Coordination Chemistry Reviews 293–294 (2015) 327–356

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Biomimicry in metal–organic materials

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Contents

ARTICLE INFO

Article history:
Received 31 March 2014
Received in revised form 24 May 2014
Accepted 28 May 2014
Available online 6 June 2014

Keywords:
Metal–organic framework
Metal–organic polyhedron
Biomimetic chemistry
Metalloporphyrin
Catalysis

ABSTRACT

Nature has evolved a great number of biological molecules which serve as excellent constructional or functional units for metal–organic materials (MOMs). Even though the study of biomimetic MOMs is still at its embryonic stage, considerable progress has been made in the past few years. In this critical review, we will highlight the recent advances in the design, development and application of biomimetic MOMs, and illustrate how the incorporation of biological components into MOMs could further enrich their structural and functional diversity. More importantly, this review will provide a systematic overview of different methods for rational design of MOMs with biomimetic features.

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1. Introduction

Naturally occurring materials are renowned for their combination of a great number of inspirational attributes that have been seldom observed in traditionally-used artificial materials, such as sophistication, miniaturization, hierarchical organization, and hybridization [1,2]. Evolution has optimized biological materials and biological processes for more than 3.8 billion years since the emergence of unicellular simple cells (i.e. prokaryotes) [3], which has resulted in the structural and functional variety of biological molecules on the planet Earth. Researchers have increasingly been looking to nature for inspiration to design novel breakthrough technology and to solve previously long-standing problems. Biomimicry is the study of the structure and function of biological systems, for the purpose of synthesizing materials that

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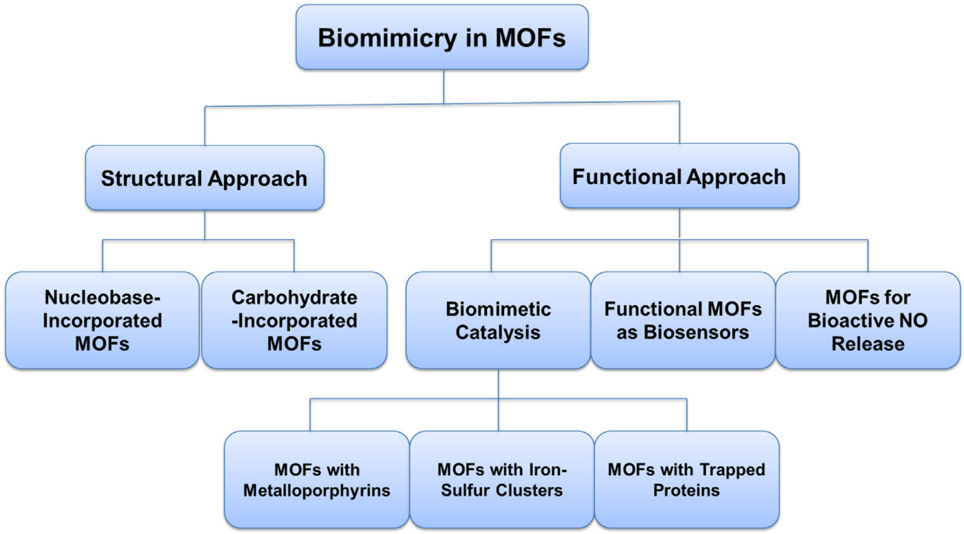
http://dx.doi.org/10.1016/j.ccr.2014.05.031
0010-8545/Published by Elsevier B.V.



Scheme 1. Recent progress on biomimetic MOFs can be cataloged into two different approaches: a structural approach and a functional approach.

mimic natural ones. The goal is to use these observations of nature to create materials that are both more compatible with life and provide functionality that has previously not been seen in artificial materials. Biomimicry is on the forefront of scientific and technological research, because it brings about novel insights for the synthesis of biologically-compatible, environmentally-friendly and energetically-efficient materials.

For the past decades, Metal–organic materials (MOMs) [4,5] have attracted a tremendous amount of attention due to their intriguing structures and diverse applications. Metal–organic frameworks (MOFs) and Metal–organic polyhedra (MOPs) are two important categories of MOMs. MOFs are crystalline polymeric coordination networks that consist of both metal units (ions or clusters) and organic linkers that form repeating three-dimensional architectures with potential inner porosity [6–9]. Due to their enormous surface areas, tunable structures and convenient functionalization processes, MOFs are promising materials for gas storage [10–25], separation process [26–47], carbon dioxide sequestration [48–62], sensors [63–78], drug delivery [79–96], photosensitive materials [97–107], magnetic materials [108–118], heterogeneous catalysts [119–130], and many other applications. MOPs, on the other hand, are discrete coordination assemblies that typically possess well-defined structures and confined cavities [131–134]. In biomimetic chemistry, while many other accomplishments have been achieved in areas such as artificial enzymes [135–147], artificial bones [148–161], biomimetic catalysts [162–169], biomimetic membranes [170–178], tissue engineering [179–188], and many other related areas, research on biomimetic MOMs still remains underdeveloped in comparison to the rapid growth of MOF/MOP chemistry. Herein, we would like to write this comprehensive review paper to summarize the research results of biomimetic metal–organic materials in recent years. In particular, we will focus on the recent advances of biomimetic MOFs, and a few examples of biomimetic MOPs will be provided.

By taking advantage of the structural and functional diversity of biological molecules, it is suggested that the incorporation of biomimetic units into MOFs will further enrich the variety of MOF architectures and applications, as the exploration of new structures or functions of MOFs is the core activity of MOF research. In a recent highlight review from our group, we have classified the contemporary progress on rational MOF designs into a structural and a functional approach [189]. Similarly, in this review, we would like to categorize the recent advances of biomimetic MOFs into those two distinct catalogs as well. The structural approach includes the incorporation of biological molecules into MOFs to explore new possible structures, while the functional approach involves the incorporation of biological/biomimetic components into MOFs to investigate their new possible applications (Scheme 1).

2. Biomolecules as organic linkers for MOF/MOP synthesis

Many biomolecules, such as amino acids, oligopeptides, proteins, nucleobases, and saccharides, are naturally good ligands and have already been successfully incorporated into coordination polymers. However, some restrictions generally prevent these biomolecules from being good candidates as MOF constituents. The symmetry deficiency in many biological building blocks makes the synthesis of ordered materials (such as MOMs) much more difficult, where the utilization of high-symmetry constructional components will significantly facilitate the packing of the repetitive units to form crystalline materials [22]. Additionally, aside from some aromatic molecules and a few cyclic non-aromatic molecules, most biomolecules are too flexible to generate a framework with potential permanent porosity. To overcome this problem, several different strategies were developed by MOF scientists: first, to construct MOFs with highly-symmetric secondary building units (SBUs) from asymmetric biological ligands; second, to introduce a highly-symmetric co-ligand to offset the low-symmetry nature of biomolecules; and third, to utilize a cyclic oligomer consisting of "small molecules" with lower symmetry. These strategies will be described in detail in this section.

We have noticed that incorporation of some selected biomolecules into coordination polymers (two-dimensional or three-dimensional structures, with or without gas adsorption data) has recently been reviewed [190]. However, this section of our review significantly differs from their work in at least two aspects. Firstly, our work offers a comprehensive review of the majority of the latest advances of biomolecule-incorporated MOFs, where many of them were not covered by the previous review. Secondly and more importantly, except for a limited number of adenine-incorporated [191,192] or γ-cyclodextrin-incorporated [193] frameworks, most coordination polymers summarized in the previous review paper possess very limited porosity, which are far less than what is needed for these materials to be an excellent candidates for gas storage, separation or other applications. However, according to the latest IUPAC definition, MOFs are infinite crystalline coordination networks with potential inner porosity [8,9]. It