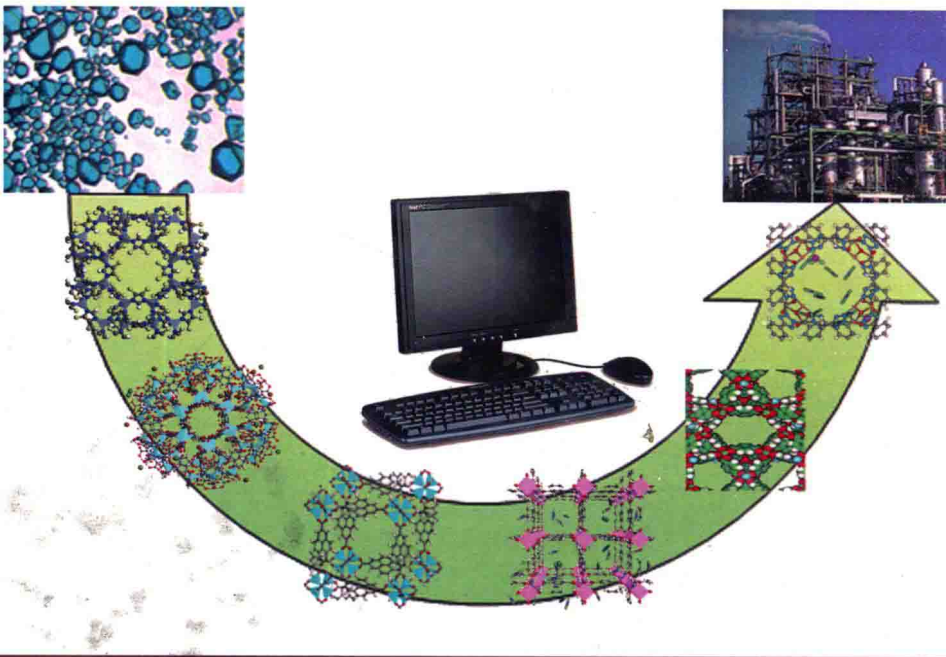
Metal–Organic Frameworks

Materials Modeling towards Potential Engineering Applications

edited by
Jianwen Jiang



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Foreword

Thanks to the diligent work of Omar Yaghi and other creative synthetic chemists, it is now possible to synthesize a variety of metal–organic frameworks (MOFs) that show much promise for gas storage (e.g., methane and hydrogen) and for gas separations, especially those that separate climate-warming carbon dioxide from nitrogen as desired for stack gases from power plants prior to release to the atmosphere.

The possible number of different MOFs is very large. In a finite time, it is not feasible to synthesize even a small fraction of these possible structures. To guide experimentalists toward those structures that are likely to be most useful, theoretical or computational methods are needed. Fortunately, such methods have been under active development for some time. It is therefore now appropriate to assemble a set of articles that describe these methods to indicate their present and future utility.

The worldwide community of chemists and chemical engineers is grateful to the authors of these assembled articles and especially to Jianwen Jiang for his diligent service as editor of this timely volume.

John Prausnitz
University of California, Berkeley, USA

Preface

Metal–organic frameworks (MOFs), also called porous coordination polymers or porous coordination networks, have emerged as a special class of nanoporous materials. Constituted by the enormous choices of metal clusters and organic linkers, MOFs possess a wide range of surface area, pore volume, and functionality; thus they have been considered versatile materials for storage, separation, catalysis, etc. Over the past decade, thousands of MOFs have been synthesized, characterized and tested. The number of MOFs is constantly growing and in principle unlimited. It is, therefore, practically infeasible to experimentally test and select appropriate MOFs from infinite candidates for applications.

With rapidly evolving computational resources, atomistic/molecular modeling has become an indispensable tool in materials science and engineering. Sophisticated modeling at a microscopic level provides wealthy insights that are otherwise experimentally inaccessible and elucidates underlying physics from the bottom up. Furthermore, modeling can secure the fundamental interpretation of experimental observations and guide the rational selection and design of materials.

This book compiles a broad collection of recent modeling studies in the field of MOFs toward potential engineering applications. It contains 13 chapters and is categorized into 5 different topics:

- In Chapter 1, Caroline Mellot-Draznieks, Ben Slater, and Raimondas Galvelis give an overview of computational approaches for the crystal structure prediction of MOFs. They highlight the simulation-informed principles to design and characterize new MOFs and more systematically understand structure–property relationships.

- Adsorption phenomenon and associated properties of MOFs are summarized in Chapters 2–4. While David Dubbeldam and Krista S. Walton discuss the classical molecular simulations, Michael Fischer and Michael Fröba, as well as Lukáš Grajciar, Miroslav Rubeš, Ota Bludský, and Petr Nachtigall, review theoretical approaches, particularly density functional theory, to describe adsorption on coordinatively unsaturated metal sites in MOFs.
- Chapters 5 and 6 are devoted to both adsorption and diffusion in MOFs. George K. Papadopoulos presents statistical mechanics–based modeling for sorbate equilibria and transport in MOFs. On the other hand, Giovanni Garberoglio highlights the importance of quantum effects to accurately describe hydrogen behavior in MOFs.
- Numerous modeling studies of MOFs are focused on separation, as summarized in a series of chapters. In Chapter 7, Qingyuan Yang, Dahuan Liu, and Chongli Zhong review both adsorption- and membrane-based separation processes for CO_2-related systems, olefin/paraffin mixtures, and other gas mixtures. Seda Keskin discusses, in Chapter 8, adsorption-based separation for typical CO_2-containing gas mixtures in MOFs and membrane-based CO_2 separation in MOFs and mixed-matrix membranes. In Chapter 9, Carlos Nieto-Draghi and Javier Pérez-Pellitero survey the modeling of gas separation in zeolitic imidazolate frameworks. Alternatively, Alexandre F. P. Ferreira, Ana M. Ribeiro, João C. Santos, Marta C. Campo, and Alírio E. Rodrigues demonstrate the modeling of cyclic adsorptive separation in Chapter 10, with emphasis on pilot-scale modeling and process simulation. In Chapter 11, Anjaiah Nalaparaju and Jianwen Jiang review the simulation studies of ionic MOFs for gas adsorption and separation, water treatment, biofuel purification, and drug loading.
- Modeling studies of catalysis in MOF-based compounds are documented in Chapters 12 and 13. Qiuju Zhang and Liang Chen, as well as Remedios Cortese and Dario Duca, discuss the catalytic properties of MOFs and several typical chemical reactions catalyzed by MOFs.

From this book, one can clearly witness the increasingly important role of computational modeling in the characterization, screening, and design of MOFs for potential engineering applications. Microscopic insights from the bottom up are imperative to quantitatively unravel fundamental mechanisms, cohesively complement experiments, and effectively facilitate new development in this burgeoning field.

I wish to express my gratitude to the outstanding authors for their invaluable contribution to this book and the editorial team of Pan Stanford Publishing for its technical support.

Jianwen Jiang
Singapore

Contents

Chapter 1

Computational Approaches to the Design, Crystal Structure Prediction, and Structure–Property Relationships of Metal–Organic Frameworks

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1.1 Introduction

The purpose of this chapter is to give an overview of some recent developments in the area of computational crystal structure prediction (CSP) of metal–organic frameworks (MOFs) or hybrid inorganic-organic framework materials over recent years and further highlight its use in the discovery and synthesis of new

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MOFs and a more systematic understanding of structure–property relationships. This is indeed a distinct subfield from the much larger field of MOF computational chemistry, whereby CSP aims to genuinely predict (existing or hypothetical) crystal structures at the atomic level without recourse to any experimental crystal structure data, that is, ab initio. While CSP has a longstanding history in the field of molecular solids such as pharmaceuticals [1] and more recently molecular cage materiáls [2], a number of recent reviews have highlighted how the field of CSP of periodic solid MOFs is still relatively young and presents significant challenges to methodologies. Nevertheless it has evolved dramatically over the last decade with major methodological developments in the area of inorganic solids and, later, in the area of MOFs [3, 4].

We will not cover the following specific topics, which were recently reviewed: force field development [5], simulation of guest-responsive flexible MOFs [6], and simulation of the adsorption properties of MOFs [7, 8] except when it involves the exploration of computationally generated hypothetical MOFs, and instead aim to give a general overview of the modeling of MOFs.

We will formally divide the predictive computational approaches of MOFs into six categories. Section 1.2 gives an overview of the various strategies developed so far for the genuine prediction of the crystal structure of MOFs, including large-scale computational methods. Section 1.3 discusses structure determination of MOFs, highlighting how computational approaches may be used in a predictive fashion when new MOFs are synthesized where their structures cannot be determined through the conventional structure solution methods from powder diffraction data. In Section 1.4 the computational modification of MOFs, typically through virtual ligand functionalization of MOFs or topologies, is addressed. Such approaches appeared only recently and have been adopted with the aim to develop more systematic functional and topological screening for MOFs for targeted adsorption properties. Quantitative structure–property relationship (QSPR) methods, beginning to emerge from the literature using a database of hypothetical MOFs or virtually modified ones, will also be presented. Section 1.5 presents one of most speculative and heuristic use of CPS in the computational design and evaluation of new families of MOFs and