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Review

Snapshots of encapsulated porphyrins and heme enzymes in metal-organic materials: A prevailing paradigm of heme mimicry

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ABSTRACT

Literature sources on metal-organic materials encapsulating versatile porphyrinoids and heme enzymes have been discussed in this review. General fundamentals and structural and chemical requisites of these architectures are discussed in introduction followed by historical perspectives of the initial composites. We have categorized the structural aspects of this class of compounds according to the host and guest skeletons as well as encapsulating strategies in a sequential manner. Heme mimetic, as well as some novel applications of the materials including oxidation, electron transfer, carbene transfer and biomolecule sensing, are then discussed and compared with each other and their homogeneous analogues based on mechanistic similarities, wherever possible.

Contents

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1. Introduction

Metal-organic materials (MOMs) are a distinctive class of compounds which have attracted the attention of a number of scientists [1–3]. In a definitive sense, MOMs include all the compounds possessing metal center(s) ligated to organic struts crafted with suitable functionalities. Such a broad domain comprises a variety of materials that can be categorized into four subclasses: (i) simple coordination complexes, (ii) metal-organic polyhedra (MOP), (iii) metal organic frameworks (MOF) and (iv) metal organic gels (MOG) (Fig. 1). Coordination complexes are the simplest form of MOMs consisting of mono- or polymetallic center(s) ligated to versatile linkers. The ones possessing only inorganic ligands are excluded from the domain of MOMs. MOPs, also known as metal organic cages, on the other hand, feature well-defined regular discrete 3D geometric shapes (any form of Platonic, Archimedean or Johnson solids) and consist of more than three metal centers connected by suitable organic struts. MOFs or coordination polymers are periodically repeating 2D or 3D infinite frameworks composed of metal ions and organic ligands. Though crystallinity is observed in maximum MOF skeletons, amorphous coordination polymers are also quite prevailing in the literature [4,5]. MOGs are jelly-like materials made of cross-linked coordination polymers [6–8]. MOGs are often observed as by-products while synthesizing MOFs possessing high valent metal ions and multipodal ligands. Though these materials are porous and possess high surface area similar to MOPs or MOFs, the basic difference between them lies in the fact that MOGs are not uniformly porous and can be easily molded to any desired shape because of their inherent jelly-like nature [9]. Here in this review, we will discuss the structures and applications of porphyrinoids and heme enzymes entrapped within first three categories of MOMs briefly. The potential of MOGs as suitable hosts are yet to be exploited.

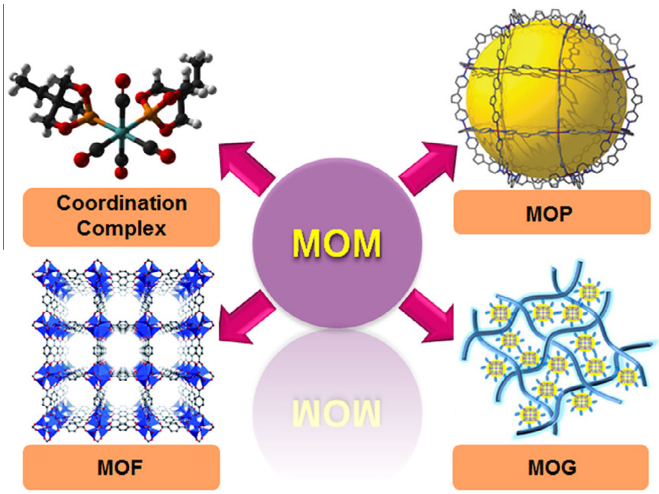
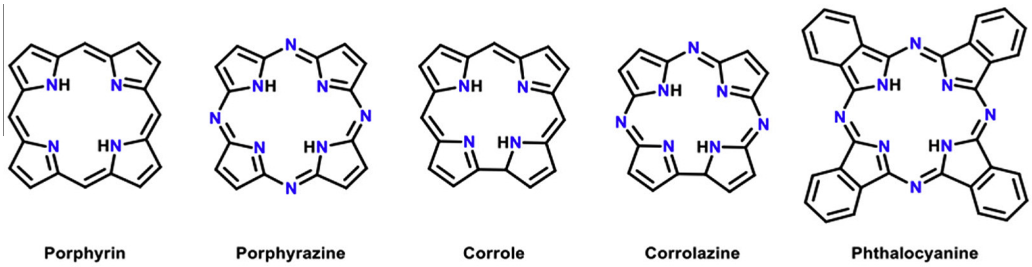


Fig. 1. Four subclasses of metal organic materials (MOMs) coordination complex, MOP, MOF, and MOG.

Some authors prefer the name MOMzymes to address these materials. However in a broader sense, MOMzyme accounts for MOMs that exhibit structural or functional resemblance to any sort of enzyme. In other words, the name is not specific towards encapsulated porphyrinic struts. Contrary to this nomenclature, porph@-MOMs precisely indicate immobilization of porphyrinic moieties, either designed or as natural heme enzymes, inside a MOM pore. Thus, the term "porph@MOM" has been used throughout this review and a general abbreviation A@B has been adopted in order to describe encapsulation of A into the interior of B. Though immobilization of different metalloporphyrinic systems including heme enzymes in or onto solid surfaces had been an issue of interest for more than last three decades because of their recyclability and capability to catalyze a number of reactions, [10,11] MOMs are a relatively recent addition to this family of solid supports. Despite the fact that porph@MOMs have stimulated much enthusiasm amongst researchers, it is still in its initial stage.

Metalloporphyrins are one of the most important class of compounds, on which the existence of life depends. Structures of major synthetic porphyrinoids are shown in Scheme 1. Porphyrins are stable organic chromophores that absorb visible light and possess very strong characteristic absorption bands (Soret band) around 400–450 nm with absorptivities, ε, on the order of $10^5\ \mathrm{M^{-1}\,cm^{-1}}$ [12]. Applications of these tetrapyrrolic macrocycles in oxygen transportation, light harvesting, and enzymatic catalysis are quite abundant [13]. The catalytic activities of heme proteins, as well as the activities of many other metalloporphyrins, include oxidation of olefins [14]. Nonetheless, most of the homogeneous metalloporphyrin-based catalysts endure reduced lifetime and activity due to self-degradation and/or formation of μ-oxodimers [15]. Thus, immobilizing these units into solid matrices that offer enough room to catalyze a reaction, provide assuring approach to overcome such drawbacks and make them good candidates to imitate versatile biological processes [16,17]. In order to develop novel biomimetic catalysts, scientists tried to entrap these moieties in inorganic materials like zeolites [18–26], intercalated clays [27–29], detergent micelles [30] and polymer films [31,32] as well as in organic materials like ion exchange resins [33] and in other organic polymers [34,35] and supramolecular struts [36]. MOMs are a relatively recent addition to this family of solid supports. With suitable interstitial pores, MOMs offer platforms to entrap porphyrinoids which possibly accounts for the growth of the porph@MOM field.

Usually, in porph@MOMs, the enzymes are incorporated into MOM skeletons post-synthetically with a few examples of *in situ* immobilization, whereas *in situ* or even metal cation directed post-synthetic *de novo* protocols are adopted to afford metalloporphyrin guests. The core of the porphyrins can be pre-metallated or



Scheme 1. Different types of porphyrinoid structures. Reproduced with permission from Ref. [12]. Copyright © 2009, American Chemical Society.