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Photoactive Metal–Organic Frameworks for the Selective Synthesis of Thioethers: Coupled with Phosphine to Modulate Thiyl Radical Generation

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ABSTRACT: Metal–organic framework (MOF) materials are intriguing photocatalysts to trigger radical-mediated chemical transformations. We report herein the synthesis and characterization of a series of isomorphic MOFs which show a novel structure, wide visible-light absorption, high chemical stability, and specific redox potential. The prepared MOFs were explored for the photoinduced single-electron oxidation of thiol compounds, generating reactive thiyl radicals to afford thioethers via a convenient thiol–olefin reaction. Importantly, we provide a widely applicable strategy by combing a photoactive MOF with phosphine to modulate the generation of thiyl radical in the reaction, thereby producing a single product of the thioether without the formation of a disulfide byproduct due to the dimerization of thiyl radicals.



The photocatalytic reaction takes advantage of this strategy, showing great generality where tens of thiols and olefins have been examined as coupling partners. In addition, the strategy has also been demonstrated to be effective for the reactions catalyzed by other MOFs. Mechanism studies reveal that the selective synthesis of C–S products relies on a synergy between the photoinduced generation of a thiyl radical over the MOF and the *in situ* cleavage of S–S bond into a S–H bond by phosphine. It is notable that the synthesized MOFs show advanced performance in comparison with classical MOFs. The work not only provides a series of novel MOF photocatalysts that are capable of photoinduced thiol–olefin coupling but also indicates the great potential of MOFs for photochemical transformations mediated by reactive radicals.

■ INTRODUCTION

One approach toward photoinduced chemical transformations to address energy and environment concerns is the photocatalytic technique, in which the synthesis of the photocatalyst and the exploration of its reactivity have always been at the frontiers of photocatalysis studies.¹⁻⁵ Recently, the use of a metal-organic framework (MOF) as a photocatalyst has attracted much attention in the field of photocatalysis due to the rapid development of coordination chemistry in the past few decades.⁶ The great flexibility of components, structures and properties of a MOF material makes it a designable platform to prepare novel heterogeneous photocatalysts with excellent photophysical properties and desirable catalytic activities. Successful studies have demonstrated that methodologies including linker modification, dye inclusion, and others are feasible to construct visible-light-responsive MOFs, thereby achieving various photocatalytic reactions such as dye degradation, water splitting, carbon dioxide reduction, and organic transformation.⁷⁻¹⁶ Studies reveal that these photocatalytic reactions depend primarily on the ability of an excited MOF to either remove an electron from or donate an electron to a substrate molecule under mild conditions. As a result, highly reactive radical species are typically generated to initiate target reactions. Fox example, the photoinduced electron transfer of an MOF to a ubiquitous oxygen molecule to form a superoxide radical has been widely observed for dye degradation.¹⁷ In addition, the superoxide radical has also been recognized as a reactive intermediate to trigger the photocatalytic oxidation of amines and thioethers to produce valuable imines and sulfoxides, respectively.^{13–15} Despite these successful investigations, important issues such as the activation of diverse substrates by MOFs to generate different reactive radicals and the control of the reaction to afford a single-phase product have still been less addressed.

Among the various candidates that could be activated by photoactive MOFs, the oxidation of a thiol to generate a thiyl radical is of much interest to us, since thiol compounds are

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Article

cheap and easily available. More importantly, thiyl radicals have been demonstrated as versatile intermediates to construct C-S bonds via convenient thiol-olefin reactions that have been widely adopted for the synthesis of natural products, pharmaceuticals, polymers, and bioconjugated materials.¹⁸⁻²³ In addition, thiyl radicals have also been recognized as hydrogen atom transfer (HAT) species to activate carbonhydrogen and heteroatom-hydrogen bonds.²⁴⁻²⁶ Conventionally, the generation of radicals from thiols can be achieved by heating a radical initiator, using strong ultraviolet irradiation, or adding oxidants to the reaction.^{20,21,27} Recent studies showed that thiols could be oxidized expediently by photoactive Ir^{III}(ppy)₃ and Ru(bpz)₃²⁺ to afford thiyl radicals.^{19,28} However, a literature survey suggests that the activation of thiols by a photoactive MOF has been rarely studied so far. We envisaged that the generation of thiyl radicals would be achievable using a MOF photocatalyst, and the MOF-mediated reaction would be useful to prepare functional complexes and materials via convenient thiol-olefin reactions under mild conditions.

We report herein a series of novel MOFs with properties of wide visible-light absorption, high chemical stability, and specific redox potential to activate thiol substrates via a singleelectron-oxidation process, generating reactive thiyl radicals to couple with olefins for the synthesis of thioethers. In addition, we provide a facile and widely applicable strategy by combing a photoactive MOF with organophosphine catalysis to modulate the photogeneration of the thiyl radical in the reaction, thus providing a single thioether product without the formation of a disulfide byproduct due to the rapid dimerization of generated thiyl radicals.

RESULTS AND DISCUSSION

Synthesis, Structures, and Characterizations of MOFs. To achieve visible-light absorption of the prepared MOFs, the conjugated anthracene ligand (4,4'-anthracene-9,10-diylbis(ethyne-2,1-diyl))dibenzoic acid (ADBEB) was synthesized according to previous reports (Figure S1).^{29,30} Then, a series of novel orange lanthanide MOFs were prepared via solvothermal reactions between ADBEB and lanthanide nitrate (Ln = Gd^{3+} , Eu^{3+} , Sm^{3+}) at 120 °C for 2 days (see the Experimental Section). It is expected that the strong coordination interaction between the carboxylate group and the lanthanide ion would be helpful to synthesize MOFs with good stability.³¹⁻³⁴ The crystal structures of the prepared MOFs (1Gd, 1Eu, and 1Sm) were determined by singlecrystal X-ray diffraction. The structure analysis indicates that these compounds crystallize in the monoclinic $P2_1/c$ space group (Table S1), showing an isomorphic framework structure with a general formula of Ln(ADBEB)(DMF)(HCOO). In the structure, the trivalent lanthanide ion coordinates with ADBEB, DMF, and HCOO⁻, in which HCOO⁻ results from the decomposition of the DMF solvent molecule (Figure 1a).^{35,36} Adjacent lanthanide ions in the structure are interconnected via oxygen atoms to form dimers containing Ln–O–Ln bonds (Figure 1a). The Ln–O bond lengths are in the ranges of 2.331(5)-2.622(4) Å for 1Gd, 2.358(7)-2.628(6) Å for 1Eu, and 2.377(5)-2.635(6) Å for 1Sm. These values are in good agreement with those reported for other lanthanide MOFs.^{37,38} As shown in Figure 1b, the coordination between ADBEB and the lanthanide ion constructs the twodimensional MOFs, where the conjugated ADBEB ligands



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Figure 1. (a) Coordination mode of lanthanide ion in the structure. (b) Structure of the MOFs showing a dense stacking between different layers. (c) Single layer in the MOFs in which the coordinated DMF molecules are omitted. Gray, blue, red, and cyanine represent carbon, nitrogen, oxygen, and lanthanide atoms, respectively. All hydrogen atoms are omitted for clarity.

appear in pairs with a face to face distance of 3.64 Å (Figure 1c and Figure S2).

Scanning electron microscopy (SEM) suggests that the prepared MOF compounds are strip-shaped crystals (Figure S3). The microcrystalline samples of these compounds were then studied by powder X-ray diffraction (PXRD). Simulated PXRD patterns of the isostructural Ln-MOFs are almost the same as the experimental patterns. As shown in Figure 2a, the experimental PXRD patterns of the MOFs fit well with those simulated from the crystal structures, suggesting that the prepared samples are in a single phase. In addition, the chemical stability of the prepared MOF was also studied by PXRD (Figure 2b). When the MOF was soaked in different solvents such as methanol, acetonitrile, DMF, chloroform, and dioxane for 1 day, it showed original the PXRD pattern with high intensity, indicating the good chemical stability of the MOF in common organic solvents. FTIR spectra of the MOFs show very similar absorption peaks (Figure S4). The characteristic absorption of the alkynyl group in ADBEB is observed at 2193 cm⁻¹. In addition, the absorption of the phenyl group in ADBEB appears at 861, 787, and 758 cm⁻¹. These peaks indicate the existence of an aromatic ligand in the structure. The vibration peaks of carboxylate groups in the structure are observed at 1568 and 1408 cm^{-1.39} The presence of DMF is confirmed by a series of weak peaks from 3056 to 2846 cm⁻¹ ($\nu_{\rm C-H}$) along with an intense peak at 1625 cm⁻¹ $(\nu_{\rm C=0}).^{40}$

Ultraviolet–visible diffuse reflectance spectroscopy (UV–vis DRS) measurements shows that the synthesized MOF exhibits intense absorption before 520 nm in the visible-light region, followed by weak and broadened absorption extending to 700 nm (Figure 2c). As the optical absorption of lanthanide ions falls usually into the UV region, the visible-light absorption of the MOF should result primarily from the aromatic ADEBE (Figure S1).^{41–43} In comparison with the transition absorption of ADBEB, the optical absorption of the prepared MOF is broadened, due possibly to a ligand to ligand charge transfer interaction.^{44,45} The band gap energies of the MOF were

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Figure 2. (a) Experimental PXRD of the MOFs and the simulated PXRD of 1Gd, which is isostructural with 1Eu and 1Sm. (b) PXRD patterns for 1Gd soaked in organic solvents. (c) UV-vis DRS spectra of the MOFs. (d) Band-gap energy of the MOFs.

estimated to be 2.23 eV for **1Gd**, 2.26 eV for **1Eu**, and 2.24 eV for **1Sm** from Tauc plots (Figure 2d); it is believed that the electronic bands in the MOFs are contributed primarily from the HOMO–LUMO levels of the aromatic ligand.^{46–49}

Photocatalytic Reactions. Visible-light-induced oxidation of thiol and its subsequent coupling with olefin was studied under ambient conditions using 1Gd as a prototype. At first, the coupling between benzyl thiol (1) and styrene (2) in acetonitrile was carried out with a commercially available blue LED (32 W) as the light source (Table S2, entry 1). The reaction at a scale of 0.1 mmol of the olefin gave a 76% yield of the thioether. The formation of the target product suggests the successive oxidation of thiol by excited 1Gd, generating a reactive thiyl radical to initiate a thiol-olefin reaction. However, a GC-MS analysis indicated that the reaction suffers from a certain amount of disulfide byproduct with an S-S bond. The presence of the disulfide byproduct hindered the promotion of the reaction yield and complicated product purification. Solvent optimization was then carried out to diminish the formation of disulfide. As shown in Table S2, the reaction in either polar or nonpolar solvents such as methanol, DMF, acetonitrile, chloroform, dioxane, and their mixture showed a major product of the thioether, accompanied by a certain amount (4-9%) of disulfide. Among these solvents, the reaction in the mixture of DMF/MeCN gave an ideal performance (89% for thioether) in comparison to that carried out in other solvents. Control experiments were carried out in DMF/MeCN as the model condition to study the nature of the reaction. The results show that the reaction is photocatalytic, where 1Gd and visible light are essential in the system (Table 1, entries 2 and 3).

To enhance the selectivity of the reaction to produce a thioether, parameters such as the thiol/olefin ratio and photocatalyst dosage were optimized to avoid the generation of disulfide (Table 1, entries 4-10). Reducing thiol/olefin

 Table 1. Visible-Light-Induced Thiol–Olefin Coupling under Different Conditions^a

SH	+ Contract (10 mol %) MeCN/DMF, N2 blue-LED, 8 h		C S-S
entry	reaction	thioether (%) ^a	disulfide (%) ^a
1	typical	89	4
2	no light	0	0
3	no 1Gd	15	12
4	thiol/olefin (4/1)	92	7
5	thiol/olefin (1/1)	72	2
6	thiol/olefin (1/2)	58	3
7	thiol/olefin (1/4)	50	2
8	1Gd (15 mol %)	95	5
9	1Gd (5 mol %)	79	3
10	1Gd (2.5 mol %)	72	3
11	TEA (1 equiv)	2.5	88
12	KI (1 equiv)	38	23
13	NH ₂ -UiO-66	31	11
14	MIL-101(Fe)	8	92
15	NH ₂ -MIL-101(Fe)	12	87
16	TCEP (1 equiv)	99	0

Reaction conditions: MOF (7.4 mg, 10 mol %), MeCN/DMF (V/V 1/1, 500 μ L), benzyl thiol (24.8 mg, 0.2 mmol), styrene (11.5 μ L, 0.1 mmol), blue LED (32 W), N₂ atmosphere, 8 h. ^{*a*}The yields were determined by GC.

ratio from 4 to 0.25 seems to be effective to decrease the relative content of disulfide from 7% to 2%, whereas the yield of the thioether decreased significantly from 92% to 50% (Table 1, entries 4-7). Similarly, the optimization of photocatalyst dosage exhibits the same trend, where the yield of thioether and disulfide decreased simultaneously when the dosage of 1Gd was lowered gradually (Table 1, entries 8-10). It is well-known that the generation of disulfide in thiol-olefin

Article

Table 2. Scope of Thiols for 1Gd-Mediated Reactions^a



^aReaction conditions: **1Gd** (7.4 mg), MeCN/DMF (V/V 1/1, 500 μ L), thiol (0.2 mmol), styrene (0.1 mmol), TCEP (28.6 mg, 0.1 mmol), blue LED (32 W), N₂ atmosphere, 8 h.

coupling is commonly encountered due to the presence of excessive thiyl radicals in the system,^{20,21} in which the dimerization between thivl radicals occurs rapidly since the reaction exhibits a large rate constant of ca. $10^{9} M^{-1} s^{-1.27,50,51}$ In this context, we attempted to control the photoinduced generation of the thiyl radical by the addition of a hole scavenger such as triethylamine (TEA) or potassium iodide (KI). However, the addition of these chemicals depressed the target reaction (Table 1, entries 11 and 12). The results showed that it is difficult to directly eliminate the formation of the disulfide byproduct via optimization experiments. Thereafter, photoinduced thiol-olefin coupling was studied using other visible-light-responsive MOFs, such as NH2-UiO-66, MIL-101(Fe) and NH₂-MIL-101(Fe) (Table 1, entries 13-15). Under the same conditions as with the 1Gd-mediated reaction, NH_2 -UiO-66 gave a major product of thiother (31%), but this was accompanied by relatively more disulfide (11%). MIL-101(Fe) and NH₂-MIL-101(Fe) produced the major product disulfide (92% and 87%) and minor product thioether (8% and 12%). Further optimization of the thiol/olefin ratio and catalyst dosage in these reactions has been demonstrated to be unable to produce a single product of thioether. These experiments suggest that the heterogeneity of the reaction may be responsible for the generation of disulfide. A comparison between the performance shown by 1Gd and classical MOFs

indicates that the synthesized MOF is more advanced for thioether synthesis via a photoinduced thiol-olefin reaction.

Then, we assorted to promote the reaction by cleaving the disulfide into the starting thiol compound to cause it to be involved in the reaction again. Previous reports have disclosed that organophosphine tris(2-carboxyethyl)phosphine (TCEP) is a promising agent for the rapid and irreversible reduction of disulfides into thiols.⁵² It has been recently adopted for the cleavage of S-S bonds on proteins and peptides.⁵³ However, the use of TCEP to modulate thiol-olefin coupling has rarely been explored. A preliminary study was inspiring as the reaction exhibited an excellent yield of 99% of the thioether upon the addition of TCEP in a molar stoichiometry, without the formation of disulfide (Table 1, entry 16). The role of TCEP in the reaction was then studied by contrasting experiments where dibenzyl disulfide was used as the substrate, instead of benzyl thiol (Table S3). In the absence of TCEP, no thioether formed in the 1Gd-mediated reaction. In contrast, the photocatalytic reaction exhibits a 70% yield of thioether upon the addition of TCEP, due to the in situ cleavage of an S-S bond into an S-H bond. This has been affirmed by the direct observation of the irreversible reduction of dibenzyl disulfide into benzyl thiol (Figure S5).

Under these optimized conditions, the versatility of the **1Gd**-mediated photocatalytic reaction was then explored using a diverse set of reaction partners. As shown in Table 2, a wide

Article

Table 3. Scope of Olefins for 1Gd-Mediated Reactions^a



^aReaction conditions: **1Gd** (7.4 mg), MeCN/DMF (V/V 1/1, 500 μ L), benzyl thiol (0.2 mmol), olefin (0.1 mmol), TCEP (28.6 mg, 0.1 mmol), blue LED (32 W), N₂ atmosphere, 8 h.

range of thiols (8-13) including benzyl thiols, thiophenol, and alkanethiols (14-17) have been demonstrated to be efficient partners to couple with styrene. The reactions of these thiols exhibit excellent isolated yields of 90-96% to produce the corresponding thioethers (8-17). Reactions with secondary and tertiary thiols exhibit moderate yields of 75% and 70% (18, 19), due probably to the steric effect of the thiol. Beyond thiol substrates, a series of olefins were also examined to further highlight the generality of 1Gd-mediated photocatalytic reactions. As shown in Table 3, styrene derivatives with methoxy and halide substituents gave excellent yields of 90-95% (20–23). For the derivatives of p- α -methylstyrene (24, 25), the substrate modified with an electron-donating group showed a much higher yield (91%) in comparison to that with an electron-withdrawing group (58%), suggesting that the electronic effect of the olefin substrate is important for the reaction. Cyclohexene and other substrates with a vinyl group on the terminal position exhibit moderate yields of 56-85% (26 - 31).

It is worth noting that there was no disulfide detected in any of these reactions. Comparative experiments exhibit that the same reaction produced both a thioether and a disulfide if TCEP was absent (Table S4). These studies indicate the combination of **1Gd** and TCEP has wide applicability for the synthesis of a thioether as a single product via a thiol-olefin reaction. Cycling experiments demonstrated that **1Gd** is stable enough to survive five cycles (Figure S6), maintaining its crystal structure and catalytic activity (Figures S7–S9). Moreover, an enlarged model reaction has been performed with a lower photocatalyst loading of 1.9 mol %. As a result, 1.3 g of the thioether was isolated, suggesting that the synthesized MOF is promising for the preparation of the target product in large amounts.

To explore the feasibility of the strategy by combining the photoactive MOF with TCEP, visible-light-induced thiololefin reactions over the MOFs of NH₂-UiO-66, MIL-101(Fe), and NH₂-MIL-101(Fe) were studied in the presence of TCEP. For the reaction of NH₂-UiO-66, the yield of the thioether increased from 31% to 48% upon the addition of equimolar TCEP, accompanied by a decrease in disulfide from 11% to 4% (Table S5). For the reactions of MIL-101(Fe) and NH₂-MIL-101(Fe), they exhibit the same trend to increase the amount of thioether (from 8-12% to 18-25%) when TCEP was introduced (Table S5). These results indicate that the strategy is widely feasible for other heterogeneous photocatalysts to prepare thioethers via thiol-olefin reactions. The same strategy has also been applied for the 1Gd analogues 1Eu and 1Sm. As shown in Table S6, the MOFs exhibited comparable photocatalytic performance when various coupling partners of thiols and olefins were used to prepare thioethers, indicating that these isostructural MOFs are promising photocatalysts to prepare a single thioether in the presence of TCEP. To understand the photocatalytic activity of the synthesized Ln-MOFs, control experiments using lanthanide



Figure 3. (a) Transient photocurrent response under visible light ($420 \le \lambda \le 800$ nm). (b) Mott–Schottky plots at different frequencies. (c) Redox potentials of 1Gd and PhCH₂SH.



Figure 4. (a) EPR trapping of thiyl radical from benzyl thiol. (b) EPR trapping of thiyl radical from disulfide in the presence of TCEP. The simulated $a_{\rm H}$ and $a_{\rm N}$ of values of the thiyl–DMPO adduct are 13.78 and 13.26 G, respectively. (c) Proposed mechanism for TCEP-mediated synthesis of a thioether over the MOF.

nitrates as photocatalysts were conducted under the same conditions (Table S7). The results show that these metal salts are incapable of carrying out the target reaction. In contrast, a photocatalytic reaction using ADBEB as the catalyst shows a moderate yield of 62% (Table S7). Then mixtures of the ligand ADBEB and lanthanide nitrates were tested for the photocatalytic thiol—ene coupling. These reactions showed a 6-10% increase in the yield in comparison with the reaction using solely ADBEB (Table S7). These control experiments suggest the photocatalytic activity of the synthesized MOFs results from the photoactive ligand, and the interaction between ligand and lanthanide ion plays a role in the reaction.

Mechanistic Studies. In addition to the photocatalytic experiments, more physical measurements have been carried out on **1Gd** to understand the photoinduced activation of thiol initiating the thiol-olefin reaction. The transient photocurrent response of the photocatalyst was studied at first under ambient conditions. As shown in Figure 3a, **1Gd** exhibits a

significant and reproducible photocurrent signal, suggesting an efficient photoinduced electron—hole separation upon visiblelight excitation, leading to the subsequent oxidation of thiol on its valence band (VB). To evaluate the redox potential of the synthesized MOF, Mott—Schottky measurements were conducted. Positive slopes of C^2 versus the applied potential were observed at 1500–2500 Hz, indicating a semiconductor-like behavior (Figure 3b).¹³ The conduction band (CB) of **1Gd** is ca. –1.17 V versus the Ag/AgCl electrode. Hence, the valence band (VB) of **1Gd** was estimated to be 1.06 V versus the Ag/AgCl electrode: i.e., 1.26 V versus the normal hydrogen electrode (NHE). This value is much more positive than that of the thiol compound (+0.70 V versus NHE, benzyl thiol),¹⁹ indicating that the excited **1Gd** is thermodynamically feasible to oxidize thiols, generating thiyl radicals (Figure 3c).

To gain a deeper insight into the reaction, the photoinduced generation of the thiyl radical has been studied by electron paramagnetic resonance (EPR). The EPR response of a pubs.acs.org/IC

CONCLUSION

suspension containing benzyl thiol and 1Gd was tested at room temperature, in which the spin-trapping agent 5,5dimethyl-1-pyrroline N-oxide (DMPO) was added to capture the resulting thiyl radicals. As shown in Figure 4a, the suspension shows no EPR response under dark conditions. In contrast, the same suspension exhibits characteristic EPR peaks belonging to a DMPO-thiyl adduct under visible-light irradiation from a xenon lamp.⁵⁴ The measured EPR spectrum fits well with that simulated by SpinFit, and the parameters $a_{\rm H}$ and a_N were calculated to be 13.78 and 13.26 G, respectively. EPR results show clearly the visible-light-induced generation of thiyl radical by 1Gd. In addition, the influence of TCEP on the 1Gd-mediated reaction was also studied by EPR, where dibenzyl disulfide was adopted instead of benzyl thiol. As shown in Figure 4b, the suspension containing 1Gd, disulfide, and DMPO is EPR-silent under visible-light irradiation, suggesting that the photoinduced generation of thiyl radical from disulfide cannot be directly achieved in the absence of TCEP. When TCEP was added to the suspension, significant EPR signals belonging to a DMPO-thiyl adduct were observed, indicating the generation of a thiyl radical from disulfide due to the synergistic effect of photoactive MOF and TCEP.

According to our experimental findings and previous reports, a plausible mechanism for the reaction was then proposed, as shown in Figure 4c. The excited 1Gd oxidizes the thiol compound upon visible-light irradiation, resulting in the generation of reactive thiyl radicals (4). The thiyl radical then attacks the vinyl group on an olefin in anti-Markownikoff fashion to form a transient carbon-centered radical (5). This radical species (5) would then be reduced by 1Gd via a proton-coupled electron transfer (PCET) mechanism to produce a thioether (6) containing a C-S bond.⁵⁵ However, the rapid dimerization of photogenerated thiyl radicals produces an undesirable disulfide (7) with an S-S bond. The addition of organophosphine irreversibly reduces 7 into the starting thiol ,which can be oxidized by 1Gd to regenerate thiyl radicals (4). In this case, the synergy between the photoactive MOF and the organophosphine provides a single product of the thioether in C-S bonding. Alternatively, the alkyl radical (5) could participate in a classical radical chain transfer pathway to produce the thiol-ene product (Figure 4c). This has been confirmed by the measurement of the quantum yield of the reaction (Table S8).^{56–60} The quantum yields under blue-light irradiation were estimated to be 1.13 (450 nm) and 1.46 (475 nm), indicating the existence of the radical chain transfer pathway. In addition, we studied the influence of the light source on the reaction. As shown in Table S8, a model reaction using a blue LED (440-485 nm) with lower powers of 8 and 24 W gave lower yields of 70% and 90%, respectively. The reaction under a green LED (495-530 nm) gave a relatively low yield of 53%. The quantum yield of the reaction under green light at 520 nm was measured to be 0.43. These studies suggest that the photophysical properties of the MOF are vital to control the photocatalytic performance. In addition, it is worth noting that the solvent also plays an important role in the reaction (Table S2). Upon the detection of thiyl radical, it is conjectured that influence of the solvent on the reaction might be attributed to the relative stabilization of the thiyl radical induced by solvents of different nature.^{27,61}

In summary, a series of visible-light-responsive MOFs with novel structure, excellent visible-light absorption, high chemical stability, and specific redox potential have been successfully synthesized. Photocatalytic studies suggest that they are intriguing photocatalysts for the synthesis of thioethers via thiol-olefin reactions. We provide here a facile strategy to promote the reaction by combining a photoactive MOF and organophosphine catalysis, resulting in the generation of a single product of the thioether, without the formation of disulfide byproduct due to the self-coupling of thiyl radicals. By this strategy, tens of thioethers have been synthesized using the synthesized MOF as a photocatalyst. Photocatalytic experiments indicate the strategy is also effective for photoinduced thiol-olefin coupling catalyzed by other MOFs to produce thioether. Mechanism studies reveal that the generation of a single product in C-S bonding depends on the synergy between the photoinduced generation of a thiyl radical by MOFs and the in situ cleavage of an S-S bond into an S-H bond by phosphine to regenerate a thivl radical. The work provides a series of rarely reported MOFs serving as heterogeneous photocatalysts for the photoinduced synthesis of thioethers via thiol-olefin reactions, showing the great potential of photoactive MOFs for radical-mediated transformations.

EXPERIMENTAL SECTION

Synthesis of the MOFs [Ln(ADBEB)(DMF)(HCOO)]. Typically, the MOF was prepared via a solvothermal reaction as follows: a mixture of the organic ligand ADBEB (0.26 mmol, 120 mg), gadolinium nitrate hexahydrate (1.04 mmol, 469 mg), 2-fluorobenzoic acid (10 mmol, 1.4 g), and nitric acid (0.3 M, 3 mL) was stirred in DMF (15 mL) for 10 min. Then the mixture was transferred to a Teflon-lined autoclave and heated to 120 °C for 2 days under autogenous pressure. After the solvothermal reaction, the autoclave was cooled naturally to ambient temperature. The orange crystals of 1Gd were washed with DMF and ethanol and then dried under ambient conditions for further use. The yield of 1Gd is calculated to be 85.8% on the basis of the ligand. 1Eu and 1Sm were prepared by the same solvothermal method, where the lanthanide (Eu/Sm) nitrate hexahydrate was used. The yields for 1Eu and 1Sm were 74.6% and 78.6% on the basis of the ligand, respectively. A structure analysis suggests that they possess isomorphic structures on the basis of the single-crystal X-ray diffraction (SCXRD) data in Table S1. IR (KBr, cm⁻¹): 3056-2846 (m), 2193 (s), 1625 (s), 1568 (s), 1408 (s), 861 (s), 787 (s) and 758 (s). Elemental analysis for the synthesized MOFs is as follows. Anal. Found for [Gd(ADBEB)(DMF)(HCOO)]: C, 58.34%; H, 3.54%; N, 1.93%; Gd, 21.35%. Calcd: C, 58.46%; H, 3.25%; N, 1.89%; Gd, 21.24%. Found for [Eu(ADBEB)(DMF)-(HCOO)]: C, 58.91%; H, 3.82%; N, 2.04%; Eu, 20.05%. Calcd: C, 58.85%; H, 3.27%; N, 1.91%; Eu, 20.68%. Found for [Sm(ADBEB)-(DMF)(HCOO)]: C, 59.10%; H, 3.62%; N, 1.96%; Sm, 19.95%. Calcd: C, 59.02%; H, 3.28%; N, 1.91%; Sm, 20.49%.

Electrochemical Measurements. Photocurrent measurements were performed in a standard three-electrode system with MOF-coated ITO as the working electrode, a Pt plate as the counter electrode, and Ag/AgCl as the reference electrode.¹³ A solution of 0.2 M Na₂SO₄ was used as the electrolyte with nitrogen bubbling for 30 min. A suspension of the MOF was made by adding 40 mg of the MOF and 5 mg of polyvinylidene fluoride (PVDF) to 1.0 mL of ethanol. Then the working electrode was prepared by dropping the suspension (20 μ L) onto the surface of an ITO plate covering approximately 1 cm² and then drying at 85 °C for 2 h. The photocurrent signal of the working electrode was measured under a 300 W Xe lamp, where optical filters were used to remove light of less than 420 nm and greater than 800 nm. Mott–Schottky measurements

were conducted on the basis of the same electrochemical setting. During the test, the frequencies of the impedance were set to be 1500, 2000, and 2500 Hz, respectively.

General Photocatalytic Reactions. Photocatalytic Thiol-Olefin Coupling. Typically, the MOF (7.4 mg, 10.0 μ mol), thiol (0.2 mmol), TCEP (28.6 mg, 0.1 mmol), anhydrous MeCN (99.8%, 250 μ L), and DMF (99.8%, 250 μ L) were mixed under an N₂ atmosphere in a vial (4 mL). Then, the olefin (0.1 mmol) was injected with a syringe. After that, the reaction mixture was irradiated with a 32 W blue LED and fanned to maintain the temperature (ca. 25 °C) for 8 h. Then the filtrate was extracted three times with EtOAc, and the extracts were washed with NaCl aqueous solution. Then the organic phase was dried by anhydrous magnesium sulfate for 30 min, followed by concentration and purification by flash chromatography on silica gel with a hexane/EtOAc mixture to obtain the isolated yield. The structures of the synthesized thioethers were determined by ¹H NMR spectra in reference to structures reported in previous studies.^{19,} To confirm the correctness of the structures, we also measured the ¹³C NMR and HR-MS data for thioethers such as 3, 12, 16, and 17. The data are provided in the Supporting Information, and they confirm the correctness of the molecular structure of the products.

The large-scale photocatalytic reaction was performed as follows: the MOF (105 mg, 0.14 mmol, 1.9 mol %), benzyl thiol (15 mmol), TCEP (429 mg, 1.5 mmol, 0.2 equiv), anhydrous MeCN (99.8%, 18.75 mL), and DMF (99.8%, 18.75 mL) were mixed under an N_2 atmosphere in a round-bottom flask (50 mL). Then, styrene (7.5 mmol) was injected with a syringe. After that, the reaction was irradiated with a 32 W blue LED and fanned to maintain the temperature at about 25 °C for 8 h. The product was purified by flash chromatography on silica gel to isolate the thioether (1.3 g, yield 76%).

Photocatalytic Reaction of Dibenzyl Disulfide with Styrene. The MOF (7.4 mg, 10.0 μ mol), TCEP (28.6 mg, 0.1 mmol), dibenzyl disulfide (24.6 mg, 0.1 mmol), anhydrous MeCN (99.8%, 250 μ L), and DMF (99.8%, 250 μ L) were mixed in a vial (4 mL) under a nitrogen atmosphere. Then styrene (11.5 μ L, 0.1 mmol) was injected with a syringe. The reaction was irradiated with a 32 W blue LED and fanned to maintain the temperature at ca. 25 °C for 8 h. The resulting suspension was filtered using a membrane (22 μ m in diameter) and analyzed by GC.

Electron Paramagnetic Resonance (EPR) Measurements. The EPR response of the reaction solutions was recorded on the a spectrometer (X-band) operated at a frequency of 9.41 GHz at 298 K. General spectrometer parameters are as follows: scan range, 200 G; center field set, 3359.0 G; conversion time, 34.18 ms; sweep time, 35.00023 s; modulation amplitude, 1.0 G; modulation frequency, 100 kHz; receiver gain, 1.00×20 ; microwave power, 19.1 mW.⁵⁴

EPR Detection of Radical Generated from Thiol. An ovendried tube (4 mL) containing MeCN (500 μ L, nitrogen bubbled for 30 min) was equipped with a stirring bar under an N₂ atmosphere. Then benzyl thiol (24.8 mg, 0.2 mmol) and **1Gd** (7.4 mg, 10.0 μ mol) were placed in the tube with stirring in the dark. Before the EPR measurement, 0.2 mmol of DMPO was injected into the system as a trapping agent for thiyl radicals. A small portion of the mixture was taken out quickly using a capillary and placed into a quartz EPR tube (4 mm diameter) for EPR measurement. There was no EPR response. Thereafter, the mixture was irradiated by a 300 W Xe lamp where light of less than 420 nm and greater than 800 nm was removed by an optical filter. An EPR signal for the DMPO–thiyl adduct was observed.

EPR Detection of Radical Generated from Dibenzyl Disulfide. At first, a mixture of **1Gd** (7.4 mg, 10.0 μ mol), dibenzyl disulfide (24.6 mg, 0.1 mmol), and 0.2 mmol of DMPO in N₂-saturared MeCN (500 μ L) was tested under visible-light irradiation. There was no EPR response in this case, indicating that the direct generation of a thiyl radical from disulfide is not achievable in the presence of only **1Gd**. TCEP (28.4 mg, 0.1 mmol) was then added to the system, whereupon an EPR signal for the DMPO-thiyl adduct was detected, indicating the generation of a thiyl radical from disulfide.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00642.

Materials, single-crystal structure analysis, supporting tables and figures, experimental methods, and compound characterization data (PDF)

Accession Codes

CCDC 1963656–1963658 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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