Supplementary Information

Synthesis and structural properties of a 2D Zn(II) dodecahydroxy-*closo*-dodecaborate coordination polymer

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Density Functional Theory Calculations

Calculations were performed using SCM ADF software. XYZ coordinates for $[B_{12}(OH)_{12}]^{2-}$ determined by refinement of the powder pattern were imported, and the structure was subsequently modified within the software to create a monodentate, bidentate, and fully bound cluster (two monodentate and one bidentate). To reduce the computational complexity, Zn(II) ions were replaced by electron-withdrawing $-CF_3$ or $-CF_2$ groups for the monodentate and bidentate interactions, respectively. Geometry pre-optimizations were performed, followed by full geometry optimizations at the GGA:PBE-D3(BJ) theory level with a DZP basis set and scalar relativistic effects considered. Electron densities were approximated by visualizing the Mulliken charges from the optimized geometries.

DFT Geometry Coordinates

Monodentate Model

B	10.03641626	0.70477989	4.25036940
B	9.86041612	0.91832069	1.37492897
B	10.84443567	1.33883616	2.78722167
B	9.07410742	1.39416003	2.90217249
B	11.31314064	-0.04102169	1.77195483
B	8.54657298	-0.09218594	3.70593632
B	8.42750664	0.04862699	1.92450214
B	11.41759731	-0.17551100	3.52625271
O	10.21046734	1.28710518	5.57590467
O	9.99484615	1.89312023	0.28857152
O	11.48592717	2.65127162	2.72393846
O	8.48212971	2.73171711	2.97793617
O	12.36948369	-0.03293479	0.76586790
O	7.28673613	-0.25303660	4.42409684

O	7.06594926	0.01815626	1.40161372
H	11.22138264	-3.03849040	1.42303935
B	9.97828320	-1.08937531	4.11664441
B	10.78877609	-1.56982927	2.59658628
B	8.99458501	-1.47693594	2.67298394
O	9.99988404	-1.85179240	5.34778269
B	9.81877147	-0.86904833	1.24406481
O	11.49367255	-2.80285841	2.33816524
O	8.02003400	-2.56062674	2.64587197
O	9.93512675	-1.58607964	-0.02013589
H	10.80854249	-1.28004740	-0.36118097
H	6.85130685	-0.94406827	1.42243947
H	8.34409045	2.98684693	2.04042765
H	10.58658644	2.57268760	0.69629076
H	10.77948059	3.25148754	3.05999258
H	11.17900886	1.31654313	5.72463849
H	12.15587060	0.74865946	0.20958506
H	9.90880745	-1.17696623	6.05535366
H	7.50484123	-2.41734468	3.47324682
H	6.61891362	0.03994560	3.76280987
O	12.61098248	-0.22071594	4.43161112
F	14.17446441	1.06937723	3.41185957
C	13.84397960	-0.12734681	4.02309306
F	14.69883623	-0.22062261	5.12404294
F	14.25598674	-1.11026051	3.15308815

Bidentate Model

B	10.08719002	0.83793251	4.15365152
B	10.18662900	0.79277030	1.28647311
B	11.11471683	1.21897185	2.73540103
B	9.35549107	1.45676299	2.65381487
B	11.50970186	-0.24497295	1.82647977
B	8.55528105	0.14078610	3.51174597
B	8.60383452	0.10338866	1.72206769
B	11.43804108	-0.25566632	3.63989979
O	10.23660844	1.51496346	5.42453822
O	10.09559733	1.92362691	0.30471646
O	12.10555178	2.28715480	2.72355915
O	8.94010744	2.79169955	2.10445065
O	12.75523581	-0.36703017	1.08153225
O	7.31536502	0.08890406	4.27346873
O	7.42048922	0.34954394	0.92752469
H	10.93590742	-3.29790186	1.74685850
B	9.86503450	-0.93063877	4.08601227
B	10.74907619	-1.60839435	2.67368650
B	8.96720243	-1.36559770	2.60135901
O	9.54118560	-1.71819790	5.26905963
B	9.97678742	-0.95042308	1.18308019
O	11.26956112	-2.96080580	2.60766596
O	8.05001624	-2.48683434	2.75053682
O	10.05367393	-1.77959689	-0.01232610
H	10.93785569	-1.58173621	-0.38816698

H	7.38928567	1.30880236	0.73402787
C	9.48363918	2.97139570	0.88358002
F	8.50142775	3.49698087	0.00698543
H	11.71540497	3.06394657	2.27038897
H	11.07810032	1.15089475	5.78003634
H	13.08809235	0.55388509	1.01592287
H	8.72380334	-1.28382750	5.60657253
H	8.34924905	-2.90421935	3.59168397
H	6.84084819	-0.67665694	3.87673939
O	12.60710806	-0.29535529	4.51024218
F	10.41364934	4.08817725	0.94332260
H	13.20874009	0.39807322	4.16827063

Full Structure Model

B	10.15980135	0.84130150	4.23769295
B	10.02051420	0.96177166	1.39389812
B	11.09379991	1.34778550	2.77642402
B	9.32285272	1.51991925	2.84546883
B	11.39727113	-0.07891761	1.75123265
B	8.57656421	0.16948167	3.70524412
B	8.48861840	0.22324826	1.92577006
B	11.46372227	-0.19458711	3.54593532
O	10.25373992	1.39206930	5.57515991
O	9.82711525	2.13613075	0.49298370
O	11.98521916	2.47772394	2.70761641
O	8.85930751	2.88354963	2.45171684

O	12.52307139	-0.22589488	0.85944380
O	7.43984764	0.32955100	4.58030387
O	7.22327202	0.48467757	1.28776126
H	10.90561051	-3.12990936	1.56014048
B	9.93666727	-0.94077548	4.14293646
B	10.71783061	-1.51370271	2.61583974
B	8.93099182	-1.29149142	2.71858643
O	9.93328829	-1.65944814	5.38522198
B	9.82085626	-0.78161505	1.23633201
O	11.27148747	-2.82295234	2.41870835
O	8.11512355	-2.52503344	2.57006013
O	9.79530136	-1.55935952	0.01373016
H	10.66121397	-1.37890537	-0.41222802
H	7.28175476	1.34217488	0.81799614
F	6.58266741	-4.07187360	2.85392118
F	7.96495809	3.42957580	0.43942726
H	11.47861182	3.25233489	2.38781232
H	9.32424349	1.46022163	5.88310144
H	13.00652706	0.62617694	0.88444732
H	10.22247482	-1.00578547	6.05925699
F	7.20326518	-2.89574551	4.61158577
H	6.66707091	0.48512425	3.99753694
O	12.65141053	-0.38385628	4.41675496
F	14.42058207	0.46030100	3.27293347
C	13.87348685	-0.57770580	4.01600546
F	14.70393867	-0.70407129	5.12504894
F	14.08342540	-1.71269257	3.26686175

C	7.04537611	-2.82069411	3.24799400
F	5.96954203	-1.96116088	3.05063756
C	9.16332276	3.10734403	1.15474564
F	9.88479304	4.33011229	1.04765589

Monodentate Model

Fig. S1 Mulliken charges on boron atoms for monodentate model

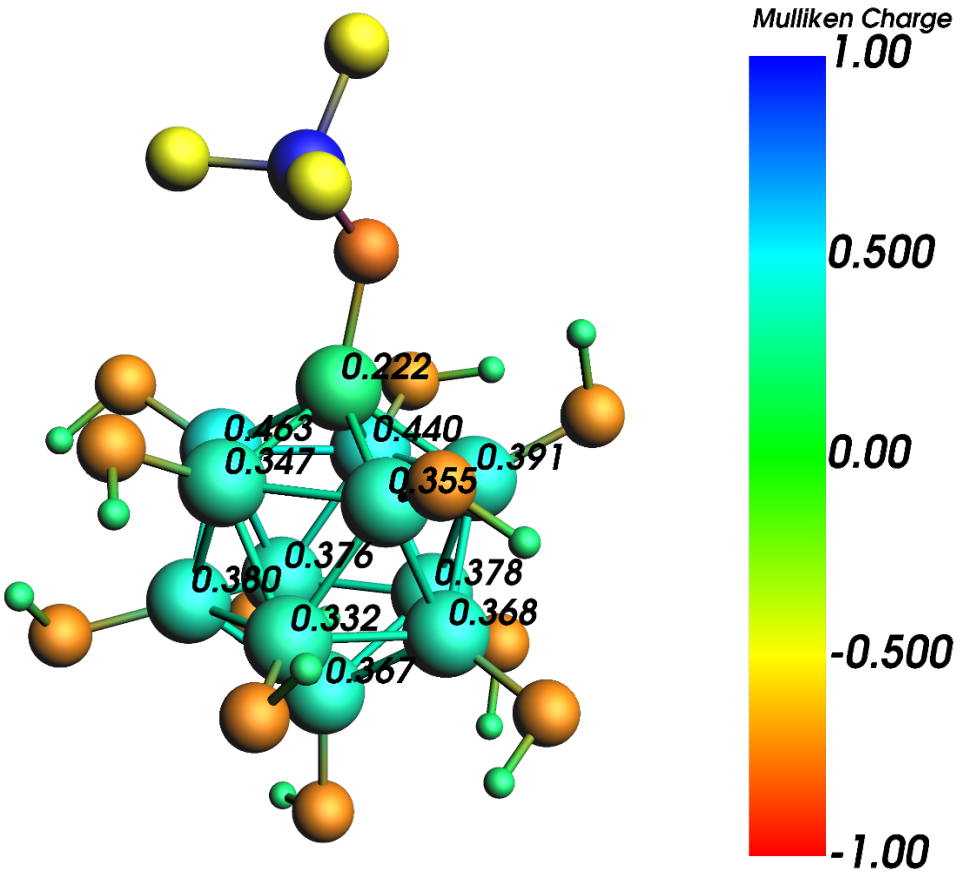


Fig. S2 Mulliken charges on oxygen atoms for monodentate model

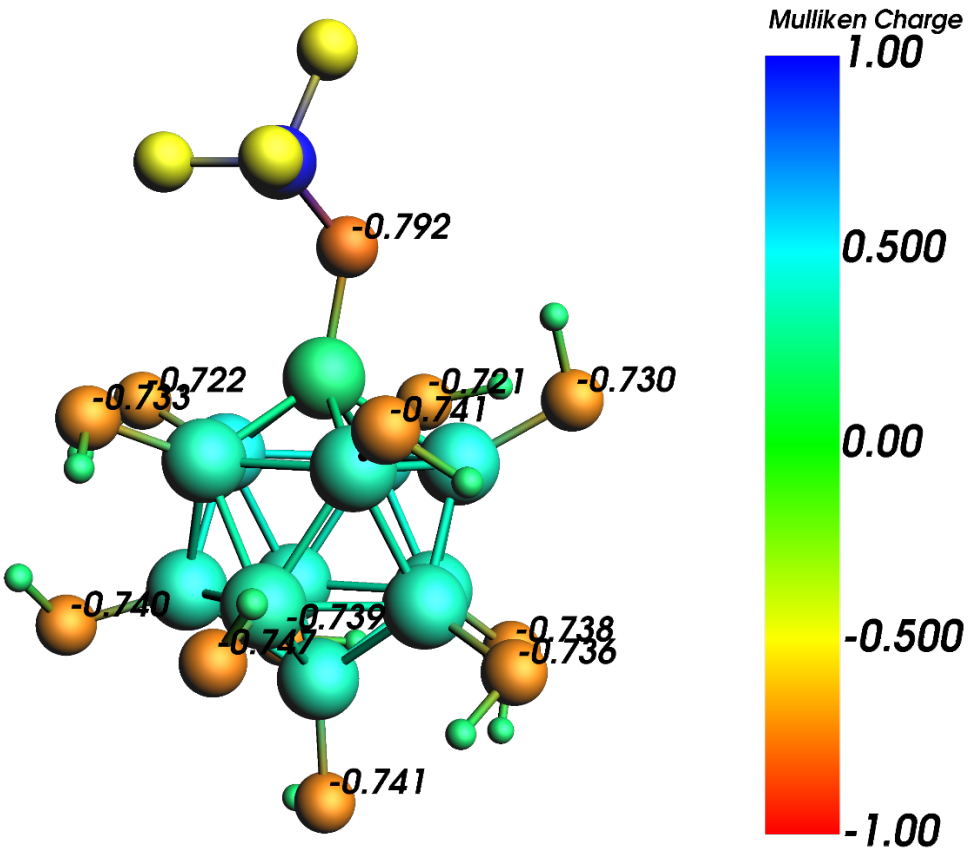
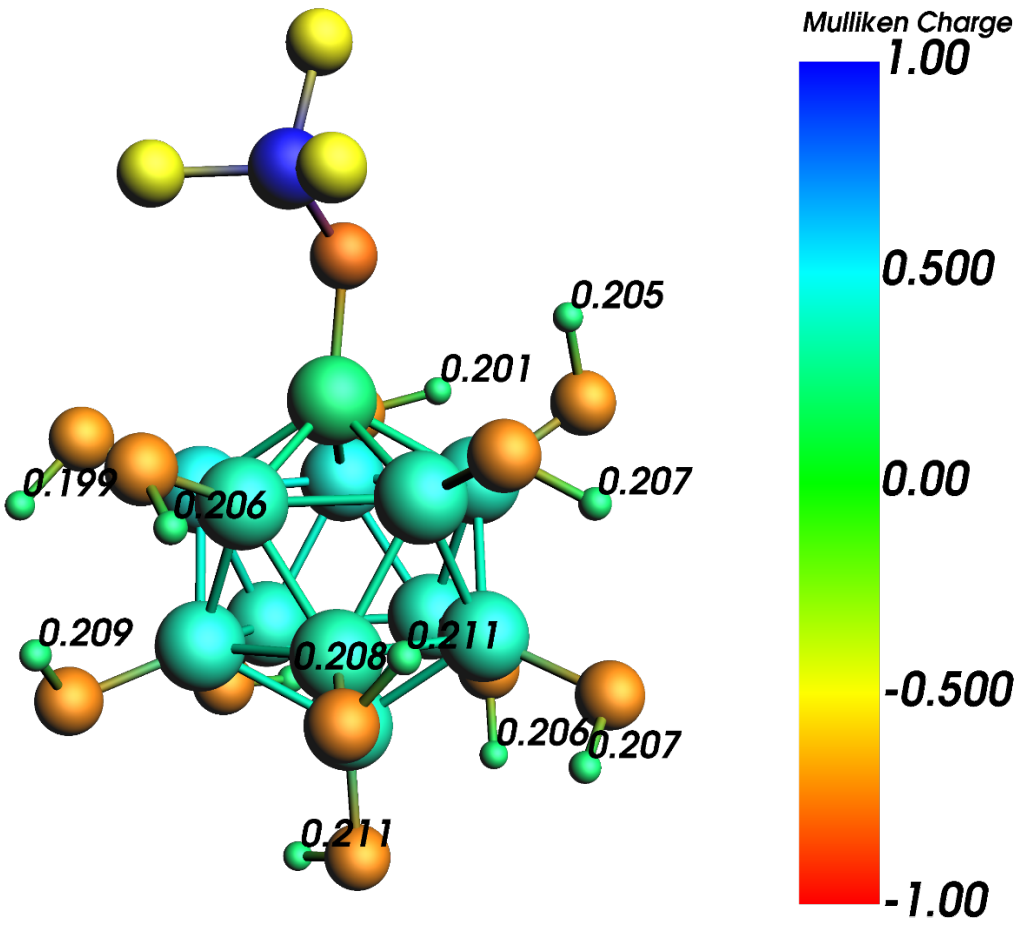


Fig. S3 Mulliken charges on hydrogen atoms for monodentate model



Bidentate Model

Fig. S4 Mulliken charges on boron atoms for bidentate model

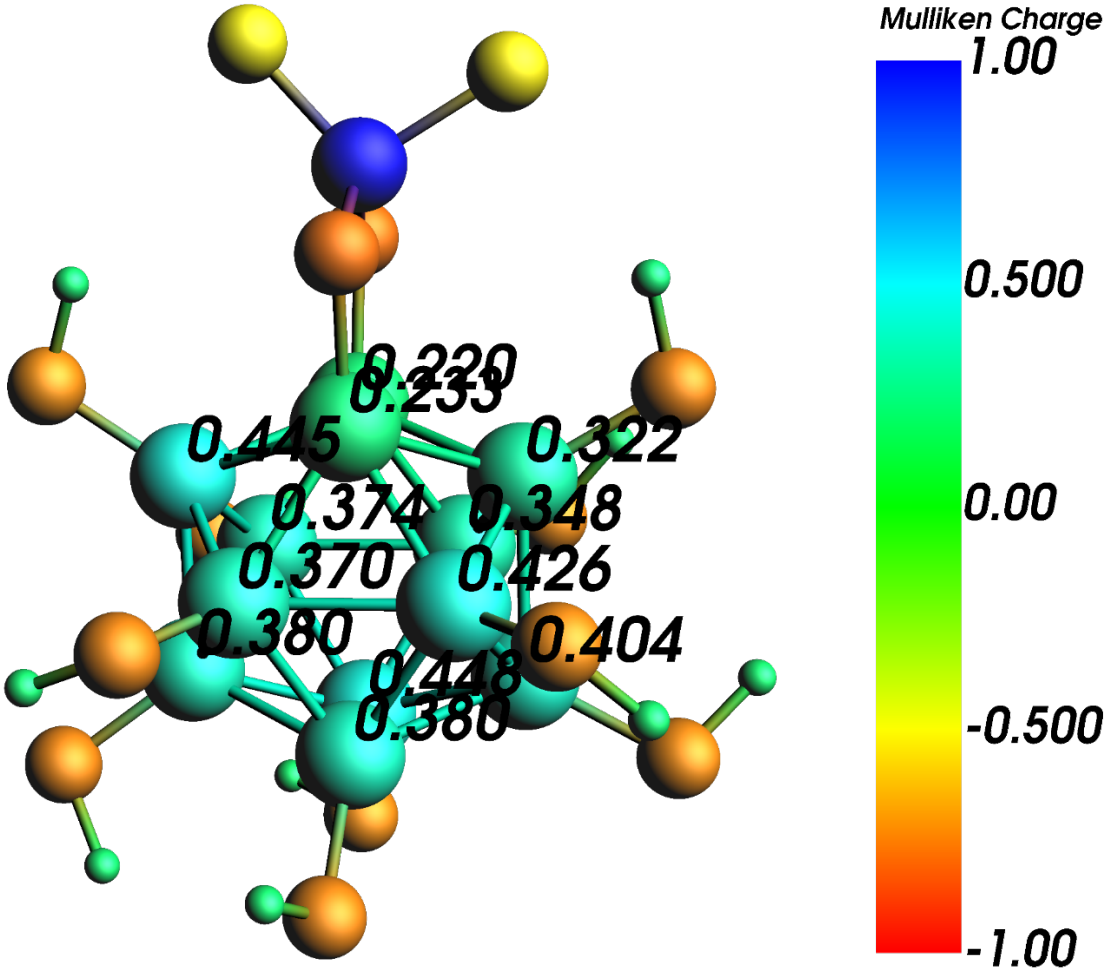


Fig. S5 Mulliken charges on oxygen atoms for bidentate model

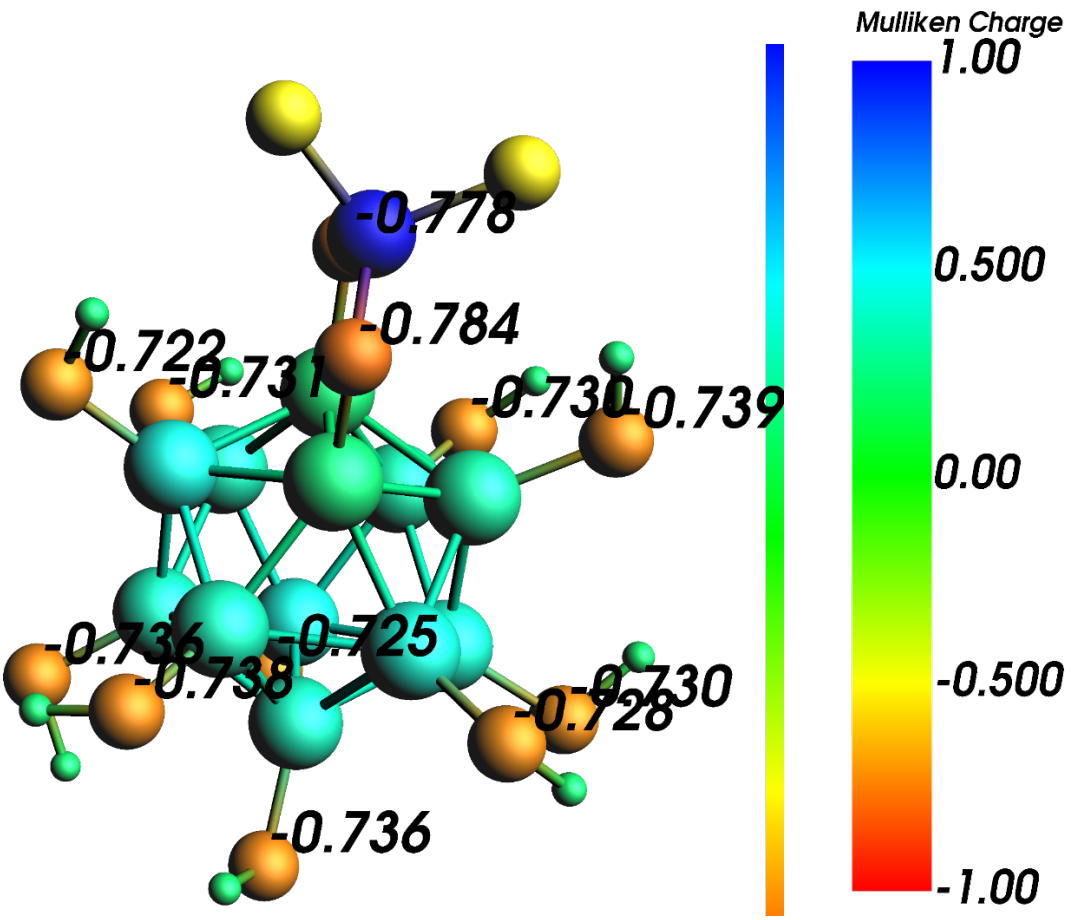
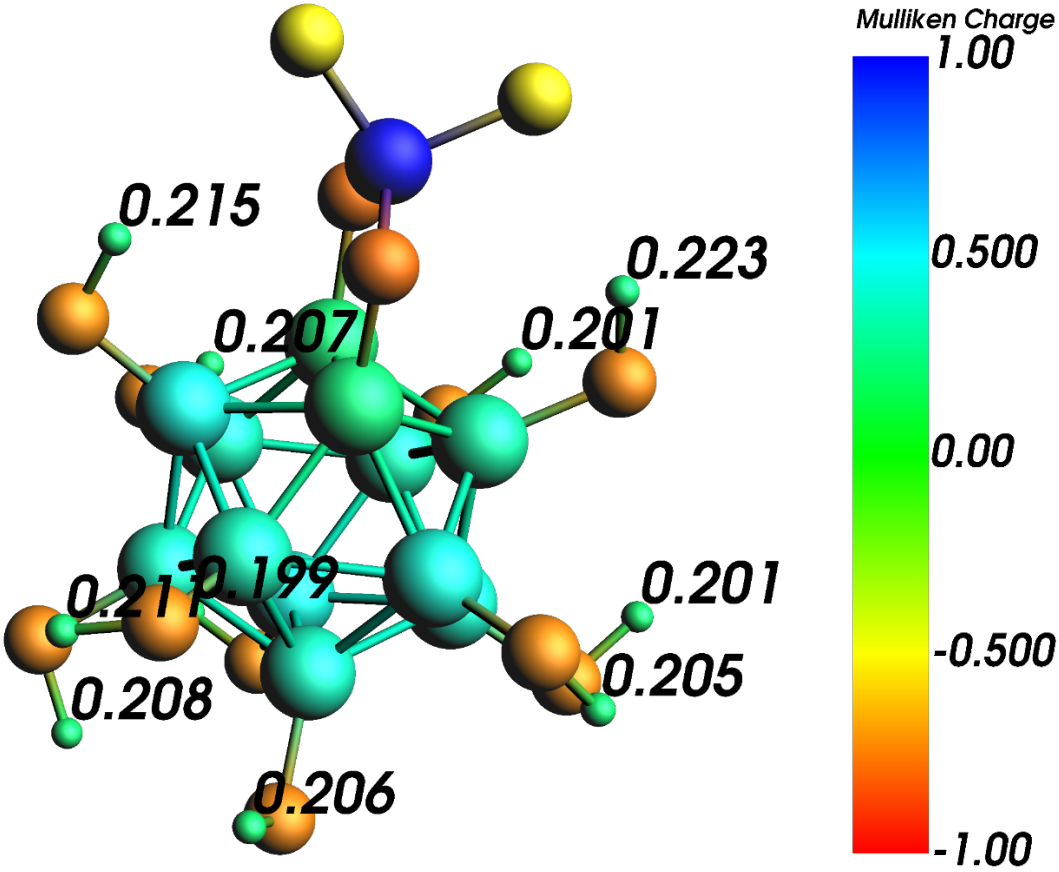


Fig. S6 Mulliken charges on hydrogen atoms for bidentate model



Full Structure Model

Fig. S7 Mulliken charges on boron atoms for full structure model

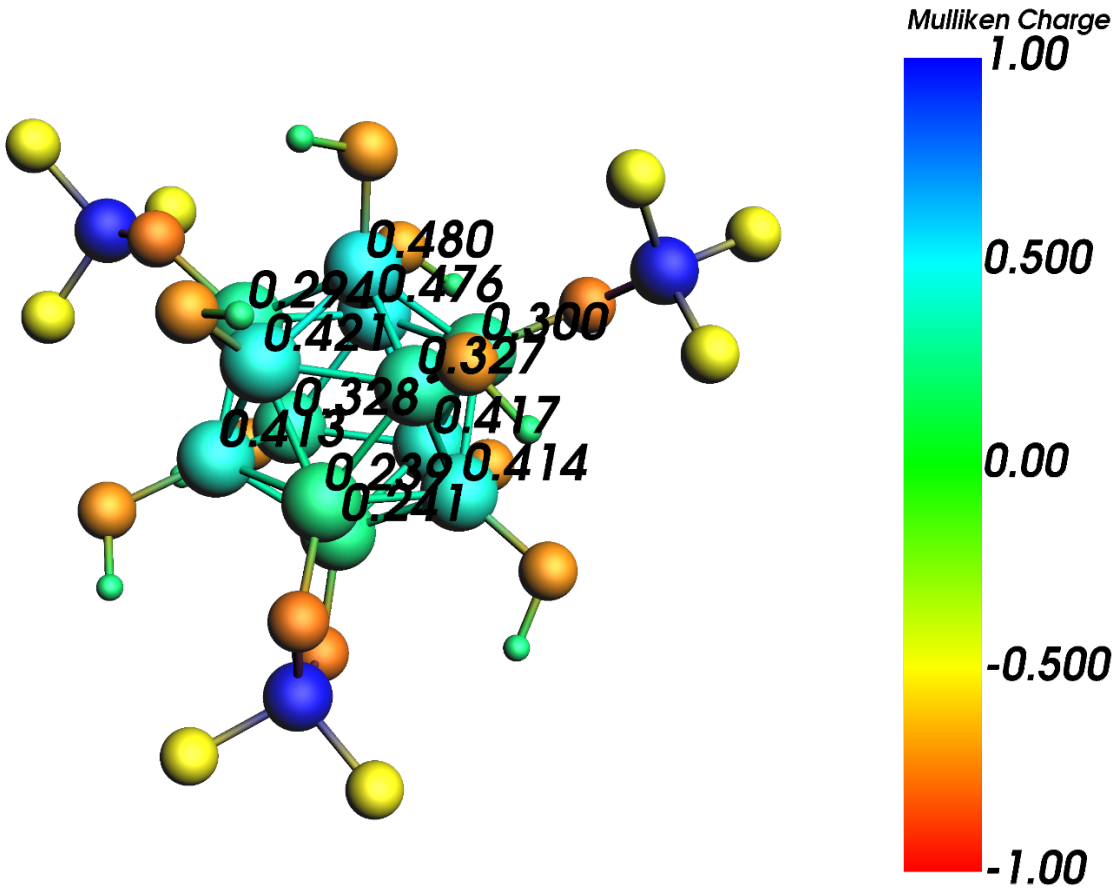


Fig. S8 Mulliken charges on oxygen atoms for full structure model

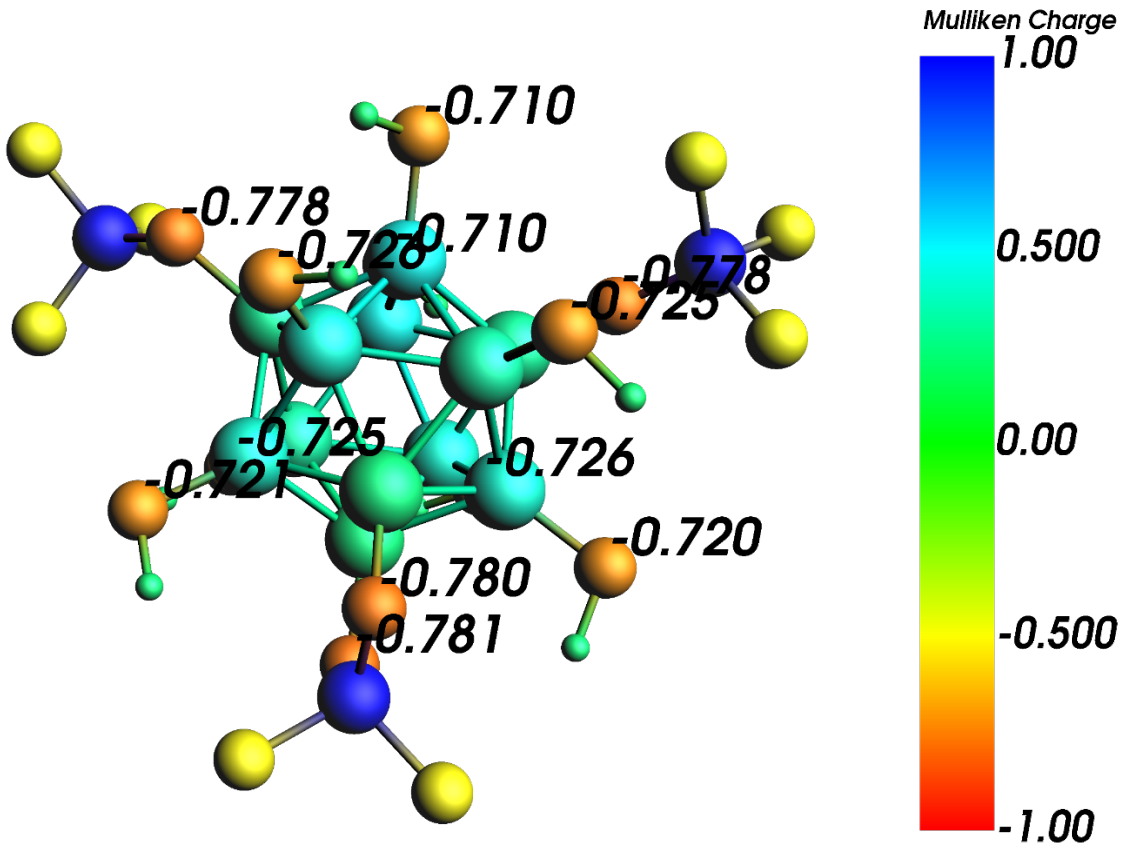


Fig. S9 Mulliken charges on hydrogen atoms for full structure model

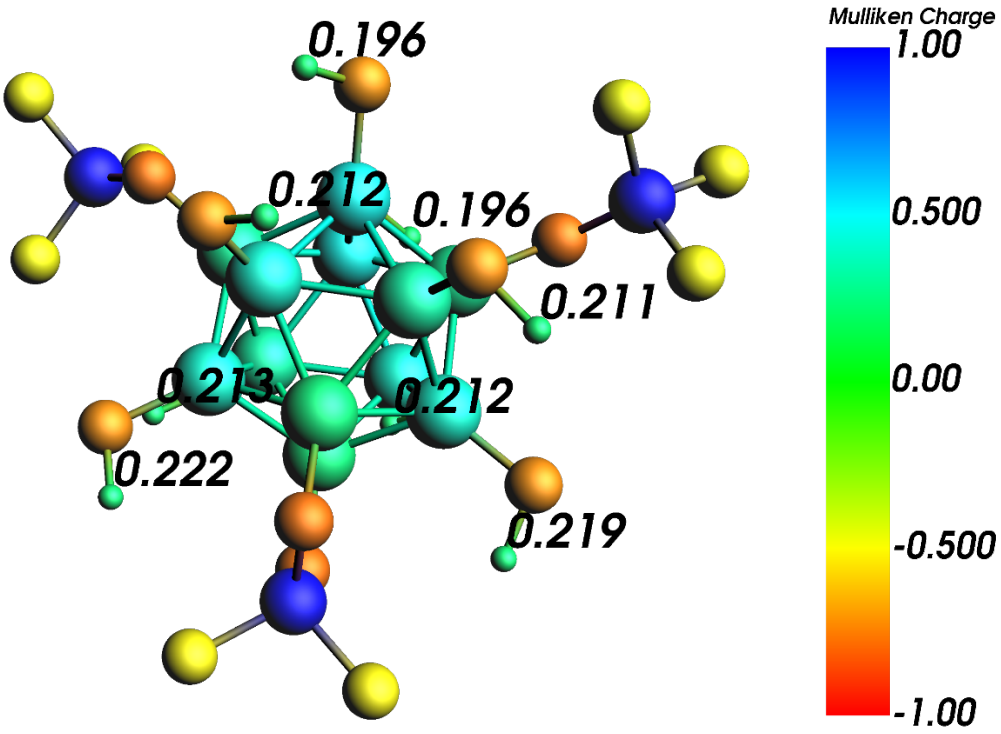


Fig. S10 Rietveld plot for as-synthesized $ZnB_{12}(OH)_{12}$, with green arrows designating the small peaks which corresponding to an unidentified impurity phase

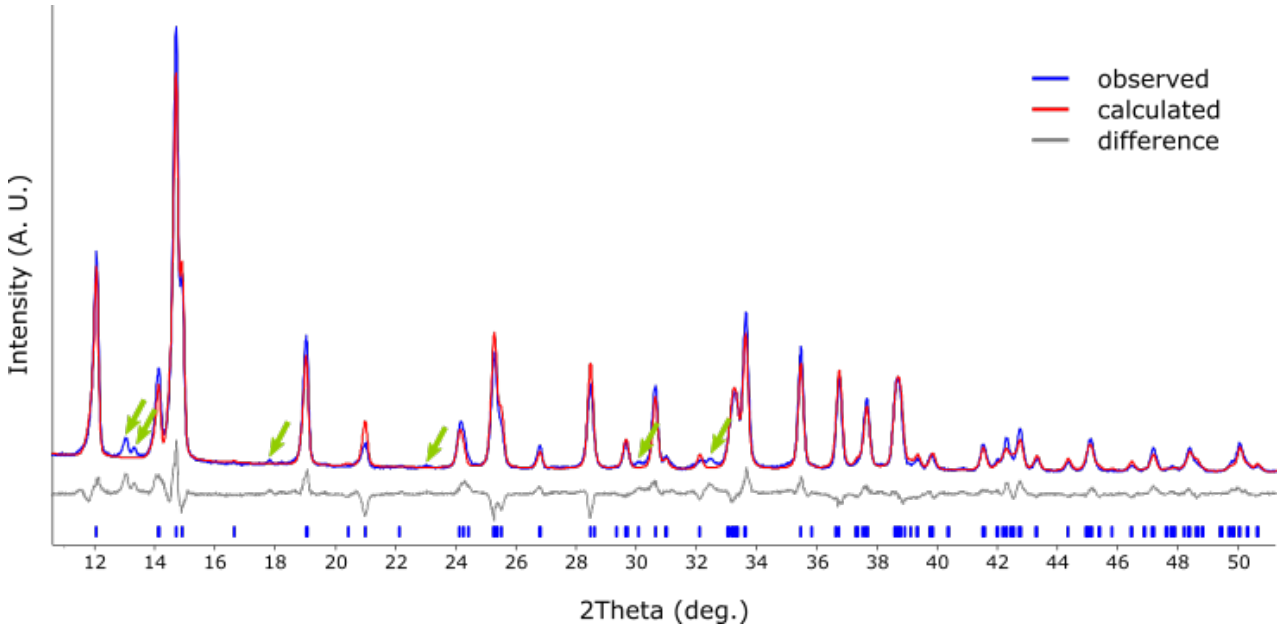


Fig. S11 CIF of $ZnB_{12}F_{12}$, determined through refinement of the powder pattern of as-synthesized $ZnB_{12}(OH)_{12}$

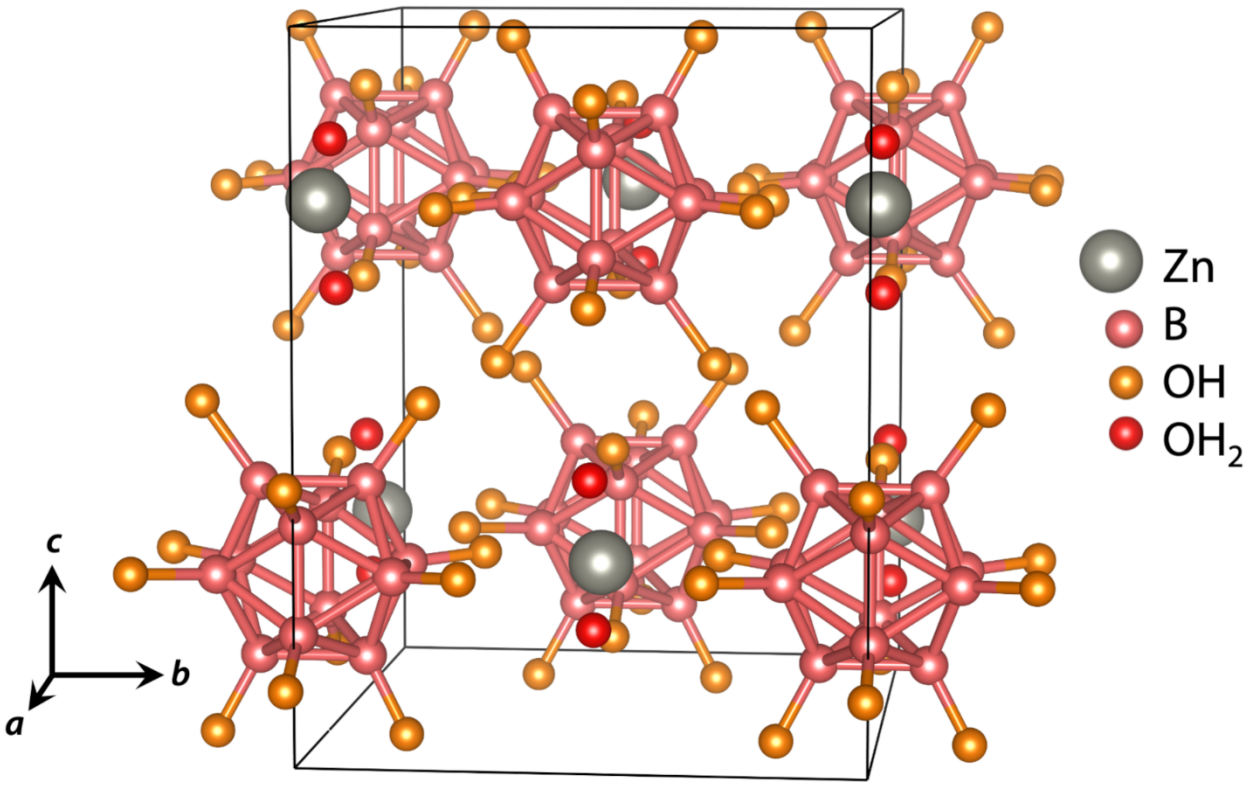


Table S1 Reliability Factors for Refinement

Reliability Factors	
R_{wp}	12.9810467
R_{exp}	3.92036972
R_P	10.0065068
GOF	3.31117921
R_B	8.364317

Table S2 Crystallographic Information for $ZnB_{12}F_{12}$

Lattice Parameters	
Crystal System	Monoclinic
Space Group	C2/m
a	11.8767 (3)
b	9.3221 (2)
c	12.0457 (3)
β	90.082 (6)
Cell Volume	1333.09 (8)
Phase Density	2.2975 (1)

Table S3. Atomic positions for one $ZnB_{12}F_{12}$ moiety (3 zinc ions and one boron cluster)

Listing of all 32 visible atoms:

Elmt	Label	Orthogonal Coordinates [Å] xor	yor	zor
B	B1	2.63149	-9.75698	4.18518
B	B17	0.90676	-9.84821	4.67223
B	B19	0.03369	-10.82450	3.44986
B	B2	1.85292	-9.86305	1.39107
B	B21	0.11923	-9.95475	1.88065
B	B22	-0.08030	-9.03219	3.40770
B	B3	2.82910	-10.67664	2.66046
B	B4	2.72855	-8.88362	2.61450
B	B5	1.22149	-11.33509	2.20238
B	B6	1.53322	-8.37646	3.86045
B	B7	1.05132	-8.44280	2.14152
B	B8	1.70567	-11.26850	3.92943

F	F10	2.18342	-10.08676	-0.01525
F	F11	4.10309	-11.57334	2.45887
F	F12	3.88287	-8.18605	2.37220
F	F13	1.09575	-12.57833	1.52424
F	F14	1.66027	-7.13308	4.54323
F	F15	0.77258	-7.57612	1.31680
F	F16	1.97333	-12.46135	4.65383
F	F18	0.35561	-9.88652	6.20776
F	F20	-1.06358	-11.84663	3.91789
F	F23	-0.87272	-10.24841	0.84778
F	F24	-1.25316	-8.45772	3.82257
F	F26	6.30118	-9.90268	3.28545
F	F27	5.57406	-9.42550	0.79998
F	F28	7.70649	-7.98381	1.29244
F	F29	5.23820	-6.41326	0.17483
F	F30	6.11578	-6.29628	3.30442
F	F9	3.90345	-9.69886	5.20587
Zn	Zn25	5.76756	-8.22414	1.71021

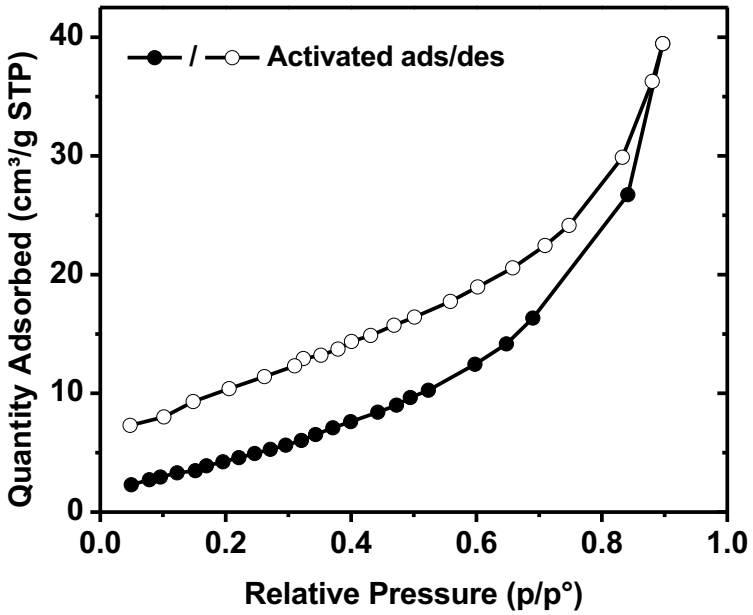
Zn Zn31 -3.19209 -8.69805 4.24034

Zn Zn32 1.62511 -14.38920 3.05961

Water Adsorption Studies

Water isotherms were collected on a Micromeritics 3Flex, and the water uptake in $g \cdot g^{-1}$ units is calculated as [(adsorbed amount of water)/(amount of adsorbent)]. Prior to the water adsorption measurements, water (analyte) was flash frozen under liquid nitrogen and then evacuated under dynamic vacuum at least 3 times to remove any gases in the water reservoir. The temperature was controlled with a Micromeritics ISO Controller. Prior to measurement, the sample was activated under dynamic vacuum on SmartVapPrep (SVP) at 120 °C for 24 hours.

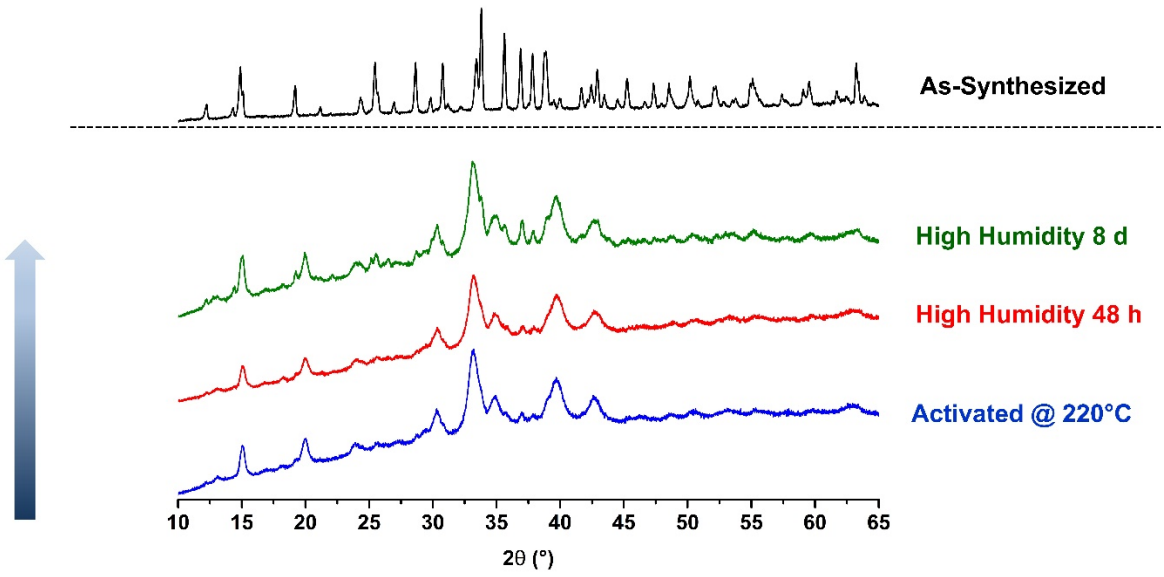
Fig. S12 H_2O sorption isotherm for an activated sample of $ZnB_{12}(OH)_{12}$



Rehydration in Humidity Chamber

50 mg of freshly activated material was placed on a weigh boat on top of a stand in an airtight chamber. The bottom of the chamber was lined with large filter papers and then filled with water to create a humid environment. The humidity within the chamber was measured to be 85% RH with a SmartPro Digital Hygrometer. The sample was left in the saturated chamber for 48 h and then removed, lyophilized and the PXRD pattern was measured. The sample was then returned to the chamber for 6 more days and the analysis was repeated, showing negligible changes in the PXRD pattern.

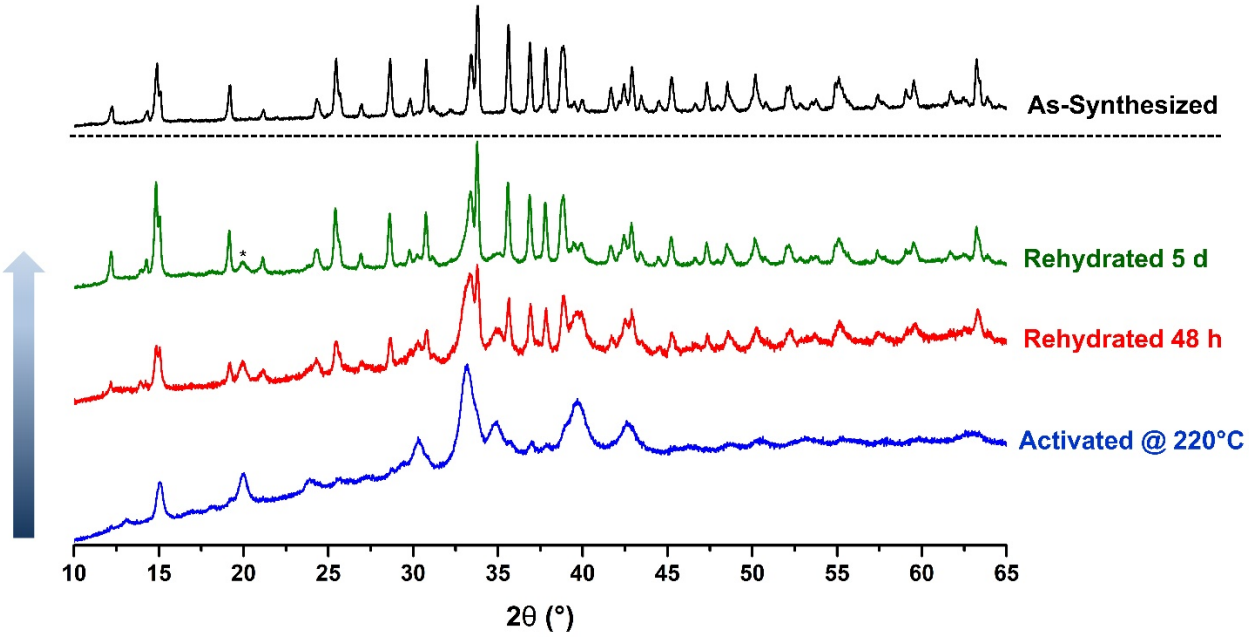
Fig. S13 PXRD patterns at various time points of activated $ZnB_{12}(OH)_{12}$ in a humidity chamber



Rehydration in H_2O

35 mg of freshly activated material was stirred as a slurry in 10 mL MilliQ H_2O. After 48 hours, the sample was centrifuged, lyophilized, and then the PXRD pattern was measured. It was then returned to 10 mL of fresh MilliQ H_2O for 3 more days and then analyzed in the same manner, showing full reversion back to the as-synthesized pattern, except for the presence of a small peak at 20° (marked with an asterisk).

Fig. S14 PXRD patterns at various time points of activated $ZnB_{12}(OH)_{12}$ stirred in H_2O



Solvent Exchange with Acetone

16 mg of as-synthesized material was vigorously stirred as a slurry in 5 ml of dry acetone. Every 24 hours the sample was centrifuged, the solvent was removed, and a fresh portion of acetone was added. After 72 hours, the sample was centrifuged, the powder was air-dried overnight, and the PXRD pattern and TGA were measured.

Fig. S15 PXRD patterns of starting material and product after attempting solvent exchange with acetone

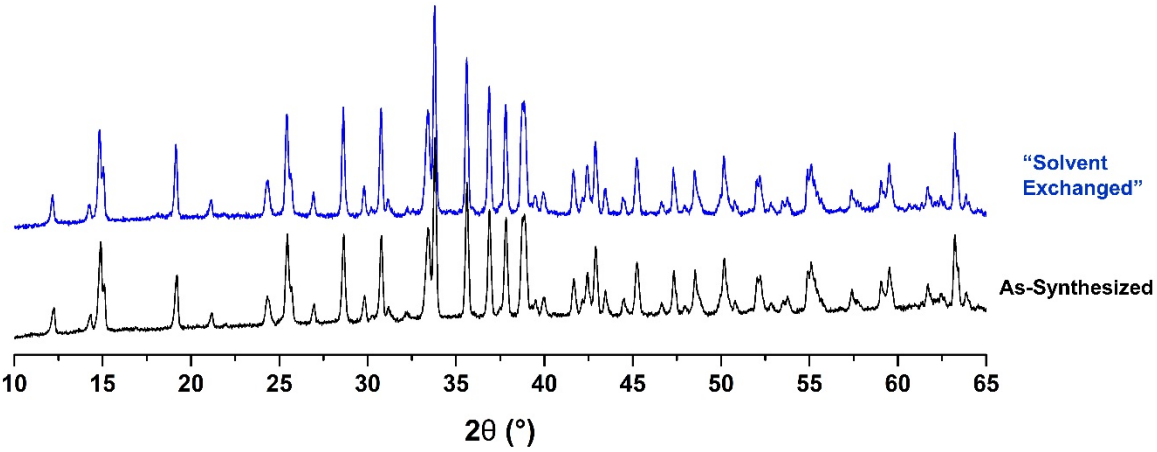
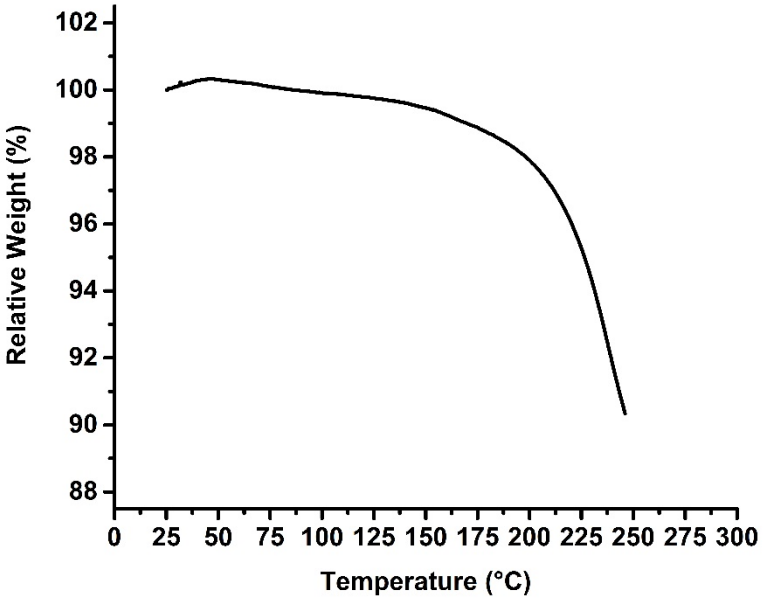


Fig. S16 TGA of material after attempted solvent exchange with acetone



Nitrogen adsorption isotherms

N_2 isotherms were collected at 77 K on a Micromeritics Tristar II 3020. Prior to measurement, the as-synthesized sample was soaked in acetone, washed with acetone, and dried under vacuum at 80 °C for 24 h. Then the sample was activated under dynamic vacuum on SmartVapPrep (SVP) at 120 °C for 24 h. No porosity was observed.

Fig. S17 N_2 adsorption isotherms for as-synthesized (left) and activated (right) samples