawa, Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615–851 Japan; Kitagawa Integrated Pore Project, Exploratory Research for Advanced Technology (ERATO), Japan Science and Technology Agency (JST), Shimogyo-ku, Kyoto 600-8815, Japan; Institute for Cell Materials Sciences (iCeMS), Kyoto University, Sokyoku-ku, Kyoto, Japan

Wenbin Lin, Department of Chemistry, CB3290, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, USA

Xiang Lin, School of Chemistry, The University of Nottingham, University Park, Nottingham, NG7 2RD, UK

Shengqian Ma, Department of Chemistry and Biochemistry, Miami University, Oxford, OH 45056, USA; Department of Chemistry, Texas A&M University, College Station, TX 77843, USA

Leonard R. MacGillivray, Department of Chemistry, University of Iowa, Iowa City, IA 52242, USA

Martin Schröder, School of Chemistry, The University of Nottingham, University Park, Nottingham, NG7 2RD, UK

Randall Q. Snurr, Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road E136, Evanston, IL 60208, USA

A. Özgür Yazaydin, Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road E136, Evanston, IL 60208, USA

Shuting Wu, Department of Chemistry, CB3290, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, USA

Hong-Cai Zhou, Department of Chemistry and Biochemistry, Miami University, Oxford, OH 45056, USA; Department of Chemistry, Texas A&M University, College Station, TX 77843, USA
FROM HOFMANN COMPLEXES TO ORGANIC COORDINATION NETWORKS

MAKOTO FUJITA
Department of Applied Chemistry, School of Engineering, University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

1.1 INTRODUCTION

Recently, there has been a considerable upsurge in the study of porous hybrid organic–inorganic materials referred as organic coordination networks. Porous organic coordination networks can be prepared via self-assembly of a connector (a metal) and a link (a ligand) where connectors and ligands are bound together through a metal–ligand bond to form porous crystalline structures. It is in the pores that a wide range of processes can be carried out. One salient feature of coordination networks is the possibility to design the pores. Now it is possible to create pores with determined sizes just by selecting ligands with determined shapes, and particular environments through functionalization of the ligands. Therefore, certain reactions that are not possible to be carried out in solution are now being carried out within the porous space.

Another feature of organic coordination networks is their flexibility, which differentiates them from the robust frameworks of zeolites. This flexibility enables a dynamic behavior in porous coordination networks, which facilitate structural modifications (guest exchange or chemical reactions within the pores) without loss of its structural integrity. Hence, chemical reactions that occur in the pore can be monitored in situ in great detail by X-ray crystallography and other spectroscopic techniques.