

Introduction to Metal–Organic Frameworks

Metal–organic frameworks, or MOFs, have emerged as an extensive class of crystalline materials with ultrahigh porosity (up to 90% free volume) and enormous internal surface areas, extending beyond 6 000 m²/g. These properties, together with the extraordinary degree of variability for both the organic and inorganic components of their structures, make MOFs of interest for potential applications in clean energy, most significantly as storage media for gases such as hydrogen and methane, and as high-capacity adsorbents to meet various separation needs. Additional applications in membranes, thin-film devices, catalysis, and biomedical imaging are increasingly gaining importance. On a fundamental level, MOFs epitomize the beauty of chemical structures and the power of combining organic and inorganic chemistry, two disciplines often regarded as disparate. Since the 1990s, this area of chemistry has experienced an almost unparalleled growth, as evidenced by not only the sheer number of research papers published but also the ever-expanding scope of the research. Although the number of review articles and monographs has also escalated in the last five years, we believe this thematic issue of *Chemical Reviews*, comprising the most up-to-date contributions from leading MOF researchers all over the world, is necessary to mark the progress made thus far in a comprehensive manner. The scope of the volume ranges from topology analysis and molecular simulations to synthesis, from adsorptive and optical to ferroelectric properties, and from gas storage, separations, and catalysis to applications in biomedicine. As such, we hope that it will serve as a valuable resource for new and current researchers in the field alike.

One of the hallmarks of MOFs is their topologically diverse and aesthetically pleasing structures, many of which are derived from minerals in nature. Designing a target structure with specific properties and functions represents an eternal aspiration for materials scientists. To reverse-engineer the beautiful structures from nature, the first step is to understand the underlying geometric principles. O’Keeffe and Yaghi demonstrate such an approach by deconstructing crystal structures of MOFs into their underlying topological nets, thereby laying a foundation for the subsequent description and design of other MOF structures.

MOFs are known for their extraordinarily high surface areas, tunable pore size, and adjustable internal surface properties. The next five articles focus on applications in gas storage and separations stemming from the characteristic adsorptive properties of MOFs. First, Snurr and co-workers summarize recent computational studies on the adsorption of methane, hydrogen, and acetylene within these materials. In addition, state-of-the-art techniques and challenges in molecular simulations are discussed. One of the hottest topics in MOF research in recent years has been carbon dioxide capture, which is directly related to clean energy and environmental protection. In this regard, Long and co-workers analyze the considerations associated with using MOFs to reduce emissions of carbon dioxide from coal-fired power plants via post-combustion capture, precombustion capture, or oxy-fuel

combustion routes. One of the key technologies in the utilization of hydrogen as an energy carrier is storage, which has been extensively explored over the past decade. In the next article, Suh and co-workers review and classify representative MOFs developed for hydrogen storage and discuss the difficulties and prospects of using MOFs for this application. The following treatise, by Li and co-workers, discusses the adsorption of hydrocarbons in MOFs, with an emphasis on “commensurate” adsorption, which refers to the adsorption and packing of guest molecules in a porous host with ideal matching in size and orientation. Finally, Li, Sculley, and Zhou survey selective adsorption and separations for an extensive list of gases and liquids using MOFs, while further highlighting several approaches developed to evaluate the performance of MOFs in separation-related applications.

Synthetic-method development has been playing a major role in the advancement of this field. Accordingly, the next five articles deal with the all-important issue of MOF synthesis. The first, by Stock and Biswas, provides an account of various synthetic methods, including microwave, electrochemical, mechanochemical, ultrasonic, and high-throughput syntheses. Cohen then details the latest progress in postsynthetic modification (PSM), an alternative way of introducing functional groups within MOFs, covering covalent and dative modifications, as well as postsynthetic deprotection. Although the majority of MOFs are based on carboxylate linkers, the next two articles in this section focus specifically on azolate- and phosphonate-based frameworks. The first, by Chen and co-workers, provides an overview of metal–azolate frameworks, including MOFs constructed from imidazolate, pyrazolate, 1,2,4-triazolate, 1,2,3-triazolate, and tetrazolate. In the article by Clearfield and co-workers, phosphonate takes the center stage. Bétard and Fischer then review the growing literature on the fabrication, characterization, and potential application of MOF films, which show promise for applications in catalysis, membrane separations, and sensing.

The combination of the two components of a MOF, the metal ion or cluster and the organic linker, provides endless possibilities. The sum of the physical properties of the inorganic and organic components and the possible synergistic play between the two provide intriguing properties for a MOF. In the next five articles, optical and ferroelectric properties become the main focus. First, Lin and co-workers discuss the design principles and examples of MOFs displaying second-harmonic generation for use in nonlinear optics. Allendorf, Hupp, and co-workers then provide a comprehensive review of MOFs that function as chemical sensors. In this article, solvatochromism/vapochromism, luminescence-based sensing, interferometry, localized surface plasmon resonance, colloidal crystals, impedance spectroscopy, and electromechanical sensors are highlighted. In the next article, Qian, B. Chen, and co-workers present an inclusive overview of luminescent MOFs, with

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emphasis on their unique characteristics, analyzing the origin of MOF luminescence, and exploring their potential applications. In the last article of this section, Zhang and Xiong provide highlights on ferroelectric MOFs, considered a new class for this type of material, with inherent advantages in synthesis and structure and filling a gap between pure inorganic and organic ferroelectrics.

The final two contributions represent some of the newest developments in the MOF field. In the first, Kim and co-workers give an overview of MOF-based asymmetric heterogeneous catalysis, highlighting the state-of-the-art in MOF catalysis and analyzing its potential and limitations. Finally, Horcajada, Serre, and co-workers give an account of the advantages of using MOFs for the adsorption and release of drugs. Here, the biodegradable character of the material can be modified through the proper choice of the metal, organic linker, and structure.

Finally, readers will find that, among these developments, the following is fundamentally important: the ability to control the connectivity of vertices in a MOF structure, as well as the metrics and functionality of a given structure without altering its underlying connectivity. This allows for the control one needs to achieve many of the structures and properties discussed. Indeed, this volume showcases a wide array of topics that highlight the importance and diversity of MOF chemistry, as well as its impact on other fields. We hope that readers will find it beneficial to their future research and teaching endeavors. Toward this end, we greatly appreciate the outstanding contribution of all authors, as well as the strenuous efforts from the editorial staff members, especially Dr. Guy Bertrand of *Chemical Reviews*.

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Biographies



Hong-Cai "Joe" Zhou was born in Hubei, China, in 1964. He obtained his B.S. in 1984 and M.S. in 1989 from Beijing Normal University. He attended Texas A & M University in 1996, studying metal–metal bonds under the guidance of F. A. Cotton and obtained his Ph.D. in 2000. After a postdoctoral stint working on iron–sulfur clusters under

R. H. Holm at Harvard University, he joined the faculty of Miami University, Oxford, in 2002. He moved back to Texas A & M University and has been Professor of Chemistry since 2008. His research group specializes in the synthesis and characterization of metal–organic frameworks and porous polymer networks for gas storage, separation, and other potential applications.



Jeffrey R. Long was born in Rolla, Missouri, USA, in 1969. He received his B.S. in Chemistry from Cornell University in 1991 and his Ph.D. in Chemistry at Harvard University in 1995. Following postdoctoral work at Harvard and the University of California, Berkeley, he joined the faculty at Berkeley in 1997, where he is currently Professor of Chemistry. He is also a Faculty Senior Scientist in the Materials Sciences Division of Lawrence Berkeley National Laboratory. His research involves the synthesis of new inorganic clusters and solids, with emphasis on magnetic and microporous materials.



Omar M. Yaghi was born in Amman, Jordan, in 1965. He received his Ph.D. from the University of Illinois—Urbana (1990) with Professor Walter G. Klemperer. He was an NSF Postdoctoral Fellow at Harvard University (1990–1992) with Professor Richard H. Holm. He has been on the faculties of Arizona State University (1992–1998) and University of Michigan (1999–2006). His current position is the Professor of Chemistry at the University of California, Berkeley, and the Director for the Molecular Foundry at the Lawrence Berkeley National Laboratory. His work encompasses the synthesis, structure, and properties of inorganic compounds and the design and construction of new crystalline porous materials, most notably metal–organic frameworks and covalent organic frameworks. He has also pioneered a global mentoring model for building centers of excellence for scientific collaborations between the United States and other countries.