

Integration of Earth-Abundant Photosensitizers and Catalysts in Metal–Organic Frameworks Enhances Photocatalytic Aerobic Oxidation

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ABSTRACT: We report here the construction of two metal—organic frameworks (MOFs), Zr_6 -**Cu/Fe-1** and Zr_6 -**Cu/Fe-2**, by integrating earth-abundant cuprous photosensitizers (Cu-PSs) and Fe catalysts for photocatalytic aerobic oxidation. Site isolation and pore confinement stabilize both Cu-PSs and Fe catalysts, while the proximity between active centers facilitates electron and mass transfer. Upon visible light irradiation and using O₂ as the only oxidant, Zr_6 -**Cu/Fe-1** and Zr_6 -**Cu/Fe-2** efficiently oxidize alcohols and benzylic compounds to afford corresponding carbonyl products with broad substrate scopes, high turnover numbers of up to 500 with a 9.4-fold enhancement over homogeneous analogues, and excellent recyclability in four consecutive runs. Control experiments, spectroscopic evidence, and computational studies revealed the photo-oxidation mechanism: oxidative quenching of [Cu-PS]* by O₂ affords [Cu^{II}-PS], which efficiently oxidizes Fe^{III}–OH to generate a hydroxyl radical for substrate oxidation. This work highlights the potential of MOFs in promoting earth-abundant metal-based photocatalysis.



KEYWORDS: aerobic oxidation, photoredox catalysis, metal–organic framework, heterogeneous catalysis, earth-abundant metal, cuprous photosensitizer, site isolation

INTRODUCTION

With increasing emphasis on environmental sustainability and green chemistry, 1,2 O₂ has established its irreplaceable role as a green, cheap, and abundant oxidant for the synthesis of oxygen-containing chemical feedstocks.³ The development of efficient and cost-effective catalytic systems for aerobic oxidation processes has become an important research topic, with significant progress made in recent years.⁴⁻⁹ However, to activate the triplet O₂ and control the radical reaction during the oxidation process, traditional transition-metal-catalyzed aerobic oxidation reactions typically rely on hash reaction conditions and (sub)stoichiometric amounts of expensive radical initiators, which limits their practical applications.^{10–13} In contrast, by utilizing light to provide energy for the activation of ground-state O2 and to facilitate electron transfer between the substrates and oxidants, photocatalytic aerobic oxidation reactions can be performed under ambient temperature and atmospheric pressure without cocatalysts, thus providing an attractive platform for the development of novel catalytic systems for environmentally benign synthetic processes.^{14–18}

Despite the advantages offered by and the progress made in photocatalytic aerobic oxidation systems, significant challenges remain and limit their widespread applications. For example, reliance on rare, expensive, and toxic noble metals, such as Ru, Ir, Os, and Pt, for efficient photosensitization presents a significant roadblock for practical photocatalytic processes.¹⁹⁻²⁷ Although semiconductor-based photocatalysts can address some of these challenges, they tend to have a distribution of active centers, which makes it difficult to study the reaction mechanism in detail and tune the active sites for enhanced reactivity or selectivity.^{14,28-32} Thus, there is a strong need for developing well-defined photocatalytic systems based on inexpensive earth-abundant metals (EAMs).³³⁻⁴⁰ We envisioned that metal-organic frameworks (MOFs), a class of crystalline and porous molecular solid materials, could provide a tunable platform to design efficient photocatalytic aerobic oxidation systems based on EAMs. MOFs have recently been shown to stabilize homogeneously inaccessible EAM complexes for catalytic or photocatalytic applications through active site isolation and pore confinement.^{18,41-45} Meanwhile, high local concentrations and proximity of multiple active sites in MOFs can enhance electron and mass transfer, which is critically important in photocatalytic processes.^{46–48} The welldefined active centers in MOF catalysts allow an in-depth understanding of reaction mechanisms to facilitate catalyst optimization.

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We previously showed that MOFs stabilize cuprous photosensitizers (Cu-PSs) as potent photoreductants.⁴⁹ As Cu-PSs are also effective photo-oxidants^{50,51} and Fe catalysts have been successfully used in many homogeneous oxidation reactions,^{9,52-54} we surmised that earth-abundant Cu-PSs and Fe catalysts could be integrated into MOFs for photocatalytic oxidation using O2 as the oxidant. The MOF catalysts with both Cu-PSs and Fe catalysts, Zr₆-Cu/Fe-1 and Zr₆-Cu/Fe-2, were highly active in photocatalytic aerobic oxidation of alcohols and benzylic compounds to selectively afford corresponding carbonyl products with turnover numbers (TONs) as high as 500. No additives were required and the aerobic process could proceed smoothly at room temperature. Due to the stabilization of both EAM complexes by the MOF framework and enhanced electron transfer between proximate Cu-PSs and Fe catalysts, Zr₆-Cu/Fe-1 showed a nearly tenfold enhancement in TONs than the homogeneous analogue. Indepth mechanistic studies by combining control experiments, spectroscopic data, and computational results revealed that, upon light irradiation and with O_2 as the oxidant, $[Cu^{II}-PS]$ efficiently oxidizes Fe^{III}-OH to generate a hydroxyl radical as the key reactive species for substrate oxidation (Figure 1).



Figure 1. MOFs integrate earth-abundant Cu-PSs and Fe catalysts for photocatalytic aerobic oxidations.

RESULTS AND DISCUSSION

Synthesis and Characterization of MOF Catalysts. We targeted cuprous diimine–diphosphine photosensitizing complexes for the construction of visible-light-responsive MOF catalysts. The initial attempt of using ZrCl_4 as the Zr source failed to give the targeted MOF due to the decomposition of Cu-PSs by the highly Lewis acidic ZrCl_4 . $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{McO})_{12}$ cluster ($\text{Zr}_6\text{-Mc}$, Mc = methacrylate),⁵⁵ which was compatible with the cuprous complex, was applied as an alternative Zr source. After optimization, Cu-PSs $\text{Cu}(\text{H}_2\text{bypdc})(\text{XantP})$](PF₆) (XantP = dimethyl-4,5-bis-

(diphenylphosphino)xanthene, H_2 bpydc = 2,2'-bipyridine-5,5'-dicarboxylic acid) and Cu(H₂bpydc)(POP)(PF₆) (POP = bis(2-diphenylphosphino)phenyl ether) were successfully incorporated into UiO-type MOFs through solvothermal reactions of H_2 bpydc, $[Cu(H_2$ bpydc)(XantP)](PF_6), or [Cu- $(H_2bpydc)(POP)](PF_6)$ and Zr_6-Mc in oxygen-free N,Ndimethylformamide (DMF) to afford Zr₆-Cu-1 and Zr₆-Cu-2, respectively (Figure 2a). Zr₆-Cu/Fe-1 and Zr₆-Cu/Fe-2 were obtained as light olive solids through subsequent metalation of the bipy sites in Zr_6 -Cu-1 and Zr_6 -Cu-2, respectively, with FeCl₂. Powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM) studies showed that Zr₆-Cu-1, Zr₆-Cu-2, Zr₆-Cu/Fe-1, and Zr₆-Cu/Fe-2 all adopted UiO-67type topology with near-octahedral morphologies of ~40 nm in dimensions (Figures 2b,c, S7, and S8). Such nanosizes and uniform morphologies are expected to facilitate light penetration and substrate diffusion as well as efficient adsorption of oxygen for photocatalytic aerobic processes. N2 sorption measurements showed Brunauer-Emmett-Teller surface areas of 930, 1192, and 2563 m^2/g for $Zr_6\text{-}Cu/Fe\text{-}1,$ $Zr_6\text{-}Cu/Fe\text{-}2,$ and UiO-67-bpy, 56 respectively (Figure 2d). ^{1}H NMR spectra of digested MOFs revealed a 1:5 [Cu(H₂bpydc)-(XantP)]⁺ to H₂bpydc ratio in Zr₆-Cu-1 (17% Cu loading) and a 1:4 $[Cu(H_2bpydc)(POP)]^+$ to H_2bpydc ratio in Zr_6 -Cu-2 (20% Cu loading, Figure S6). Inductively coupled plasmamass spectrometry (ICP-MS) measurements showed Fe loadings of 63 and 60% in Zr₆-Cu/Fe-1 and Zr₆-Cu/Fe-2 (relative to bipy), respectively.

X-ray absorption spectroscopy was used to determine the electronic properties and coordination environments of Cu and Fe centers in Zr₆-Cu/Fe-1 and Zr₆-Cu/Fe-2. X-ray absorption near-edge structure (XANES) spectroscopy indicated Cu^I oxidation state in both Zr₆-Cu/Fe-1 and Zr₆-Cu/ Fe-2 by comparing the pre-edge features with corresponding Cu salts, all displaying a similar pre-edge peak corresponding to the spin-allowed 1s \rightarrow 4p electronic transition at 8981-8983 eV (Figure S13). Extended X-ray absorption fine structure (EXAFS) features of Zr₆-Cu/Fe-1 and Zr₆-Cu/Fe-2 at both Cu K-edge and Fe K-edge were well fit with the reported crystal structures of corresponding Cu¹ and Fe¹¹ complexes with nearly identical coordination environments. Specifically, for Zr₆-Cu/Fe-1, EXAFS results revealed that the tetrahedral Cu¹ center coordinates to one bidentate bipy with Cu-N distances of 1.98 and 2.05 Å, and one bidentate XantP with Cu–P distances of 2.25 and 2.25 Å (Figure 2e), while the tetrahedral Fe^{II} center coordinates to one bidentate bipy with the same Fe-N distance of 2.08 Å and two equivalent chloride groups with Fe–Cl distance of 2.25 Å (Figure S14). Zr₆-Cu/ Fe-2 adopted similar tetrahedral Cu^I centers with one bidentate bipy and one bidentate POP and tetrahedral Fe^{II} centers with one bidentate bipy and two chloride groups (Figures S12 and S15). No EXAFS features corresponding to metallic nanoparticles were detected at either Cu K-edge or Fe K-edge. These results confirm the successful integration of Cu-PSs and Fe catalysts with well-defined electronic and local coordination structures into the UiO frameworks.

Photocatalytic Aerobic Oxidation Reactions. As a proof of concept, we focused on the oxidation of alcohols to aldehydes and the direct oxidation of benzylic C–H bonds to aromatic carbonyl derivatives to test the photocatalytic performance of our EAM MOF catalysts. The carbonyl products, including aldehydes, ketones, and esters, are important feedstocks for pharmaceutical synthesis and



Figure 2. (a) Synthesis of MOF-based photocatalytic aerobic oxidation systems Zr_6 -Cu/Fe-1 and Zr_6 -Cu/Fe-2 with Zr_6 -Mc as the Zr source. (b) PXRD patterns of Zr_6 -Cu-1 (orange), Zr_6 -Cu/Fe-1 (olive), and Zr_6 -Cu/Fe-1 (AR, violet) and the simulated pattern of UiO-67 (black). (c) TEM images of Zr_6 -Cu-1 and Zr_6 -Cu/Fe-1. (d) N₂ sorption isotherms of Zr_6 -Cu/Fe-1 (orange), Zr_6 -Cu/Fe-2 (olive), and UiO-67-bpy (gray). (e) EXAFS spectra (gray solid line) and fits (black circles) of Zr_6 -Cu/Fe-1 in R-space at the Cu K-edge.

Table 1. Photocatalytic Aerobic Oxidation of 4-Methylbenzyl Alcohol by MOF and Homogeneous Catalytic Systems⁴

$OH + O_2 - Cu Fe \rightarrow I \rightarrow O$							
entry	catalyst	yield (24 h) (%)	TON				
1	0.5 mol % Zr ₆ -Cu/Fe-1	98 (73% in 6 h)	196				
2	0.5 mol % Zr ₆ -Cu/Fe-2	82	164				
3	0.2 mol % Zr ₆ -Cu/Fe-1	68	340				
4	0.5 mol % Zr ₆ -Cu/Fe-1 (dark)	0	0				
5	1.5 mol % Zr ₆ -Fe	9	-				
6	0.5 mol % Zr ₆ -Cu-1	1	-				
7	none	0	_				
8	UiO-67-bpy	0	_				
9	0.5 mol % [Cu(H ₂ bpydc)(XantP)](PF ₆) + 1.5 mol % Fe(bpy)Cl ₂	18	36				
10	1.5 mol % Fe(bpy)Cl ₂	5	_				
11	0.5 mol % [Cu(H ₂ bpydc)(XantP)](PF ₆)	0	-				

^aUnless noted, reactions were conducted with 0.05 mmol 4-methylbenzyl alcohol in 1.0 mL of DMSO under light irradiation for 24 h. Catalyst loadings were based on Cu-PS for dual-metallated MOFs.

commodity chemicals.^{57,58} Traditional synthesis protocols typically relied on elevated reaction temperatures or radical initiators, which put a significant burden on the cost and environment.^{12,59}

Merging of Cu-PSs and Fe catalysts in robust MOFs resulted in efficient photocatalytic aerobic oxidation of alcohols to corresponding aldehydes under mild reaction conditions and without any additives. In the presence of 0.5 mol % of Zr_6 -Cu/ Fe-1 and irradiation with a 13.9 W 350–700 nm solid-state plasma light source (equipped with a cooling fan), a solution of 4-methylbenzyl alcohol in dimethylsulfoxide (DMSO) was efficiently oxidized to 4-methylbenzaldehyde in 73% yield in 6 h and 98% yield in 24 h under ambient O₂ atmosphere and at room temperature (Table 1). No significant overoxidized products were detected. A slightly lower 4-methylbenzaldehyde yield of 82% was obtained for \mathbf{Zr}_{6} - $\mathbf{Cu}/\mathbf{Fe-2}$ in 24 h. Further lowering the \mathbf{Zr}_{6} - $\mathbf{Cu}/\mathbf{Fe-1}$ loading to 0.2 mol % led to a TON of 340, exhibiting a 9.4-fold enhancement over the homogeneous control using $[Cu(H_2bpydc)(XantP)](PF_6)$ and $Fe(4,4'-bipyridine)Cl_2$ in a 1:3 mole ratio (18% yield with a TON of 36). This enhancement of photocatalytic activity can be attributed to active center stabilization and confinement as well as the close proximity (<1 nm) between MOF-incorporated Cu-PS and Fe catalyst. As a heterogeneous catalyst, \mathbf{Zr}_6 - $\mathbf{Cu}/\mathbf{Fe-1}$ was recovered and reused in four consecutive runs without a significant decrease in photocatalytic activity (Figure S20). PXRD studies indicated the maintenance of the crystallinity of both \mathbf{Zr}_6 - $\mathbf{Cu}/\mathbf{Fe-1}$ and \mathbf{Zr}_6 -



Table 2. Zr₆-Cu/Fe-1 Catalyzed Photocatalytic Aerobic Oxidation of Alcohols and Benzylic Compounds^a

Cu/Fe-2 after photocatalysis (Figures 2b and S7). ICP-MS revealed minimal leaching of Cu (0.8%) and Fe (0.7%) into the supernatant after one reaction run.

 Zr_6 -Cu/Fe-1 catalyzed photocatalytic aerobic oxidation of a wide scope of alcohols (Table 2a). Under standard conditions, Zr_6 -Cu/Fe-1 converted various primary and secondary benzylic alcohols to corresponding carbonyl compounds. Both electron-donating groups, e.g., methyl, methoxyl, and hydroxymethyl, and electron-withdrawing groups, e.g., chloride before trifluoromethyl, were well tolerated in the photocatalytic processes with good to excellent yields. Moreover, aliphatic alcohols were also smoothly and selectively oxidized to corresponding aliphatic aldehydes, ketones, or α,β -unsaturated aldehydes without interference from the unsaturated bonds. All of the reactions were conducted at room

temperature and atmospheric pressure, suggesting the potential utility of this process.

Besides the outstanding performance in photocatalytic aerobic oxidation of alcohols, Zr_6 -Cu/Fe-1 was also highly active for direct aerobic oxidation of benzylic compounds to afford aromatic carbonyl derivatives (Table 2b). Upon photoirradiation, 4-methylanisole was quantitively oxidized to 4-methoxylbenzaldehyde in the presence of 0.5 mol % Zr_6 -Cu/Fe-1 within 24 h. Several substrates containing benzylic C–H bonds, including 4-ethylanisole, indane, tetralin, fluorene, and xanthene, were all successfully oxidized to afford desired ketones in 60–99% yields under similar reaction conditions. Higher photocatalytic activity was observed for substrates with adjacent oxygen atoms, e.g., phthalane and isochromane, to afford lactones in excellent yields with lower catalyst loadings.



Figure 3. (a) CV curves of $[Cu(H_2bpydc)(XantP)]^+$ (orange) and $[Cu(H_2bpydc)(POP)]^+$ (olive). (b) Normalized XANES features at Fe K-edge in Zr_6 -Cu/Fe-1 (navy), Zr_6 -Cu/Fe-1 (AR, olive), FeCl₂ (black), and FeCl₃ (red). (c) CV curve of Zr_6 -Fe coated on the electrode. (d) EPR signal of the BMPO-^oOH adduct generated by Zr_6 -Cu/Fe-1 in H_2O /toluene under N_2 .

Mechanistic Studies. The well-defined active site structures of the MOF catalysts provide an opportunity for in-depth mechanistic studies. To gain insights into the Zr₆-Cu/ Fe-1-catalyzed photocatalytic alcohol to aldehyde transformation, we performed several control experiments with 4methylbenzyl alcohol. When O_2 was replaced by air and N_2 the yields of 4-methylbenzaldehyde dropped from 73 to 32 and 0%, respectively (Table S6), demonstrating the crucial role of O_2 as the oxidant. The removal of either light source, Cu-PS, or Fe catalyst significantly decreased the yields of 4methylbenzaldehyde or completely shut down the reaction (Table 1). A significantly lower yield of 4-methylbenzaldehyde (4%) was found when 4 Å molecular sieve was added as a water absorbent (Table S6), indicating the involvement of water in the photo-oxidation process. A low yield of 7% 4methylbenzaldehyde was obtained with H2O2 as the oxidant (Table S6), ruling out the contribution of the Fenton reaction.

To further identify the role of potential reactive oxygen species (ROS) in the photocatalytic oxidation process, specific ROS quenching agents were added to Zr_6 -Cu/Fe-1-catalyzed oxidation of 4-methylbenzyl alcohol. In the presence of 50 mM 1,4-benzoquinone (as an O_2^{-1} scavenger)⁶⁰ or 50 mM NaN₃ (as an ${}^{1}O_2$ scavenger),⁶¹ no obvious decrease of 4-methylbenzaldehyde yields was detected (Table S6). However, the addition of hydroxyl radical capturing agent TEMPO (50 mM)⁶² completely shut down the reaction (Table S6), thus

suggesting the *in situ* generated hydroxyl radical from water as the key ROS for photocatalytic oxidation. Furthermore, a radical clock experiment with 4-penten-1-ol as a substrate afforded 87% cyclic products along with 13% primary aldehydes, confirming the alkoxyl radical as the photo-oxidation intermediate (Figure S19).⁶³

Spectroscopic evidence was obtained to shed light on the electron-transfer pathways across the metal centers. Zr₆-Cu/ Fe-1 and Zr₆-Cu/Fe-2 displayed characteristic [Cu(diimine)-(diphosphine)]⁺ luminescence at 491 and 489 nm, respectively (Figure S23),⁶⁴ which correspond to ground-state to excitedstate energy gaps of 2.52 eV for Zr₆-Cu/Fe-1 and 2.54 eV for Zr₆-Cu/Fe-2. These emissions were effectively quenched by the increasing concentration of O2, indicating the efficient electron transfer between [Cu-PS]* and O₂ (Figure S23). Furthermore, CV curves of $[Cu(H_2bpydc)(XantP)]^+$ and $[Cu(H_2bpydc)(POP)]^+$ showed similar one-electron oxidation peaks at +1.58 and +1.55 V vs NHE for the [Cu^{II}-PS]/[Cu^I-PS] couple (Figure 3a), indicating the strong oxidation power of both [Cu^{II}-PS] species. XANES analysis gave the Fe^{III} oxidation state for Zr₆-Cu/Fe-1 (AR) recovered from photocatalytic oxidation, suggesting the oxidation of Fe^{II} precatalyst during the photocatalytic oxidation process (Figure 3b). The CV curve of the MOF-stabilized Fe catalyst, Zr₆-Fe, displayed a reversible one-electron oxidation peak at +0.42 V vs NHE and an irreversible one-electron oxidation peak at



Figure 4. Gibbs free energy changes for the photocatalytic oxidation steps on the Fe centers via the metal—oxo pathway or the hydroxyl radical pathway as calculated by DFT.

+1.43 V vs NHE (Figure 3c). The first peak can be assigned to the reversible Fe^{II}/Fe^{III} couple, while the second peak can be attributed to the further irreversible oxidation of the Fe^{III} species. Both Cu-PSs in the MOFs have enough oxidation potential to drive such steps for subsequent substrate oxidation.

Density functional theory (DFT) calculations with the B3LYP functional were carried out to gain insights into the second electron oxidation process on the Fe^{III} centers and the subsequent substrate oxidation. As shown in Figure 4, two possible transformation pathways were proposed: (a) the metal-oxo pathway with the involvement of a key Fe^{IV}-oxo intermediate (IN-FeO) before the hydrogen atom transfer (HAT) process or (b) the hydroxyl radical pathway with the generation of [•]OH from the oxidation of Fe^{III}-OH intermediate followed by HAT between the highly reactive •OH and the substrate. With the energy input from the oxidant $[Cu(H_2bpydc)(XantP)]^{2+}$, the hydroxyl radical pathway from IN-FeOH to IN-Fe required a ΔG of +39.1 kcal/mol, while the metal—oxo pathway required a much higher ΔG of +78.5 kcal/ mol for the generation of IN-FeO. Although both processes were driven by exothermic HAT between the active intermediates and alcoholic substrates, the hydroxyl radical pathway is favored to occur to form alkoxyl radicals.

Finally, electron paramagnetic resonance (EPR) experiments were conducted to detect the *in situ* generated ROS. The generation of $O_2^{\bullet^-}$ was confirmed by detecting the characteristic EPR signal for the BMPO- $O_2^{\bullet^-}$ adduct when BMPO was added to the suspension of \mathbf{Zr}_6 -Cu-1 in anhydrous MeOH/ toluene in air with irradiation (Figure S25). We also detected the characteristic quartet EPR signal for the BMPO-^oOH adduct at g = 2.006 when Ag⁺ (sacrificial electron acceptor)

and BMPO were added to a suspension of $Zr_6-Cu/Fe-1$ in H_2O /toluene under N_2 and light irradiation (Figure 3d). EPR signals from other BMPO-radical adducts were also evident in the spectrum, which were likely generated from the reactions between highly reactive [•]OH and organic solvents.

Based on these control experiments, computational results, and spectroscopic evidence, we propose a dual Cu–Fe photocatalytic cycle for Zr_6 -Cu/Fe-1 catalyzed aerobic oxidation (Figure 5). Upon photoirradiation, the [Cu¹-PS] in the MOF is first excited to [Cu-PS]*, which is subsequently oxidized by O₂ to generate O₂^{•-} and [Cu^{II}-PS]. The strongly oxidizing [Cu^{II}-PS] efficiently oxidizes [Fe^{III}-OH], which is



Figure 5. Proposed mechanism for photocatalytic aerobic oxidation of alcohols to generate alkoxyl radicals with Zr_6 -Cu/Fe-1.

formed by deprotonation of H_2O on the acidic Fe^{III} center, to generate highly reactive [•]OH. Through HAT, [•]OH rapidly oxidizes the alcohol to generate alkoxyl radical species as the key intermediate, which subsequently transforms into the aldehyde product. In the presence of H_2O , the generated $[Fe^{III}]$ undergoes hydrolysis to afford $[Fe^{III}-OH]$ for the next oxidation cycle. Akin to natural enzymes, the product selectivity of the MOFs is likely controlled by the uniform and small hydrophobic channels, which facilitate substrate and product diffusion and minimize overoxidized products. Similarly, [•]OH can efficiently oxidize alkanes with benzylic C–H bonds to generate benzylic radicals, which are further converted to the corresponding carbonyl products (Figure S26).

CONCLUSIONS

In summary, we hierarchically integrated earth-abundant cuprous photosensitizers and Fe catalysts into two robust MOF catalysts for visible-light-driven aerobic oxidation. Spectroscopic evidence shows that the well-defined Cu-PSs and Fe catalysts in the MOFs are significantly stabilized by site isolation and pore confinement to afford robust and reusable heterogeneous EAM-based photocatalysts. The close proximity between Cu-PSs and Fe catalysts further enhances electron and mass transfer during the photocatalytic process to significantly increase catalytic performance. Under mild reaction conditions and without additives, Zr₆-Cu/Fe-1 displays excellent activity in photocatalytic aerobic oxidation of alcohols and benzylic compounds to corresponding carbonyl products with broad substrate scopes, high TONs, which are nearly an order of magnitude higher than those of their homogeneous counterparts, and excellent recyclability. Benefitting from uniform active centers, a combination of control experiments, spectroscopic evidence, and computational results established the mechanism of the aerobic photo-oxidation process: [Cu^I-PS] is first photoexcited to [Cu-PS]* and then oxidized by O₂ to generate [Cu^{II}-PS]. As a potent oxidant, [Cu^{II}-PS] oxidizes in situ generated Fe^{III}-OH to afford a highly reactive hydroxyl radical, which further oxidizes alcohols and benzylic C-H bonds to corresponding carbonyl products through a radical process. To the best of our knowledge, this work reports the first example of MOF-based dual-EAM catalysts for photocatalytic oxidation processes, thus highlighting the great potential of MOFs in stabilizing EAM complexes for photocatalytic organic synthesis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c05053.

Synthesis and characterization of Zr₆-Cu-1, Zr₆-Cu-2, Zr₆-Cu/Fe-1, and Zr₆-Cu/Fe-2; reaction procedures and supplementary experiment results of photocatalytic aerobic oxidation; and supplementary photophysical and electrochemical data (PDF)

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Notes

The authors declare no competing financial interest.

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