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Review

Biologically derived metal organic frameworks

Samantha L. Anderson, Kyriakos C. Stylianou *

Laboratory of Molecular Simulation (LSMO), Institut des Sciences et Ingénierie Chimiques (ISIC), École Polytechnique Fédérale de Lausanne (EPFL Valais Wallis), Rue de l'Industrie 17, CH-1951 Sion, Switzerland

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ABSTRACT

Metal organic frameworks (MOFs) are extended structures composed of a network of organic ligands and metal ions or clusters connected to each other *via* coordination bonds. The numerous choices of organic ligands and metal coordination geometries have led to the construction of porous MOFs with various compositions, network topologies, pore sizes and shapes and they possess high surface areas and low densities. The structures of MOFs can be tailor-tuned in such a way that any desired ligand or/and metal ion can be incorporated; this has given to researchers the advantage of designing MOFs for a targeted application. Within this review, we overview recent examples of a sub-class of MOFs namely biologically derived MOFs (bio-MOFs), made of multifunctional and commercially available biologically derived ligands (bio-ligands) such as: amino acids, peptides, nucleobases and saccharides and focus on their coordination chemistry with a variety of metals. Central to this review are four tables detailing the coordination modes of bio-ligands to metals, along with a visual representation of the bio-MOF that is subsequently formed. Through the detailed analysis of these structures, we highlight the structural impact of these ligands on the structure, and their contribution to the MOF properties and applications. Finally, we showcase the potential of bio-MOFs in several research areas such as CO_2 capture, separation, catalysis, drug delivery and sensing.

Contents

Abbreviations: MOFs, metal organic frameworks; Bio-MOFs, biologically derived MOFs; Bio-ligands, biologically derived ligands; MTV-MOF, multivariate MOF; IRMOF, isoreticular MOF; GFP, green fluorescent protein; HTCPB, tetradentate carboxylic acid; BET, Brunauer–Emmett–Teller; SCSC, single crystal to single crystal; I, intensity; CPO, coordination polymer; LEDs, light-emitting diodes; DMF, *N,N′*-dimethyl formamide; DEF, *N,N′*-diethyl formamide; FITC, fluorescein isothiocyanate; NMOFs, nanoscale MOFs; BTAsp, benzene-1,3,5-tris aspartic acid; Gly, glycine; Phe, phenylalanine; Gln, glutamine; Asp, aspartic acid; SOD, sodalite; Met, methionine; Glu, glutamic acid; His, histidine; Cys, cysteine; Tyr, tyrosine; Bipy, 4,4′-bipyridyl; Py3T, tris(4-pyridyl)-35bpp, 3,5-bis(4-pyridyl)pyridine; IDS, *meso*-iminodisuccinic acid; Im, imidazole; Trp, tryptophan; bpe, bis(4-pyridyl)ethylene; ser, serine; val, valine; BDC, benzene dicarboxylic acid; GlyGly, glycyl-glycine; GlyGlu, glycyl-glutamic acid; GlyThr, glycyl-threonine; AlaThr, alanyl-threonine; GlyAla, glycyl-alanine; GlyAsp, glycyl-aspartate; GlySer, glycyl-serine; MTV, multivariate; Car or AlaHis, carnosine or alanyl-histidine; GlyHis, glycyl-histidine; GlyPhe, glycyl-phenalanine; GlyGlyGly, glycyl–glycyl-glycine; GlyProPro, glycyl–prolinyl-proline; BPDC, 4,4′-biphenyldicarboxylic acid; GlyHisLys, glycyl–histidyl-lysine; GlyHisGly, glycyl–histidyl-glysine; NH_2-Glu-pCO_2Phe-pCO_2Phe-Ala-Gly-OH, penta-peptide composed of the sequence of glutamic acid-phenylamine-phenylamine-alanine-glycine; Ade, adenine; Thy, thymine; TATB, 4,4′,4″-*s*-triazine-2,4,6-triyl-tribenzoic acid; BTeC, 1,2,4,5-benzene tetracarboxylic acid; Gua, guanine; MOP, metal organic polyhedron; TMOP, thymine based MOP; MDPI, 5-((5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)methyl)isophthalate; DMA, dimethyl acetimide; XRD, X-ray diffraction; α-CD, alpha-cyclodextrin; β-CD, beta-cyclodextrin; γ-CD, gamma-cyclodextrin; TCPB, 1,2,4,5-tetrakis(4-carboxyphenyl)benzene; CDMOF, cyclodextrin based MOF; α-1,4-D-Glup, α-1,4-linked D-glucopyranosyl; SBUs, secondary building units; ZABUs, zinc-adeninate octahedral building units; NDC, 2,6-napthalene dicarboxylic acid; ABDC, azo-benzene-4,4′-dicarboxylic acid; TPDC, terphenyldicarboxylic acid; NH_2-TPDC, 2′-amino-1,1′:4,1″-terphenyl-4,4″-dicarboxylate; BTC, 1,3,5-benzene tricarboxylic acid; PfH^+, proflavine hemisulfate ion; MB^+, methylene blue ion; Azobipy, 4,4′-azobipyrine; Azinebipy, 4,4′-azinebipyridine; Bpeb, 1,4-bis(4-pyridylethenyl)-benzene; Azpy, 4,4′-azopyridine; 3rbp, 1,4-bis(4-pyridyl)benzene; TMA^+, tetramethyl-ammonium cations; TEA^+, tetraethyl-ammonium cations; TBA^+, tetrabutyl-ammonium cations; pzdc, pyrazole dicarboxylic acid; 9Hade, adenine with protonated N9; 7Hade, adenine with protonated N7; TiF6, titanium hexafluoride; IAST, ideal adsorbed solution theory calculations; GND^+, guanidium cations; $AmGND^+$, aminoguanidinium cations; $DiAmGND^+$, diaminoguanidinium cations; DMA^+, dimethyl ammonium cations; TIF, tetrahedral imidazolate frameworks; int, isonicotinic acid; CA-CDMOF-2, carbonic acid cyclodextrin based MOF; e.e., enantioselectivity; HPLC, high performance liquid chromatography; BTEX, acronym that stands for benzene, toluene, ethylbenzene, and xylenes; 4-Pca, 4-pyrazolecarboxylic acid; $HNEt_2$, diethanaloamine; TTA, 2-thenoyltrifluoroacetonate.

* Corresponding author.
E-mail address: kyriakos.stylianou@epfl.ch (K.C. Stylianou).

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1. Introduction

Metal organic frameworks (MOFs) are crystalline coordination based materials consisting of an infinite network of metal–ions, or metal–ion clusters, bridged by organic ligands through coordination bonds into porous two- or three-dimensional extended structures [1,2]. The judicious selection of the metal ion and ligand has led to the discovery of a broad array of highly porous MOF materials with various topologies, compositions and properties such as record-breaking internal surface areas (up to 7000 m^2/g) [3], high void volumes (up to 90%) [4], and low densities (as low as 0.126 g/cm^3) [5]. The ability to chemically modify the pore surface of MOFs through pre- and post-synthetic introduction of functional groups, combined with the potential for the formation of open metal coordination sites, can also provide the means to tailor internal surfaces for applications related to gas separation and storage, catalysis, and sensing [6]. Compared with other frequently used ligands for MOF synthesis, biologically related ligands (such as amino acids, peptides, nucleobases and saccharides) offer the potential to utilize multiple coordination sites, and contain a variety of functional groups that can be advantageous in areas such as CO_2 capture, separation and catalysis. They also, have added advantages such as controlling hydrogen-bonding interactions, resulting in structures that can be flexible or robust. Ultimately, bio-ligands allow researchers to buy any combination of chirality, aromaticity, cyclic or aliphatic features desired, or by buying the necessary backbone and synthetically altering it for further research investigations. This saves time, and can accelerate the rate of MOF discovery. With the vast amount of bio-ligands readily available, it is not surprising that these ligands have found their way into several applications, such as CO_2 capture/storage, enantioselective synthesis, etc. that other well-known MOFs (e.g. HKUST-1, MOF-74) have been known for [7]. To control the size and shape of a cavity in a particular MOF for a given application can still prove challenging to researchers, however the ligand design strategy (and their incorporation within the MOF structure) plays a significant role in the construction of functional MOFs.

In this review, we highlight the importance of ligands in general and more specifically the impact of biologically related ligands (hereafter bio-ligands), in the design, structure and applications of biologically derived MOFs (hereafter bio-MOFs). More so, we will discuss the current work and challenges of incorporating bio-ligands into MOFs, and offer insights into this exciting sub-discipline of research.

2. Ligand design in MOFs

Typically, the self-assembly of metal ions or clusters with ligands to form MOFs can be achieved through classical coordination chemistry methods (<100 °C) [1,8], diffusion methods, solvothermal synthesis (>100 °C) [9], electrochemical methods, microwave synthesis [10,11], or high-throughput techniques [12–14]. While a variety of metal ions throughout the periodic table can be used, rigid organic ligands are generally preferred (over flexible) since the resulting MOFs can be robust and/or porous [15–17]. Commonly used organic ligands within MOFs are divided into families such as: (i) carboxylic acid containing ligands, (ii) nitrogen containing ligands (pyridyl, pyrryl, imidazolyl, etc), (iii) cyano ligands, (iv) phosphonic acids ligands, (v) ligands based on mixed functional groups, (vi) sulfonyl ligands and (vii) metal-bearing ligands [18,19]. While cationic ligands are less common in the synthesis of MOFs (low affinity to coordinate to metal cations), both neutral and charged ligands can be used [8]. Functionalities pointing toward their internal pore surface are often utilized to introduce strong interactions with a target molecule and can influence the framework structure [18]. In addition, they may have interconnecting functions, which could extend the coordination motifs, creating secondary interactions such as hydrogen bonding and aromatic stacking [18,20–23].

With a wide variety of ligands available, many different strategies have been used to synthesize MOFs that target a specific application. Some of them can be summarized into six different categories:

(i) Using ligands that are identical in size but contain different functional groups can afford multivariate MOFs (MTV-MOFs) [22,23]. This was demonstrated by Reimer et al., who combined Zn_4O and BDC to form a MTV-MOF-5 family, which showed fourfold selectivity for CO_2 over CO [22].
(ii) Replacing the organic ligands in a MOF with units that are topologically similar or identical, but instead increasing in length, can extend the pore size, resulting in the construction of new families of isoreticular MOFs (IRMOFs) with unique properties [24–29]. This method can be used to increase the BET, CO_2 capacity, and pore of the material. For example, in the IR-MOF-74-I to -IX series the pore apertures were increased for 14–98 Å, allowing for molecules such as vitamin B_{12}, or green fluorescent protein (GFP) to reside in their pores [27].
(iii) Using ligands with specific functionalities to target applications such as CO_2 capture and storage, or ligands that have specific functionalities to enhance their interaction with target molecules. For example, amine functionalized MOFs can be used to achieve a higher total adsorption energy of CO_2 molecules [28].
(iv) Increasing the conjugation of organic ligand can aid in the formation of MOFs with hydrophilic pores, or that can be used for light absorbing or sensing applications [30–39]. Ligands such as H_4TCPB have been incorporated into MOFs, allowing for selective uptake of *p*-xylene over other isomers