An international and interdisciplinary team of leading experts from both academia and industry report on the wide range of hot applications for MOFs, discussing both the advantages and limits of the material. The resulting overview covers everything from catalysis, H₂ and CH₄ storage and gas purification to drug delivery and sensors.

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- Design of Porous Coordination Polymers/Metal-Organic Frameworks: Past, Present and Future
- Design of Functional Metal-Organic Frameworks by Post-Synthetic Modification
- Thermodynamic Methods for Prediction of Gas Separation in Flexible Frameworks
- Separation and Purification of Gases by MOFs
- Opportunities for MOFs in CO₂ Capture from Flue Gases, Natural Gas and Syngas by Adsorption
- Manufacture of MOF Thin Films on Structured Supports for Separation and Catalysis
- Research Status of Metal-Organic Frameworks for On-board Cryo-Adsorptive Hydrogen Storage Applications
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A must-have for every scientist in the field.

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Metal-Organic Frameworks

Applications from Catalysis to Gas Storage

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Preface

Are porous metal–organic frameworks (MOFs) breakthrough materials, or are they simply an illusion reminiscent of “The Emperor’s New Clothes?”

Over the past three decades, the domain of porous solids has been expanded by the discovery of various “cornerstone” materials, such as ALPO molecular sieves (1982), carbon nanotubes (1991), ordered silica mesoporous materials (1992), and CMK (1999), to name just a few. Porous MOFs were first described in Volume 4 of the *Handbook of Porous Solids*, published by Wiley-VCH in 2002. Since that time, this class of materials has become much better known and much more widely studied. The number of publications dealing with MOFs and porous coordination polymers is currently increasing at an exponential rate – with the total doubling every 2 years. In 2009, we could count about 1200 new publications, a rate similar to that observed for ordered mesoporous materials.

Thanks to their hybrid formulation, MOFs bridge the gap between pure inorganic and organic materials, thereby pushing the frontiers of knowledge ever further forward. Initially, MOFs were regarded only as a new type of molecular sieve material with a pore size between those of inorganic zeolites (<1 nm) and ordered mesoporous silica materials (>2 nm). On the other hand, their stimuli-induced flexibility, or more generally their softness, is a common trait with organic enzymes. It is acknowledged that MOFs could mimic enzymes using the concept of molecular recognition, allowing high chemo-, regio-, and enantioselectivity – the ultimate goal in catalysis. With respect to mechanical properties such as hardness and elasticity, the domain corresponding to MOFs can, to some extent, be considered to straddle the borders between purely organic polymers, purely inorganic ceramics, and metallic materials. Some MOFs possess unique features, such as luminescence, that already allow them to surpass benchmark materials.

The ever-increasing demand to develop more complex and integrated processes drives the research and development of advanced “smart” materials, with specific engineering at the molecular level but also at higher scales from the micron to the millimeter. Clearly, MOFs are promising new candidates for addressing current challenges in a number of domains of application. A few MOF solids have recently become commercially available under the trade name Basolite™ – this should
greatly accelerate the development of MOF-based processes. Currently, the emphasis of research and development is shifting towards converting the unique properties of MOFs into efficient processes.

This brings us to the purpose of this book – to perform a critical assessment of the properties of MOFs, taking into account the process specifications and performance targets required to allow these solids to be introduced on to the market. It seems that MOF performances are rarely discussed with respect to those of state-of-the-art materials or commercial targets. Furthermore, their shaping and further processing in physical and chemical processes have rarely been reported so far. The ambitious goal here is to measure the gap that exists between the state of the art of MOF and commercial applications in the domains of energy, chemistry, physics, and medicine.

This deliberately application-oriented book is divided into six parts. Each chapter refers to the original literature and can be read independently of the other chapters.

The first part of this book emphasizes the uniqueness of MOFs compared with other porous solids in terms of intrinsic material properties and engineering capabilities. In particular, MOFs are characterized by their softness and by their associated host–guest dynamic properties that make them “smart” materials. The first chapter establishes the mechanisms and provides an outlook on how to proceed in designing multifunctional MOFs, using techniques for addition or modification of physical or chemical features within the frameworks. The second chapter gives a critical review of post-modification methods with emphasis on catalytic applications.

The second part deals with gas storage and separation. The different types of flexibility and the thermodynamic description of breathing are given in Chapter 3, and the associated solids and applications are detailed in Chapter 4. Carbon dioxide capture is treated in detail for PSA/TSA processes in Chapter 5 and for membrane processes in Chapter 6. The topic of hydrogen storage is discussed in Chapter 7.

The third part deals with bulk chemistry. Chapter 8 deals with the separation of xylenes, and Chapter 9 provides a review of MOF applications in catalysis, with particular focus placed on structure–activity relationships.

The fourth part encompasses an overview of medical applications of MOFs (Chapter 10) and imaging (Chapter 11).

In the fifth part, the use of MOFs in the design of small-scale devices and sensors is discussed. Luminescence properties and possible applications are described in Chapter 12. Thin-film preparations for sensor applications are detailed in Chapter 13.

The sixth part discusses the mass production of MOFs, with attention devoted to economic criteria (Chapter 14), and also the shaping of MOFs as large bodies and their immobilization as composite materials with polymer fibers (Chapter 15).

I hope that the information in this book will be of interest both to researchers involved in the development of chemical and physical processes and to scientists focusing on porous solids. I also hope that it will help establish a common ground
between different communities by providing a multidisciplinary point of view, including solid-state chemistry, materials science, and process engineering.

The European Community is acknowledged for supporting R&D in this field through the Integrated Projects NanoMOF and Macademia (FP7-NMP).

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Part One
Design of Multifunctional Porous MOFs
1
Design of Porous Coordination Polymers/Metal–Organic Frameworks: Past, Present and Future
Satoshi Horike and Susumu Kitagawa

1.1
Introduction

At the end of the 1990s, a new porous compound with an inorganic–organic hybrid framework had an impact on the field of porous materials and represented a new family for porous chemistry. Porous coordination polymers (PCPs), also known as metal–organic frameworks (MOFs), have regular pores ranging from micro- to mesopores, resulting in a large pore surface area, and a highly designable framework, pore shape, pore size, and surface functionality. Their structures are based on organic ligands as linkers and metal centers as the connectors. The rich functionality and designability of the organic ligands and the directability and physical properties of the metal ions are fascinating for the design of various functions, not only conventional adsorptive functions such as storage, separation, and catalysis, but also other physical/chemical functions that can be integrated in the frameworks. Whereas the components of PCPs are connected by coordination bonds and other weak interactions or noncovalent bonds (H-bonds, π-electron stacking, or van der Waals interactions), the interactions lead to structural flexibility and dynamics in the crystalline state, which also promotes the unique character of PCPs in the field of porous materials. As synthetic techniques and knowledge have increased in the last decade, we are now ready to design advanced porous functions by making full use of the chemical components and structural topologies. In this chapter, we introduce the background of PCPs/MOFs with some of the main framework designs and describe the unconventional porous properties of multifunctional porous materials based on ligand–metal networks.

1.2
Background and Ongoing Chemistry of Porous Coordination Polymers

Coordination polymers (CPs) are a family of compounds with extended structures formed by metal ions and organic and/or inorganic ligands with coordination bonds.
They can provide various frameworks constructed from one-, two-, and three-dimensional networks. The late transition metal elements (Cu, Ag, Zn, and Cd) tend to provide this type of framework and the chemistry of CPs has been elucidated with the development of single-crystal X-ray crystallography. The term “coordination polymer” was used in a paper in 1916 [1], but there was no means of demonstrating infinite frameworks without single-crystal X-ray crystallography. A three-dimensional coordination framework connected by a CN bridge was realized in 1936 [2], namely the well-known Prussian Blue compounds. Currently, coordination polymers having porous properties are termed PCPs or porous MOFs, and therefore we suggest “coordination framework” as an all-inclusive term because the chemistry of the background is defined as “chemistry of coordination space.” To understand the background of this chemistry, there are three important concepts: (1) framework, (2) molecular metal–organic hybrid, and (3) porosity.

1) Concept of Framework

It is well known that CPs provide us with one-, two-, and three-dimensional motifs. In particular, the structural concept of a framework was demonstrated by Hofmann and Küspert [3], whose compounds are known as the family of Hofmann compounds having a two-dimensional layer-based architecture. The first X-ray crystallographic structure was obtained in 1949 [4]. The complete three-dimensional framework, the so-called Prussian Blue complex, appeared in 1936 and a comprehensive study was performed by Iwamoto et al. in 1967 [2, 5].

2) Molecular Metal–Organic Hybrid

Hofmann and Prussian Blue compounds have structures bridged by the inorganic ion CN⁻, and therefore have a restricted variety of structures. On the other hand, frameworks having organic linkers afford not only designability but also functionality of frameworks. The X-ray crystal structure of the metal–organic coordination framework of [Cu(adiponitrile)₂]⁻⋅NO₃ appeared in 1959 [6]. Since then, many compounds in this category have been synthesized and characterized crystallographically. Yaghi et al. termed these compounds “metal–organic frameworks (MOFs)” in 1995 [7]. [Cu(adiponitrile)₂]⁻⋅NO₃ contains the NO₃⁻ anion in the voids. Such compounds are regarded as clathrate-type CPs, however, which are not categorized as “porous” compounds. By the late 1990s, many clathrate-type CPs/MOFs had been synthesized.

3) Porosity

Porosity means “the quality or state of being a porous entity, which has many small holes that allow water, air, and so on, to pass through.” The porosity is antithesis to Aristotle’s proposition, “Nature abhors a vacuum.” Indeed, closely packed solid structures formed by molecules and ions can easily form. Researchers have often misunderstood that the crystallographic structure of MOFs having guest species in their voids is a porous material. In 1997, “porosity” was demonstrated to give a compound that maintains a porous structure without guests in the pores; gas sorption experiments under ambient conditions were carried out for stable apohosts [8, 9]. Reversible gas storage properties were identified and the PCPs have attracted wide attention as new porous materials.
Since that point, the number of reports on PCPs has been increasing rapidly, and many researchers have been developing strategies for the design of porosity, some of which are intrinsically unique to PCP materials.

1.2 Background and Ongoing Chemistry of Porous Coordination Polymers

1.2.1 Frameworks with High Surface Area

One of the great advantages of PCPs/MOFs is their high surface area, attributable to the low density of the porous structure. An MOF composed of Zn₄O clusters connected by benzenedicarboxylate (bdc), [Zn₄O(bdc)₃] (MOF-5), was synthesized in 1999 and possesses a cubic structure with an ordered three-dimensional (3D) porous system (Figure 1.1a) [10]. This compound has a BET surface area of 3800 m² g⁻¹ [11]. Many porous compounds have been synthesized on the basis of this structural motif, and this approach has been intensively developed to design important porous frameworks. Some related frameworks, [Zn₄O(btb)₂] (MOF-177) and [Zn₄O(bbc)₂] (MOF-200) {btb = 1,3,5-benzenetribenzoate; bbc = 4,4',4''-[benzene-1,3,5-triylis(benzene-4,1-diyl)]tribenzoate} also possess high porosity; the reported BET surface areas for these compounds are 4746 and 6260 m² g⁻¹, respectively [12, 13]. The self-assembly process of structure growth often faces network interpenetration, which precludes a high surface area, but further

![Figure 1.1](image_url)  
**Figure 1.1** Partial crystal structures of (a) [Zn₄O(bdc)₃] (MOF-5, BET surface area = 3800 m² g⁻¹) and (b) Zn₄O(t₂dc)(btb)₄/₃ (UMCM-2, t₂dc = thieno-3,2-bithiophene-2,5-dicarboxylate, BET surface area = 5200 m² g⁻¹) constructed from Zn₄O clusters.
improvements in the design of pore network topologies could avoid interpenetration to achieve extremely high surface areas.

Porous frameworks constructed from two or more kinds of ligands are in some cases effective in the design of high surface area compounds. Zn₄O(t₂dc)(bbl)₄/₃ (UMCM-2) (t₂dc = thieno-3,2-bithiophene-2,5-dicarboxylate) (Figure 1.1b) is also made up of Zn₄O clusters and two distinct ligands contribute to the construction of the porous framework [14]. There is a narrow distribution of micropores at 1.4–1.6 and 1.6–1.8 nm and a mesopore at 2.4–3.0 nm and the calculated BET surface reaches 5200 m² g⁻¹.

Another framework, [Cr₃F(H₂O)O(bdc)₃] (MIL-101), is made from the linkage of terephthalate and chromium trimer units that consist of three Cr cations and the μ₃O oxygen anion [15]. The pore space is constructed from two cages with diameters of 2.9 and 3.4 nm which are connected with windows with diameters of 1.2 and 1.45 nm, respectively. The compound has a BET surface area of 4100 m² g⁻¹ and, compared with the Zn₄O-type metal cluster, the framework is more stable against water and other chemical species and it has also been utilized as a porous matrix for post-synthesis or hybridization with other species such as metal particles [16].

A paddle-wheel-type dimetal cluster is a popular building unit to construct frameworks. Many transition metals can form this type of cluster and it affords square grid extended networks. [Cu(H₂O)]₃(n-tei) (PCN-66) is prepared by the combination of 4,4',4''-nitrilotris(benzene-4,1-diyl)tris(ethyne-2,1-diyl)tissuexphthalate (n-tei) and a Cu²⁺ paddle-wheel cluster and the BET surface area is 4000 m² g⁻¹ [17]. Isostructures have been made using other hexatopic carboxylate ligands and it is anticipated that even higher surface areas can be designed.

So far, these compounds represent carbon-containing materials with one of the highest surface areas and the feature of complete crystallinity is a significant platform for a high capacity of gas uptake and it also acts as accumulation areas for other materials such as metal particles, functional molecules and polymers, and gases with high density.

1.2.2 Lewis Acidic Frameworks

The design of porous frameworks having guest interaction sites has also been intensively investigated. Especially unsaturated metal sites on the pore interior, which act as Lewis acid sites, have been synthesized because of interest in the storage of gases such as H₂ and CO₂ and for heterogeneous catalysis.

[Cu₃(btc)₂] (HKUST-1), based on Cu₂ paddle-wheel units linked by benzenetri-carboxylic acid (btc) is one of the early PCPs with unsaturated metal sites [18]. This compound possesses a 3D channel with a pore size of 1 nm and has high thermal stability and aqueous durability. The axial sites of Cu²⁺ are accessible to guests and gas capture and heterogeneous catalysis have been reported [19, 20]. This motif is available for other metal ions such as W, Fe, and Cr, and [Cr₃(btc)₂] shows O₂ adsorption at 298 K with a Type I isotherm with which adsorption occurs at very low