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# Bifunctional Metal–Organic Layer with Organic Dyes and Iron Centers for Synergistic Photoredox Catalysis

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**ABSTRACT:** Here we report the design of a bifunctional metal—organic layer (MOL), **Hf-EY-Fe**, by bridging eosin Y (EY)-capped Hf<sub>6</sub> secondary building units (SBUs) with Fe-TPY (TPY = 4'-(4-carboxyphenyl)[2,2':6',2''-terpyridine]-5,5''-dicarboxylate) ligands. With the organic dye EY as an efficient photosensitizer and TPY-Fe(OTf)<sub>2</sub> as the catalytic center, **Hf-EY-Fe** efficiently catalyzes aminotrifluoromethylation, hydroxytrifluoromethylation, and chlorotrifluoromethylation of alkenes. **Hf-EY-Fe** also catalyzes the synthesis of CF<sub>3</sub>-substituted derivatives of large bioactive molecules such as rotenone, estrone, and adapalene with sizes of up to 2.2 nm. The proximity between EY and iron centers and their site isolation in **Hf-EY-Fe** enhance catalytic activity while inhibiting their mutual deactivation, leading to high turnover numbers of up to 1840 and good recyclability of the MOL catalyst.

Metal-organic frameworks (MOFs) are a class of 3D porous materials built from metal-cluster second building units (SBUs) and bridging ligands.<sup>1–15</sup> The synthetic tunability of both SBUs and bridging ligands has endowed MOFs with interesting properties for many potential applications. For example, the integration of Ir- and Rubased photosensitizers into MOFs has afforded photoactive MOFs for photodynamic therapy, solar energy conversion, and photoredox catalysis (Figure 1a).<sup>16-24</sup> On the other hand, nonmetal photosensitizers have recently received considerable research interest owing to their environmental friendliness and sustainable nature. In particular, organic dyes have been actively explored as promising alternatives to noble-metalbased photosensitizers in photoredox catalysis with relatively low costs, wide availability, and good performance.<sup>25,26</sup> However, organic dyes cannot be readily integrated into MOFs owing to their large steric demands and typically low symmetry. We surmised that organic dyes can be integrated into metal-organic layers to afford novel 2D molecular nanomaterials for photoredox catalysis.

As a monolayered version of MOFs, 2D metal-organic layers (MOLs) are structurally regular, compositionally tunable, and highly stable under catalytic conditions.<sup>27,28</sup> MOLs can also be readily functionalized postsynthetically to afford a new class of highly dispersible 2D molecular materials with free substrate access to active sites.<sup>29-38</sup> The 2D morphology of MOLs can not only facilitate the integration of typically complex organic dyes but also suppress selfdegradation of organic dyes via site-isolation, one of the major challenges in photocatalysis with organic dyes.<sup>39</sup> Herein we report the design of the first bifunctional MOL, Hf-EY-Fe, consisting of eosin Y (EY)-capped Hf<sub>6</sub> SBUs and TPY- $Fe(OTf)_2$  (TPY = 4'-(4-carboxyphenyl)[2,2':6',2''-terpyridine]-5,5''-dicarboxylate) ligands for synergistic photoredox catalysis (Figure 1b). At 0.05-0.1 mol % catalyst loading, Hf-EY-Fe competently catalyzed trifluoromethylative difunctionalization of alkenes with turnover numbers of up to 1840. Hf-



**Figure 1.** (a) Schematic showing the integration of noble metal-based photosensitizers into MOFs for photoinduced transformations. (b) First bifunctional MOL with organic dyes and iron centers for sustainable photoredox catalysis.

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**Figure 2.** Synthesis and characterization of **Hf-EY-Fe**. (a) Synthetic route to **Hf-EY-Fe**. (b) PXRD patterns of **Hf-MOL**, **Hf-EY**, and **Hf-EY-Fe** (freshly prepared or after catalytic reaction) in comparison to the simulated pattern for the  $Hf_6$  MOL. (c, d) UV-vis (c) and fluorescence (d) spectra of EY (black), **Hf-EY** (red), and **Hf-EY-Fe** (blue). (e-h) TEM image (e), HRTEM image (f), AFM topography (g), and height profile (h) of **Hf-EY-Fe**. (i-k) Fe XPS (i), XANES spectra (j), and EXAFS fitting (k) of **Hf-EY-Fe**.

**EY-Fe** was also used for the functionalization of complex bioactive molecules with sizes of 1.4–2.2 nm, demonstrating substrate accessibility and versatility of the MOL catalyst.

Free-standing **Hf-MOL** of the composition  $Hf_6(\mu_3-O)_4(\mu_3-OH)_4(HCO_2)_6(TPY)_2$  was first synthesized via a solvothermal reaction of  $HfCl_4$  and  $H_3TPY$  in *N,N*-dimethylformamide (DMF) at 120 °C using formic acid and water as modulators.<sup>40</sup> The  $Hf_6$ -SBUs in **Hf-MOL** are laterally bridged by TPY ligands and vertically terminated by formate groups to afford an infinite 2D network (Scheme S1). Transmission electron microscopy (TEM, Figures S1a) and atomic force microscopy

(AFM, Figures S1b) imaging proved the monolayer morphology of Hf-MOL with a thickness of  $\sim 1.5$  nm (Figures S1c).

The metathesis reaction between the formate capping groups of **Hf-MOL** and EY afforded **Hf-EY** MOL with EY-capped Hf<sub>6</sub>–SBUs (Figures 2a and S2). The loading of EY was determined to be 10 mol % (relative to Hf<sub>6</sub>–SBU) by UV–vis spectroscopy (Figure S3), leading to a formula of Hf<sub>6</sub>( $\mu_3$ -O)<sub>4</sub>( $\mu_3$ -OH)<sub>4</sub>(HCO<sub>2</sub>)<sub>5.9</sub>(EY)<sub>0.1</sub>(TPY)<sub>2</sub> for **Hf-EY**. The EY loading was increased to 20 mol % in **Hf-EY**(H) when the mixture of EY and **Hf-MOL** was heated at 90 °C for 24 h (Figure S3). Treatment of **Hf-EY** with Fe(OTf)<sub>2</sub> in CH<sub>3</sub>CN at

TEM (Figure 2e) and AFM (Figure 2g) imaging confirmed the monolayer morphology of Hf-EY-Fe with a thickness of ~1.9 nm (Figure 2f). The increased thickness over Hf-MOL is attributed to the coordination of EY to  $Hf_6$ -SBUs (Figure S4). High-resolution TEM (HRTEM) exhibited a 6-fold symmetry (Figure 2f), consistent with the projection of Hf-EY-Fe structure along the vertical direction. Hf-EY-Fe retained the crystallinity of Hf-MOL as evidenced by their similar PXRD patterns (Figure 2b). Hf-EY and Hf-EY-Fe exhibited absorption peaks in their UV-vis spectra similar to those of EY (Figure 2c). The luminescence spectrum of Hf-EY showed an emission peak at ~560 nm similar to that of EY, but this emission peak completely disappeared in Hf-EY-Fe (Figure 2d), due to luminescence quenching of EY by the Fe(OTf)<sub>2</sub> center in Hf-EY-Fe (Figure 3a).

X-ray absorption near edge structure (XANES) analysis indicated the +2 oxidation state of iron in **Hf-EY-Fe** by comparing the energy of its pre-edge peak to that of the  $Fe(OTf)_2$  reference (Figure 2j). The  $Fe^{2+}$  oxidation state was further verified by X-ray photoelectron spectroscopy (XPS). As shown in Figure 2i, the peaks at 709.9 eV ( $2p_{3/2}$ ) and 723.3 eV

![](_page_2_Figure_4.jpeg)

**Figure 3.** (a) Luminescence quenching of **Hf-EY-Fe** with different Fe loadings. (b) Emission spectra of **Hf-EY** after the addition of different amounts of CF<sub>3</sub>SO<sub>2</sub>Cl. Insets show plots of  $I_0/I$  of EY as a function of equivalents of [Fe] compound (a) or CF<sub>3</sub>SO<sub>2</sub>Cl (b). (c) Timedependent yields of **1c** with different catalysts. (d) Yields of **19c** with recovered **Hf-EY-Fe** in five consecutive runs. (e) Proposed reaction mechanism.

 $(2p_{1/2})$  were assignable to the  $Fe^{II}$  species. In addition, the extended X-ray absorption fine structure (EXAFS) feature of iron centers in Hf-EY-Fe was well-fit to the  $(terpy)Fe(OTf)_2$  (terpy = terpyridine) structure with nearly identical coordination geometry (Figures 2k and S6).

In view of the importance of the CF<sub>3</sub> group in smallmolecule drugs,<sup>41-46</sup> we chose trifluoromethylative difunctionalization of alkenes as the model reaction to evaluate the catalytic performance of Hf-EY-Fe. Upon blue LED irradiation at room temperature, Hf-EY-Fe (0.05–0.1 mol % based on EY) competently catalyzed aminotrifluoromethylation, hydroxytrifluoromethylation, and chlorotrifluoromethylation of alkenes with turnover numbers of up to 900, 850, and 1840, respectively. Aryl alkenes bearing electron-withdrawing or electron-donating groups underwent aminotrifluoromethylation reactions with Umemoto's reagent and nitriles smoothly to give corresponding products 1c-8c in good to excellent isolated yields (Tables 1 and S2). The amination resulted from

# Table 1. Hf-EY-Fe-Catalyzed Trifluoromethylative Difunctionalization of Alkenes $^a$

![](_page_2_Figure_11.jpeg)

<sup>*a*</sup>Reactions at 0.1 mmol scale with **Hf-EY-Fe** (0.05–0.1 mol % based on EY) at room temperature, CF<sub>3</sub>-1 = Umemoto's reagent, CF<sub>3</sub>-2 = CF<sub>3</sub>SO<sub>2</sub>Cl. Comparation on TON among MOL catalyst, Ruphotosensitizer<sup>47,48</sup> and (diarylamino)anthracene organic catalyst.<sup>49</sup>

electrophilic attack on nitriles by the in situ generated carbon cation followed by hydrolysis. In the presence of Hf-EY-Fe (0.1 mol % based on EY), aryl alkenes reacted with Umemoto's reagent and water to afford CF<sub>3</sub>-substituted alcohols 9c-14c efficiently (Tables 1 and S2). Furthermore, Hf-EY-Fe efficiently catalyzed the chlorotrifluoromethylation of alkenes by using CF<sub>3</sub>SO<sub>2</sub>Cl as the bifunctional agent (Tables 1 and S2). Corresponding products 15c-17c and 20c were obtained in 70–86% isolated yields. Long-chain alkenes 1-hexadecene and 7-bromo-1-heptene also coupled with  $CF_3SO_2Cl$  to generate **18c** and **19c** in 90 and 95% yields, respectively. The reactions at 1 and 10 mmol scales afforded **19c** in 92 and 90% yields, respectively.

To further illustrate the synthetic utility and versatility of the MOL catalyst, Hf-EY-Fe was used for late-stage functionalization of bioactive molecules (Tables 1 and S2). Nootkatone (an environmentally friendly insecticide) and rotenone (an organic pesticide) underwent chlorotrifluoromethylation efficiently to obtain CF3-functionalized products 21c and 22c in good yields. The vinyl derivatives of large biomolecules including Fmoc-phenylalanine (an essential  $\alpha$ -amino acid), adapalene (an effective antiacne drug), and dehydrocholic acid (a useful hydrocholeretic) also reacted with CF<sub>3</sub>SO<sub>2</sub>Cl to give products 24c-26c in 58-80% isolated yields. In addition, the vinyl derivative of estrone, one of three major endogenous estrogens, was also compatible with the aminotrifluoromethylation reaction to afford CF<sub>3</sub>-substituted product 23c in 56% yield. These products exhibit large sizes ranging from 1.4 to 2.2 nm and cannot readily diffuse through the channels of 3D MOFs (Figure S8). The successful trifluoromethylative difunctionalization of large bioactive molecules supports the freely accessible active sites in the MOL catalyst and its potential applications in drug discovery and synthesis.

Hf-EY-Fe exhibits much higher TON numbers for trifluoromethylative difunctionalization (Table 1) over Ruphotosensitizer<sup>47,48</sup> and (diarylamino)anthracene organic catalyst.<sup>49</sup> In addition, the 0.05-0.1 mol % loading of Hf-**EY-Fe** (based on EY) is much lower than the typical 1-5 mol % loading in homogeneous EY-catalyzed reactions.<sup>50</sup> The low catalyst loading and high TON numbers of Hf-EY-Fe may be attributed to the proximity between EY and [Fe] centers for facile transfer of radical intermediates and their site isolation which prevents the deactivation and poisoning of both EY and [Fe] centers. Hf-EY-Fe was stable under catalytic conditions as evidenced by the maintenance of PXRD patterns in the recoverd MOLs (Figure 2b). Furthermore, Hf-EY-Fe was readily recovered and used in five runs of chlorotrifluoromethylation of 7-bromo-1-heptene without significant decrease in product yields (Figure 3d). Interestingly, the homogeneous control reaction using a combination of EY and  $(terpy)Fe(OTf)_2$  did not afford aminotrifluoromethylation product 1c (Figure 3c), likely due to the low loading (0.1 mol %) of EY and its deactivation by excess (terpy)Fe(OTf)<sub>2</sub>.

We conducted several control experiments to probe the reaction mechanism. The replacement of Hf-EY-Fe by Hf-EY-FeBr<sub>21</sub> or Hf-EY in aminotrifluoromethylation of styrene gave the target product 1c in 15 and 12% yields, respectively, suggesting the crucial role of Fe center in the reaction (Schemes S4 and S5). In the absence of EY, Hf-Fe MOL catalyzed the aminotrifluoromethylation of styrene to afford 1c in <5% yield (Scheme S6). No reaction was observed without light radiation (Scheme S7). These results indicate the photocatalytic nature of the synergistic catalysis. In addition, radical capture by (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) completely shut down the aminotrifluoromethylation reaction, but afforded 1-trifluoromethoxy-2,2,6,6-tetramethylpiperidine quantitatively (Scheme S8). This result suggests the involvement of trifluoromethyl radical in the aminotrifluoromethylation reaction. Furthermore, the visible-light irradiation on/off experiment showed that chlorotrifluoromethylation of 7-bromo-1-heptene was completely stopped when light was turned off and restarted when the light was turned on (Figure S10). The results exclude the radical chain mechanism.

Upon excitation at 400 nm, luminescence quenching of Hf-EY-Fe with different Fe loadings was evaluated, with a  $K_{sv}$ (Fe) of 0.72 for the fitted Stern–Völmer equation (Figures 3a and S9a,b). This result explains the absence of the emission peak in the luminescence spectrum of Hf-EY-Fe but the existence of an emission peak at ~560 nm for Hf-EY (Figure 2d). In addition, the luminescence of Hf-EY was quenched by the added CF<sub>3</sub>-agent or (terpy)Fe(OTf)<sub>2</sub> with  $K_{sv}$ (CF<sub>3</sub>SO<sub>2</sub>Cl) of 0.21 and  $K_{sv}$ [(terpy)]Fe(OTf)<sub>2</sub>] of 0.16, respectively (Figures 3b and S9c–f). The substantially different  $K_{sv}$  values (0.72 vs 0.16) indicate the different electron transfer rates between EY and Fe centers in the MOL and homogeneous systems, which may account for the much enhanced catalytic performance of Hf-EY-Fe (Figure 3c).

On the basis of these experimental results and literature precedents,<sup>51</sup> we propose a possible reaction mechanism as shown in Figure 3e. Single electron transfer from [Fe<sup>II</sup>] to the photoexcited EY in Hf-EY-Fe affords the [Fe<sup>III</sup>] species and the strongly reducing EY radical anion, which reduces the CF<sub>3</sub>agent to deliver open-shell trifluoromethyl radical A and regenerate EY. The EY photosensitizer is excited by blue LED to restart the photocatalytic cycle. The radical addition reaction of A to alkene generates carbon radical B, which is subsequently oxidized by the  $[Fe^{III}]$  center that is only ~1.0 nm away, to give carbon cation C and regenerate the  $[Fe^{II}]$ species to finish the metal catalytic cycle. The reaction of C with nucleophiles delivers the trifluoromethylative difunctionalization product. In this mechanistic scenario, the close proximity of EY and iron sites in Hf-EY-Fe facilitates the electron and radical transfer between the two catalytic centers, thus enhancing the synergistic catalytic performance. The site isolation of synergistic catalytic centers also suppresses the potential mutual deactivation and results in high turnover numbers of up to 1840 and good recyclability (Table 1 and Figure 3d).

In summary, we have designed the first bifunctional MOL, Hf-EY-Fe, containing EY as the non-noble metal photosensitizer and TPY-Fe(OTf)<sub>2</sub> as the metal catalytic center. Hf-EY-Fe effectively catalyzed aminotrifluoromethylation, hydroxytrifluoromethylation and chlorotrifluoromethylation of alkenes with turnover numbers of up to 900, 850, and 1840, respectively. Hf-EY-Fe also competently catalyzed trifluoromethylative difunctionalization of bioactive molecules including nootkatone, rotenone, estrone, Fmoc-phenylalanine, adapalene, and dehydrocholic acid derivatives. The compatibility with large bioactive molecules (up to 2.2 nm) supports the free accessibility of active sites and versatility of the MOL catalyst. MOLs thus provide an excellent 2D molecular material platform to incorporate readily available organic dyes for sustainable photoredox transformations.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c01083.

Synthesis and characterization of Hf-MOL, Hf-EY, and Hf-EY-Fe, synergistically catalytic reactions, and mechanistic study (PDF)

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# **Author Contributions**

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#### Notes

The authors declare no competing financial interest.

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