

# Postsynthetic Oxidation of the Coordination Site in a Heterometallic Metal–Organic Framework: Tuning Catalytic Behaviors

Yi Han,\* Michael A. Sinnwell, Robert G. Surbella, III, Wenjuan Xue, Hongliang Huang, Jian Zheng, Bo Peng, Gaurav Verma, Yang Yang, Lili Liu, Shengqian Ma, and Praveen K. Thallapally\*

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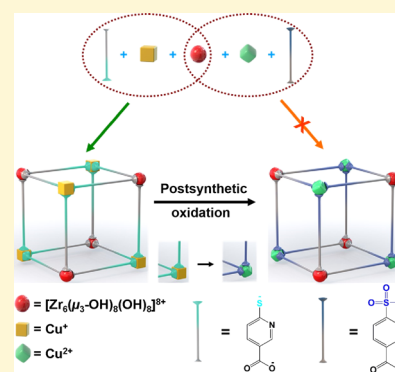
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**ABSTRACT:** Postsynthetic modification (PSM) in metal–organic frameworks (MOFs) can introduce multiple functionalities and alter the structural function for the desired application. However, the PSM of the coordination site faces the challenges of structural collapse or incompatibility between the original metal site and the newly formed coordination group. Herein, we developed a novel concept of introducing “primary” and “secondary” nodes, coexisting in a water-stable, Zr-based heterometallic MOF,  $[\text{Zr}_6(\mu_3\text{-OH})_8(\text{OH})_8][\text{Cu}_4^{\text{I}}(\text{L}_1)_4]_2$  (**1-SH-a**,  $\text{H}_2\text{L}_1 = 6\text{-mercaptopyridine-3-carboxylic acid}$ ). The postsynthetic oxidation at the coordination site was successfully achieved in the secondary nodes  $[\text{Cu}_4^{\text{I}}(\text{L}_1)_4]^{4+}$ , while the robust primary nodes  $[\text{Zr}_6(\mu_3\text{-OH})_8(\text{OH})_8]^{8+}$  stabilized the whole framework to form  $[\text{Zr}_6(\mu_3\text{-OH})_8(\text{OH})_8][(\text{Cu}_{0.44}^{\text{I}}\text{Cu}_{0.56}^{\text{II}}(\text{OH})_{0.56})_4(\text{L}_2)_4]_2$  (**1-SO<sub>3</sub>H**,  $\text{H}_2\text{L}_2 = 6\text{-sulfonicotinic acid}$ ). Attempts to directly synthesize **1-SO<sub>3</sub>H** through the reactions of Zr(IV), Cu(II), and  $\text{H}_2\text{L}_2$  failed. Furthermore, the PSM of **1-SH-a** to form **1-SO<sub>3</sub>H** was utilized to tune the catalytic behaviors toward the styrene oxide ring-opening reaction to give an improved regioselectivity of the primary alcohol (A) of ~99% compared with that of **1-SH-a** (~71%).

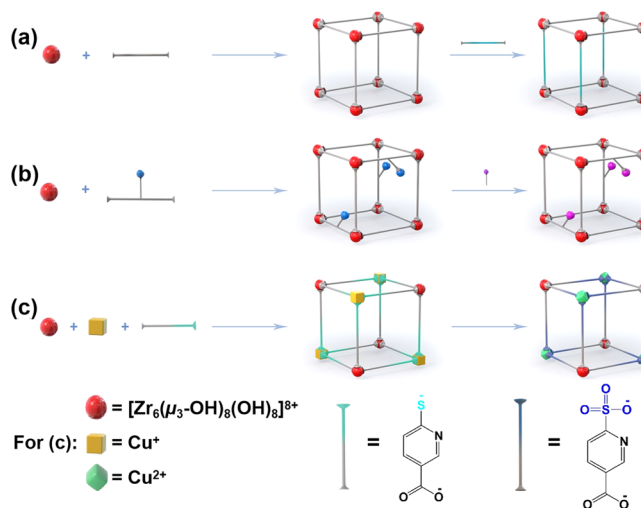


## INTRODUCTION

Postsynthetic modification (PSM) of porous materials such as mesoporous silica and porous carbons has been successfully used to control and analyze their organization and functionalization.<sup>1,2</sup> In the past decades, much interest has been focused on tailoring metal–organic frameworks (MOFs) using PSM.<sup>3,4</sup> PSM has been extensively used and has become a much sought-after method compared to de novo synthesis because PSM offers the ability to (i) facilitate the introduction of a wide variety of chemical functionalities, (ii) maximize the rejection of undesirable byproducts in unpredictable ways, and (iii) endow functions that are thermally labile, which are thwarted almost in solvothermal conditions. Accordingly, MOFs have been vested with significant multifunctionalities, thus adapting the modified functions in response to exploration for the associated applications.

The PSM of MOFs can be broadly divided into three major divisions: unique reactions in terms of (i) metal or linker exchange,<sup>5,6</sup> (ii) covalent modification,<sup>7</sup> and (iii) oxidation/reduction.<sup>8–10</sup> Most of these modifications are carried out on the organic components of the framework. Specifically, linker exchange in readily accessible isorecticular MOF analogues leads to progressively diverse functionalities and properties.<sup>11–15</sup> By contrast, covalent modification allows for chemically modifying the organic struts to either introduce the functionality or functionalize the inherent reactive tags<sup>16–19</sup> (Scheme 1). On the other hand, PSM on the coordination site has not yet been exploited by the MOF

## Scheme 1. Generic Schemes for (a) Linker Exchange, (b) Covalent PSM, and (c) Coordination Site PSM

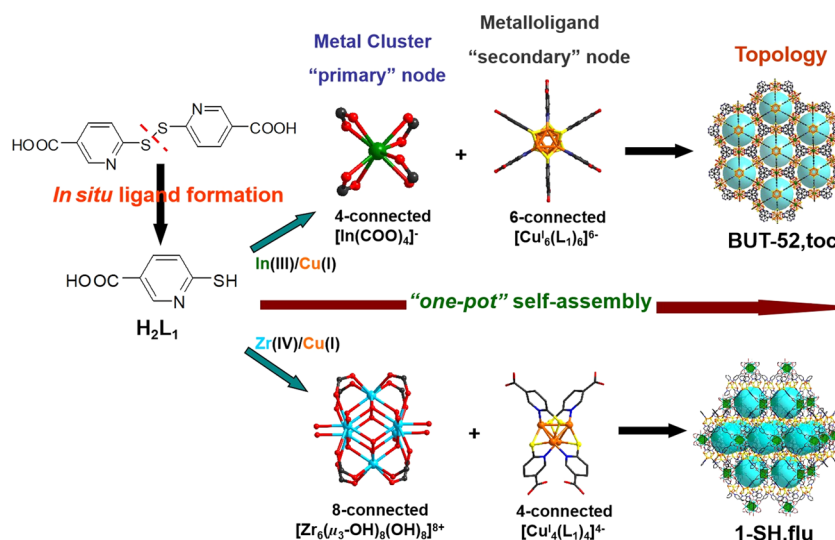


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**Figure 1.** Rational design of BUT-52 and 1-SH on the basis of In(III) or Zr(IV), Cu(I), and the *in situ*-synthesized  $\text{L}_1^{2-}$ .

community, possibly due to the structural collapse under the conditions required or incompatibility between the original metal and the newly formed coordination group.

The coordination ability of thiol and sulfonic groups has been popularized by their extensive use in material science.<sup>20,21</sup> Generally, thiol preferentially coordinates with soft Lewis acids (*i.e.*, Cu(I), Ag(I), Au(III)), while the sulfonic group shows affinity for the harder ones (*i.e.*, Cu(II), Ni(II), Fe(II)). In addition, the vulnerability of thiol compounds to oxidize to the sulfonate derivatives assisted by  $\text{H}_2\text{O}_2$  is well documented even in porous supports, such as thiol-grafted single-walled carbon nanotubes.<sup>22</sup> The unique use in coordination chemistry and the ready conversion toward thiol and sulfonic groups would enable the preparation of a specific thiolated MOF and permit the formation of the isolated sulfonate one employing postsynthetic oxidation.

Herein, we report a water-stable heterometallic Zr-MOF  $[\text{Zr}_6(\mu_3\text{-OH})_8(\text{OH})_8][\text{Cu}_4^+(\text{L}_1)_4]_2 \cdot x\text{guest}$  (**1-SH**,  $\text{H}_2\text{L}_1 = 6$ -mercaptopyridine-3-carboxylic acid), which can undergo a guest-dependent structural transformation to form **1-SH-a**. As expected, in the presence of  $\text{H}_2\text{O}_2$ , the coordination site modification was successfully achieved in **1-SH-a** by the postsynthetic oxidation of  $\text{L}_1^{2-}$  to the corresponding  $\text{L}_2^{2-}$  ( $\text{H}_2\text{L}_2 = 6$ -sulfonicotinic acid) (**Scheme 1c**). The resulting **1-SO<sub>3</sub>H** was determined by powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), and nuclear magnetic resonance ( $^1\text{H}$  NMR). Significantly, the styrene oxide ring-opening reactions catalyzed by **1-SH-a** and **1-SO<sub>3</sub>H** were thoroughly investigated to compare their catalytic behaviors derived from their modified organic fragments and copper species, indicating that the functionalization of **1-SH-a** to form **1-SO<sub>3</sub>H** tuned the catalytic behavior to give an improved regioselectivity of the primary alcohol (A) of  $\sim 99\%$  compared with that of **1-SH-a** ( $\sim 71\%$ ).

## EXPERIMENTAL SECTION

Unless otherwise noted, all starting materials were directly purchased from commercial suppliers and used without further purification. The compounds were purchased as follows:  $\text{ZrCl}_4$  ( $>99.5\%$ , Alfa Aesar), CuI (99.0%, ARCOS), 6,6'-dithiodinicotinic acid ( $\text{H}_2\text{L}$ ) ( $>98.0\%$ , TCI), 6-mercaptopyridine-3-carboxylic acid ( $\text{H}_2\text{L}_1$ ) (90%, Sigma-Aldrich), benzoic acid ( $>99\%$ , TCI), hydrogen peroxide solution ( $\text{H}_2\text{O}_2$ ) (30 wt % in  $\text{H}_2\text{O}$ , ACS reagent, Sigma-Aldrich), *N,N*-

dimethylformamide (DMF) ( $>99.8\%$ , GR ACS), acetonitrile ( $\text{CH}_3\text{CN}$ ) (99.8%, Sigma-Aldrich), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), ( $>99.5\%$ , Alfa Aesar), acetone (99.5%, Fisher), styrene oxide ( $>98\%$ , Alfa Aesar), isopropanol (99.6%, ARCOS), 1-bromo-3,5-difluorobenzene (98%, Alfa Aesar), tetrahydrofuran (THF) (99.9%, Sigma-Aldrich), methanol (95%, Fisher), and ethanol (95%, Fisher). 6-Sulfonicotinic acid ( $\text{H}_2\text{L}_2$ ) was synthesized according to the reported literature.<sup>23</sup>

**Synthesis of 1-SH.** A mixture of  $\text{ZrCl}_4$  (100 mg), CuI (142.5 mg), and  $\text{H}_2\text{L}$  (61.6 mg) in the presence of benzoic acid (2 g) dissolved in *N,N*-dimethylformamide (DMF, 10 mL) and acetonitrile ( $\text{CH}_3\text{CN}$ , 5 mL) in a 20 mL vial was heated at  $120^\circ\text{C}$  for 96 h. Yellow single crystals in a 56% yield (based on  $\text{H}_2\text{L}$ ) were harvested.

**Synthesis of 1-SH-a.** As-synthesized single crystals of **1-SH** were thoroughly washed with fresh DMF and then soaked in acetone for 12 h to produce single crystals of **1-SH-a**. Elemental analysis (EA) (%): calcd for  $\text{C}_{57}\text{H}_{62}\text{Cu}_8\text{N}_8\text{O}_{37}\text{S}_8\text{Zr}_6 = [\text{Zr}_6(\mu_3\text{-OH})_8(\text{OH})_8][\text{Cu}_4^+(\text{L}_1)_4]_2 \cdot 3(\text{C}_3\text{H}_6\text{O}) \cdot 2\text{H}_2\text{O}$ : C, 24.77; H, 2.26; N, 4.06; S, 9.28; found: C, 25.01; H, 1.99; N, 4.02; S, 9.32. The resulting molecular formula was derived from the combination of EA and thermogravimetric analysis (TGA). The solid was continued to soak in acetone for 5 days, during which acetone was decanted, freshly replenished two times, and then dried at  $120^\circ\text{C}$  under vacuum for 12 h to yield the activated sample.

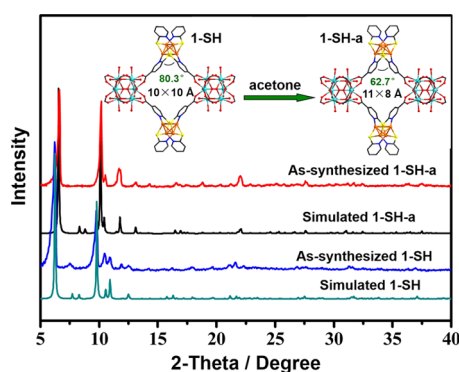
**Synthesis of 1-SO<sub>3</sub>H.** As-synthesized single crystals of **1-SH-a** ( $\sim 30$  mg) were immersed in a mixture of THF (4 mL)/ $\text{H}_2\text{O}_2$  (0.1 mL) for 12 h, during which THF/ $\text{H}_2\text{O}_2$  was decanted and freshly replenished two times. The resulting green crystals were washed with THF and dried in air. EA (%): calcd for  $\text{C}_{63}\text{H}_{74}\text{Cu}_8\text{N}_8\text{O}_{38}\text{S}_8\text{Zr}_6 = [\text{Zr}_6(\mu_3\text{-OH})_8(\text{OH})_8][(\text{Cu}_{0.44}^{\text{I}}\text{Cu}_{0.56}^{\text{II}}(\text{OH})_{0.56})_4(\text{L}_2)_4]_2 \cdot 3(\text{C}_4\text{H}_8\text{O}) \cdot (\text{C}_3\text{H}_6\text{O}) \cdot 2\text{H}_2\text{O}$ : C, 26.42; H, 2.60; N, 3.91; S, 8.96; found: C, 26.22; H, 3.01; N, 3.88; S, 9.10. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) confirmed the ratio of Zr/Cu upon digestion of **1-SO<sub>3</sub>H** in dilute  $\text{H}_2\text{O}/\text{HNO}_3$ , showing that the concentrations of Zr and Cu are 49.8 and 49.6 ppm, respectively, corresponding to the molar ratio of Zr/Cu of  $\sim 0.7$ , which is close to the ratio of Zr/Cu (0.75) in **1-SH**. The activated sample was obtained by soaking in acetone for 5 days and drying at room temperature under vacuum for 24 h.

## RESULTS AND DISCUSSION

Solvothermal reactions of  $\text{ZrCl}_4$ , CuI, 6,6'-dithiodinicotinic acid ( $\text{H}_2\text{L}$ ), and benzoic acid in a mixture of DMF/ $\text{CH}_3\text{CN}$  at  $120^\circ\text{C}$  afforded yellow single crystals of **1-SH**. Single-crystal X-ray diffraction (SCXRD) revealed that **1-SH** crystallizes in the tetragonal space group  $P4_2/mnm$  and has a three-dimensional flu topology, which consists of the 8-connected  $[\text{Zr}_6(\mu_3\text{-$

$(\text{OH})_8(\text{OH})_8]^{8+}$  clusters (denoted as “primary” nodes) linked by tetrahedral  $[\text{Cu}_4^{\text{I}}(\text{L}_1)_4]^{4-}$  metalloligands (denoted as “secondary” nodes). Similar to our previously reported BUT-52,<sup>24</sup> both  $\text{H}_2\text{L}_1$  are originated from the cleavage of the S–S bond during the solvothermal reaction and are allowed to form distinct cuprous sulfur cluster-based heterometallic MOFs (Figure 1). Unlike the 6-connected  $[\text{Cu}_6^{\text{I}}(\text{L}_1)_6]^{6-}$  moiety observed in BUT-52, in **1-SH**, a 4-connected  $[\text{Cu}_4^{\text{I}}(\text{L}_1)_4]^{4-}$  tetrahedron with a  $D_{2d}$  symmetry is achieved (Figure S1). Moreover, an open dodecahedral cage is observed, with dimensions of about  $22.8 \times 22.8 \times 29.3 \text{ \AA}$ , which is constructed by 6  $[\text{Zr}_6(\mu_3\text{-OH})_8(\text{OH})_8]^{8+}$  and 8  $[\text{Cu}_4^{\text{I}}(\text{L}_1)_4]^{4-}$  tetrahedra as vertices and 24  $\text{L}_1^{2-}$  linkers as edges (Figure S2).

An interesting feature in the PXRD pattern of the dried bulk **1-SH** after acetone washing is the peak shift, compared to the calculated pattern from the single-crystal data, inferring a guest-dependent structural transformation (Figure 2). The size

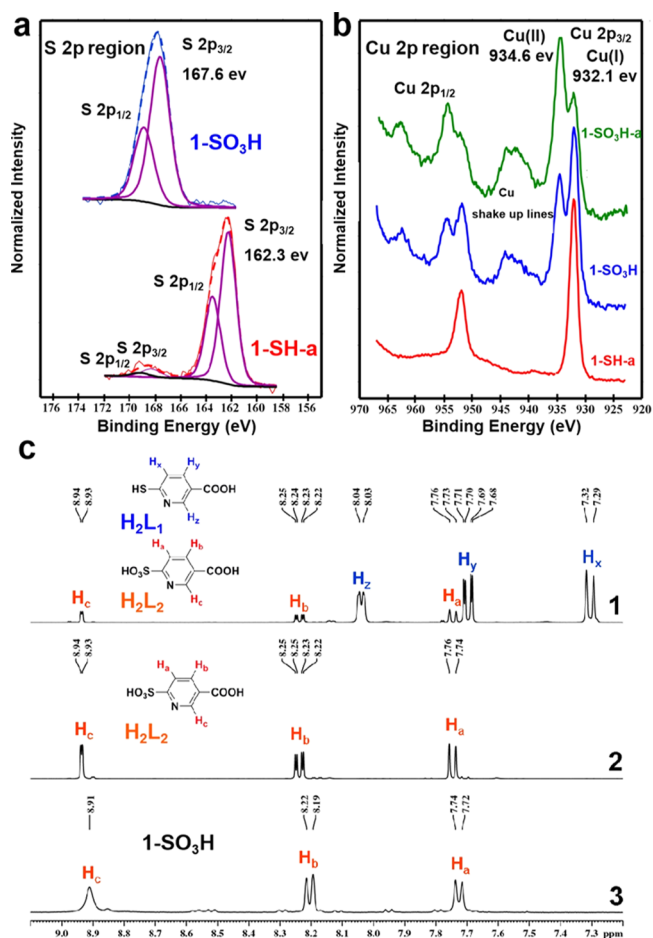


**Figure 2.** Experimental and simulated PXRD patterns of **1-SH** and **1-SH-a**; the inset is the structural transformation from **1-SH** to **1-SH-a**.

and shape of single crystals after acetone treatment remain unaltered, indicative of a single-crystal to single-crystal transformation (Figure S3). This prompted us to obtain the transformed structure (**1-SH-a**) using SCXRD. **1-SH-a** exhibits very similar unit cell parameters (Table S1), but with a shrink angle in the window compared to **1-SH** (Figure 2, inset). Significantly, the calculated PXRD pattern matched well with that of the as-synthesized **1-SH-a**. Unlike the varied flexibility presented by the previously reported Zr-MOFs in response to guest molecules,<sup>25,26</sup> **1-SH** was found to exclusively maintain its contracted conformation upon immersion in different solvents, showing no guest solvent dependence (Figure S4). TGA and PXRD indicated that **1-SH-a** did not decompose until 350 °C in air (Figures S4 and S5). Upon acetone exchange and activation at 120 °C, **1-SH-a** showed no  $\text{N}_2$  uptake at 77 K, which is most likely due to the insufficient activation and pore size selectivity.<sup>27</sup> However, the effective  $\text{CO}_2$  adsorption at 273 K was measured with a maximum capacity of  $40.1 \text{ cm}^3 \text{ g}^{-1}$ , which showed type I adsorption isotherm (Figure S6). The chemical stability of **1-SH-a** was measured by soaking it in water for 12 h, where the crystallinity and porosity were maintained, as evidenced by PXRD and  $\text{CO}_2$  adsorption (Figures S5 and S6). These results demonstrate that the high-connectivity primary ( $\text{Zr}_6$ ) nodes<sup>28</sup> and robust secondary  $\text{Cu}_4\text{S}_4$  nodes ( $\text{p}K_{\text{a}}(\text{Cu}_2\text{S}) = 47.6$ )<sup>29</sup> in **1-SH-a** are responsible for the excellent thermal and chemical stability.

Due to the combination of the exceptional thermal and chemical stability of **1-SH-a** and the nature of vulnerability of thiol compounds to oxidize to the sulfonate derivatives, the

exploration for the postsynthetic oxidation of coordination site seemed to be very promising. Therefore, as-synthesized **1-SH-a** was treated in a mixed solution of THF/ $\text{H}_2\text{O}_2$  ( $v/v = 4/0.1$ ) at room temperature for 12 h to produce **1-SO<sub>3</sub>H** (Figure S7). XPS data showed that the sulfur 2p region of **1-SH-a** exhibited a peak centered at  $\sim 162.3 \text{ eV}$ , which corresponded to a reduced oxidation state of sulfur as in  $\text{L}_1^{2-}$ , while in **1-SO<sub>3</sub>H**, this peak is absent and a new characteristic band at  $\sim 167.6 \text{ eV}$  formed, which is assigned to a higher oxidation state of sulfur ( $\text{L}_2^{2-}$ ) (Figure 3a).<sup>30</sup> Similarly, an intense asymmetrical Cu



**Figure 3.** XPS spectra in the regions of (a) Cu 2p and (b) S 2p for **1-SH-a** and **1-SO<sub>3</sub>H**. (c)  $^1\text{H}$  NMR spectrum of the commercially available  $\text{H}_2\text{L}_1$  (1), as-synthesized  $\text{H}_2\text{L}_2$  (2), and DCl/ $\text{D}_2\text{O}$ -digested **1-SO<sub>3</sub>H** in  $\text{DMSO-}d_6$  solution (3). Note: We found that there is trace  $\text{H}_2\text{L}_2$  in the commercially available  $\text{H}_2\text{L}_1$  from Sigma-Aldrich Co. (purity: 90%).

$2p_{3/2}$  photoelectron peak together with shakeup satellite peaks indicated a mixed-valence state of Cu in green crystals of **1-SO<sub>3</sub>H** (Figure S7), which can be deconvoluted into two contributions located at 932.1 and 934.6 eV, corresponding to Cu(I)  $2p_{3/2}$  and Cu(II)  $2p_{3/2}$ , respectively. Integration of the Cu(I)  $2p_{3/2}$  and Cu(II)  $2p_{3/2}$  peaks with Cu(II) satellite peaks gives a calculated ratio of Cu(II)/Cu(I) of  $\sim 0.56/0.44$  in **1-SO<sub>3</sub>H**. In **1-SH-a**, a strong characteristic band at 932.1 eV is consistent with Cu(I)  $2p_{3/2}$ , indicating that the Cu species possess a 1+ oxidation state (Figure 3b).<sup>31</sup> Further,  $^1\text{H}$  NMR upon digestion of **1-SO<sub>3</sub>H** in dilute DCl/ $\text{D}_2\text{O}$  and  $\text{DMSO-}d_6$  solutions confirmed the degree of conversion by oxidation. The appearance of pure resonances centered at  $\delta$  8.91, 8.21,

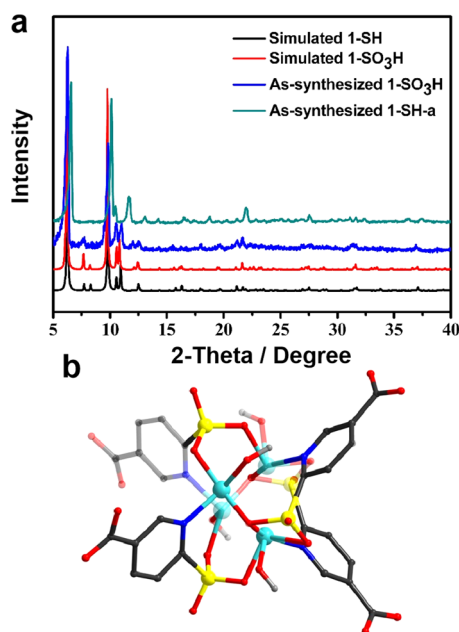
and 7.73 ppm is obvious, corresponding to the different hydrogen signals in  $H_2L_2$  (Figure 3c). The conversion from  $-S^-$  to  $-SO_3^-$  highlights the fact that the oxidation can access both the exterior and the interior of the MOF crystal, contributing to the overall modification of the organic linkers. Fourier transform infrared (FT-IR) spectra also indicated that the characteristic S–O stretches of  $R-SO_3^-$  in  $1-SO_3H$  were evident at 1244 and 1201  $cm^{-1}$ ,<sup>21</sup> which were absent in  $1-SH-a$  (Figure S8). Continuous oxidation of  $1-SO_3H$  for another 12 h can lead to  $1-SO_3H-a$ , with an increased ratio of Cu(II)/Cu(I) ( $\sim 0.78/0.22$ ), however, causing partial structural collapse (Figures 3b and S4). Despite the incomplete conversion of Cu(I), the percent sulfonation of  $1-SH-a$  is 100% during the oxidation, indicating the first example of coordination site modification through PSM in MOF materials. In addition, no obvious reversible process from  $-SO_3^-$  to  $-S^-$  was observed when soaking  $1-SO_3H$  ( $\sim 30$  mg) in a saturated THF/ $H_2O$  (2/2 mL) solution of a reduced agent, such as  $NaNO_2$ , for 10 days (Figure S11). Attempts to directly synthesize  $1-SO_3H$  from the reactions of Zr(IV), Cu(I)/Cu(II), and pure  $H_2L_2$ , however, failed. Furthermore, BUT-52 was also investigated under the same condition for this modification. The PXRD patterns indicated that the material lost crystallinity, albeit the color change from red to green was observed (Figures S4 and S7). Clearly, the access of robust primary nodes seems extremely critical for stabilization of the whole framework, while postsynthetic oxidation can occur in secondary nodes.

PXRD revealed that the pattern of  $1-SO_3H$  was not consistent with that of  $1-SH-a$  but changed to match the PXRD pattern of  $1-SH$  (Figure 4a). The resulting formula of  $[Zr_6(\mu_3-OH)_8(OH)_8][(Cu_{0.44}^{I}Cu_{0.56}^{II}(OH)_{0.56})_4(L_2)_4]_2 \cdot 3 \cdot (C_4H_8O) \cdot (C_3H_6O) \cdot 2H_2O$  ( $1-SO_3H$ ) was defined from the combination of PXRD, XPS,  $^1H$  NMR, IR spectra, ICP-AES, EA, and TGA along with the reasonable deduction of oxidation

states based on  $L_1^{2-}$  and Cu(I) (Section VI, Supporting Information).<sup>32</sup> Although scanning electron microscopy (SEM) confirmed that the shapes of single crystals of  $1-SO_3H$  remain, the structure of  $1-SO_3H$  could not be determined by SCXRD due to the cracking of crystals (Figures S3 and S9), leading to very weak diffraction. Thus, we modeled  $1-SO_3H$  using the framework of  $1-SH$  as a constraint and geometrically optimized the models using periodic density functional theory (DFT) calculations using the CP2K code (Section VII, Supporting Information).<sup>33</sup> The newly formed sulfonate anions coordinate in a bidentate fashion to Cu(II), either in a bridging mode or in chelating and bridging modes to two Cu(II) ions. Cu(II) was then allowed to coordinate to the N atom of a pyridine unit and further coordinated to one  $-OH$  terminal to form 4- or 5-coordinated species (Figure 4b). TGA shows that  $1-SO_3H$  is not thermally stable and the activated sample was achieved by the exchange with acetone and dried at room temperature under vacuum for 24 h (Figure S5).  $1-SO_3H$  exhibits  $CO_2$  adsorption at 273 K with a maximum capacity of 32.0  $cm^3 g^{-1}$  (Figure S6).

Compared with ideal 12-connected Zr-MOFs, such as UiO-type series,<sup>34</sup>  $1-SH-a$  and  $1-SO_3H$  with lower connectivity (8-connected) can be seen with “inherent defects”, and the terminal hydroxide groups (Zr–OH) can be considered as catalytic Brønsted acid sites.<sup>35–39</sup> To test the catalytic activities of  $1-SH-a$  and  $1-SO_3H$ , the ring opening of styrene oxide with a monohydric alcohol (*i.e.*, isopropanol) was selected as a model reaction. This reaction is hardly processed in the absence of a catalyst, due to the poor nucleophilicity of alcohols.<sup>40,41</sup> As shown in Scheme 2a, the reaction was carried out at 55 °C with a 1 mol % MOF catalyst. In accordance with the two possible sites of nucleophilic attack of isopropanol on styrene oxide, two products are possible: the primary alcohol (A) and the secondary alcohol (B). After 8 h, the reactions led to a >90% conversion of styrene oxide, and the final conversion reached  $\sim 100\%$  after 24 h for both catalysts (Scheme 2b and Table S2). PXRD indicated that the crystallinity of both MOFs remained intact after catalysis (Figure S4). Recycling tests with three consecutive runs were performed without any significant loss of their catalytic activities to indicate that the catalysts can be reused (Table S2).

Interestingly, for  $1-SH-a$  tested, both products A and B were achieved with  $\sim 71\%$  of the regioselectivity toward the primary alcohol (A), whereas  $1-SO_3H$  gave a regioselectivity of  $\sim 99\%$  (Scheme 2c, Figures S13 and S14, and Table S2). The regioselectivity of  $1-SH-a$  (71%) and  $1-SO_3H$  (99%) toward the primary alcohol (A) was almost identical throughout the reaction course. This observation can be further rationalized by a first-order parallel reaction model (Section VIII, Supporting Information). From the mechanistic point of view, generally, the ring-opening reaction of epoxides can proceed by either  $S_N1$  or  $S_N2$  mechanisms, depending on the nature of the catalyst and reaction conditions. Accordingly, plausible reaction mechanisms are proposed: (1) When styrene oxide undergoes reaction in the presence of an acidic catalyst, ring opening occurs by an  $S_N1$  mechanism, and the more-substituted carbon is the site of the attack, leading to product A. (2) Conversely, when initiated with a basic catalyst, the reaction takes place by a mechanism with a substantial  $S_N2$  character, and the less-substituted carbon is the site of nucleophilic attack. As a result, product B predominates.<sup>42</sup> As shown in Figure 5,  $1-SH-a$  possesses  $[Zr_6(\mu_3-OH)_8(OH)_8]^{8+}$  ( $Zr_6$  nodes) and cuprous sulfur clusters ( $R-$



**Figure 4.** (a) PXRD patterns of simulated or as-synthesized  $1-SH$ ,  $1-SH-a$ , and  $1-SO_3H$ . (b) DFT-optimized structure of  $1-SO_3H$ . (Only the optimized unit of the  $R-SO_3-Cu^{II}$  is shown; the remaining atoms and hydrogen atoms in  $1-SO_3H$  are omitted for clarity.) C, black; O, red; N, blue; S, yellow; H, gray; and  $Cu^{II}$ , cyan.

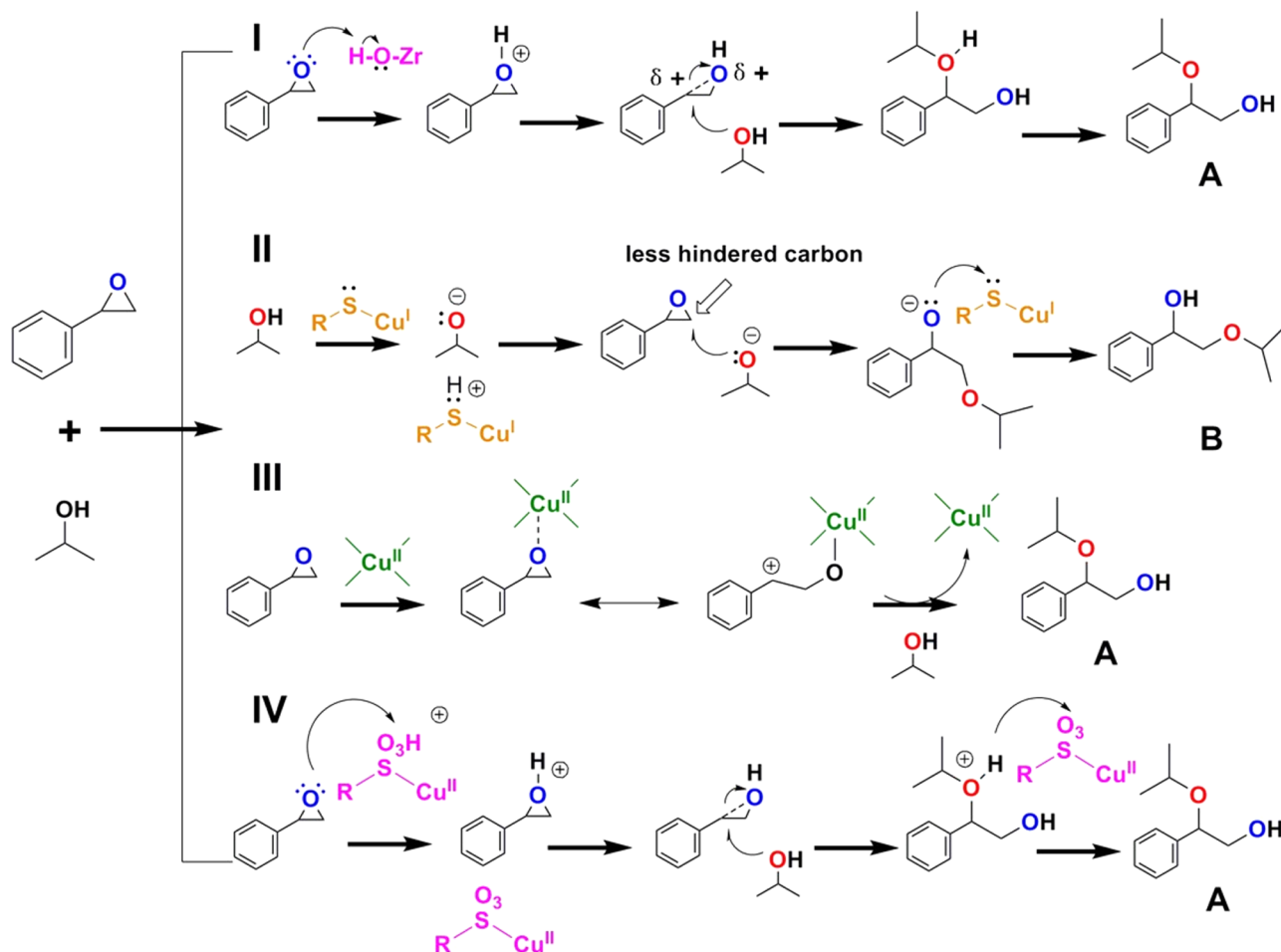
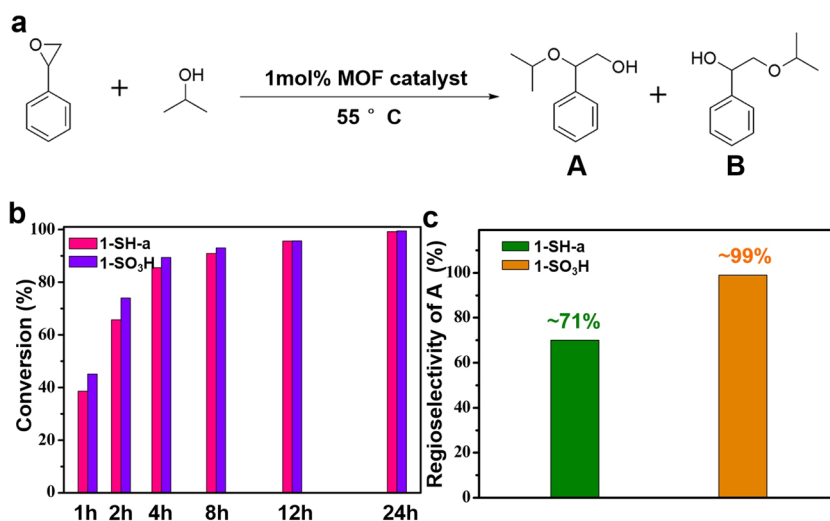
Scheme 2. (a) Styrene Oxide Ring-Opening Reaction with Isopropanol, (b) Conversion, and (c) Regioselectivity of A Catalyzed by 1-SH-a and 1-SO<sub>3</sub>H

Figure 5. Plausible mechanisms for the styrene oxide ring-opening reaction catalyzed by different catalytic sites.

S-Cu<sup>I</sup>), in which there is Zr<sub>6</sub> node-based Brønsted acid available to protonate the oxygen atom in styrene oxide to create a good leaving group, resulting in product A (I). This matched well with the product catalyzed by the previously reported benchmark Zr-MOFs.<sup>40,41</sup> For R-S<sup>-</sup>, divalent organic sulfides are well-known strong Lewis bases and have stronger electron-donating ability. Thus, a deprotonated, negatively

charged alkoxide is preferentially created. An alkoxide is a poor leaving group, making the ring unlikely to open without a “push” from the nucleophile, and the reaction is very likely to proceed by an S<sub>N</sub>2 mechanism (II). Clearly, this illuminates that both products A and B were observed when using Brønsted acid sites and strong Lewis basis dual-functionalized 1-SH-a. After postsynthetic oxidation, 1-SH-a was completely

accessible to form **1-SO<sub>3</sub>H**, with retained Zr<sub>6</sub> nodes and newly formed R-SO<sub>3</sub>-Cu<sub>0.56</sub><sup>II</sup>-OH<sub>0.56</sub> units. Cu(II)-MOFs were found to be effective for the ring-opening reaction of styrene oxide with unsaturated coordinated Cu(II) sites as Lewis acids.<sup>43–45</sup> In this case, three types of plausible mechanisms could probably be adopted simultaneously and give an integrative contribution to the catalytic performance in **1-SO<sub>3</sub>H**. Besides mechanism I, Lewis acidic Cu(II) binds to styrene oxide to produce an enhanced electrophilic nature of the carbon attached to the phenyl group through an acid–base interaction. Subsequently, the carbon with a partial positive charge is attacked by isopropanol to give product A (III). In addition, R-SO<sub>3</sub><sup>-</sup> moieties might be protonated by inherent -OH from Zr-OH or Cu<sup>II</sup>-OH in **1-SO<sub>3</sub>H** and form strong Brønsted acidic R-SO<sub>3</sub>H sites for alcoholysis of epoxides (IV).<sup>46</sup> Nevertheless, only product A is exclusively obtained within the above three proposed mechanisms, which is consistent with the experimental data observed in this work.

## CONCLUSIONS

In conclusion, a water-stable heterometallic Zr-MOF with primary and secondary nodes has been reported, and the guest-dependent structural dynamic was studied by SCXRD. The presence of primary nodes in the framework plays a vital role in the improvement of structural stability. Subsequently, post-synthetic oxidation-induced coordination site modification was successfully observed in secondary nodes. In addition, the catalytic behavior toward the styrene oxide ring-opening reaction after PSM was tuned, and plausible mechanisms were also unambiguously verified. The present work not only demonstrates a suitable MOF model for investigating the coordination site modification but also provides a potential prediction on the unique design of heterogeneous catalysts at the molecular level. Furthermore, postsynthetic oxidation of the coordination site is expected to become a promising strategy for the introduction of multifunctionalities in MOFs for advanced applications.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.0c01267>.

Crystallographic data for **1-SH** and **1-SH-a**; synthesis of MOFs, PXRD, FT-IR, TGA, SEM, <sup>1</sup>H NMR, XPS, and catalysis reaction (PDF)

## AUTHOR INFORMATION

### Corresponding Authors

**Yi Han** – Key Laboratory of Eco-Chemical Engineering, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao, Shandong 266042, P. R. China; [orcid.org/0000-0003-0395-1111](https://orcid.org/0000-0003-0395-1111); Email: [roberthan@yeah.net](mailto:roberthan@yeah.net)

**Praveen K. Thallapally** – Pacific Northwest National Laboratory, Richland, Washington 99352, United States; [orcid.org/0000-0001-7814-4467](https://orcid.org/0000-0001-7814-4467); Email: [praveen.thallapally@pnnl.gov](mailto:praveen.thallapally@pnnl.gov)

### Authors

**Michael A. Sinnwell** – Pacific Northwest National Laboratory, Richland, Washington 99352, United States; [orcid.org/0000-0002-6733-8335](https://orcid.org/0000-0002-6733-8335)

**Robert G. Surbella, III** – Pacific Northwest National Laboratory, Richland, Washington 99352, United States

**Wenjuan Xue** – State Key Laboratory of Separation Membranes and Membrane Processes, Tianjin Polytechnic University, Tianjin 300387, P. R. China

**Hongliang Huang** – State Key Laboratory of Separation Membranes and Membrane Processes, Tianjin Polytechnic University, Tianjin 300387, P. R. China

**Jian Zheng** – Pacific Northwest National Laboratory, Richland, Washington 99352, United States; [orcid.org/0000-0003-2054-9482](https://orcid.org/0000-0003-2054-9482)

**Bo Peng** – Pacific Northwest National Laboratory, Richland, Washington 99352, United States

**Gaurav Verma** – Department of Chemistry, University of South Florida, Tampa, Florida 33620, United States

**Yang Yang** – Pacific Northwest National Laboratory, Richland, Washington 99352, United States

**Lili Liu** – Pacific Northwest National Laboratory, Richland, Washington 99352, United States; [orcid.org/0000-0002-9595-4303](https://orcid.org/0000-0002-9595-4303)

**Shengqian Ma** – Department of Chemistry, University of South Florida, Tampa, Florida 33620, United States; [orcid.org/0000-0002-1897-7069](https://orcid.org/0000-0002-1897-7069)

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.chemmater.0c01267>

## Notes

The authors declare no competing financial interest.

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