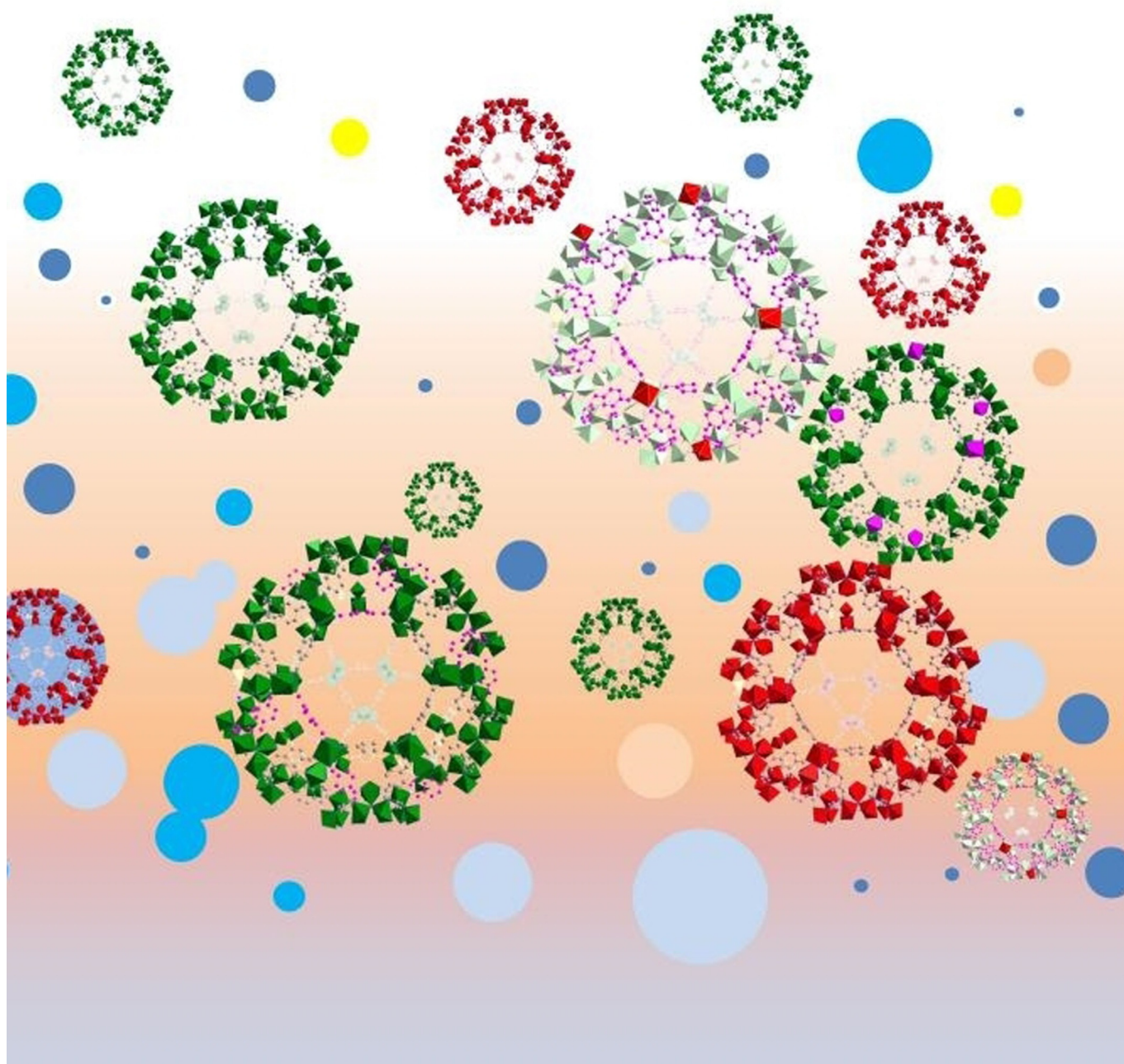


Single-Site Photocatalysts



Design of Single-Site Photocatalysts by Using Metal–Organic Frameworks as a Matrix

Meicheng Wen,^[a, b] Kohsuke Mori,^[a, c, d] Yasutaka Kuwahara,^[a, c] Taicheng An,^[b] and Hiromi Yamashita^{*[a, c]}



Abstract: Single-site photocatalysts generally display excellent photocatalytic activity and considerably high stability compared with homogeneous catalytic systems. A rational structural design of single-site photocatalysts with isolated, uniform, and spatially separated active sites in a given solid is of prime importance to achieve high photocatalytic activity. Intense attention has been focused on the design and fabrication of single-site photocatalysts by using porous materials as a platform. Metal–organic frameworks (MOFs) have great potential in the design and fabrication of single-site photocatalysts due to their remarkable porosity, ultrahigh

surface area, extraordinary tailorability, and significant diversity. MOFs can provide an abundant number of binding sites to anchor active sites, which results in a significant enhancement in photocatalytic performance. In this focus review, the development of single-site MOF photocatalysts that perform important and challenging chemical redox reactions, such as photocatalytic H₂ production, photocatalytic CO₂ conversion, and organic transformations, is summarized thoroughly. Successful strategies for the construction of single-site MOF photocatalysts are summarized and major challenges in their practical applications are noted.

Introduction

Photocatalysis is closely concerned with many aspects of human life, such as solar energy conversion, water remediation, antibacterial compounds, and air purification.^[1] Efficient charge separation and transfer greatly influence the photocatalytic performance of a photocatalyst.^[2] Additionally, the number of active sites, the surface area, and the porosity of photocatalysts also play vital roles in determining photocatalytic activity.^[3] Current research into photocatalysts is predominantly based on semiconductors.^[4] Although considerable achievements have been obtained, semiconductors still suffer from low surface area, poor electron–hole pair separation, limited active sites, and large bandgaps, which hinder their practical applications.^[5] Increasing efforts are being dedicated to the development of molecular-based photocatalytic reaction systems constructed from a organometallic compound catalyst, a sacrificial reagent, and a photosensitizer; such homogeneous reaction systems usually display high photocatalytic activity.^[6] However, the thermal stability of this homogeneous reaction system is very low and it is unrecoverable. With the aim of obtaining photocatalysts with high surface area, abundant cata-

lytic active sites, recyclability, and efficient charge separation and transfer, tremendous research has been focused on the development of single-site photocatalysts by integrating organometallic compounds within porous materials.^[7] Great breakthroughs in the design of single-site photocatalysts with porous materials have also been reported. For example, Yamashita and co-workers reported a series of V oxide, Mo oxide, Cr oxide, and Ti oxide single sites anchored on porous silica and zeolites, and the high photocatalytic activity of these single-site photocatalysts has been observed.^[3,8] However, due to the inert chemical surface of the inorganic porous material, it is difficult to increase the degree of anchored active sites. Furthermore, strict synthetic conditions and complicated surface chemical modifications are required to anchor active sites onto inorganic porous material at the atomic level.^[9]

Metal–organic frameworks (MOFs) are an attractive class of organic–inorganic porous material constructed from inorganic secondary building units (metal oxide clusters or metal ions) coordinated to organic moieties.^[10] Differing from traditional inorganic materials, these coordination polymers, with their unique and uniform pore structures, extraordinary tailorability, and ultrahigh surface area, have received much attention and opened new possibilities in the field of photocatalysis for the engineering of single-site photocatalysts.^[11] The significant chemical diversity of MOFs endows them with many advantages shared by both heterogeneous and homogeneous catalysts.^[12]

MOFs are a class of highly crystalline solid materials with remarkable thermal stability and considerable recyclability, and can be easily separated from gas and liquid phases.^[13] Despite their heterogeneous nature, MOFs are built from well-defined organic molecular building blocks, which can be considered as organic molecules arranged in a crystalline lattice. Therefore, organometallic compounds that possess high catalytic activity and selectivity toward some identical chemical reactions can be incorporated into the MOF framework.^[14] In addition, due to the atomic-level crystal structure of MOFs and their high surface area, a large number of catalytic active sites can be chemically incorporated into MOFs, which provides activity and selectivity comparable to their homogeneous analogues.^[15] Moreover, the coordinatively unsaturated metal in a MOF can serve as a single-site reaction center to catalyze

[a] Dr. M. Wen, Dr. K. Mori, Dr. Y. Kuwahara, Prof. H. Yamashita
Graduate School of Engineering
Osaka University
Suita, 565-0871 (Japan)
E-mail: yamashita@mat.eng.osaka-u.ac.jp

[b] Dr. M. Wen, Prof. T. An
Guangzhou Key Laboratory of Environmental Catalysis and Pollution Control
School of Environmental Science and Engineering
Institute of Environmental Health and Pollution Control
Guangdong University of Technology
Guangdong, 510006 (China)

[c] Dr. K. Mori, Dr. Y. Kuwahara, Prof. H. Yamashita
Unit of Elements Strategy Initiative for Catalysts & Batteries
Kyoto University
Kyoto (Japan)

[d] Dr. K. Mori
JST, PRESTO
4-1-8 Honcho, Kawaguchi, Saitama 332-0012 (Japan)

✉ The ORCID identification number(s) for the author(s) of this article can be found under:
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chemical redox reactions or as a binding site to anchor a catalytically active site.^[16] Numerous approaches have been proposed to create single-site catalytic reaction centers on the organic linkers or metal clusters of MOFs or confined single-site catalytic centers within the MOF cavities.^[17] Undoubtedly, MOFs display great potential as an ideal homo–hetero bridge that can open the door to novel photocatalysts with stable and high photocatalytic activity for various chemical redox reactions.^[18]

As discussed above, MOFs are able to offer sufficient design opportunities in the architecture of novel single-site MOF solid photocatalysts. Herein, we summarize recent synthetic strategies for the development of single-site photocatalysts with MOFs and their photocatalytic performance. Single-site MOF-based photocatalysts are conceptually divided into four categories: 1) For active sites located on the MOF organic linkers, different methods have been used to obtain single-site MOF photocatalysts with catalytic active sites isolated on the organ-

ic linkers of MOFs, such as in situ synthesis strategies, post-synthetic metalation methods, and ion-exchange methods; detailed synthetic routes will be discussed further herein. 2) For redox-active metal sites located at MOF nodes, it is known that MOFs are composed of transition-metal ions coordinated to oxygen atoms of the organic linkers to form transition-metal oxide nodes; these nodes contain a large number of geometrically uncoordinated metal ions that can be considered as open metal sites, which gives significant opportunities to design single-site MOF photocatalysts. 3) For single-site photocatalysts confined in the MOF cavities, active single-site MOF photocatalysts can also be synthesized by incorporating organometallic compounds within the MOF cavities. Due to the large size and narrow window of the cavities, organometallic compounds can be confined within the MOF, which can efficiently prevent diffusion and leaching of the organometallic compound during the photocatalytic reaction process. 4) For single noble metal atoms confined in the MOF framework, MOFs with a large surface area and abundant micro- and mesopores can prevent the diffusion and aggregation of metal-atom precursors during the reduction process, which results in the formation of single noble metal atoms. Apart from the discussion on the design and architecture of single-site MOF photocatalysts, the application of these photocatalysts in various heterogeneous photocatalytic reactions and the related reaction mechanisms are also summarized and highlighted. Finally, a brief perspective on the challenges and possibilities in the design of single-site photocatalysts with MOFs as a matrix for photocatalysis applications is also discussed. We sincerely believe that single-site MOF photocatalysts with porous structure have the potential

Meicheng Wen received his Ph.D. degree in engineering from Osaka University under the supervision of Prof. Hiromi Yamashita in 2016. He was a specially appointed Assistant Professor in the Division of Materials and Manufacturing Science at Osaka University in 2016–2017. He has been an Associate Professor at Guangdong University of Technology, China. His research mainly focuses on the preparation of nanomaterials and their applications in energy conversion and environmental remediation.



Kohsuke Mori received his Ph.D. degree from the Graduate School of Engineering Science at Osaka University under the supervision of Prof. K. Kaneda in 2003. In 2004, he joined Prof. T. Don Tilley's group at the University of California, Berkeley, as a postdoctoral fellow. He moved to his current faculty in 2005 and then became an Associate Professor in 2009. His current research interests focus on hybrid photocatalysts based on visible-light-responsive metal complexes and metal and alloy nanoparticle catalysts to establish clean and environmentally friendly chemical processes, and diesel automobile catalysts.



Yasutaka Kuwahara received his Ph.D. degree in engineering from Osaka University in 2011. He was a postdoctoral research fellow at the Georgia Institute of Technology, USA, in 2011. He was a researcher at the National Institute of Advanced Industrial Science and Technology (AIST), Japan, in 2012–2014. Since 2014, he has been appointed as an Assistant Professor at Osaka University. His current research interests include the design of nanostructured catalysts with multiple functionalities by using porous materials, and their applications in green chemical reactions and the conversion of energy and resources.



Taicheng An received his Ph.D. degree from Sun Yat-sen University in 2002. He is currently a Full Professor at the School of Environmental Sciences and Engineering and Director of the Institute of Environmental Health and Pollution Control, Guangdong University of Technology. He is the holder of 40 issued patents and has published more than 220 SCI papers in reputable journals. His research interests mainly focus on the transportation mechanisms, fate prediction, and health effects of emerging organic contaminants, and the synthesis of nanostructured photocatalysts and their applications in environmental remediation.



Hiromi Yamashita has been a Professor of Osaka University since 2004. He received his Ph.D. degree from Kyoto University in 1987. He was an Assistant Professor at Tohoku University, an Associate Professor at Osaka Prefecture University, and an Invited Professor at University Pierre and Marie Curie (UPMC). He was also the visiting research fellow at Pennsylvania State University, the University of Texas at Austin, and the California Institute of Technology. His research interests include the design of single-site photocatalysts and nanostructured catalysts.



to replace traditional photocatalysts, which are dominated by semiconductor-based heterogeneous photocatalysts and organometallic-compound-based homogeneous photocatalysts. This would be of significant importance for protection of the environment and the exploration of sustainable and renewable energy.

Fundamentals of MOF photocatalysts

MOFs have been demonstrated as a semiconducting material and widely used in photocatalytic H_2 production, organic pollutant degradation, and CO_2 reduction.^[19] The hallmark of a semiconducting MOF is the generation of a photoinduced electron upon light irradiation.^[20] The photocatalytic reaction mechanism is similar to that of semiconductors, the energy levels of MOFs are typically identified as the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital). After the absorption of solar energy by a MOF, an electron is excited from the HOMO to the LUMO, which leaves a hole in the HOMO. The photoinduced electron is then transferred to the MOF node through a linker-to-metal charge transfer (LMCT) mechanism and is subsequently involved in a photoreduction reaction that takes place on the MOF node.^[16,21] The MOF nodes usually behave as active sites and are formed by a transition-metal cation coordinated with oxygen atoms of the organic linkers. Simultaneously, the hole is used in a photooxidation reaction.^[22] In 2006, Natarajan reported the synthesis of three novel MOFs, $[Co_2(C_{10}H_8N_2)] [C_{12}H_8O(COO)_2]_2$, $[Ni_2(C_{10}H_8N_2)] [C_{12}H_8O(COO)_2]_2$, and $[Zn_2(C_{10}H_8N_2)] [C_{12}H_8O(COO)_2]_2$, with three-dimensional structures and light-responsive properties.^[23] The photocatalytic degradation of orange G and rhodamine B (RhB) was carried out to investigate the photocatalytic activity of the as-synthesized MOFs, and all showed considerable photocatalytic activity. Alvaro employed MOF-5 (zinc ions coordinated with terephthalic acid) in the photocatalytic degradation of organic pollutants.^[12b] In this work, MOF-5 behaved as a microporous semiconductor that was able to degrade phenol photocatalytically. Recently, MIL-125(Ti) (Ti cations coordinated with terephthalic acid) was widely used for photocatalytic H_2 production from an aqueous solution that contained an electron donor, and photocatalytic CO_2 reduction to formic acid.^[19b,24] Li and co-workers used 2-aminophthalic acid as an organic linker to fabricate NH_2 -MIL-125(Ti) for the photocatalytic reduction of CO_2 to formate under visible light irradiation.^[19a] The amino functionality can significantly reduce the bandgap of NH_2 -MIL-125(Ti) and increase the adsorption capacity of CO_2 . After the absorption of visible light, a photoexcited electron is transferred to the MOF cluster, which results in the generation of a Ti^{3+} single active site. Then the CO_2 captured by the MOF is subsequently reduced at the Ti^{3+} single active site as proposed by the authors. Triethanolamine (TEOA) donates an electron to regenerate the pristine MOF, as shown in Figure 1. Very recently, Jiang and co-workers synthesized a porphyrin-based MOF (PCN-222) for photocatalytic CO_2 reduction.^[25] The photocatalytic performance in the conversion of CO_2 to formate was greatly improved compared with the corresponding porphyrin

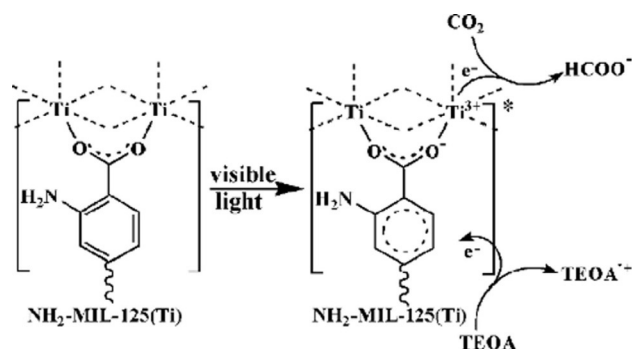


Figure 1. Proposed reaction mechanism for CO_2 reduction to formate with NH_2 -MIL-125(Ti), reproduced with permission from Ref. [19a].

ligand. The porphyrin incorporated within the MOF created a deep electron trap state, which facilitated the formation of active Zr^{3+} single sites for CO_2 reduction.

The possible mechanisms for the photocatalytic degradation of organic pollutants and CO_2 reduction mentioned above are all based on LMCT, in which the transition-metal ions in the MOF nodes behave as active sites. Additionally, the band structure and the redox-active metal of the MOF can be systematically modified by substituting the organic linker with different functional groups and doping foreign metal ions or anions at the MOF nodes.^[26] In addition to the LMCT mechanism, metal-to-ligand charge transfer (MLCT), ligand-to-ligand charge transfer (LLCT), and metal-to-metal-to-ligand charge transfer (MMLCT) mechanisms have also been proposed for photocatalytic reactions with MOFs. The MLCT mechanism is observed for Ir and Pt metal complexes incorporated in MOFs, in which a photocatalytically active Pt complex and an Ir complex as the photosensitizer are integrated within the MOF. Photocatalytic H_2 production proceeds on the Pt species anchored within the framework, based on a MLCT mechanism.^[27] Huang and co-workers reported a highly efficient MOF (Bi^{3+} connected with 2-mercaptosuccinic acid) photocatalyst for the photocatalytic degradation of RhB, based on the LLCT mechanism.^[28] The MMLCT mechanism is achieved by rational control of the electron transfer distance between two Pt complexes.^[29] In this case, the Pt complex serves as a bifunctional catalyst that enables both visible-light sensitization and H_2 evolution. The photocatalytic activity in H_2 production is highly affected by Pt–Pt interactions.

To date, many photocatalytic MOFs that are able to degrade organic pollutants, generate hydrogen from water, or reduce CO_2 have transition metal oxide clusters. It has been proven that the transition metal plays an important role as single active sites in photocatalytic reactions. However, their exact roles are still unclear and the photocatalytic activity is still low. To investigate the mechanisms of photocatalytic reactions on single-site MOF photocatalysts and improve photocatalytic activity, chemical modifications to link the single sites in MOFs can be used to control the position and the degree of coordinated active sites.

Synthesis of single-site MOF photocatalysts through ligand modification

Pre-synthetic method for organometallic compounds incorporated in MOF photocatalysts

Owing to the ability to fine-tune the physical and chemical properties of MOFs at the molecular level, a large number of highly active MOF catalysts with well-defined active sites anchored on the ligands have been synthesized by directly mixing a given amount of catalytically active component (organometallic compound) into the MOF precursor as a building block, which leads to the generation of easily recoverable and reusable single-site MOF photocatalyst.^[30] This presynthetic strategy is very popular because MOFs are usually synthesized in a one-step procedure. The integrity of the organometallic compounds is well preserved during MOF formation because MOFs are generally synthesized under mild conditions, and this synthetic method allows a high loading of organometallic compound to be homogeneously distributed within the MOF framework.^[31] Generally, a mix-and-match synthetic strategy is applied to the in situ synthesis of single-site MOF photocatalysts, in which the length of the catalytically active organometallic compound should match that of the original MOF linker.^[12a] The matching ligand length of the original ligands allows the formation of a highly crystalline MOF. Normally, the synthetic conditions for MOF preparation are mild, and the framework structure of the single-site MOF photocatalyst is well retained. This presynthetic strategy provides a rational opportunity for the heterogenization of homogeneous organometallic compound catalysts. Extensive work has demonstrated that metallic single atoms as an active site can be covalently linked to a MOF during the MOF preparation procedure, which endows the supported catalysts with remarkable activity in a variety of redox reactions.

Three catalytic components, Ir, Ru, and Re organometallic compounds (Figure 2a, b, and e), have been doped by Lin and co-workers into a highly stable and porous Zr-based MOF (UiO-67) by using a mix-and-match synthetic strategy.^[32] UiO-67 is originally composed of bpdc (*para*-biphenyldicarboxylic acid) as the organic linker and a zirconium oxide cluster as the

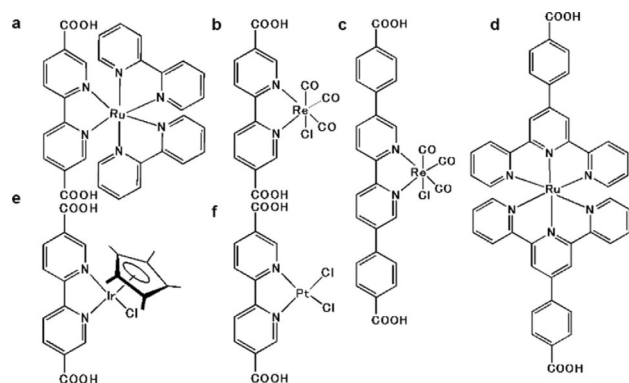


Figure 2. Typical organometallic compounds as linkers for the in situ synthesis of single-site MOF photocatalysts.

connecting center. Due to the steric demand of the large organometallic compound, it is difficult to obtain a single-site MOF photocatalyst by only using organometallic compounds as MOF building blocks. However, organometallic compounds can partially substitute the original bpdc linker according to structure modeling studies. In this work, the length of the doped organometallic compound with dicarboxylic acid functionality matches the original linker (bpdc) well, which allows the successful fabrication of a porous MOF with a high surface area and a framework that is isostructural to that of the parent UiO-67. Various characterization methods, such as X-ray diffraction, SEM images, N₂ adsorption, and inductively coupled plasma mass spectrometry analysis, have proven the successful fabrication of single-site MOF photocatalysts. Doping of these precious organometallic compounds into porous MOF is highly desirable to prolong catalytic reaction time by taking advantage of the stabilization effect and recyclability of solid MOFs. MOFs with single-atom active sites show high catalytic activity and stability in photocatalytic water oxidation, photochemical CO₂ reduction, and photocatalytic organic transformations, as shown in Figure 3.

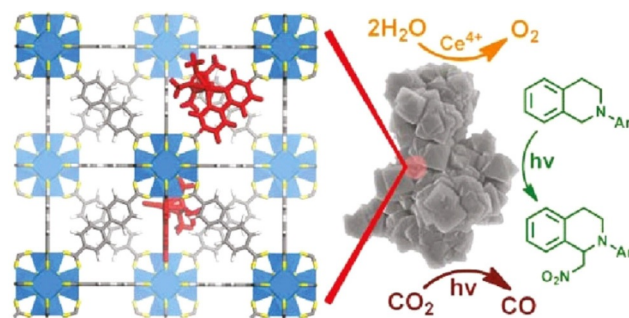


Figure 3. Schematic illustration of organometallic-compound-doped UiO-67 for photocatalytic water oxidation, CO₂ reduction, and organic transformations. Reprinted with permission from Ref. [32].

To increase the degree of active sites and meet the steric requirements of large organometallic compounds, two Ir and Re organometallic compounds with elongated dicarboxylate ligands (see Figure 2c and d) were employed as the organic linker to synthesize single-site MOF photocatalysts. The Ir-complex-derived MOF (Ir-MOF) can be obtained by heating a mixture that contained the Ir organometallic compound, ZrCl₄, and DMF at 100 °C for 3 d.^[33] Ir-MOF is a highly porous crystal with a triangular open channel and an octahedral cavity. The as-prepared MOF was employed to deposit Pt nanoparticles within the MOF pores under visible-light irradiation; tiny and uniform Pt nanoparticles were observed by using TEM after visible-light irradiation. The Pt-entrapped MOF displayed a high photocatalytic activity towards H₂ production from a solution that contained an electron donor. Conversely, the Re-complex-derived MOF (Re-MOF) was synthesized by using the same procedure as Ir-MOF.^[34] Re-MOF served as an effective single-site photocatalyst for CO₂ reduction. The heterogeneous Re-MOF showed higher photocatalytic activity than the homo-

geneous catalyst. The incorporation of a homogeneous catalyst for CO₂ reduction (Re complexes) into a stable Zr-based MOF with three-dimensional structure to create isolated catalytic active sites highlights an exciting opportunity for the rational design of single-site MOF photocatalysts.

Another example of the in situ synthesis of single-site MOF photocatalysts was contributed by Matsuoka and co-workers.^[35] In a solvothermal method, they used a bis[4'-(4-carboxyphenyl)terpyridine] Ru^{II} complex ([Ru(tpy)₂]) as an organic linker and a Ti cation as a metal center to prepare a visible-light-responsive single-site MOF photocatalyst (Ti-MOF-Ru(tpy)₂) for photocatalytic H₂ evolution. A new diffraction peak in the Ti-MOF-Ru(tpy)₂ XRD pattern at low angles, compared with the pattern for the organic linker, revealed the formation of a framework. The as-prepared MOF was thermally stable up to 650 K, which suggested the successful formation of a Ru complex incorporated in the MOF. The chemical environment and electronic structure of Ru were carefully studied by using X-ray absorption measurements (XAFS) and the results show that the chemical environment and electronic structure of incorporated Ru are well preserved compared to [Ru(tpy)₂], which suggests that the single-atom Ru was successfully linked to the MOF linkers. Additionally, Ti-MOF-Ru(tpy)₂ shows wide absorption in the visible-light region. H₂ generation can be achieved from an aqueous solution that contains a sacrificial reagent as an electron donor under visible-light irradiation up to $\lambda = 620$ nm over Ti-MOF-Ru(tpy)₂, whereas no H₂ can be detected with the organic linker [Ru(tpy)₂] as the catalyst. Importantly, Ti-MOF-Ru(tpy)₂ can be reused three times without significant loss of photocatalytic activity. Recently, four isostructural porphyrinic MOFs (UNLPF-10a, -10b, -11 and -12) were fabricated by using free base, In^{III}-, Sn^{IV}Cl₂-, and Sn^{IV}-porphyrin complex as the organic linkers and [In(COO)₄]⁻ as the connecting center.^[36] The electronic structure of the porphyrin macrocycle was significantly changed by the metalation of In^{III} and Sn^{IV}, which resulted in high photostability and efficient photocatalytic performance in the aerobic hydroxylation of arylboronic acids, amine coupling, and the Mannich reaction. More recently, a series of Zr-based MOFs (ZrPP-1-M) were synthesized by using THPP-M (THPP = 5,10,15,20-tetrakis(3,4,5-trihydroxyphenyl); M = H₂, Zn, Cu, Fe, Co) as the organic linker and applied for CO₂ conversion under visible-light irradiation.^[37] Of these MOFs, ZrPP-1-Co displayed high CO₂ adsorption capacity and high stability over a large pH range, and remarkable photocatalytic activity towards CO₂ reduction.

Pre-synthetic method for MOF photocatalysts with multiple components

MOFs are built of molecular building blocks, and this molecularly tunable character makes it an ideal platform to incorporate multicomponent functional moieties. Normally, a molecular-based H₂ production system requires a catalyst for proton reduction, a photosensitizer for light harvesting, and an electron mediator for photoexcited electron transfer from the photosensitizer to the catalyst.^[7c, 38] However, the catalytic activity

of this homogeneous system is hindered by poor electron transfer between the photosensitizer and the proton-reduction catalyst, and an electron mediator is necessary for electron transfer from the photosensitizer and proton-reduction catalyst. Reducing the distance between photosensitizer and proton-reduction catalyst is very beneficial for efficient electron transfer and to eliminate toxic electron mediators. Fu and co-workers reported a bifunctional photocatalyst (Ru-Pt@UiO-67) for H₂ production by using a MOF as the platform to integrate a molecular proton-reduction catalyst ([Pt(dcbpy)]Cl₂; dcbpy = 2,2'-bipyridyl-5,5'-dicarboxylic acid (RuDCBPY)) and a molecular photosensitizer ([Ru(dcbpy)(bpy)]₂²⁺; bpy = 2,2'-bipyridine (PtDCBPY)).^[39] The bifunctional photocatalyst was synthesized by thermal treatment of a solution that contained ZrCl₄ as the connecting metal centers and bpdc, RuDCBPY, and PtDCBPY as the organic linkers. Figure 4 illustrates the synthetic strategy

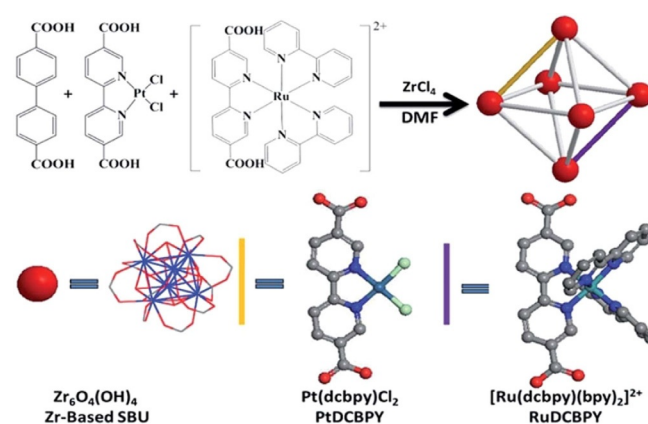


Figure 4. Schematic illustration of the synthetic strategy to prepare a MOF co-doped with Pt and Ru complexes, reprinted with permission from Ref. [39].

used to prepare the bifunctional photocatalyst. The incorporation of both the photosensitizer and the proton-reduction catalyst within the MOF is very interesting for efficient photocatalytic H₂ production. The XRD and BET characterization suggested that Ru-Pt@UiO-67 is a highly porous crystal and isostructural to the parent UiO-67 framework. The HAADF-STEM and EDX analysis demonstrated that the Ru and Pt complexes are well isolated in the MOF. As expected, significant H₂ was produced with Ru-Pt@UiO-67 dispersed in aqueous solution without any electron mediator under visible-light irradiation, much more than with a homogeneous solution of Pt complex and electron mediator (methyl viologen). The enhanced photocatalytic efficiency can be attributed to efficient electron transfer from the photosensitizer (Ru complex) to the proton-reduction catalyst (Pt complex). This work will stimulate further research into the fabrication of MOFs that incorporate multiple components for various photocatalytic reactions.

The molecular [Pt(dcbpy)]Cl₂ complex is widely used in photocatalytic reactions; however, the reduction of the Pt complex to Pt colloids during the photocatalytic reaction process significantly decreases its activity and stability. In this case, Park and

co-workers used a bipyridine-embedded UiO-67 MOF as a self-healing platform to integrate the photosensitizer (Ir complex) and the photocatalyst (Pt complex).^[27] The integration of Pt, Ir, and dcbpy within a single solid greatly improves the stability of the [Pt(dcbpy)]Cl₂ complex in the H₂ evolution reaction by varying the ratio of organic linker (dcbpy) and the [Pt(dcbpy)]Cl₂ complex.

Post-synthetic metalation method

MOFs are very interesting porous materials that allow precise spatial control of chemical moieties and catalytic active sites within their pores and cavities.^[40] Thus, a large number of functional groups can be incorporated for the post-synthetic metalation of MOFs.^[41] In natural photosynthesis, a highly ordered porphyrin-like pigment plays an important role in the conversion of solar light into chemical energy. Therefore, considerable attention has been focused on the synthesis of porphyrin-based MOFs with high crystallinity and surface area.^[42] Ye and co-workers synthesized ordered porphyrin-based MOF-525 by using TCPP (4,4',4''',4''''-(porphyrin-5,10,15,20-tetrayl)tetrabenzoate) as an organic linker and Zr₆ clusters as the connecting center.^[42d] The as-synthesized MOF-525 is a porous material with metal-free porphyrin rings, which can be employed to bind extraneous metal ions as displayed in Figure 5. Subse-

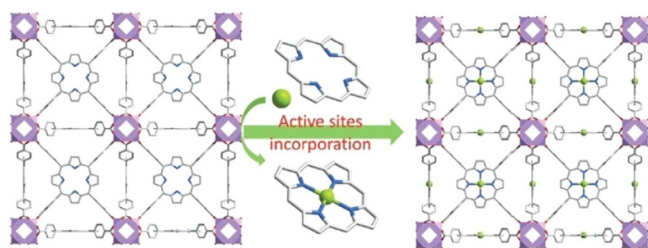


Figure 5. View of MOF-525-Co with a highly porous framework and incorporated active sites. Reprinted with permission from Ref. [42d].

quently, a new composite (MOF-525-Co) was produced by the metalation of coordinatively unsaturated Co sites within the porphyrin units, with the aim of enhancing CO₂ adsorption and facilitating CO₂ activation. The X-ray adsorption measurements clearly demonstrated the successful incorporation of Co into the MOF frameworks. Indeed, the CO₂ adsorption capacity of MOFs-525-Co is enhanced by a strong interaction between CO₂ and the coordinatively unsaturated Co sites, as suggested by the IR spectra. The photocatalytic activity of MOFs-525-Co for CO₂ conversion is higher than that of MOF-525 and the H6TCPP [TCPP = 4,4',4''',4''''-(porphyrin-5,10,15,20-tetrayl) tetrabenzoate] organic linker. The enhanced catalytic activity for CO₂ reduction can be assigned to the unique electron-transfer pathways, in which photogenerated electrons transfer to coordinatively unsaturated Co sites from high-spin-state Co^{II} to low-spin-state Co^I under visible-light irradiation. Subsequently, CO₂ is reduced by Co^I to produce CO and CH₄, which results in the regeneration of Co^{II}. This work offers an exciting way to

construct a multifunctional photocatalyst for CO₂ adsorption, activation, and reduction in a single solid material.

MOF-253, with open 2,2'-bipyridine binding sites (constructed from 2,2'-bipyridine-5,5'-dicarboxylic acid coordinated with oxophilic Al³⁺ ions), was designed and fabricated by Yaghi and co-workers.^[43] The open 2,2'-bipyridine binding sites within MOF-253 are able to chelate metal ions for various applications. Xu's group employed MOF-253 as a matrix for the post-synthetic immobilization of a Pt complex within its framework.^[29] The Pt complex was successfully incorporated within MOF-253 by heating a suspension of MOF-253, acetonitrile, and *cis*-[Pt(DMSO)₂Cl₂] at reflux for 15 h. The structure of MOF-253-Pt is shown in Figure 6. The Pt-complex-modified MOF-253

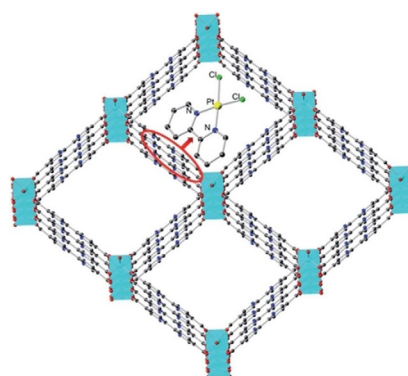


Figure 6. View of MOF-253-Pt with a highly porous framework and incorporated active sites, reprinted with permission from Ref. [29].

(MOF-253-Pt) serves as a bifunctional photocatalyst for solar light harvesting and proton reduction. The as-obtained MOF-253-Pt displays intense visible-light adsorption with an adsorption edge of around $\lambda = 650$ nm. The photocatalytic activity of MOF-253-Pt for H₂ production was investigated in the presence of TEOA as an electron donor under visible-light irradiation. A great amount of H₂ was produced over MOF-253-Pt, much higher than with the corresponding Pt complex under certain reaction conditions. The enhanced photocatalytic activity of MOF-253-Pt can be explained by the rational distribution of Pt active sites on the organic linkers of the MOF, which is beneficial for efficient solar energy conversion and reduces the photogenerated electron transfer distance. Similarly, Cohen and co-workers synthesized a Zr^{IV}-based MOF that incorporated a manganese bipyridine complex for CO₂ reduction.^[57] The intrinsic catalytic activity and stability of the Mn complex is enhanced by fixation in the MOF. These studies open new opportunities for the immobilization and protection of organometallic compounds in MOFs, which leads to enhancement of their photocatalytic performance.

Post-synthetic ligand exchange method

It is known that the strength of coordination bonds between metals and organic linkers is weak compared with chemical bonds. Recent studies have demonstrated that organic ligand

exchange can occur in MOFs with less chemical stability.^[44] Therefore, the exchange of organic linkers between an intact MOF and an organometallic compound can be used to design single-site MOF photocatalysts under mild conditions. Post-synthetic ligand exchange can occur in MOFs. Fontecave and co-workers reported the synthesis of a series of Rh-complex-containing MOFs (UiO-67-Rh) with different amounts incorporated by post-synthetic linker exchange.^[45] As shown in Figure 7,

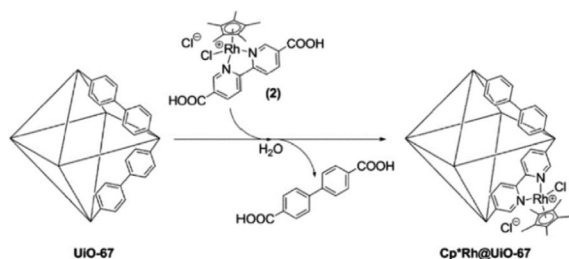


Figure 7. Post-synthesis ligand exchange to incorporate a rhodium complex into the framework of UiO-67, reprinted with permission from Ref. [45].

UiO-67-Rh is obtained by stirring an aqueous solution of Rh complex and UiO-67 at room temperature for 1 d, which allows the Rh complex to replace the 4,4'-biphenyldicarboxylate (bpdc) linker gradually. Then the precipitate is collected and washed with DMF and isopropanol, and finally dried under vacuum. The whole post-synthetic modification method is carried out under mild conditions. Importantly, loading of the Rh complex can be controlled by varying its concentration. During the stirring process, bpdc is slowly released from the parent UiO-67, as detected by using ¹H NMR spectroscopy after replacement with the Rh complex. Characterization by using BET, XRD, and UV/Vis spectroscopy studies suggested the successful incorporation of the Rh complex within UiO-67. The photocatalytic performance of UiO-67-Rh was probed for CO₂ reduction in a mixture of acetonitrile and TEOA. The photocatalytic activity of UiO-67-Rh towards CO₂ reduction is comparable to that of the homogeneous system, which suggests the excellent photocatalytic performance of the MOF-based system. Importantly, UiO-67-Rh displayed high selectivity for formate over H₂, and can be continuously used three times without a significant reduction in photocatalytic activity.

Synthesis of single-site MOF photocatalysts by node engineering

MOFs are composed of metal oxide clusters (nodes) and organic molecules (linkers). The node is usually based on a transition-metal oxide, which can be considered as a semiconductor quantum dot capable of photocatalytic H₂ production from an aqueous solution with an electron donor and organic pollutant degradation. It is known that quantum-sized nanoparticles possess high surface energy due to coordinatively unsaturated metal sites on their surfaces. There are a large number of coordinatively unsaturated metal sites in MOFs.^[13a] These open metal sites are electron-deficient centers that can interact with

electron-rich reagents. This unique characteristic is beneficial for driving the photocatalytic applications. In this way, MOF nodes that contain open metal sites can also be used as a promising matrix to design single-site photocatalysts. Considerable attention has been focused on the introduction of redox-active metals into MOF nodes. Doping a foreign metal ion into a cluster is a promising way to drive photochemical reactions for the purpose of solar-energy utilization.^[46]

Pre-synthetic method for doping redox-active metal into MOF nodes

Our group have developed a one-step synthetic method for the fabrication of Ce-doped, Cr-based MOFs (Ce-MIL-101(Cr)) through the hydrothermal treatment of chromic nitrate hydrate and cerium nitrate hexahydrate as metal precursors and 2-aminoterephthalic acid as an organic linker in water as the solvent.^[47] X-ray adsorption measurements were used to investigate whether Ce ions were doped in the MOF clusters. Intense peaks similar to that of cerium nitrate were observed in the normalized Ce L_{III}-edge XANES spectra, which suggested successful doping of Ce ions into the nodes. However, the peak of the Ce-doped MOF is broader than that of cerium nitrate, which suggests the formation of a valence fluctuation of Ce³⁺/Ce⁴⁺ in the nodes. The Ce-doped MOF is expected to promote photogenerated electron and hole separation by recycling the valence fluctuation of Ce³⁺/Ce⁴⁺. Indeed, the intrinsic catalytic activity of Pd nanoparticles for H₂ production from ammonia borane is significantly enhanced with Ce-MIL-101(Cr) under visible-light irradiation, and the enhancement is much larger than the MOF without doped Ce, as shown in Figure 8. The enhanced photocatalytic activity of Ce-MIL-101(Cr) is attributed to the isolated Ce ions in the nodes, which facilitate electron transfer from the MOF to the Pd nanoparticles by recycling the valence fluctuation of Ce³⁺/Ce⁴⁺. This results in the efficient separation of photogenerated holes and electrons. This one-step synthetic method was also applied for the fabrication of a Ti-ion-doped, Zr-based MOF with the aim to achieve the photocatalytic deposition of Pd on Au/MOFs.^[48] This bimetallic-doped MOF showed high catalytic activity and significant enhancement effects when tested in the formic acid

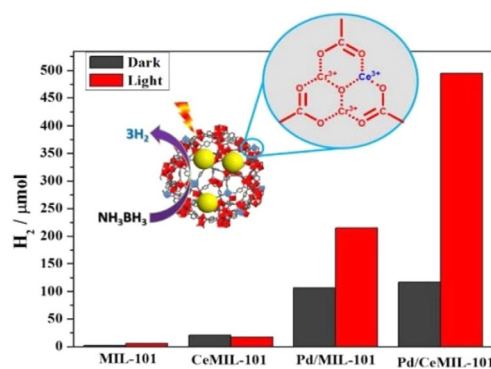


Figure 8. Visible-light-enhanced H₂ production from ammonia borane decomposition over different samples.

dehydrogenation reaction in the dark and under light irradiation. A volcano-type relationship between the catalytic activity and amount of Ti doping was obtained and a Ti/Zr ratio of 15:85 exhibited the highest enhancement under mild reaction conditions.

Post-synthetic ion exchange for doping redox-active metals into MOF nodes

It is important to note that open metal sites in MOFs have been used as active sites for various photocatalytic reactions.^[19a,20b] It can be imagined that the node on which the photocatalytic reaction takes place obviously affects the photogenerated charge transfer, as discussed above. Adding redox-active metal ions at the nodes as electron-transfer promoters can greatly accelerate photogenerated charge separation. In addition to the one-step synthetic method to introduce electron-transfer promoters at nodes, post-synthetic modification has proved to be an alternative.

Cation exchange at MOF nodes has attracted growing interest. Li and co-workers have reported a post-synthetic metal-ion-exchange method for the preparation of a Ti-doped UiO-66 photocatalyst for CO₂ reduction.^[49] Ti-doped UiO-66 (UiO-66(Zr/Ti)) is synthesized by soaking UiO-66 in a solution of TiCl₄(THF)₂ in DMF as the Ti-doping precursor. Zr in the original UiO-66 is gradually substituted by Ti moieties, and the substitution rate is highly dependent on the incubation temperature. More Ti moieties are substituted at the MOF nodes at high incubation temperatures than at relatively low incubation temperatures. The X-ray absorption measurements suggested that Ti is successfully substituted at nodes with an eightfold coordination environment. The photocatalytic performance of UiO-66(Zr/Ti) was investigated for the photocatalytic reduction of CO₂ in MeCN with TEOA as an electron donor. UiO-66(Zr/Ti) with heteroatoms to generate potential active sites and an electron-transfer promoter exhibits the requisite activity and selectivity to reduce CO₂ to formate.

Apparently, the photocatalytic activity of UiO-66(Zr/Ti) for CO₂ reduction is much higher than that of UiO-66 without Ti doping. This is presumably because the Ti moieties within the MOF framework are able to accelerate the transfer of photogenerated electrons from Ti³⁺ to Zr⁴⁺. This unique electron transfer is confirmed by ESR analyses. Two ESR signals, corresponding to Zr³⁺ and Ti³⁺, were observed upon light irradiation. The Zr³⁺ signal gradually increased after the light was switched off, whereas the Ti³⁺ signal gradually decreased. This observation clearly proves the electron transfer from Ti³⁺ to Zr⁴⁺. This study demonstrated that a highly dispersed metal ion in an isolated state, serving as an electron mediator for accelerated electron transfer, can be easily implanted in MOF nodes through post-synthetic ion exchange.

Post-synthetic addition of redox-active metals on the surface of MOF nodes

As discussed above, pre- and post-synthetic ion exchange methods for the in situ doping of a redox-active metal at MOF

nodes have been demonstrated as efficient ways to design single-site MOF photocatalysts, and the active sites are usually doped inside the metal cluster. An alternative strategy for the design of single-site MOF photocatalysts is to graft the redox-active metal onto the surface of the nodes at a linker vacancy site. Recent studies have suggested that there are a large number of linker vacancies in the MOF framework,^[50] which can allow a considerable amount of redox-active metal moieties to be grafted to the MOF nodes. Gascon and co-workers have fabricated novel single-site MOF photocatalysts by grafting Ti onto nodes in UiO-66.^[30c] The authors claimed that the Ti precursor significantly affected the Ti location and the photocatalytic activity of the Ti-modified UiO-66. It was found that a single Ti active site can be successfully grafted onto the node surface, rather than replacing Zr in the node, by using the basic Ti(OnBu)₄ as the Ti precursor. The grafting of Ti on the surface of UiO-66 gave an excellent photocatalyst for H₂ production from a CH₃CN, Et₃N, and H₂O mixture under light irradiation. The hydrogen production rate is 14 times greater than the parent UiO-66 without Ti grafting. On the basis of the above elucidation, the MOF nodes can be systematically engineered to introduce redox-active metals inside or on the MOF nodes at the atomic level through an in situ synthetic method, a metal-ion-exchange method, or a post-synthetic grafting method. These studies have demonstrated that the linker can be used for the design of single-site MOF photocatalysts, and that the metal oxide clusters are also equally important in the development of novel MOF photocatalysts with isolated active sites.

Incorporation of single-site photocatalysts within the MOF cavities

MOFs with three-dimensional microporous materials with prodigious porosity and numerous cavities can provide a more suitable environment to incorporate single-site photocatalysts. Feng and co-workers have synthesized a new photocatalyst by immobilizing the biomimetic [Fe₂S₂] catalyst inside the cavity of a zirconium-porphyrin MOF (ZrPF) with zinc at the center of the porphyrin ring.^[51] ZrPF is composed of Zr oxide clusters (Figure 9a) and Zn metal complexes (Figure 9b). Linking the biomimetic [Fe₂S₂] proton-reduction catalyst (Figure 9d) with zinc open metal sites through a chemical bond to form [FeFe]@ZrPF can reduce the photogenerated charge transfer distance and avoids using the electron mediator to transfer electrons from the photosensitizer to the catalytically active biomimetic [Fe₂S₂] site. Before immobilizing biomimetic [Fe₂S₂] within the MOF, the MOF displayed two intense fluorescence emission peaks centered at $\lambda = 668$ and 717 nm, the intensities of which decreased with the incorporation of biomimetic [Fe₂S₂] due to electron transfer from the Zn complex to the diiron complex, which demonstrated the efficient charge transfer. The photocatalytic activity of [FeFe]@ZrPF for H₂ production was tested in water with ascorbic acid as an electron donor under visible-light irradiation. A remarkable enhancement in H₂ production was observed with [FeFe]@ZrPF. The amount of H₂ produced with [FeFe]@ZrPF is almost four times

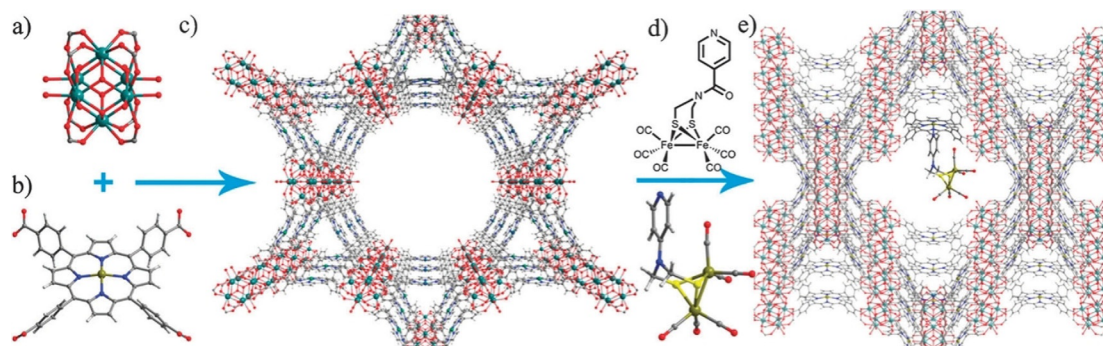


Figure 9. Structural building blocks of a) a zinc oxide cluster and b) tetrakis(4-carboxyphenyl porphyrin)-zinc complex, c) zirconium-porphyrin MOFs (ZrPF), and d) biomimetic $[\text{Fe}_2\text{S}_2]$ catalyst. e) Model structure of $[\text{FeFe}]@\text{ZrPF}$. Reprinted with permission from Ref. [51].

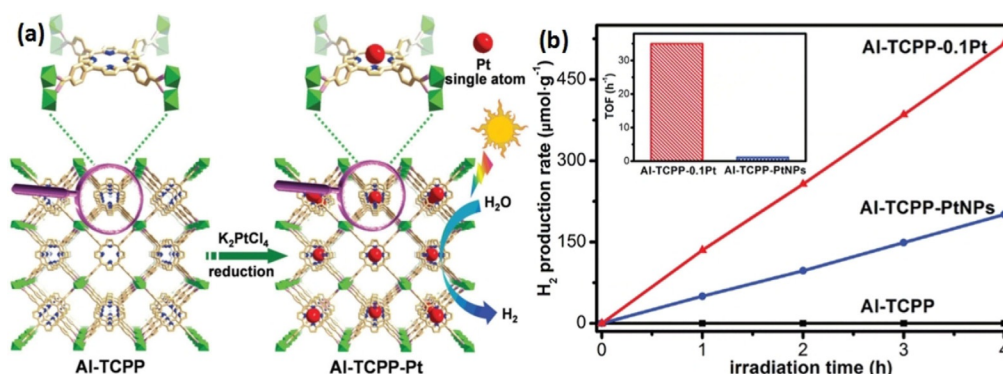


Figure 10. a) Schematic illustration of the synthetic strategy for the fabrication of Pt single atoms confined in Al-TCPP. b) Hydrogen production on Al-TCPP-0.1Pt and Al-TCPP-PtNPs. Reproduced with permission from Ref. [55].

that with the corresponding homogeneous catalyst. The high performance of $[\text{FeFe}]@\text{ZrPF}$ results from the enhanced stability and electron transfer efficiency obtained by anchoring biomimetic $[\text{Fe}_2\text{S}_2]$ at Zn open sites.

A proton reduction catalyst was fabricated by first absorbing the $N^2,N^{2'}$ -propanediyl bis(2,3-butanedione-2-imine-3-oxime) ligand in the cage of MOF, then introducing CoBr_2 under aerobic conditions to form a well-defined cobaloxime proton reduction catalyst.^[52] The as-formed Co metal complex was confined within the cavity of MOFs due to the larger size of complex than the MOF pore size. The photocatalytic activity for H_2 production was investigated in a mixture of acetonitrile, (triethylamine) TEA, and water. The Co-complex-encapsulating MOF exhibited higher activity than a homogeneous system in the absence of photosensitizer. In a similar strategy, a Co^{II} molecular photocatalyst $[\text{Co}^{\text{II}}(\text{TPA})\text{Cl}][\text{Cl}]$ (TPA = tris(2-pyridylmethyl)amine) was incorporated inside the cage of a MIL-125- NH_2 matrix as a noble-metal-free composite ($\text{Co}^{\text{II}}@\text{MIL-125-NH}_2$) for visible-light-driven H_2 production by a “ship-in-a-bottle” synthetic strategy.^[53] $\text{Co}^{\text{II}}@\text{MIL-125-NH}_2$ behaves as a photosensitizer to harvest visible light and a catalyst for H_2 production, and greatly facilitates the spatial charge separation, which results in an enhancement in H_2 production.

Incorporation of single metal atoms within MOF cavities

To maximize atomic efficiency, the loading of single metal atoms on porous materials for various catalytic reactions has been extensively studied in recent years.^[54] However, single metal atoms loaded on silica or alumina surfaces easily aggregate due to their high surface energy. Therefore, stabilizing single metal atoms by dispersing them within a designed chemical environment is particularly important. In this case, MOFs with a large number of free binding sites have proved to be an excellent candidate to stabilize single metal atoms.

A unique MOF (Al-TCPP; TCPP = 4,4',4''-(porphyrin-5,10,15,20-tetrayl)tetrabenzoate) with a free porphyrin ring was synthesized and used to stabilize Pt single atoms by Jiang and co-workers.^[55] Figure 10 illustrates the synthetic strategy for the fabrication of Pt single atoms confined in Al-TCPP. Al-TCPP, with a three-dimensional structure, is constructed by using Al^{3+} as the connecting centers and TCPP as the organic linker. The free porphyrin ring is used to contain the Pt^{II} ions. Pt-doped Al-TCPP (Al-TCPP- Pt^{II}) can be easily obtained by treating K_2PtCl_4 with Al-TCPP in the liquid phase. Subsequently, Pt^{II} is reduced to Pt at 180°C under a H_2 atmosphere to give single-atom-confined Al-TCPP-Pt (denoted as Al-TCPP-Pt). The optimized Pt loading was found to be 0.1 wt%; higher loading

amounts result in the formation of Pt clusters. The single Pt atoms are stabilized by the porphyrin rings through the formation of Pt–N interactions, as confirmed by the X-ray adsorption results, in which one prominent peak centered at around 1.5 Å, corresponding to Pt–N, was observed. The photocatalytic performance of Al-TCPP-Pt was investigated for H₂ production from an aqueous solution. As displayed in Figure 10b, Al-TCPP-Pt showed a higher catalytic activity than Pt-nanoparticle-supporting Al-TCPP (Al-TCPP-PtNPs) or pure Al-TCPP. This can be explained by the efficient charge transfer in Al-TCPP-Pt. The isolated Pt atoms are able to promote photocatalytic H₂ production through efficient electron transfer from the photosensitizer to the Pt active site and improve hydrogen bond energy. Moreover, the agglomeration of Pt atoms into large Pt nanoparticles was not observed after four catalytic runs and the recovered Al-TCPP-Pt could be reused without significant deterioration in the catalytic activity. At about the same time, Wang and co-workers synthesized a series of noble-metal (Ir, Pt, Ru, Au, Pd) single atoms immobilized in MOFs with a hollow nanotube structure.^[56] The bimetallic Pt–Ir single-atom-immobilized MOF displayed excellent photocatalytic activity due to a unique structure, fast mass transformation, and improved charge separation efficiency. These works provide new strategies for implanting single metal atoms within MOFs for various photocatalytic applications.

Summary and outlook

Owing to the tunable structure, high porosity, and remarkable crystallinity of MOFs, these materials are superior to other porous materials in the design of single-site photocatalysts and proven to be an ideal platform for the integration of organometallic compounds and heterogeneous photocatalysts into a single, solid, single-site photocatalyst. The cavity, metal oxide cluster, and organic linker offer sufficient opportunities for the design of photoactive sites. Indeed, the last few years have witnessed impressive achievements in the design of single-site MOF photocatalysts through various synthetic methods, including the incorporation of organometallic compounds through in situ synthetic methods, post-synthetic ligand engineering, and post-synthetic ligand exchange; doping of redox-active metals within the MOF nodes through in situ synthetic methods and post-synthetic ion exchange, and grafting of redox-active metals onto the node surfaces; and the incorporation of single atoms within the MOF. It is obvious that single-site MOF photocatalysts displayed higher photocatalytic activity and stability for various photocatalytic reactions compared with their homogeneous counterparts or parent MOFs, owing to their advantages of a highly porous structure to facilitate reagent diffusion, intense crystallinity for fast photogenerated electron transfer, and controllable active-site design at the atomic level. However, their poor stability and recyclability still need to be enhanced for practical applications.

The bonding interactions between metal oxide clusters and organic linkers are weaker than ionic bonds. The entire MOF framework is not so chemically stable when applied in photocatalytic applications. During the photocatalytic application

process, photogenerated reactive species, such as superoxide anions and hydroxyl radicals, can easily react with the organic linker, which leads to decomposition of the organic linker and collapse of the MOF framework. Additionally, most MOFs with open metal sites have a high affinity towards water, and the hydrolysis reaction between water and the metal organic clusters significantly affects the MOF stability. Therefore, tuning the hydrophobic properties of the MOF nodes to make them water-resistant is of great importance. Attention can also be paid to the creation of a crowding effect around the metal oxide cluster to prevent water interacting with the open metal sites, with the aim of enhancing the stability of the MOF. Recent studies have also suggested that MOFs built from hard metal ions (e.g., Cr³⁺, Ti⁴⁺, Zr⁴⁺, Fe³⁺) and linkers with carboxylate groups have exhibited considerably high stability in the presence of water due to the strong coordination force and the optimized coordination number. Therefore, the reagent hydrophobicity, molecular size, catalytic active site locations, and reaction solvent need to be considered overall when anchoring active sites in MOFs.

Considering that most photocatalytic reaction systems require an electron mediator, the migration rate of the electron mediator (to relay electrons from the photosensitizer to the active sites) and the electron donor (to recover the photooxidized photocatalyst) greatly affects the photocatalytic performance of single-site MOFs. To enhance the migration rate of the electron mediator and the electron donor, the activation method for removing unreacted organic linkers and residual solvent under mild conditions should be explored. The breakthrough strategy of incorporating both photosensitizer and catalytic active sites has proved to be an ideal way to eliminate the use of electron mediation in photocatalytic reaction systems and promote photogenerated electron transfer by reducing the electron relay distance.

Much attention has been paid to the creation of redox-active metals on/in MOF nodes with unprecedented catalytic activity, particularly for redox-active metals exposed on the MOF surfaces, which are easily accessed by the reagent. The redox-active metal is generally grafted on the surface of node at a linker vacancy site. However, a high concentration of linker vacancies easily leads to the collapse of the MOF framework. Searching for the optimal linker vacancy concentration is highly important to achieve single-site MOF photocatalysts with robust frameworks. The incorporation of small organic molecules with functional groups as rigid pillars and electron donors into MOFs is providing an alternative to the fabrication of single-site MOFs with robust structure.

Most of the reported single-site MOF photocatalysts are composed of noble metals as the catalytic active sites and expensive organic molecules as the MOF building blocks; for example, Ir, Re, Pt, and Ru complexes incorporated within porphyrin- or bipyridine-based MOFs. These starting materials are very expensive, which hinders their future applications. Recent studies have suggested that non-noble-metal complexes incorporated within porous structures may also exhibit excellent photocatalytic activity in various reactions. Therefore, the incorporation of non-noble-metal complexes or non-noble-metal

atoms within MOFs is also suggested for the development of low-cost MOF photocatalysts with isolated active sites.

As a potential matrix for the development of single-site photocatalysts, MOFs have attracted a great deal of interest. However, remarkable progress has been obtained in the photocatalysis area in recent years. The future development of single-site MOF photocatalysts with high catalytic activity and stability for visible-light-driven photocatalytic reactions still needs deeper understanding. The idea of using MOFs to anchor active sites in a porous framework is a new and promising methodology for the design and construction of new types of photocatalysts for visible-light-driven photocatalytic reactions. We believe that MOF photocatalysts with isolated active sites can serve as alternatives to replace traditional semiconductors in the future.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: ligand-ion exchange · metal-organic frameworks · post-synthetic modifications · redox chemistry · single-site photocatalysts

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