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Title

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Journal

Nature Chemistry, 11(2)

ISSN

1755-4330

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Publication Date

2019-02-01

DOI

10.1038/s41557-018-0171-z

Peer reviewed

# 1 Identification of the Strong Brønsted Acid Site in a Metal-Organic 2 Framework Solid Acid Catalyst

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21 **Abstract:** It remains difficult to understand the surface of solid acid catalysts at the molecular  
22 level, despite their importance for industrial catalytic applications. A sulfated zirconium-based  
23 metal-organic framework, MOF-808-SO<sub>4</sub>, has previously been shown to be a strong solid  
24 Brønsted acid material. In this report, we probe the origin of its acidity through an array of  
25 spectroscopic, crystallographic, and computational characterization techniques. The strongest  
26 Brønsted acid site is shown to consist of a specific arrangement of adsorbed water and sulfate  
27 moieties on the zirconium clusters. When a water molecule adsorbs to one zirconium atom, it  
28 participates in a hydrogen bond with a sulfate moiety that is chelated to a neighboring zirconium  
29 atom; this motif in turn results in the presence of a strongly acidic proton. On dehydration, the  
30 material loses its acidity. The hydrated sulfated MOF exhibits good catalytic performance for the  
31 dimerization of isobutene (2-methyl-1-propene), achieving 100% selectivity for C<sub>8</sub> products  
32 with good conversion efficiency.

33  
34 The chemistry at the surface of solid acid catalysts is of vital importance for industrial catalytic  
35 applications, yet a precise molecular picture of these surfaces remains elusive. Attempts to obtain  
36 a clear view of the Brønsted acid sites in solid acids such as sulfated zirconia have resulted in  
37 multiple proposed models, in part due to the difficulty in characterizing the structure of this

38 amorphous material, but also because of wildly variable properties depending on preparation  
39 conditions (1-11). Discerning the molecular structures responsible for the activity of solid acid  
40 catalysts provides a richer perspective on the functional properties and catalytic mechanisms of  
41 these materials, and illuminates the fundamental surface chemistry relating the molecular  
42 structures and their functions. Recently, the synthesis of a metal-organic framework (MOF) solid  
43 acid catalyst was reported, achieved by treating a Zr-based MOF, MOF-808, with sulfuric acid to  
44 yield the solid acid MOF, MOF-808-SO<sub>4</sub>, which was shown to be capable of performing several  
45 acid-catalyzed reactions (12,13). In this report, we conclusively identify the structure of the  
46 strong Brønsted acid site in MOF-808-SO<sub>4</sub>, as being a hydrogen bond pair of two species, water  
47 and chelating sulfate, adsorbed on the surface of its zirconium clusters, where the acidic proton is  
48 arises as a result of the hydrogen bond. We achieve this through a union of crystallographic,  
49 spectroscopic, and computational studies. We also show that MOF-808-SO<sub>4</sub> exhibits good  
50 activity and selectivity for the dimerization of isobutene to isooctene, and that dehydration of the  
51 material significantly reduces the catalytic activity, confirming the role of water as necessary to  
52 the strong acidity of the site.

53

## 54 **Results and Discussion**

55 The preparation of MOF-808-SO<sub>4</sub> was performed by first synthesizing pristine MOF-808  
56 (Fig. 1a), Zr<sub>6</sub>O<sub>5</sub>(OH)<sub>3</sub>(BTC)<sub>2</sub>(HCOO)<sub>5</sub>(OH<sub>2</sub>)<sub>2</sub>, with a subsequent exchange of the formate ions  
57 on the zirconium clusters for sulfate ions simply by washing the MOF in dilute sulfuric acid (12).  
58 The MOF-808 backbone is comprised of an octahedron of zirconium atoms that are triply  
59 bridged by μ<sup>3</sup>-O and μ<sup>3</sup>-OH groups. The formate groups in the pristine structure each bridge two  
60 zirconium atoms to form a six-membered belt around the cluster (13). One cluster is connected to  
61 six other clusters through benzene tricarboxylate (BTC) linkers, three above and three below the  
62 belt of formates, resulting in a framework with spn topology. Once the formate ions are  
63 exchanged for sulfate to yield MOF-808-SO<sub>4</sub> (Fig. 1b), these sulfates may take on multiple  
64 binding modes and can take one of several positions along the belt interspersed between  
65 additional ligated water molecules, resulting in long-range disorder from one cluster to the next.  
66 As this disorder is confined to the surface species on the zirconium clusters, the surface of each  
67 cluster has a slightly different local molecular ‘decoration,’ (Fig. 1c) while the structural  
68 backbone of MOF-808 is still conserved throughout (14-17). Our challenge is to understand the  
69 molecular decoration of the zirconium clusters in MOF-808-SO<sub>4</sub> by first identifying the  
70 structures that decorate the cluster surface, and from there, discerning which arrangement of  
71 decorating structures results in a strong Brønsted acid site.

### 72 **Understanding the molecular decoration of the zirconium clusters**

73 Elucidating the coordination mode of sulfate is essential for discerning the local  
74 structures that exist on the surface of the clusters. From single crystal X-ray diffraction (SXRD)  
75 analysis of a crystal in aqueous solution, the sulfate groups are found to be coordinated in both a  
76 bridging and chelating mode (Supplementary Fig. 1), with the bridging mode dominating in a 4:1  
77 ratio over chelating (Supplementary Section 3). To obtain further insight into what factors  
78 control the coordination mode of these ions, selenated MOF-808 (MOF-808-SeO<sub>4</sub>) was  
79 synthesized in a similar manner to sulfated MOF-808. The MOF-808-SeO<sub>4</sub> framework in  
80 aqueous solution was found to possess only one coordination mode for selenate, where selenate  
81 bridges two zirconium atoms, suggesting that perhaps the increased atomic radius of selenium

82 enforces the bridging coordination mode. However, upon activation of these two MOFs under  
83 dynamic vacuum and heating at 120 °C, both sulfate and selenate were found to have shifted into  
84 the chelating mode exclusively. This was confirmed using Rietveld refinement of the samples  
85 measured by powder X-ray diffraction (PXRD) in an argon atmosphere. The solid acid nature of  
86 MOF-808-SO<sub>4</sub> is only observed following activation at 120 °C, suggesting that the chelating  
87 coordination mode of sulfate is a key contributor to its catalytic activity.

88 Quantifying the average molecular formula for MOF-808-SO<sub>4</sub> constrains further the  
89 possibilities for ligand disorder on the surface of the zirconium clusters. Here, balancing the  
90 charge on the zirconium clusters guides our stoichiometric analysis. Using inductively coupled  
91 plasma-optical emission spectroscopy for elemental analysis, 2.3 sulfur atoms per 6 zirconium  
92 atoms were found, meaning an average of 2.3 sulfate groups per zirconium cluster. Since each  
93 zirconium atom is in the +4 oxidation state, there is an excess of positive charge that is not  
94 properly accounted for within the model so far. To probe this, we turned to powder neutron  
95 diffraction (PND) to obtain more precise information on the occupancies and thermal ellipsoids  
96 of light elements within the framework (Fig. 2a). A sample of MOF-808-SO<sub>4</sub> with deuterated  
97 BTC linker was measured at 10 K and 300 K and refined simultaneously against a structure  
98 model, revealing a 1:1 ratio of  $\mu^3\text{-O}$  to  $\mu^3\text{-OH}$  in both independent crystallographic positions  
99 within two standard deviations (Supplementary Section 2). An excess of  $\mu^3\text{-O}$  is therefore not  
100 what balances the excess positive charge. There is substantially more electron density located  
101 around the position of the oxygen that connects zirconium to sulfur, O6, which is the same  
102 location as coordinated water molecules bound to the cluster in the as-synthesized MOF-808-  
103 SO<sub>4</sub>. It is noteworthy to mention that the sulfate position could not be located by PND due to the  
104 low occupancy and extremely weak neutron scattering factor of sulfur, thus information from  
105 PXRD was used in combination with elemental analysis to confirm its presence in this sample.

106 As the only electron density unaccounted for in this model is located at position O6,  
107 where water is present in the structure prior to activation, we can infer that balance of the excess  
108 positive charge is achieved here by terminal hydroxide, produced by the deprotonation of water  
109 molecules. This assumption is plausible considering terminal water molecules bound to  
110 zirconium hydroxide clusters have been found to be acidic (18, 19). The position thus accounts  
111 for crystallographically superimposed oxygen from sulfate groups, hydroxide and water  
112 molecules that were not removed during the activation process. This overlap excludes the  
113 possibility of determining the precise coordinates of hydroxide, water and sulfate oxygen, but the  
114 total occupancy of these species was refined freely, converging to 78.4 ± 1.1%. This corresponds  
115 to 9.4 oxygen atoms per cluster, out of a possible 12. Since there must be 4.6 oxygen atoms from  
116 2.3 bidentate sulfate groups as found by elemental analysis, and 1.4 hydroxide groups for charge-  
117 balancing, this leaves 3.4 ± 0.1 oxygen atoms unaccounted for, and are assigned to ligated water.  
118 This was confirmed by thermogravimetric analysis - mass spectrometry (TGA-MS) on the  
119 activated sample, which demonstrated the loss of 3.1 water molecules per cluster prior to  
120 structure decomposition (Supplementary Fig. 16). The first water signal observed from the mass  
121 spectrometer peaked at 143 °C, and indicates water is still present following evacuation and  
122 heating. After a small, second water loss event at 236 °C, the structure decomposes at around 350  
123 °C. This trend can be explained by considering that losing neutral, terminal water ligands would  
124 not collapse the structure, but once the framework is completely dehydrated any further mass  
125 loss leads to structure decomposition, as this involves the loss of charged species. Evidence from  
126 elemental analysis, PND, <sup>1</sup>H nuclear magnetic resonance (NMR) of the digested MOF and TGA-



127 MS, lead to the average molecular formula of  
128  $Zr_6O_4(OH)_4(BTC)_2(SO_4)_{2.3}(OH)_{1.4}(OH_2)_{3.1}(DMF)_{0.4}$  for the activated form of MOF-808-SO<sub>4</sub>.

### 129 **Identifying the strong Brønsted acid site**

130 With the average chemical formula now known, the possible species that decorate each  
131 zirconium cluster are constrained, simplifying the task of identifying the Brønsted acid site in  
132 MOF-808-SO<sub>4</sub>. The potential acidic sources are discussed in turn. Firstly, terminal hydroxide  
133 may be eliminated simply because terminal water is present and bound to the cluster in the same  
134 manner as hydroxide, with terminal water being known to be more acidic (17,18). Protons on  
135 sulfate can also be ruled out since the pH of the solution when the MOF is washed with water  
136 following incorporation of sulfate is 3.5, while the  $pK_{a2}$  value of sulfuric acid is 1.92 (20).  
137 Therefore, sulfate must be fully deprotonated at this stage. A direct comparison between  $\mu^3$ -OH  
138 and terminal water is not as straightforward; however, we found that the water molecules bound  
139 to the framework could be successfully removed by holding the temperature at 220 °C overnight  
140 while maintaining crystallinity and porosity. This sample will be hereafter referred to as  
141 dehydrated MOF-808-SO<sub>4</sub>. If the water molecules are indeed the most acidic species present, the  
142 material should lose its strong acid properties upon dehydration.

143 To determine if water molecules are the source of the most acidic protons, we adsorbed  
144 trimethylphosphine oxide (TMPO) into MOF-808-SO<sub>4</sub> as a probe of acidity and performed <sup>31</sup>P  
145 solid state NMR with magic angle spinning (MAS). TMPO interacts with Brønsted and Lewis  
146 acid sites via the lone pairs on its oxygen atom. Strong acid sites polarize the phosphorus-oxygen  
147 bond, resulting in a linear relationship between <sup>31</sup>P chemical shift values of adsorbed TMPO and  
148 the strength of the acid site, where a higher <sup>31</sup>P chemical shift corresponds to a stronger acid site  
149 (21-25). MOF-808-SO<sub>4</sub> with adsorbed TMPO shows a <sup>31</sup>P resonance at 69 ppm associated with a  
150 strongly acidic site (Fig. 2b, i), consistent with what has been previously observed for this  
151 material (12). This resonance at 69 ppm is found to be absent when TMPO is used in dehydrated  
152 MOF-808-SO<sub>4</sub> (Fig. 2b, ii). As the loss of a water molecule is associated with the loss of the  
153 strongest acid site, this result supports the role of terminal water as the strongest Brønsted acid  
154 source.

155 At this point, two key molecular features decorating the zirconium clusters have been  
156 identified as essential to the acidity of MOF-808-SO<sub>4</sub>: the chelating mode of sulfate and terminal  
157 water ligand. In isolation, neither of these two species is sufficient to account for the acidity of  
158 this MOF, therefore its strong Brønsted acidity must arise from a specific arrangement of these  
159 species on the cluster surface. Given the many possible ways to decorate the belt of the cluster  
160 with terminal water, terminal hydroxide, and chelating sulfate, several arrangements were chosen  
161 to be modeled and geometrically optimized using density functional theory (DFT). The formula  
162  $Zr_6O_4(OH)_4(C_2H_3O_2)_6(SO_4)_2(OH)_2(OH_2)_x$  was used as a representation of an average cluster,  
163 where  $x = 2$  or  $3$ . The restrictions on structural arrangement of the cluster included (i) the core  
164  $[Zr_6O_4(OH)_4(C_2H_3O_2)_6]^{6+}$  being fixed, with  $\mu^3$ -O and -OH groups arranged in the commonly  
165 reported alternating arrangement to minimize charge repulsion, (ii) modeling sulfate as chelating  
166 to zirconium as opposed to bridging, (iii) using terminal hydroxide to charge-balance the cluster,  
167 (iv) including two to three water molecules per cluster. Additionally, individual clusters were  
168 modeled by truncating the linker with acetate groups, which assumes the clusters are  
169 electronically decoupled. The most enlightening result obtained from the different modeled  
170 arrangements on the clusters is from the comparison of terminal water in isolation versus  
171 adjacent to a chelating sulfate group. An O-H bond length of 0.98 Å was observed on the

172 terminal water molecules that have no significant interactions with neighboring adsorbed  
173 molecules. However, when the terminal water molecule is adjacent to chelating sulfate, there is a  
174 strong hydrogen bonding interaction, with an O-H bond length ranging from 1.02 – 1.05 Å  
175 depending on the particular cluster modeled, significantly longer than the O-H bond with no  
176 hydrogen bonding. This is accompanied by an O-H...O angle of 163-166° and a short H...O  
177 hydrogen bonding distance of 1.50 – 1.66 Å, indicating that the proton is very weakly bound.  
178 Indeed, the system can be viewed as a protonated conjugate of an adsorbed pair of hydroxide and  
179 sulfate, with the proton sitting between the two groups but localized mostly on the hydroxide.  
180 One example of this site on a modeled cluster is represented in Fig. 3, which was modeled with  
181 overall two water molecules and two chelating sulfate groups located on opposite sides of the  
182 zirconium cluster.

183 The broken symmetry of the water molecule at this proposed acid site implies that the  
184 water participating in a hydrogen bond to chelating sulfate should have distinctly different  
185 spectroscopic signatures for its two proton environments. We will refer to these two sites as H<sub>a</sub>  
186 for the acidic proton on water participating in the hydrogen bond to chelating sulfate, and H<sub>b</sub> for  
187 the other proton pointing into free space. To probe these proton chemical environments directly,  
188 we performed <sup>1</sup>H solid state NMR. Fig. 4a shows the <sup>1</sup>H MAS spectrum of MOF-808-SO<sub>4</sub> at 6  
189 kHz MAS taken before and after dehydration, and their difference. The difference spectrum  
190 shows that two peaks at around 2.5 ppm and 8.1 ppm are lost as a result of dehydration.  
191 Assigning the identity of these resonances is informed by comparing to the DFT-calculated <sup>1</sup>H  
192 NMR chemical shifts of two of the modeled zirconium clusters (Section S7, Tables S4 and S5).  
193 The difference in chemical shift ( $\Delta\delta$ ) between the H<sub>a</sub> and H<sub>b</sub> protons in the acid site is calculated  
194 for two cases to be  $\Delta\delta = 5.1$  ppm and  $\Delta\delta = 9.1$  ppm. Water lacking a strong hydrogen bonding  
195 interaction to chelating sulfate is calculated to have only  $\Delta\delta = 2.0$  ppm between the two protons.  
196 The changes in the spectra in Fig. 4a after dehydration suggest that the two lost resonances  
197 belong to the H<sub>a</sub> and H<sub>b</sub> protons on the water molecule in the acid site with  $\Delta\delta = 5.6$  ppm, where  
198 H<sub>a</sub>, the acidic proton, is the downfield resonance.

199 In order to confirm that these two resonances are the H<sub>a</sub> and H<sub>b</sub> protons belonging to the  
200 same water molecule, a rotor-synchronized double-quantum (DQ) MAS NMR experiment with  
201 the back-to-back (BABA) recoupling sequence was performed. This experiment correlates  
202 proton resonances in the standard, single-quantum (SQ) spectrum by their proximity to one  
203 another through space. A peak in the DQ dimension indicates that a pair of protons is in close  
204 enough proximity to generate a double quantum coherence (26). As the closest pairs of protons  
205 in MOF-808-SO<sub>4</sub> belong to those on  $\mu^1$ -water molecules, we expect these to be the primary  
206 coherences observed. The intensity of these peaks is dependent upon the number of duplicate  
207 pairs exhibiting this coherence, as well as the efficiency at which this coherence is excited, i.e.  
208 the internuclear distance (27). The SQ H<sub>a</sub> and H<sub>b</sub> resonances at 8.7 ppm 2.5 ppm, respectively,  
209 exhibit strong cross peaks at a DQ frequency of 11.2 ppm, indicating their close spatial  
210 proximity and confirming that these two resonances must arise from a single water species (Fig.  
211 4b). The low-intensity cross peaks between 8.7 and 3.1 ppm may arise from a small subset of H<sub>a</sub>  
212 and H<sub>b</sub> protons in acid sites with a slightly different local arrangement of nearest neighbor  $\mu^1$ -OH  
213 and  $\mu^3$ -OH groups. Along the diagonal, a strong autocorrelation DQ peak at around 5.0 ppm is  
214 observed for an SQ resonance at around 2.5 ppm, which arises from pairs of protons belonging to  
215 isolated terminal water at other sites on the zirconium cluster. The chemical environment of the  
216 protons on water molecules not neighboring a chelating sulfate is similar to the chemical  
217 environment of the H<sub>b</sub> proton in the acid site, and accordingly, their chemical shifts should be

218 similar. This is supported by our DFT calculations, where the chemical shifts of protons in these  
219 environments were calculated to be within about  $\pm 1$  ppm of one another. The  $^1\text{H}$  solid state  
220 NMR results reveal a picture consistent with the proposed molecular conformation of the  
221 Brønsted acid site, where water hydrogen-bonded to sulfate has two protons with inequivalent O-  
222 H bond lengths and inequivalent chemical shifts. The subsequent loss of these peaks after  
223 dehydration at 220 °C is correlated with a loss of acidity, resulting in the conclusion that the  
224 strong Brønsted acid site arises from this hydrogen bonding interaction between water and  
225 chelating sulfate.

## 226 **Removal of water at the acid site impacts catalytic performance**

227 These results suggest a structure-property relationship in MOF-808-SO<sub>4</sub>, where water  
228 must be present and adjacent to chelating sulfate to yield strong acidity. We sought to test this  
229 hypothesis by measuring the activity of MOF-808-SO<sub>4</sub> in catalyzing the dimerization of  
230 isobutene (2-methylprop-1-ene), and to see whether removing the water molecule in the active  
231 site by dehydration would affect this activity. The dimerization of isobutene may yield two  
232 products, either 2,4,4-trimethyl-1-pentene or 2,4,4-trimethyl-2-pentene, both referred to as  
233 isooctene (Fig. 5a). The terminal alkene product is prized as a starting material for synthesizing  
234 terminal aldehydes and alcohols, but both alkene products may be hydrogenated to form 2,4,4-  
235 trimethylpentane, known as isooctane, a valuable gasoline octane booster (28-30). In the process  
236 of dimerizing isobutene, higher order alkene oligomer products greater than C8 may form, which  
237 is typically disfavored, as a separation step is required to isolate the C8 species. Selectivity for  
238 C8 products is crucial if isooctane is the desired product (31,32). To that end, MOF-808-SO<sub>4</sub> was  
239 benchmarked against other solid acid catalysts for C8 selectivity and conversion efficiency  
240 (sulfated zirconia, Amberlyst, and H-ZSM-5) using a continuous gas flow setup, with isobutene  
241 diluted in helium and at atmospheric pressure (Supplementary Section 11). The advantage of  
242 using a gas flow setup over a solvent-based process is that it allows for continuous production,  
243 and negates the need to purify isooctene from solvent mixtures. Our benchmark materials were  
244 chosen based on their capacity to operate under these conditions, and their catalytic activities  
245 were evaluated with respect to the mass of the catalyst. MOF-808-SO<sub>4</sub> was found to be active  
246 even at room temperature, with conversion peaking at 160 °C at 21.5%, outperforming  
247 Amberlyst, sulfated zirconia and H-ZSM-5 under these conditions (Fig. 5b). The C8 selectivity  
248 of MOF-808-SO<sub>4</sub> is found to be 100% at 80 °C and lower, yet remains at 92.8% at 160 °C,  
249 similar to sulfated zirconia (Fig. 5c). The C8 product distribution for both MOF-808-SO<sub>4</sub> and  
250 sulfated zirconia runs about 4:1 in favor of the terminal alkene product (Supplementary Figs. 28-  
251 30). H-ZSM-5 and Amberlyst exhibit C8 selectivity under 35% at all temperatures, forming a  
252 mixture of many different higher order oligomers. Though the C8 selectivity and product  
253 distribution for MOF-808-SO<sub>4</sub> and sulfated zirconia are comparable, under longer experiments of  
254 up to 15 days at 80 °C, MOF-808-SO<sub>4</sub> does not lose activity or selectivity, maintaining a  
255 constant 15% conversion while the conversion efficiency of sulfated zirconia drops by around  
256 60% from its starting value of 5.2% (Fig. 5d). MOF-808-SO<sub>4</sub> does begin lose activity at 120 °C  
257 and 160 °C, and at a faster rate with increasing temperature, consistent with the notion that  
258 desorption of water from the zirconium clusters at higher temperatures should affect the  
259 Brønsted acid site. Indeed, when dehydrated MOF-808-SO<sub>4</sub> was tested as a catalyst, the  
260 conversion was found to be 80 % less than that of MOF-808-SO<sub>4</sub> at 80 °C (Fig. 5b). The great  
261 majority of the catalytic activity of the material can thus be attributed to this acid site, where  
262 water is adjacent and hydrogen bonded to chelating sulfate. The C8 selectivity and product

263 distribution for dehydrated MOF-808-SO<sub>4</sub> are almost identical to that of MOF-808-SO<sub>4</sub> and  
264 sulfated zirconia, indicating that this acid site alone is not responsible for the selectivity.

265 We conclude that perturbing the strong Brønsted acid site by removing the water adjacent  
266 to chelating sulfate has a significant negative impact on the catalytic performance of MOF-808-  
267 SO<sub>4</sub>. The remaining activity of the material in the absence of this water molecule suggests that  
268 Lewis acid sites in the material may also contribute to its activity but to a lesser extent, a  
269 possibility supported by the observation of open metal sites in the PND refinement of the  
270 structure (Supplementary Section 2). Regeneration of the catalyst thus only requires replacing  
271 the water molecule adjacent to sulfate, which can be done by repeating the solvent exchange and  
272 activation process. Future work may find a more efficient process whereby the catalyst is  
273 regenerated continuously during operation by the addition of water vapor into the product  
274 stream, maintaining the active site even at higher temperatures.

275 The relative strength of this acid site compared to other acids is of interest, as its structure  
276 may serve as a model for the design of new strong acid sites. While MOF-808-SO<sub>4</sub> has been  
277 previously stated to be superacidic by colorimetric methods (12), these methods can sometimes  
278 prove unreliable for acid sites existing at the interface of the solid and gas phase (33). We can  
279 provide a thermodynamically-based estimate of the acidity of this specific Brønsted acid site  
280 based on a previously calculated relationship between the <sup>31</sup>P chemical shift of adsorbed TMPO  
281 and the deprotonation energy of simulated Brønsted acid sites (20,21). The TMPO resonance at  
282 69 ppm correlated to the acid site in this material corresponds to a deprotonation energy of 1214  
283 kJ/mol. It is generally accepted that a superacid is a medium in which the chemical potential of  
284 the proton is higher than in sulfuric acid (34). The deprotonation energy for gas-phase sulfuric  
285 acid has been experimentally determined to be 1295 kJ/mol (35), which suggests that this  
286 Brønsted site in MOF-808-SO<sub>4</sub> is at the very least comparable to sulfuric acid, and may even be  
287 considered superacidic by this measure. At its core, the structure of this site in MOF-808-SO<sub>4</sub> is  
288 characterized by the pairing of two bases (chelating sulfate and μ<sup>1</sup>-OH) supported on two  
289 neighboring zirconium atoms and sharing a weakly bound proton between them. Thus such a  
290 Brønsted acid site construct may be quite generalizable, as it may be possible to reduce the  
291 deprotonation energy of this proton to yield even stronger acidity by manipulating the identities  
292 of these two bases or of the support atoms.

293  
294 **Data availability.** Synthetic and experimental procedures, as well as crystallographic, spectroscopic  
295 and computational data are provided in the Supplementary Information. All other data are available  
296 from the authors upon reasonable request.

297

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381

## 382 Acknowledgements

383 This work, including synthesis, characterization and crystal structure analysis was funded by  
384 BASF SE (Ludwigshafen, Germany) and the U.S. Department of Defense, Defense Threat  
385 Reduction Agency (HDTRA 1-12-1-0053). Work performed at the Advanced Light Source is

386 supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S.  
387 Department of Energy under Contract No. DE-AC02-05CH11231. A portion of this research  
388 used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated  
389 by the Oak Ridge National Laboratory. NMR work was supported as part of the Center for Gas  
390 Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center funded  
391 by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-  
392 SC0001015. T.O.P. acknowledges funding from the NSF Graduate Research Fellowship  
393 Program. C.Y. acknowledges support from a Hewlett-Packard Stanford Graduate Fellowship.  
394 P.U. acknowledges the German Research Foundation (DFG, PU 286/1-1). M.J.K is grateful for  
395 financial support through the German Research Foundation (DFG, KA 4484/1-1). We  
396 acknowledge Bunyarat Rungtaweivoranit for his assistance with electron microscopy; Simon  
397 Teat and Laura McCormick for the synchrotron X-ray diffraction data acquisition support at  
398 beamline 11.3.1 of the Advanced Light Source, Lawrence Berkeley National Laboratory.

399

#### 400 **Author Contributions**

401 C.T. and T.O.P co-wrote the manuscript. C.T. performed the PND modeling, SXRD and PXRD  
402 experiments. T.O.P. performed the solid state NMR experiments and NMR DFT calculations,  
403 with support and advice from J.R. J.S., Q.L. and J.B. performed the dimerization catalysis  
404 experiments with the support and advice of G.S. C.Y. performed the IR experiments. J.W.  
405 performed the DFT calculations on the cluster models, with support and advice from M.H.G.  
406 A.H. performed the PND experiments. P.U. performed the PXRD Rietveld refinements. M.K.  
407 helped with TGA experiments. J.J. supported and advised the synthesis. O.Y. supervised the  
408 project. All authors reviewed and edited the manuscript and contributed useful discussions.

409

#### 410 **Competing interests**

411 The authors declare no competing interests.

412

413

#### 414 **Additional information**

415 Supplementary information is available in the online version of the paper. Reprints and  
416 permissions information is available online at [www.nature.com/reprints](http://www.nature.com/reprints).

417

418 Correspondence and requests for materials should be addressed to O.Y.

419

420

#### 421 **Figure Captions**

422

423 **Fig. 1. MOF-808, MOF-808-SO<sub>4</sub>, and visualization of differences in molecular ‘decoration.’**  
424 **(a)** Pristine MOF-808 is comprised of 6-connected zirconium-based metal clusters containing  
425 five formate groups and linked by benzenetricarboxylate (BTC) into the depicted spn topology  
426 framework. These formates may be substituted with sulfate anions as in **(b)**, which coordinate in  
427 a bidentate fashion to zirconium, either in chelating mode to a single zirconium atom, or in a  
428 bridging mode to two zirconium atoms. Sulfate is predominantly in the bridging mode in the  
429 solvated MOF, and converts exclusively to the chelating mode following activation by heating  
430 under dynamic vacuum. **(c)** Two representations of modeled zirconium clusters, with BTC-  
431 linkers omitted beyond the coordinating carboxylate group, highlight the differences in

432 molecular ‘decoration’ between clusters in the overall structure. A similar stoichiometry of  
433 hydroxide, water and sulfate groups are present on each cluster, but the local arrangement and  
434 apportionment of these groups differs between each cluster.

435 **Fig. 2. Structural characterization of MOF-808-SO<sub>4</sub> by Rietveld refinement of powder**  
436 **neutron data, and NMR evidence for presence of water being central to the strong acid site.**  
437 **(a)** The data obtained from powder neutron diffraction (red) is compared against the calculated  
438 pattern from the structural model (black), and their difference (blue).  $wRp = 2.91\%$ ,  $R_p = 9.59\%$ .  
439 **(b)** <sup>31</sup>P MAS solid state NMR spectra of trimethylphosphine oxide (TMPO) adsorbed into (i)  
440 MOF-808-SO<sub>4</sub> (blue) and (ii) dehydrated MOF-808-SO<sub>4</sub> (red). The peak at 69 ppm, assigned to  
441 TMPO interacting with the strong Brønsted acid site, is lost upon dehydration. The peak centered  
442 at 42 ppm is due to excess TMPO that is not interacting with acid sites directly. Other peaks in  
443 the spectra belong to TMPO adsorbed at various  $\mu^1$ -OH,  $\mu^3$ -OH, and terminal water sites.

444 **Fig. 3. Depiction of the zirconium cluster and Brønsted acid site in MOF-808-SO<sub>4</sub> as**  
445 **determined by DFT geometry optimization. (a)** the overall cluster, **(b)** a close-up view of the  
446 acid site with relevant bond lengths and angles, with the acidic proton participating in the  
447 hydrogen bond labeled as H<sub>a</sub>, and the other as H<sub>b</sub>. Atoms not directly part of the active site are in  
448 grey, with zirconium in blue, oxygen in red, sulfur in yellow and hydrogen in white.

449 **Fig. 4. Identification of the resonances attributable to adsorbed water using <sup>1</sup>H solid state**  
450 **NMR, comparing MOF-808-SO<sub>4</sub> before and after dehydration. (a)** <sup>1</sup>H MAS spectrum of  
451 MOF-808-SO<sub>4</sub> at 6 kHz MAS (blue), <sup>1</sup>H MAS spectrum of dehydrated MOF-808-SO<sub>4</sub> at 6 kHz  
452 MAS (red), and their difference (black) showing the loss of two prominent peaks assigned as the  
453 two inequivalent protons on a water molecule hydrogen-bonded to sulfate. **(b)** <sup>1</sup>H DQ-MAS  
454 NMR spectrum of MOF-808-SO<sub>4</sub> with SQ and DQ skyline projections (blue). The spectrum was  
455 recorded at 12.5 kHz with two cycles of the BABA recoupling sequence for excitation and  
456 reconversion of DQ coherence. The two peaks that are lost upon dehydration appear at 2.5 and  
457 8.7 ppm and exhibit a DQ coherence at 11.2 ppm, and are assigned as the inequivalent protons  
458 on terminal water hydrogen bonded to chelating sulfate. The prominent peak along the  
459 autocorrelation diagonal at 5 ppm is assigned as terminal water elsewhere on the zirconium  
460 cluster, not adjacent to sulfate.

461  
462  
463 **Fig. 5. Comparison of the catalytic conversion, selectivity, and long-term stability of MOF-**  
464 **808-SO<sub>4</sub> and dehydrated MOF-808-SO<sub>4</sub> against benchmark catalysts. (a)** General reaction  
465 scheme for the dimerization of isobutene (2-methylprop-1-ene) to isooctene (2,4,4-trimethylpent-  
466 1-ene, 2,4,4-trimethylpent-2-ene). **(b)** Plot of the percent conversion of isobutene to isooctene for  
467 MOF-808-SO<sub>4</sub> (blue), dehydrated MOF-808-SO<sub>4</sub> (red), sulfated zirconia (green), Amberlyst  
468 (orange) and H-ZSM-5 (pink) from room temperature up to 200 °C. Amberlyst is the most active  
469 at low temperatures while MOF-808-SO<sub>4</sub> has a strong temperature dependence. Dehydrated  
470 MOF-808-SO<sub>4</sub> has significantly lower conversion efficiency, indicating that the presence of  
471 water adjacent to chelating sulfate is responsible for the majority of the activity. **(c)** Plot of the  
472 selectivity for dimer products over higher order oligomers. Both Amberlyst and H-ZSM-5 have  
473 poor selectivity, favoring higher order oligomers at all temperatures. MOF-808-SO<sub>4</sub>, dehydrated  
474 MOF-808-SO<sub>4</sub>, and sulfated zirconia have nearly 100% selectivity for dimer products up to 80  
475 °C **(d)** Plot of the long-term catalytic performance of MOF-808-SO<sub>4</sub> for the dimerization of



476 isobutene at 80 °C (blue), 120 °C (violet) and 160 °C (dark red), against sulfated zirconia (green)  
477 at 80 °C. The conversion efficiency for MOF-808-SO<sub>4</sub> is maintained at 80 °C, but at higher  
478 temperatures the material loses activity with an increasing rate, likely due to desorption of  
479 terminal water from the clusters at these temperatures. Sulfated zirconia at 80 °C has  
480 approximately one third of the activity of MOF-808-SO<sub>4</sub> at 80 °C, but falls to about half this  
481 value by 240 hours, while MOF-808-SO<sub>4</sub> maintains its conversion level throughout this period.

Table of contents graphic:

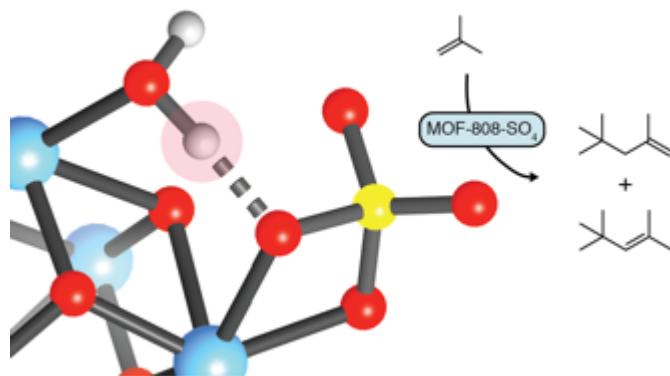


Figure 1:

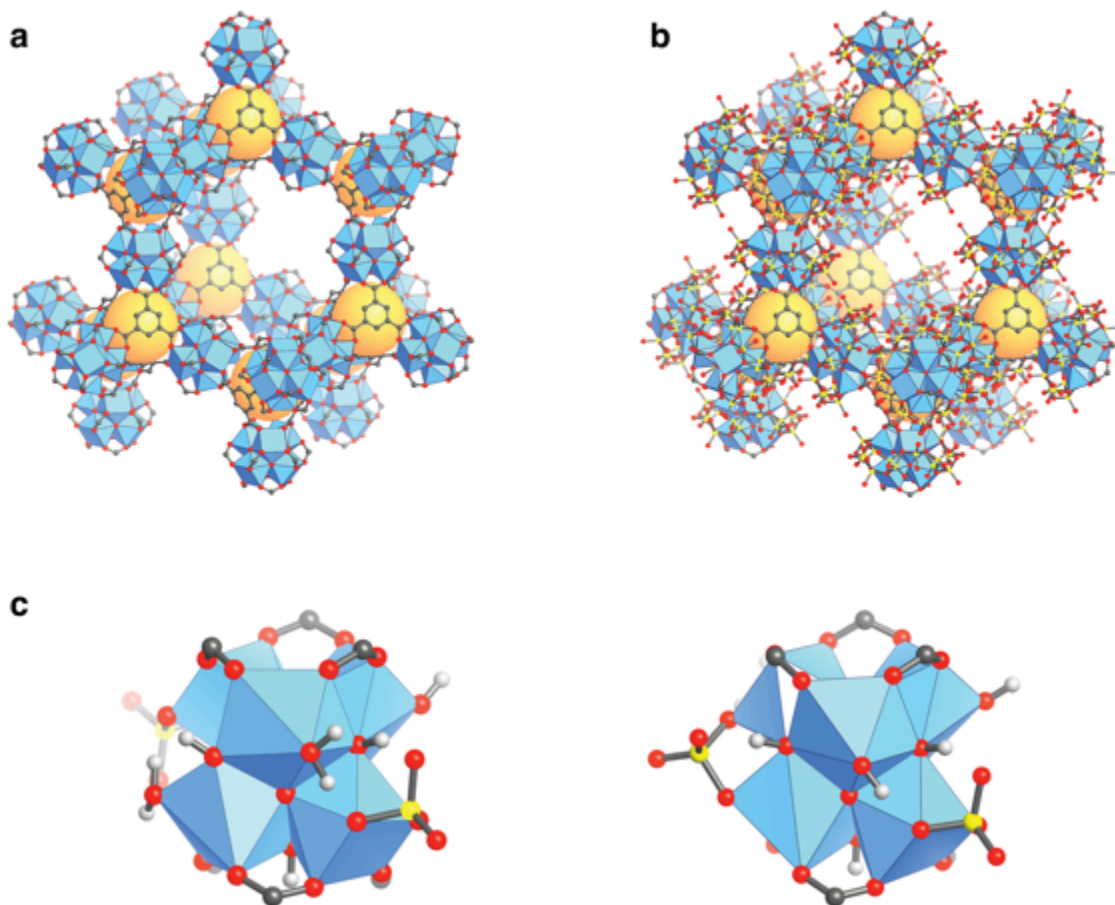


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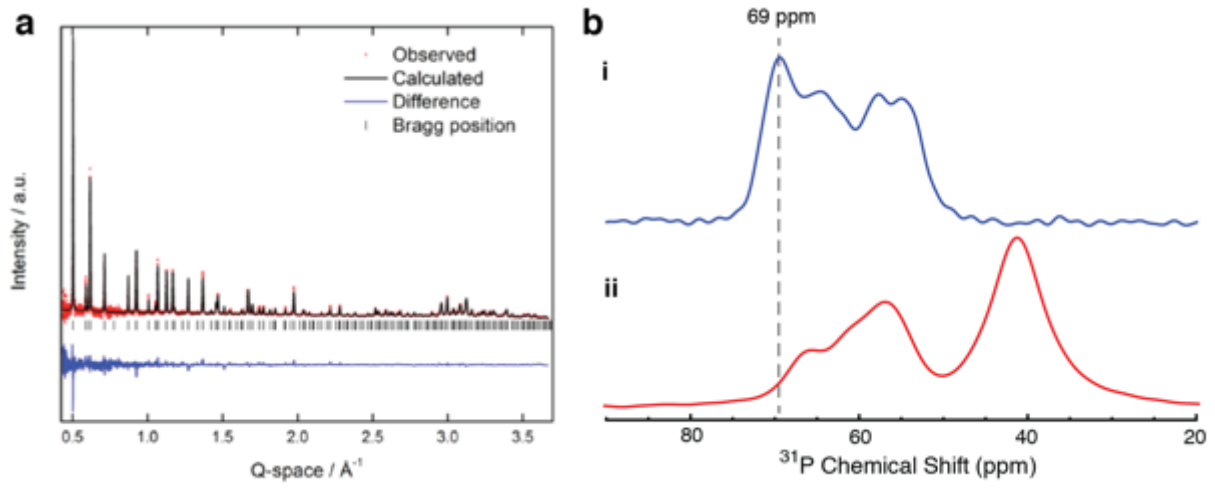


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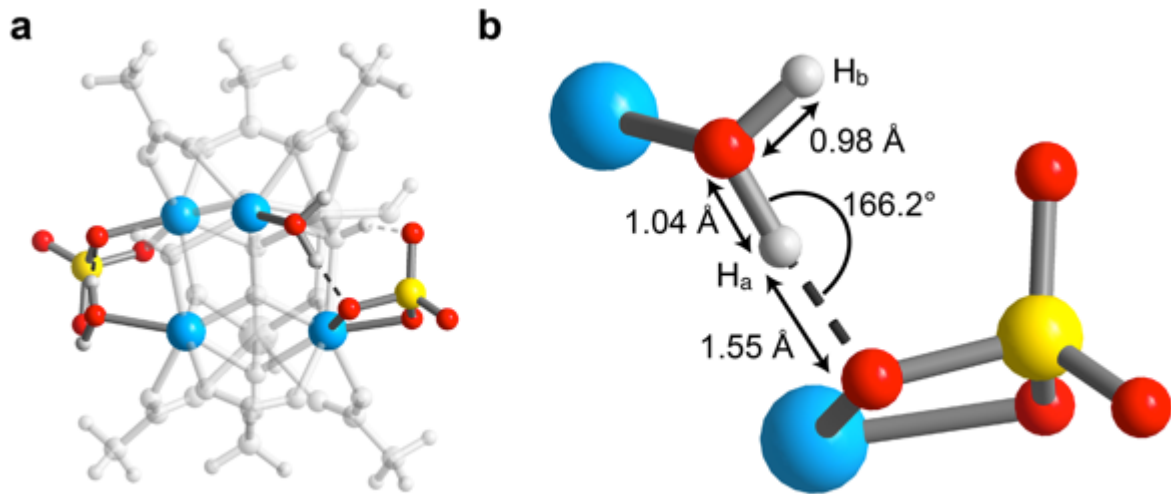


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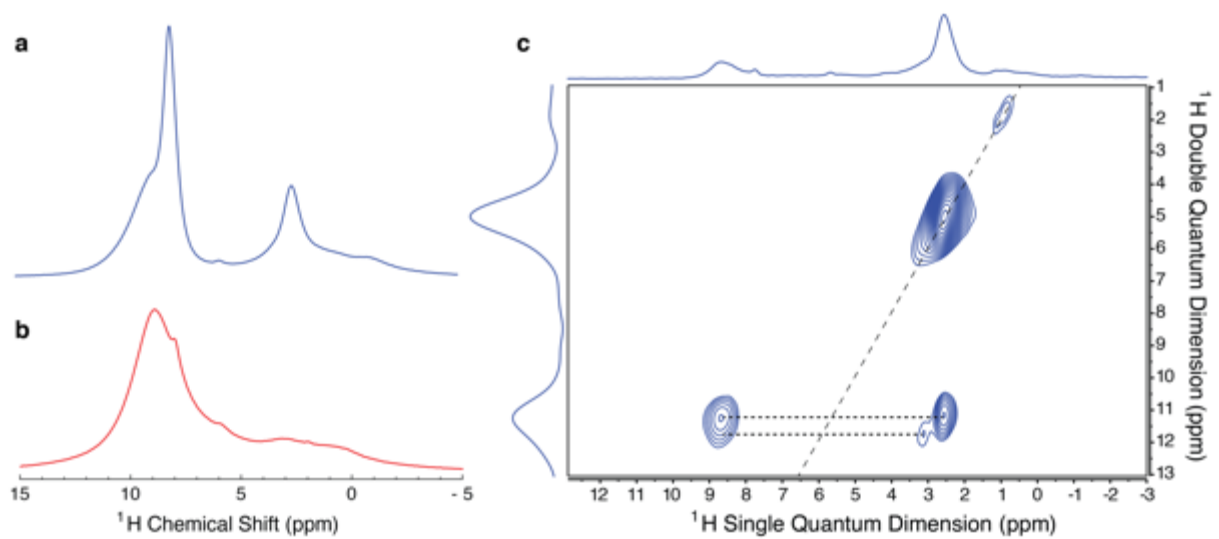
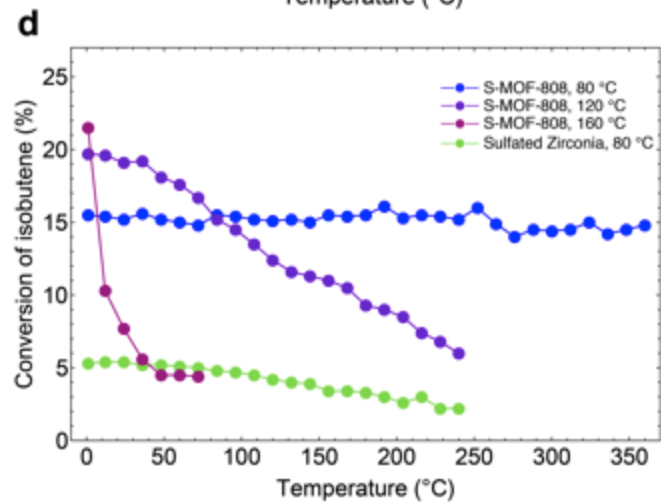
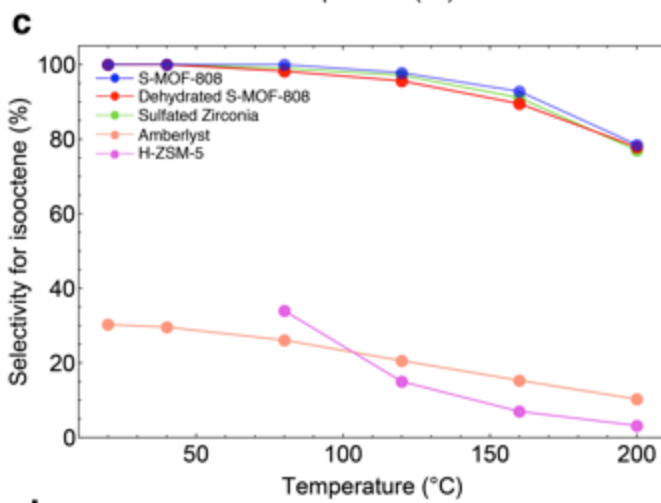
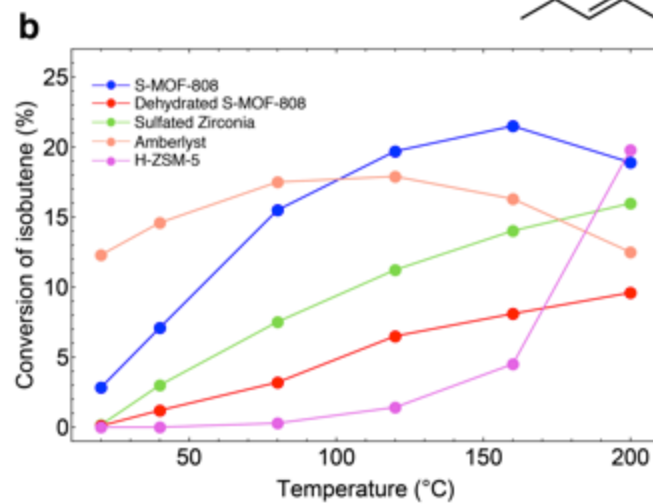
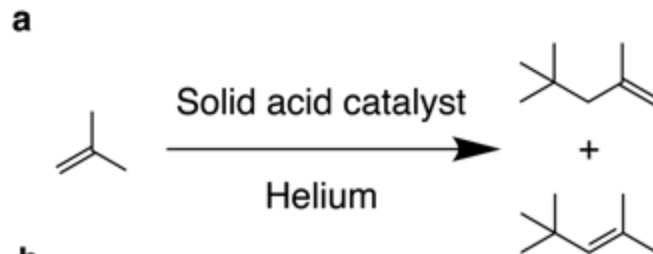


Figure 5:



# Supplementary Information

## Identification of the Strong Brønsted Acid Site in a Metal-Organic Framework Solid Acid Catalyst

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## Section 1: Syntheses of Materials

### Methods.

**Chemicals used in this work.** *N,N*-dimethylformamide (DMF) was obtained from Fisher Scientific. Formic acid (purity > 98%) and anhydrous chloroform were obtained from EMD Millipore Chemicals. Anhydrous acetone was obtained from Acros Organics. Zirconium oxychloride octahydrate (>99.5%), hydrofluoric acid (aqueous, 48%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, purity ≥ 95%), 1,3,5-benzenetricarboxylic acid (H<sub>3</sub>BTC), selenic acid (aqueous, 40%) deuterated sulfuric acid (D<sub>2</sub>SO<sub>4</sub>, 96-98%, 99.5 atom % D) and D<sub>2</sub>O (99.9 atom % D) was obtained from Aldrich. Deuterated 1,3,5-benzenetricarboxylic acid (D<sub>3</sub>DBTC, 97%, 98 atom % D) was obtained from CDN Isotopes. Trimethylphosphine oxide (TMPO) was obtained from Alfa Aesar. Ammonium hydroxide (28%) was obtained from EMD Millipore. All starting materials and solvents, unless otherwise specified, were used without further purification.

**Analytical techniques.** Single-crystal x-ray diffraction (SXRD) data were collected on beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Lab. Samples were mounted on MiTeGen® kapton loops and placed in a 100(2) K nitrogen cold stream provided by an Oxford Cryostream 700 Plus low temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with a PHOTON100 CMOS detector operating in shutterless mode. Diffraction data were collected using synchrotron radiation monochromated using a silicon (111) reflection to a wavelength of 0.7749(1) Å. An approximate full-sphere of data was collected using a combination of phi and omega scans with scan speeds of 2 seconds per 4 degrees for the phi fast scans, and 5 and 15 seconds per degree for the omega scans at 2θ = 0 and -45, respectively. In all cases, the data were processed using the Bruker APEX2 software package (1, 2), structures were solved by intrinsic phasing (SHELXT) and refined by full-matrix least squares on F<sup>2</sup> (SHELXL-2014) using the Olex2 software package (3). All non-hydrogen atoms were refined anisotropically unless otherwise specified. Hydrogen atoms were geometrically calculated and refined as riding atoms. See Section 3 for more details.

Powder x-ray diffraction patterns (PXRD) were recorded using a Bruker D8 Advance diffractometer (Göbel-mirror monochromated Cu K<sub>α</sub> radiation λ= 1.54056 Å). Elemental microanalyses (EA) for carbon, hydrogen, nitrogen and sulfur were performed in the Microanalytical Laboratory of the College of Chemistry at UC Berkeley, using a Perkin Elmer 2400 Series II CHNS elemental analyzer. Solution <sup>1</sup>H NMR spectra were acquired on a Bruker AVB-400 NMR spectrometer. N<sub>2</sub> sorption isotherms were measured on a Quantachrome Quadrasorb instrument, held at 77 K using a liquid nitrogen bath. Helium was used for the estimation of dead space for gas adsorption measurements. Ultra-high purity grade N<sub>2</sub> and He were used throughout the adsorption experiments.

Powder neutron diffraction data (PND) were collected at POWGEN at Oak Ridge National Laboratory, Tennessee. Two diffraction patterns were collected for each sample using center wavelengths 1.066 Å and 4.797 Å covering a d-spacing range of 0.5-15 Å.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed on a PerkinElmer Optical Emission Spectrometer Optima 7000DV instrument. Scanning electron microscope (SEM) images were obtained using a Zeiss Gemini Ultra-55 analytical scanning electron microscope. FTIR spectra were collected in-house using a Bruker ALPHA Platinum ATR-FTIR Spectrometer equipped with a single reflection diamond ATR module.

**General procedure for sample preparation.** To reduce nucleation in the growth of MOF single-crystals, the inner surface of glass containers were rinsed with Sigmacote® siliconizing reagent, washed three times with acetone, and dried in oven before use. Following synthesis, the MOFs were washed with DMF. The molecular formulae of the MOFs were determined using a combination of elemental analysis (C, H, N and S), <sup>1</sup>H NMR (ratio of linker to formate) and ICP-OES (Zr, Se), and TGA-MS. A mixture of containing 20 μL of DMSO-*d*<sub>6</sub> and 580 μL of hydrofluoric acid (48 wt% in water) was used to digest 10 mg of each MOF for NMR measurements.

79 **Native MOF-808 synthesis.** Single crystals of MOF-808 was prepared following the reported  
80 procedure (4). Briefly,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (0.032 g, 0.10 mmol) and  $\text{H}_2\text{BTC}$  (0.022 g, 0.10 mmol) were  
81 dissolved separately in 2 ml DMF, then both solutions were combined in a 20 ml scintillation vial and 4  
82 ml formic acid was added. This mixture was then placed in a pre-heated oven at 100 °C for three days.  
83 Colorless block crystals were collected in 81% yield based on Zr. As-synthesized MOF-808 single  
84 crystals were immersed in anhydrous DMF for three days followed by water for three days, during which  
85 time the solvent was exchanged three times per day. The same conditions were used for the preparation of  
86 deuterated MOF-808, except deuterated  $\text{D}_2\text{BTC}$  was used as the starting reagent, and washing was  
87 performed in  $\text{D}_2\text{O}$  instead of  $\text{H}_2\text{O}$ .

88 **Preparation of Sulfated MOF-808.** Approximately 50 mg of MOF-808 was immersed in 0.05  
89 M sulfuric acid in  $\text{H}_2\text{O}$  for 24 hours and stirred at regular intervals. The treated solid was then washed  
90 with  $\text{H}_2\text{O}$ , then solvent exchanged by immersion in anhydrous acetone before exchanging into chloroform.  
91 For each step, the samples were washed for three days with the solvent being decanted and freshly  
92 replenished three times per day. The chloroform in the solvent-exchanged crystals was removed under  
93 dynamic vacuum (30 mTorr) for 24 h at room temperature, followed by 8 h at 80 °C and a further 16 h at  
94 120 °C. The same conditions were used for the preparation of deuterated sulfated MOF-808, except  
95 deuterated deuterated sulfuric acid in  $\text{D}_2\text{O}$  was used, and all aqueous washings were carried out with  $\text{D}_2\text{O}$ .

96  $^1\text{H}$  solution NMR spectra of the digested, activated and sulfated MOF-808 (400 MHz,  $\text{DMSO-}$   
97  $d_6$ ): 8.61 (s, BTC), 8.10 (s, HCOOH), 7.92 (s, DMF), peak area ratio (BTC:HCOOH:DMF) =  
98 6.0:0.05:0.3. Anal calcd for  $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{C}_6\text{H}_3\text{O}_6)_2(\text{SO}_3)_{2.3}(\text{OH})_{1.4}(\text{OH}_2)_{3.1}(\text{C}_3\text{H}_7\text{NO})_{0.4} = \text{Zr}_6\text{O}_{34.1}\text{C}_{19.2}\text{H}_{20.4}\text{S}_{2.3}\text{N}_{0.4}$ ;  
99 C = 16.2%; H, 1.4%; N, 0.4%; S, 5.2%. Found: C = 17.2%; H, 1.3%; N, 0.6%; S, 5.4%.

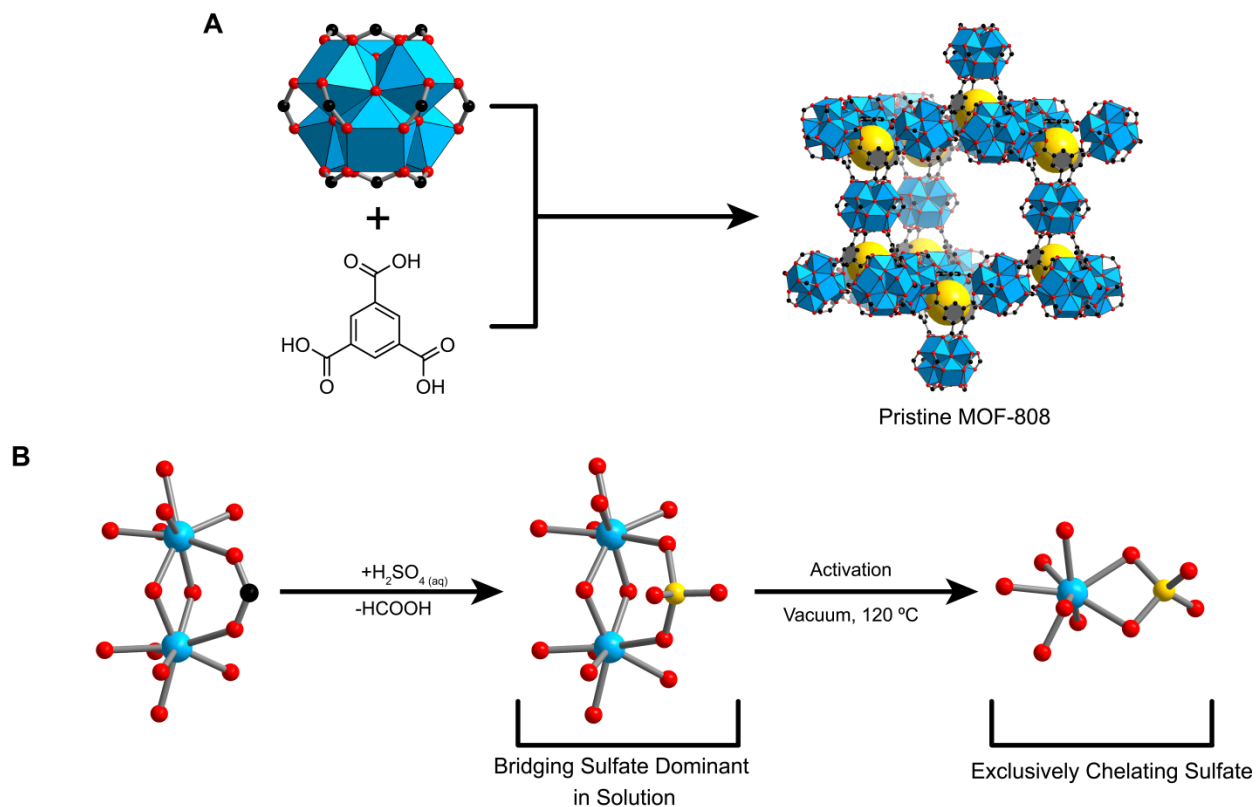
100 **Preparation of Selenated MOF-808.** Approximately 50 mg of MOF-808 was immersed in 0.05  
101 M selenic acid in  $\text{H}_2\text{O}$  for 24 hours and stirred at regular intervals. The treated solid was then washed with  
102  $\text{H}_2\text{O}$ , then solvent exchanged by immersion in anhydrous acetone before exchanging into chloroform. For  
103 each step, the samples were washed for three days with the solvent being decanted and freshly  
104 replenished three times per day. The chloroform in the solvent-exchanged crystals was removed under  
105 dynamic vacuum (30 mTorr) for 24 h at room temperature, followed by 8 h at 80 °C and a further 16 h at  
106 120 °C.

107  $^1\text{H}$  solution NMR spectra of the digested, activated and selenated MOF-808 (400 MHz,  $\text{DMSO-}$   
108  $d_6$ ): 8.64 (s, BTC), 7.85 (s, DMF), peak area ratio (BTC:HCOOH:DMF) = 6.00:0.00:0.5. Calculated  
109 formula  $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{C}_6\text{H}_3\text{O}_6)_2(\text{SeO}_4)_{2.3}(\text{OH})_{1.4}(\text{C}_3\text{H}_7\text{NO})_{0.5}(\text{H}_2\text{O})_{2.9} = \text{Zr}_6\text{O}_{34}\text{C}_{19.5}\text{H}_{20.7}\text{N}_{0.5}\text{Se}_{2.3}$ ; C, 15.3%; H, 1.4%; N,  
110 0.5%. Found: C, 15.4%; H, 0.9%; N, 0.7%.

111 **Preparation of sulfated zirconia.** The synthesis of sulfated zirconia was performed following a  
112 literature report of conventional sulfated zirconia with an additional step to prepare  $\text{Zr}(\text{OH})_4$  from  
113  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ .(5) Briefly, 1g  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was placed in 10 mL  $\text{NH}_4\text{OH}$  (28%) and stirred overnight at  
114 room temperature. The slurry was filtered and washed in deionized water before being dried at 50 °C. 1g  
115 of the product,  $\text{Zr}(\text{OH})_4$ , was stirred for 2 h in 10 mL aqueous  $\text{H}_2\text{SO}_4$  (0.05 M). The solid product was  
116 subsequently filtered and dried at 100 °C for 24 h, followed by calcination at 550 °C for 2 h. The sulfur  
117 loading was found to be 3.45%.

118





119

120 **Supplementary Figure 1. Synthesis and coordination mode of sulfate in MOF-808-SO<sub>4</sub>.** (A) The  
 121 synthesis of pristine MOF-808 constructed by 6-coordinate zirconium-based metal clusters containing  
 122 formate groups and linked by benzenetricarboxylate into the diamond topology is depicted. Note that only  
 123 five out of a possible six formates coordinate to the cluster, with water ligands replacing the last formate.  
 124 These formates may be substituted with sulfate anions as in (B), which coordinate in a bidentate fashion  
 125 to zirconium, predominantly by a bridging mode to two zirconium atoms when in solution, and convert to  
 126 exclusively the chelating mode to a single zirconium atom following activation by heating under dynamic  
 127 vacuum.

## 128 Section 2: Powder Neutron Diffraction Experiments

129 Approximately 300 mg activated pristine deuterated MOF-808 was packed into a 6 mm vanadium  
 130 can sealed with a titanium collar, copper gasket and aluminum lid in an argon glove box. After post-  
 131 synthetic exchange with 0.05 M D<sub>2</sub>SO<sub>4</sub> in D<sub>2</sub>O followed by activation described in Section 1, sulfated  
 132 deuterated MOF-808 was similarly loaded into the vanadium can. In both cases, data was collected at 10  
 133 K and 300 K for comparison.

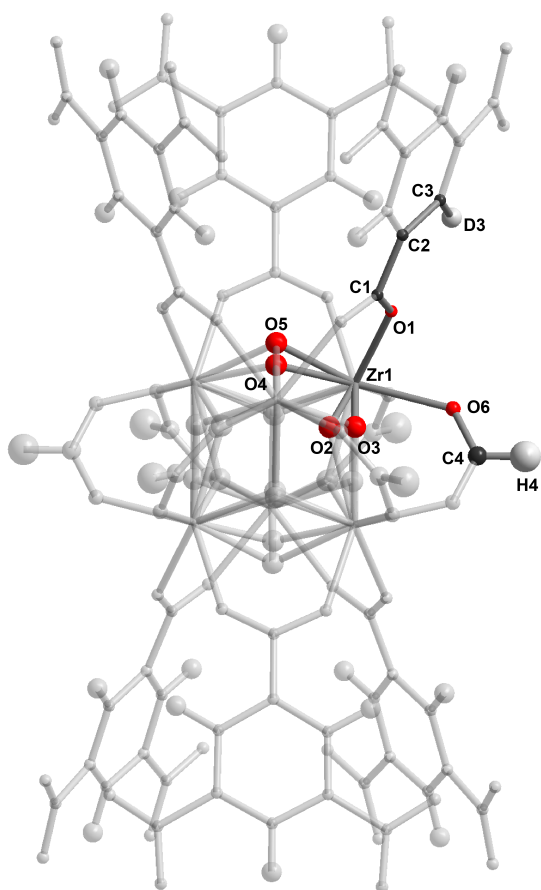
134  
 135 Structure models were initially developed in Materials Studio 7.0 using the models from single  
 136 crystal x-ray diffraction experiments as a starting point. These models were then refined against the  
 137 powder neutron data, with atomic coordinates of the cluster and linker allowed to refine freely, with  
 138 occupancies fixed based on the activated pristine MOF-808 model and knowledge of sulfate coordinates  
 139 from the MOF-808-SO<sub>4</sub> sample prior to activation from single crystal and powder x-ray data.

### 140 Pristine MOF-808 modeling

141 An initial structural model was developed based on MOF-808 single crystal data collected prior  
 142 to activation. All hydrogen atoms in the structure were converted to deuterium atoms except for hydrogen

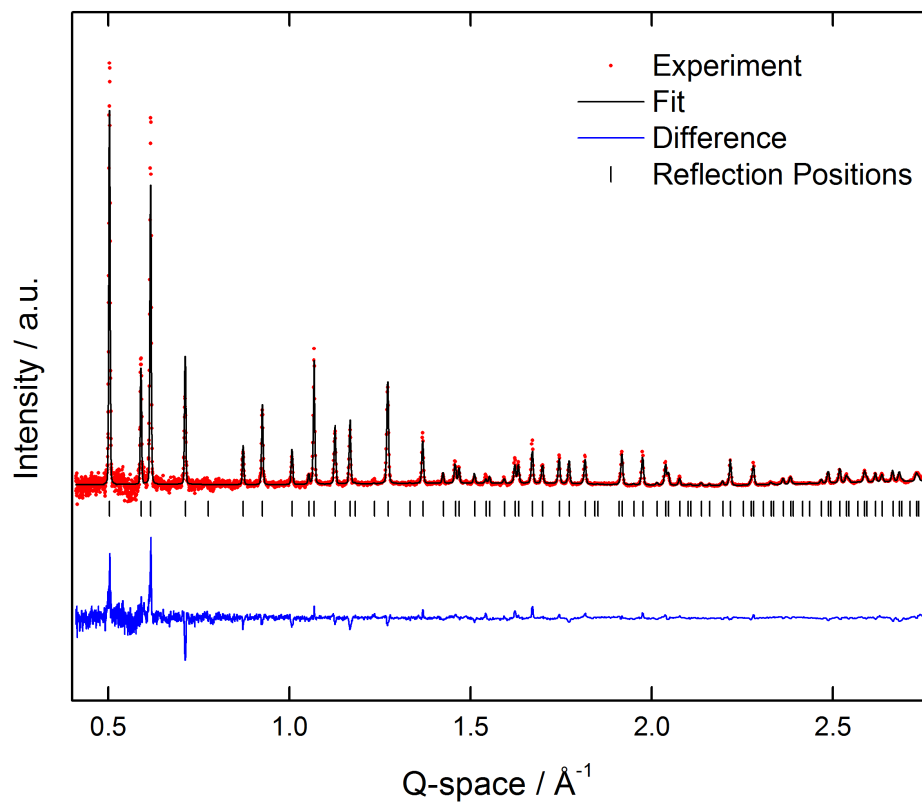
143 on formate, which was not deuterated. To begin with, atomic coordinates were allowed to refine freely  
144 before being fixed at their converged values. With the linker and zirconium occupancies fixed at 100%,  
145 the thermal ellipsoids and occupancies of the remaining atoms were systematically refined. Note that the  
146 ellipsoids on the linker C1, C2, C3, and the ellipsoids of the  $\mu$ -O and -OH pairs were constrained to be  
147 identical in order to aid refinement. The occupancies of the  $\mu$ -O and -OH groups O2, O3, O4 and O5  
148 refined to  $47.9 \pm 1.0$ ,  $48.7 \pm 1.0$ ,  $50.7 \pm 3.2\%$  and  $49.5 \pm 3.2\%$  respectively, meaning there has been no  
149 deprotonation of the  $\mu$ -OH groups to account for charge-balancing. Note however that the data set  
150 collected at room temperature failed to converge O5, and allowing the position of O4 to refine freely  
151 moved it to intermediate coordinates between O4 and O5 in the data set collected at 10 K. This is not an  
152 indication that O5 is not present as it is observed in the 10 K data set, but simply an averaging of the two  
153 positions due to thermal motion.

154 The ellipsoids of D3A and D5, corresponding to  $\mu$ -OD, failed to converge indicating only partial  
155 exchange of hydrogen with deuterium. If hydrogen is partially present, this does not reflect the true  
156 occupancy of deuterium at this position as  $^1\text{H}$  and  $^2\text{D}$  signals cancel each other out. This could be  
157 additionally compounded from the terminal position of the deuterium atoms that increase disorder and  
158 thermal motion as is observed for H4 on formate. The formate carbon and hydrogen atoms, C4 and H4,  
159 refine to  $84.1 \pm 1.1\%$  and  $85.5 \pm 2.3\%$ , fixed to 83.3% as consistent with NMR data. Refinement of O6,  
160 which accommodated oxygen from formate and terminal water molecules coordinated zirconium,  
161 converged at  $97.9 \pm 0.8\%$ , which is consistent with terminal hydroxide groups completing the charge-  
162 balancing of the framework, and hence not being removed following activation as was found in MOF-  
163 808-SO<sub>4</sub>. The final refinement converged to  $wR_p = 3.20\%$  and  $R_p = 11.20\%$ .



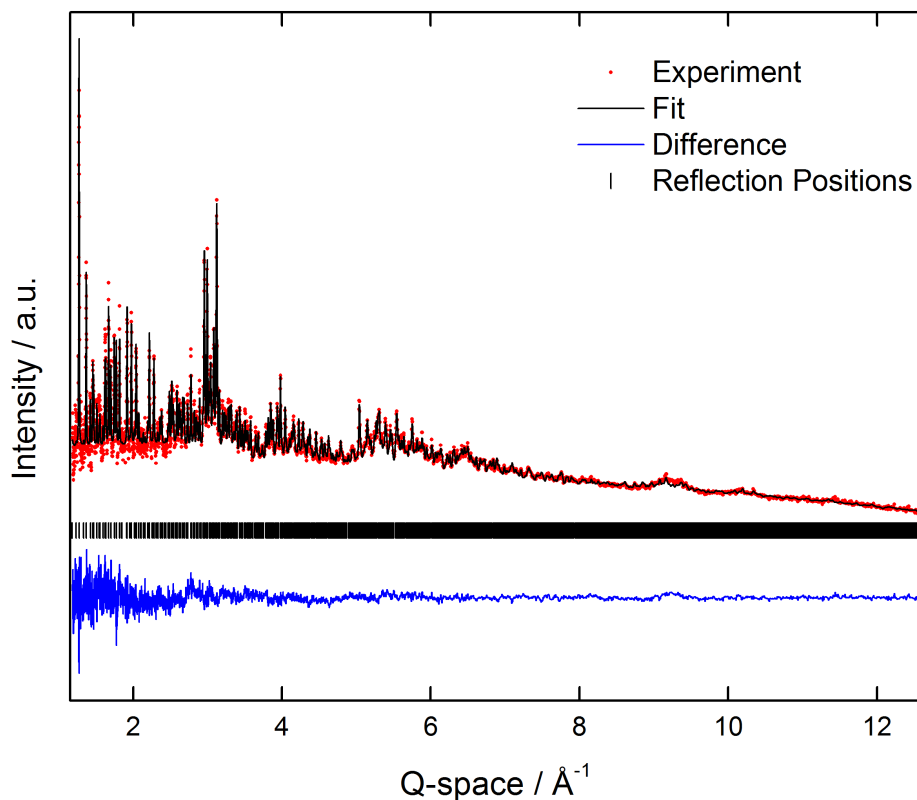
164

165 **Supplementary Figure 2.** Representation of metal oxide cluster in pristine MOF-808 as found by powder  
166 neutron diffraction. The asymmetric unit is colored and labeled with zirconium in blue, oxygen in red,  
167 carbon in black and hydrogen/deuterium in white, while the remaining atoms are shaded in order to show  
168 how the framework extends. Thermal ellipsoids are represented at 50% probability, with all refined  
169 isotropically.  $wRp = 3.20\%$ ,  $Rp = 11.20\%$



170

171 **Supplementary Figure 3.** Powder neutron diffraction pattern of data for pristine MOF-808 activated at  
172 120 °C, displaying the experimental pattern (red) and the fitted pattern obtained by Rietveld refinement of  
173 the structure (black). The difference plot (blue) as well as the Bragg positions (black) are provided.



174

175 **Supplementary Figure 4.** Powder neutron diffraction pattern of data collected at high Q-space values for  
 176 pristine MOF-808 activated at 120 °C, displaying the experimental pattern (red) and the fitted pattern  
 177 obtained by Rietveld refinement of the structure (black). The difference plot (blue) as well as the Bragg  
 178 positions (black) are provided.

179

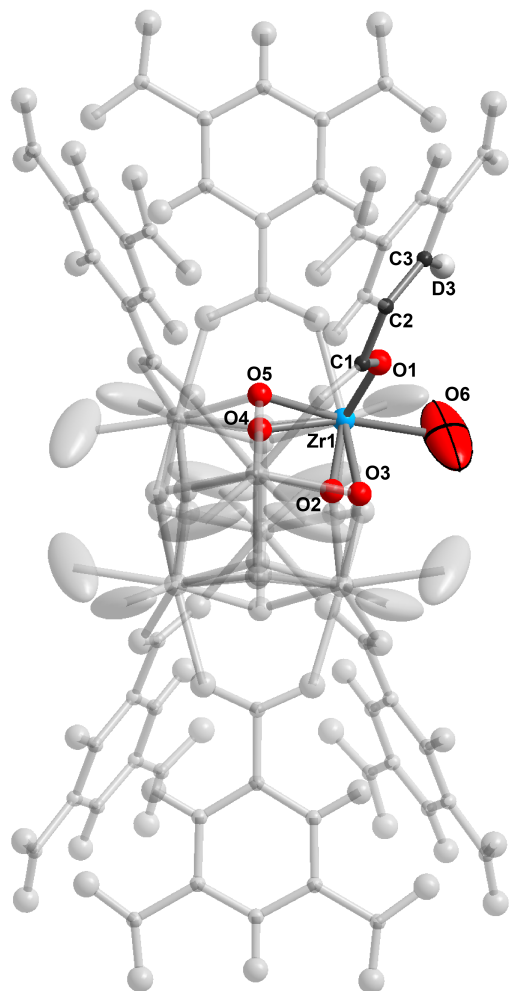
## 180 MOF-808-SO, modeling

181 The coordinates and occupancies from the sulfated MOF-808 model prior to activation were  
 182 imported and used as a starting point for Rietveld refinement. To begin with, atomic coordinates were  
 183 allowed to refine freely before being fixed at their converged values. With the linker and zirconium  
 184 occupancies fixed at 100%, the thermal ellipsoids and occupancies of the remaining atoms were  
 185 systematically refined. Note that the ellipsoids on the linker C1, C2, C3, and the ellipsoids of the  $\mu$ -O and  
 186 -OH pairs were constrained to be identical in order to aid refinement. It was found that modeling S1, S2,  
 187 O8A, O8B, O9A and O9B based on coordinates from single crystal data failed to converge with  
 188 reasonable thermal ellipsoids. This is due to the very low occupancies of sulfate, found to be 12% and 6%  
 189 for S1 and S2 in MOF-808-SO, respectively, and prior to activation. It should be noted that the coherent  
 190 neutron scattering length for sulfur is less than half that of oxygen, in contrast with x-ray diffraction  
 191 where sulfur contains double the number of electrons as oxygen and thus scatters x-rays much more  
 192 readily. Since the refinement quality indicators,  $wR_r$  and  $R_w$ , displayed no significant difference between  
 193 modeling and neglecting the sulfate groups, and requiring significant restraints to model whilst worsening  
 194 the overall refinement quality, all sulfate atoms except for O6, which is oxygen bound to zirconium  
 195 directly, were neglected in the final structure model. The presence of sulfate in the activated structure was  
 196 however confirmed by elemental analysis and lack of formate by <sup>1</sup>H NMR, and evidence for the sulfate

197 position in the framework was identified through PXRD as being exclusively in the chelating mode (see  
198 Section 4).

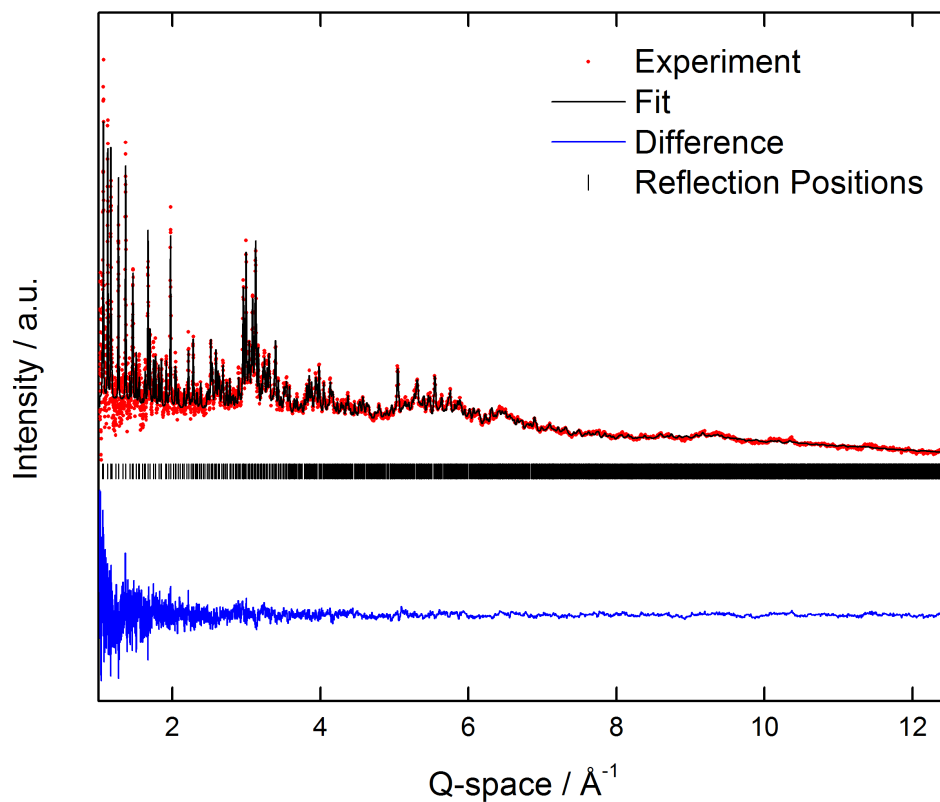
199 Additionally, it was found that the thermal ellipsoid of D3A and D5, corresponding to deuterium  
200 on  $\mu$ -OD in the framework, failed to converge. This could be evidence for deprotonated  $\mu$ -OD in the  
201 framework; however, free refinement of the occupancies of the corresponding oxygen atoms on the  $\mu$ -O  
202 and -OD groups, O2 ( $53.5 \pm 1.1\%$ ) and O3 ( $48.5 \pm 1.1\%$ ) for D3 and O4 ( $49.8 \pm 2.1\%$ ), O5 ( $50.8 \pm 2.1$ ) for  
203 D5 were found to be, within two standard deviations, in an equal ratio as in the sample prior to activation.  
204 It is therefore presumed not all deuterium was successfully exchanged into the framework, since any  
205 hydrogen present in the same position has a negative scattering length and would negate the signal from  
206 deuterium. Indeed, a roughly 1:2 ratio of D to H would contribute overall no scattering. This could be  
207 additionally compounded from the terminal position of the deuterium atoms that increase disorder and  
208 thermal motion.

209 At position O6, where sulfate and water coordinate to zirconium in the sample prior to activation,  
210 the occupancy refines to  $78.7 \pm 1.1\%$ , yet the contribution from sulfate only accounts for 38.3%, or 4.6  
211 oxygen atoms out of 12 possible sites per cluster. Since the remaining density must be derived from  
212 water, and having established charge-balancing is not achieved elsewhere, we postulate some of this  
213 density must be deprotonated water to become terminal hydroxide. Based on the chemical formula, there  
214 is an average charge of -1.4 per cluster unaccounted for, and therefore 11.7% of this density is assigned to  
215 hydroxide, or 1.4 out of the 12 possible positions per cluster, (two per zirconium). In total, sulfate and  
216 hydroxide account for 50% of the observed density, leaving  $28.7 \pm 1.1\%$  as water molecules bound to the  
217 zirconium cluster, which translates to  $3.4 \pm 0.1$  water molecules per cluster, and the remaining  $21.6 \pm 1.1\%$   
218 unoccupied positions corresponding to open metal sites. This result is consistent with previous  
219 experimental data indicating Lewis acid sites alongside Brønsted acid sites in MOF-808-SO<sub>4</sub> (4). While  
220 the thermal ellipsoid for O6A is relatively large compared to other atoms in the structure, with at least  
221 three different species in different local environments and slightly different positions for each, this is  
222 reasonable. In the sample prior to activation with single crystal data, a larger anisotropic ellipsoid is also  
223 observed at position O6, reflecting the slightly strained conformation of the two binding modes of sulfate,  
224 which are not perfectly overlapping with the oxygen atom from coordinated water, which illustrates this  
225 point.



226

227 **Supplementary Figure 5.** Representation of metal oxide cluster in MOF-808-SO<sub>4</sub> as found by powder  
 228 neutron diffraction. The asymmetric unit is colored and labeled with zirconium in blue, oxygen in red,  
 229 carbon in black and deuterium in white, while the remaining atoms are shaded in order to show how the  
 230 framework extends. Note the large ellipsoid for O6 relative to other atoms is expected as this position is  
 231 representing at least four different sources of oxygen atoms including from water, hydroxide, bridging  
 232 and chelating sulfate. Thermal ellipsoids are represented at 50% probability, with all except O6 refined  
 233 isotropically.  $wR_p = 2.91\%$ ,  $R_p = 9.59\%$



234

235 **Supplementary Figure 6.** Powder neutron diffraction pattern of data collected at high Q-space values for  
236 MOF-808-SO<sub>4</sub> activated at 120 °C, displaying the experimental pattern (red) and the fitted pattern  
237 obtained by Rietveld refinement of the structure (black). The difference plot (blue) as well as the Bragg  
238 positions (black) are provided.

239



240 **Section 3: Single Crystal X-ray Diffraction Analyses**

241

242 **Supplementary Table 1.** Crystal structure data for pristine MOF-808 prior to activation.

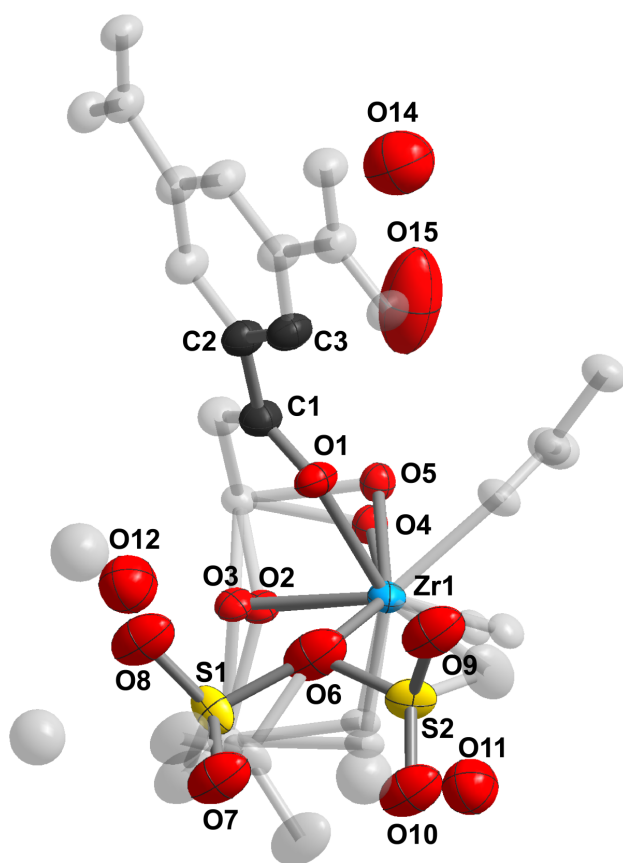
243

<b>Sample</b>	<b>Pristine MOF-808</b>
<b>chemical formula</b>	Zr <sub>6</sub> O <sub>7.12</sub> C <sub>23</sub> H <sub>15</sub>
<b>formula mass</b>	1432.67
<b>crystal system</b>	cubic
<b>space group</b>	<i>Fd-3m</i>
<b>λ (Å)</b>	0.77490
<b>a (Å)</b>	35.1364(13)
<b>Z</b>	16
<b>V (Å<sup>3</sup>)</b>	43378(5)
<b>temperature (K)</b>	100
<b>size /mm</b>	0.015 × 0.015 × 0.010
<b>density (g/cm<sup>3</sup>)</b>	0.877
<b>measured reflections</b>	60241
<b>unique reflections</b>	2487
<b>parameters</b>	78
<b>restraints</b>	0
<b>R<sub>m</sub></b>	0.0858
<b>θ range (deg)</b>	2.10-30.74
<b>R<sub>i</sub>, wR<sub>i</sub></b>	0.0531, 0.1907
<b>S (GOF)</b>	1.110
<b>max/min res. dens. (e/Å<sup>3</sup>)</b>	0.75/-0.89

244



Sample	MOF-808-SO <sub>4</sub>
chemical formula	Zr <sub>6</sub> O <sub>43.09</sub> C <sub>18</sub> H <sub>10</sub> S <sub>1.79</sub>
formula mass	1520.35
crystal system	cubic
space group	<i>Fd-3m</i>
λ (Å)	0.77490
a (Å)	35.2075(13)
Z	16
V (Å <sup>3</sup> )	43642(5)
temperature (K)	100
size /mm	0.015 × 0.015 × 0.010
density (g/cm <sup>3</sup> )	0.926
measured reflections	70715
unique reflections	3175
parameters	101
restraints	7
R <sub>int</sub>	0.0849
θ range (deg)	2.09-33.75
R <sub>1</sub> , wR <sub>2</sub>	0.0556, 0.1911
S (GOF)	1.117
max/min res. dens. (e/Å <sup>3</sup> )	1.1/-0.6

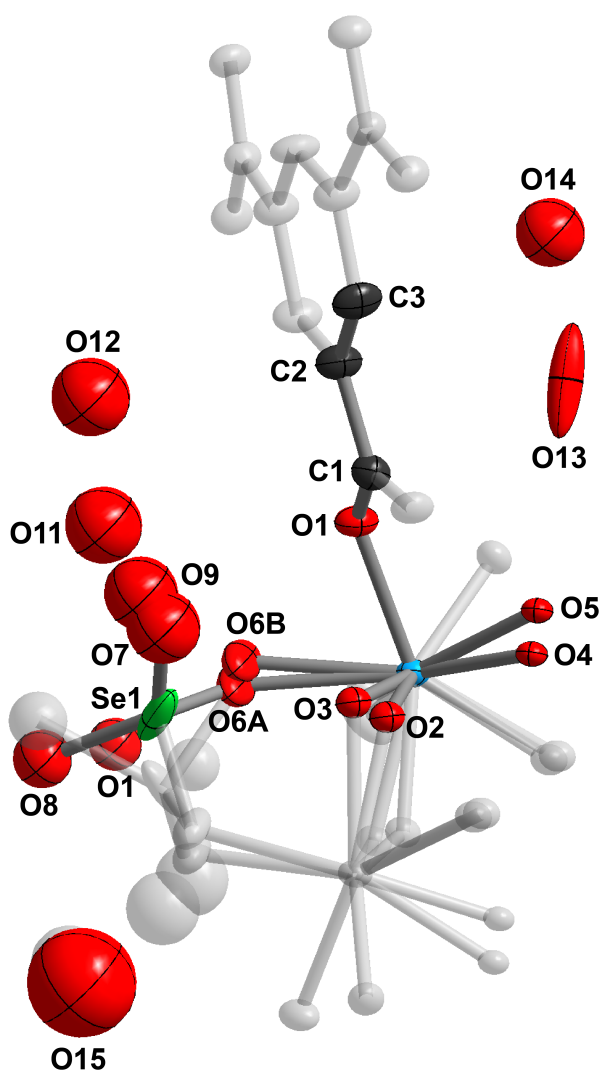


267  
 268 **Supplementary Figure 8.** Representation of MOF-808-SO<sub>4</sub> prior to activation from SXR data. The  
 269 asymmetric unit is displayed in color, with additional atoms in gray to aid visualizing the structure.  
 270 Thermal ellipsoids are displayed at 50% probability and atom colors are as follows: zirconium (blue),  
 271 oxygen (red), carbon (black), sulfur (yellow). Hydrogen atoms are omitted for clarity.

272  
 273 The single crystal structure of MOF-808-SeO<sub>4</sub> was modeled where the occupancy of sulfur was  
 274 permitted to refine freely, with Se1 exclusively existing in the bridging mode in the pre-activated form.  
 275 Note this configuration changes to exclusively chelating upon activation under dynamic vacuum at 120  
 276 °C. Ellipsoids of O2 and O3, O4 and O5, O6A and O6B were constrained in their pairs to be identical due  
 277 to their close proximity. Oxygen atoms have been modeled within the cavity of the structure, representing  
 278 highly disordered solvent molecules which are typically hydrogen bonding to the framework and are  
 279 likely a combination of water and DMF molecules. Note that O7 through to O15 have been modeled  
 280 isotropically due to their low occupancy and proximity to other atoms in the model. The geometry of  
 281 selenate was restrained to its known tetrahedral configuration using distance and angle restraints due to  
 282 partial occupancy and positional overlap with solvent molecules. Two low-angle reflections, (222) and  
 283 (044), were omitted from the refinement due to their large discrepancy between calculated and  
 284 experimental values. The reason for discrepancy is likely related to not fully accounting for the highly  
 285 disordered solvent within the cavity.

286  
 287 **Supplementary Table 3.** Crystal structure data for MOF-808-SeO<sub>4</sub> prior to activation.

Sample	MOF-808-SeO <sub>4</sub>
chemical formula	Zr <sub>6</sub> O <sub>43.90</sub> C <sub>18</sub> H <sub>10</sub> Se <sub>1.28</sub>
formula mass	1579.22
crystal system	cubic
space group	<i>Fd-3m</i>
λ (Å)	0.77490
a (Å)	35.2645(10)
Z	16
V (Å <sup>3</sup> )	43854(4)
temperature (K)	100
size /mm	0.015 × 0.015 × 0.010
density (g/cm <sup>3</sup> )	0.955
measured reflections	79733
unique reflections	2245
parameters	98
restraints	17
R <sub>int</sub>	0.0858
θ range (deg)	1.8-29.5
R <sub>1</sub> , wR <sub>2</sub>	0.0510, 0.1672
S (GOF)	1.144
max/min res. dens. (e/Å <sup>3</sup> )	0.8/-0.4



289

290 **Supplementary Figure 9.** Representation of MOF-808-SeO, prior to activation from SXRD data. The  
 291 asymmetric unit is displayed in color, with additional atoms in gray to aid visualizing the structure.  
 292 Thermal ellipsoids are displayed at 50% probability and atom colors are as follows: zirconium (blue),  
 293 oxygen (red), carbon (black), selenium (green). Hydrogen atoms are omitted for clarity.

294

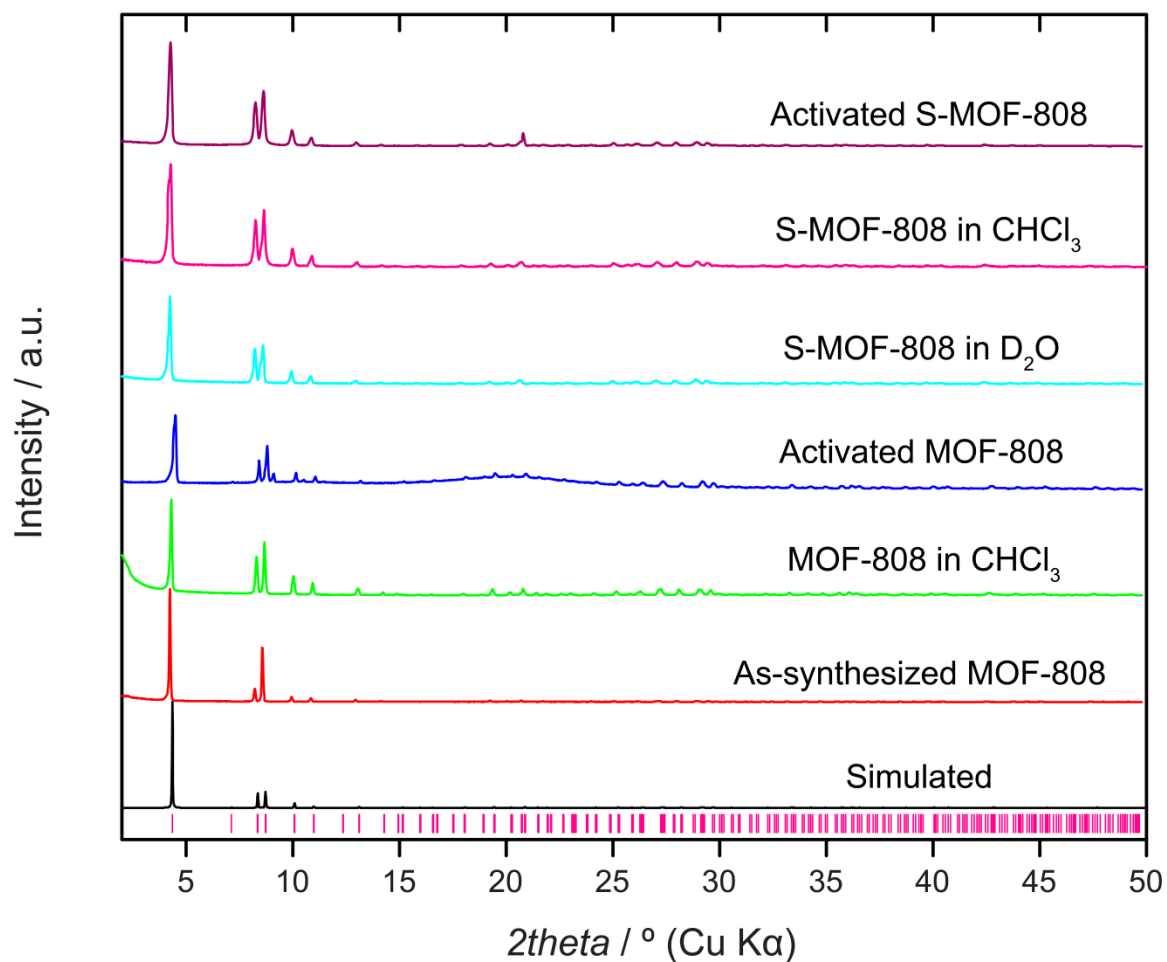
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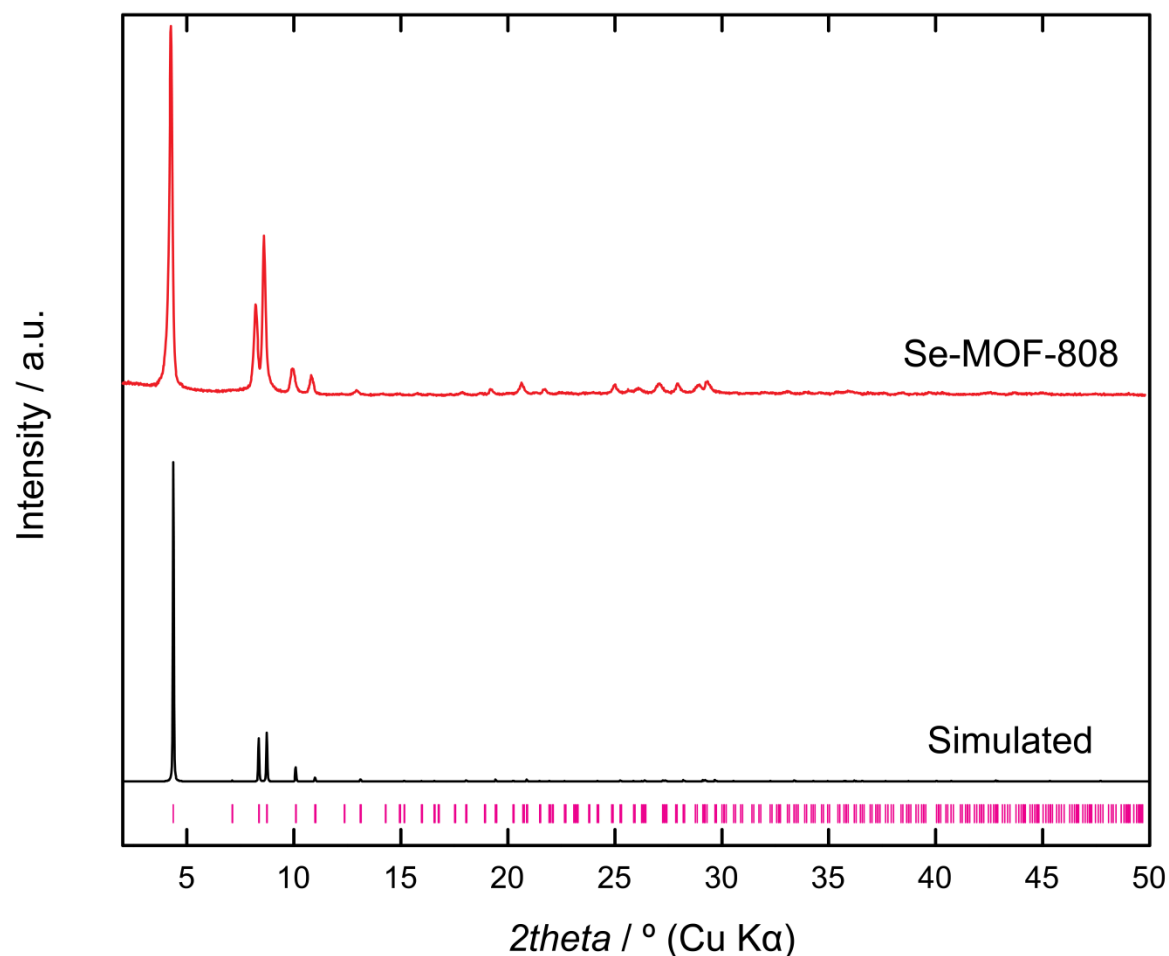
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299



302  
303 **Supplementary Figure 10.** PXRD patterns of deuterated MOF-808 after various stages of treatment. The  
304 pristine simulated pattern (black) is compared to the as-synthesized (red), after CHCl<sub>3</sub> (green), and after  
305 activation under dynamic vacuum (dark blue) of the pristine sample. The remaining patterns are  
306 immediately after treatment with D<sub>2</sub>SO<sub>4</sub> in D<sub>2</sub>O (light blue), exchanging with CHCl<sub>3</sub> (pink) and activation  
307 of the sulfated sample (violet), showing crystallinity is retained.



309

310 **Supplementary Figure 11.** PXRD patterns of simulated MOF-808 (black) and after immersion with 0.05  
 311 M of selenic acid, solvent exchange and activation (red).

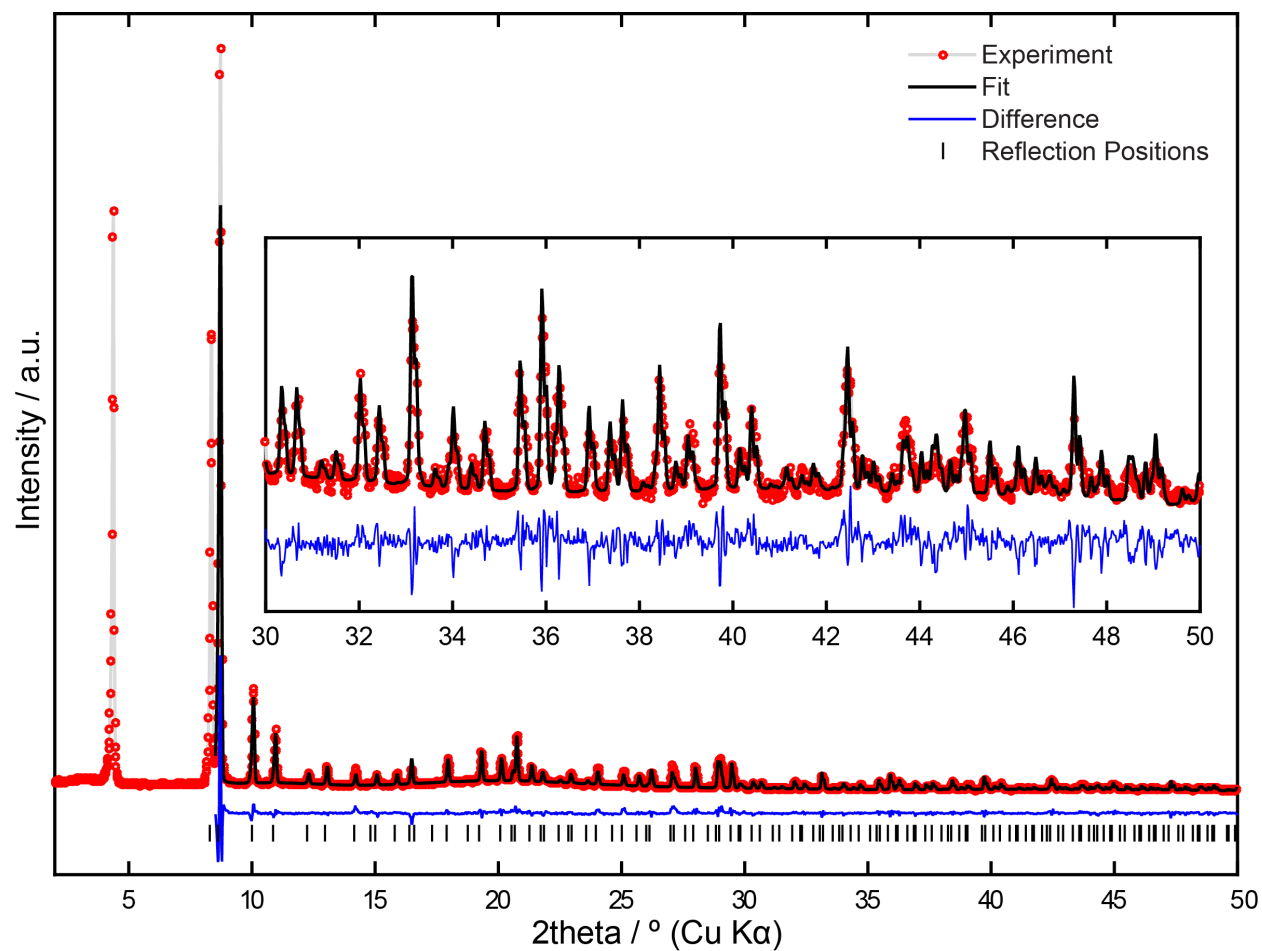
312 X-ray powder Rietveld refinements of the activated samples under argon (both MOF-  
 313 808-SeO<sub>4</sub> and MOF-808-SO<sub>4</sub>) were carried out using TOPAS 5 (6). Regarding the overall quality  
 314 of the fits, it is noted that there is no routine like Platon SQUEEZE used, which could take the  
 315 contribution of any residual density in the pores into account, such as the disordered argon atoms  
 316 or any other remaining molecules. Thus, there are small systematic deviations visible in the  
 317 difference plots, which might be due to anything what is left in the pores. Also, reflections 111  
 318 and 022 had to be excluded from the refinements, as the inclusion of those two reflections  
 319 rendered the refinement unstable and yielded chemically unreasonable electron densities in the  
 320  $F_{\text{obs}}-F_{\text{calc}}$  plots. This data was used to determine the position of selenate and sulfate only, and the  
 321 neutron data collected from the spallation source was used for occupancies and thermal ellipsoid  
 322 parameters discussed in the main text due to the superior data quality and resolution obtained.

323

324 In the first steps of the refinement, a structure model was used without selenate/sulfate  
 325 groups. In subsequent steps, those groups were located after inspection of the  $F_{\text{obs}}-F_{\text{calc}}$  plots.  
 326 Geometrical constraints were applied during the refinement to retain symmetry  $Fd\bar{3}m$ : In

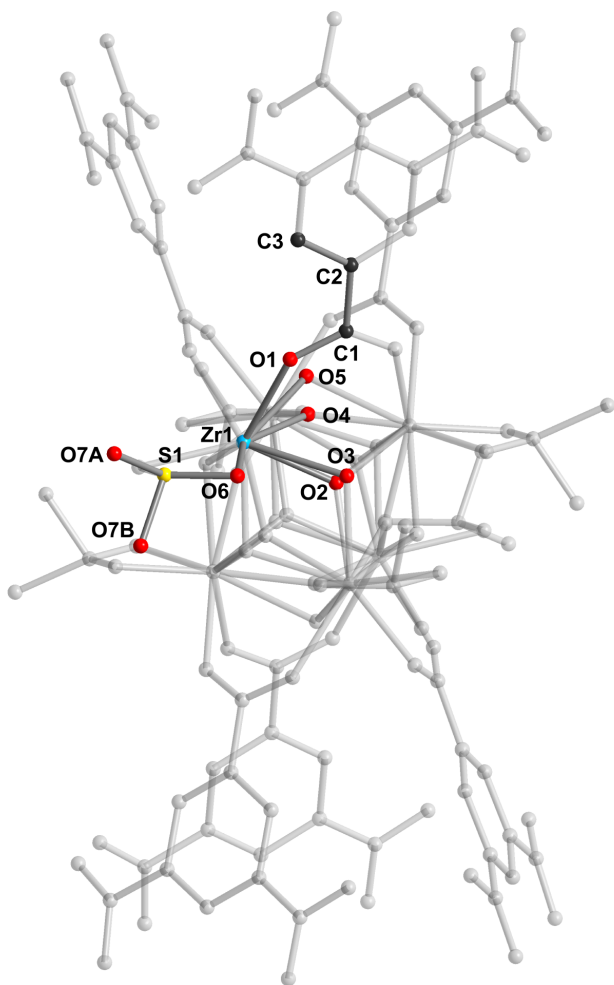


327 particular, the Zr<sub>6</sub>-octahedra were allowed to expand/contract isotropically. The phenyl ring of  
328 the BTC linker was allowed to move along the 3-fold axis. The angle between the center of the  
329 phenyl ring, the carbon atom the carboxylate group is binding to and the carboxylate carbon,  
330 however, were refined freely, as a slight distortion of the linker was observed in previous work  
331 (4). Interatomic distances within the linker were constrained to their ideal values. Further  
332 constraints were applied to all oxygen atoms bound to the cluster and the selenate/sulfate as well  
333 as S/Se atoms themselves, to ensure they stayed on their ideal Wyckoff position. Anti-bump  
334 restraints were applied to the terminal oxygen atoms bound to S/Se. As of the low x-ray  
335 scattering contrast of hydrogen, no hydrogen atoms were refined other than the ones directly  
336 bound to the linker. In total, 3 isotropic displacement parameters were refined for the Se data.  
337 Specifically, one displacement parameter for the zirconium atom, one for all light elements  
338 besides the oxygens bridging zirconium and Se, and one for the selenate group. The results are as  
339 expected:  $U_{\text{iso}}(\text{Zr}) < U_{\text{iso}}(\text{light atoms}) < U_{\text{iso}}(\text{selenate})$ . The occupancy of the selenate/sulfate group  
340 was allowed to refine freely and is within the limits of the method and in reasonable agreement  
341 with the results from ICP and EA respectively. It has to be noted that the fit is worse for the S  
342 data than for Se. A reason for this could be the lower resolution. As a consequence, less  
343 parameters were refined. In particular the displacement parameters were fixed at reasonable  
344 values (0.03 for Zr, 0.05 for light atoms and 0.08 for the sulfate group). The chelating position of  
345 the sulfate group however was verified by inspecting the  $F_{\text{obs}} - F_{\text{calc}}$  plots. No significant electron  
346 density was found at a hypothetical bridging position.



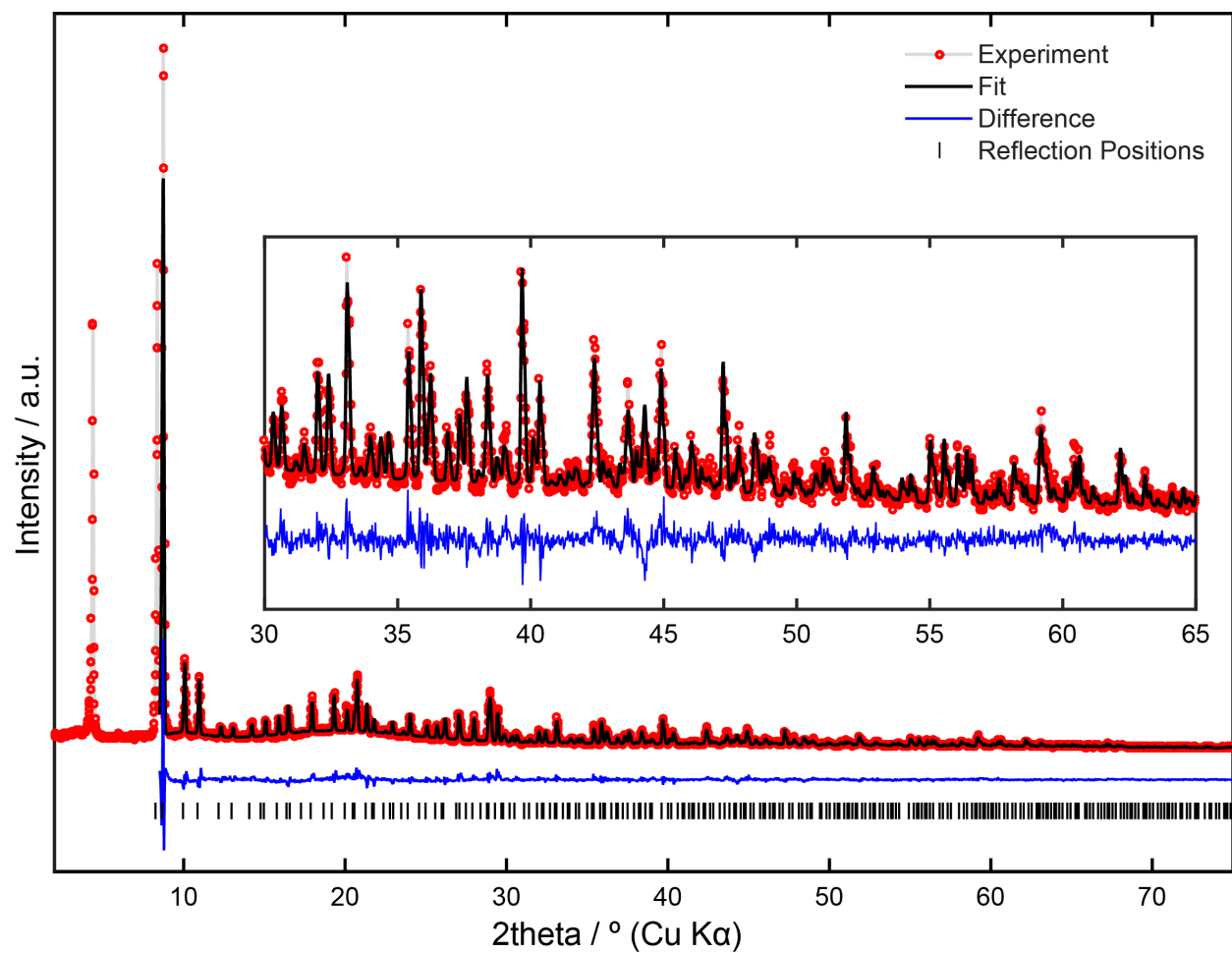
347

348 **Supplementary Figure 12.** Powder x-ray diffraction pattern of MOF-808-SO<sub>4</sub> activated at 120 °C,  
349 displaying the experimental pattern (red) and the fitted pattern obtained by Rietveld refinement of the  
350 structure (black). The difference plot (blue) as well as the Bragg positions (black) are provided. The data  
351 was collected under argon atmosphere at room temperature.



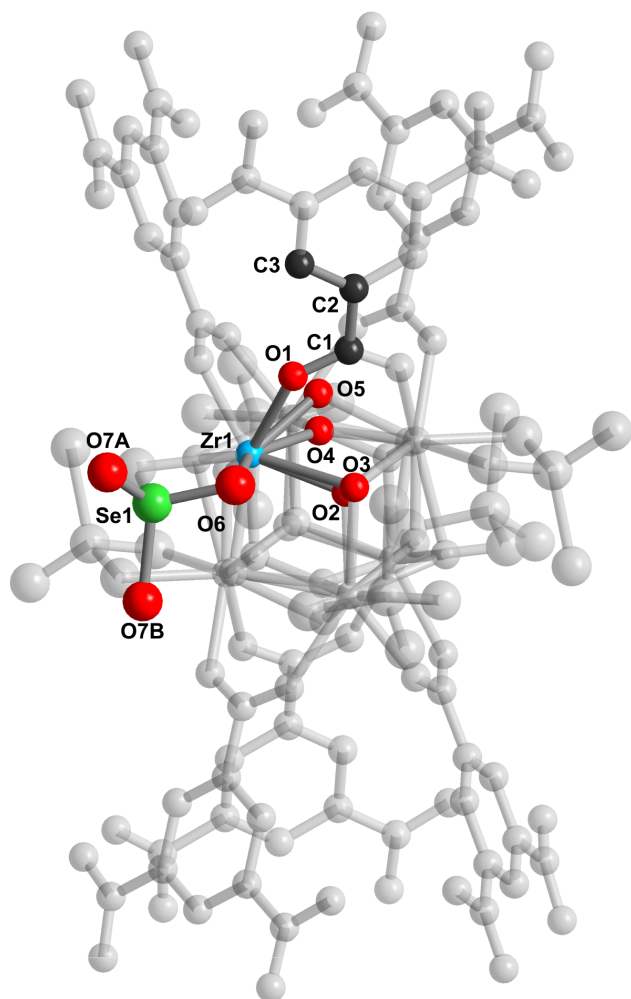
352

353 **Supplementary Figure 1.** Representation of metal oxide cluster in MOF-808-SO<sub>4</sub> as found by powder x-  
354 ray diffraction, revealing the exclusively chelating mode of sulfate. The asymmetric unit is colored and  
355 labeled with zirconium in blue, oxygen in red, carbon in black and sulfur in yellow, while the remaining  
356 atoms are shaded in order to show how the framework extends. Hydrogen atoms were omitted for clarity.  
357 Thermal ellipsoids are represented at 50% probability, with all refined isotropically. Rp = 11.6%.



358

359 **Supplementary Figure 2.** Powder x-ray diffraction pattern of MOF-808-SeO<sub>2</sub>, activated at 120 °C,  
 360 displaying the experimental pattern (red) and the fitted pattern obtained by Rietveld refinement of the  
 361 structure (black). The difference plot (blue) as well as the Bragg positions (black) are provided. The data  
 362 was collected under argon atmosphere at room temperature.



363

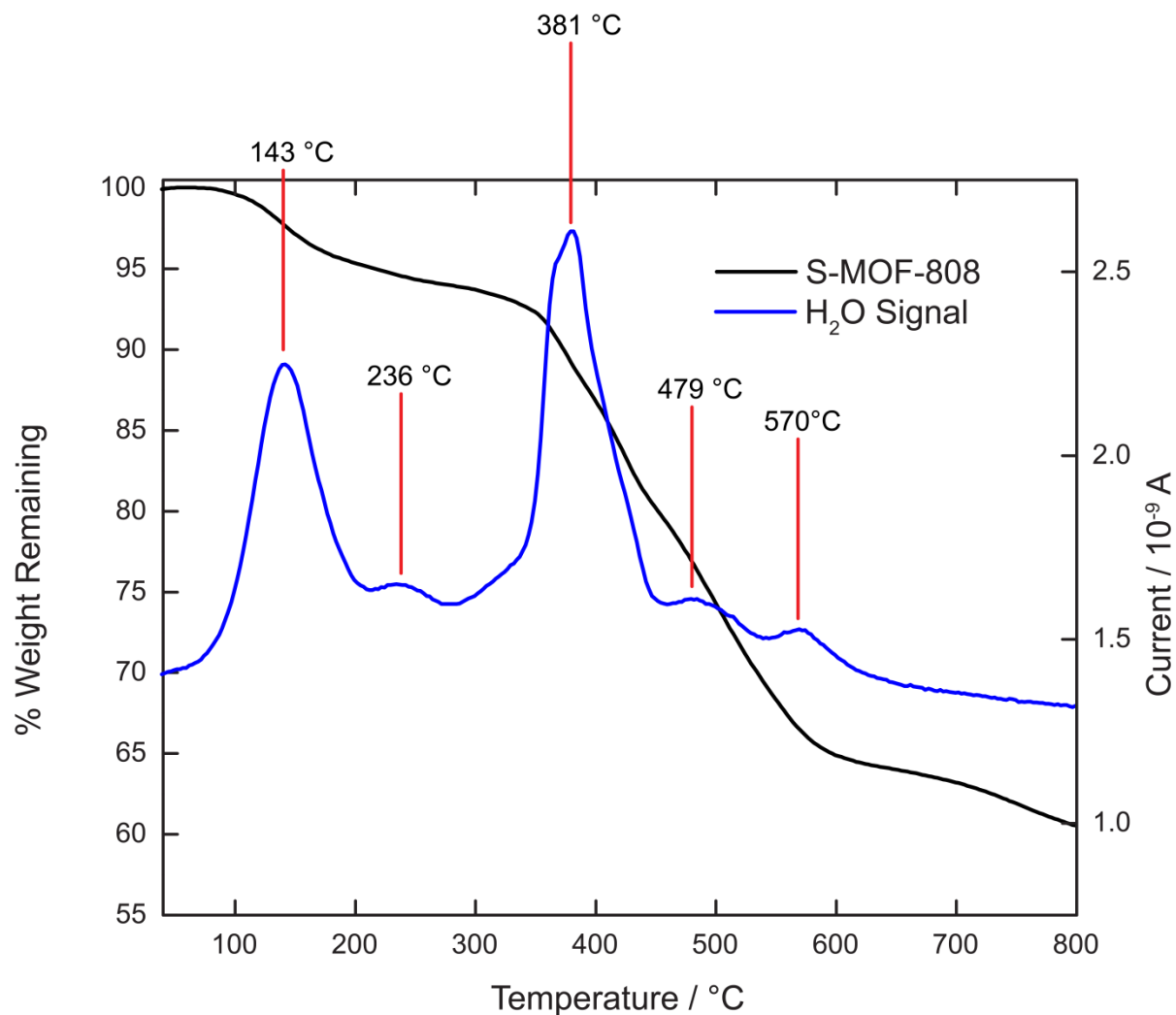
364 **Supplementary Figure 3.** Representation of metal oxide cluster in MOF-808-SeO, as found by powder x-  
365 ray diffraction, revealing the exclusively chelating mode of selenate. The asymmetric unit is colored and  
366 labeled with zirconium in blue, oxygen in red, carbon in black and sulfur in yellow, while the remaining  
367 atoms are shaded in order to show how the framework extends. Hydrogen atoms were omitted for clarity.  
368 Thermal ellipsoids are represented at 50% probability, with all refined isotropically.  $R_p = 10.5\%$ .

369

## 370 Section 5: Thermogravimetric Analysis

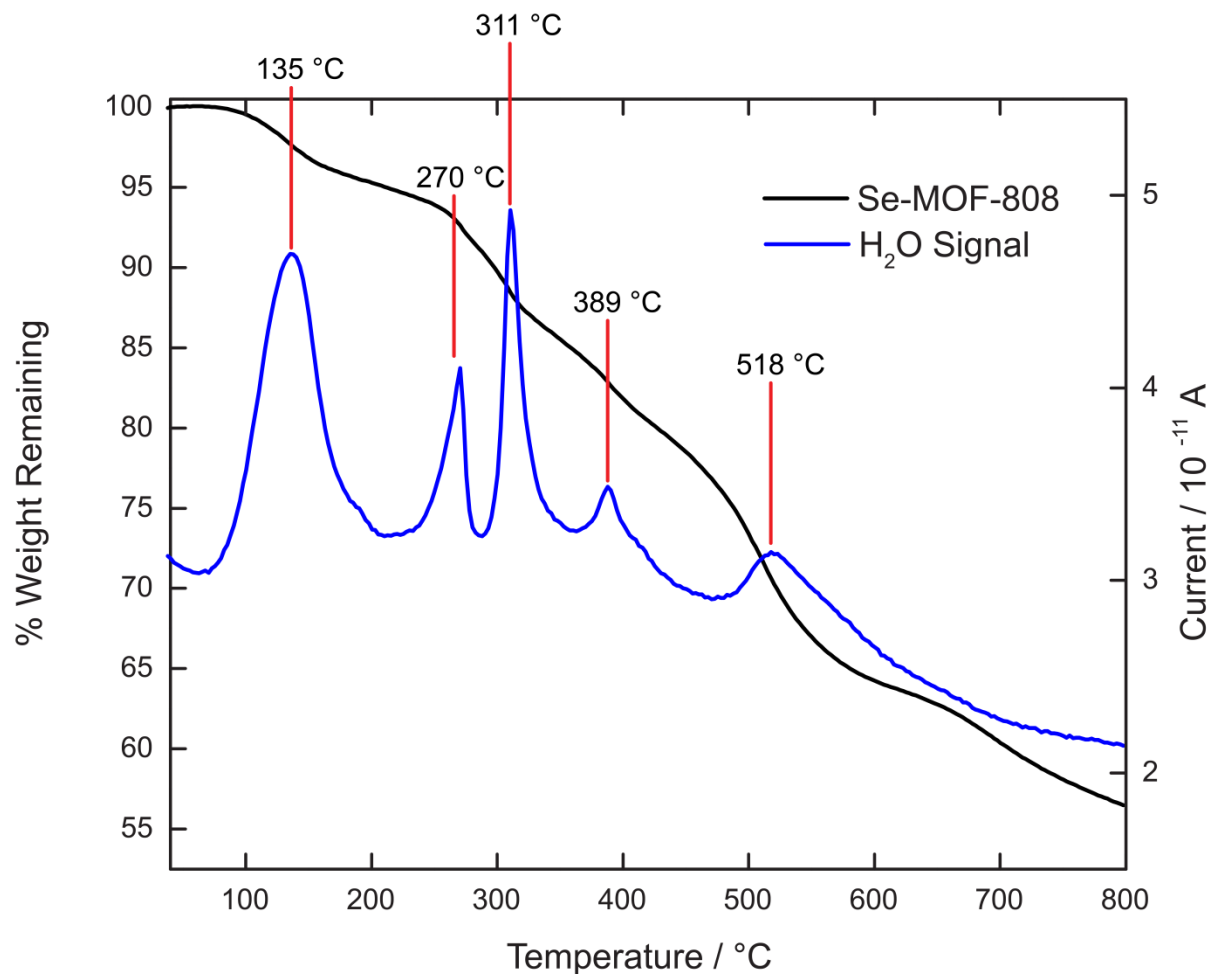
371

372 Thermogravimetric analysis coupled to a mass spectrometer (TGA-MS) was performed  
373 using a Netzsch STA 449 F5 Jupiter thermogravimetric analyzer coupled to a Netzsch QMS 403  
374 D Aeolos mass spectrometer. A typical sample preparation method is as follows: the activated  
375 MOF sample was weighed in a glove box under argon atmosphere and transferred under argon to  
376 the TGA-MS. The sample chamber was then evacuated three times, refilling the chamber each  
377 time with argon. Next, the sample was heated at a rate of 2 °C min<sup>-1</sup> to 800 °C with an argon flow  
378 rate of 20 ml min<sup>-1</sup>. The water signal was quantified by repeating the experiment under identical  
379 conditions but with copper sulfate pentahydrate as a standard since this compound has well-  
380 characterized water loss steps. The area underneath the water signal plot was then used to  
381 quantify the amount of water being lost in the MOF by relating this to the known amount lost in  
382 the standard. The first water signal, peaking at 143 °C, corresponds to 0.96 mg H<sub>2</sub>O in 24.5 mg  
383 MOF-808-SO<sub>4</sub>, which is 3.9% of the total mass. Taking the chemical formula of  
384  $Zr_6O_4(OH)_4(C_9H_3O_6)_2(SO_4)_{2.3}(OH)_{1.4}(OH_2)_x(DMF)_{0.4} = Zr_6O_{31+x}C_{19.2}H_{14.2+2x}S_{2.3}N_{0.4}$ , and assuming all terminal  
385 water molecules are lost after the first peak, then  $x = 3.1$ . This result is consistent with the PND  
386 data which indicates  $3.4 \pm 0.1$  water molecules per cluster. A similar calculation was performed  
387 on MOF-808-SeO<sub>4</sub>, containing 3.4% H<sub>2</sub>O by weight. Considering the formula  
388  $Zr_6O_4(OH)_4(C_9H_3O_6)_2(SeO_4)_{2.3}(OH)_{1.4}(C_2H_7NO)_{0.5}(H_2O)_1 = Zr_6O_{31}C_{19.5}H_{14.5}N_{0.5}Se_{2.3} + xH_2O$ , then  $x = 2.9$ .



389

390 **Supplementary Figure 4.** TGA-MS plot of activated MOF-808-SO<sub>4</sub> under argon atmosphere with the  
 391 thermogravimetric plot (black) and corresponding water loss signal (blue). The first mass loss, with the  
 392 water signal peaking at 143 °C, corresponds of water coordinated to the framework that is lost prior to full  
 393 structure decomposition beginning around 320 °C. Quantification of the water signals correspond to 3.1  
 394 water molecules per cluster for the first peak centered at 143 °C, 0.05 water molecules per cluster at 236  
 395 °C, and 4.5 water molecules at 381 °C.



396

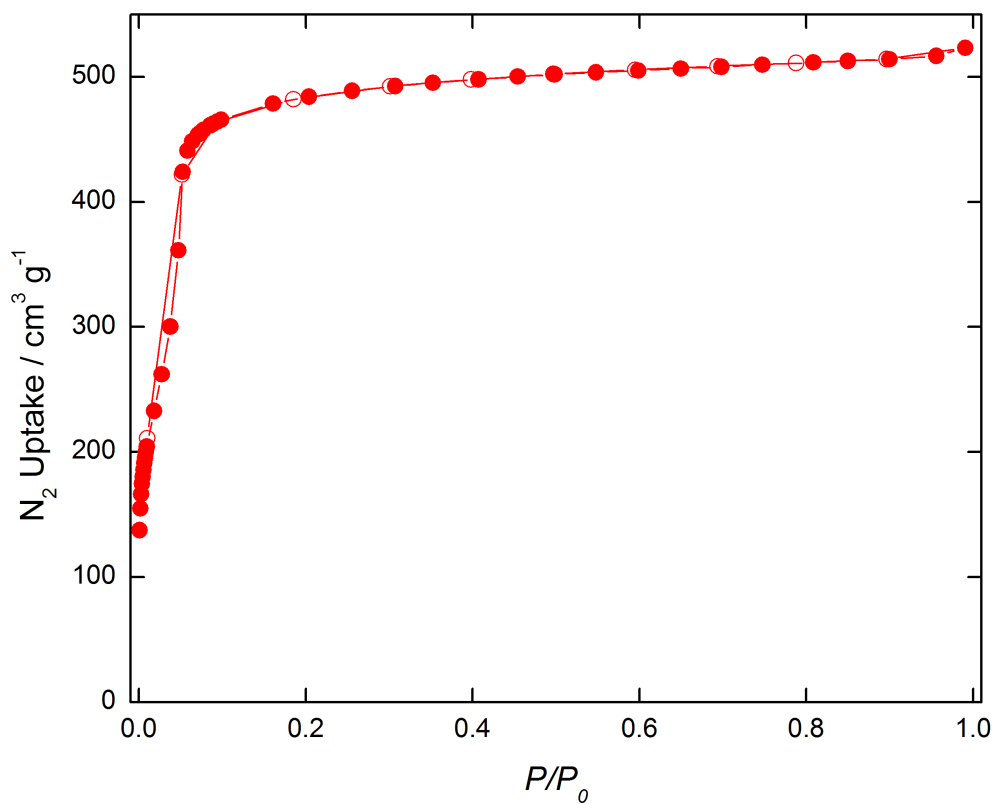
397 **Supplementary Figure 5.** TGA-MS plot of activated MOF-808-SeO<sub>4</sub> under argon atmosphere with the  
 398 thermogravimetric plot (black) and corresponding water loss signal (blue). The first mass loss, with the  
 399 water signal peaking at 135 °C, corresponds to water coordinated to the framework that is lost prior to full  
 400 structure decomposition beginning around 270 °C. The most credible explanation for the lower  
 401 temperature decomposition of MOF-808-SeO<sub>4</sub> compared to MOF-808-SO<sub>4</sub> is the much larger strain on  
 402 chelating selenate, since the former is distorted to a much greater degree compared with chelating sulfate.  
 403 Quantification of the water signals correspond to 2.9 water molecules per cluster for the first peak  
 404 centered at 135 °C.

405

406

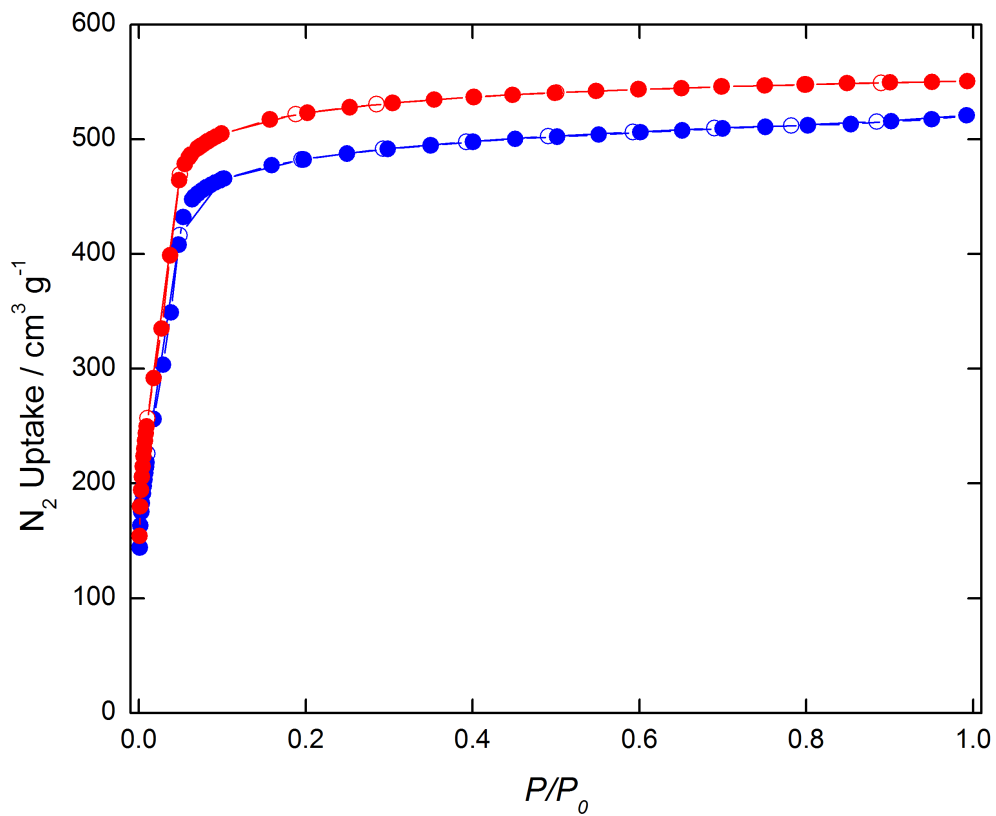
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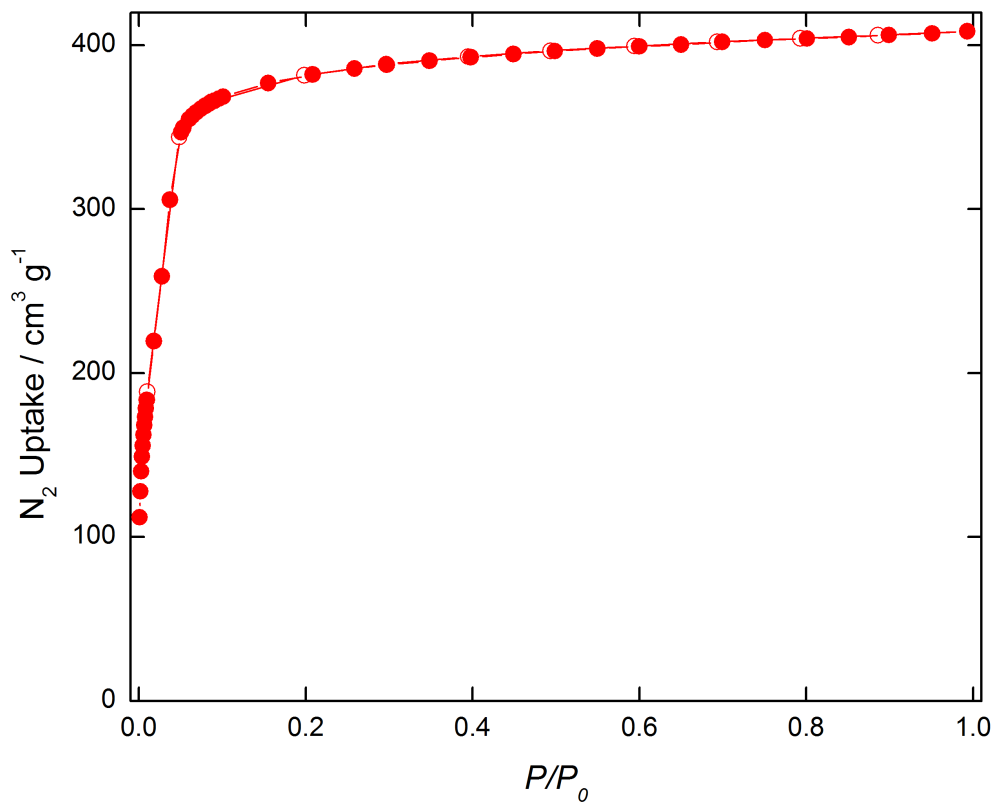


409

410 **Supplementary Figure 6.** N<sub>2</sub> adsorption isotherm of pristine MOF-808 at 77K.



411  
412 **Supplementary Figure 19.** N<sub>2</sub> adsorption isotherms of MOF-808-SO<sub>4</sub> (blue circles) and dehydrated  
413 MOF-808-SO<sub>4</sub> (red circles) at 77K.



414

415 **Supplementary Figure 20.** N<sub>2</sub> adsorption isotherm of at 77K.

416

## 417 Section 7: Solid State NMR Spectroscopy

418

419 **<sup>31</sup>P Solid State NMR experiments.** Samples for <sup>31</sup>P Solid State NMR were prepared  
420 following a slightly modified procedure based on the previously reported method (4). Briefly,  
421 around 100 mg MOF sample was activated as described in Section 1, and 1.5 mL of 0.2 M  
422 TMPO in chloroform was added and mixed with the MOF sample. This suspension was then  
423 evacuated under dynamic vacuum at room temperature overnight, then at 50 °C for 8 hours. The  
424 resulting solid was then packed into 75 uL Doty XC5 Kel-F sealing cells under argon  
425 atmosphere, and inserted into a Doty 5 mm thin-wall zirconia rotor with Kel-F turbine caps.  
426 Solid state NMR spectra were collected using a 7.05 T magnet with a Tecmag Discovery  
427 spectrometer operating at 300.13 MHz for <sup>1</sup>H and 121.5 MHz for <sup>31</sup>P. <sup>31</sup>P chemical shifts were  
428 externally referenced to aqueous H<sub>3</sub>PO<sub>4</sub> (85%) at 0 ppm. Experiments were performed on a Doty  
429 5-mm triple resonance MAS probe operating in <sup>1</sup>H/<sup>31</sup>P/<sup>87</sup>Sr mode. Magic angle spinning (MAS)  
430 was used to collect high resolution NMR spectra at a spinning rate of 8 kHz. <sup>31</sup>P NMR  
431 experiments were performed with a <sup>31</sup>P 90° pulse time of 6 μs and a continuous wave <sup>1</sup>H  
432 decoupling B<sub>1</sub> field of 60 kHz. Spectra were collected with a recycle delay time of 11 s, and were  
433 processed with 5 Hz line broadening.

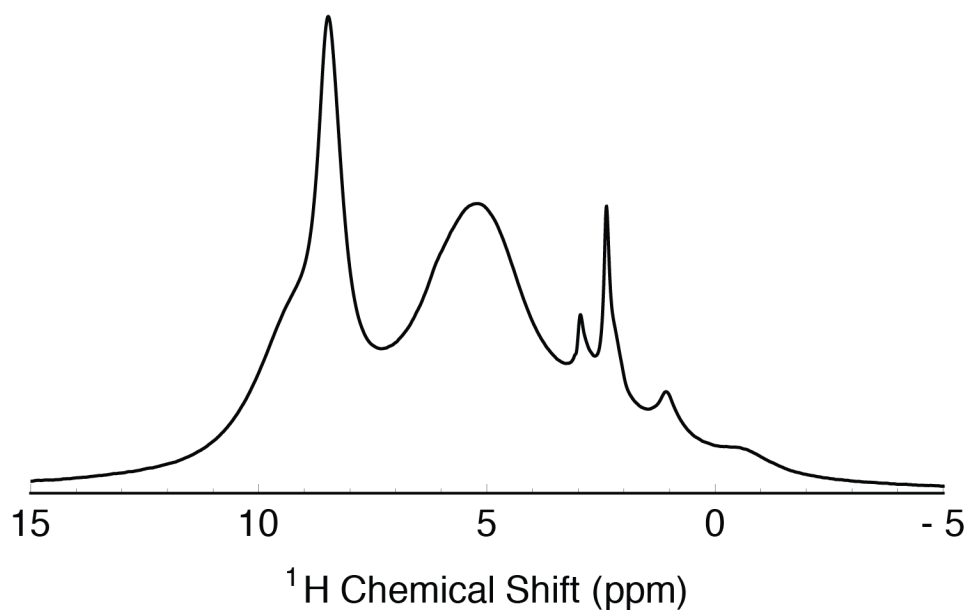
434 **<sup>1</sup>H Solid State NMR experiments.** For direct <sup>1</sup>H MAS experiments, samples of MOF-  
435 808-SO<sub>4</sub> and dehydrated MOF-808-SO<sub>4</sub> were packed into Doty 5 mm thick-wall zirconia rotors  
436 with Kel-F turbine caps under argon atmosphere. Solid state NMR spectra were collected using a  
437 7.05 T magnet with a Tecmag Apollo spectrometer operating at 300.27 MHz for <sup>1</sup>H. <sup>1</sup>H chemical  
438 shifts were externally referenced to TMS at 0 ppm. Experiments were performed on a Doty 5-  
439 mm triple resonance MAS probe. Magic angle spinning (MAS) was used to collect high  
440 resolution NMR spectra at a spinning rate of 6 kHz. Pulse-acquire <sup>1</sup>H NMR experiments were  
441 performed with a <sup>1</sup>H 90° pulse time of 4 μs and a recycle delay time of 5 s. The <sup>1</sup>H back-to-back  
442 (BABA) rotor-synchronized DQ recoupling experiment was run at 11.74 T field using a Bruker  
443 AV-500 spectrometer operating at 500.2 MHz for <sup>1</sup>H. The experiment was performed using a  
444 Bruker 4 mm CP-MAS probe at an MAS rate of 12.5 kHz, with a 4 μs <sup>1</sup>H 90° pulse time and  
445 recorded using two rotor period cycles with the BABA sequence for excitation and reconversion  
446 of the double quantum coherences. Spectra were processed without apodization.

447 The MOF-808-SO<sub>4</sub> system differs from typical organic molecular solids in that there is  
448 not a dense network of protons. The majority of proton-proton distances on a single zirconium  
449 cluster are greater than 2 Å, and distance between clusters imposed by the MOF framework  
450 reduces the influence of long-range homonuclear dipolar couplings. The spin interactions in this  
451 system thus approach the limit of isolated two-spin dipolar couplings, which can be easily  
452 resolved with magic-angle spinning (MAS) even at relatively low spinning rates.

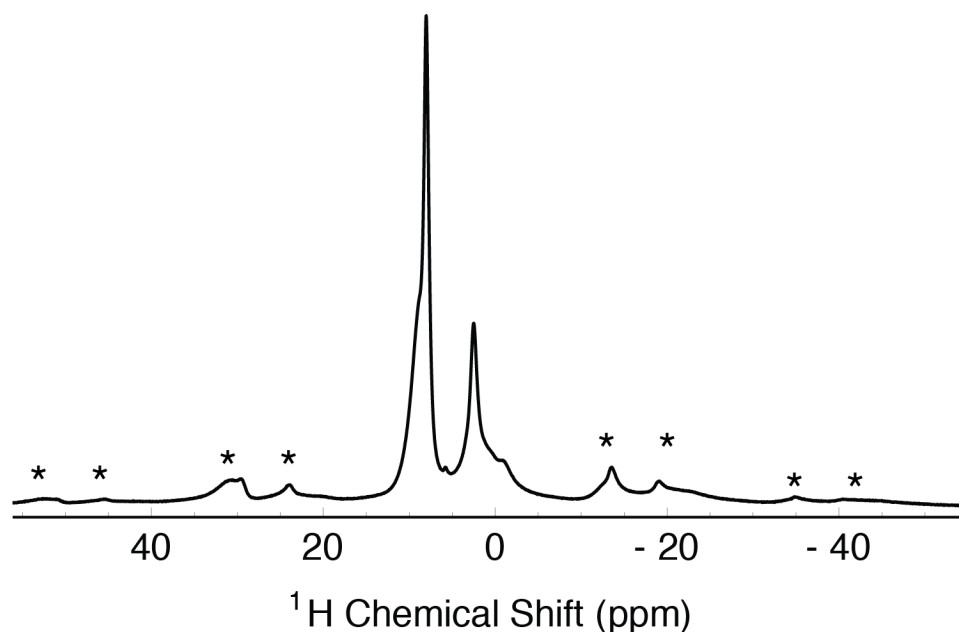
453 **<sup>1</sup>H NMR Chemical shift calculations.** The NMR chemical shielding tensors for the  
454 atoms in two of the DFT structure-optimized clusters were calculated using mPW1PW91 and the  
455 default gauge-independent atomic orbital (GIAO) method available in Gaussian 09 with the basis  
456 set 6-311++G(2d,2p) for all atom types excluding Zr, for which the basis lan12dz, 5d, 7f was  
457 used (7 - 9). <sup>1</sup>H chemical shifts were referenced to tetramethylsilane, for which the structure and  
458 NMR shifts were calculated at the same level of theory. No scaling factor was applied to the <sup>1</sup>H  
459 chemical shifts, and as such we expect significant deviation from experimentally observed shifts;  
460 instead the relative magnitudes of, and differences between, the calculated shift values were used  
461 as a tool to inform the assignment of peaks in the experimental <sup>1</sup>H NMR results.

462

463 Exposure to atmospheric moisture (approximately 50% RH at 20 °C) also results in the  
464 loss of acidity as observed previously (4), meaning water is a key component in the acidic  
465 properties of MOF-808-SO<sub>4</sub>, but not when it is in excess. This observation in MOF-808-SO<sub>4</sub> is  
466 consistent with the proposition that the acid catalysis of its analogue, sulfated zirconia, only  
467 operates in a specific humidity range (10). Supplementary figure 21 shows a <sup>1</sup>H NMR spectrum  
468 after exposure to atmospheric moisture. There is a broad resonance centered about 5.2 ppm  
469 which we assign as adsorbed water. The presence of this excess water should level the material's  
470 acidity to the acidity level of the hydronium ion. As the resonance of bulk water is 4.8 ppm, the  
471 slight upfield shift could be due to a lowering of the pH of the adsorbed water by some  
472 deprotonation of the active site. Several other new peaks are present in the spectrum of the  
473 hydrated MOF, which are likely protons in new hydroxide and adsorbed water species resulting  
474 from the introduction of water vapor, but it is difficult to assign them precisely.  
475



476  
477 **Supplementary Figure 21.** Plot of the <sup>1</sup>H NMR spectra of MOF-808-SO<sub>4</sub> exposed to atmospheric  
478 moisture (approximately 50% RH at 20 °C).  
479



480

481 **Supplementary Figure 22.** Plot of the  $^1\text{H}$  NMR spectra of MOF-808- $\text{SO}_4$  seen in main text figure  
 482 5a, but displayed with the frequency range extended to show the manifold of spinning sidebands  
 483 (denoted by asterisks).

484

485 **Supplementary Table 4.** Calculated  $^1\text{H}$  NMR Chemical Shifts for ‘2wopp\_optS,’ a cluster model  
 486 with two chelating sulfates with adjacent water molecules

Atom Label	Chemical Group	Chemical Shift (ppm)	Notes
18	$\mu^i\text{-OH}$	9.3889	H-bonded to a chelating $\text{SO}_4$
23	$\mu^i\text{-OH}$	5.7650	Adjacent to $\text{H}_2\text{O}$ but not H-bonded
26	$\mu^i\text{-OH}$	5.1614	Isolated on cluster
34	$\mu^i\text{-OH}$	2.8991	Enclosed between the three terminal acetates at the end of the cluster
52	$\mu^i\text{-OH}$	7.1503	
53	$\mu^i\text{-OH}$	6.2171	
54	$\text{H}_2\text{O}$	13.7517	Strongly H-bonded to a chelating $\text{SO}_4$ , and $\text{SO}_4$ is H-bonded to 18, aka “ $\text{H}_a$ ” in the acid site
74	$\text{H}_2\text{O}$	4.6606	On $\text{H}_2\text{O}$ with 54, aka “ $\text{H}_b$ ” in the acid site
79	$\text{H}_2\text{O}$	5.6023	On $\text{H}_2\text{O}$ with 80, aka “ $\text{H}_c$ ” in the

acid site

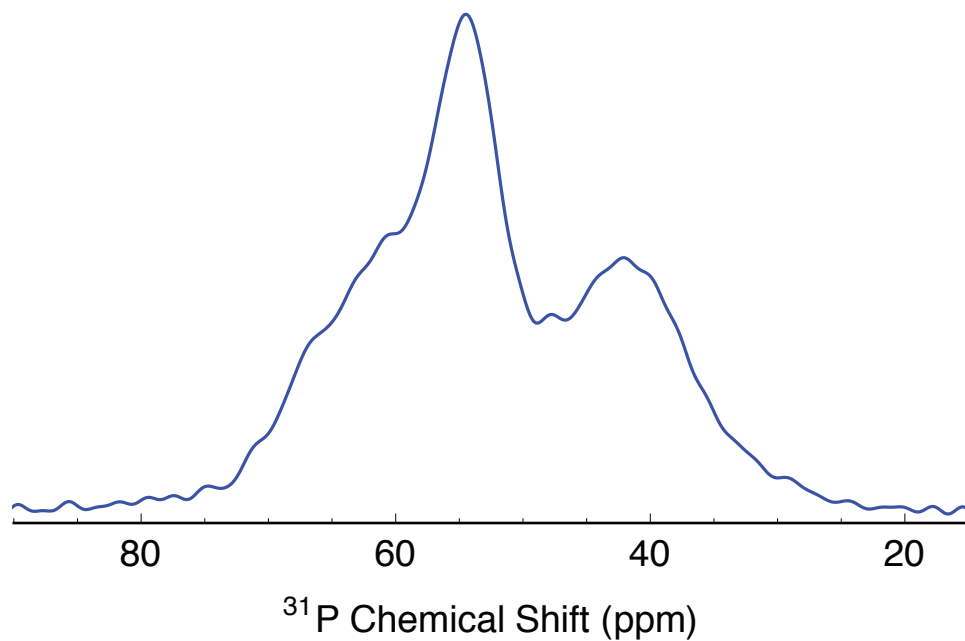
80	H <sub>2</sub> O	10.7284	Strongly H-bonded to a chelating SO <sub>4</sub> , which itself has no H-bond to μ <sup>-</sup> -OH, aka “H <sub>a</sub> ” in the acid site
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487

488 **Supplementary Table 5.** Calculated <sup>1</sup>H NMR Chemical Shifts for ‘2opthighS,’ a cluster model  
489 with one bridging and one chelating sulfate, and one adsorbed water molecule.

Atom Label	Chemical Group	Chemical Shift (ppm)	Notes
21	μ <sup>-</sup> -OH	9.4348	H-bonded to chelating SO <sub>4</sub>
26	μ <sup>-</sup> -OH	10.0635	H-bonded to bridging SO <sub>4</sub>
29	μ <sup>-</sup> -OH	5.4765	
37	μ <sup>-</sup> -OH	3.1569	Enclosed between the three terminal acetates at the end of the cluster
54	μ <sup>-</sup> -OH	5.0904	
55	μ <sup>-</sup> -OH	10.979	Partial H-bond to SO <sub>4</sub>
76	H <sub>2</sub> O	3.2215	On H <sub>2</sub> O with 77
77	H <sub>2</sub> O	5.2524	Adjacent to bridging SO <sub>4</sub>

490



491

492 **Supplementary Figure 23.** Plot of the  $^{31}\text{P}$  NMR spectra of trimethylphosphine oxide (TMPO)  
493 adsorbed into MOF-808- $\text{SeO}_4$ . Though not as prominent as the peak at 69 ppm for MOF-808- $\text{SO}_4$   
494 (Main text figure 3), there is signal intensity in the region of 60-70 ppm, suggesting the presence  
495 of strong acid sites in MOF-808- $\text{SeO}_4$ . The peak centered at 42 ppm is due to excess TMPO that  
496 is not interacting with acid sites directly. Other peaks in the spectrum belong to TMPO adsorbed  
497 at various  $\mu^1\text{-OH}$ ,  $\mu^3\text{-OH}$ , and water sites.

498

499



## 500 Section 8: Infrared Absorption Spectroscopy

501

502 Infrared (IR) absorption spectra of activated and dehydrated MOF samples were  
503 measured in transmission mode on a Thermo Scientific Nicolet 6700 FTIR spectrometer with a  
504 resolution of 1  $\text{cm}^{-1}$ . The sample cell assembly process was performed in a  $\text{N}_2$  glove box. A  
505 minute amount of the MOF powder sample was sandwiched between two  $\text{CaF}_2$  windows to form  
506 a thin layer of 100 microns. The sample thickness was controlled by a Teflon spacer. Then the  
507 windows with the sample were assembled into a gas-tight IR sandwich sample cell to seal. After  
508 the assembly, the sample cell can be taken outside of the glove box without being compromised  
509 by moisture in air. The sample cell was then transferred to the measurement chamber of the  
510 FTIR spectrometer purged with  $\text{CO}_2$ -free dry air. The background spectrum was simply taken on  
511 the  $\text{CO}_2$ -free dry air for calculating the absorbance. Since the sample spectra were acquired in  
512 transmission mode on a powder sample, a large offset due to scattering is present in all the  
513 measurements.

514 Infrared spectroscopy of MOF-808- $\text{SO}_4$  before and after dehydration reveals changes in  
515 the region associated with O-H vibrations, where at least seven O-H stretches are observed in the  
516 spectral region of 3550-3800  $\text{cm}^{-1}$  (Supplementary figures 24, 25). Prior to dehydration, there is a  
517 group of overlapping peaks in the range of 3550-3725  $\text{cm}^{-1}$ , and two more distinct stretches  
518 located at 3737 and 3767  $\text{cm}^{-1}$ . After dehydration, these two peaks at 3737 and 3767  $\text{cm}^{-1}$  are no  
519 longer present, indicating that they originate from O-H vibrations belonging to adsorbed water.  
520 We assign the peaks in the range of 3550-3725  $\text{cm}^{-1}$  as O-H vibrations belonging to various  $\mu$ -  
521 OH and  $\mu$ -OH groups. The strong blue shift of two O-H stretches at 3737 and 3767  $\text{cm}^{-1}$  is  
522 characteristic of exposed hydroxyl groups not participating in hydrogen bonding (11, 12). One of  
523 these two peaks must belong to the O-H<sub>s</sub> stretch in the acid site, while the other is likely an  
524 asymmetric stretching mode for terminal water not participating in a hydrogen bond to chelating  
525 sulfate. Our assignments are consistent with DFT calculations for the vibrational modes of our  
526 modeled clusters which were done using M06-L in Gaussian 09 with the basis set 6-31+G(d,p)  
527 for all atom types excluding Zr, for which the basis lan12dz, 5d, 7f was used (9,13,14). The  
528 values for the O-H<sub>s</sub> vibrational frequencies were calculated to be within 100-200  $\text{cm}^{-1}$  of the  
529 peaks associated with O-H vibrations on water not participating in a hydrogen bond. However,  
530 the values for O-H<sub>s</sub> vibrations were calculated to be present 1000-1500  $\text{cm}^{-1}$  lower than the O-H<sub>s</sub>  
531 vibrations. The O-H<sub>s</sub> vibration should be located at a lower frequency due to the hydrogen  
532 bonding interaction with sulfate. However, no absorption features between 2000-3500  $\text{cm}^{-1}$  were  
533 observed in the experiment that were not otherwise attributable to C-H modes on the BTC linker,  
534 due to a low signal to noise ratio (Supplementary figure 24b). We believe that the O-H<sub>s</sub> vibration  
535 likely is not at such a low frequency as calculated by DFT, but rather may be present in the  
536 region between 3550-3725  $\text{cm}^{-1}$ . However, due to the large degree of overlapping peaks in the  
537 region below 3700  $\text{cm}^{-1}$ , it is difficult to see changes in this region after the water loss, but the  
538 presence of these blue-shifted O-H stretches and their subsequent loss after dehydration is  
539 consistent with our proposed Brønsted acid site.

540

541

542 **Supplementary Table 6.** Calculated IR frequencies for O-H vibrational modes in '2wopp\_optS,' a  
543 cluster model with two chelating sulfates with adjacent water molecules.

Frequency ( $\text{cm}^{-1}$ )	Chemical Group primarily associated with the calculated vibrational mode
--------------------------------	--

3779	$\mu$ -OH
3747	$\mu$ -OH
3745	$\mu$ -OH
3718	$\mu$ -OH
3679	$\mu$ -OH
3657	O-H <sub>s</sub> on H <sub>2</sub> O for site 1
3588	O-H <sub>s</sub> on H <sub>2</sub> O for site 2
3220	$\mu$ -OH
2988	O-H <sub>i</sub> on H <sub>2</sub> O for site 2
2604	O-H <sub>i</sub> on H <sub>2</sub> O for site 1

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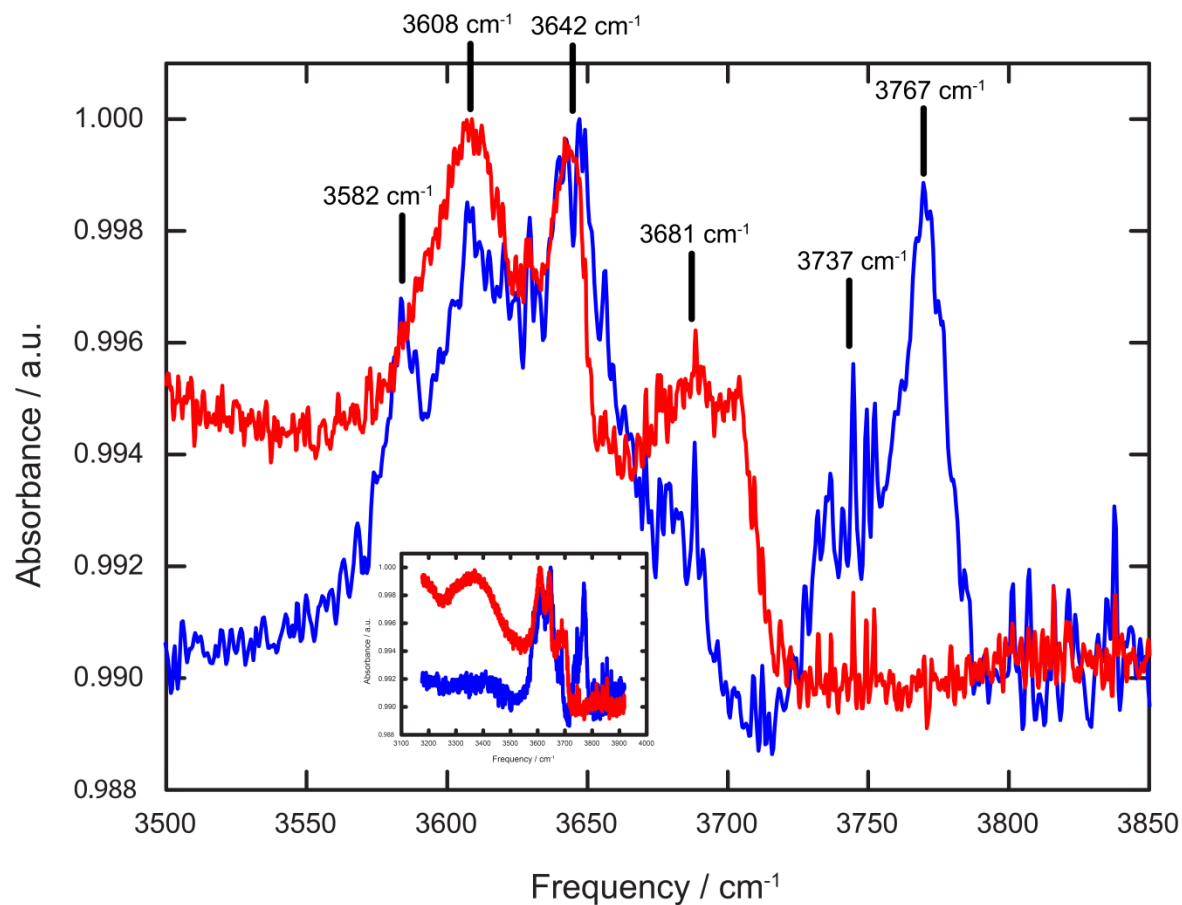
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545 **Supplementary Table 7.** Calculated <sup>1</sup>H NMR Chemical Shifts for ‘2opthighS,’ a cluster model  
546 with one bridging and one chelating sulfate, and one adsorbed water molecule.

Frequency (cm <sup>-1</sup> )	Chemical Group primarily associated with the calculated vibrational mode
3824	$\mu$ -OH
3780	$\mu$ -OH
3766	$\mu$ -OH
3750	Asymmetric stretch H <sub>2</sub> O
3532	$\mu$ -OH
3526	Symmetric stretch H <sub>2</sub> O
3241	$\mu$ -OH
3223	$\mu$ -OH

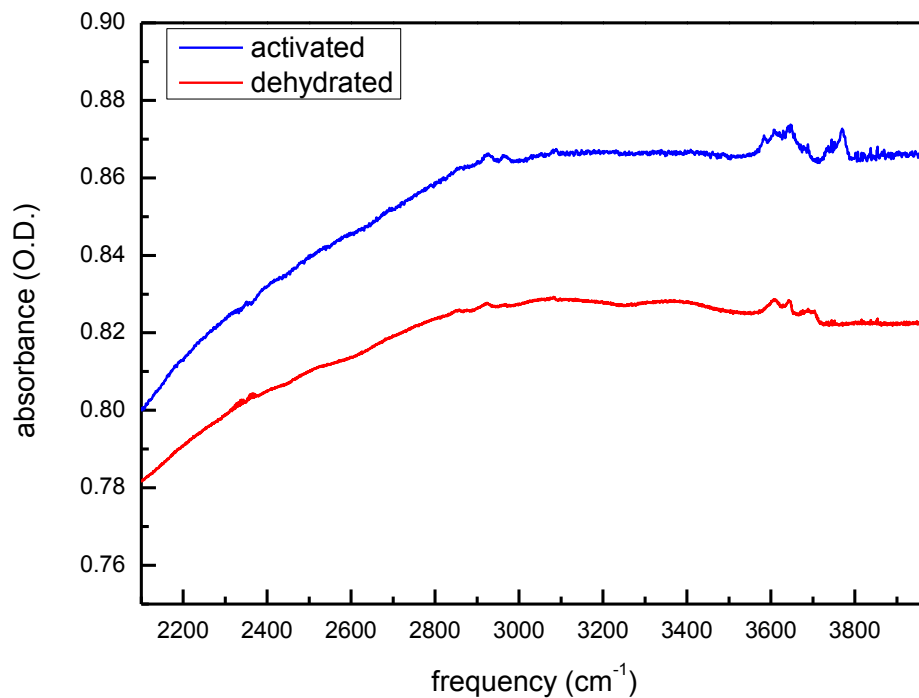
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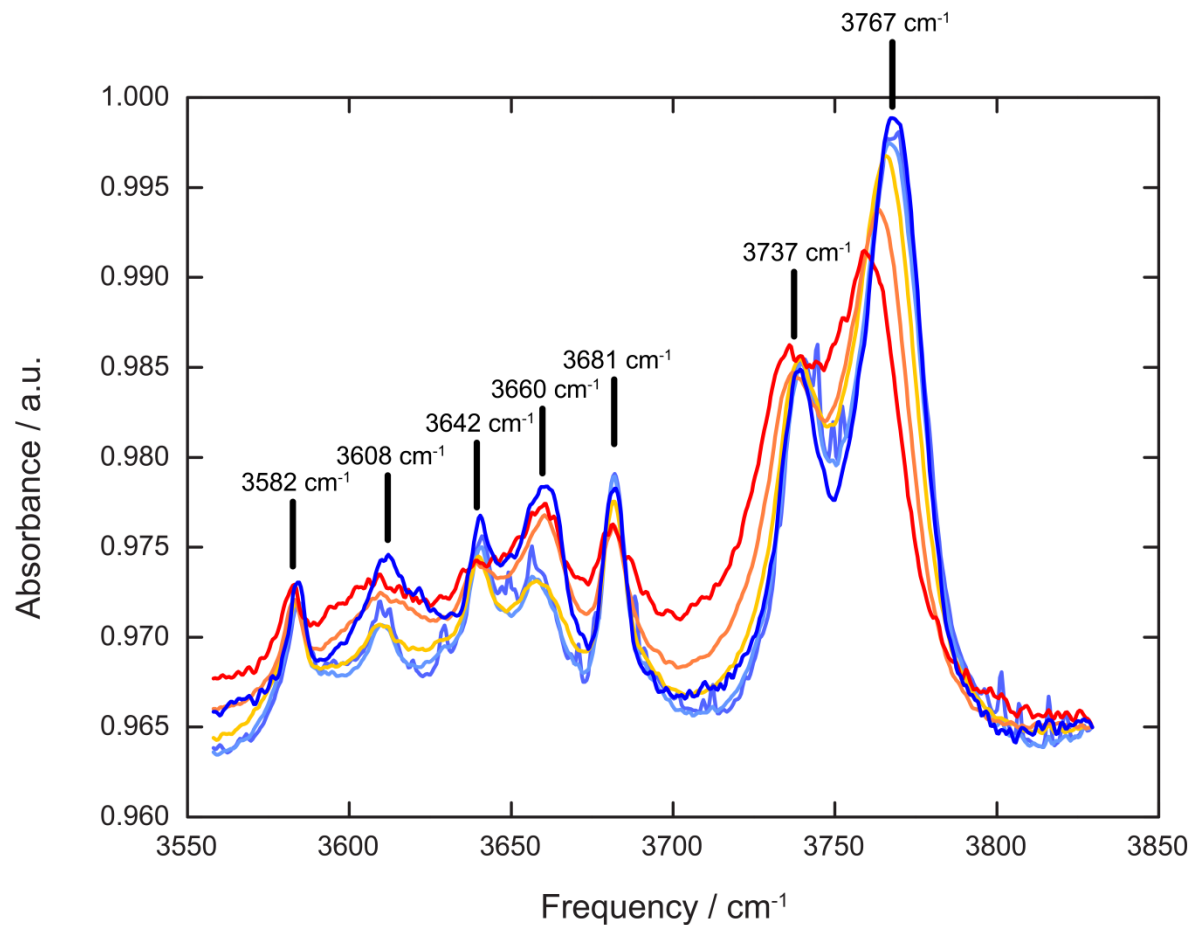
549 **Supplementary Figure 24a.** A comparison of the IR spectra of activated (blue) and dehydrated (red)  
 550 stages of MOF-808-SO<sub>4</sub> in the spectral region relevant to O-H stretches. The most notable feature is the  
 551 loss of the two blue-side peaks at 3737 and 3767 cm<sup>-1</sup>. The inset is included to show the broad feature  
 552 centered around 3350 cm<sup>-1</sup> in the dehydrated structure, which corresponds to a minute amount of water  
 553 adsorbed onto the MOF-808-SO<sub>4</sub> crystals.



554

555 **Supplementary Figure 24b.** Expanded range IR spectra shown in supplementary figure 24a, showing the  
556 lack of distinct features between 2000-3000 cm<sup>-1</sup> that cannot otherwise be attributed to aromatic C-H  
557 vibrational modes of the linker, and the low signal-to-noise in the region between 3000-4000 cm<sup>-1</sup> that was  
558 characteristic of our IR studies for multiple batches of this material.

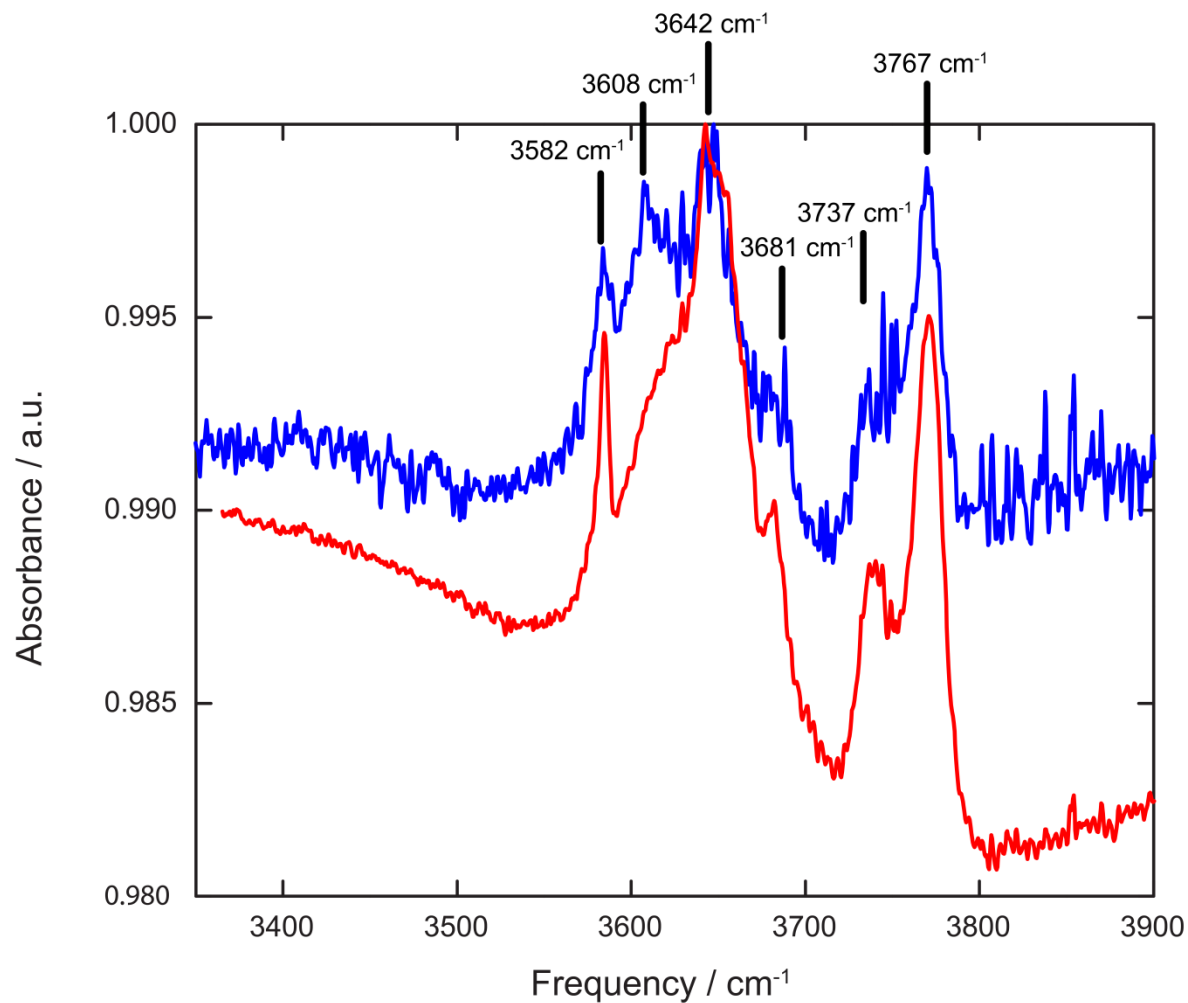
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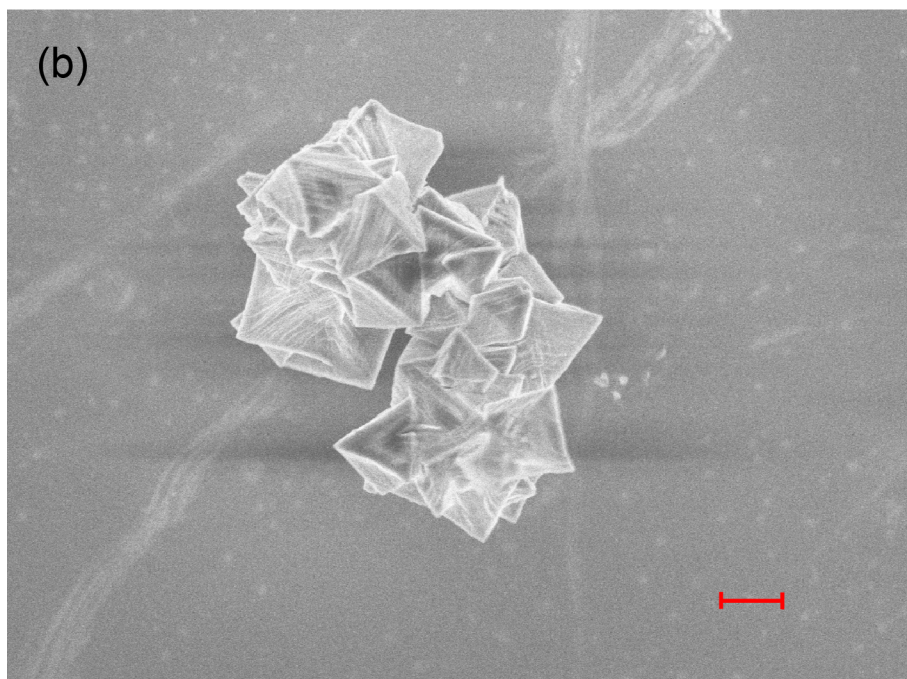
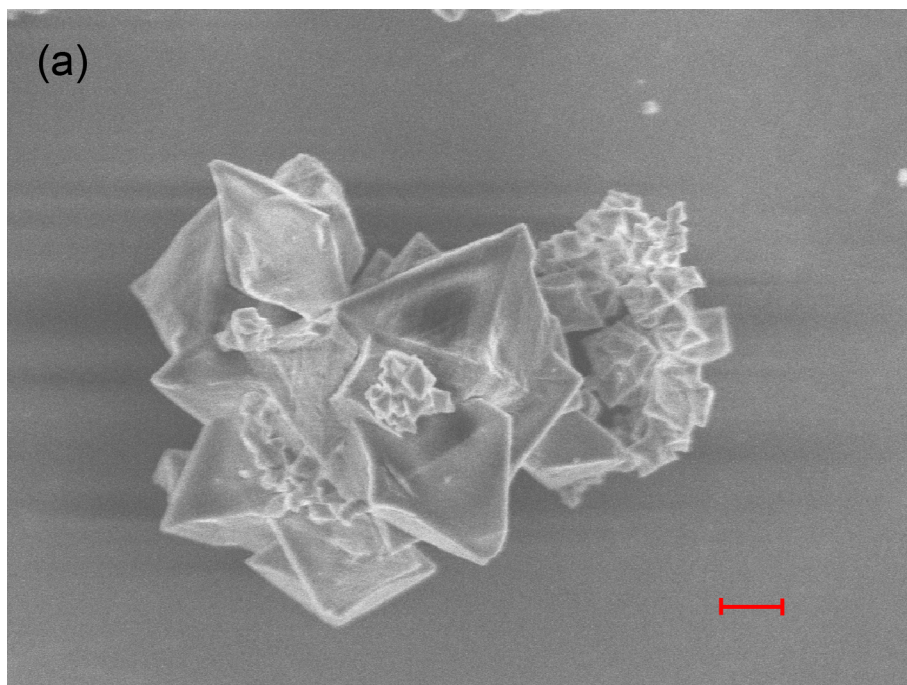
561 **Supplementary Figure 25.** A comparison of the IR spectra of a different batch (compared to  
 562 supplementary figure 24) of activated MOF-808-SO<sub>4</sub> measured at different temperatures. Heating the  
 563 sample broadens the peaks as the local environment becomes more disordered due to thermal motion. The  
 564 process is reversible between room temperature and 200 °C. The measurement was started at room  
 565 temperature (light blue) then heated gradually to 40 °C (light purple), 80 °C (yellow), 125 °C (orange),  
 566 200 °C (red), and cooled back down to room temperature (dark blue).

567



568  
 569 **Supplementary Figure 26.** A comparison of the *in situ* IR spectra of activated MOF-808-SO<sub>4</sub> (blue) and  
 570 MOF-808-SeO<sub>4</sub> (red) in the energy region relevant to O-H stretches. Both samples display the same O-H  
 571 stretch features, indicating the water and hydroxide environments in both samples are similar.

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582  
583 **Supplementary Figure 27.** Scanning electron microscope (SEM) images of (a) MOF-808-SO<sub>4</sub> and (b)  
584 MOF-808-SeO<sub>4</sub> following activation under dynamic vacuum at 120 °C (scale bar 1 μm).

587 Cluster optimizations were performed and geometrically optimized using density  
588 functional theory (DFT), based on the formula  $Zr_6O_4(OH)_4(C_2H_3O_2)_6(SO_4)_2(OH)_2(OH_2)_x$ , where  $x = 2$   
589 or 3. Acetate groups were used instead of BTC as a terminal ligand. The functional B97-D3 was  
590 chosen, which is the B97 functional with Grimme's dispersion term added on to account for  
591 dispersive effects that B97 misses. The chosen basis set was 6-31G\* for all non-Zr atoms. For  
592 Zr, the CRENBL effective core potential was used for core electrons, with the matching  
593 CRENBL basis for valence electrons. A very fine grid consisting of 90 radial points and 590  
594 angular points was selected for the numerical integration step to account for exchange-  
595 correlation. Early evaluation of cluster models by classical force field geometry optimization  
596 followed by energy calculation found that an uneven distribution of charge or chemical species  
597 resulted in much higher energy configurations, or even failed to converge. For instance, a  
598 configuration where two hydroxides are localized on one zirconium atom and two open metal  
599 sites are assigned to another was 300-400 kJ mol<sup>-1</sup> higher in energy than both zirconium atoms  
600 assigned a single hydroxide group each, depending on the exact configuration.  
601

602



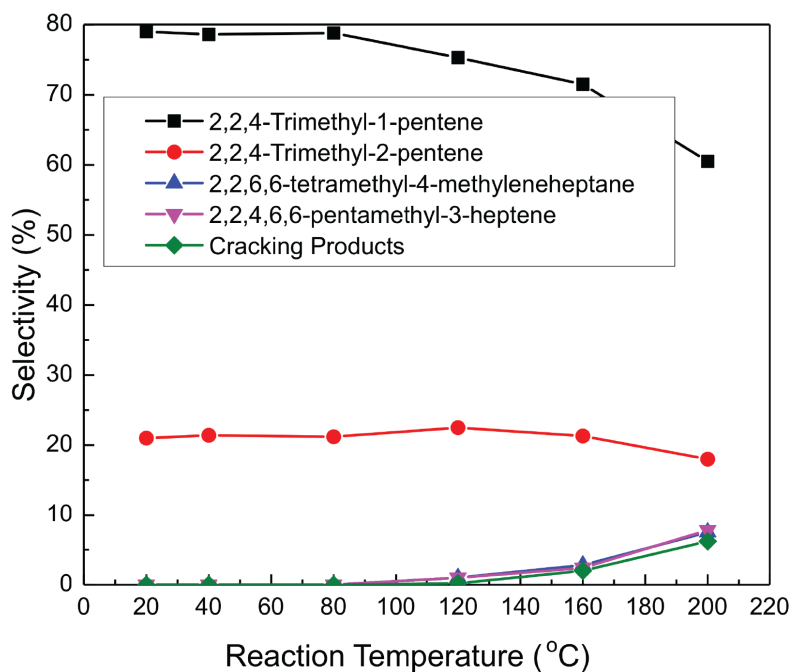
603 **Section 11: Acid Catalysis of Isobutene**  
604

605 A flow reactor set-up was used to test the catalytic performance of various acid catalysts:  
606 H-ZSM-5 (ammonium type, Si/Al ratio 20/1, Alfa Aesar), Amberlyst (Sigma Aldrich) and  
607 sulfated zirconia. Sulfated zirconia was prepared as explained in section 1. Gas feeds of 2 mL  
608 min<sup>-1</sup> isobutene and 20 mL min<sup>-1</sup> He regulated by a mass flow controller to be at 1 atm, were  
609 mixed together and directed towards the catalyst (90 mg), loaded into a tube furnace. The  
610 temperature of the catalyst bed was monitored by a K-type thermocouple controlled by a PID  
611 controller. The products were analyzed using an HP 6890 series GC-MS with a Supelco column  
612 (phase 23% SP-1700 support, 80/100 chromosorb PAW). Since the number of acid sites for each  
613 catalyst is unknown, the catalysts were compared by mass. The conversion and selectivity of  
614 isobutene and isoootene were calculated using the following equations:

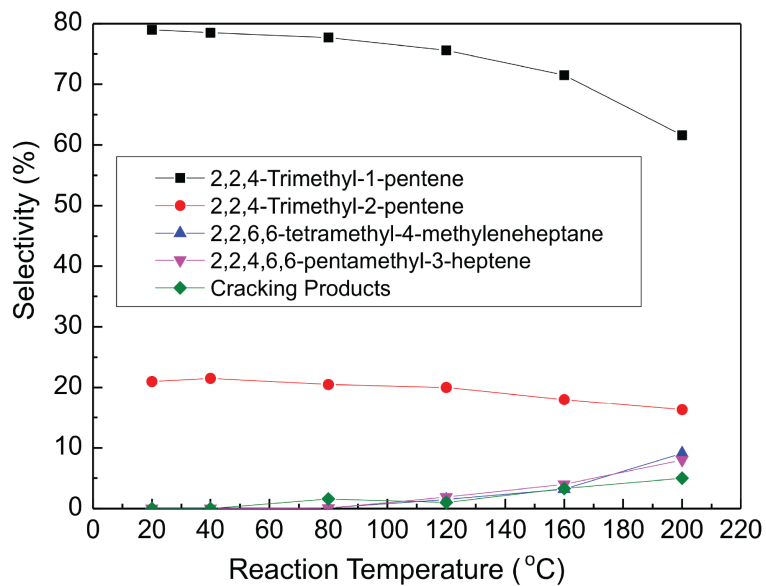
$$\text{Isobutene conversion (\%)} = \frac{\text{Isobutene}_{\text{in}} - \text{Isobutene}_{\text{out}}}{\text{Isobutene}_{\text{in}}} \times 100$$

$$\text{Isooctene selectivity (\%)} = \frac{n\text{Isooctene}}{n\text{Dimers} + n\text{Trimers}} \times 100$$

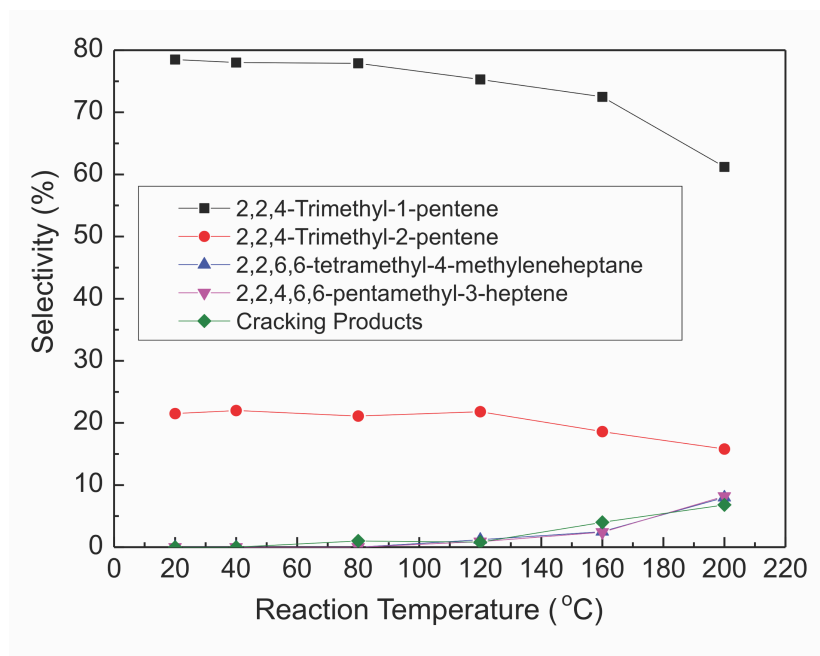
615 where n is number of hydrocarbons in moles.



616  
617 **Supplementary Figure 28.** Product distribution for the dimerization of isobutene using MOF-808-SO<sub>4</sub>.



618  
 619 **Supplementary Figure 29.** Product distribution for the dimerization of isobutene using dehydrated  
 620 MOF-808-SO<sub>4</sub>.  
 621



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 623 **Supplementary Figure 30.** Product distribution for the dimerization of isobutene using sulfated zirconia.  
 624

625 **Section 12: References**

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