Biomimicry in Metal-Organic Materials

Muwei Zhang,^a Zhi-Yuan Gu,^a Mathieu Bosch,^a Zachary Perry,^a and Hong-Cai Zhou^{a,b,*}

^a Address: Department of Chemistry, Texas A&M University, College Station, Texas, U.S.A 77842
Email: zhou@mail.chem.tamu.edu Fax: +1 979 845 1595; Tel: +1 979 845 4034

^b Department of Materials Science and Engineering, Texas A&M University, College Station, Texas, 77842, USA.

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.

Keywords: Metal-Organic Framework; Metal-Organic Polyhedron; Biomimetic Chemistry; Metalloporphyrin; Catalysis.

1. Introduction

2. Biomolecules as Organic Linkers for MOF/MOP Synthesis

2.1 Nucleobase-incorporated MOFs

2.2 Carbohydrate-incorporated MOFs

2.3 Nucleobase-incorporated MOPs

3. Functional MOFs for Biomimetic Applications

3.1 MOFs as biomimetic catalysts

3.1.1 MOFs with unsaturated metal centers (UMCs)

3.1.2 MOFs with trapped metalloporphyrin

3.1.3 MOFs with metalloporphyrin as organic linker

3.1.4 MOFs with iron-sulfur clusters

3.1.5 MOFs with trapped proteins

3.2 Functional MOFs as biosensors

3.3 MOFs for bioactive nitric oxide release

4. Conclusion and Perspective

1. Introduction

Naturally occurring materials are renowned for their combination of a great number of inspirational and sophisticated 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 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)

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

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 is important to offer a review that focuses on *porous* MOFs with biological/biomimetic components for a careful examination of their potential applications. For the purpose of this review, we define a MOF as a hybrid organic-inorganic material with potential permanent porosity, reversible adsorption-desorption of adsorbates, and an extended three-dimensional framework with crystalline structure that can be evaluated by instrumentation methods (primarily single crystal X-ray diffraction and powder X-ray diffraction) [194]. Thus, the coordination polymers that are porous but lack long-range order and the coordination polymers that are crystalline but not porous are beyond the

scope of this review. The biomedical applications of nano-sized coordination polymers are not included and have been already reviewed comprehensively elsewhere [79-84].

2.1 Nucleobase-incorporated MOFs

Nucleobases are of central significance of the emergence, maintenance and proliferation of life on the planet Earth. With the selectivity of these base pair interactions, nucleobases are excellent components to construct supramolecular structures [195]. At the same time, nucleobases appear to be good ligands for coordination compounds as well. The presence of accessible nitrogen and oxygen lone pairs has brought about a rich field of nucleobase coordination chemistry [196]. For a single nucleobase, it is possible for metal ions to coordinate with almost any site of the molecules. This coordination versatility has led to the investigation of nucleobase-incorporated MOFs. However, to the best of our knowledge, only a few examples of MOFs with nucleobase incorporation have been currently reported [191, 192, 197-200]. This probably has in part resulted from the lack of intrinsic symmetry of nucleobases and from undesired binding modes to metal ions.

Scheme 2 Representation of (a) an adenine molecule and its possible coordination modes. (b) an imidazole molecule and its coordination mode in ZIFs. (c) the resemblance of carboxylic acids and an adenine molecule in MOF coordination chemistry.

Adenine contains a purine ring with four imino nitrogens and an exocyclic amino group, and all five nitrogen atoms are potential coordination sites. (Scheme 2 (a)) [201]. The coordination chemistry of adenine has been well-established for quite some time [196, 201]; however, it was not until recently that chemists started to investigate MOFs constructed by adenine [190]. The imidazole moiety in adenine is the primary constructional unit of zeolitic imidazolate frameworks (ZIFs) (Scheme 2 (b)) [202]. Additionally, the N3, N9 imino nitrogens resemble the carboxylic acid group by replacing the two coordinating oxygen atoms with two coordinating imino

nitrogens (Scheme 2 (c)), where carboxylate groups are currently the best-studied MOF ligands. With the use of carboxylates, paddlewheel structures are commonly obtained as secondary building units (SBUs) in MOFs (Figure 1 (a)) [203]. Similarly, paddlewheel structures were also observed by using adenine as a ligand (Figure 1 (b)) [204].

Fig. 1 (a) Representation of the dicopper paddlewheel with carboxylic acid groups (b) Representation of the crystal structure of adeninate-copper complex, with four adenine molecules coordinating to two central copper atoms by N3, N9 imino nitrogens, which exactly resembles the paddle-wheel structure in MOFs. Color Scheme: green, Cu; blue, N; red, O; and gray, C. H atoms are omitted for clarity.

Bio-MOF-1 is one of the earliest examples of biomolecule-incorporated MOFs with a significant porosity [191]. It is constructed from adenine and 4,4'-biphenyldicarboxylic acid (BPDC) with Zn(II) where the formation of infinite zinc-adeninate columnar SBUs made by apex-sharing zinc-adeninate octahedral cages leads to a 3D porous material. (Figure 2 (a)) Unlike the other reported mixed-ligand MOFs (UMCM-1 [205], UMCM-2 [206], MOF-210 [207], *etc.*) constructed from two highly symmetric ligands, the synthesis of bio-MOF-1 utilizes a low-symmetry building block (adenine) which, upon assembly, forms high-symmetry SBUs. By adopting this particular coordination, the symmetry of the framework is greatly improved, which significantly facilitates the packing of the repetitive units and the formation of crystalline materials. The Zn(II)-adeninate columns were then connected by BPDC linkers, resulting in a three-dimensional framework with one-dimensional channels which are stable after the removal of solvent guest molecules. (Figure 2 (b)) In the SBU, adenine ligands bridge eight Zn(II) ions via N1, N3, N7, N9 coordination, which leaves the exocyclic amino group uncoordinated in the framework. All of the adenine molecules coordinate to Zn(II) ions uniformly in this fashion, eliminating other unnecessary coordination modes. This framework has a permanent porosity after the removal of guest solvent molecules, with a Brunauer-Emmett-Teller (BET) surface area around $1700 \text{ m}^2 \cdot \text{g}^{-1}$.

Fig. 2 The representation of (a) the zinc-adeninate columns in Bio-MOF-1 and (b) its three-dimensional structure with one-dimensional SBU chain (Color Scheme: dark blue tetrahedra, Zn; gray spheres, C; red spheres, O; light blue spheres, N. H was omitted for clarity) (Reprinted with permission from Ref. [191], copyright by 2009 American Chemical Society)

Following the same strategy, bio-MOF-100 was developed by the same group as another nucleobase-incorporated framework [197]. Bio-MOF-100 also possesses highly symmetric Zn(II)-adeninate SBUs. Unlike the columns of fused zinc-adeninate cages observed in Bio-MOF-1 (Figure 2 (a)), this SBU exists as discrete octahedral cages which can be topologically represented as truncated tetrahedra (Figure 3 (a)). The SBUs were bridged by the BPDC ligands to yield an exceptionally porous MOF with exclusively mesoporous cavities (Figure 3(b)). This MOF possessed the largest pore volume [197] until NU-110E [208] was recently published. It was also reported as the first MOF with entirely mesoporous cavities. This framework is stable after the removal of the solvent molecules. Supercritical CO_2 activation was applied to activate this MOF because of its highly porous nature. It possesses one of the largest surface areas to date with a BET surface area of $4300 \text{ m}^2\cdot\text{g}^{-1}$ (Figure 3 (c)) [208].

Fig. 3 (a) The large cavity produced by discrete Zn(II)-Adenine SBUs (b) The crystal structure of bio-MOF-100. (Color Scheme: dark blue tetrahedra, Zn; gray spheres, C; red spheres, O; light blue spheres, N. H was omitted for clarity) (c) The N_2 uptake isotherm at 77 K of bio-MOF-100. (d) The microscope image of solvated bio-MOF-100 single crystals. (Reprinted with permission from Ref. [197], copyright by 2012 Nature Publishing Group)

An isoreticular series of bio-MOF-100 was also reported recently [198]. Instead of using the traditional solvothermal reactions, these MOFs were obtained by a single crystal to single crystal transformation via a stepwise ligand exchange strategy (Figure 4 (a)). Larger mesoporous cavities can be achieved by progressively replacing the BPDC linkers with longer dicarboxylate ligands (Figure 4 (b)). Bio-MOF-102 and bio-MOF-103 were prepared by the introduction of azobenzene-4,4'-dicarboxylate (ABDC) and 2'-amino-1,1':4,1"-terphenyl-4,4"-dicarboxylate (NH_2 -TPDC), respectively. An obvious volume expansion was observed when the longer ligands were incorporated into the framework. All these MOFs exhibit a Type IV adsorption isotherm, indicating the existence of mesoporous cavities. The calculated pore volumes of bio-MOF-102 and bio-MOF-103 are 4.36 and 4.13 $cm^3 g^{-1}$, respectively, making them among the MOFs with the largest pore volumes.

Fig. 4 (a) The graphic representation of generation of larger cavities via the ligand exchange strategy. (b) A stepwise replacement of linear ligand in bio-MOF-100 by longer dicarboxylate linkers. (Reprinted with permission from Ref. [198], copyright by 2013 American Chemical Society)

Another metal-adenine framework, bio-MOF-11, was solvothermally synthesized from adenine and cobalt acetate. This structure contains a cobalt-adenine-acetate paddlewheel SBUs (Figure 5 (a)) in which two Co(II) was bridged by two adeninates via N3 and N9 and two acetates [192]. The formation of this SBU yields a higher symmetry structure than an adenine linker possesses itself. These SBUs were connected by apical coordination of the N7 nitrogen atom of adeninate to the Co(II) ions in neighboring clusters to generate a three-dimensional structure (Figure 5 (b)). The N1 imino nitrogen in the pyrimidine ring and the exocyclic amino group remained uncoordinated in this framework. Thus, the other undesirable coordination modes between adenine and metal ions are avoided. The existence of the Lewis-basic nitrogen atoms in the cavity of this framework has further facilitated its selective adsorption of carbon dioxide [209]. The calculated selectivity of CO₂ over N₂ is 81:1 at 273K and 75:1 at 298 K, making it a promising candidate for CO₂ sequestration in industrial applications (Figure 5 (c)). This framework is also permanently porous with a calculated BET surface area of 1040 m²·g⁻¹.

Fig. 5 (a) The illustration of the Co(II)-adeninate-acetate paddlewheel structure. (b) The representation of the crystal structure of bio-MOF-11, which has an extended three-dimensional structure with channels along a and b crystallographic directions. (Color Scheme: light purple tetrahedra, Co; gray spheres, C; red spheres, O; light blue spheres, N. H was omitted for clarity) (c) The adsorption isotherms of CO₂ (circles) and N₂ (triangles) at 273K (black) and 298K (red). (d) Isosteric heat of adsorption of CO₂ for bio-MOF-11. (Reprinted with permission from Ref. [210], copyright 2010 American Chemical Society)

Besides being good ligands, nucleobases are also excellent motifs for supramolecular chemistry in the preparation of complicated molecular architectures. Nature has been taking advantage of supramolecular structures of nucleotides to store, transmit and replicate biological information with a very limited number of structural units [195]. Utilization of these nucleobases provides a new direction towards biomimetic self-assembly. Inspired by multiple hydrogen bonding interactions between nucleobases, another metal-adeninate framework was constructed with the assistance of hydrogen bonding formation between adenine moieties (Figure 6 (a)) [211]. Strictly speaking, this framework is not a MOF, but it is a rare example of MOM that consists of macrocyclic metal-organic assemblies interconnected by hydrogen bonds to generate a three-dimensional framework with permanent inner porosity. It comprises a hexameric Zn(II)-adeninate macrocycle as the repetitive unit, where each Zn(II) coordinates tetrahedrally by two nitrogens on the imidazolate ring of adenine, one pyridine molecule and one dimethylcarbamate anion formed *in situ* (Figure 6 (b)). The formation of the macrocycle has significantly improved the symmetry of repeating unit of the crystalline materials. It should be noted that only the imidazole nitrogens (N7, N9) of the adeninate are coordinated to the metal. The N1 and the exocyclic amino group on the pyrimidine ring remain uncoordinated and thus are available for supramolecular assembly. The periodic packing of the macrocycles via hydrogen-bonding resulted in a three-dimensional supramolecular framework with one-dimensional channels in the framework (Figure 6 (c)). Although many three-dimensional macrocyclic structures exhibit large cavities in the solid state, few of them are permanently

porous after the removal of the guest molecules [212]. However, due to the strong adenine-adenine hydrogen bonding interactions between the neighboring metal-adeninate macrocycles, the framework remains its porosity upon activation [211]. The pyridine ligands were removed upon activation at 125 °C, resulted in a comparatively large uptake of both H₂ (Figure 6 (d)) and CO₂ (Figure 6 (e)). The maximum H₂ uptake at 77 K and 1 bar is about 1 weight percent, which is similar to many other microporous MOFs [213, 214]. The ability for such macrocycles to show similar behavior to MOFs is a promising aspect of biomolecule inclusion in self-assembled materials.

Fig. 6 (a) The adenine-adenine hydrogen bonding interaction (b) The representation of an individual hexameric Zn(II)-adeninate macrocycle (Color Scheme: dark blue tetrahedra, Zn; gray spheres, C; red spheres, O; light blue spheres, N. H was omitted for clarity) (c) The crystal structure of this material after supramolecular assembly shows a one-dimensional channel (d) Hydrogen sorption isotherm (77 K) for material activated at 125°C and (e) Carbon dioxide sorption isotherms (273 K) for material activated at 125 °C (Reprinted with permission from Ref. [211], copyright 2009 American Chemical Society)

Despite the low-symmetry of nucleobase molecules, the aforementioned work has demonstrated that the incorporation of highly symmetric metal-adeninate units into MOMs appears to be an efficient way to generate porous structures. Apart from this approach, the introduction of a highly symmetric co-ligand may also be an effective way to construct nucleobase-incorporated MOFs. PCN-530 (PCN represents “Porous Coordination Network”) were synthesized between zinc acetate and adenine with the presence of H₃TATB (TATB = 4,4',4''-s-triazine-2,4,6-triyl-tribenzoate) as a co-ligand [200]. In this MOF, the one-dimensional zinc-adeninate chains (Figure 7 (a)) are linked by the TATB ligands, generating a three-dimensional structure with potential porosities. Like many other MOFs constructed from the TATB ligand, the polar nature of the s-triazine core has allowed the adjacent TATB ligands to stagger themselves to maximize the $\pi\cdots\pi$ interaction (Figure 7 (b)) [215, 216]. This MOF possesses open channels of 7.4×11.9 Å along the *a* axis (Figure 7 (c)).

Fig. 7 (a) The graphic representation of the one-dimensional zinc-adeninate chain in the framework. (b) The stacking pattern of TATB ligands. (c) The packing diagram of PCN-530 along a axis where open channels of $7.4 \times 11.9 \text{ \AA}$ can be found. Color scheme: grey, C; red, O; blue, N; and cyan, Zn. H atoms were omitted for clarity. (Reprinted with permission from Ref. [200], copyright 2014 Royal Society of Chemistry)

2.2 Carbohydrate-incorporated MOFs

Inspired by the novel structures and interesting properties of these adenine-incorporated architectures, it is worthwhile to initiate the study of other categories of biomolecules and their inclusion into MOFs. Carbohydrates (Saccharides) have a multitude of functions in living organisms, from structural components (*e. g.*, cellulose in plants) to energy storage (*e. g.*, starch and glycogen). They also play a vital role in genetics (backbones of DNA and RNA), immune systems, cell recognition, signaling, and many other biological functions. However, due to their intrinsically low symmetry, naturally flexible structure, difficulty in deprotonation, and relatively unexplored coordination chemistry, saccharides were rarely used as constructional units for any metal-organic materials [190]. This problem could be addressed by utilizing oligosaccharides with improved symmetry, and employing a novel synthetic method other than the traditional solvothermal conditions. The first example of a metal-saccharide MOF with permanent porosity was reported by Yaghi, Stoddart and coworkers [193]. Utilizing γ -cyclodextrin (γ -CD) as the linker, the MOFs were constructed with K^+ or Rb^+ metal centers. Cyclodextrins are a group of cyclic oligosaccharides made from 5 or more α -D-glucopyranoside units. Particularly, γ -cyclodextrin is a symmetric cyclic molecule with eight monosaccharide units (Figure 8 (a)). The symmetric arrangement of eight asymmetric α -1,4-linked D-glucopyranosyl residues is the key step to this assembly process [193]. After slow vapor diffusion of methanol into the aqueous mixture of γ -CD and KOH or RbOH, CD-MOF-1 and CD-MOF-2 (CD-MOF represents “ γ -Cyclodextrin-incorporated Metal-Organic Framework”) were obtained as colorless cubic single crystals suitable for X-ray crystallography (Figure 8 (b)). Importantly, after the removal of the guest solvents by heating to nearly 200°C , the activated framework exhibits permanent porosity with a BET surface area of $1220 \text{ m}^2\cdot\text{g}^{-1}$ for K^+ , and $1030 \text{ m}^2\cdot\text{g}^{-1}$ for Rb^+ , respectively. More recent work has demonstrated the synthesis of CD-MOF-3 and CD-MOF-4 from γ -CD and cesium hydroxide [217]. CD-MOF-3 and CD-MOF-4 formed simultaneously in the same reaction. Although the crystals of CD-MOF-3 and CD-MOF-4 could be separated manually, obtaining phase-pure materials still remains difficult. CD-MOF-3 has the same topology as that observed in CD-MOF-1 and 2; while CD-MOF-4 (Figure 8 (c)) displays a channel structure where γ -CD stack in one dimension. Crystals built from γ -CDs and NaOH (Figure 8 (d)) or SrBr_2 (Figure 8 (e)) were also reported by the same author simultaneously.

Fig. 8 (a) A conformational representation of γ -cyclodextrin (γ -CD) with its $-\text{OCCO}-$ units. (b) A representation of the porous nature of the CD-MOF-1 structure. CD-MOF-2 and CD-MOF-3 are isostructural to CD-MOF-1. (c) The structure of CD-MOF-4. (d) The structure of $[(\text{NaOH})_2 \cdot (\gamma\text{-CD})]_n$. (e) Solid-state structure of $[(\text{SrBr}_2)_3 \cdot (\gamma\text{-CD})]_n$. (Reprinted with permission from Ref. [217], copyright by 2012 American Chemical Society)

2.3 Nucleobase-incorporated MOPs

Metal-Organic Polyhedra (MOPs) are another category of MOMs that exist as supramolecular coordination assemblies between organic linkers and metal-containing SBUs. Unlike 3D extended MOFs, MOPs typically exist as 0D discrete cages with well-defined cavities and predictable structures [131-134]. Currently, the investigation of biomimetic MOPs is at an embryonic stage, and examples of biomimetic MOPs are exceedingly rare. Fujita group has reported a DNA-coated metal-organic cage. However, due to the complexity of their systems, this material cannot be obtained in its crystalline form [218]. Nevertheless, MOPs are usually regarded as supramolecular coordination assemblies whose crystallinity can be assessed by instrumentation methods such as XRD. Despite their low-symmetry nature, incorporation of a nucleobase molecule onto an isophthalate moiety may be an efficient way to construct nucleobase-incorporated MOPs [200]. TMOP-1 (TMOP represents “Thymine-incorporated Metal-Organic Polyhedron”) was successfully constructed from MDPI ligands (MDPI = 5-((5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)methyl)isophthate, See Figure 9 (a)) with dicopper paddlewheels. Similar to many other MOPs made from isophthalate ligands, single crystal XRD reveals the structure of TMOP-1 as a cuboctahedral cage consisting of 24 MDPI ligands and 12 dicopper paddlewheel SBUs. (Figure 9 (a)) It is suggested that the DMA solvent molecules coordinating to the axial position of some dicopper paddlewheel SBUs have facilitated the packing of this MOP by $\pi \dots \pi$ interaction with adjacent thymine moieties. (Figure 9 (b)) This is the first example of a nucleobase-incorporated MOP characterized by X-ray diffraction [200].

Fig. 9 (a) The crystal structure of TMOP-1. The yellow sphere indicates the empty space inside its cuboctahedral cage. (b) The $\pi \cdots \pi$ interaction between a coordinating DMA solvent molecule and an adjacent thymine moiety. Color scheme: grey, C; red, O; blue, N; and green, Cu. H atoms were omitted for clarity. (Reprinted with permission from Ref. [200], copyright 2014 Royal Society of Chemistry)

3. Functional MOFs for Biomimetic Applications

There exist a great number of biomolecules that are capable of performing complicated biological activities with exceptional accuracy and efficiency. This has inspired the study of “biomimetic chemistry” [219] or “artificial enzymes” [220] and motivated researchers to imitate the enzymatic activities *in vitro*. The incorporation of either proteins / peptide segments [221–227] or their prosthetic groups / active sites (like metalloporphyrins or iron-sulfur clusters) into permanently porous materials has opened up another possible way of building artificial enzymes. This section of the review will focus on the incorporation of any structures that contain or mimic the enzymatic prosthetic groups into MOFs that can perform functions, especially for biomimetic catalysis, biosensing/imaging, and biomedical applications.

3.1 MOFs as biomimetic catalysts

3.1.1 MOFs with unsaturated metal centers (UMCs)

Early studies on biomimetic MOFs were focused on the imitation of the coordination environments that exist in hemes or cobalamins. The iron in a heme adopts a square pyramidal geometry coordinated by the porphyrin ring and the axial histidine residue (Figure 10 (a)), engendering an uncoordinated site on iron which can bind gas molecules. Similar to hemes, cobalamin found in Vitamin B₁₂ consists of a cobalt center which, in the base-on mode [228], adopts a distorted square pyramidal geometry by a corrin ligand [229]. Similar structures were discovered in PCN-9 whose SBUs contain four Vitamin B₁₂-like cobalt centers sharing a μ_4 -oxo bridge, generating four unsaturated metal centers (UMCs) that are suitable for selective binding of gases (Figure 10 (b)) [230]. Cobalamin is

often found coordinated to methyl (methylcobalamin) [231] or cyano (Vitamin B₁₂) groups on its uncoordinated metal site. PCN-9, with SBUs resembling the structure of cobalamin cofactors, should have a high CH₄ affinity as well. Indeed, the adsorption enthalpies of H₂ and CH₄ in PCN-9 are extraordinarily high values. Its adsorption enthalpy for H₂ is 10.1 kJ·mol⁻¹, and for CH₄ is 23.3 kJ·mol⁻¹ [230].

Fig. 10 (a) A schematic representation of the active site of hemoglobin. The golden sphere represents the iron center. (b) The Co₄(μ₄-O)(carboxylate)₄ SBU in PCN-9 which resembles the UMC in cobalamin. Color scheme: gray, C; pink, Co; and red, O. (Figure 10(a) was reprinted with permission from Ref. [230], copyright 2006 American Chemical Society)

Similar interactions between entatic metal centers and H₂ have also been observed in manganese-based MOFs and corroborated by neutron powder diffraction (NPD) experiments [232]. This MOF, with the formula [Mn(DMF)₆]₃[(Mn₄Cl)₃(BTT)₈(H₂O)₁₂]₂, consists of the Mn₄(μ₄-Cl)(tetrazolate)₄ SBU connected by BTT linkers (BTT= 1,3,5-benzenetristetrazolate). (Figure 11) In this MOF, square pyramidal geometry is adopted by the Mn-containing SBU that resembles the coordination mode of metalloporphyrins with four UMCs per SBU. Based on both computational and experimental studies, it has been well-established that UMCs can enhance the H₂ adsorption enthalpy via increased metal-H₂ interactions. The H₂ adsorption enthalpy of this MOF is 10.1 kJ·mol⁻¹. The enhancement of H₂ adsorption enthalpy by introducing UMCs into MOFs has already been comprehensively reviewed elsewhere [11].

Fig. 11 (a) A graphic representation of the Mn₄(μ₄-Cl)(tetrazolate)₄ SBU in this MOF. After activation, each Mn center adopts a square pyramidal geometry. (b) The crystal structure of this MOF. Color scheme: gray, C; blue, N; pink, Mn; and green, Cl. The H atoms and the trapped counterions were omitted for clarity.

3.1.2 MOFs with trapped metalloporphyrin

Metalloporphyrins are one of the most famous and well-studied enzymatic prosthetic groups. Porphyrins are a group of highly conjugated heterocyclic organic compounds which, upon metallation, carry out many important biochemical processes. One of the most well-known metalloporphyrin families, the heme, consists of an iron atom located in the center of a porphyrin ring. In proteins such as hemoglobin and myoglobin, reversible binding of O₂ occurs at the metalloporphyrin center. It is conceivable that synthetic metalloporphyrins can perform catalytic transformations in a similar fashion as enzymes without complicated protein machinery [220]. The thermal and chemical stability of metalloporphyrins make them promising building units for porous biomimetic solids with tunable chemical, physical, and catalytic properties [233].

However, some limitations have been revealed for this type of chemistry. The most notable problem is that metalloporphyrins are susceptible to dimerization via oxo-bridging interactions, which terminates its catalytic activity via blocking of the active site [220]. In order to solve this problem and construct metalloporphyrin-incorporated artificial enzymes, several distinctive strategies were developed: (1) encapsulation of porphyrins into the cavities of porous materials (silica [234], surface modified silica [235, 236], synthetic molecular sieves [237], clays [238], layered metal oxide semiconductors (LMOS) [239], zeolites [240], diamond nano-particles [241], and MOFs [242-246]), (2) immobilization of the porphyrin into the struts of a framework (hydrogen bond network solids [247] and MOFs [248-265]), and (3) appending the porphyrin onto a surface (Fullerenes [266, 267] and nanotubes [268, 269]).

Due to their structural regularity and permanent porosity, MOFs are promising materials for the construction of artificial enzymes [220]. They can be used to incorporate the entire protein or peptide. Most MOFs have pores too small for enzyme incorporation, but the inclusion of a few selected proteins into MOFs with ultra-large pores was successful [270-272]. On the other hand, incorporation of active sites and their mimics into MOFs is a convenient way to build biomimetic catalysts. In this section of the review, we would like to focus on the incorporation of such features into MOFs and discuss the resulting structures and activities.

A straightforward way to construct biomimetic catalysts is to trap the biomimetic centers, such as a metalloporphyrins, into porous materials. A number of considerations must be taken to plan such an experiment. The host that is suitable for the incorporation of porphyrin should possess several attributes [242]: (1) the cavity should be large enough for the encapsulation of porphyrin; (2) the framework should be synthesized in mild conditions and should retain its integrity upon subsequent metalation or catalytic processes; (3) host-guest interactions are preferred to facilitate the encapsulation process; (4) the framework should have a low affinity toward the products, allowing an effective separation of final products from starting materials.

Rho-ZMOF [273] (topologically analogous to zeolite **rho**) was selected as a candidate to form a porphyrin encapsulated framework. Free porphyrin was trapped during formation of the framework due to electrostatic interactions. The **rho**-ZMOF is formulated as [In₄₈(HImDC)₉₆]⁴⁸⁻ (H₃ImDC= 4,5-imidazoledicarboxylic acid), where the negatively charged framework is balanced by cationic guest molecules. Introduction of 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin tetra(*p*-toluenesulfonate) ([H₂TMPyP][*p*-tosyl]₄) during its synthesis provides a trapped [H₂TMPyP]⁴⁺ cation (See Electronic Supplementary Material, Section 1). (Figure 12 (a)) The incorporation of porphyrin units was confirmed by solid-state UV-Vis studies of the resulting product, the spectrum shows five characteristic absorption bands of free porphyrin (λ_{max} = 434, 522, 556, 593, 648 nm) (Figure 12 (b)). To investigate its catalytic properties, the oxidation of hydrocarbons was tested. Under mild conditions, the cyclohexane was oxidized by *tert*-butyl hydroperoxide (TBHP) to yield cyclohexanol or cyclohexanone. A total yield (from cyclohexane to cyclohexanol/cyclohexanone) of 91.5% and a corresponding turn over number (TON) of 23.5 were observed (Figure 12 (c)).

Fig. 12 The crystal structure of rho-ZMOF and an illustrative representation of the incorporation of [H₂TMPyP]⁴⁺ cation into its cavity. (b) the solid-state UV-Vis spectroscopy confirms the encapsulation of free porphyrin. (c) the catalytic activity of rho-ZMOFs with Mn[TMPyP] incorporated (Reprinted with permission from Ref. [242], copyright 2008 American Chemical Society)

The porphyrin was encapsulated into the **rho**-MOF cage by the electrostatic attractions between the negatively charged framework and the positively charged [H₂TMPyP]⁴⁺ cations. Consequently, there is no preference for the orientation of the encapsulated metalloporphyrin in the framework, which means that the inclusion of the porphyrin could not be verified by single-crystal XRD due to the highly disordered porphyrin molecules [242]. In most enzymatic structures, the metalloporphyrin has a specific orientation in the peptide scaffold allowing for greater control over reactions. To construct such a material with regular orientation of its “active sites”, porphyrin encapsulation within specific cages associated with HKUST-1 was demonstrated [243].

HKUST-1 is constructed from benzene-1,3,5-tricarboxylate (BTC) and copper(II) [274] or zinc(II) [275] paddlewheels. As expected, the metalloporphyrin, tetrakis(4-sulphonatophenyl)porphyrin (TSP, see Electronic Supplementary Material, Section 1), was encapsulated within the octahedral cage of HKUST-1-Cu, presumably because the octahedral cages have appropriate size and symmetry. (Figure 13 (a)) The remaining cavities create channels that allow small molecules to reach the active sites. This is analogous to substrate channels in heme proteins [243]. The penetration of the benzenesulfonic acid groups on each porphyrin molecule into neighboring cages locks the metalloporphyrin into a well-defined orientation. Both axial sites of the metalloporphyrin remain exposed to the cavities of the framework (Figure 13 (b)) [243]. Although the porphyrin possesses a specific orientation in an

individual cage, overall the porphyrin may occupy any of the three equivalent orientations in the octahedral cages (Figure 13 (c)). This MOF has been demonstrated as a biomimetic catalyst with its peroxidase activity. This was confirmed by utilization of 2,2'-azinodi(3-ethylbenzthiazoline)-6-sulfonate (ABTS) as a redox indicator. Metalloporphyrin units were successfully incorporated in to HKUST-1-Zn in a similar way [244], where the HKUST-1-Zn is topologically equivalent to HKUST-1-Cu.

Fig. 13 (a) The graphic representation of three different cages in HKUST-1. Metalloporphyrin molecules are exclusively encapsulated in its octahedral cages. (b, c) The encapsulation of metalloporphyrin into the octahedral cages in two equivalent orientations. (Reprinted with permission from: Ref. [243], copyright by 2011 American Chemical Society)

The incorporated metalloporphyrins have not only been validated as effective biomimetic catalysts, but have also demonstrated to function as MOF formation templates. In this aspect, they facilitate the construction of MOFs with new structures or metal centers that had previously not been seen. Development of the aforementioned work has been slowed by the fact that the **tbo** topology MOFs such as HKUST-1 require “square paddlewheel” nodes that are not readily accessible by metals other than Cu^{2+} and Zn^{2+} [274, 275]. However, in a recent paper, the metalloporphyrin units appear to be an efficient template for the synthesis of HKUST-1 analogs. In particular, porph@MOM-4, -5, and -6 (“porph@MOM” represents “Porphyrin at Metal-Organic Materials”) are constructed from BTC and Fe, Co and Mn respectively. These frameworks are isostructural with HKUST-1-Cu and HKUST-1-Zn. (Figure 14 (a)) Porph@MOM-7 and -8 were constructed using Ni and Mg; and porph@MOM-9 was constructed from BTC and Zn in DMA. During their syntheses, the meso-tetra(N-methyl-4-pyridyl)porphine tetratosylate (TMPyP, see Electronic Supplementary Material, Section 1) serves as a template to form these frameworks. (Figure 14 (b)) It should be noted that there are three types of cages in the structure of HKUST-1: rhombicuboctahedral, octahemioctahedral, and tetrahedral cages. (Figure 14 (c)) However, the TMPyP molecules are exclusively encapsulated in the octahemioctahedral cages for two reasons. First, the O_h symmetry of the octahemioctahedral cages closely matches the D_{4h} symmetry of the TMPyP molecules, since D_{4h} is a subgroup of O_h . Second, the octahemioctahedral cages has the right size and shape to accommodate the bulky TMPyP molecule, while its four arms (N-methyl-4-pyridyl groups) could extend to four adjacent cages. (Figure 14 (b)) The successful incorporation of metalloporphyrin units can be crystallographically substantiated, and the units are disordered in three equivalent positions. The incorporated metalloporphyrin was able to catalyze the olefin oxidation reaction, a classic heme-catalyzed reaction [245].

Fig. 14 (a) The building units of porph@MOMs where porphyrin was used as a template. (b) The representation of an octahedral cage (in turquoise) in which the porphyrin was encapsulated. (c) The framework structure of HKUST-1 that contains three distinct cages: large rhombihexahedral cages (pink), medium-sized octahedral cages (turquoise), and small tetrahedral cages (green). Porphyrin was encapsulated exclusively in the turquoise octahedral cages. (Reprinted with permission from Ref. [245], copyright by 2012 American Chemical Society)

Similarly, porph@MOM-10 was prepared using an analogous tritopic ligand, biphenyl-3,4',5-tricarboxylate (H_3BPT) with $Cd(II)$ in the presence of metalloporphyrin molecules acting as a template [246]. Projection of its crystal structure along the c axis reveals that there is a 1:1 ratio of two types of square channels (Figure 15 (a)): Channel A with pore size of about $12.6 \text{ \AA} \times 12.6 \text{ \AA}$ and Channel B with pore size of about $11.9 \text{ \AA} \times 11.9 \text{ \AA}$, where channel A was exclusively occupied by the $CdTMPyP$ cations, and channel B was occupied by solvent molecules. A closer examination of its SBUs reveals that there are two distinct types of $Cd(II)$ center ($Cd1$ and $Cd2$). $Cd2$ adopts a distorted octahedral geometry via coordination to four carboxylate oxygen atoms, an aqua ligand, and a μ_2 -chloride anion, while $Cd1$ possesses distorted octahedral geometry through four carboxylate oxygen atoms and two μ_2 -chloride anions (Figure 15 (b)) [246]. With a longer ligand and thus a larger cavity, porph@MOM-10 catalyzes the epoxidation of larger olefins such as *trans*-stilbene.

Fig. 15 (a) The representation of the crystal structure of porph@MOM-10 viewed along c axis. (b) The representation of the coordination modes of Cd(II) in porph@MOM-10. (c) An illustration of Channel A with the metalloporphyrin encapsulated. (Reprinted with permission from Ref. [246], copyright by 2012 American Chemical Society)

3.1.3 MOFs with metalloporphyrin as organic linker

The incorporation of metalloporphyrins into MOF struts has been demonstrated as another efficient way to construct MOFs with various functionalities. The artificial synthesis of porphyrins [276] has inspired scientists to synthesize MOF structural ligands with both a porphyrin center and coordinating moieties (carboxylic acids, pyridines, *etc.*). Currently, a variety of metalloporphyrin-incorporated MOFs have been synthesized [248-265]. Their ligands, catalytic / biomimetic activities and the corresponding references are summarized in Table 1. While this manuscript is under review, a few other reviews that discuss porous MOFs with metalloporphyrin linkers were published [277, 278].

The majority of the metalloporphyrin-incorporated MOFs possess catalytic activity. When the axial ligands are removed, UMCs in the center of metalloporphyrins are created. It is at the UMC where the catalytic reactions can take place. This is quite similar to a great number of metalloporphyrin enzymes such as cytochrome P450. An illustrative example of the catalytic capability of these MOFs is ZnPO-MOF developed by Hupp, Nguyen and coworkers [249]. ZnPO-MOF is constructed from a metalloporphyrin pyridyl ligand with Zn (II) with TCPB as a co-ligand (TCPB=1,2,4,5-tetrakis(4-carboxyphenyl)benzene, See Table 1 and Electronic Supplementary Material, Section 1). This MOF is permanently porous, with a surface area of approximately $500 \text{ m}^2 \cdot \text{g}^{-1}$. It performs an acyl-transfer reaction between N-acetylimidazole (NAI) and 3-pyridylcarbinol (3-PC). A 2420-fold rate enhancement relative to the uncatalyzed reaction was observed and a reaction mechanism of the catalytic process was provided (Scheme 3).

Table 1 A list of selected metalloporphyrin-incorporated MOFs and their catalytic/biomimetic activities

MOF	Metalloporphyrin ligand	Co-ligand ^b	Metal	Catalytic / biomimetic activities	Ref
NAFS-1		Py	Cu(II)	N/A	[248]
Co-TCPP					
ZnPO-MOF		TCPB	Zn(II)	acyl-transfer reaction	[249]
Zn-Porphyrin					
RPMs		metal-TCPP complexes	Zn(II)	epoxidation of styrene, and hydroxylation of cyclohexane	[250]
Al ³⁺ , Zn ²⁺ , Pd ²⁺ , Fe ³⁺ , Mn ³⁺ complexes					

Mn-Porphyrin MOF rods ^a		N/A	In(III)	olefin epoxidation	[251]
Mn-Porphyrin					
Metalloporphyrin-POM-based hybrid framework ^a		N/A	Cd(II) as metal center; (P W ₁₂ O ₄₀) ³⁻ as counter ions	oxidation reaction of alkylbenzene	[252]
Mn-TPyP					
MMPF-1		isophthalic acid	Cu(II)	N/A	[253]
Cu-BDCPP					
Pd(II)-porphyrin-based MOF ^a		N/A	Cd(II)	selective oxidation of styrene	[254]
Pd-TPyP					

Al-PMOF	Free base TCPP	N/A	Al(III)	photocatalysis of water splitting (upon metalation of Zn)	[255]
PCN-222 ^c	Free base TCPP	N/A	Zr(IV)	biomimetic phenol oxidation (upon metalation of Fe)	[256]
MMPF-6 ^c	Fe(III)Cl-TCPP	N/A	Zr(IV)	biomimetic oxidation of THB and ABTS	[257]
MOF-525 ^c	Free base TCPP	N/A	Zr(IV)	N/A	[258]

MIL-141	Ni-TCPP	N/A	Fe(III)	preferentially O ₂ adsorption over N ₂	[259]
ZJU-18,19,20	Mn(III)Cl-TDCPP or Ni(II)Cl-TDCPP	N/A	Mn(II) or Cd(II)	selective catalytic oxidation of alkylbenzenes	[260]
MMPF-2,4,5	Free base TDCPP	N/A	Co(II), Zn(II) or Cd(II)	N/A	[261, 262]
PCN-221	Free base TCPP	N/A	Zr(IV)/Hf(IV)	cyclohexane oxidation (upon metalation of Fe)	[263]

PCN-224		N/A	Zr(IV)	CO ₂ and propylene oxide coupling reaction (upon metalation of Co)	[264]
Free base TCPP					
PCN-225		N/A	Zr(IV)	fluorescent pH sensor	[265]
Free base TCPP					

^a The author didn't provide a name for this MOF in the original paper.

^b The chemical structure of co-ligands are summarized in Electronic Supplementary Material, Section 1.

^c PCN-222 is also known as MOF-545 and MPPF-6. This MOF was independently reported by Yaghi, Zhou and Ma groups [257, 258].

Scheme 3 A proposed mechanism of acyl-transfer reaction catalyzed by ZnPO-MOF.

To accurately mimic many biological systems, it is highly desirable to design MOFs with improved water stability [279]. The majority of MOFs are composed of coordination bonds between divalent metal ions and carboxylate ligands. These bonds are often susceptible to hydrolysis, greatly limiting their application in an aqueous medium. However, judicious choice of metals used in the construction of MOFs will help overcome the current instability issue. Carboxylate based MOFs are usually water-stable when they contain high-valence metals such as Al(III), Cr(III), Fe(III), Zr(IV), and Hf(IV) [8, 280]. Most of the reported MOFs with these metal ions have excellent mechanical, chemical and thermal stability due to the strength of the M–L bonds, which can be ascribed to the high charge densities (Z/r values) of these metal ions. Two recent examples clearly prove this concept and demonstrate promising biomimetic catalytic applications.

A porphyrin-incorporated MOF, PCN-222, reported by Zhou group, was constructed from zirconium metal nodes and four-connected TCPP ligands (TCPP= 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin, See Table 1 and Electronic Supplementary Material, Section 1) [256]. In an optimized procedure, FeCl_2 and ZrCl_4 were reacted with H_4TCPP in the presence of benzoic acid in DMF. Under solvothermal conditions crystalline PCN-222(Fe) (Fe-porphyrin) was prepared with properties (such as chemical stability and catalytic activity) superior to those of many existing MOFs. PCN-222 has a large open channel of 3.7 nm in diameter, one of the largest reported for mesoporous MOFs (Figure 16). Activated PCN-222 samples possess permanent pores. Nitrogen adsorption isotherm at 77 K showed typical type IV behavior with a steep increase at the point of $P/P_0 = 0.3$, indicative of its mesoporous nature (Figure 17). The BET surface area was calculated to be $2200 \text{ m}^2\cdot\text{g}^{-1}$, and the total pore volume is $1.56 \text{ cm}^3\cdot\text{g}^{-1}$, which is among the highest values reported for all porous materials containing porphyrins. Most importantly, PCN-222 exhibits extraordinary stability among all MOFs. From powder X-ray diffraction patterns, PCN-222 retains its crystallinity upon immersion in boiling water, and 2 M, 4 M, 8 M, and concentrated hydrochloric acid solutions for 24 h, suggesting no phase transition or framework collapse during these treatments (Figure 17A). The N_2 adsorption isotherms also remained the same after each treatment of water or acid, which further confirmed the remarkable stability of PCN-222 (Figure 17B). To the best of our knowledge, PCN-222 is the only reported MOF that can undergo treatment with concentrated hydrochloric acid and retain its structure. We postulate that the Zr_6 cluster is responsible for the exceptional stability of PCN-222(Fe). The Zr(IV) ion, with its high charge density, polarizes the oxygen atoms of the carboxylate groups to form strong Zr–O bonds with significant covalent character. Furthermore, the chelating effect between porphyrin and Fe^{3+} further stabilizes the overall framework.

The peroxidase-like catalytic activity of PCN-222 was evaluated with a variety of metalloporphyrins for the oxidation of several substrates. In natural systems, peroxidases regulate the concentration of hydrogen peroxide in biofluids. PCN-222 with iron centers exhibited excellent peroxidase-like catalytic activity, while PCN-222 with other metal centers did not show significant activity under identical conditions. An enzyme kinetics study for PCN-222(Fe) was performed and the kinetic parameters k_{cat} and K_m were derived. The k_{cat} value gives the maximum number of substrate molecules catalyzed per molecule of catalyst per unit time. K_m is the Michaelis constant and indicates the affinity of the catalyst molecules for the substrate. For the pyrogallol oxidation reaction, k_{cat} of the PCN-222(Fe) catalyst shows a high value of 16.1 min^{-1} , which is 7-times higher than k_{cat} of free hemin (2.4 min^{-1}). The K_m value (around 0.33 mM) is lower than that of the natural enzyme HRP (horseradish peroxidase, 0.81 mM), indicating a better affinity of the substrate to PCN-222(Fe), resulting from the high porosity of PCN-222(Fe). Other substrates such as 3,3',5,5'-tetramethylbenzidine and *o*-phenylenediamine have also been tested for peroxidase-like oxidation to demonstrate the general applicability of PCN-222(Fe) as an enzyme mimic. PCN-222(Fe) showed superior catalytic activity over free hemin, as its k_{cat} was nearly ten times higher than that of free hemin [141]. It should be noted that a similar MOF, MMPF-6, was also reported by Ma group, where similar biomimetic oxidation reactions was observed. MMPF-6 efficiently catalyzes the oxidation of 1,2,3-trihydroxybenzene (THB) to purpurogallin, and the oxidation of 2,2'-azinodi(3-ethylbenzothiazoline)-6-sulfonate (ABTS) to ABTS cation radical [257]. Another similar MOF with free base porphyrin as its organic linker was independently reported by Yaghi group [258].

Fig. 16 Crystal structure and underlying network topology of PCN-222(Fe). The M-TCPP (blue square, A) is connected to four 8-connected Zr₆ clusters (light orange cuboid, B) with twisted angle to generate a 3D network in Kagome-like topology with 1-D large channels (green pillar, C). The overall structure is shown in D, and topology in E. (Reprinted with permission from Ref. [256], copyright 2012 John Wiley and Sons)

Fig. 17 (a) Powder X-ray diffraction pattern and (b) N₂ adsorption isotherms for PCN-222(Fe) at 77 K, showing the framework stability of PCN-222(Fe) upon the treatments with water, boiling water, 2 M, 4 M, 8 M and concentrated hydrochloric acid. (Reprinted with permission from Ref. [256], copyright 2012 John Wiley and Sons)

The ongoing study of zirconium porphyrinic MOFs led to the discovery of a series of MOFs, namely the PCN-22X series (PCN-221, 222, 224 and 225). PCN-222, PCN-224 and PCN-225 are based on the extremely stable Zr₆ clusters. Meanwhile, PCN-221 is based on a rarely seen Zr₈ cluster, which was unknown in both cluster and MOF chemistry. The dihedral angle between the phenyl ring of a TCPP ligand and the porphyrin plane is 54.12° in Zr₆-based PCN-222. In contrast, the four peripheral phenyl rings are perpendicular to the porphyrin in PCN-221 [263]. Each TCPP ligand connects four Zr₈ clusters in a 4-connected mode, in which each carboxylic acid coordinates one Zr₈ cluster (Figure 18 (a)). The structure of PCN-221 features two types of polyhedral cages with pore openings of ~0.8 nm. The small cage, an octahedral cage with a cavity diameter of ~1.1 nm, comprises two Zr₈ clusters in the axial sites and four TCPP ligands in the equatorial plane (Figure 18(d)). The other cage, a cubic cage with edge length of ~2.0 nm, is surrounded by eight Zr₈ clusters at the vertices and six TCPP ligands at the faces (Figure 18(e)). The solvent accessible volume of PCN-221 is 70.5%. The BET surface areas are 1936 and 1549 m²·g⁻¹ for Zr-PCN-221(no metal) and Zr-PCN-221(Fe), respectively. Zr-PCN-221(Fe) was then explored as a heterogeneous catalyst for cyclohexane oxidation in the presence of tert-butyl hydroperoxide (TBHP) as an oxidant. After 11h, the TBHP utilization efficiency was close to 100%, while the selectivity of the PCN-221 catalyst is mainly toward cyclohexanone (86.9%) and a small amount of cyclohexanol (5.4%) is also produced. The high reactivity and selectivity can be attributed to the high density of accessible active porphyrinic iron(III) centers within the porous framework.

Fig. 18 (a) TCPP-Cu ligand is 4-connected to four Zr₈ clusters. (b) Schematic representation of the (4,12)-connected 3D network of PCN-221 with ftw topology, in which Zr₈ cluster and TCPP ligand are simplified as aqua dodecahedral and brown square nodes, respectively. (c) View of the 3D structure of PCN-221 along the a-axis. (d) Octahedral and (e) cubic cages comprised Zr₈ clusters and organic linkers in PCN-221. Color Scheme: Zr, aqua; C, dark gray; O, red; N, blue; Cu, gold. H atoms are omitted for clarity. (Reprinted with permission from Ref. [263], copyright 2013 American Chemical

Society)

PCN-224, another zirconium porphyrinic MOF with 3D nanochannels, has been assembled with six-connected Zr_6 clusters and metalloporphyrins by a linker-elimination strategy. (Figure 19) The PCN-224 series not only exhibits the highest BET surface area ($2600 \text{ m}^2\cdot\text{g}^{-1}$) among all the reported porphyrinic MOFs, but also remains intact in a wide pH range, from pH = 0 to pH = 11 in aqueous solution. This is a great improvement over PCN-222, which is not stable in basic conditions. PCN-224(Co) exhibits high catalytic activity for the CO_2 /propylene oxide coupling reaction and can be used as a recoverable heterogeneous catalyst [264]. PCN-225 with two types of open channels was synthesized by the same group. It features a (4,8)-connected net with **sqc** topology. Due to the remarkably extensive pH stability and pH-dependent fluorescent intensity, PCN-225 can potentially be applied in fluorescent pH sensing [265].

Fig. 19 (a, b) Microscope images of PCN-224(Ni) and PCN-224(no metal), respectively. (c) The 6-connected D_{3d} symmetric Zr_6O_8 clusters in PCN-224. (d) Tetratopic TCPP ligands (violet square) with twisted dihedral angles generate a framework with 3D nanochannels. (e) The crystal structure of PCN-224(Ni). Color scheme: Zr, green spheres; C, gray; O, red; N, blue; Ni, orange; and H, white. (f) The underlying network topology of PCN-224(Ni) (Reprinted with permission from Ref. [264],

A water-stable aluminum porphyrin MOF, named as Al-PMOF, was reported by Rosseinsky and coworkers. This porous MOF, with a BET surface area of $1400 \text{ m}^2\text{g}^{-1}$, performs visible-light-driven hydrogen generation from water with the help of Pt as co-catalyst and ethylenediaminetetracetic acid (EDTA) as a sacrificial electron donor (Figure 20) [255]. The reaction of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ with H_2TCPP in water under hydrothermal conditions at 180°C gives the red, crystalline compound Al-PMOF. Each porphyrin linker is coordinated to eight aluminum centers (Figure 20) through the four carboxylate groups. Like the common motif for Al^{3+} frameworks with carboxylate ligands, Al-PMOF has an infinite $\text{Al}(\text{OH})\text{O}_4$ chain constructed by two μ_2 axial OH bridges adjacent Al^{3+} centers and four carboxylate oxygen atoms in the equatorial plane. The structure of Al-PMOF was solved and refined from synchrotron powder X-ray diffraction and further confirmed by solid-state NMR spectroscopy. The freebase porphyrin in Al-PMOF is metalated with zinc in the MOF structure, resulting in a purple solid with high potential for hydrogen evolution. Two experimental approaches were compared for hydrogen generation, both with and without the methyl viologen dication (MV^{2+}) as an electron acceptor and transfer mediate to Pt. In the absence of MV^{2+} , MOF/EDTA/Pt system produces H_2 at a $100 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ rate for zinc-substituted Al-PMOF and a $200 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ rate for Al-PMOF. A control experiment in MOF-filtered solution confirms the H_2 is produced by heterogeneous photocatalytic activity of the MOF.

Demonstrated by the above stable biomimetic MOFs, the focus of current research is not only to establish new series of water-stable and biocomponent-containing MOFs but to also enhance the properties of the materials with large open channels and tunable functionalities towards biomimetic catalysis.

Fig. 20 (a) Structure of the Zn^{2+} -metalated porphyrin unit. (b) Crystal structure of Al-PMOF viewed from [010] direction. (c) The photocatalytic reaction through two approaches. (d) Photocatalytic evolution of hydrogen from water by Al-PMOF (1) and Zn-metalated Al-PMOF (2) under visible-light illumination, using sacrificial EDTA with catalytic colloidal platinum. (Reprinted with permission from Ref. [255], copyright by 2012 John Wiley and Sons)

3.1.4 MOFs with iron-sulfur clusters

Besides metalloporphyrins, iron-sulfur clusters are another important family of prosthetic groups, which, upon incorporation into proteins, perform a great variety of important biological functions, including catalysis, electron transfer, oxygen sensing and stabilization of protein conformations [281, 282]. In particular, hydrogenase is a category of metalloenzymes that efficiently catalyzes the proton reduction reaction to produce molecular hydrogen. [283-285] The majority of the discovered hydrogenases contain iron-sulfur clusters [286]. Much effort has been made in the preparation of the structural or functional analogs of hydrogenases, for the purpose of designing biomimetic hydrogen generation catalysts [287, 288]. However, most of these biomimetic catalysts suffer from limited stability, particularly when used in conjunction with photosensitizers [289]. There are several advantages associated with incorporating analogous structures of the iron-sulfur cluster into MOFs. First, the MOF struts serve as an external matrix to support the biomimetic active sites, and thus the stability of these biomimetic hydrogen generation catalysts should be improved [290]. Second, the channels or cavities in MOF can serve as the “grooves” or “pockets” of enzymes, which resemble the active site machinery of metalloenzymes.

An organometallic diiron complex that is structurally analogous to the active site of [FeFe] hydrogenase was successfully incorporated into MOFs [290]. A water-stable MOF, UiO-66, was selected to be the host of the biomimetic diiron structure [279]. However, direct incorporation of the diiron complex into UiO-66 during solvothermal synthesis resulted in a decomposition of the cluster. Post-synthetic ligand exchange was employed to incorporate the biomimetic diiron structure, where the original BDC ligand (BDC=1,4-benzenedicarboxylate, see Figure 21) was exchanged with the diiron-complex-bearing DCBDT ligand (DCBDT=1,4-dicarboxylbenzene-2,3-dithiolate, see Figure 21) in deoxygenated ultrapure water at room temperature. (See Figure 21) The diiron-complex-incorporated UiO-66 was separated as an orange crystalline material, which, upon activation, possesses a BET surface area of $1357 \pm 25 \text{ m}^2\cdot\text{g}^{-1}$, suggesting that a genuine post-synthetic ligand exchange, rather than a simple encapsulation of DCBDT ligand into the MOF cavities, takes place in the UiO-66 structure. Powder XRD study shows retention of the crystallinity of UiO-66 framework.

Fig. 21 A graphic illustration of the post-synthetic ligand exchange process of UiO-66 Structure. (Reprinted with permission from Ref. [290], copyright 2013 American Chemical Society)

A catalytic activity test was conducted on the diiron-complex-incorporated UiO-66. This MOF demonstrates a photochemical hydrogen production activity in the presence of $[\text{Ru}(\text{bpy})_3]^{2+}$ as the photosensitizer and ascorbate as the sacrificial electron donor at pH=5. Under these conditions, hydrogen production can be observed and quantified by a hydrogen-specific solid-state sensor. The diiron centers can be reduced and then catalyze the reduction of protons to generate molecular hydrogen (See Figure 22 (a)). It should be noted that the hydrogen production activity of this MOF is significantly improved over the homogenous catalytic system where an equivalent concentration of the diiron complex is present in the solution under the same reaction condition. Additionally, a control experiment was carried out on the unmodified UiO-66, where no hydrogen generation was observed. (See Figure 22 (b)) [290].

Fig. 22 (a) A schematic representation of the process of photochemical hydrogen productions. (b) Photocatalytic hydrogen production of the diiron-complex-incorporated UiO-66 (blue), the homogeneous solution of the diiron complex (red), the original UiO-66 (black) and the background (gray). (Reprinted with permission from Ref. [290], copyright 2013 American Chemical Society)

3.1.5 MOFs with trapped proteins

In the previous sections, we have covered the construction of biomimetic catalysts by incorporating an enzyme's active site into the struts or cavities of a MOF. A more intuitive and straightforward way is to incorporate the entire enzyme into the MOF cavities. Regardless of their high selectivity and specificity, the utilization of enzymes is largely limited by their low stability and recyclability under industrially necessary conditions [291]. The enzymatic activity of a protein that is isolated from biological system is largely dependent on its structural stabilization within the unnatural environment [221]. Much effort has been made in the incorporation of enzymes

into mesoporous silica, presumably due to its easy synthesis and tunable pore size. However, the lack of specific interaction between enzymes and mesoporous silica has significantly reduced the reactivity and reusability of the incorporated enzymes [272]. Alternatively, the large porosity, high crystallinity and easy functionalization process of MOFs have made them especially promising for enzyme stabilization. In particular, many MOFs with ultralarge cavities were reported in recent years [292, 293]. Ma and coworkers have investigated the incorporation of enzymes into MOFs [270-272]. In their work, a reported mesoporous MOF named Tb-TATB was utilized. This MOF contains microscopic cages with diameters of 3.9 and 4.7 nm (Figure 23), and exhibits a characteristic type-IV sorption isotherm [293]. The mesoporous cavities inside this MOF are large enough to accommodate some small proteins such as microperoxidase-11 [272] (MP-11, with a size of $3.3 \times 1.7 \times 1.1$ nm [294], Figure 24 (a)), cytochrome c [271] (Cyt c, with a size of $2.6 \times 3.2 \times 3.3$ nm [295], Figure 24 (b)) and even myoglobin [270] (Mb, with a size of $2.1 \times 3.5 \times 4.4$ nm [296], Figure 24 (c)).

Fig. 23 (a) A graphic representation of the topology and the cavities of the mesoporous Tb-TATB MOF. The two types of cages are highlighted in green and pink. (b) A 3.9 nm diameter cage and a 4.7 nm diameter cage interconnected through 1.3 and 1.7 nm windows in Tb-TATB MOF. Color scheme: C, gray; O, red; N, blue; Tb, turquoise. (Reprinted with permission from Ref. [271], copyright 2012 American Chemical Society)

Fig. 24 The molecular structures and sizes of (a) microperoxidase-11 (MP-11), (b) cytochrome c (Cyt c), (c) myoglobin (Mb).

The protein-included MOFs possess both permanent porosity and catalytic activity. For example, MP-11 catalyzes the peroxidation process of organic molecules in the presence of hydrogen peroxide [297]. However, the aggregation of free MP-11 molecules has severely limited its catalytic activity [298]. Incorporation of MP-11 into a solid matrix, such as a MOF, has significantly improved the stability of the “free” molecules of this enzyme [272]. The Tb-TATB MOF with MP-11 incorporated is still porous, even though its BET surface area has dropped from $1935 \text{ m}^2 \text{ g}^{-1}$ to $400 \text{ m}^2 \text{ g}^{-1}$ after the MP-11 uptake was saturated. The porosity of MP-11@Tb-TATB allows substrate to access the active center of the trapped MP-11 molecules. The catalytic activity of MP-11@Tb-TATB was evaluated by observing the reaction rate of oxidation of polyphenols in the presence of hydrogen peroxide. The catalytic activity of MP-11@Tb-TATB is almost 29 times larger than the original Tb-TATB framework. It should be noted that free MP-11 enzymes have shown an even higher catalytic activity at the initial stage; however,

they quickly lost their activity after a few minutes owing to MP-11's aggregation in solution [272]. The high catalytic activity and recyclability of MP-11@Tb-TATB has provided a novel way to immobilize enzymes into solid matrices for catalytic applications.

3.2 Functional MOFs as biosensors

MOFs were explored as sensors for metal ions in organic solvents as well as for volatile organic compounds and explosive species in the gas phase. The interaction between targets and MOFs are due to the unsaturated metal sites and/or functionalized frameworks. The selectivity is obtained from the shape and size compatibility between targets and MOFs, and this topic has been extensively reviewed [299, 300]. Here we summarize a new topic, the recent developments of MOFs as biosensors. For a practical biomimetic sensor, it needs durable stability and proper recognition mechanisms in aqueous conditions. Thanks to the recent rapid increase in the number of stable MOFs, especially those constructed from carboxylates with high-valence metals (such as Fe(III) and Zr(IV)) as well as nitrogen-donor ligands (such as ZIFs), it is now more feasible to functionalize MOFs as biomimetic sensors with appropriate recognition mechanisms. The MOFs provide several advantages over natural enzymes, such as ease of preparation, low cost, and good stability, which indicate MOFs should be investigated for potential applications in medical diagnostics.

Jiang and coworkers explored two water-stable Fe(III)-based MOFs, MIL-68 and MIL-100, as biomimetic sensors for either H₂O₂ or ascorbic acid [301]. These two MOFs could perform catalysis of oxidation and show intrinsic peroxidase-like activities because of the active unsaturated Fe(III) centers in MOFs. The catalysis is highly sensitive to H₂O₂ concentration, which could be easily detected by employing 3,3',5,5'-tetramethylbenzidine as substrate and monitoring the absorbance changes at 653 nm, thus generating a biomimetic colorimetric assay for H₂O₂. Moreover, ascorbic acid could inhibit the peroxidase-like activity of Fe(III)-based MOFs. Based on this principle, a colorimetric biosensor for ascorbic acid was developed.

Mao and coworkers exploited the first example of ZIFs as the matrix for integrating dehydrogenase and constructing electrochemical biosensors [302]. *In vivo* measurement of neurochemicals, such as glucose, could be performed with the ZIF-based sensor (Figure 25A). In this study, a series of ZIFs were synthesized and studied as coimmobilizing matrices for integrating electrocatalysts and dehydrogenases because of their advantages, such as tunable pore size, great water stability, biocompatibility and ability to form thin films onto the electrode. The adsorption capabilities toward electrocatalysts (methylene green, MG) and glucose dehydrogenase, GDH) of these ZIFs are studied with UV-Vis spectroscopy, confocal laser scanning microscopy, and Fourier transform-infrared spectroscopy. Among all the ZIFs, ZIF-70 shows excellent adsorption capacities toward both MG and GDH and is thus selected as the matrix for the glucose biosensor. The as-prepared ZIF-70 biosensor is sensitive to glucose with a linear range of 0.1–2 mM (Figure 25B). Moreover, the ZIF-based biosensor is more highly selective to glucose over other endogenous electroactive species in the cerebral system. In the end, the biosensor was tested with the brains of guinea pigs to monitor the dialysate glucose (Figure 25C).

Fig. 25 A) The electrochemical monitoring of glucose in the cerebral system. B) Response for glucose standards from 0.1 mM to 2 mM using the ZIF-70-based biosensor. C) Brain microdialysates of guinea pigs using ZIF-70-based biosensor to validate the glucose detection (red). The control experiments were also established in GDH-free ZIF-70-based sensor (black) and insulin controlled experiment (blue) (Reprinted with permission from Ref. [302], copyright 2013 American Chemical Society)

Lee and coworkers developed “biomimetic tongues” based on the photoluminescence responses of MOFs by multiple recognition mechanisms to discriminate between five basic tastants [303]. The taste sensing capabilities of $[\text{In}(\text{OH})(\text{BDC})]_n$ (BDC=1,4-benzenedicarboxylate), $[\text{Tb}(\text{BTC})]_n$ (MOF-76, BTC=benzene-1,3,5-tricarboxylate), and $[\text{Ca}_3(\text{BTC})_2(\text{DMF})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ were tested in aqueous solutions of five basic tastants: sucrose (sweet), caffeine (bitter), citric acid (sour), sodium chloride (salty) and monosodium glutamate (umami). Successful discrimination between five basic tastants was obtained with three MOFs. The $[\text{In}(\text{OH})(\text{BDC})]_n$ mimics the taste receptor cells (TRCs) for their structural flexibility. The Weber-Fechner law of human sensing, which indicates that sensation is proportional to the logarithm of the stimulus intensity, is observed between the PL emission response of MOF-76 and the concentration of tastant. The tastant is identified by the shape of the 3D principal component analysis contour map.

3.3 MOFs for bioactive nitric oxide release

Nitric oxide (NO) is an important gaseous neurotransmitter and signaling molecule. MOFs are promising candidates for the transportation and release of bioactive NO because of their high porosity and multi-functionality. Although the concepts were proposed for a long time, the development of biocompatible MOFs with high-loading and controlled release for NO is still challenging. The early results measuring NO adsorption in MOFs inevitably followed the prevalent research paradigm in MOFs at that time, just like other famous gas-storage-related applications, such as hydrogen storage, carbon dioxide capture, and methane storage. However, the adsorption measurement of NO in MOFs could only demonstrate its potential NO uptake. It could not be directly shown as evidence for the practical use of these MOFs as NO release materials, especially when Van de Waals interactions are crucial. Possible triggers for NO release from MOFs were then investigated by different means. Water activation, structural dynamics, and immobilization of thermal/light-active molecules into MOFs provided concrete and feasible routes to design practical NO release materials [80, 304].

Morris and coworkers designed and constructed two porous MOFs with metals Co and Ni, which are isostructural to MOF-74 [305]. These two MOFs perform exceptionally well for the adsorption, storage, and delivery of NO (Figure 26). Each UMC in the MOFs fixes one NO molecule, which was investigated by adsorption measurements and powder X-ray diffraction techniques. The adsorption capacity of NO could be as high as $7 \text{ mmol} \cdot \text{g}^{-1}$ on MOF-74-Ni, which is higher than HKUST-1 ($3 \text{ mmol} \cdot \text{g}^{-1}$). More importantly, the MOF-74-Ni could perform well over the whole adsorption-storage-delivery cycle which is particularly difficult for MOFs like HKUST-1 because

of their high binding energy. HKUST-1 only releases $1 \mu\text{mol}\cdot\text{g}^{-1}$, although adsorbing $3 \text{ mmol}\cdot\text{g}^{-1}$, giving 0.03% release efficiency. Meanwhile, MOF-74-Ni nearly delivers all $7 \text{ mmol}\cdot\text{g}^{-1}$ of adsorbed NO by contact with a simple trigger (moisture). Long-term high storage stability was also observed on this material, which is necessary for extended use. The activity of the NO storage materials is proved further in myography experiments showing that the NO-releasing MOFs cause relaxation of porcine arterial tissue. The same group explored flexible MOF as hosts for selective NO adsorption and release. The dynamic MOFs show considerable structural flexibility in response to various external stimuli. A flexible Cu-MOF shows unprecedented low-pressure selectivity towards NO through a gating mechanism driven by coordination [306]. In a perspective, Morris and coworkers further summarized the triggered release methods that can be used to biologically deliver NO, and then showed Ni, Co and Cu-containing MOFs are biologically active materials in other potential applications, such as for anti-thrombosis, wound healing, anti-bacterial use, and vasodilation. The chemical and biological stability and the toxicology of MOFs were discussed in general [307].

Fig. 26 The cycle of activation, loading, storage and delivery of NO in MOF-74-Co and Ni, which are isostructural to MOF-74-Mg. Color Scheme: cyan, Ni/Co; red, O; gray, C; blue, N. (Reprinted with permission from Ref. [305], copyright 2008 American Chemical Society)

Cohen and coworkers successfully developed covalently NONOate-functionalized MOFs via post synthetic modification. The NONOate functional group could release NO with the trigger of protonation under different MOF chemical environments (Scheme 4). Specifically, MOFs containing the NH_2 -BDC ligand could result in as high as $0.5 \text{ mmol}\cdot\text{g}^{-1}$ amounts of NO which were liberated from NONOate-MOFs under aqueous conditions. Although the MOFs are susceptible to hydrolysis and decomposition in water, these results pioneer the demonstration of chemical triggers to produce NO from MOFs [308].

Scheme 4 The mechanism of release of NO from NONOate functional group.

Kitagawa and coworkers employed laser irradiation to release NO from MOFs and tested with localized cells [309]. The nitro group functionalized two ZIF materials were prepared and named NOF-1 and NOF-2. Due to the excellent stability of ZIFs, NOF-1 and NOF-2 could be used in aqueous conditions within a proper pH range. Poly dimethyl silicone (PDMS) was utilized to integrate with NOFs as substrates due to the good diffusion properties of PDMS for gases (Figure 27 (a)). Localized cells with intracellular NO fluorescent indicator were put on the matrices/substrates. At the same time, two-photon near-infrared laser irradiation was developed and applied to photoactivate the NOF materials in order to avoid interference from the fluorescence of the cell itself. It was the first attempt to develop a localized cell stimulation platform by exogenous NO, and provide an opportunity to control and monitor cell signaling networks chemically in time and space. The precise localization of gaseous biomolecules at the single-cell level was achieved (Figure 27 (b)).

Fig. 27 a) An illustration of the localized cell-stimulation platform. Two-photon near-infrared laser irradiates a ZIF-8 analog (NOF-1), modified with nitro group, releasing NO. The generated NO diffuses through PDMS layer and reacts with an intracellular NO fluorescent indicator, DAF-FM. b) Matrix of NOF-1/PDMS by SEM with scale bar of 10 μm in cross-section view. c) Confocal microscopy images of NOF-1-integrated matrices with HEK293 cells introduced via DAF-FM. The emitting green fluorescence demonstrated the NO released from NOF-1 crystals (white dashed line) could locally light up the DAF-FM indicator in the cell through PDMS via diffusion. (Reprinted with permission from Ref. [309], copyright 2013 Nature Publishing Group)

4. Conclusion and Perspective

Biochemical processes have been refined for billions of years and have yielded a great variety of biological molecules with an extraordinarily large diversity in their structures and functions. Borrowing ideas from nature and introducing biological/biomimetic constituents into MOMs appears to be the most straightforward way to construct MOMs with biomimetic functionality. Compared with the rapid growth of MOM chemistry and the ever-expanding database of MOM materials, the study of biomimetic MOMs is still at its initial stage. Nevertheless, it is highly desirable to incorporate greater biomimetic study into MOM chemistry, because it will not only significantly enrich the MOM diversity in architectures and applications, but also bring about a novel perspective to design MOMs with enhanced biological/environmental compatibility, working efficiency, and reduced cost. By dividing the recent advances on biomimetic MOMs into a structural and functional approach, this review also offers a systematic overview on rational design of MOMs with biomimetic features. In particular, utilization of nucleobases or oligosaccharides as organic linkers has yielded a series of MOFs with novel structures, among which the bio-MOF-100 series are among porous materials with the largest pore volumes to date. Incorporation of biological catalysts or their mimics into MOFs has generated a variety of MOFs as biomimetic catalysts or biochemical sensors. For example, the encapsulation of metalloporphyrin units into MOF cavities and integration of them into MOF struts have provided a great assortment of MOFs. PCN-222 is a representative example of a mesoporous MOF with superior chemical stability and biomimetic activities. Biomimetic hydrogen production should be achievable by the incorporation of iron-sulfur complexes into water stable MOFs via post-synthetic modification. Additionally, as new types of MOF with greater stability and larger porosity are reported, incorporating entire enzymes into large-cavity MOFs appears to be a more convenient and straightforward way to construct biomimetic catalysts.

In general, the study of biomimetic MOMs is still in its initial phase and there are several key research challenges to be addressed. First, beside the rich functionalities in MOMs, construction of materials with enhanced chemical stability that will stand up to physiological conditions for biomimetic activities still remains problematic. A few representative cases have been successfully reported, but examples of MOMs that exhibit high stability, large porosity and reduced cost are still relatively rare. Nevertheless, this concern has partially been addressed by the use of abundant, high valence metal ions or clusters. Second, development of new synthetic techniques appears to be necessary in order to synthesize and crystallize biocompatible MOMs, where the utilization of biological molecules with low symmetry and limited solubility in common solvents are often unavoidable. Finally, further exploration of MOMs with ultralarge cavities, preferably with a particular shape, polarity, or with protein-anchoring functional groups, is necessary for study of enzyme immobilization in MOMs. Thanks to the extraordinarily large variety of MOM structures and the exceedingly rapid growth of the MOM field, we believe these challenges can be solved in the near future.

Acknowledgements

This work was supported as part of the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001015, part of the Hydrogen and Fuel Cell Program under Award Number DE-FC36-07G017033, part of the Methane Opportunities for Vehicular Energy (MOVE) Program, an ARPA-e project under Award Number DE-AR0000249 and part of the Welch Foundation under Award Number A-1725. M. B. also acknowledges the Texas A&M graduate merit fellowship.

Notes

† Electronic Supplementary Materials Available: The chemical structure of all the ligands, the abbreviations and acronyms can be found in Electronic Supplementary Materials. This is available free of charge from the publisher.

References

- [1] C. Sanchez, H. Arribart, M.M. Giraud Guille, *Nat. Mater.*, 4 (2005) 277-288.
- [2] J. Aizenberg, P. Fratzl, *Adv. Mater.*, 21 (2009) 387-388.
- [3] J.O. McInerney, J.A. Cotton, D. Pisani, *Trends Ecol. Evol.*, 23 (2008) 276-281.
- [4] A. Carne, C. Carbonell, I. Imaz, D. MasPOCH, *Chem. Soc. Rev.*, 40 (2011) 291-305.
- [5] J.J. Perry IV, J.A. Perman, M.J. Zaworotko, *Chem. Soc. Rev.*, 38 (2009) 1400-1417.
- [6] N.L. Rosi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O'Keeffe, O.M. Yaghi, *Science*, 300 (2003) 1127-1129.
- [7] H.-C. Zhou, J.R. Long, O.M. Yaghi, *Chem. Rev.*, 112 (2012) 673-674.
- [8] M. Zhang, Y.-P. Chen, M. Bosch, T. Gentle, K. Wang, D. Feng, Z.U. Wang, H.-C. Zhou, *Angew. Chem. Int. Ed.*, 53 (2014) 815-818.
- [9] S.R. Batten, N.R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, O.K. Michael, M.P. Suh, J. Reedijk, *Pure Appl. Chem.*, 85 (2013) 1715-1724.
- [10] L. Schlapbach, A. Züttel, *Nature*, 414 (2001) 353-358.
- [11] M.P. Suh, H.J. Park, T.K. Prasad, D.-W. Lim, *Chem. Rev.*, 112 (2012) 782-835.
- [12] O.K. Farha, Ö.Y. A., I. Eryazici, C.D. Malliakas, B.G. Hauser, M.G. Kanatzidis, S.T. Nguyen, R.Q. Snurr, J.T. Hupp, *Nat. Chem.*, 2 (2010) 944-948.
- [13] S. Ma, H.-C. Zhou, *Chem. Commun.*, 46 (2012) 44-53.
- [14] Y. Liu, J.F. Eubank, A.J. Cairns, J. Eckert, V.C. Kravtsov, R. Luebke, M. Eddaoudi, *Angew. Chem. Int. Ed.*, 46 (2007) 3278-3283.
- [15] S.S. Kaye, A. Dailly, O.M. Yaghi, J.R. Long, *J. Am. Chem. Soc.*, 129 (2007) 14176-14177.
- [16] R.E. Morris, P.S. Wheatley, *Angew. Chem. Int. Ed.*, 47 (2008) 4966-4981.
- [17] Y. Li, R.T. Yang, *Langmuir*, 23 (2007) 12937-12944.
- [18] Y. Hu, S. Xiang, W. Zhang, Z. Zhang, L. Wang, J. Bai, B. Chen, *Chem. Commun.*, (2009) 7551-7553.
- [19] D. Zhao, D.Q. Yuan, H.C. Zhou, *Energy Environ. Sci.*, 1 (2008) 222-235.
- [20] J. Sculley, D.Q. Yuan, H.C. Zhou, *Energy Environ. Sci.*, 4 (2011) 2721-2735.
- [21] D. Yuan, D. Zhao, D. Sun, H.-C. Zhou, *Angew. Chem. Int. Ed.*, 49 (2010) 5357-5361.
- [22] M. Zhang, Y.-P. Chen, H.-C. Zhou, *CrystEngComm*, 15 (2013) 9544-9552.
- [23] C. Yang, X. Wang, M.A. Omary, *J. Am. Chem. Soc.*, 129 (2007) 15454-15455.
- [24] M. Gallo, D. Glossman-Mitnik, *J. Phys. Chem. C*, 113 (2009) 6634-6642.
- [25] T.A. Makal, J.-R. Li, W. Lu, H.-C. Zhou, *Chem. Soc. Rev.*, 41 (2012) 7761-7779.
- [26] J.-R. Li, R.J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev.*, 38 (2009) 1477-1504.
- [27] S. Ma, D. Sun, D. Yuan, X.-S. Wang, H.-C. Zhou, *J. Am. Chem. Soc.*, 131 (2009) 6445-6451.
- [28] J.-R. Li, J. Sculley, H.-C. Zhou, *Chem. Rev.*, 112 (2012) 869-932.
- [29] B. Chen, S. Ma, E.J. Hurtado, E.B. Lobkovsky, H.-C. Zhou, *Inorg. Chem.*, 46 (2007) 8490-8492.
- [30] S. Ma, D. Sun, X.-S. Wang, H.-C. Zhou, *Angew. Chem. Int. Ed.*, 46 (2007) 2458-2462.
- [31] D. Britt, D. Tranchemontagne, O.M. Yaghi, *Proc. Natl. Acad. Sci. U.S.A.*, 105 (2008) 11623-11627.
- [32] Y.S. Bae, K.L. Mulfort, H. Frost, P. Ryan, S. Punnnathanam, L.J. Broadbelt, J.T. Hupp, R.Q. Snurr, *Langmuir*, 24 (2008) 8592-8598.
- [33] B. Chen, C. Liang, J. Yang, D.S. Contreras, Y.L. Clancy, E.B. Lobkovsky, O.M. Yaghi, S. Dai, *Angew. Chem. Int. Ed.*, 45 (2006) 1390-1393.
- [34] M.R. Kishan, J. Tian, P.K. Thallapally, C.A. Fernandez, S.J. Dalgarno, J.E. Warren, B.P. McGrail, J.L. Atwood, *Chem. Commun.*, 46 (2010) 538-540.
- [35] L. Pan, B. Parker, X. Huang, D.H. Olson, Lee, J. Li, *J. Am. Chem. Soc.*, 128 (2006) 4180-4181.
- [36] J.Y. Lee, D.H. Olson, L. Pan, T.J. Emge, J. Li, *Adv. Funct. Mater.*, 17 (2007) 1255-1262.
- [37] L. Pan, D.H. Olson, L.R. Ciemnomolonski, R. Heddy, J. Li, *Angew. Chem. Int. Ed.*, 45 (2006) 616-619.
- [38] Z.-Y. Gu, X.-P. Yan, *Angew. Chem. Int. Ed.*, 49 (2010) 1477-1480.
- [39] S.R. Venna, M.A. Carreon, *J. Am. Chem. Soc.*, 132 (2009) 76-78.
- [40] S. Ma, X.-S. Wang, C.D. Collier, E.S. Manis, H.-C. Zhou, *Inorg. Chem.*, 46 (2007) 8499-8501.
- [41] D. Liu, C. Zhong, *J. Mater. Chem.*, 20 (2010) 10308-10318.
- [42] E.D. Bloch, W.L. Queen, R. Krishna, J.M. Zadrozny, C.M. Brown, J.R. Long, *Science*, 335 (2012) 1606-1610.
- [43] R. Custelcean, B.A. Moyer, *Eur. J. Inorg. Chem.*, (2007) 1321-1340.

- [44] H. Bux, C. Chmelik, R. Krishna, J. Caro, *J. Membr. Sci.*, 369 (2011) 284-289.
- [45] J.A. Bohrman, M.A. Carreon, *Chem. Commun.*, 48 (2012) 5130-5132.
- [46] Z.-Y. Gu, C.-X. Yang, N. Chang, X.-P. Yan, *Acc. Chem. Res.*, 45 (2012) 734-745.
- [47] Y.B. He, R. Krishna, B.L. Chen, *Energy Environ. Sci.*, 5 (2012) 9107-9120.
- [48] K. Sumida, D.L. Rogow, J.A. Mason, T.M. McDonald, E.D. Bloch, Z.R. Herm, T.-H. Bae, J.R. Long, *Chem. Rev.*, 112 (2012) 724-781.
- [49] D. Britt, H. Furukawa, B. Wang, T.G. Glover, O.M. Yaghi, *Proc. Natl. Acad. Sci. U.S.A.*, 106 (2009) 20637-20640.
- [50] A.O.z.r. Yazaydin, R.Q. Snurr, T.-H. Park, K. Koh, J. Liu, M.D. LeVan, A.I. Benin, P. Jakubczak, M. Lanuza, D.B. Galloway, J.J. Low, R.R. Willis, *J. Am. Chem. Soc.*, 131 (2009) 18198-18199.
- [51] L. Bastin, P.S. Barcia, E.J. Hurtado, J.A.C. Silva, A.E. Rodrigues, B. Chen, *J. Phys. Chem. C*, 112 (2008) 1575-1581.
- [52] J.R. Li, Y.G. Ma, M.C. McCarthy, J. Sculley, J.M. Yu, H.K. Jeong, P.B. Balbuena, H.C. Zhou, *Coord. Chem. Rev.*, 255 (2011) 1791-1823.
- [53] R. Vaidhyanathan, S.S. Iremonger, K.W. Dawson, G.K.H. Shimizu, *Chem. Commun.*, (2009) 5230-5232.
- [54] A. Demessence, D.M. D'Alessandro, M.L. Foo, J.R. Long, *J. Am. Chem. Soc.*, 131 (2009) 8784-8786.
- [55] A.R. Millward, O.M. Yaghi, *J. Am. Chem. Soc.*, 127 (2005) 17998-17999.
- [56] J.A. Mason, K. Sumida, Z.R. Herm, R. Krishna, J.R. Long, *Energy Environ. Sci.*, 4 (2011) 3030-3040.
- [57] A.L. Dzubak, L.C. Lin, J. Kim, J.A. Swisher, R. Poloni, S.N. Maximoff, B. Smit, L. Gagliardi, *Nat. Chem.*, 4 (2012) 810-816.
- [58] S. Couck, J.F.M. Denayer, G.V. Baron, T. Rémy, J. Gascon, F. Kapteijn, *J. Am. Chem. Soc.*, 131 (2009) 6326-6327.
- [59] T.M. McDonald, D.M. D'Alessandro, R. Krishna, J.R. Long, *Chem. Sci.*, 2 (2011) 2022-2028.
- [60] A. Phan, C.J. Doonan, F.J. Uribe-Romo, C.B. Knobler, M. O'Keeffe, O.M. Yaghi, *Acc. Chem. Res.*, 43 (2010) 58-67.
- [61] P.D.C. Dietzel, V. Besikiotis, R. Blom, *J. Mater. Chem.*, 19 (2009) 7362-7370.
- [62] S. Keskin, T.M. van Heest, D.S. Sholl, *ChemSusChem*, 3 (2010) 879-891.
- [63] L.E. Kreno, K. Leong, O.K. Farha, M. Allendorf, R.P. Van Duyne, J.T. Hupp, *Chem. Rev.*, 112 (2012) 1105-1125.
- [64] G. Lu, J.T. Hupp, *J. Am. Chem. Soc.*, 132 (2010) 7832-7833.
- [65] Z. Xie, L. Ma, K.E. deKrafft, A. Jin, W. Lin, *J. Am. Chem. Soc.*, 132 (2010) 922-923.
- [66] B. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian, E.B. Lobkovsky, *Adv. Mater.*, 19 (2007) 1693-1696.
- [67] B. Chen, L. Wang, F. Zapata, G. Qian, E.B. Lobkovsky, *J. Am. Chem. Soc.*, 130 (2008) 6718-6719.
- [68] B.V. Harbuzaru, A. Corma, F. Rey, J.L. Jordá, D. Ananias, L.D. Carlos, J. Rocha, *Angew. Chem. Int. Ed.*, 48 (2009) 6476-6479.
- [69] W.J. Rieter, K.M.L. Taylor, W. Lin, *J. Am. Chem. Soc.*, 129 (2007) 9852-9853.
- [70] K.L. Wong, G.L. Law, Y.Y. Yang, W.T. Wong, *Adv. Mater.*, 18 (2006) 1051-1054.
- [71] M.D. Allendorf, R.J.T. Houk, L. Andruszkiewicz, A.A. Talin, J. Pikarsky, A. Choudhury, K.A. Gall, P.J. Hesketh, *J. Am. Chem. Soc.*, 130 (2008) 14404-14405.
- [72] S. Achmann, G. Hagen, J. Kita, I. Malkowsky, C. Kiener, R. Moos, *Sensors*, 9 (2009) 1574-1589.
- [73] A. Lan, K. Li, H. Wu, D.H. Olson, T.J. Emge, W. Ki, M. Hong, J. Li, *Angew. Chem. Int. Ed.*, 48 (2009) 2334-2338.
- [74] Z.-Z. Lu, R. Zhang, Y.-Z. Li, Z.-J. Guo, H.-G. Zheng, *J. Am. Chem. Soc.*, 133 (2011) 4172-4174.
- [75] B.V. Harbuzaru, A. Corma, F. Rey, P. Atienzar, J.L. Jorda, H. Garcia, D. Ananias, L.D. Carlos, J. Rocha, *Angew. Chem. Int. Ed.*, 47 (2008) 1080-1083.
- [76] M. Cametti, K. Rissanen, *Chem. Commun.*, (2009) 2809-2829.
- [77] H.-L. Jiang, Y. Tatsu, Z.-H. Lu, Q. Xu, *J. Am. Chem. Soc.*, 132 (2010) 5586-5587.
- [78] L.G. Qiu, Z.Q. Li, Y. Wu, W. Wang, T. Xu, X. Jiang, *Chem. Commun.*, (2008) 3642-3644.
- [79] P. Horcajada, R. Gref, T. Baati, P.K. Allan, G. Maurin, P. Couvreur, G. Férey, R.E. Morris, C. Serre, *Chem. Rev.*, 112 (2012) 1232-1268.
- [80] A.C. McKinlay, R.E. Morris, P. Horcajada, G. Férey, R. Gref, P. Couvreur, C. Serre, *Angew. Chem. Int. Ed.*, 49 (2010) 6260-6266.
- [81] J. Della Rocca, D. Liu, W. Lin, *Acc. Chem. Res.*, 44 (2011) 957-968.

- [82] S. Keskin, S. Kızılel, *Ind. Eng. Chem. Res.*, 50 (2011) 1799-1812.
- [83] Z. Ma, B. Moulton, *Coord. Chem. Rev.*, 255 (2010) 1623-1641.
- [84] R.C. Huxford, J. Della Rocca, W. Lin, *Curr. Opin. Chem. Biol.*, 14 (2010) 262-268.
- [85] K.M.L. Taylor-Pashow, J.D. Rocca, Z. Xie, S. Tran, W. Lin, *J. Am. Chem. Soc.*, 131 (2009) 14261-14263.
- [86] P. Horcajada, C. Serre, G. Maurin, N.A. Ramsahye, F. Balas, M.a. Vallet-Regí, M. Sebban, F. Taulelle, G.r. Férey, *J. Am. Chem. Soc.*, 130 (2008) 6774-6780.
- [87] P. Horcajada, C. Serre, M. Vallet-Regí, M. Sebban, F. Taulelle, G. Férey, *Angew. Chem. Int. Ed.*, 45 (2006) 5974-5978.
- [88] P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J.F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J.S. Chang, Y.K. Hwang, V. Marsaud, P.N. Bories, L. Cynober, S. Gil, G. Férey, P. Couvreur, R. Gref, *Nat. Mater.*, 9 (2010) 172-178.
- [89] I. Imaz, M. Rubio-Martinez, L. Garcia-Fernandez, F. Garcia, D. Ruiz-Molina, J. Hernando, V. Puentes, D. MasPOCH, *Chem. Commun.*, 46 (2010) 4737-4739.
- [90] D. Zhao, S. Tan, D. Yuan, W. Lu, Y.H. Rezenom, H. Jiang, L.-Q. Wang, H.-C. Zhou, *Adv. Mater.*, 23 (2010) 90-93.
- [91] W.J. Rieter, K.M. Pott, K.M.L. Taylor, W. Lin, *J. Am. Chem. Soc.*, 130 (2008) 11584-11585.
- [92] F. Ke, Y.P. Yuan, L.G. Qiu, Y.H. Shen, A.J. Xie, J.F. Zhu, X.Y. Tian, L.D. Zhang, *J. Mater. Chem.*, 21 (2011) 3843-3848.
- [93] H.N. Wang, X. Meng, G.S. Yang, X.L. Wang, K.Z. Shao, Z.M. Su, C.G. Wang, *Chem. Commun.*, 47 (2011) 7128-7130.
- [94] C. Gaudin, D. Cunha, E. Ivanoff, P. Horcajada, G. Cheve, A. Yasri, O. Loget, C. Serre, G. Maurin, *Microporous Mesoporous Mater.*, 157 (2012) 124-130.
- [95] J.S. Qin, D.Y. Du, W.L. Li, J.P. Zhang, S.L. Li, Z.M. Su, X.L. Wang, Q. Xu, K.Z. Shao, Y.Q. Lan, *Chem. Sci.*, 3 (2012) 2114-2118.
- [96] K.M.L. Taylor, A. Jin, W. Lin, *Angew. Chem. Int. Ed.*, 47 (2008) 7722-7725.
- [97] Y. Cui, Y. Yue, G. Qian, B. Chen, *Chem. Rev.*, 112 (2012) 1126-1162.
- [98] C. Wang, T. Zhang, W. Lin, *Chem. Rev.*, 112 (2012) 1084-1104.
- [99] M.D. Allendorf, C.A. Bauer, R.K. Bhakta, R.J.T. Houk, *Chem. Soc. Rev.*, 38 (2009) 1330-1352.
- [100] B.D. Chandler, D.T. Cramb, G.K.H. Shimizu, *J. Am. Chem. Soc.*, 128 (2006) 10403-10412.
- [101] C.A. Bauer, T.V. Timofeeva, T.B. Settersten, B.D. Patterson, V.H. Liu, B.A. Simmons, M.D. Allendorf, *J. Am. Chem. Soc.*, 129 (2007) 7136-7144.
- [102] K.C. Stylianou, R. Heck, S.Y. Chong, J. Bacsá, J.T.A. Jones, Y.Z. Khimyak, D. Bradshaw, M.J. Rosseinsky, *J. Am. Chem. Soc.*, 132 (2010) 4119-4130.
- [103] J. Park, D. Yuan, K.T. Pham, J.-R. Li, A. Yakovenko, H.-C. Zhou, *J. Am. Chem. Soc.*, 134 (2012) 99-102.
- [104] A.J. Blake, N.R. Champness, T.L. Easun, D.R. Allan, H. Nowell, M.W. George, J. Jia, X.-Z. Sun, *Nat. Chem.*, 2 (2010) 688-694.
- [105] J. Rocha, L.D. Carlos, F.A.A. Paz, D. Ananias, *Chem. Soc. Rev.*, 40 (2011) 926-940.
- [106] X.-H. Jin, J.-K. Sun, X.-M. Xu, Z.-H. Li, J. Zhang, *Chem. Commun.*, 46 (2010) 4695-4697.
- [107] D.T. de Lill, N.S. Gunning, C.L. Cahill, *Inorg. Chem.*, 44 (2004) 258-266.
- [108] M. Kurmoo, *Chem. Soc. Rev.*, 38 (2009) 1353-1379.
- [109] M.-H. Zeng, B. Wang, X.-Y. Wang, W.-X. Zhang, X.-M. Chen, S. Gao, *Inorg. Chem.*, 45 (2006) 7069-7076.
- [110] R.D. Poulsen, A. Bentien, M. Chevalier, B.B. Iversen, *J. Am. Chem. Soc.*, 127 (2005) 9156-9166.
- [111] K.M.L. Taylor, W.J. Rieter, W. Lin, *J. Am. Chem. Soc.*, 130 (2008) 14358-14359.
- [112] B.-B. Ding, Y.-Q. Weng, Z.-W. Mao, C.-K. Lam, X.-M. Chen, B.-H. Ye, *Inorg. Chem.*, 44 (2005) 8836-8845.
- [113] Z. Li, G. Zhu, X. Guo, X. Zhao, Z. Jin, S. Qiu, *Inorg. Chem.*, 46 (2007) 5174-5178.
- [114] M. Wriedt, H.C. Zhou, *Dalton Trans.*, 41 (2012) 4207-4216.
- [115] D. MasPOCH, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira, J. Veciana, *Nat. Mater.*, 2 (2003) 190-195.
- [116] D. MasPOCH, D. Ruiz-Molina, J. Veciana, *J. Mater. Chem.*, 14 (2004) 2713-2723.
- [117] V. Niel, A.L. Thompson, M.C. Munoz, A. Galet, A.S.E. Goeta, J.A. Real, *Angew. Chem. Int. Ed.*, 42 (2003) 3760-3763.
- [118] P.D.C. Dietzel, Y. Morita, R. Blom, H. Fjellvag, *Angew. Chem. Int. Ed.*, 44 (2005) 6354-6358.
- [119] J. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, *Chem. Soc. Rev.*, 38 (2009)

1450-1459.

- [120] A. Corma, H. García, F.X. Llabrés i Xamena, *Chem. Rev.*, 110 (2012) 4606-4655.
- [121] M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.*, 112 (2012) 1196-1231.
- [122] J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim, *Nature*, 404 (2000) 982-986.
- [123] C.-Y. Sun, S.-X. Liu, D.-D. Liang, K.-Z. Shao, Y.-H. Ren, Z.-M. Su, *J. Am. Chem. Soc.*, 131 (2009) 1883-1888.
- [124] L. Ma, J.M. Falkowski, C. Abney, W. Lin, *Nat. Chem.*, 2 (2010) 838-846.
- [125] C.-D. Wu, W. Lin, *Angew. Chem. Int. Ed.*, 46 (2007) 1075-1078.
- [126] D. Farrusseng, S. Aguado, C. Pinel, *Angew. Chem. Int. Ed.*, 48 (2009) 7502-7513.
- [127] S.-H. Cho, B. Ma, S.T. Nguyen, J.T. Hupp, T.E. Albrecht-Schmitt, *Chem. Commun.*, (2006) 2563-2565.
- [128] S. Horike, M. Dinca, K. Tamaki, J.R. Long, *J. Am. Chem. Soc.*, 130 (2008) 5854-5855.
- [129] L. Ma, C. Abney, W. Lin, *Chem. Soc. Rev.*, 38 (2009) 1248-1256.
- [130] C.-D. Wu, A. Hu, L. Zhang, W. Lin, *J. Am. Chem. Soc.*, 127 (2005) 8940-8941.
- [131] M. Eddaoudi, J. Kim, J.B. Wachter, H.K. Chae, M. O'Keeffe, O.M. Yaghi, *J. Am. Chem. Soc.*, 123 (2001) 4368-4369.
- [132] J.-R. Li, A.A. Yakovenko, W. Lu, D.J. Timmons, W. Zhuang, D. Yuan, H.-C. Zhou, *J. Am. Chem. Soc.*, 132 (2010) 17599-17610.
- [133] J.-R. Li, H.-C. Zhou, *Nat. Chem.*, 2 (2010) 893-898.
- [134] J.-R. Li, J. Yu, W. Lu, L.-B. Sun, J. Sculley, P.B. Balbuena, H.-C. Zhou, *Nat. Commun.*, 4 (2013) 1538.
- [135] R. Breslow, L.E. Overman, *J. Am. Chem. Soc.*, 92 (1970) 1075-1077.
- [136] R. Breslow, *Acc. Chem. Res.*, 13 (1980) 170-177.
- [137] H.R. Luckarift, J.C. Spain, R.R. Naik, M.O. Stone, *Nat. Biotech.*, 22 (2004) 211-213.
- [138] R. Breslow, S.D. Dong, *Chem. Rev.*, 98 (1998) 1997-2012.
- [139] R. Breslow, J. Yang, J. Yan, *Tetrahedron*, 58 (2002) 653-659.
- [140] R. Breslow, M. Hammond, M. Lauer, *J. Am. Chem. Soc.*, 102 (1980) 421-422.
- [141] Q. Wang, Z. Yang, X. Zhang, X. Xiao, C.K. Chang, B. Xu, *Angew. Chem. Int. Ed.*, 46 (2007) 4285-4289.
- [142] H. Ye, W. Tong, V.T. D'Souza, *J. Am. Chem. Soc.*, 114 (1992) 5470-5472.
- [143] L.G. Marinescu, M. Bols, *Angew. Chem. Int. Ed.*, 45 (2006) 4590-4593.
- [144] R. Breslow, Y. Huang, X. Zhang, J. Yang, *Proc. Natl. Acad. Sci. U.S.A.*, 94 (1997) 11156-11158.
- [145] V.T. D'Souza, M.L. Bender, *Acc. Chem. Res.*, 20 (1987) 146-152.
- [146] J.J. Ramsden, *Biosens. Bioelectron.*, 13 (1998) 593-598.
- [147] R. Li, V. Dowd, D.J. Stewart, S.J. Burton, C.R. Lowe, *Nat. Biotech.*, 16 (1998) 190-195.
- [148] Z. Tang, N.A. Kotov, S. Magonov, B. Ozturk, *Nat. Mater.*, 2 (2003) 413-418.
- [149] M. Kikuchi, T. Ikoma, S. Itoh, H.N. Matsumoto, Y. Koyama, K. Takakuda, K. Shinomiya, J. Tanaka, *Compos. Sci. Technol.*, 64 (2004) 819-825.
- [150] G. Daculsi, *Biomaterials.*, 19 (1998) 1473-1478.
- [151] I. Sopyan, M. Mel, S. Ramesh, K.A. Khalid, *Sci. Tech. Adv. Mater.*, 8 (2007) 116-123.
- [152] S.I. Stupp, G.W. Ciegler, *J. Biomed. Mater. Res.*, 26 (1992) 169-183.
- [153] E.D. Spoerke, S.G. Anthony, S.I. Stupp, *Adv. Mater.*, 21 (2009) 425-430.
- [154] A. Mata, Y. Geng, K.J. Henrikson, C. Aparicio, S.R. Stock, R.L. Satcher, S.I. Stupp, *Biomaterials.*, 31 (2010) 6004-6012.
- [155] S.-H. Rhee, J. Tanaka, *J. Am. Ceram. Soc.*, 81 (1998) 3029-3031.
- [156] K. Hata, T. Kokubo, T. Nakamura, T. Yamamuro, *J. Am. Ceram. Soc.*, 78 (1995) 1049-1053.
- [157] M. Tanahashi, T. Yao, T. Kokubo, M. Minoda, T. Miyamoto, T. Nakamura, T. Yamamura, *J. Biomed. Mater. Res.*, 29 (1995) 349-357.
- [158] A. Tampieri, G. Celotti, E. Landi, *Anal. Bioanal. Chem.*, 381 (2005) 568-576.
- [159] Y. Shikinami, Y. Kotani, B.W. Cunningham, K. Abumi, K. Kaneda, *Adv. Funct. Mater.*, 14 (2004) 1039-1046.
- [160] E. Landi, G. Logroscino, L. Proietti, A. Tampieri, M. Sandri, S. Sprio, *J. Mater. Sci.: Mater. Med.*, 19 (2008) 239-247.
- [161] J. Song, V. Malathong, C.R. Bertozzi, *J. Am. Chem. Soc.*, 127 (2005) 3366-3372.
- [162] M. Costas, K. Chen, L. Que Jr, *Coord. Chem. Rev.*, 200-202 (2000) 517-544.
- [163] R.H. Crabtree, J.A. Loch, K. Gruet, D.-H. Lee, C. Borgmann, *J. Organomet. Chem.*, 600 (2000) 7-11.

- [164] F. Bedioui, *Coord. Chem. Rev.*, 144 (1995) 39-68.
- [165] J. Bernadou, B. Meunier, *Adv. Synth. Catal.*, 346 (2004) 171-184.
- [166] J.D. Stevenson, N.R. Thomas, *Nat. Prod. Rep.*, 17 (2000) 535-577.
- [167] J.-i. Kadokawa, A. Kokubo, H. Tagaya, *Macromol. Biosci.*, 2 (2002) 257-260.
- [168] K.M. Roth, Y. Zhou, W. Yang, D.E. Morse, *J. Am. Chem. Soc.*, 127 (2004) 325-330.
- [169] Y. Yuan, H. Ji, Y. Chen, Y. Han, X. Song, Y. She, R. Zhong, *Org. Process. Res. Dev.*, 8 (2004) 418-420.
- [170] A. Mecke, C. Dittrich, W. Meier, *Soft Matter*, 2 (2006) 751-759.
- [171] S. Kolusheva, R. Kafri, M. Katz, R. Jelinek, *J. Am. Chem. Soc.*, 123 (2001) 417-422.
- [172] K. Morigaki, T. Baumgart, U. Jonas, A. Offenhäusser, W. Knoll, *Langmuir*, 18 (2002) 4082-4089.
- [173] S.H. Rhee, J. Tanaka, *J. Am. Ceram. Soc.*, 81 (1998) 3029-3031.
- [174] D. Vaknin, P. Krüger, M. Lösche, *Phys. Rev. Lett.*, 90 (2003) 178102.
- [175] S. Kolusheva, R. Kafri, M. Katz, R. Jelinek, *J. Am. Chem. Soc.*, 123 (2000) 417-422.
- [176] A. Mecke, C. Dittrich, W. Meier, *Soft. Matter.*, 2 (2006) 751-759.
- [177] C. Nielsen, *Anal. Bioanal. Chem.*, 395 (2009) 697-718.
- [178] A.L. Plant, M. Gueguetchkeri, W. Yap, *Biophys. J.*, 67 (1994) 1126-1133.
- [179] L.G. Griffith, G. Naughton, *Science*, 295 (2002) 1009-1014.
- [180] R. Langer, J.P. Vacanti, *Science*, 260 (1993) 920-926.
- [181] K.Y. Lee, D.J. Mooney, *Chem. Rev.*, 101 (2001) 1869-1879.
- [182] S.J. Hollister, *Nat. Mater.*, 4 (2005) 518-524.
- [183] M.P. Lutolf, J.A. Hubbell, *Nat. Biotechnol.*, 23 (2005) 47-55.
- [184] J.L. Drury, D.J. Mooney, *Biomaterials.*, 24 (2003) 4337-4351.
- [185] H. Shin, S. Jo, A.G. Mikos, *Biomaterials.*, 24 (2003) 4353-4364.
- [186] P.X. Ma, *Adv. Drug Deliver. Rev.*, 60 (2008) 184-198.
- [187] S. Liao, C.K. Chan, S. Ramakrishna, *Materials Science and Engineering: C*, 28 (2008) 1189-1202.
- [188] Z.Y. Tang, Y. Wang, P. Podsiadlo, N.A. Kotov, *Adv. Mater.*, 18 (2006) 3203-3224.
- [189] M. Zhang, M. Bosch, T. Gentle, H.-C. Zhou, *CrystEngComm*, 16 (2014) 4069-4083.
- [190] I. Imaz, M. Rubio-Martinez, J. An, I. Sole-Font, N.L. Rosi, D. Maspoch, *Chem. Commun.*, 47 (2011) 7287-7302.
- [191] J. An, S.J. Geib, N.L. Rosi, *J. Am. Chem. Soc.*, 131 (2009) 8376-8377.
- [192] J. An, S.J. Geib, N.L. Rosi, *J. Am. Chem. Soc.*, 132 (2010) 38-39.
- [193] R.A. Smaldone, R.S. Forgan, H. Furukawa, J.J. Gassensmith, A.M.Z. Slawin, O.M. Yaghi, J.F. Stoddart, *Angew. Chem. Int. Ed.*, 49 (2010) 8630-8634.
- [194] A. Bétard, R.A. Fischer, *Chem. Rev.*, 112 (2012) 1055-1083.
- [195] S. Sivakova, S.J. Rowan, *Chem. Soc. Rev.*, 34 (2005) 9-21.
- [196] D.K. Patel, A. Domínguez-Martín, M.d.P. Brandi-Blanco, D. Choquesillo-Lazarte, V.M. Nurchi, J. Niclós-Gutiérrez, *Coord. Chem. Rev.*, 256 (2012) 193-211.
- [197] J. An, O.K. Farha, J.T. Hupp, E. Pohl, J.I. Yeh, N.L. Rosi, *Nat. Commun.*, 3 (2012) 604.
- [198] T. Li, M.T. Kozłowski, E.A. Doud, M.N. Blakely, N.L. Rosi, *J. Am. Chem. Soc.*, 135 (2013) 11688-11691.
- [199] P.S. Nugent, V.L. Rhodus, T. Pham, K. Forrest, L. Wojtas, B. Space, M.J. Zaworotko, *J. Am. Chem. Soc.*, 135 (2013) 10950-10953.
- [200] M. Zhang, W. Lu, J.-R. Li, M. Bosch, Y.-P. Chen, T.-F. Liu, Y. Liu, H.-C. Zhou, *Inorg. Chem. Front.*, 1 (2014) 159-162.
- [201] S. Verma, A.K. Mishra, J. Kumar, *Acc. Chem. Res.*, 43 (2009) 79-91.
- [202] H. Hayashi, A.P. Cote, H. Furukawa, M. O'Keeffe, O.M. Yaghi, *Nat. Mater.*, 6 (2007) 501-506.
- [203] S. Ma, D. Sun, P.M. Forster, D. Yuan, W. Zhuang, Y.-S. Chen, J.B. Parise, H.-C. Zhou, *Inorg. Chem.*, 48 (2009) 4616-4618.
- [204] J.M. González-Pérez, C. Alarcón-Payer, A. Castiñeiras, T. Pivetta, L. Lezama, D. Choquesillo-Lazarte, G. Crisponi, J. Niclós-Gutiérrez, *Inorg. Chem.*, 45 (2005) 877-882.
- [205] K. Koh, A.G. Wong-Foy, A.J. Matzger, *Angew. Chem. Int. Ed.*, 47 (2008) 677-680.
- [206] K. Koh, A.G. Wong-Foy, A.J. Matzger, *J. Am. Chem. Soc.*, 131 (2009) 4184-4185.
- [207] H. Furukawa, N. Ko, Y.B. Go, N. Aratani, S.B. Choi, E. Choi, A.Ö. Yazaydin, R.Q. Snurr, M. O'Keeffe, J. Kim, O.M. Yaghi, *Science*, 329 (2010) 424-428.
- [208] O.K. Farha, I. Eryazici, N.C. Jeong, B.G. Hauser, C.E. Wilmer, A.A. Sarjeant, R.Q. Snurr, S.T. Nguyen, A.Ö. Yazaydin, J.T. Hupp, *J. Am. Chem. Soc.*, 134 (2012) 15016-15021.

- [209] M. Zhang, Z. Perry, J. Park, H.-C. Zhou, *Polymer*, 55 (2014) 335-339.
- [210] J. An, S.J. Geib, N.L. Rosi, *J. Am. Chem. Soc.*, 132 (2010) 38-39.
- [211] J. An, R.P. Fiorella, S.J. Geib, N.L. Rosi, *J. Am. Chem. Soc.*, 131 (2009) 8401-8403.
- [212] S. Lim, H. Kim, N. Selvapalam, K.-J. Kim, S.J. Cho, G. Seo, K. Kim, *Angew. Chem. Int. Ed.*, 47 (2008) 3352-3355.
- [213] J.L.C. Rowsell, O.M. Yaghi, *Angew. Chem. Int. Ed.*, 44 (2005) 4670-4679.
- [214] M. Dincă, J.R. Long, *Angew. Chem. Int. Ed.*, 47 (2008) 6766-6779.
- [215] D. Sun, S. Ma, Y. Ke, T.M. Petersen, H.-C. Zhou, *Chem. Commun.*, (2005) 2663-2665.
- [216] V. R. Thalladi, R. Boese, S. Brasselet, I. Ledoux, J. Zyss, R. K. R. Jetti, G. R. Desiraju, *Chem. Commun.*, (1999) 1639-1640.
- [217] R.S. Forgan, R.A. Smaldone, J.J. Gassensmith, H. Furukawa, D.B. Cordes, Q. Li, C.E. Wilmer, Y.Y. Botros, R.Q. Snurr, A.M.Z. Slawin, J.F. Stoddart, *J. Am. Chem. Soc.*, 134 (2012) 406-417.
- [218] T. Kikuchi, S. Sato, M. Fujita, *J. Am. Chem. Soc.*, 132 (2010) 15930-15932.
- [219] R. Breslow, *Acc. Chem. Res.*, 28 (1995) 146-153.
- [220] J.T. Hupp, *Nat. Chem.*, 2 (2010) 432-433.
- [221] S. Hudson, J. Cooney, E. Magner, *Angew. Chem. Int. Ed.*, 47 (2008) 8582-8594.
- [222] R. Ravindra, S. Zhao, H. Gies, R. Winter, *J. Am. Chem. Soc.*, 126 (2004) 12224-12225.
- [223] M. Quirós, A.B. García, M.A. Montes-Morán, *Carbon*, 49 (2011) 406-415.
- [224] A. Manton, L. Massüger, P. Rabu, C. Palivan, L.B. McCusker, A. Taubert, *J. Am. Chem. Soc.*, 130 (2008) 2517-2526.
- [225] M. Ikemi, T. Kikuchi, S. Matsumura, K. Shiba, S. Sato, M. Fujita, *Chem. Sci.*, 1 (2010) 68-71.
- [226] D. Peri, J. Ciston, F. Gándara, Y. Zhao, O.M. Yaghi, *Inorg. Chem.*, 52 (2013) 13818-13820.
- [227] X.-L. Yang, C.-D. Wu, *CrystEngComm*, 16 (2014) ASAP, 10.1039/C3CE42508H.
- [228] I. Bertini, H.B. Gray, E.I. Stiefel, J.S. Valentine, *Biological Inorganic Chemistry: Structure and Reactivity*, University Science Books, Sausalito, 2007.
- [229] M.K. Geno, J. Halpern, *J. Am. Chem. Soc.*, 109 (1987) 1238-1240.
- [230] S. Ma, H.-C. Zhou, *J. Am. Chem. Soc.*, 128 (2006) 11734-11735.
- [231] R.G. Matthews, *Acc. Chem. Res.*, 34 (2001) 681-689.
- [232] M. Dinca, A. Dailly, Y. Liu, C.M. Brown, D.A. Neumann, J.R. Long, *J. Am. Chem. Soc.*, 128 (2006) 16876-16883.
- [233] K.S. Suslick, P. Bhyrappa, J.H. Chou, M.E. Kosal, S. Nakagaki, D.W. Smithenry, S.R. Wilson, *Acc. Chem. Res.*, 38 (2005) 283-291.
- [234] A. Yoshida, N. Kakegawa, M. Ogawa, *Res. Chem. Intermediat*, 29 (2003) 721-731.
- [235] S.M. Ribeiro, A.C. Serra, A.M.d.A. Rocha Gonsalves, *J. Mol. Catal. A: Chem.*, 326 (2010) 121-127.
- [236] E.M. Serwicka, J. Połtowicz, K. Bahrnowski, Z. Olejniczak, W. Jones, *Appl. Catal. A*, 275 (2004) 9-14.
- [237] A. Kalilur Rahiman, S. Sreedaran, K. Shanmuga Bharathi, V. Narayanan, *J. Porous. Mat.*, 17 (2010) 711-718.
- [238] T. Shichi, K. Takagi, *J. Photochem. Photobiol. C: Photochem. Rev.*, 1 (2000) 113-130.
- [239] Z. Tong, T. Shichi, K. Takagi, *J. Phys. Chem. B*, 106 (2002) 13306-13310.
- [240] L. Persaud, A.J. Bard, A. Campion, M.A. Fox, T.E. Mallouk, S.E. Webber, J.M. White, *J. Am. Chem. Soc.*, 109 (1987) 7309-7314.
- [241] E. Chevallier, E. Scorsone, H.A. Girard, V. Pichot, D. Spitzer, P. Bergonzo, *Sensor Actuat. B:Chem*, 151 (2010) 191-197.
- [242] M.H. Alkordi, Y. Liu, R.W. Larsen, J.F. Eubank, M. Eddaoudi, *J. Am. Chem. Soc.*, 130 (2008) 12639-12641.
- [243] R.W. Larsen, L. Wojtas, J. Perman, R.L. Musselman, M.J. Zaworotko, C.M. Vetromile, *J. Am. Chem. Soc.*, 133 (2011) 10356-10359.
- [244] R.W. Larsen, J. Miksovská, R.L. Musselman, L. Wojtas, *J. Phys. Chem. A*, 115 (2011) 11519-11524.
- [245] Z. Zhang, L. Zhang, L. Wojtas, M. Eddaoudi, M.J. Zaworotko, *J. Am. Chem. Soc.*, 134 (2012) 928-933.
- [246] Z. Zhang, L. Zhang, L. Wojtas, P. Nugent, M. Eddaoudi, M.J. Zaworotko, *J. Am. Chem. Soc.*, 134 (2012) 924-927.
- [247] P. Dastidar, Z. Stein, I. Goldberg, C.E. Strouse, *Supramol. Chem.*, 7 (1996) 257-270.
- [248] R. Makiura, S. Motoyama, Y. Umemura, H. Yamanaka, O. Sakata, H. Kitagawa, *Nat. Mater.*, 9 (2010) 565-571.

- [249] A.M. Shultz, O.K. Farha, J.T. Hupp, S.T. Nguyen, *J. Am. Chem. Soc.*, 131 (2009) 4204-4205.
- [250] O.K. Farha, A.M. Shultz, A.A. Sarjeant, S.T. Nguyen, J.T. Hupp, *J. Am. Chem. Soc.*, 133 (2011) 5652-5655.
- [251] D.H. Lee, S. Kim, M.Y. Hyun, J.-Y. Hong, S. Huh, C. Kim, S.J. Lee, *Chem. Commun.*, 48 (2012) 5512-5514.
- [252] C. Zou, Z. Zhang, X. Xu, Q. Gong, J. Li, C.-D. Wu, *J. Am. Chem. Soc.*, 134 (2012) 87-90.
- [253] X.-S. Wang, L. Meng, Q. Cheng, C. Kim, L. Wojtas, M. Chrzanowski, Y.-S. Chen, X.P. Zhang, S. Ma, *J. Am. Chem. Soc.*, 133 (2012) 16322-16325.
- [254] M.-H. Xie, X.-L. Yang, C.-D. Wu, *Chem. Commun.*, 47 (2012) 5521-5523.
- [255] A. Fateeva, P.A. Chater, C.P. Ireland, A.A. Tahir, Y.Z. Khimyak, P.V. Wiper, J.R. Darwent, M.J. Rosseinsky, *Angew. Chem. Int. Ed.*, 51 (2012) 7440-7444.
- [256] D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei, H.-C. Zhou, *Angew. Chem. Int. Ed.*, 51 (2012) 10307-10310.
- [257] Y. Chen, T. Hoang, S. Ma, *Inorg. Chem.*, 51 (2012) 12600-12602.
- [258] W. Morris, B. Voloskiy, S. Demir, F. Gándara, P.L. McGrier, H. Furukawa, D. Cascio, J.F. Stoddart, O.M. Yaghi, *Inorg. Chem.*, 51 (2012) 6443-6445.
- [259] A. Fateeva, S. Devautour-Vinot, N. Heymans, T. Devic, J.-M. Grenèche, S. Wuttke, S. Miller, A. Lago, C. Serre, G. De Weireld, G. Maurin, A. Vimont, G. Férey, *Chem. Mater.*, 23 (2011) 4641-4651.
- [260] X.-L. Yang, M.-H. Xie, C. Zou, Y. He, B. Chen, M. O'Keeffe, C.-D. Wu, *J. Am. Chem. Soc.*, 134 (2012) 10638-10645.
- [261] X.-S. Wang, M. Chrzanowski, C. Kim, W.-Y. Gao, L. Wojtas, Y.-S. Chen, X. Peter Zhang, S. Ma, *Chem. Commun.*, 48 (2012) 7173-7175.
- [262] X.-S. Wang, M. Chrzanowski, W.-Y. Gao, L. Wojtas, Y.-S. Chen, M.J. Zaworotko, S. Ma, *Chem. Sci.*, 3 (2012) 2823-2827.
- [263] D. Feng, H.-L. Jiang, Y.-P. Chen, Z.-Y. Gu, Z. Wei, H.-C. Zhou, *Inorg. Chem.*, 52 (2013) 12661-12667.
- [264] D. Feng, W.-C. Chung, Z. Wei, Z.-Y. Gu, H.-L. Jiang, Y.-P. Chen, D.J. Darensbourg, H.-C. Zhou, *J. Am. Chem. Soc.*, (2013).
- [265] H.-L. Jiang, D. Feng, K. Wang, Z.-Y. Gu, Z. Wei, Y.-P. Chen, H.-C. Zhou, *J. Am. Chem. Soc.*, 135 (2013) 13934-13938.
- [266] H. Hayashi, A. Kira, T. Umeyama, Y. Matano, P. Charoensirithavorn, T. Sagawa, S. Yoshikawa, N.V. Tkachenko, H. Lemmetyinen, H. Imahori, *J. Phys. Chem. C*, 113 (2009) 10819-10828.
- [267] D. Sun, F.S. Tham, C.A. Reed, P.D.W. Boyd, *Proc. Natl. Acad. Sci. U.S.A.*, 99 (2002) 5088-5092.
- [268] D.M. Guldi, H. Taieb, G.M.A. Rahman, N. Tagmatarchis, M. Prato, *Adv. Mater.*, 17 (2005) 871-875.
- [269] D. Baskaran, J.W. Mays, X.P. Zhang, M.S. Bratcher, *J. Am. Chem. Soc.*, 127 (2005) 6916-6917.
- [270] Y. Chen, V. Lykourinou, T. Hoang, L.-J. Ming, S. Ma, *Inorg. Chem.*, 51 (2012) 9156-9158.
- [271] Y. Chen, V. Lykourinou, C. Vetromile, T. Hoang, L.-J. Ming, R.W. Larsen, S. Ma, *J. Am. Chem. Soc.*, 134 (2012) 13188-13191.
- [272] V. Lykourinou, Y. Chen, X.-S. Wang, L. Meng, T. Hoang, L.-J. Ming, R.L. Musselman, S. Ma, *J. Am. Chem. Soc.*, 133 (2011) 10382-10385.
- [273] Y. Liu, V.C. Kravtsov, R. Larsen, M. Eddaoudi, *Chem. Commun.*, (2006) 1488-1490.
- [274] S.S.-Y. Chui, S.M.-F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams, *Science*, 283 (1999) 1148-1150.
- [275] S.A. Bourne, J. Lu, A. Mondal, B. Moulton, M.J. Zaworotko, *Angew. Chem. Int. Ed.*, 40 (2001) 2111-2113.
- [276] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, *J. Org. Chem.*, 32 (1967) 476-476.
- [277] M. Zhao, S. Ou, C.-D. Wu, *Acc. Chem. Res.*, 47 (2014) 1199-1207.
- [278] W.-Y. Gao, M. Chrzanowski, S. Ma, *Chem. Soc. Rev.*, 43 (2014) ASAP, 10.1039/C4CS00001C.
- [279] J.H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K.P. Lillerud, *J. Am. Chem. Soc.*, 130 (2008) 13850-13851.
- [280] H. Chevreau, T. Devic, F. Salles, G. Maurin, N. Stock, C. Serre, *Angew. Chem. Int. Ed.*, 52 (2013) 5056-5060.
- [281] H. Beinert, R.H. Holm, E. Münck, *Science*, 277 (1997) 653-659.
- [282] D.H. Flint, R.M. Allen, *Chem. Rev.*, 96 (1996) 2315-2334.
- [283] J.C. Fontecilla-Camps, A. Volbeda, C. Cavazza, Y. Nicolet, *Chem. Rev.*, 107 (2007) 4273-4303.

- [284] Z. Cao, M.B. Hall, *J. Am. Chem. Soc.*, 123 (2001) 3734-3742.
- [285] P.M. Vignais, B. Billoud, *Chem. Rev.*, 107 (2007) 4206-4272.
- [286] J.W. Peters, W.N. Lanzilotta, B.J. Lemon, L.C. Seefeldt, *Science*, 282 (1998) 1853-1858.
- [287] C.d. Tard, C.J. Pickett, *Chem. Rev.*, 109 (2009) 2245-2274.
- [288] C.-H. Lai, W.-Z. Lee, M.L. Miller, J.H. Reibenspies, D.J. Darensbourg, M.Y. Darensbourg, *J. Am. Chem. Soc.*, 120 (1998) 10103-10114.
- [289] R. Lomoth, S. Ott, *Dalton Trans.*, (2009) 9952-9959.
- [290] S. Pullen, H. Fei, A. Orthaber, S.M. Cohen, S. Ott, *J. Am. Chem. Soc.*, 135 (2013) 16997-17003.
- [291] M. Hartmann, D. Jung, *J. Mater. Chem.*, 20 (2010) 844-857.
- [292] H. Deng, S. Grunder, K.E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A.C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O’Keeffe, O. Terasaki, J.F. Stoddart, O.M. Yaghi, *Science*, 336 (2012) 1018-1023.
- [293] Y.K. Park, S.B. Choi, H. Kim, K. Kim, B.-H. Won, K. Choi, J.-S. Choi, W.-S. Ahn, N. Won, S. Kim, D.H. Jung, S.-H. Choi, G.-H. Kim, S.-S. Cha, Y.H. Jhon, J.K. Yang, J. Kim, *Angew. Chem. Int. Ed.*, 46 (2007) 8230-8233.
- [294] H.M. Marques, *Dalton Trans.*, (2007) 4371-4385.
- [295] H.A. Harbury, P.A. Loach, *J. Biol. Chem.*, 235 (1960) 3640-3645.
- [296] M.A. Bos, Z. Shervani, A.C.I. Anusiem, M. Giesbers, W. Norde, J.M. Kleijn, *Colloids and Surfaces B: Biointerfaces*, 3 (1994) 91-100.
- [297] C. Veeger, *J. Inorg. Biochem.*, 91 (2002) 35-45.
- [298] E.N. Kadnikova, N.M. Kostić, *J. Org. Chem.*, 68 (2003) 2600-2608.
- [299] L.E. Kreno, K. Leong, O.K. Farha, M. Allendorf, R.P. Van Duyne, J.T. Hupp, *Chem. Rev.*, 112 (2011) 1105-1125.
- [300] D. Liu, K. Lu, C. Poon, W. Lin, *Inorg. Chem.*, (2013).
- [301] J.-W. Zhang, H.-T. Zhang, Z.-Y. Du, X. Wang, S.-H. Yu, H.-L. Jiang, *Chem. Commun.*, 50 (2014) 1092-1094.
- [302] W. Ma, Q. Jiang, P. Yu, L. Yang, L. Mao, *Anal. Chem.*, 85 (2013) 7550-7557.
- [303] T. Lee, H. Lin Lee, M. Hsun Tsai, S.-L. Cheng, S.-W. Lee, J.-C. Hu, L.-T. Chen, *Biosens. Bioelectron.*, 43 (2013) 56-62.
- [304] J. Della Rocca, D. Liu, W. Lin, *Acc. Chem. Res.*, 44 (2011) 957-968.
- [305] A.C. McKinlay, B. Xiao, D.S. Wragg, P.S. Wheatley, I.L. Megson, R.E. Morris, *J. Am. Chem. Soc.*, 130 (2008) 10440-10444.
- [306] B. Xiao, P.J. Byrne, P.S. Wheatley, D.S. Wragg, X. Zhao, A.J. Fletcher, K.M. Thomas, L. Peters, S.O. EvansJohn, J.E. Warren, W. Zhou, R.E. Morris, *Nat. Chem.*, 1 (2009) 289-294.
- [307] N.J. Hinks, A.C. McKinlay, B. Xiao, P.S. Wheatley, R.E. Morris, *Microporous Mesoporous Mater.*, 129 (2010) 330-334.
- [308] J.G. Nguyen, K.K. Tanabe, S.M. Cohen, *CrystEngComm*, 12 (2010) 2335-2338.
- [309] S. Diring, D.O. Wang, C. Kim, M. Kondo, Y. Chen, S. Kitagawa, K.-i. Kamei, S. Furukawa, *Nat. Commun.*, 4 (2013) 2684.