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REVIEW PAPER

Design and bio-applications of biological metal-organic frameworks

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Abstract−Biological metal-organic frameworks (bioMOFs) are a new subclass of the MOF family. In comparison with traditional MOFs, the bioMOFs are made of multifunctional biologically related ligands (bio-ligand) and metal ions. The bio-ligands confer biological compatibility for traditional MOFs, thus providing many opportunities for a wide array of biological applications. This review highlights the recent advances in the synthesis of bioMOFs comprising multifunctional bio-ligands and metal ions. These bio-ligands include nucleobases, amino acids, peptides, proteins, cyclodextrin, saccharides, and other biomolecules. Furthermore, the potential bio-applications of bioMOFs in several fields such as biomedicine, biosensing and bioimaging, antimicrobial applications, biomimetic catalysis, chiral separation, and environmental protection are also demonstrated.

Keywords: Biological Metal-organic Frameworks (bioMOFs), Bio-ligand, Biodesign, Bioapplication

INTRODUCTION

Metal-organic frameworks (MOFs) are constructed from metal ions and organic linkers [1-3]. They are a class of porous hybrid materials with high surface areas, tunable pore structures, and high thermal stability [4-6]. Therefore, in the past twenty years, MOFs have been widely applied in gas storage and separation, sensing, catalysis, nonlinear optics, biomedicine, and so on [7,8]. Generally, highly active nanomaterials are designed by maximizing integrated functional building units while minimizing inactive components [9]. Therefore, the overall vision for MOF nanoparticle chemistry is to integrate functional molecular building blocks into artificial multifunctional nanosystems that are able to operate in different environments. In MOFs, metal ions and organic linkers play a key role in the structure and properties of MOFs. Most of the metal ions can be used to synthesize MOFs. Some metal ions such as paramagnetic metal ions have magnetic resonance active. Therefore, these paramagnetic metal ions not only become the ligands to form the MOFs but also use as magnetic resonance tomography (MRT) [10]. Besides, it is necessary to carefully select organic ligands since they directly affect the performance of MOFs [11-13]. There are many kinds of organic ligands such as carboxylic ligands, nitrogen-containing ligands, sulfonyl ligands, and metal-bearing ligands [14,15]. However, many organic ligands exhibit intrinsic toxicity and low biocompatibility, limiting the bio-application of the MOFs. Therefore, it is necessary to synthesize new MOFs to satisfy various biological applications. In recent years, biological metal-organic frameworks (bioMOFs) have attracted the attention of green chemistry. These bioMOFs are made up of biologically related ligands (bio-ligands) and metal ions [16,17]. The bio-ligands include amino acids (AAs), peptides, nucleobases, proteins, and saccharides. Compared with the conventional organic ligands, these bio-ligands can provide multiple coordination modes for metal ions, thus increasing the structural diversity of the bioMOFs. Meanwhile, chiral bioMOFs can be prepared by various functional groups of bio-ligands and used in gas separation, enantioselective synthesis, catalysis, and so on [18,19]. Furthermore, the structure of MOF can be adjusted by changing hydrogen-bonding interactions in bio-ligands. Especially, bioMOFs exhibit potential biomedical applications due to good biocompatibility, and high level functionality. However, there are only a few reviews about the design and bio-applications of bioMOFs. Therefore, this review focuses on the design method and potential bio-applications of bioMOFs using various biomolecules as bio-ligands. It also covers some aspects that were not considered in the previous literature. Potential challenges and future prospects for bioMOFs application in different sectors were also discussed.

DESIGN OF bioMOFs

MOFs are made of metal ion and organic molecules containing metal-binding sites through coordination bonds. Similarly, biomolecules also have many different metal-binding sites, so they can be used as an organic ligand to connect metal nodes into metal-biomolecule frameworks. Compared with other organic molecules, biomolecules including amino acids, nucleobases, peptides, proteins, and saccharides have several advantages. On the one hand, the diverse structures of biomolecules can directly influence the performance

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of the bioMOFs. On the other hand, the bioMOFs are more suitable for numerous bio-applications because of the presence of biomolecules compared with the conventional MOFs. Furthermore, the biomolecules with intrinsic self-assembly properties can directly modify the structure and function of bioMOFs. Especially, chiral bioMOFs can be developed by using biomolecules with chiral characteristics and used in the recognition, separation, and catalysis [20,21]. In short, biomolecule properties have played a major role in the applicability of bioMOFs. Therefore, the choice of the biomolecules is a key factor in the synthesis of bioMOFs. This section highlights the recent advances in the synthesis of bioMOFs.

1. bioMOFs Using Nucleobases as Organic Ligands

Nucleobases are nitrogenous bases with many self-assembly characteristics. They exhibit rich metal binding and H-bonding capabilities, and rigid molecular structures. Therefore, nucleobases are suitable bio-ligands for the design and synthesis of bioMOFs [22, 23]. To date, there have been a large number of reports about the nucleobases-based bioMOFs [24]. Generally, the nucleobases include purines and pyrimidines. Compared with the pyrimidines, purines have been used widely as bio-ligands for bioMOFs preparation since they contain many heteroatoms and hydrogen bonding donor/acceptor [25]. To the best of our knowledge, only a few bioMOFs have been prepared by using pyrimidines. The most reported nucleobases-based bioMOFs are synthesized by adenine [17,26]. Furthermore, unlike pyrimidines, an adenine can provide five potential metal-binding sites, a purine ring with four imino nitrogen's and an exocyclic amino group (Fig. 1) [27]. Therefore, adenine-based bioMOFs are the most important nucleobases-based bioMOFs. The first nucleobase-based bioMOFs was reported in 1964 by Gillen et al. [28], who demonstrated that Ag(I) ions can react with the N1, N3 and N6 coordination of 9-methyladenine to form 2-D bioMOFs. Subsequently, many nucleobase-based bioMOFs were prepared. However, majority of the reported nucleobase-based bioMOFs exhibit 1D or 2D structures. 3D nucleobase-based bioMOFs are scarce in the literature. This could be due to the intrinsically low symmetry and limited length of single adenine molecules. The first 3D nucleobase-based bioMOFs were synthesized by García-Terán et al. [29]. Subsequently, An et al. prepared 3D zinc-adeninate bioMOFs through adenine-adenine hydrogen bonding interactions [30]. They demonstrated that the 3D bioMOFs formation could be due to the fact that symmetry of bioMOFs was increased by using symmetric zinc-adeninate secondary building unit [31]. The same group further reported that the cavity aperture dimensions of the 3D bioMOFs can be controlled by the removal of the coordinated pyridine molecules. Based on the same strategy, a porous Bio-MOF-1 ($[Zn_8(ad)_4(bpdc)_6O{\cdot}2Me_2NH_2]{\cdot}8DMF{\cdot}11H_2O$) was also synthesized and used to adsorb CO_2 [32]. However, these bioMOFs cannot be used in biomedicine because of the presence of toxic molecules (e.g. bpdc) [33]. To overcome the low symmetry of nucleobase-based bioMOFs, some highly symmetric co-ligands were used to prepare bioMOFs. For example, a highly symmetric co-ligand, 4,40,400-s-tria zine-2,4,6-triyl-tribenzoate (TATB) was introduced into adenines-based bioMOFs [34]. The highly symmetric TATB promoted the formation of 3D adenines-based bioMOFs. Although the adenines have been used widely as bio-ligands, the use of guanine and cytosine as bio-ligands is rare. Recently, Sharma et al. synthesized 3D bioMOF hydrogels by adding Ag^{2+} ions into a deprotonated solution of adenine, cytosine, thymine or uracil. They found that Ag^{2+} could induce hydro-gelation of guanine under acidic conditions [35]. The same group further pre-

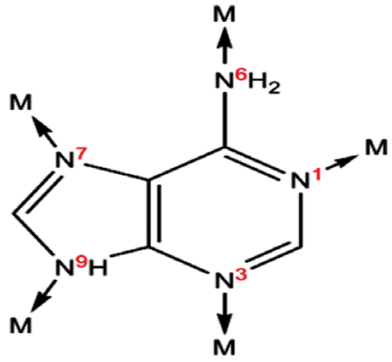


Fig. 1. Illustration of an adenine molecule and its possible coordination modes. Reproduced from Ref. [27] with permission from copyright holders.

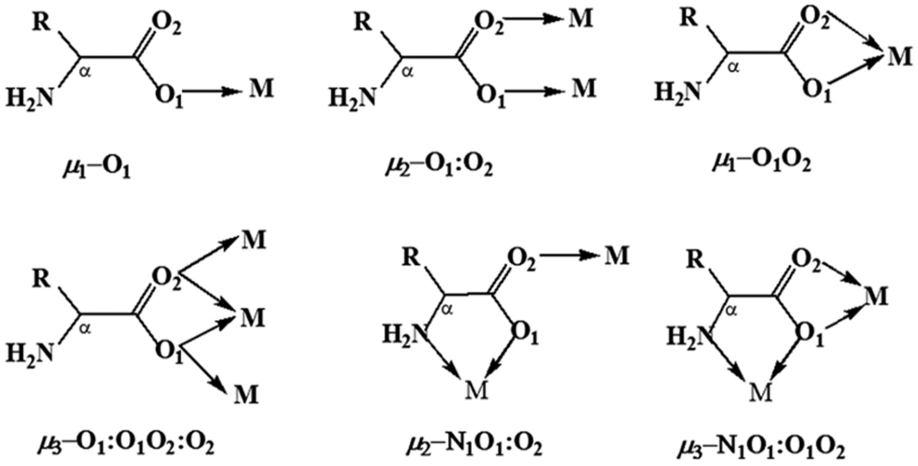


Fig. 2. The possible coordination models of amino acids and metal ions. Reproduced from Ref. [16] with permission from copyright holders.

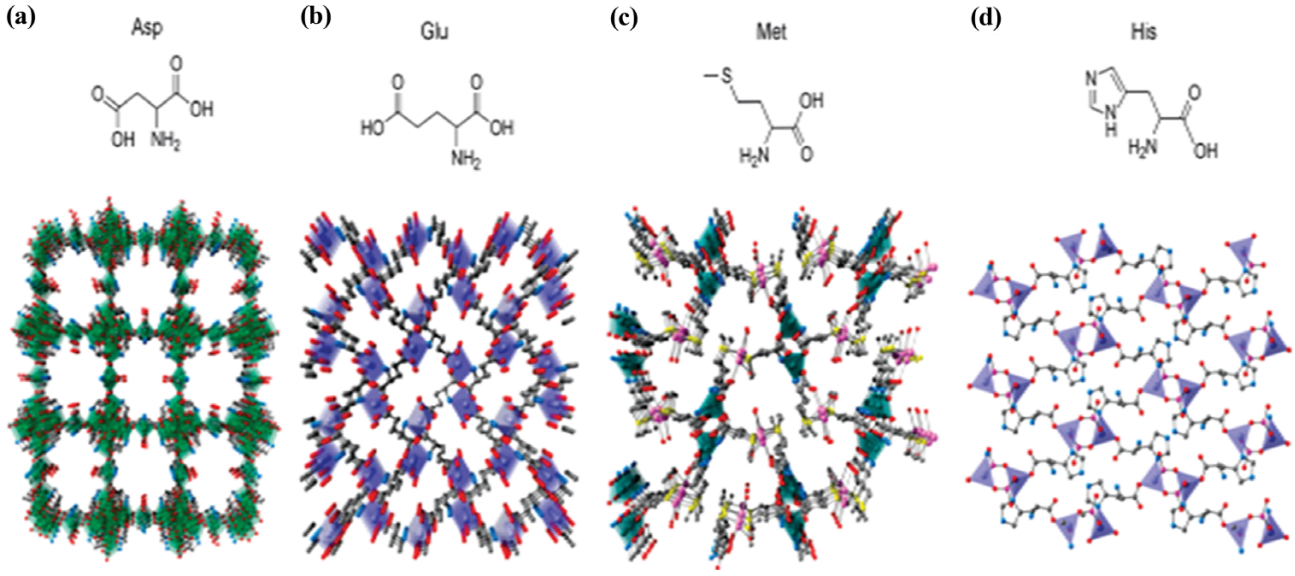


Fig. 3. 3D AAs-based bioMOFs by linking between metal ions and AAs containing side chains with metal binding groups. (a) [Ni2.5(OH)(L-Asp)$_2$]6.55H_2O; (b) Zn(L-Glu)(H_2O)]H_2O; (c) [Ag_3Cu_3(L-Met)6(NO_3)3(H_2O)$_3$]7H_2O; (d) Zn(HPO_3)(His)(H_2O)$_{1/2}$. Reproduced from Ref. [20] with permission from copyright holders.

pared stable bioMOF metallogels in water by adding Zn^{2+} ions into the guanine solution [36]. They observed that bioMOF metallogels with flower shape could be formed when Zn^{2+} ions were added into a mixed solution of cytosine and guanine. Although nucleobase-based bioMOFs have been extensively investigated, 3D bioMOFs by pure nucleobases are still rare. Therefore, it is necessary to develop new 3D bioMOFs based on pure nucleobases.

2. bioMOFs Using Amino Acids as Organic Ligands

Amino acids (AAs) are biomolecules with both carboxyl and amino groups. Therefore, AAs are excellent bio-ligands for the synthesis of bioMOFs (Fig. 2). AAs-based bioMOFs exhibit potential application in enantioselective preparation of drugs and release due to their inherent chirality [37,38]. Generally, the AAs used as bio-ligands can be categorized into three major types: (1) natural AAs; (2) mixture of natural AAs and additional organic ligands; and (3) chemically-modified natural AAs. However, natural AAs-based bioMOFs usually exhibit low dimensional and compact frameworks. Consequently, bioMOFs constructed purely from AAs are rare [39]. To overcome this problem, polydentate organic ligands, anions, or chemically modified AAs are usually used to increase the dimensionality of the AAs-based bioMOFs. Until now, natural AAs-based bioMOFs mainly exhibit 1D structure. In comparison, 2D AAs-based bioMOFs can be prepared by coordinating AAs to metal ions in a 2 : 1 fashion. Meanwhile, 2D AAs-based bioMOFs could also be obtained by the coordination of two AAs to an octahedral metal ion. For example, 2D glycine-based bioMOFs can be prepared when glycine is coordinated to Ni(II), Mn(II), and Co(II)) in a 2 : 1 fashion [40-42].

As mentioned, although 3D AAs-based bioMOFs are rare, some 3D AAs-based bioMOFs could be constructed by the linkage between metal ions and AAs containing side chains with metal binding groups. Generally, the metal binding groups on these AAs include β-carboxylate groups of aspartic and glutamic acids, the imidazole group of histidine, the thiol or thioether groups of cysteine and methionine, and the phenol ring of tyrosine [20] (Fig. 3). For the first time, Gramaccioli prepared the biocompatible 3D AAs-based bioMOFs by mixing Zn(II) and glutamate (L-Glu) in 1966 [43]. Subsequently, a 3D bioMOF was synthesized by mixing $Dy(ClO_4)_3$ and L-aspartic acid [44]. Lu et al. prepared a homochiral heterobimetallic bioMOF by binding Cu(II) ions and Ag(I) to carboxylate sites and thioether groups of methionine [45]. However, these prepared 3D AAs-based bioMOFs are still rare and low dimensional. To increase the dimensionality of bioMOF, the mixture of both AAs and additional organic ligands or inorganic anion was used as linkers to prepare 3D bioMOF. Xu et al. synthesized a 3D homochiral bioMOF by connecting Cu(II)-L or D-Pro chains through polyoxometalate $[BW_{12}O_{40}]^{5-}$ clusters [46]. Chen et al. prepared a non-chiral 3D bioMOF with Gly and azide. The Gly-based bioMOF exhibited an unusual 4-connected 3D net with a hexagonal diamond shape [47]. Likewise, Luo et al. developed a non-chiral 3 D Ala-based bioMOF by using chiral L-Ala, Cu and Gd [48]. Two 3D homochiral bioMOFs were designed and fabricated in a layered-pillar fashion by binding an Asp to three CoII ions [49]. The dimensionality of AAs-based bioMOFs could also be increased by chemically-modified natural AAs. For instance, instead of traditional 1- and 2D bioMOFs with non-modified Phe, two 3D homochiral bioMOFs were prepared by modifying the phenyl ring in Phe with a tetrazole [50] (Fig. 4). Using the same strategy, Wang et al. found that the size and the shape of 2-D Zn(II) and Cd(II) chiral bioMOFs could be regulated by introducing different functionalities to the phenyl ring of Phe [51]. 3D bioMOFs can also be synthesized by coordinating Cu(II) and Cd(II) ions with the carboxylate and amino groups of cysteic acid [52].

3. bioMOFs Using Peptides as Organic Ligands

Peptide is a product constructed by AAs, and despite having the property of AAs is quite different from AAs. Due to the use of

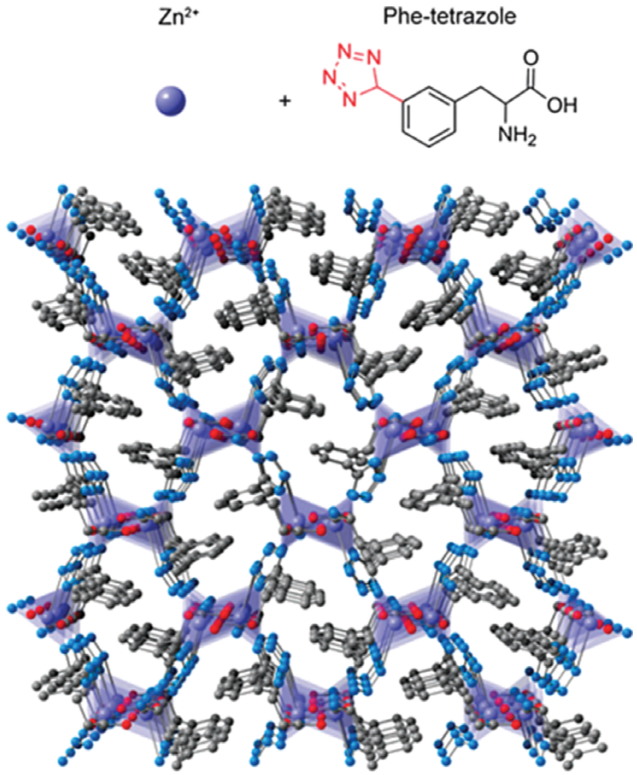


Fig. 4. Representation of the structure [Zn(Phe-tetrazole)] generated by using Phe functionalized with a tetrazole moiety. Reproduced from Ref. [50] with permission from copyright holders.

amino acids as substrates, peptides also have the ability to act as bio-ligands. Usually, peptides can react with metal ions to form diverse 2D or 3D peptide-based bioMOFs. As compared to AAs, the use of peptides as bio-ligands has several advantages. For example, peptides with double-bond character exhibit higher degree of adaptability, which prevents rotation about this bond. Peptide structures can be regulated by changing the type and order of AAs. Furthermore, chiral characteristics of peptides render them the excellent candidates for preparing chiral bioMOFs. Therefore, various peptide-based bioMOFs were successfully prepared. Dipeptides such as Gly-Gly are the simplest and often used to prepare peptide-based bioMOFs. Takayama et al. first synthesized peptide-based bioMOFs by Zn(II) or Cd(II) ions and GlyGly peptide [53]. Ueda et al. used glythr dipeptides and Zn(II) ions to prepare peptide-based bioMOFs [54]. Two dipeptide-based bioMOFs were also synthesized by the coordination of dipeptides with cadmium ions [55]. One of them exhibited porous structures with 1D channels, while the other one displayed a non-porous structure. Likewise, Gasque et al. prepared two dipeptide-based bioMOFs by Pb(II) or Cd(II) ions and GlyGlu. One formed 2D bioMOFs structure, whereas another exhibited 3D porous bioMOF [56]. They demonstrated that 3D porous dipeptide-based bioMOF could be formed by the addition of a metal-binding site to the peptides. Emami et al. developed a new approach to prepare 3D porous dipeptide-based bioMOF. They used Asp and the substitution of the metal ion (Zn^{2+} by Co^{2+}) to synthesize two different 3D bioMOFs [57] (Fig. 5). Martí-Gastaldo et al. prepared a peptide-based bioMOF by coordinating glycyl-serine dipeptides to Zn metal centers. The dipeptide-based bioMOF structure can be regulated from a solvated porous state to a desolvated non-porous state when confirmation of the glycyl-serine dipeptides is changed. They considered that the phenomenon could be due to hydrogen bonding in the side-chain hydroxyl groups of the serine [58].

Until now, most of the reported peptide-based bioMOFs were synthesized from dipeptides. In recent years, some tripeptides have also been used as ligands to develop the peptide-based bioMOFs. However, tripeptides are more expensive and challenging for synthesis as compared to the dipeptides. Lee et al. synthesized a tripeptides-based bioMOF by cadmium and Gly. The resultant tripeptide-based bioMOFs exhibited a 2D structure [59]. Recently, Martí-Gastaldo et al. prepared two-isoreticular 3D tripeptide-based porous bioMOF by coordinating the Gly-L-His-Gly and Gly-L-His-L-Lys to CuII. The 3D tripeptide-based bioMOF exhibited sponge-like behavior [60]. They found that urea-functionalized networks could be obtained by modifying the lysine in the peptide backbone.

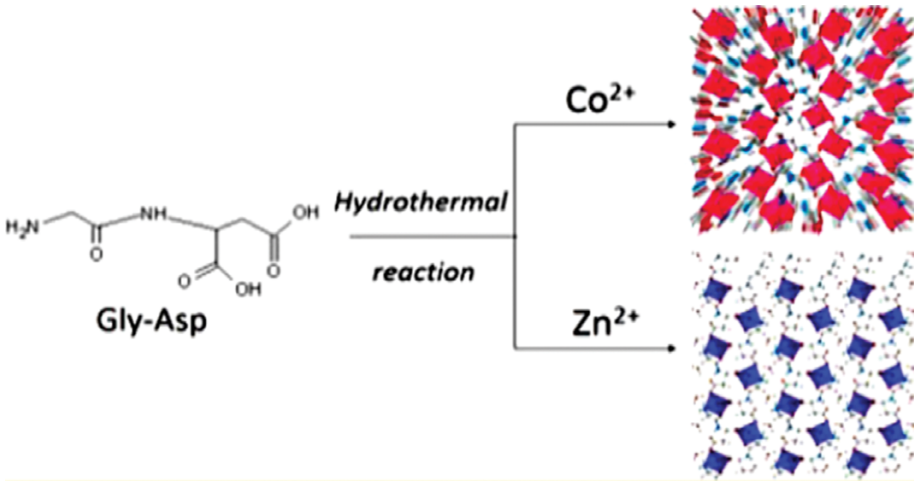


Fig. 5. Representation of the structure [Zn(GlyAsp)]·H_2O and [Co(Gly-Asp)]·H_2O generated by using side chain coordination (Asp) and the substitution of the metal ion (Zn^{2+} by Co^{2+}). Reproduced from Ref. [57] with permission from copyright holders.

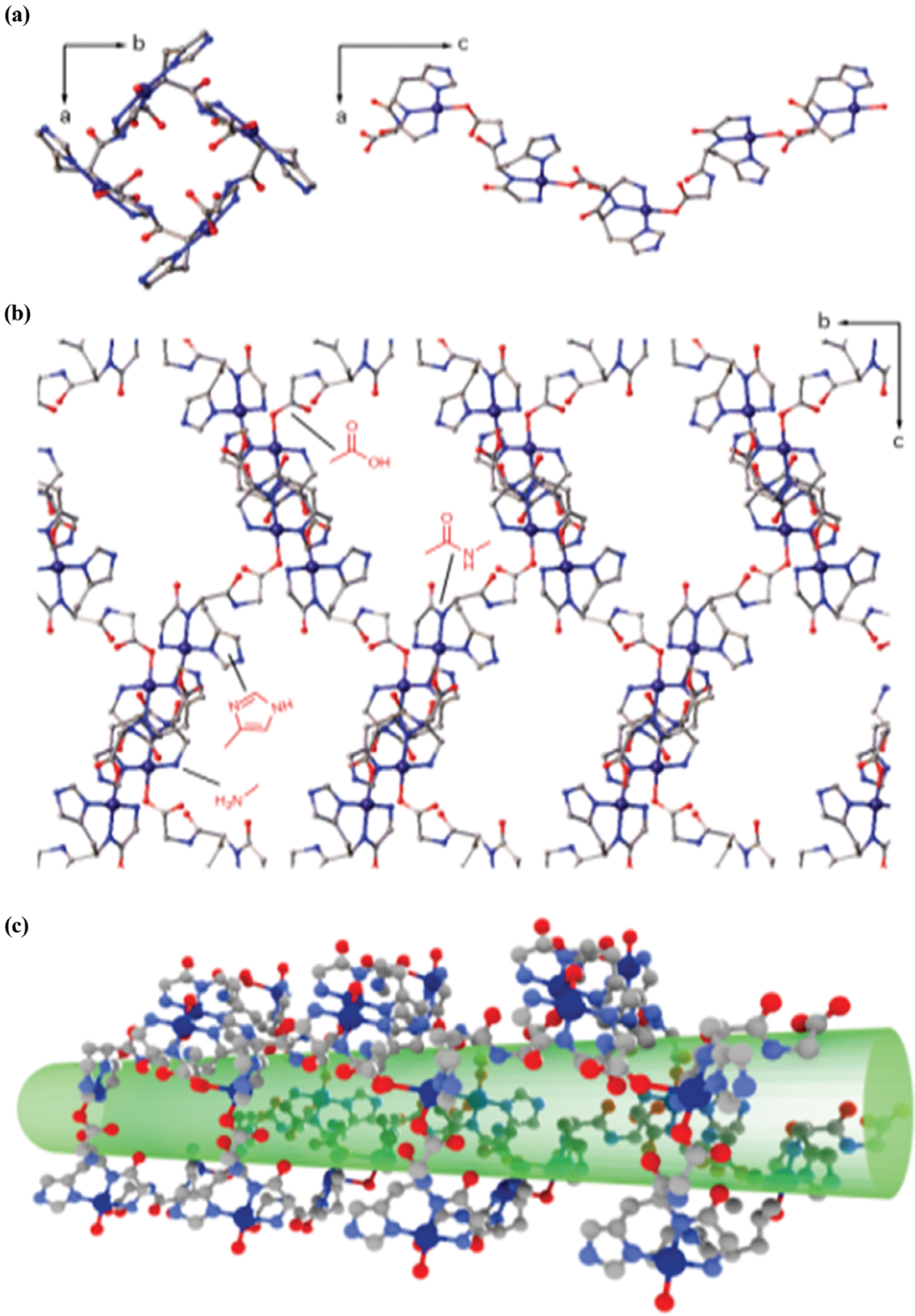


Fig. 6. Schematic synthesis of the Cu(GHG) bioMOF. (a) Structure of helicoidal chains in Cu(GHG) bioMOF. (b) Functional groups in the peptidic backbone decorating the surface of the pores. (c) 1D channels in Cu(GHG) are surrounded by functional sites prone to establish supramolecular interactions, well fitted for chiral recognition and discrimination. Reproduced from Ref. [61] with permission from copyright holders.

Navarro-Sánchez et al. prepared a chiral 3D tripeptide-based bioMOF by Cu(II) and Gly-L-His-Gly [61] (Fig. 6), and found that chiral recognition was linked to preferential binding of one of the enantiomers. The result could be due to the fact that the presence of H-bonds makes diastereomeric adducts more stable. Pentapeptide-based bioMOFs were also prepared [62]. In this case, two CdII

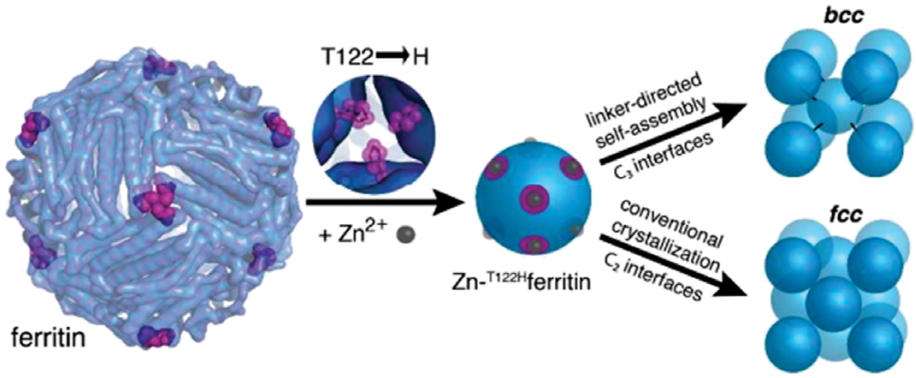


Fig. 7. Scheme for metal/linker-directed self-assembly of ferritin into 3D crystals. Reproduced from Ref. [64] with permission from copyright holders.

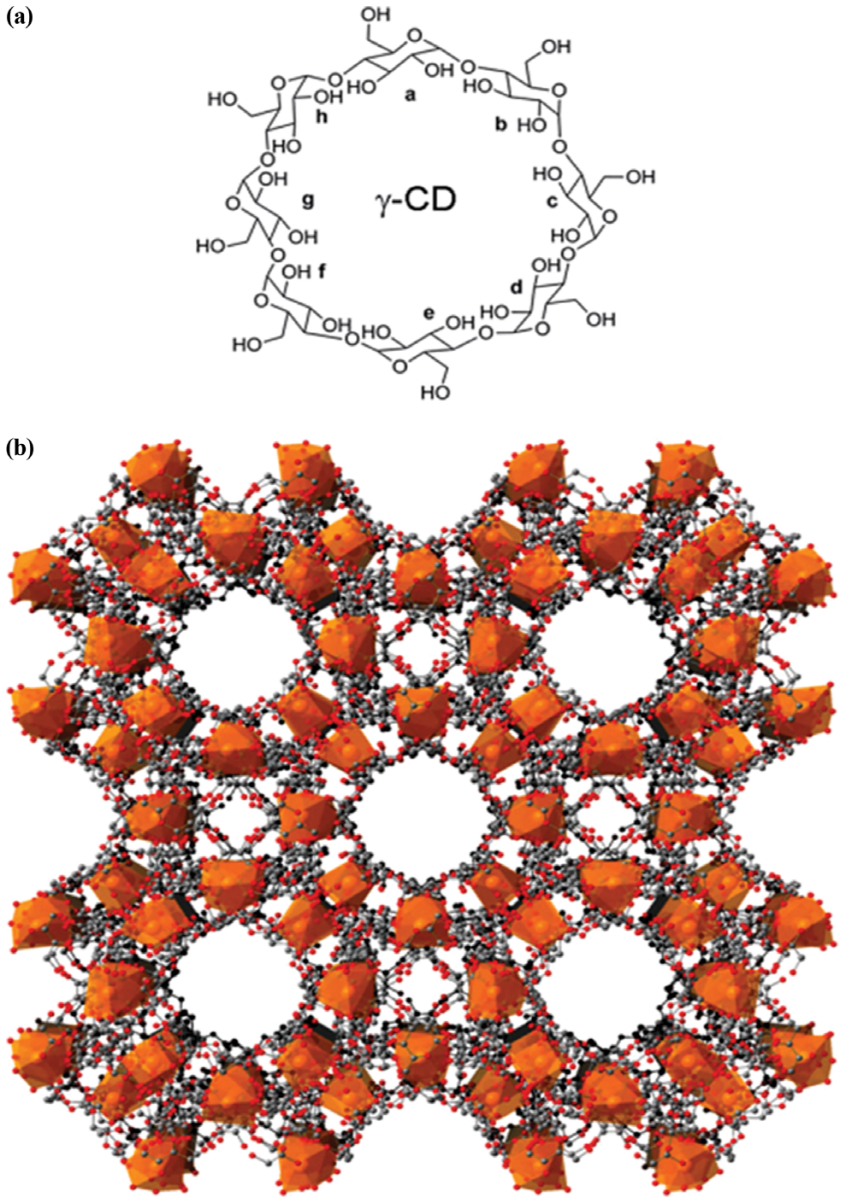


Fig. 8. Representation of (a) γ-cyclodextrin (γ-CD), and (b) the porous structure of (γ-CD)$(KOH)_2$. Reproduced from Ref. [68] with permission from copyright holders.

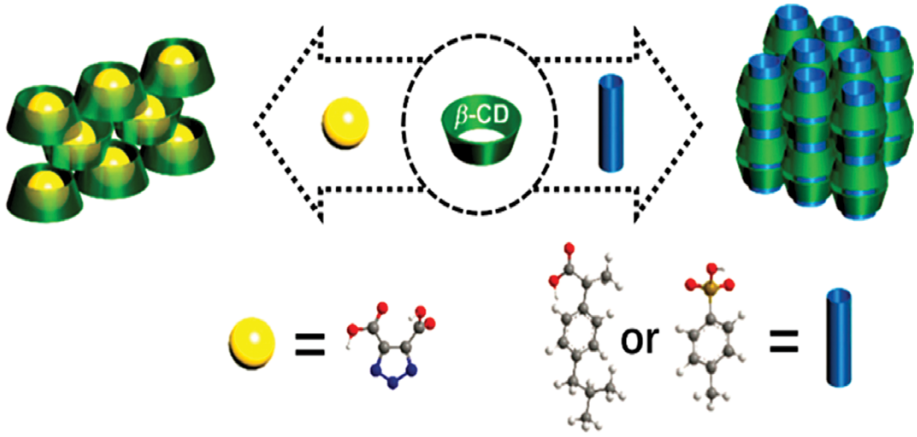


Fig. 9. Schematic view of structural forming of CD-MOF-1 (left) and CD-MOF-2 (right) by using different templates in the reaction process. Reproduced from Ref. [70] with permission from copyright holders.

chains were linked with the pentapeptide. However, there are very few reports about polypeptide-based bioMOFs. This might have been due to the flexibility of longer-chain polypeptides being able to increase the difficulty of forming 3D frameworks.

4. bioMOFs Using Proteins as Organic Ligands

It is known that proteins have the ability to coordinate metal ions due to their AA and peptide constituents. However, it is difficult to control the coordination of metal ions at the interfaces of proteins due to the complexity and flexibility of protein structures. Therefore, there are few proteins based 3D bioMOFs. Radford et al. prepared a porous protein-derived bioMOF for the first time [63]. In the protein-based bioMOF, two engineered proteins based on the four-helix bundle hemeprotein cytochrome were connected through Ni(II) and Zn(II) ions. Subsequently, the same group developed a 3D porous spherical protein-based bioMOFs by linking ferritin and Zn(II) ions [64] (Fig. 7). The same group also synthesized various protein-based bioMOFs with cubic or tetragonal shapes by changing metal ions [65]. Until now, although the number of protein-based bioMOFs is still rare, it is speculated that the development of protein-based bioMOFs will be rapid due to multi-functionality and diversity of protein molecules.

5. bioMOFs Using Saccharides as Organic Ligands

As mentioned, the majority of bioMOFs are prepared using AA, peptide, and nucleobases. In fact, as organic molecules, saccharides have frequently been used as building blocks for self-assembled structures, and become efficient host molecules in host-guest chemistry. Therefore, saccharides can be used as bio-ligand to synthesize a range of bioMOFs. Among various saccharides, cyclodextrins (CDs) with a special structure such as hydrophobic internal cavity and hydrophilic external surface are important host molecules [66, 67]. This special structure enables CDs to have a hydrophobic binding site. Generally, CDs-based bioMOFs are synthesized using alkali metal salts including K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, Cu^{2+}, and Zn^{2+}. Stoddart et al. synthesized a porous γ-CD-based bioMOF, for the first time, by combining γ-CD with KOH [68]. The γ-CD-based bioMOF were constructed by connecting six γ-CD units with K^+ or Rb^+ ions (Fig. 8). The same group then prepared new α-CD-based bioMOFs with hollow long needle shape [69]. In this hollow α-CD-based bioMOFs, the Rb^+ cations were linked to the α-1,4-D-Glup residues. However, they found that not every α-1,4-D-Glup residue was coordinated to an Rb^+ cation. Lan et al. constructed two β-CD-based bioMOFs through a template-induced approach [70], and found that β-CD-based bioMOFs with pentagonal pyramid shape contained only one Cs^+ and four contiguous β-CD molecules (Fig. 9). In contrast, another β-CD-based bioMOFs with 3D structure contained one and one half Cs^+ ions and one β-CD molecule. However, it is difficult to prepare crystalline highly porous CD-based bioMOFs. Recently, Patel et al. developed a synthetic methodology to overcome the limitation of preparing porous CD-based bioMOFs. In this case, porous CD-based bioMOFs were prepared by co-crystallization of Li^+ and K^+ ions with γ-CD [71]. Besides, CD-based bioMOFs are easily degraded in water, limiting their bio-application in physiological conditions. Therefore, Furukawa et al. prepared uniform cubic CD-based bioMOF-1 to improve the stability of CD-based bioMOF in the water. The original cubic shape of the CD-bioMOF-1 was retained in the water, indicating high water stability [72]. Although the majority of the saccharides-based bioMOFs are prepared by using CD as ligand, saccharic or glucaric acid can also be used as ligand. Robson et al. synthesized a 3D bioMOF by linking glucaric acid with Zn(II) ions [73]. In this case, Zn(II) ions were chelated at both ends of the glucarate ligand. Moreover, the same group also prepared a series of bioMOFs using saccharic acid and mucic acid galactaric [74]. However, to date, saccharide-based bioMOFs are still very rare.

6. bioMOFs Using other Active Small Biomolecules as Organic Ligands

Besides AAs, peptides, proteins, and saccharide, some active small biomolecules, such as formic, oxalic, fumaric, glutaric, malic and succinic acids can also be used as ligands to synthesize bioMOFs since these biomolecules contain carboxylate group. As the simplest carboxylic acid, formic acid has been widely used as a ligand to synthesize bioMOFs. Miller et al. prepared a microporous bioMOF structure with the biocompatible and bioactive calcium metal and 3,3′,5,5′-azobenzenetetracarboxylate ligand for the first time. The Ca-based bioMOF exhibited coordinatively Ca^{2+} Lewis acid

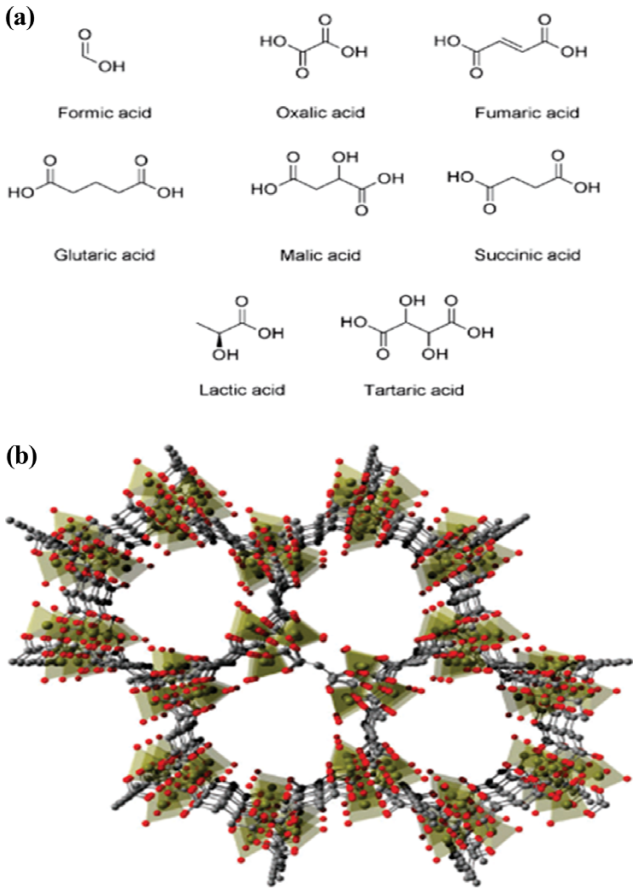


Fig. 10. Representation of some carboxylate ligands (a); Representation of the porous structure $[Fe_3O(MeOH)_3(fum)_3(CO_2CH_3)]\cdot 4.5MeOH$ (b). Reproduced from Ref. [20] with permission from copyright holders.

sites able to trap and deliver nitric oxide at a biological level, making this new Ca-MOF an interesting candidate for biomedical applications [75]. Kim et al. synthesized porous 3D bioMOFs by binding each format ligand to three Mn(II) ions [76]. Jain et al. also prepared four multiferroic formate-based bioMOFs [77]. In addition to formic acid, oxalic acid, lactic acid, succinic acid, and tartaric acid, fumaric acids were also used to prepare bioMOFs (Fig. 10). Thushari et al. prepared several tartrate-based chiral porous bioMOFs [78]. Dybtsev et al. reported a 3D porous lactic acid-based bioMOF [79]. However, these carboxylic acids-based bioMOFs are easily degraded in aqueous medium, thus limiting its practical applications. In recent years, some therapeutic molecules with coordinating groups have been used to prepare bioMOFs for biomedical applications. For example, the drug olsalazine (H_4olz) was used as a ligand to synthesize a series of mesoporous bioMOFs. The high surface area and biocompatible bioMOFs are promising candidates for drug delivery [80]. In addition, a series of zinc-based bioMOFs was also synthesized by using deferiprone as a chelating ligand [81]. Su et al. prepared a highly porous medi-bioMOF-1 by binding Zn and the pharmaceutical ingredient curcumin [82]. Although a large number of active small biomolecules have been used as ligands to prepare bioMOFs for biomedical application, the rapid degradation of these bioMOFs in aqueous medium or acidic conditions limits their widespread bio-application. Therefore, it is necessary to develop new, active biomolecules-based bioMOFs.

BIO-APPLICATIONS OF bioMOFs

In recent years, MOFs have been widely used in various fields, including gas separation, catalysis, biomedical applications, and sensors [83-86]. As a subclass of MOFs, bioMOFs also show similar properties to MOF. In addition, bioMOFs not only have practical applications in gas storage and separation, sensors, and catalysis, but also have several promising bio-applications, such as biomedicine, biosensing, bioimaging, antimicrobial applications, biomimetic catalysis, chiral separation, and environmental protection. However, although bioMOFs are built up of biomolecule components, this does not mean that the bioMOF nanoparticles are nontoxic, because the toxicity of nanoparticles is dependent on their size, shape and surface-area [87,88]. Therefore, it is necessary to con-



Fig. 11. Bioapplication of bioMOFs in various fields.

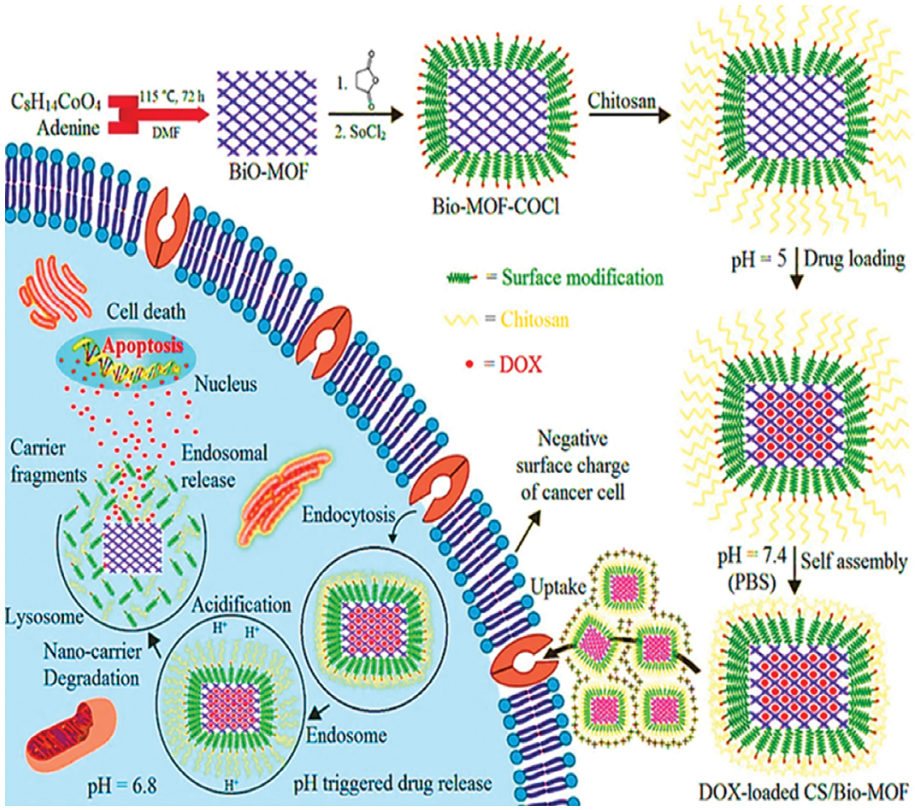


Fig. 12. Schematic view of structural forming of CS/Bio-MOF and its application as a pH-responsive and target-selective system for delivery of doxorubicin (DOX) in the treatment of breast cancer. Reproduced from Ref. [102] with permission from copyright holders.

sider the complexity of bioMOF toxicity for the bio-applications. Examples of biological applications of the bioMOFs are illustrated in Fig. 11.

1. Biomedical Applications

For biomedical application, downsizing materials to the nanoscale is a suitable strategy to develop new applications compared to the ones of their bulk analogues [89-92]. Due to high drug loading capacity and excellent biocompatibility, bioMOFs are promising candidates in biomedical applications, particularly for drug delivery hosts [93-95]. Rosi et al. reported a controlled drug release of bioMOF for the first time [96]. Horcajada et al. prepared a series of specific non-toxic porous iron(III)-based bioMOFs for the efficient controlled delivery of antitumor and retroviral drugs. These bioMOFs exhibited high drug loadings and encapsulated drugs with different characteristics and functions [97]. Bernini et al. screened a series of biocompatible bioMOFs as carriers of the anti-inflammatory and analgesic ibuprofen. They demonstrated that grand canonical Monte Carlo (GCMC) simulations could readily predict the bioMOFs performance in drug delivery [98]. In addition, aspirin was encapsulated inside the pores of bioMOF (MIL-100(Fe)). The bioMOF exhibited high drug loading efficiency (181%), and could slow the release of aspirin in an acidic environment. The slow release of aspirin from the bioMOF is beneficial for extending the duration of the therapeutic activity of aspirin in the blood [99]. Recently, a Cu@bioMOF-7 was prepared by lysine and metal ions (manganese or copper). The bioMOF possessed multifunctional properties including drug adsorption/release of a drug [100]. Besides, various cobalt-AAs based bioMOF were successfully utilized for the adsorption of terazosin, telmisartan, glimepiride, and rosuvastatin drugs [101]. Recently, a bioMOF was coated with a monodispersed layer of chitosan (CS/Bio-MOF) and applied as a pH-responsive and target-selective system for the delivery of doxorubicin [102] (Fig. 12). The CS/Bio-MOF exhibited several advantages: (1) high drug loading, (2) sustainability in aqueous media, (3) targeted pH-responsive, and stable drug release in cancer cells, and (4) bioavailability and low cytotoxicity. Therefore, the doxorubicin-loaded CS/bioMOFs displayed a greater efficacy in the treatment of cancer. In addition to drug delivery, a novel bio-metal-organic MOF (bioMOF-1) coating was formed on the surface of Mg alloy to improve the bioactivity and corrosion resistance of Mg implants. The bioMOF-1 layer exhibited a great advantage to enhance the corrosion resistance of Mg alloy, thus providing long-term protection on Mg alloy implant [103]. The authors considered that the bioMOF-1 coating was a promising method for surface modification of Mg implant. Recently, four isoreticular metal-organic frameworks (Ni-IRMOFs-74-II to -V) were prepared to encapsulate single-stranded DNA (ssDNA). The Ni-IRMOFs exhibited excellent ssDNA transfection efficiency in mammalian immune cells [104].

In addition, the surface of MOFs could be functionalized by the coordinative interaction of functionalized active molecules for biomedical application [105-108]. For example, different molecular units were anchored on the outer surface of MOF nanoparticles (MOF NPs) by the coordinative interaction of functionalized His-tags with MOF NPs for biomedical application [109]. Furthermore,

covalent post-synthetic modification of MOFs could be used to functionalize the external surface of MOF [110]. The internal surface of MOF could also be functionalized by using linker molecules with functional groups such as unsaturated functional groups [111]. Although bioMOFs exhibit excellent properties on drug delivery (chemical drug, nucleic acids, peptides, and proteins) [112-115], the drug loading efficiency of bioMOFs is still low. Therefore, it is necessary to profoundly understand the interactions between drugs and bioMOFs in the future.

2. Biosensing and Bioimaging

In recent years, bioMOFs with specific function have attracted great interest in biosensors because of their diverse structures and multi functionalities. For example, various adeninate embedded bioMOFs (bioMOF-1) were synthesized by encapsulating different lanthanide ions (e.g., Eu^{3+} or Tb^{3+}). These bioMOFs-1 exhibit high Fe^{3+} sensitivity and can be used as metal sensors in wastewater [116]. Furthermore, functionalized bioMOF-1 rare earth ion was used to synthesize various photo-functional polymer hybrid thin films. The hybrid thin films could be used as luminescent ratiometric thermometer [117]. Subsequently, Jonckheere et al. applied the bioMOF-1 to synthesize a new adeninate-based bioMOF-1 with luminescent properties. The adeninate framework bioMOF-1 displayed the ability to stabilize luminescent silver clusters [118]. Besides, two lanthanide luminescent bioMOFs were synthesized under the hydrothermal condition. These bioMOFs exhibited high-sensitivity fluorescence sensing functions to aromatic amines and used to detect Fe^{+} ions [119]. Xu et al. reported a phosphorescence/fluorescence dual-emissive bioMOF that can be used as intracellular O_2 biosensor. The bioMOFs exhibited high crystallinity and stability, and excellent ratiometric luminescence in response to O_2 partial pressure [120]. Recently, new 3D bioMOFs were synthesized by using 4,4′,4″-s-triazine-2,4,6-triyltribenzonic acid and Eu^{3+}. The 3D bioMOF could be used as a luminescent probe for highly selective sensing of Cu^{2+} [121]. In addition, a new bioMOF was prepared by using Zn_3(benzene-1,3,5-tricarboxyl)$_2$(adenine)(H_2O) (ZnBTCA) and thermosensitive fluorescent dyes. The resultant bioMOF not only exhibited highly efficient ratiometric temperature-sensing properties under physiological cellular conditions, but also could be excited under visible light [122]. So far, few sensors based on MBioFs have been reported; therefore, more research on bioMOF-based biosensors should be carried out in the future.

Generally, most of the bioMOFs exhibit structural diversity and physicochemical properties and have nanoscales from tens to hundreds of nanometers. Furthermore, compared with the conventional MOFs, bioMOFs are usually built up from low toxic ligands. Especially, bioMOFs can carry large amounts of paramagnetic metal ions. These paramagnetic metal ions such as Gd^{3+}, Fe^{3+}, and Mn^{2+} not only link the bio-ligands to form the bioMOFs but also act as magnetic resonance imaging (MRI). These magnetic properties make bioMOFs potential platforms for bioimaging [123]. Taylor et al. synthesized Mn^{2+}-based bioMOFs with controllable morphologies [124]. The surface of Mn^{2+}-based bioMOFs was modified by cell targeting molecule. The modified Mn^{2+}-based bioMOFs were used as target-specific MRI for cancer cells. They further demonstrated that the Mn^{2+}-based bioMOFs could also be used for the targeted delivery of other imaging modalities. In addition, a more biocompatible and specific non-toxic porous iron(III)-based bioMOF was synthesized that appeared as a promising candidate for MRI agents [125]. Except for MRI, bioMOFs were used in optical imaging for the biological studies [126]. For example, a series of bioMOFs based on lanthanide ions and nucleotides were synthesized and applied in optical imaging [127]. Likewise, some anionic dyes were incorporated within adenosine-based bioMOFs and successfully used for optical imaging. However, the research on bioMOF-based bioimaging is still at an early stage. Furthermore, the size and shape of the bioMOFs have a significant impact on good imaging of living cells or organisms. Therefore, it is of great significance to improve their size and shape, allowing their endocytosis by the living cells and increase their systemic circulation in blood.

3. Antimicrobial Applications

Some low-toxic cations have been reported to exhibit antimicrobial effects such as Ag, Zn, Co, and Cu ions. Therefore, bioMOFs containing these metal ions have antibacterial activity. Especially, bioMOFs have been considered to be controlled-release antimicrobial agents. These controlled-release antimicrobial components include antimicrobial metal ions and linkers from the bioMOF, as well as entrapping antimicrobial agent within the bioMOF. For example, a novel cobalt-based bioMOF was synthesized that was found to be highly effective at inactivating model microorganisms [128]. In this case, the Co active sites in the bioMOF could rapidly catalyze the lipid peroxidation, causing rupture of the bacterial membrane and thereby bacterial cells lysis. Also, two bioactive silver-bioMOFs were synthesized and exhibited notable antibacterial and antifungal activities [129]. Similarly, a silver-based bioMOF was prepared and evaluated as a bactericidal material. The silver-based bioMOF acted as a "reservoir" of Ag^{+} that could be released and inhibited various bacteria cells [130]. In addition, the Cu-based bioMOF was directly grown within the synthetic fabrics. The Cu-based bioMOF exhibited excellent antibacterial activities against three different microbial pathogens [131].

Although antibacterial effects based on metal ion release show great promise for biomedical applications. Some metal ions such as Ag^{+} and Co^{2+} are toxic to human cells, thus limiting their therapeutic applicability. As a result, bioMOFs developed from low toxicity metals (Zn^{2+}) might be more suitable for biomedical applications. Wang et al. prepared four Zn-based bioMOFs of various shapes by zinc(II) metal ions and 2,20 -bipyridine-4,40-dicarboxylic acid. The synthesized bioMOFs exhibited good antimicrobial effects, indicating potential uses in the medical and environmental applications [132]. Similarly, a biocompatible and bioactive BioMIL-5 was synthesized from a Zn^{2+} salt and azelaic acid [133]. The BioMIL-5 revealed interesting antibacterial properties. It was found to be stable in water and bacterial culture medium and showed a sustained release of Zn^{2+} ions (Fig. 13). Besides, a Zn-based bioMOF with hydrazine benzoate linkers was prepared and evaluated against the *Staphylococcus aureus*. The bioMOF showed potential bacterial growth inhibiting activity. The authors considered that the antimicrobial effect could be attributed to the release of the 4-hydrazinebenzoate linker and Zn^{2+} [134]. In addition, the encapsulated antimicrobial agent within the bioMOF also played an antibacterial role. For example, bioMOFs encapsulated with vancomycin and folic acid were used against *S. aureus* [135]. Lin et al. synthe-

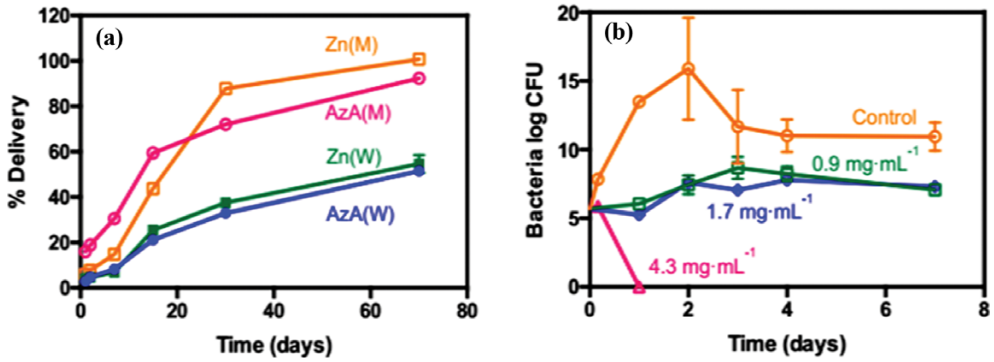


Fig. 13. (a) Delivery profile of azelaic acid (AzA) and zinc (Zn) in Mueller Hinton Cation Adjusted broth or MHCA (M) and in water (W): AzA(M) (pink), AZA(W) (blue), Zn(M) (green) and Zn (orange) (W). (b) Bacterial growth curves comparing the control group (orange) with BioMIL-5 at different concentrations. Reproduced from Ref. [133] with permission from copyright holders.

sized a carboxylate bioMOF with vancomycin encapsulation. The resultant bioMOF, which was constructed from Fe^{3+} ions and terephthalic acid, exhibited high antibacterial activity against *S. aureus* [136]. So far, the antibacterial mechanism of bioMOFs still remains to be elucidated. Furthermore, it necessitates more researches to develop appropriate methods for the improvement of antibacterial activities of environmentally friendly bioMOFs.

4. Biomimetic Catalysis

Enzymes are effective biocatalysts used in various fields owing to their ease of production, substrate specificity and selectivity, and green chemistry. However, natural enzymes exhibit low tolerances to extreme environment, limiting their practical applications. Therefore, there is a great need to develop alternatives to enzymes. Biomimetic catalysis has become a promising candidate for highly efficient catalysis [137-139]. Especially, some reports showed that bioMOFs with hydrophobic and hydrophilic pore can be used to mimic the microenvironment of the active sites in enzymes. Therefore, porous bioMOFs are becoming desirable biomimetic catalysts. Generally, biomimetic bioMOF catalysts have the following modes: (1) bioMOFs with biomimetic molecules, (2) metal nodes as biomimetic catalytic sites, and (3) incorporation of biomimetic active sites into organic linkers [140]. Especially, bioMOFs with the open metal centers have been used as catalysts. For example, Li et al. demonstrated that HKUST-1 with CuII binuclear metal centers exhibited protease-like catalytic activity. They also found that the CuII sites not only increased the interfacial interaction between HKUST-1 and substrates but also played as hydrolytic active centers, thus accelerating the hydrolysis reaction rate [141]. bioMOFs with metalloporphyrin moieties were found highly active in the aerobic oxidation of inert hydrocarbons. For example, Zhao and Wu introduced N-hydroxyphthalimide as an assistant catalyst to improve metalloporphyrinic bioMOF catalysis. The biomimetic bioMOF displayed high efficiency in the aerobic oxidation of arylalkanes [142]. Similarly, Li et al. prepared a chiral bioMOF by incorporating metalloporphyrin and metallosalen into MOF structure, and used the chiral bioMOF to catalyze the asymmetric cyanosilylation of aldehydes [143]. Instead of metalloporphyrins, metallophthalocyanines can be incorporated into bioMOFs to prepare biomimetic catalysts. For example, CoII-phthalocyanine (Co-PC) moieties were encapsulated into bioMOF-1 (C)-PC@bioMOF). The resultant Co-PC@bio-MOF-1 could catalyze the epoxidation of styrene [144]. However, compared to metalloporphyrins, metallophthalocyanines are much more easily aggregated, thus decreasing their catalytic efficiency. Generally, hydrogen bonding plays an important role in molecular recognition and activation in enzymatic catalysis. Inspired by enzymatic catalysis, some small molecules with hydrogen-bonding moieties have been used to mimic the catalytic properties of the enzyme. For example, a urea-derived bioMOF with hydrogen-bonding was prepared that exhibited excellent catalytic activity in the Friedel-Crafts alkylation reactions [145]. Likewise, an azobenzene-based bioMOF with zirconium was used to catalyze the amidation of benzoic acids. Furthermore, the bioMOF could be widely applied to synthesize bioactive amide compounds [146]. In addition, adenine-based bioMOF (AD-MOF-2) exhibited CO_2 photoreduction performance, and had a very high HCOOH production rate [147]. Overall, compared with the native enzyme, biomimetic bioMOF catalysts exhibited the wider application perspective and enhanced stability. Sometimes they also showed catalytic properties that native enzymes do not possess. However, the study of stable biomimetic bioMOF catalysts is still in an early stage that demands development of new types of stable biomimetic bioMOF catalysts.

5. Chiral Separation

Chirality is of vital importance in medicine, life science, and food chemistry, but the separation of chiral isomers is very difficult due to their unique physicochemical properties. Chiral bioMOFs have become a promising candidate for the enantioselective separation. Compared with other chiral materials, the chiral porous bioMOFs with various chiral linkers and metal ions can better interact with chiral molecules, leading to more efficient selectivity and the separation of chiral molecules. Li et al. prepared microporous zeolitic bioMOFs from four enantiopure amino acids and 5-methyltetrazole ligand (Fig. 14). These zeolitic bioMOFs exhibited enantioselective recognition ability [148]. Zhang et al. prepared six homochiral bioMOFs with amino acid ligands for HPLC separation of enantiomers [149]. Recently, Chan et al. prepared a homochiral zeolitic imidazolate framework-8 (ZIF-8) membrane for efficient chiral separation by incorporating L-histidine (L-His) into ZIF-8's framework. The homochiral L-His-ZIF-8 membrane exhibited good selectivity for the R-enantiomer of 1-phenylethanol [150]. Yang et al.

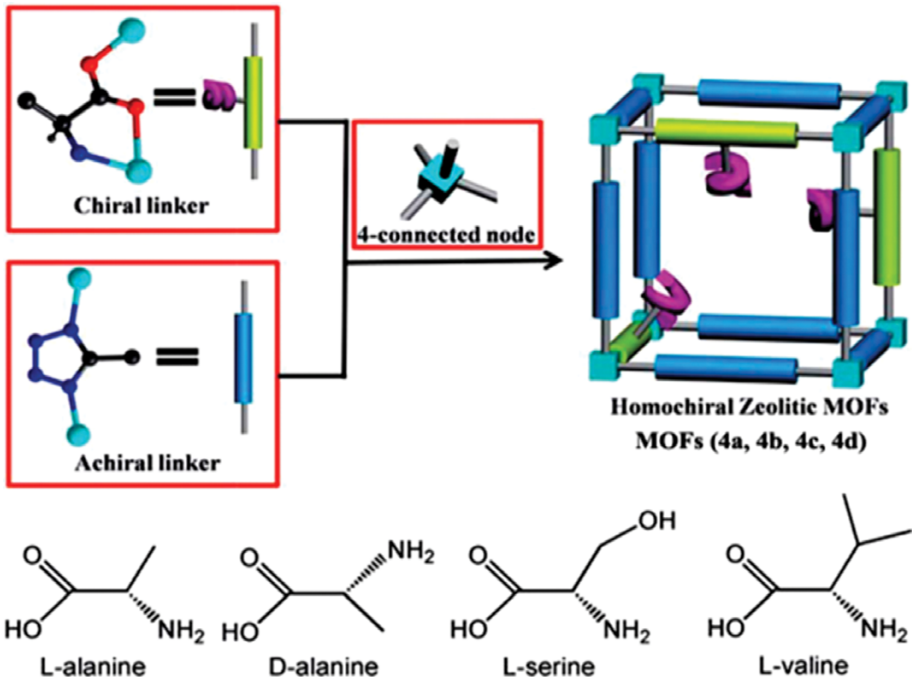


Fig. 14. The synthetic strategies of homochiral zeolitic bioMOFs 4a, 4b, 4c, and 4d. Reproduced from Ref. [148] with permission from copyright holders.

synthesized 3D Ca-based bioMOFs by bridging Ca^{2+} ions and L-lactate. The Ca-based bioMOFs could be used as a degradable carrier for pesticides [151]. In addition to AAs and small biomolecules, cyclodextrin is also well suited to produce the chiral bioMOFs. For example, a new bioMOF (CD-bioMOF) was synthesized by γ-cyclodextrin (γ-CD) and alkali metal salt, which catalyzed the separation of ethylbenzene from styrene, haloaromatics, and other chiral compounds. Importantly, the CD-bioMOF was also able to resolve the enantiomers of chiral analytes [152]. Similarly, a CD-bioMOF-1 was prepared from β-cyclodextrins and Na salts. The CD-bioMOF-1 showed a 3D structure with left-handed helical channels. The CD-MOF-1 showed higher inclusion rate than that of β-cyclodextrins and promised to become a new chiral carrier in food application [153]. In sum, chiral bioMOFs can be used as potential chiral stationary phases in HPLC and GC for enantioselective separation [154,155].

6. Environmental Protection

In the past twenty years, water pollution has become one of the most serious global problems since it threatens the survival and development of human society. Therefore, the efficient removal of contaminants from water has become a hotspot issue. In recent years, bioMOFs have proved to be the ideal adsorbents or photocatalysts for wastewater treatment due to their unique structure and multiple functions. Generally, the pollutants in wastewater usually include inorganic pollutants and organic pollutants. For the removal of inorganic pollutants such as toxic heavy metal ions, selective adsorption by bioMOFs seems to be the only way due to their non-degradability [156]. Pardo et al. prepared a 3D bioMOF by using the enantiopure bis[(S)-methionine]oxalyl diamide. The synthesized bioMOF presented excellent capture ability of mercury from water. Furthermore, the bioMOF was capable of adsorbing highly toxic CH_3Hg^+ from water [157]. Likewise, a series of $[Cu_3(BTC)_2]_n$ were prepared by coordinating unsaturated metal centers in HKUST-1. The obtained bioMOFs revealed remarkably high adsorption capacity for Hg^{2+} from water [158]. Compared with inorganic pollutants, the species of organic pollutants in wastewater are rich and more diversified. Therefore, bioMOFs have also been used as good adsorbents or catalysts for the elimination of organic pollutants from water. Yaghi group synthesized two bioMOFs by Ca^{2+} ions and lactate and acetate linkers, and used these bioMOFs to encapsulate cis-1,3-dichloroporopropene. These bioMOFs are naturally degradable in water, thus decreasing their environmental pollution [151]. In addition, Bhadra et al. synthesized a bioMOF-derived carbon (BMDC) from the pyrolysis of bioMOF-1 and successfully utilized it for the removal of bisphenol A from wastewater. The BMDC displayed five-times greater efficiency compared with a commercial activated carbon [159]. Recently, the same group used the BMDC to remove four pharmaceuticals and personal care products (PPCPs) from water. The BMDC exhibited high adsorption capacity for basic atenolol and acidic clofibric acid [160]. In addition, a magnetic cobalt adeninate based bioMOF was developed, and examined for the separation of benzodiazepines from urine and wastewater. The results showed that high extraction recoveries were obtained for urine and wastewater. The authors considered that the magnetic bioMOF was expected to become an efficient material for removal of benzodiazepines from urine and wastewater [161]. Based on the findings, the bioMOFs could be suggested as a promising adsorbent to adsorb and remove hazardous contaminants from the water.

In addition to the removal of the pollutants in wastewater, bioMOF can also be used to capture unsafe/harmful gas such as CO_2, N_2, CH_4, H_2, H_2S, SO_2, NH_3, and CO [162,163]. In this regard, the

bioMOFs with multiple groups have become promising candidates for the selective capture of gas. An et al. reported for the first time that cobalt adeninate bioMOFs exhibited exceptional ability to selectively adsorb CO_2. They speculated that adenine ligand in bioMOFs was able to interact with CO_2, thus causing high CO_2 adsorption capacity [1624]. The same group further demonstrated that adenine based bioMOFs were good candidates for the selective capture of CO_2 [165]. Li et al. prepared a water resistant core-shell bioMOF that possessed higher CO_2 uptake than bioMOF-14 and low N_2 uptake compared to the core. They observed that the shell could affect the N_2 and CO_2 adsorption behavior [166]. Some reports also demonstrated that bioMOF-11 exhibited significantly higher adsorption selectivity for CO_2 than the conventional MOFs [167]. However, to date, research efforts have focused on the removal of unsafe gas (CO_2, N_2, CH_4, and H_2) by bioMOF. There are few reports on the removal of the harmful gas (H_2S, SO_2, NH_3, and CO, etc.) by bioMOFs. Therefore, it is necessary to strengthen research in this important field.

SUMMARY AND FUTURE OUTLOOK

As one of the families of MOFs, bioMOFs are attracting interest in bio-application due to their special structure and function. The bio-application of bioMOFs has also been extended to biomedicine, biosensor, bioimaging, antimicrobial applications, biomimetic catalysis, chiral separation, and environmental protection. However, there are some key challenges to be addressed in future research. First, the interaction between the metal ions and bioligand needs to be systematically investigated, because this would provide some principles for the rational design of bioMOFs. Second, the stability of bioMOFs, such as thermostability, chemical stability, and water stability, do not yet meet the requirements of bio-applications. Third, there are very few bioMOFs reported for applications such as bioimaging and the removal of the harmful gas. Lastly, multifunctional bioMOFs based on various biomolecules have not been fully explored. In particular, operating bioMOFs in industrial or biomedical conditions also demands further insight. In addition to the above challenges, there are many other areas that require in-depth investigation. For example, there are few reports about the synthesis of multi-functional materials by combining bioMOFs and/or polymers. How to further improve the hydrolytic stability of bioMOFs in physiological conditions? Overcoming these problems will further broaden the interests of bioMOFs, allowing us further understand bioMOFs.

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