Electronic Supplementary Information

Computational Determination of Coordination Structure Impact on Adsorption and Acidity of Pristine and Sulfated MOF-808

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1. Additional computational details

Periodic models were optimized in vacuum to better than 0.003 Å for atom displacement and 0.00045 au for the forces. Cluster models were optimized in vacuum to better than 0.0018 Å for the atom displacement and 0.00045 au for the forces. Frequency analysis were performed for selected cluster models at 298.15 K and 1 atom.

The geometric surface areas of the MOFs were computed using the *RASPA* program in which the surface area is determined based on the overlap between probe (Ar) and framework atoms.[1]

2. Summary of optimized MOF-808 models

Table S1. Summary of optimized periodic MOF-808 models. Topologies are described in terms of sections and sub-sections of a Zr_6 node as indicated in Figure 2b in the main text. Averaged lattice constants ($a = b = c$) are given in Å.

Model	Zr1 - Zr2		Zr2 - Zr3		Zr3 - Zr4		Zr4 - Zr5		Zr5 - Zr6		Zr6 - Zr1		H_2O in pore	$a = b = c$
	α	β	α	β	α	β	α	β	α	β	α	β		
I	μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		—	35.282
II	μ^2 formate		κ^1 formate	—	μ^2 formate		κ^1 formate	—	μ^2 formate		κ^1 formate	—	—	35.131
III	μ^2 formate		κ^1 formate	—	κ^1 formate	—	κ^1 formate	—	κ^1 formate	—	κ^1 formate	—	—	35.000
IV	μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		hydroxo	—	—	35.270
V	μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		hydroxo	aqua	—	35.391
VI	μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		aqua	aqua	—	35.411
VII	κ^1 formate	—	κ^1 formate	—	κ^1 formate	—	κ^1 formate	—	κ^1 formate	—	κ^1 formate	—	—	34.947
VIII	κ^2 formate	—	κ^2 formate	—	κ^2 formate	—	κ^2 formate	—	κ^2 formate	—	κ^2 formate	—	—	35.362
IX	μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		1	35.278
X	μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		2	35.274
XI	μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		3	35.253
XII	μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		4	35.222
XIII	μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		5	35.186
XIV	μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		μ^2 formate		6	35.132
XV	κ^1 formate	aqua	κ^1 formate	aqua	κ^1 formate	aqua	κ^1 formate	aqua	κ^1 formate	aqua	κ^1 formate	aqua	—	35.529
XVI	κ^1 formate	aqua	κ^1 formate	aqua	κ^1 formate	aqua	κ^1 formate	aqua	κ^1 formate	aqua	κ^1 formate	aqua	5	35.298
XVII	κ^1 formate	aqua	μ^2 formate		κ^1 formate	aqua	μ^2 formate		κ^1 formate	aqua	μ^2 formate		—	35.331
XVIII	aqua	hydroxo	aqua	hydroxo	aqua	hydroxo	aqua	hydroxo	aqua	hydroxo	aqua	hydroxo	—	35.409

3. Summary of optimized sulfated MOF-808 models

Table S2. Topologies of S-MOF-808 models. Topologies are described in terms of sections and sub-sections of a Zr_6 node shown in Figure S1 below. Ligands that occupy two columns are bridging across two Zr atoms. Averaged proton affinity (PA) are given in kcal/mol. The cluster model of Model **K** was constructed based on model **A**, and the PA value for **A** was estimated based on single point calculations.

Model	Zr1		Zr2		Zr3		Zr4		Zr5		Zr6		PA
	α	β	α	β	α	β	α	β	α	β	α	β	
A	η^2 sulfate		aqua	aqua	aqua	hydroxo	η^2 sulfate		aqua	aqua	hydroxo	aqua	315.89
B	η^2 sulfate		aqua	aqua	hydroxo	aqua	hydroxo	aqua	hydroxo	aqua	hydroxo	aqua	326.53
C	η^2 sulfate		aqua	aqua	η^2 sulfate		aqua	aqua	η^2 sulfate		aqua	aqua	308.84
D*	η^2 sulfate		aqua	aqua	hydroxo	aqua	η^2 sulfate		aqua	aqua	aqua	aqua	255.14
E	hydroxo	η^2 hydrogen sulfate	hydroxo	aqua	aqua	aqua	η^2 sulfate		hydroxo	aqua	aqua	aqua	316.91
F**	η^2 sulfate		aqua	aqua	η^2 sulfate		η^2 sulfate		aqua	aqua	hydroxo	aqua	363.38
G	η^2 sulfate		aqua	aqua	hydroxo	aqua	aqua	hydroxo	η^2 sulfate		aqua	aqua	317.58
H**	η^2 sulfate		aqua	aqua	aqua	hydroxo	η^2 sulfate		hydroxo	aqua	hydroxo	aqua	374.27
J	η^2 sulfate		aqua	aqua	η^2 sulfate		η^2 sulfate		aqua	aqua	aqua	aqua	306.37
K***	η^2 bisulfate		hydroxo	aqua	aqua	hydroxo	η^2 bisulfate		aqua	hydroxo	aqua	hydroxo	309.79

*positively charged; **negatively charged; ***based on single point calcula

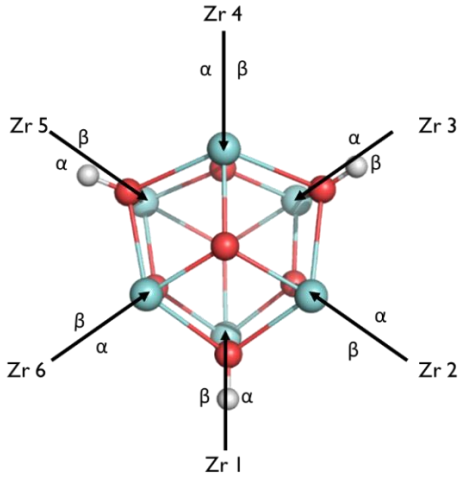

Figure S1. Bare Zr_6 node with binding ligands and linkers removed for clarity. Each Zr atom is assigned section α and β. For S-MOF-808 models, each section can be occupied by sulfate, water, or hydroxo ligands. The different arrangements of ligands give different topologies (i.e. different models) that are summarized in Table S2 above.

4. Additional discussion on ensemble-averaged proton affinities

The ensemble-averaged proton affinities (<PAs>) were calculated for three hydrogens. H1 and H2 of model **A** as shown in Figure 9 of the main text and H23 of model **XIV** (see above sections for description of this model). For H1, a total of 15 MOF-H equilibrium states were considered. These equilibrium states were constructed by protonating suitable ligands, including hydroxo, μ-oxo, and sulfate, around the Zr6 node using proton H1. The same procedure was applied to atom H2 of model **A** and atom H23 of model **XIV** with a total of 15 and 10 equilibrium states considered, respectively.

For H1, H2, and H23, the computed <PAs> are 317.05, 317.19, and 341.55 kcal/mol, respectively. The PAs as defined in Equation 1 in the main text are 317.61, 317.61, and 341.55 kcal/mol for H1, H2, and H23, respectively. The <0.6 kcal/mol differences between <PA> and PA demonstrate that not considering MOF-H equilibrium states is an accurate approximation.

5. Additional correlation between deprotonation energy and Zr–O bond dissociation energy

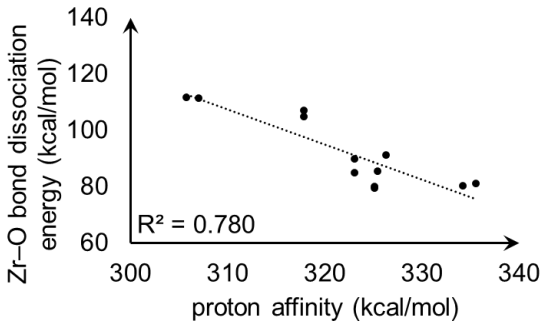

Figure S2. Correlation between deprotonation energy (kcal/mol) and heterolytic Zr–O bond dissociation energy (kcal/mol) in model **B**.

References

1. D. Dubbeldam, S. Calero, D. E. Ellis and R. Q. Snurr, *Mol. Simul.*, 2016, **42**, 81–101.