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## Role of molecular simulations in the structure exploration of Metal-Organic Frameworks: Illustrations through recent advances in the field

*Rôle de la simulation moléculaire dans l'étude structurale des matériaux hybrides poreux : illustrations à travers des travaux récents*

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### ABSTRACT

The role of molecular simulations in (i) the structure determination of existing porous Metal-Organic Framework (MOF) materials, (ii) the fundamental understanding of their structural behaviors upon diverse stimuli, and (iii) the discovery of novel architectures is illustrated through recent advances our group has made in this field.

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### R É S U M É

Le rôle de la simulation moléculaire dans (i) la détermination structurale des matériaux poreux de type MOFs, (ii) la compréhension de leur comportement sous l'effet de divers stimuli et (iii) la prédiction de nouvelles architectures est présenté à travers plusieurs illustrations empruntées à nos travaux récents dans ce domaine.

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## 1. Introduction

Crystalline porous hybrid solids known as Metal-Organic Frameworks (MOFs) are the most recent class of porous solids [1–5]. These materials are constructed of inorganic subunits (almost all the plausible di- tri- and tetraivalent metals present in the periodic table) which are linked together through organic polycomplexing moieties (carboxylates, azolates, imidazolates, phosphonates,

catecholates...). This offers an unprecedented structural and chemical diversity leading to thousands of architectures reported so far and many more to be discovered. Besides their promise for industrial application in diverse areas [6,7], this class of materials attracts tremendous curiosity from a fundamental point of view arising from the complexity and the flexibility of their architectures [1–5, 8, 9]. This makes this family of solids an ideal platform for the development and the validation of advanced experimental and computational tools.

The breathing behavior of some MOFs is one of the most fascinating structural behaviors encountered in the field of porous solids [8–10]. The fundamental understanding of the origin of such a peculiarity aroused great interest which

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led to the deployment of an arsenal of *in situ* characterization tools and multi-scale modeling techniques [9–18]. The complexity of their architectures also calls for a continuous interplay between experimental and modeling approaches integrating advanced characterization and computational tools fully intertwined during all stages of the structure determination [19–25]. Modeling tools involving energy minimization techniques at the force field (interatomic potential) and/or electronic (quantum) levels have been deployed in tandem with experimentation including X-ray diffraction and Nuclear Magnetic Resonance measurements to solve the crystal structure of several porous MOFs [19–28]. In particular, such a computational assisted structure determination strategy is currently indispensable for the structure resolution of complex (large unit cell and low symmetry) and/or poorly crystallized porous MOF solids [29], which is hardly achieved by the conventional *ab initio* direct methods applied to powder diffraction. In complement to high-throughput synthesis, there is nowadays growing interest in the development of large-scale computational toolboxes integrating efficient search algorithms and optimization methods, to boost the discovery of novel porous MOF structures and probe their adsorption/separation properties [30–37]. A huge collection of hypothetical MOF structures has been predicted; however only rarely synthesized so far.

The aim of this article is to emphasize how modeling is a valuable tool not only to aid the **structure determination** of complex architectures and to **predict novel structures** sometimes with targeted chemical and topological features for further applications, but also to capture and understand the complex structural behaviors of these MOFs upon diverse stimuli as for instance their spectacular **breathing behavior** triggered by the adsorption of guest molecules. The continuous interplay between experimental and computational tools in these three areas is highlighted through recent achievements made by our group in tandem with the experimentalists at the Institut Lavoisier Versailles (ILV). The readers can refer to recent review journals [30] and books [38] for an exhaustive review of the computational approaches applied to model MOFs.

## 2. Structure solution for MOFs

The relatively poor crystallinity of certain MOFs sometimes combined with large unit cells or low symmetries is still a hurdle on the way to obtain the structure solution of these hybrid solids solely from the indexation of the powder X-ray diffraction patterns using the conventional *ab initio* methods [39–41] as implemented in the most popular crystallography software. This called for the development of molecular simulation tools intertwined with experimental information in order to boost the resolution of the crystal structure of many MOFs. The Institut Lavoisier Versailles (ILV) is the pioneer in this field, particularly with the structure elucidation of the complex mesoporous MIL-100 [42] and MIL-101 [43] solids using a computational assisted structure determination approach. Following the concept of Secondary Building Blocks [20] and the chemical intuition raised from the analysis of the

synthetic conditions, a series of hypothetical zeotype architectures built up from the assembly of inorganic trimers and benzene-1,3,5-tricarboxylate (MIL-100) /1,4-dicarboxylate (MIL-101) linkers were first computationally generated and their associated X-ray diffraction patterns were calculated. A direct comparison between the experimental and simulated diffraction diagrams allowed the selection of the most probable structure candidate which was used for a further Rietveld refinement on the experimental powder diffraction data. The resolution of these two giant pore MOFs with huge unit cell volumes (380,000 Å<sup>3</sup> and 702,000 Å<sup>3</sup> for MIL-100 and MIL-101, respectively) comparable to some proteins is the first spectacular success of the interplay between experimental and computational approaches.

Inspired by this advance, our group contributed in collaboration with ILV to solve the structure of a series of complex isorecticular MOFs including (i) the extra-large extended and functionalized mesoporous iron carboxylate solids of cubic symmetry with the MIL-100 and MIL-101 topology [44]; the typical example is the MIL-100(BTB) built up from the 1,3,5-tris(4-carboxyphenyl)benzene linker showing an extremely large unit cell volume up to 2 million Å<sup>3</sup>, and (ii) the carboxylate interwoven structured microporous based-MIL-142 series and their functionalized derivatives of rhombohedra symmetry and associated with intermediate unit cell volumes, the 4,4'-azobenedi-carboxylate MIL-142E solid showing the largest volume (95,547 Å<sup>3</sup>) [45]. Most of these MOFs are of relatively poor crystallinity which rendered the resolution of their structures hardly feasible simply from X-ray diffraction data. A structureless pattern refinement of the experimental diffraction diagram was however possible, and the cell parameters and the space group symmetry of each phase were thus determined. A computational ligand replacement strategy was used and consisted of gradually substituting the benzene-1,3,5-tricarboxylate (btc) and the benzene-1,4-dicarboxylate (bdc) linkers of the parent MIL-100/MIL-101 and MIL-142(A) structures respectively with ligands of a longer length. Force field based-energy minimization using potential parameters selected from generic force fields was subsequently performed to optimize the geometry of these structures at fixed cell parameters experimentally obtained for each solid. The so-obtained structure models were further used for Rietveld refinement on the experimental powder diffraction data in order to deliver a final solution of the structures (Fig. 1).

A variant of this strategy can be applied when MOFs of moderate/small unit cell sizes are considered. Typically, the series of porous zirconium di-carboxylate solids, denoted MIL-140A to MIL-140D [46], of general chemical formula [ZrO(O<sub>2</sub>C-R-CO<sub>2</sub>)] where R = C<sub>6</sub>H<sub>4</sub> (MIL-140A), C<sub>10</sub>H<sub>6</sub> (B), C<sub>12</sub>H<sub>8</sub> (C) and C<sub>12</sub>N<sub>2</sub>H<sub>6</sub>Cl<sub>2</sub> (D) with unit cell volumes ranging from 2000 to 4700 Å<sup>3</sup>, fall into this category of MOF solids. In this case, the cell size is not anymore a limiting step to run calculations at the electronic level. The crystal structure of MIL-140A which was solved by direct methods, exhibits triangular channels delimited by zirconium oxide chains along the channel axis connected to six other chains through the dicarboxylate linkers (see Fig. 2). The structure models of MIL-140B to MIL-140D, built up using a ligand

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