



Review

Flexibility in Metal–Organic Frameworks: A fundamental understanding

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ABSTRACT

Expansion and contraction of structurally flexible Metal–Organic Frameworks (MOFs) or Porous Coordination Polymers (PCPs) have been extensively studied from different structural and application perspectives including crystal engineering, structural characterization, and gas adsorption–separation applications. The flexibility of the MOFs or PCPs depends on a number of factors including the nature of secondary building units (SBUs), organic linkers, pore geometry and/or solvent molecules. The flexibility can lead to unique properties, especially in gas-adsorption–separation related applications that is not observed in rigid frameworks. In this review, we offer a brief summary regarding a fundamental understanding of framework expansion–contraction in flexible porous MOFs in terms of their design and structure tunability by covering representative examples in the literature.

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1. Introduction

Metal–Organic Materials (MOMs) or Metal–Organic Frameworks (MOFs) are typically assembled from metal cations or metal cluster (nodes, also known as SBUs) that are connected by organic molecules/inorganic anions which serve as linkers to afford periodic frameworks with controllable pore size and chemistry [1–5]. The IUPAC (International Union of Pure & Applied Chemistry) task group on coordination polymers (CPs) and MOFs have given precise recommendations for the terminology and nomenclature of porous materials as numerous terminologies were introduced in the area by various research groups that could lead to unreasonable misunderstanding [6]. When we exclude the zero-dimensional structures (e.g. nanoballs, cubes and metal–organic polyhedra) from the family of MOMs/MOFs and cover polymeric one-dimensional, two-dimensional and three-dimensional structures, these are termed as CPs [7–11], if all linkers are organic in nature, the materials are termed as MOFs [12], as exemplified by HKUST-1 (Hong Kong University of Science & Technology) [13] and MOF-5 [14]. The tunable and tailorable structures [12,15–18], extra-high surface area [19–23] and modular pore functionality [7,24–28] of MOFs affords prodigious control over physicochemical properties, in comparison to their purely inorganic, porous materials such as aluminosilicate zeolites and have made them an attractive class of materials with potential for a wide range of applications such as gas storage and separation [29–33], heterogeneous catalysis [34–38], drug delivery [39,40], and conductivity [41,42]. MOMs (and MOFs) have received particular attention when the concept of crystal engineering was popularized in the early 1990's [43] and subsequently, their scientific interest has been augmented especially after pioneering work of Williams [13], Yaghi [44] and Kitagawa [45].

It was demonstrated that systematic design of the framework structure can lead to a control over its properties by studying the impact of the molecular structure upon crystal packing, crystal structure and physicochemical properties “*Form for Function*” [46–48]. Specifically, the concepts of crystal engineering and self-assembly for the design and synthesis of MOMs (or MOFs) were intensely grown, enabling the systematic study of structure/function relationship in an unprecedented way. This is distinctly different from more random, high-throughput screening approach that is traditionally used in materials discovery and development [48,46]. Though MOFs have been envisioned as being made of rigid, aromatic linkers as strut and metal clusters as nodes, a number of MOFs are known to be flexible in nature in presence of external stimuli such as pressure, temperature, and light [49–51]. The design of MOFs with expansion and contraction or “*breathing*” properties is considered as one of a pertinent idea in order to target specific applications such as gas separation, gas storage, sensing and drug delivery [50,52]. These specific types of MOFs have flexible frameworks and lack the rigidity, therefore they are termed as soft porous crystal [53], flexible MOFs, sponge-like MOFs [54,55], spring-like [56] or dynamic MOFs [57] in literature. The ordered crystal structure of these flexible MOFs has the ability to transform through different ways such as a phase change or gate opening [58,59]. Such flexibility is often observed during the adsorption–desorption process, where the interaction of adsorbate molecules with the pore–surface is believed to be the origin of such flexibility

[60]. The framework flexibility is apparent from the adsorption–desorption curve of the adsorbate molecules with a sharp change in uptake at a certain pressure or temperature, indicative of a change in pore surface properties or an associated phase change. A large number of flexible MOFs with flexible structural features have been reported till date, tailored for applications ranging from gas-adsorption and separation to catalysis and explosive sensing [50]. It should be noted that although flexible MOFs are shown to be excellent candidates for gas-separation for various industrially important gases such as small chain hydrocarbons, unless a detailed structure–property relationship for a particular system as a function of external parameters are worked out, the application of these types of materials in an industrial setting seems unlikely. In many cases, the host–guest interactions and associated flexibilities in MOFs are of fundamental importance and understanding the interaction and associated phase transition behaviours can open up a new avenue in materials design and exploration. Kitagawa's and Ferey's groups took the early lead through a variety of study on flexible MOFs such as metal paddlewheel-based pillared square grids, MIL-53 and MIL-88 (MIL = Materials Institute Lavoisier) [50,61–64]. Indeed, the flexibility in MOFs was also addressed from the computational modeling perspectives [65–69]. The earliest work on the molecular modeling of flexible MOFs was presented by Miyahara and his co-workers [68]. They conducted Grand Canonical Monte Carlo (GCMC) simulations on catenated jungle gym structures exhibiting structural transitions and gate adsorption behavior. The calculations and the grand free energy profiles revealed that the integration of the guest molecule during the adsorption process provide a stabilization of the structure that triggers the structural transition. Most recently, Smit and his co-workers have presented several studies on the flexibility of MOFs, focusing on the impact of the flexibility of MOFs on their selective adsorption of gases [65,67]. The authors have developed a simple model to calculate the flexible Henry's coefficients and selectivity for Xe and Kr gases as a function of the intrinsic flexibility of MOFs. The study gave an insight that the optimal materials for the shape selective adsorption applications should have a synergistic effect between pore size and pore chemistry as well as a minimal structural flexibility. However, for other nonoptimal materials, the selectivity could be improved in the presence of flexibility. The molecular modeling of MOFs is very critical to correctly understand the adsorption behavior of these materials and contribute to the future design of dynamic MOFs that are beneficial in certain applications such as sensing, catalysis, gas storage, gas separation and drug delivery.

Rather than covering the entire literature, in the next few sections of this review, we will briefly cover the design perspective of MOFs with expansion–contraction/dynamic behavior and its impact on their properties.

2. Intra-framework motives for the contraction or expansion in MOFs

The flexibility of MOFs is influenced by many parameters. One notable factor affecting the contraction and/or expansion of MOFs is their structural compositions including the metal ion/cluster (Molecular Building Blocks or MBBs, also known as secondary building units or SBUs) and the organic linker. Another factor

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