Metal–Organic Frameworks as Biomimetic Catalysts
Zhi-Yuan Gu, Jihye Park, Aaron Raiff, Zhangwen Wei, and Hong-Cai Zhou*[a]

In this Minireview, we have summarized the recent progress of biomimetic catalysis in the field of metal-organic frameworks (MOFs) with a focus on the implantation of biomimetic active sites into a stable MOF. In addition, the potential of creating highly selective catalytic pockets and diffusion-favored hierarchical structures in MOFs has also been explored. Furthermore, we have highlighted the achievements of MOF catalysts in the applications as mimics of peroxidase, cytochromes P450, hemoglobin, and photosynthetic systems.

Introduction

Biomimicry has been a longstanding scientific and technological endeavor because the imitation of nature not only brings about new insights into how nature works, but it also provides a novel perspective on the design of new materials or devices with a variety of functions.[1] This biomimetic effort is often based on synthetic materials with extraordinary properties. With the advent of carbon nanotubes, graphene sheets, and quantum dots, there arises an unprecedented opportunity to obtain biomimetic materials that are more efficient than natural systems by employing design principles that are inspired by nature, and by taking advantage of the characteristics of synthetic systems.[2] Many attempts have been made to incorporate ideas from nature into catalytic systems to improve their efficiency; however, an artificial enzyme with noticeable catalytic activity, good durability, and substrate selectivity remains a daunting challenge.

Metal–organic frameworks (MOFs), also known as porous coordination networks (PCNs), are a new class of hybrid inorganic–organic microporous crystalline materials, which consist of metal ions with bridging organic linkers; these form a 3D structure through coordination bonds.[3] The availability of a variety of building blocks, that is, metal ions and organic linkers, makes it possible to prepare an infinite number of new MOFs with diverse structures, topologies, and porosity. Owing to their fascinating structures and unusual properties such as permanent nanoscale porosity, high surface area, good thermostability, and uniformly-structured cavities, MOFs have great potential for hydrogen storage, gas separation, catalysis, sensing, and bioimaging.[4] Compared with traditional porous materials such as zeolites and silica, MOFs have much higher surface areas and better tunability, thus they provide an excellent platform for advancements in heterogeneous catalysis.[5]

MOFs are ideal candidates for building biomimetic systems, because their uniform cavities can generate a high density of biomimetic active centers. In addition, thermally and chemically stable MOFs can be built with a variety of metal clusters. Furthermore, the channels of MOFs provide confined pockets, which protect the catalytic centers and enhance substrate specificity. Some feature articles previously reviewed the construction of metal–biomolecule frameworks (MBioFs) and the catalytic activity of MOFs, which were usually not stable in water.[6]

To the best of our knowledge, rarely have publications discussed the principles of designing stable MOFs for the potential application of biomimetic catalysis, especially in an aqueous environment. In this Minireview, we summarize the recent progress of biomimetic catalysis in the MOF field with a focus on the implantation of biomimetic active sites into a stable MOF, and we explore the potential of creating highly selective catalytic pockets and diffusion-favored hierarchical structures in MOFs. Also, we highlight the achievements of MOF catalysts in a diverse range of biomimetic applications (Figure 1).
Implantation of Biomimetic Active Sites into a Stable MOF

As a prerequisite of potentially catalytic materials, the incorporation of active sites into MOFs is necessary. The advantages of MOFs, such as large surface areas and tunability of their pore sizes and geometries, make them a promising platform for achieving efficient catalysis. There are several ways to incorporate active sites into MOFs for catalytic purposes based on the MOF structures. One attractive approach is to construct MOFs by using metalloligands. The exploration of the metal nodes in a MOF as catalytically unsaturated metal centers has also been proven as an alternative methodology. MOFs are also good containers for active species such as small molecules, metal complexes, or even nanoparticles.[7] Comprehensive reviews have summarized the details of these methods elsewhere.[8] Here we focus on recent construction of water-stable biomimetic MOF catalysts and their potential applications as mimics of cytochrome P450 enzymes, hemoglobin and photosynthetic systems.

The stability of a heterogeneous catalytic system is another crucial factor. The majority of MOFs are composed of coordination bonds between divalent metal ions and carboxylate ligands, which are often prone to hydrolysis. This greatly limits the applicability of MOFs in an aqueous medium despite the fact their functionalized analogues show significant catalytic ability.[9] Zinc and copper in these MOFs show higher affinities for water molecules than the carboxylate group, which will inevitably cause the framework to decompose. On the other hand, metals such as aluminum, iron, chromium, titanium, and zirconium are more reactive to carboxylate ligands, which renders a series of water-stable MOFs, examples include MIL-47, MIL-53, MIL-100, MIL-101,[10] MIL-125,[11] and UiO structures.[12] Many efforts to implant catalytically active sites into these stable MOFs have been successfully demonstrated. MIL-101 has unsaturated metal centers that have catalytic activity for cyanosilylation and oxidation reactions directly[13], and through encapsulation[14] or post-synthetic modification.[15] An amine functionalized MIL-125 was shown to be a significant catalyst for the reduction of CO2 under visible light irradiation.[16] The functionalized MIL-125 was shown to be a significant catalyst for the reduction of CO2 under visible light irradiation[16].[17] The stable functionalized/doped UiO structures are highly selective catalysts for the cross-aldol condensation[18], and they act as photocatalysts for hydrogen generation,[19] water oxidation and CO2 reduction.[20]

The other possible route is to incorporate metalloligands into the aforementioned stable metal clusters to create new stable catalytic MOFs. The intention of constructing catalytic MOFs through the metalloligand approach is to incorporate molecules that have previously been demonstrated as effective catalysts in homogeneous reactions, such as metalloporphyrins, metallosalens,[20] and Ti-BINOLate complexes (BINOL = 1,1′-bi-2-naphthol).[21] Here we focus on stable metalloporphyrin MOFs. In nature, metalloporphyrins are well known for performing diverse biological functions as cofactors for many enzyme/protein families, which include peroxidases, cytochromes, hemoglobins, and myoglobins.[22] Mimicking the catalytic performance by utilization of metalloporphyrin in MOFs has been a sought-after goal for several decades. The pioneering work was reported by Robson and co-workers in 1994. The large cavities were obtained, but the framework irreversibly decomposed upon the removal of solvent.[23] Years later, Suslick and coworkers successfully built zeolite structural analogues (PIZA series) from cobalt and manganese salts with 5,10,15,20-tetraakis(4-carboxyphenyl)porphyrin. Remarkable size selectivity towards small-molecule sorption (water, methanol, ethanol and 1-butylamine) was obtained from PIZA-1, whereas PIZA-3 showed the capability of oxidative catalysis. However, the small channels in these materials restricted the catalysis of larger substrates, which occurred only on the exterior surfaces.[24] Choe and coworkers constructed many 2D metal–organic sheets with a tetra-connected porphin ligand, and paddlewheel coordination clusters. Some were further pillared in the third dimension by dipyrrolid ligands.[25] The active sites of metal ions in the porphyrin centers usually acted as structural nodes and were therefore blocked for further use as catalysts. To overcome this disadvantage, Hupp and coworkers employed Zn paddlewheel nodes to build 3D MOFs with open channels. Although paddlewheel clusters are known to be less stable in humid conditions, they succeeded in building a catalytically active MOF with this node by a mixed-ligands strategy.[26]

To further improve the design of metalloporphyrin MOFs for real applications in aqueous conditions, our group utilized stable zirconium clusters as connectors to create an ultrastable metalloporphyrin-containing MOF, named PCN-222 (See Figure 2). In an optimized procedure, ZrCl4 was reacted with Fe-TCPP (TCPP = 4-tetracarboxyphenyl porphyrin) ligands in the presence of benzoic acid in DMF under solvothermal conditions. Crystalline PCN-222(Fe) was formed, with superior properties to those of almost all existing MOFs. PCN-222(Fe) had a large open channel of 3.7 nm in diameter, one of the largest reported for mesoporous MOFs. N2 adsorption for PCN-222 at T = 77 K showed type IV behavior with a sharp increase at P/P0 of 0.3, which indicates mesoporosity. The Brunauer–Emmett–Teller (BET) surface area was 2200 m2g−1, and the total pore volume was 1.56 cm3g−1; these are amongst the highest values reported for all porous materials that contain porphyrins. Most importantly, it exhibited extraordinary stability compared to other MOFs. From powder XRD patterns, PCN-222(Fe) retained its crystallinity upon immersion in boiling water, and 2, 4, and 8 m, as well as concentrated hydrochloric acid solutions for 24 h; it showed no phase transition or framework collapse during these treatments. The N2 adsorption isotherms also remained the same after each of these treatments, which further confirmed the remarkable stability of PCN-222 (Figure 2D). To the best of our knowledge, PCN-222(Fe) is one of the most stable MOFs, as it can undergo treatment with concentrated hydrochloric acid and retain its structure. The zirconium(IV) ion is responsible for the exceptional stability of PCN-222(Fe). With its high charge density, the zirconium(IV) ion polarizes the oxygen atoms of the carboxylic groups to form strong Zr–O bonds with significant covalent character.

Similar strategies were also employed by other groups. Reinske et al. recently synthesized an Al-porphyrin MOF, which
utilized stable aluminum clusters and porphyrin ligands. This unique MOF contains 1D Al(OH)O$_4$ chains that support highly porous porphyrin networks and create a water-stable photocatalytic framework (Figure 3).\[28\] The pores range from 6 to 11 Å in size with the subtraction of van der Waals radii, and are interconnected by rectangular pores, which run along the [0 0 1] and [1 1 0] axes to render a 3D framework. It is thermally stable up to $T = 350^\circ$C in air. N$_2$ adsorption at $T = 77$ K reveals a surface area of 1400 m$^2$/g and a micropore volume of 0.625 cm$^3$/g, which is in good agreement with the calculated value of 0.63 cm$^3$/g. This ultrastable MOF has provided a valuable opportunity for pushing the limits of using MOFs as biomimetic catalysts.

Catalyst Design: Reactive Pockets and Hierarchical Structures

In addition to the use of stable clusters and catalytically active sites in MOFs, there are two more important factors for the biomimetic catalyst design. First, the selectivity towards substrate molecules largely relies on the chemical environment around the active sites. Second, the reaction kinetics and/or catalytic efficiency have a strong relationship with the molecular diffusion of the substrate towards the reactive center. Therefore, the implantation of reaction pockets and hierarchical structures into MOFs will be helpful in improving biomimetic catalysis. The creation of reactive pockets has been highly developed in the homogeneous catalysis field.\[29\] Also, the synthesis of hierarchical structures is well-established in the creation of mesoporous materials. The requirements for MOF catalyst design are not only the implementation of active sites, but also the design of the confinement effect and hierarchical structures, which will allow for accessible catalytic sites, conformational selectivity and efficient diffusion. In this section, we focus on the MOF catalyst design to fulfill the aforementioned features by two promising synthetic strategies: 1) the molecular “bottom-up” approach for designing potential reaction pockets from metal–organic polyhedra (MOPs) to MOFs and 2) the template-directed construction of MOFs that contain hierarchical structures.

From reaction pockets to MOFs: The possibilities of a molecular “bottom-up” approach

The finite molecular cages, termed in this Minireview as MOPs, are constructed through the coordination of metal ions and organic ligands, which act as the building blocks. MOPs, therefore, show the same type of chemical bonding as MOFs. This allows us to build reactive pockets in MOFs through a bottom-

Figure 2. Crystal structure and porosity of PCN-222(Fe). The metalloporphyrin (A) is connected to four Zr$_6$ clusters (B) to generate a 3D stable MOF with large 1D channels that are 3.7 nm in diameter (C). N$_2$ adsorption isotherms at $T = 77$ K show the framework stability of PCN-222(Fe) upon treatment with room-temperature water, boiling water, 2, 4, 8 M, and concentrated HCl (D). (Reprinted with permission from ref. [27], copyright 2012 John Wiley and Sons).

Figure 3. (A) Rietveld refinement of Al-porphyrin MOFs. (B) The porphyrin ligand. (C–E) The crystal structure of Al-porphyrin MOF viewed from the [0 0 1], [1 0 0], and [0 1 0] directions, respectively. (Reprinted with permission from ref. [28], copyright 2012 John Wiley and Sons).
up approach. Herein we summarize some previously reported strategies from our group that we can adopt for designing catalytic MOFs.

Zhou et al. synthesized a series of MOPs with different functionalities by a novel strategy; bridging-ligand-substitution (Figure 4).\cite{30} Direct reactions of Cu(OAc)$_2$ and various linkers yielded the corresponding MOPs. Further exploration of the bridging-ligand-substitution method resulted in a variety of new MOPs with diverse functionalities. The properties of the MOPs largely relied on the bridging linkers. This opened up the possibility of targeted synthesis for desirable MOPs with catalytic activities. Moreover, the structure of the MOPs were well adjusted, which indicated a high potential for size-selective and shape-refined cavities as well as promising catalytic activities.\cite{31}

In addition to the construction of MOPs, it is of great importance to demonstrate the potential of the bottom-up building of MOFs from molecular polyhedral structures. There are two approaches to achieve this target. One is by using molecular polyhedra as direct precursors to synthesize MOFs. For instance, it was shown in 2009 that MOFs could be assembled from MOPs by our group.\cite{32} The results clearly demonstrated the construction of MOFs in a stepwise manner with molecular polyhedra as precursors; this paved the way for developing framework materials from specifically-designed building units at a molecular level. The other approach is the connection of these polyhedra into polyhedra-based networks by designing new ligands. For example, a series of PCN-6X MOFs synthesized by our group\cite{33} are made from a set of dendritic hexacarboxylate ligands to make a series of isoreticular MOFs, which contain molecular polyhedral subunits. The results indicate that as the ligands elongated, the cavities increased in size as well. This is also supported by the BET surface areas that were measured for PCN-61, -66, and -68, as 3350, 4000, and 5109 m$^2$ g$^{-1}$, respectively. PCN-610 (also known as NU-100 with a surface area of 6143 m$^2$ g$^{-1}$) demonstrated one of the highest porosities among all existing MOFs.\cite{33b,34} The aforementioned molecular bottom-up strategy has proven effective for MOF design. Further exploration of functionalized molecular cages in MOFs for catalysis is highly promising and desirable.

**Shaping the MOFs: Template-directed synthesis of hierarchical MOFs**

In addition to the molecular bottom-up methodology, the template-directed assembly approach for the creation of hierarchical MOF structures has received extensive attention. Although some approaches have shown that morphological control can be achieved through dilution of precursors,\cite{35} the development of template-directed synthesis to build hierarchical MOFs provides a more tunable path for a range of applications. In 2008, pioneering work was reported by Qiu and coworkers, in which they applied a surfactant-templated strategy to afford hierarchical porosity-adjustable micro- and mesoporous MOFs by using [Cu$_3$(btc)$_2$(H$_2$O)$_3$] (HKUST-1), in which btc is benzene-tricarboxylate.\cite{36} A series of hierarchical porous MOF structures were prepared under solvothermal conditions with copper(II) solutions and benzene-1,3,5-tricarboxylate precursors in the presence of cetyltrimethylammonium bromide (CTAB) as a structure-directing agent. N$_2$ adsorption–desorption isotherms, small- and wide-angle XRD, and transmission electron microscopy (TEM) images showed that mesopores up to 30 nm in size were generated from microporous MOFs by tuning the amounts of CTAB. By a similar strategy, MOF nanospheres with long-range ordered mesopores were synthesized in binary solvent systems of ionic liquids and supercritical CO$_2$.\cite{37}

Our group demonstrated a cooperative templating effect by choosing CTAB as a structure-directing agent and citric acid (CA) as a chelating reagent, which enabled the rational adjustment of the interaction between MOF precursors and surfactant molecules (Figure 5).\cite{38} Structural analysis based on powder XRD, TEM, and N$_2$ adsorption–desorption isotherms indicates that mesopores are created in MOFs in which the optimal ratio of CTAB/CA is 2.3. This cooperative template-directed assembly strategy shows a possible synthetic route that one
can adopt to build hierarchical frameworks with controllable mesoporosity.

Liquid-crystal and hard-template approaches were also employed to create hierarchical MOFs. A new route of liquid-crystal templating to combine microporosity and mesoporosity was also developed by using Prussian Blue. Recently, Susumu Kitagawa and coworkers demonstrated an alternative methodology to spatially control the nucleation site, which leads to the mesoscopic architecture of MOFs. This method was based on the shaped sacrificial metal oxide as a metal precursor as well as a hard-template structure-directing agent. A highly ordered analogous MOF hierarchical structure was obtained by the morphological replacement of the metal oxide.

Although the above methodologies are not specifically designed for catalytic applications, molecular bottom-up design and synthesis of hierarchical structures can facilitate catalytic processes, especially for the improvement of selectivity and substrate diffusion. More efforts should be directed towards the demonstration of such principles in real MOF catalytic applications.

**Solid State Artificial Enzymes**

**Cytochrome P450-mimic catalysis**

Cytochromes P450, which exist as a large family of cyssteinato-heme enzymes, are prevalent in various forms of life (plants, bacteria, and mammals) and play a key role in the oxidative transformation of endogenous and exogenous molecules. The prosthetic group of P450 consists of an iron protoporphyrin IX, which is protected by polypeptides. These enzymes are potent oxidants capable of catalyzing many useful organic reactions, such as the hydroxylation of saturated carbon–hydrogen bonds, the epoxidation of double bonds, and the oxidation of aromatics. Cytochromes P450 use molecular oxygen, which inserts one of its oxygen atoms into a substrate (S), and reduces the second oxygen to a water molecule, by utilizing two electrons provided by nicotinamide adenine dinucleotide phosphate (NAD(P)H) from a reductase protein. All cytochrome P450 enzymes are involved in a complex multienzymatic system, which hampers their industrial application for selective oxygenation of chemicals. The concept of building crystalline catalytically-active solids to mimic these natural enzymes has been around for a long time. Many efforts have been made in this direction. Greater efforts have been devoted to the search for water-stable MOFs. To accurately mimic many biological systems, water-stable materials will be required. Water-stable MOFs, which contain the porphyrin group, are strongly needed to simulate the cytochrome P450 activity. The newly-developed PCN-222 from our group is an ideal synthetic platform for mimicking cytochrome P450 enzymes owing to its stability, mesoporosity and high density of metalloporphyrin centers.

To show the high potential of PCN-222 as an artificial enzyme and simplify the catalytic process, we first tested its peroxidase-like catalytic activity 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, whereas other MOFs did not show significant activities under identical conditions, which proves the stability of PCN-222 as an efficient, accessible biomimetic catalyst. An enzyme kinetics study for PCN-222(Fe) was performed and the kinetic parameters \( k_{\text{cat}} \) and \( K_m \) were derived (Figure 6). The \( k_{\text{cat}} \) 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, the \( k_{\text{cat}} \) value of the PCN-222(Fe) catalyst is 16.1 min\(^{-1}\), which is 7 times higher than the value for free hemin (2.4 min\(^{-1}\)). The \( K_m \) value (≈0.33 mM) is lower than that of the natural enzyme HRP (horseradish peroxidase, 0.81 mM), which indicates a better affinity of the substrate to PCN-222(Fe); this results 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 \( k_{\text{cat}} \) value was nearly 10 times higher than that of free hemin. Other porphyrin-containing systems, such as porphyrin-encapsulated MOFs also...
show significant catalytic activity for oxidation reactions in organic solvents.[26, 43a, c–e, g, 44]

If one considers the peroxide shunt in the P450 catalytic cycle and the similar high-valent iron-oxo intermediates shared by oxygenases and peroxidases, this test not only reflects the ability of PCN-222 to oxidize the substrates but also shows its similarity to cytochromes P450 (Scheme 1).[41] However, there is still a large discrepancy between the synthetic materials and natural P450 enzymes, which capture oxygen as oxidants and protect the iron center to finish the catalytic cycle, not to mention the construction of the complex multienzymatic system. However, the benefits that MOF catalysts will provide, such as ultrastability in water and organic solvents, a high density of reaction centers, and good recyclability, continue to inspire researchers to pursue these goals to finish the catalytic cycle of cytochromes P450 in MOF systems, which will definitely be a groundbreaking result.

Hemoglobin-like MOFs

The design of MOFs could also benefit from consideration of other natural proteins, which perform intriguing activities, such as selective binding of O₂ to hemoglobin, and light-harvesting pigments in photosystems I and II. Clever usage of active sites in MOFs shows significant similarity towards such applications, but in a stable solid state. This solid-state material is beneficial to the industrial separation of O₂ from air, which implies the potential for using purified O₂ combustion as a means of eliminating CO₂ emissions from fossil fuel-fired power plants. O₂ is separated from the N₂ in air prior to combustion instead of separating CO₂ from N₂ in postcombustion capture, which is beneficial to our environment.

Long and coworkers employed unsaturated copper(II) and iron(II)-based MOFs to systematically investigate their O₂-binding activities, which is the main role of hemoglobin in human blood. An activated Cr₃(btc)₂ MOF was obtained from heating and vacuum treatment after the reaction of Cr(CO)₆ with trimesic acid in DMF. The BET surface area from N₂ gas adsorption measurements was 1810 m² g⁻¹. At T = 298 K, the O₂ uptake for the Cr₃(btc)₂ MOF rises sharply to 11 wt %, whereas the corresponding N₂ uptake shows a capacity of 0.58 wt % at P = 1 bar. An excellent O₂/N₂ selectivity factor of 22 was obtained. Desorption of O₂ was achieved by heating at T = 50 °C under vacuum. Infrared and X-ray absorption spectra as well as neutron powder diffraction indicated the location of O₂ molecules that were near to the chromium(II) unsaturated centers (Figure 7).[45]

Similar unsaturated iron(II) sites that are effective at binding O₂ were also observed in a Fe₃(dobdc) MOF (dobdc⁻ = 2,5-dioxido-1,4-benzenedicarboxylate), which had a BET surface area of 1360 m² g⁻¹. It was synthesized from the air-free reaction between FeCl₂ and H₄dobdc in a mixture of DMF and methanol.[46] At T = 298 K, the Fe₃(dobdc) MOF irreversibly binds O₂ with a capacity of 9.3 wt % (molar ratio of O₂ to iron is 1:2). Interestingly, at a lower temperature of 211 K, reversible adsorption is observed and O₂ uptake is 18.2 wt % (molar ratio of O₂ to iron is 1:1). This temperature-dependent O₂-binding phenomenon was investigated by Mössbauer and infrared spectroscopy, as well as powder neutron diffraction. The results revealed complete charge transfer to form iron(III) and O₂⁻ ions at room temperature, which rendered a strong affinity and lower uptake, whereas partial charge transfer was observed from iron(II) ions to O₂ molecules at low temperature, which af-
forced reversible adsorption and higher uptake. This interpretation was consistent with the results of Rietveld analyses of powder neutron diffraction data, which revealed the geometry of $O_2$ molecules that were bound towards iron centers. These isolated metal centers together with large open volumes in the MOFs not only gave the high uptake of desired $O_2$ molecules but also new insights into a solid-state artificial enzyme mimic.

**Solar energy conversion and light-driven catalytic applications**

Natural photosystems I and II gave insights into how nature harvests solar energy and inspired researchers to solve the energy crisis with recent developments in photovoltaic cells, dye-sensitized solar cells, and solar-driven water splitting. Pioneering contributions were made from the MOF field to mimic natural systems for light harvesting, electron transfer, energy transfer, and photocatalytic hydrogen evolution. Kent and Lin investigated efficient MOF luminescence quenching in the presence of either oxidative or reductive quenchers to demonstrate the energy migration and electron transfer,[48] whereas other groups highlighted the advantages of the spatial energy/charge transfer effect in specific MOF structures.[48]

Nanoscale coordination polymers with guest-induced light-harvesting properties were reported from Zhang and coworkers.[48a–c] The combination of linear conjugated dicarboxylate ligands and lanthanide metal ions in organic solvent resulted in a series of self-assembled nanoscale coordination polymers that exhibit long-range ordered structures. Efficient light harvesting with energy transfer either from the framework to the guest molecule or from the framework to the framework was observed. Other than the nanoscale well-dispersed system, studies of MOF solids were also performed. The highly-ordered porphyrin-like pigments (chlorophylls) in natural photosynthesis inspired us to investigate the analogues of highly-ordered porphyrin-based MOFs, from which we might observe a similar energy migration behavior. Hupp and coworkers designed and synthesized antenna-like light-harvesting MOFs for solar energy conversion. A bodipy- and porphyrin-based MOF was capable of harvesting light across the entire visible spectrum by the efficient “strut-to-strut” energy transfer through the ordered MOF structure.[48d] The same group also explored the first example of long-distance energy migration within a MOF. The photogenerated exciton in a MOF with enhanced $\pi$-conjugation could migrate over a net distance of up to approximately 45 porphyrin struts within its lifetime, whereas in the other porphyrin MOF it could only migrate over approximately 3 struts.[48e] Not only pure MOFs, but also MOF-quantum dot hybrid materials were tested. Owing to the spectral coverage limit of porphyrin MOFs, quantum dots with broad absorption bands were introduced into MOF pores to enhance light harvesting by energy transfer from quantum dots to MOFs. Eighty percent efficiency was observed for energy transfer from quantum dots to the MOFs, which greatly enhanced the light harvesting in solar energy conversion.[48f]

In addition to light harvesting and energy transfer, water-stable MOFs have also contributed to light-driven water splitting. García and coworkers[48] applied the water-resistant Zr MOFs UiO-66 and UiO-66-NH$_2$ to this process. Both of these MOFs had photocatalytic activities for hydrogen generation upon irradiation at wavelengths longer than 300 nm. The amino group generated a bathochromic shift, which is promising for more efficient water splitting. The apparent quantum yield of 3.5% was obtained for UiO-66-NH$_2$ at $\lambda = 370$ nm UV irradiation. Recently, visible-light-driven hydrogen generation was reported by Rosseinsky and coworkers in a water-stable aluminum porphyrin MOF (Figure 8).[28] The porous MOF Al-PMOF with a BET surface area of 1400 m$^2$ g$^{-1}$ performed visible-light-driven hydrogen generation from water with the help of Pt as a co-catalyst and ethylenediaminetetraacetic acid (EDTA) as a sacrificial electron donor. The MOF/EDTA/Pt system produced H$_2$ at the rate of up to 200 μmol g$^{-1}$ h$^{-1}$. A control experiment in the MOF-filtered solution confirmed that H$_2$ was produced by heterogeneous photocatalytic activity of the MOF. It is highly promising to push the envelope of MOF research in mimicking photosynthetic systems and to develop highly efficient energy and electron transfer solid-state light-harvesting materials.

**Merits compared to other biomimetic systems**

In the category of solid materials, MOFs offer the highest surface areas, and chemical tunability. Compared with traditional heterogeneous porous catalysts such as zeolites and silica, MOFs have greater opportunity for tuning their functions, thus providing an excellent platform for biomimetic catalysis. The merits of MOFs as biomimetic catalysts over other solid-state catalysts and natural enzyme systems[49] are provided by 1) spatially and accurately isolating catalytic centers that typically degrade in solution through undesirable reactions such as $\mu$-oxo heme formation; 2) the provision of protection to enzyme active sites under extremely harsh conditions, such as...
in hydrochloric acid, through confinement in mesopores within ultrastable aluminum(III), iron(III), chromium(III), hafnium(IV), and zirconium(IV)-constructed MOFs, instead of polypeptide environments; 3) enhancing the density of porphyrin centers by incorporating them into the struts of the framework to ensure sufficient interaction between open metal sites and substrate molecules; 4) creating MOFs with large pores and channels, which will enable fast diffusion of guest molecules, which therefore increases the overall reaction rate; 5) introducing channels with multiple sizes, which allow for tuning of the reactivity of the catalytic active center through selective axial ligand binding and for tweaking of substrate selectivity through size/shape control; and 6) adjusting catalytic reactivity of metalloporphyrin moieties by systematically varying the metal ions coordinated in the porphyrin centers.

Outlook

With regards to MOF catalyst design, extremely stable MOFs with a high loading of active sites, predesigned reaction pockets, as well as hierarchical structures for the heterogeneous catalysis are highly desirable. The recent progress in the design of stable metal clusters as connection nodes for MOFs will be beneficial for stabilizing the MOF catalysts in future developments. More efforts should be put into the design of highly selective catalytic pockets in stable MOFs, as well as into the exploration of hierarchical MOF structures to reduce the diffusion resistance. For real applications, highly efficient biomimetic MOF catalysts, especially with regards to solid-state artificial enzymes, are still underdeveloped despite the significant progress made in the synthesis of stable MOFs. More fundamental innovations in MOF research will bring biomimetic catalysis a bright future.

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