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Review

Computational characterization and prediction of metal–organic framework properties

François-Xavier Coudert*,[1], Alain H. Fuchs

PSL Research University, Chimie ParisTech – CNRS, Institut de Recherche de Chimie Paris, 75005 Paris, France

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ABSTRACT

In this introductory review, we give an overview of the computational chemistry methods commonly used in the field of metal–organic frameworks (MOFs), to describe or predict the structures themselves and characterize their various properties, either at the quantum chemical level or through classical molecular simulation. We discuss the methods for the prediction of crystal structures, geometrical properties and large-scale screening of hypothetical MOFs, as well as their thermal and mechanical properties. A separate section deals with the simulation of adsorption of fluids and fluid mixtures in MOFs.

* Corresponding author. Tel.: +33 144276599.
E-mail address: fx.coudert@chimie-paristech.fr (F.-X. Coudert).
URL: http://coudert.name/ (F.-X. Coudert).
[1] @fxcoudert

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AASBU	automated assembly of secondary building units
ANN	artificial neural network
AUA	anistropic united atom
BET	Brunauer–Emmett–Teller
CC	coupled cluster
CHelpG	charges from electrostatic potentials using a grid-based method
CSD	Cambridge structural database
COF	covalent organic framework
CoRE MOF	computation-ready experimental MOF
DFT	density functional theory
GCMC	grand canonical Monte Carlo
HMC	hybrid Monte Carlo
HPC	high-performance computing
IAST	ideal adsorbed solution theory
IRMOF	iso-reticular metal–organic framework
MC	Monte Carlo
MD	molecular dynamics
MMSV	Morse–Morse–spline–van der Waals
MOF	metal–organic framework
NLC	negative linear compressibility
NTE	negative thermal expansion
OFAST	osmotic framework adsorption solution theory
PSD	pore size distribution
QSPR	quantitative structure–property relationship
RAST	real adsorbed solution theory
RCSR	reticular chemistry structure resource
RESP	restrained electrostatic potential
SBU	secondary building unit
SPC	soft porous crystal
TDDFT	time-dependent density functional theory
UA	united atom
UFF	universal force field
VST	vacancy solution theory
ZAG	zinc alkyl gate
ZIF	zeolitic imidazolate framework
ZMOF	zeolite-like metal–organic framework

1. Introduction

Since its emergence in the 1950s, molecular simulation has seen an ever-growing use in research in the fields of physical, chemical, and materials sciences, where it offers an additional dimension to the characterization and understanding of systems, complementary to experimental techniques and pen-and-paper theoretical models. The development of novel computational methodologies, together with the exponential increase in computational power available to researchers, have dramatically expanded the range of problems that can be addressed through modeling. This is true of resource-intensive calculations performed on high-performance computing (HPC) supercomputers, but it is also true of desktop workstations, and even now of laptops and mobile devices [15,16]. Several of the simulation techniques of computational chemistry have now reached the status of being relatively "routine" calculations and are nowadays considered an integral part of the researcher's toolbox, just like experimental characterization techniques like X-ray diffraction and NMR spectroscopy. Among those, we can cite Density Functional Theory calculations and Grand Canonical Monte Carlo simulations. It is possible to become a user of these tools with relatively little training, relying either on commercial or academic software with user-friendly interfaces. However, as with any technique, one should always take great care in checking the validity of the tools for the system at hand, as well as in interpreting the results obtained.

Table 1
List of reviews published on computational characterization of metal–organic frameworks.

Year	Topic	Ref.
2015	General modeling of MOFs (book)	[1]
2015	Quantum chemical characterization of MOFs, including catalysis	[2]
2014	High-throughput computational screening	[3]
2014	First-principles force fields for guest molecules	[4]
2013	Gas separation	[5]
2012	Screening for adsorption and separation	[6]
2012	Methane, hydrogen, and acetylene storage	[7]
2011	Adsorption in flexible MOFs	[8]
2011	Energy, environmental and pharmaceutical applications	[9]
2011	Screening for separation applications	[10]
2009	Hydrogen storage	[11]
2009	Adsorption	[12]
2008	Adsorption and transport	[13]
2007	Adsorption of small molecules	[14]

Given the formidable research effort focused on metal–organic frameworks (MOFs) in the past decade, with more than 20,000 papers published (at a current rate of more than 5 MOF papers per day [17]), 15,000 structures on record at the Cambridge Crystallographic Data Centre, and over 170 review articles dedicated to this topic, the published literature on computational studies of MOFs is in itself abundant. Theoretical approaches are in many cases used, in combination with experimental characterization techniques, to study newly synthesized materials and understand their properties at the microscopic level. In this *introductory review*, we give an overview of the computational chemistry methods commonly used in the field of MOFs, to describe the structures themselves and characterize (or predict) their various properties. It is by no means a systematic review of existing computational work on MOFs, of which there simply is too much to systematically enumerate here. Rather, we will try to give the reader an idea of what is possible in theoretical studies of MOFs, both at the quantum chemical level and through classical molecular simulations. For more details on specific areas of interest, we refer to existing reviews of computational MOF studies, which are listed in Table 1.[2] We finish the review by pointing out some of the open questions and challenges in the field.

2. Structural properties

2.1. Crystal structure prediction

In most cases, the structure of a newly synthesized metal–organic framework is determined experimentally, using single-crystal X-ray diffraction data when possible, or solving the structure from powder diffraction data if single crystals of sufficient size or quality cannot be obtained. In the latter case, it often happens that because of the molecular complexity of the material, a low symmetry, or a large unit cell, the structure solution is arduous or impossible to solve. Moreover, in other cases, there is a need for methodologies of true (or *ab initio*) computational prediction of MOF crystal structures, without any input of experimental data. These structures can then either be used to guide the synthesis of novel materials, or to identify materials already synthesized but

[2] In particular, we do not address in this review the very specific topic of the catalytic activity of MOFs: on this, we refer the reader to the very recent review by Odoh et al. [2].