Supporting Information: Reconciling Order, Stability, and Porosity in Phosphonate Metal-Organic Frameworks via HF-mediated Synthesis

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Synthesis Details for H_6L, ZrH_2L-A, and CALF-31:

All starting materials were purchased from commercial suppliers (Alfa Aesar and Sigma Aldrich) and were used without any further purification unless stated otherwise.

Synthesis of H_6L: the precursor, 1,3,5-tris(4-bromophenylbenzene), was synthesized from the trimerization of 1,4'-bromoacetophenone using silicon tetrachloride in dry ethanol. Following the trimerization, a modified Michaelis-Arbuzov reaction on 1,3,5-tris(4-bromophenylbenzene) with triethyl phosphite in diisopropylbenzene with nickel (II) chloride as a catalyst was performed yielding 1,3,5-tris(4-diethylphosphonophenylbenzene). Finally, a hydrolysis in neat HBr for 24 hours yielded the desired product 1,3,5-tris(4-phosphonophenylbenzene) (H_6L).

Synthesis of ZrH_2L-A: $ZrCl_4$ (0.158 g, 0.678 mmol) was dissolved in a 1:1 methanol:water solution (10 mL) and, in a separate container, H_6L (0.370 g, 0.677 mmol) was dissolved in methanol (10 mL). These two solutions were poured together into a new container instantly forming a white precipitate. This solution was stirred over night at room temperature. ZrH_2L-A (0.360 g) was collected as a white powder by vacuum filtration and rinsed with water and methanol.

Synthesis of CALF-31: $ZrCl_4$ (0.011 g, 0.047 mmol) and H_6L (0.025 g, 0.046 mmol) in 1 to 1 methanol to water solvent mixture (3.0 mL) containing HF (0.04 mL, 28.9 M, 1.2 mmol, 25 equivalents) was used in a solvothermal reaction. The reactants were mixed together in a Teflon liner, sealed in a reaction vessel, and placed in an oven at 150 °C for 6 days. A white powder (0.0215 g) was collected by vacuum filtration and rinsed with water and methanol. This white powder was subjected to 85 °C and 95 % RH for 48 hours before being washed with methanol and dried to complete the synthesis of CALF-31.

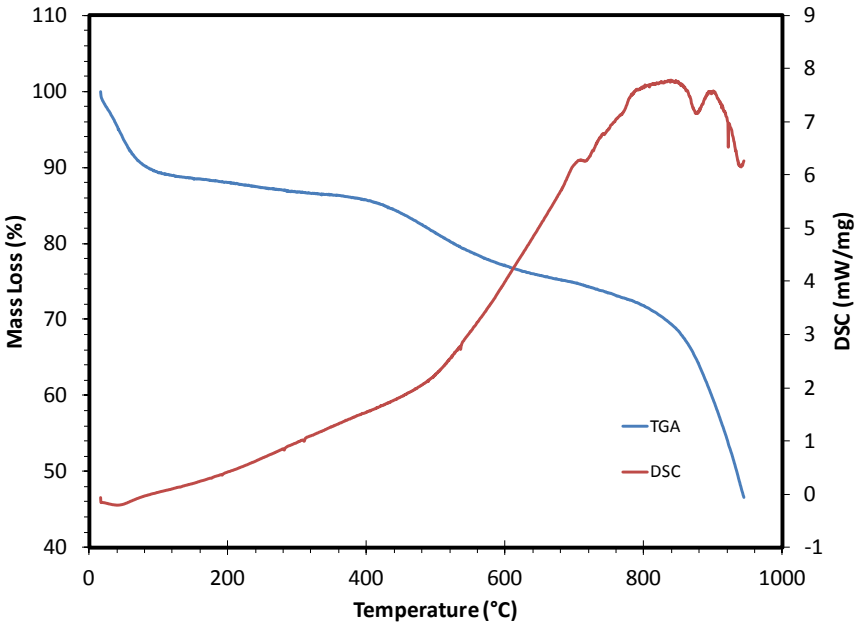
Analytical Procedures

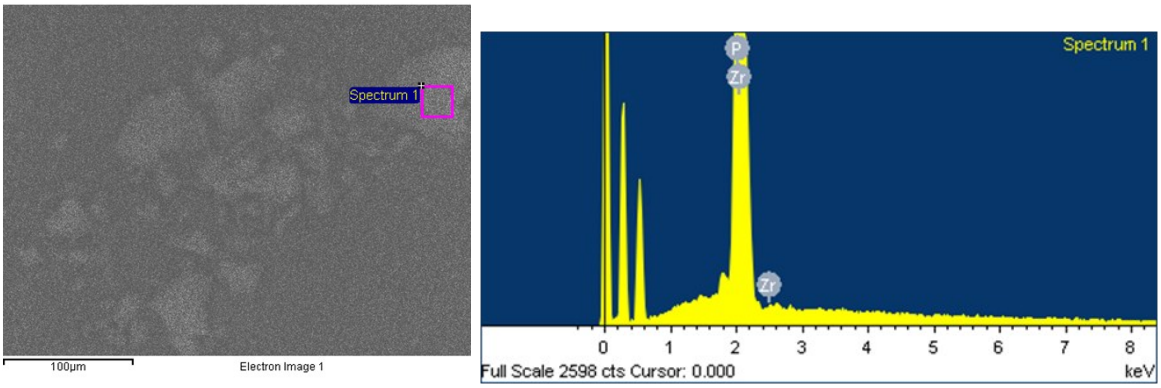
Chemical analysis: Elemental analysis was collected using a Perkin Elmer Model 2400 series II. Powder x-ray diffraction was collected with a Rigaku Miniflex II bench top PXRD equipped with a CuK_α x-ray source. SEM was collected using a Zeiss ΣIGMA VP equipped with a backscattered electron detector with an accelerating voltage of 20 keV. EDX was collected using an Oxford instruments x-act equipped with a 10 mm^2 silicon drift detector and processed using INCA analysis software. Thermogravimetric analysis was performed using a Netzsch STA 409 PC TGA/DSC analyzer under 60 ml/min flow of N_2 in an alumina crucible from room temperature to 1000 °C at 2 °C/min.

Adsorption Analysis: Adsorption isotherms for CO_2 (99.998%) and N_2 (99.999%) were conducted using an Accelerated Surface Area & Porosimetry System (ASAP) 2020 supplied by Micromeritics Instruments Inc. The dry sample (~80 mg) was loaded into the glass analysis tube. The sample was heated under vacuum (~10^{-6} mbar) in two stages, initially to 60 °C at 1 °C min^{-1} for 2 hrs then to 150 °C at 1 °C min^{-1} for 18 hrs. After this the outgas rate was less than 2 μbar hr^{-1}. The sample was then backfilled with N_2 before being transferred to the analysis port where it was evacuated for at least a further 120 min before the analysis was started.

Humidity treatment: The humidity exposure was performed using an Espec BTL-433 humidity control oven. The oven was preset to 95% relative humidity and 85 °C before loading materials into the chamber for 24 hrs. After the 24 hr period, the materials were immediately removed from the chamber before lowering the oven back to room temperature. The materials were washed with methanol then dried in a vacuum oven at 100 °C for 16 hours before analysis.

Elemental Analysis	Run 1	Run 2	ZrH2L-A · $(H_2O)_7$
% Carbon	38.0	38.2	37.9
% Hydrogen	3.7	3.8	4.1





Element	Weight %	Atomic %
P	49.81	74.51
Zr	50.19	25.49

Figure 1: Elemental analysis, TGA/DSC, and SEM-EDX data for pristine ZrH_2L-A

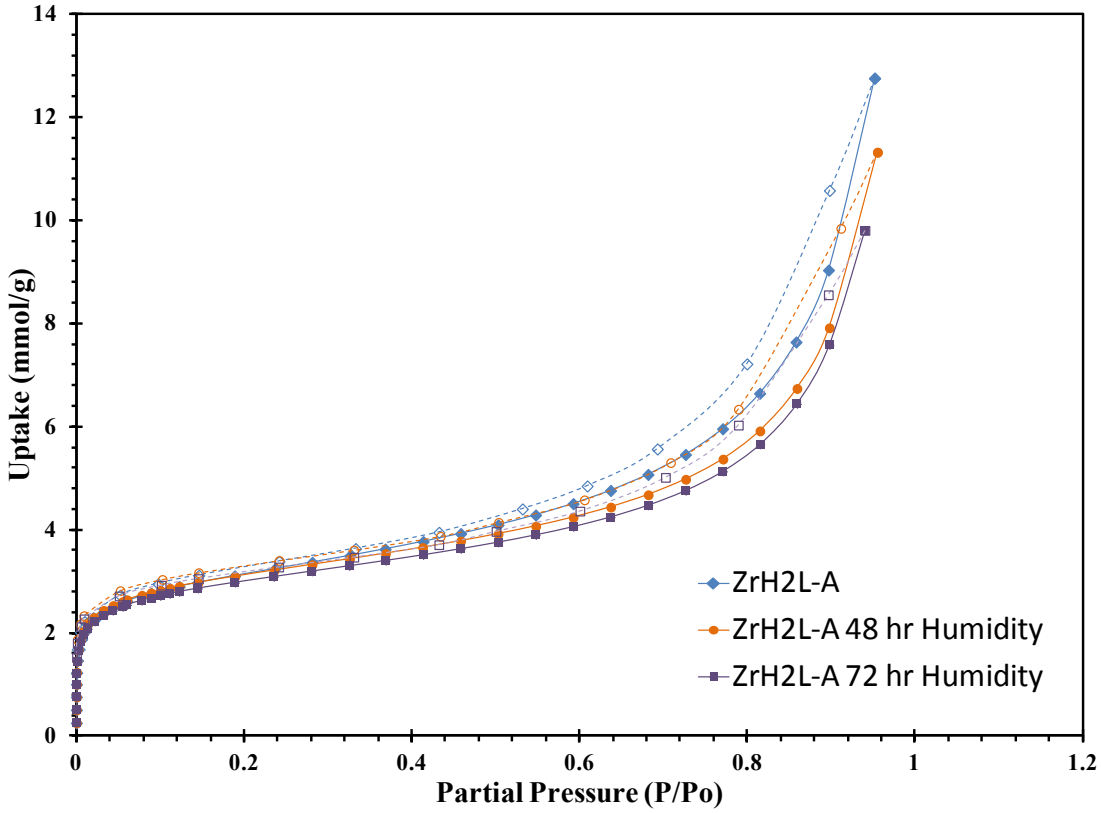


Figure 2: N_2 isotherms for ZrH_2L-A pristine (blue) and after 48 (orange) and 72 (purple) hour humidity exposure

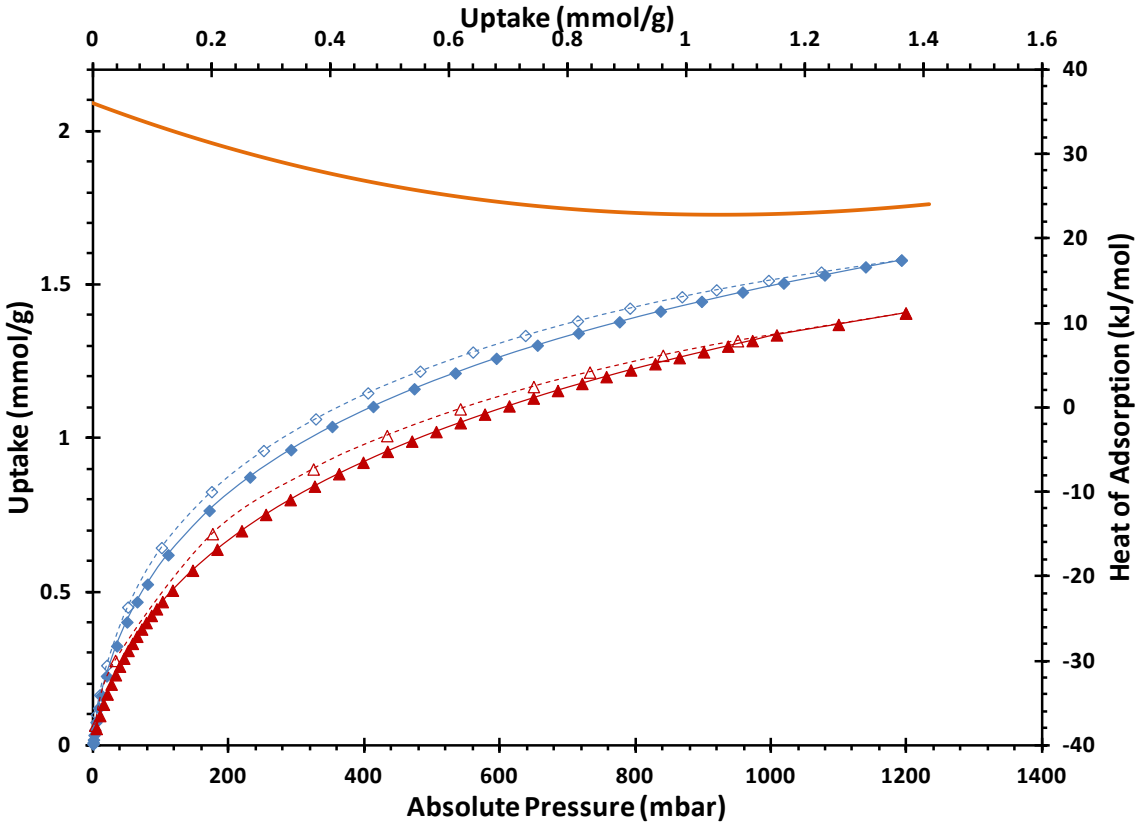


Figure 3: CO_2 isotherms for ZrH_2L-A at 263 K (blue) and 273 K (red) along with HOA (orange) on a secondary axis after 48 hours of humidity exposure.

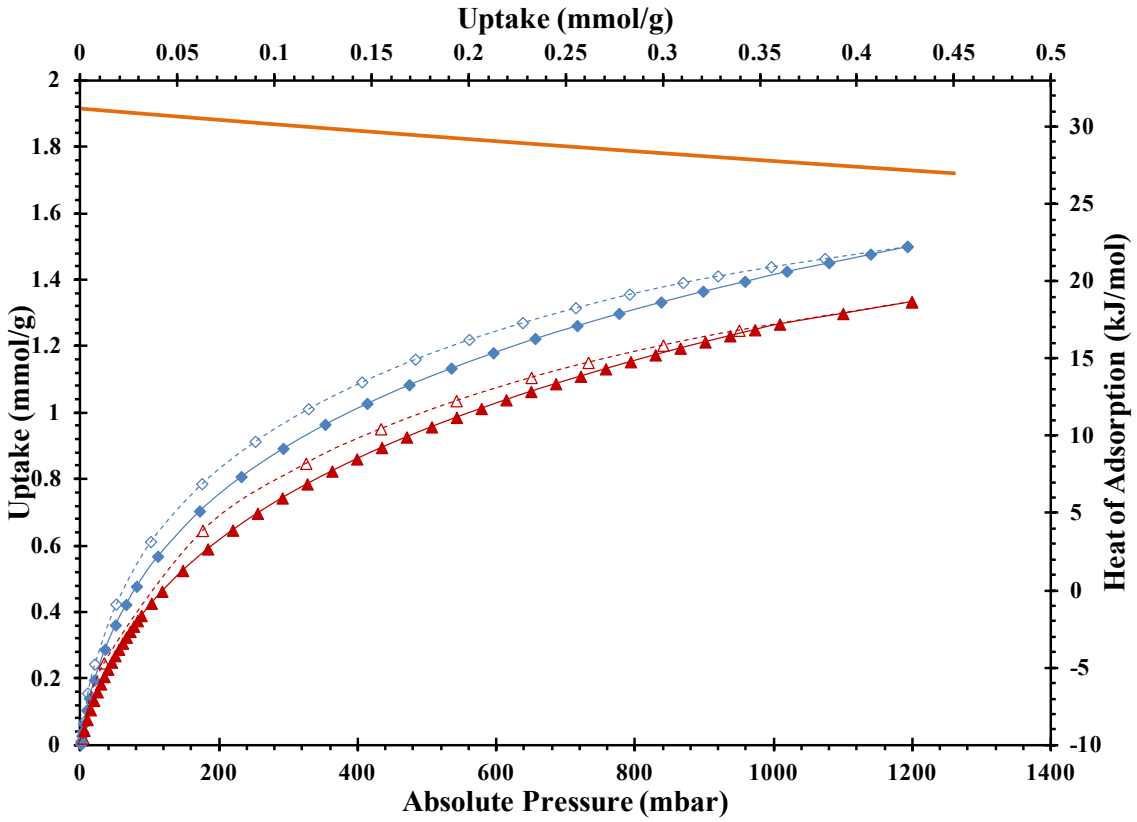


Figure 4: CO_2 isotherms for ZrH_2L-A at 263 K (blue) and 273 K (red) along with HOA (orange) on a secondary axis after 72 hours of humidity exposure.

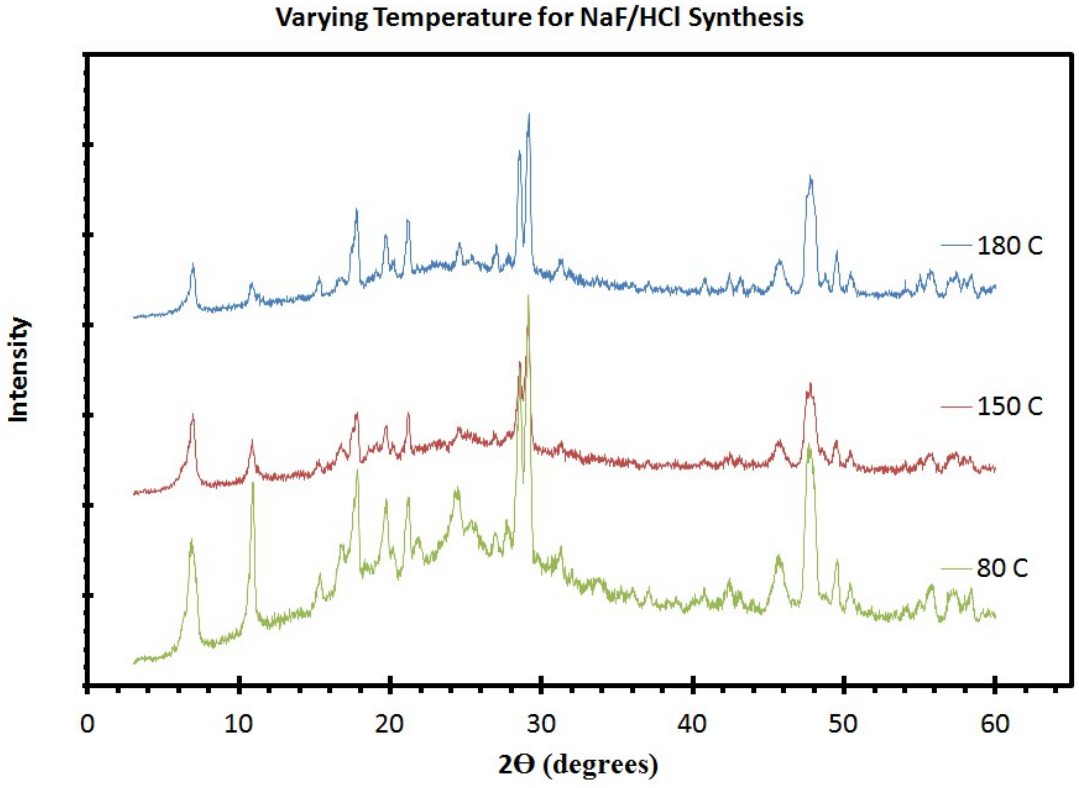
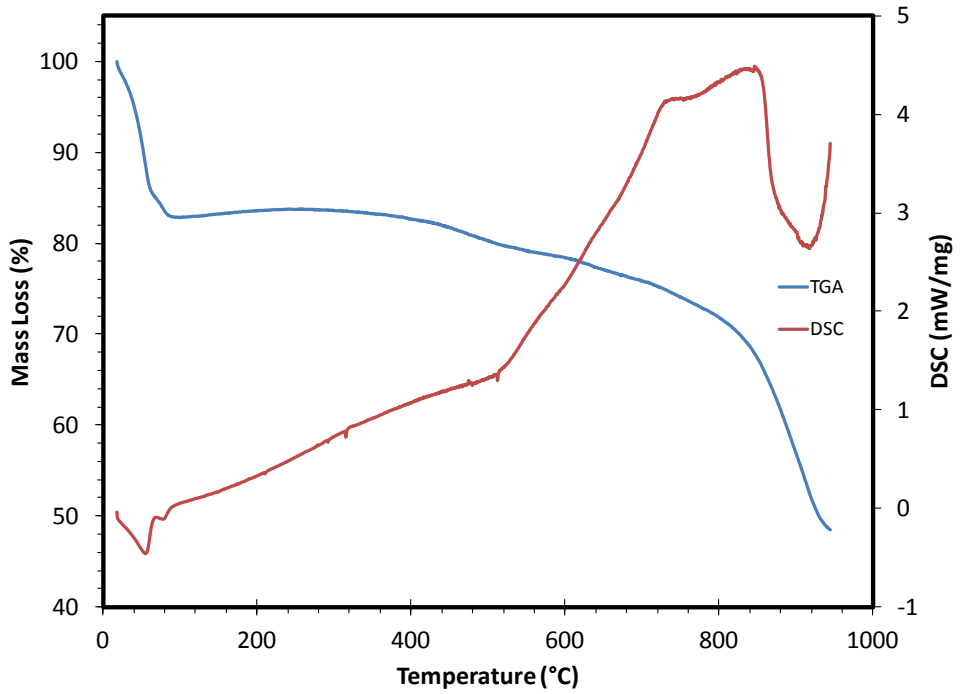
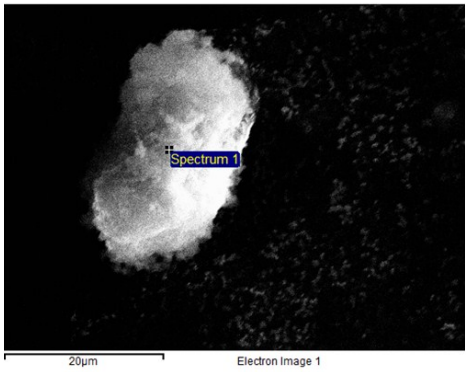
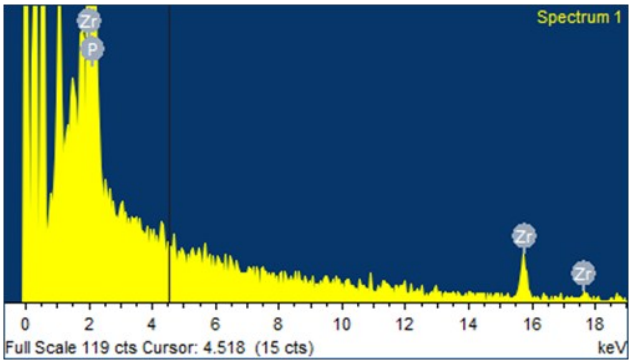


Figure 5: Material formed from in situ HF from NaF and HCl. Variable temperature shows decrease in amorphous hump up until 150 °C with impurity peaks present at 28 ° and between 46 – 52 °.

Elemental Analysis	Run 1	Run 2	$ZrH_2L \cdot (H_2O)_7$
% Carbon	37.8	37.8	37.9
% Hydrogen	3.6	3.1	4.1







Element	Weight %	Atomic %
P	51.62	75.86
Zr	48.38	24.14

Figure 6: Elemental analysis, TGA/DSC, and SEM-EDX data for CALF-31.

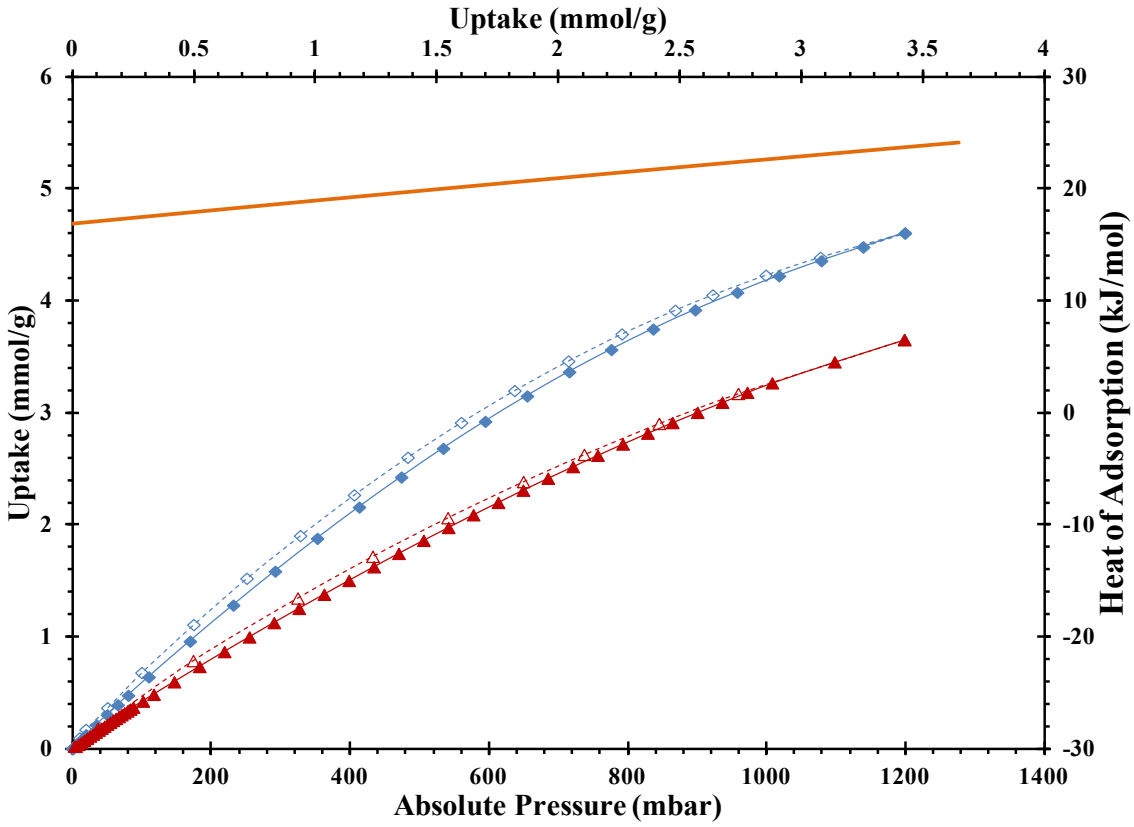


Figure 7: CO_2 isotherms of CALF-31 at 263 K (blue) and 273 K (red) with the HOA (orange) on a secondary axis.

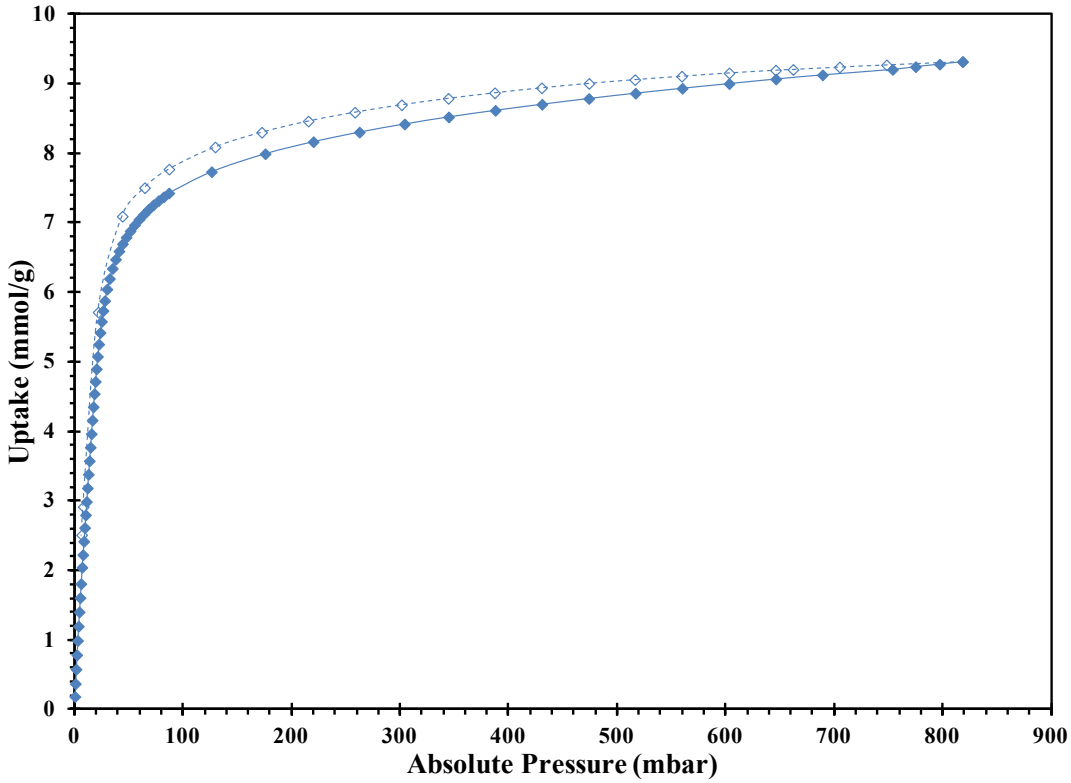


Figure 8: The CO_2 capacity of CALF-31 tested at 195 K and at 820 mbar, an uptake of 9.31 mmol/g was observed.

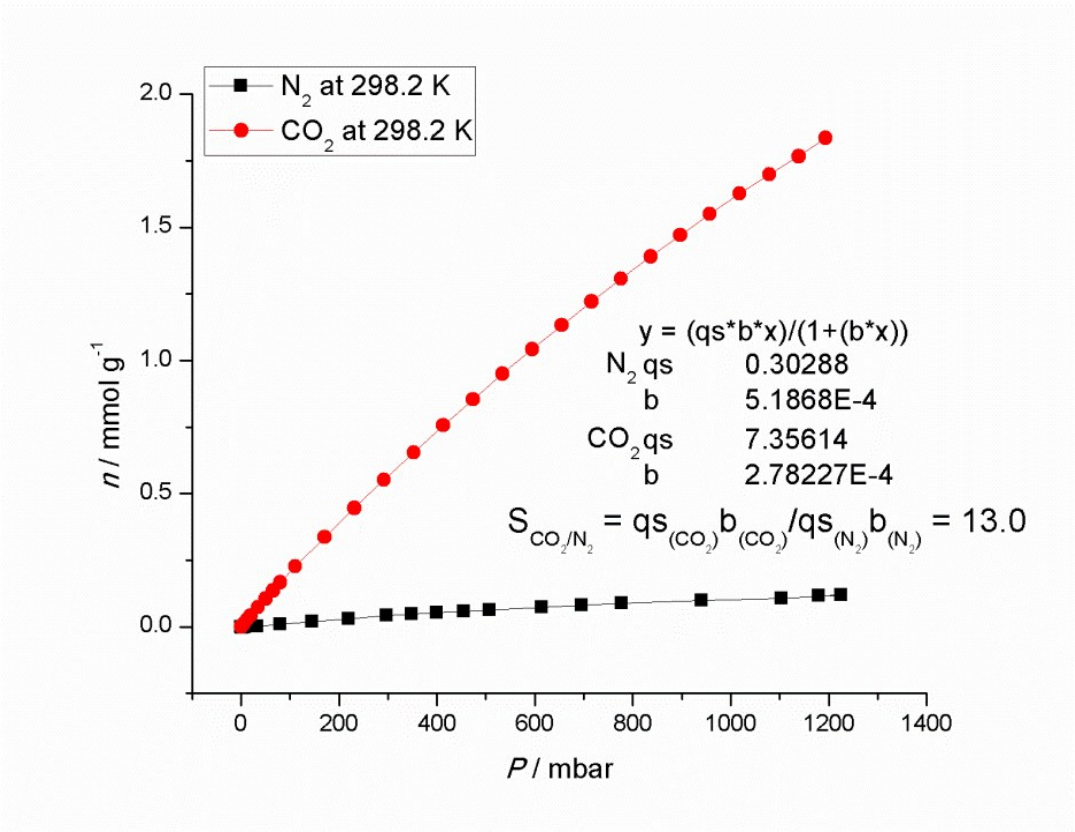


Figure 9: CO_2/N_2 selectivity of CALF-31 at 298 K with N_2 isotherm in black and CO_2 isotherm in red.

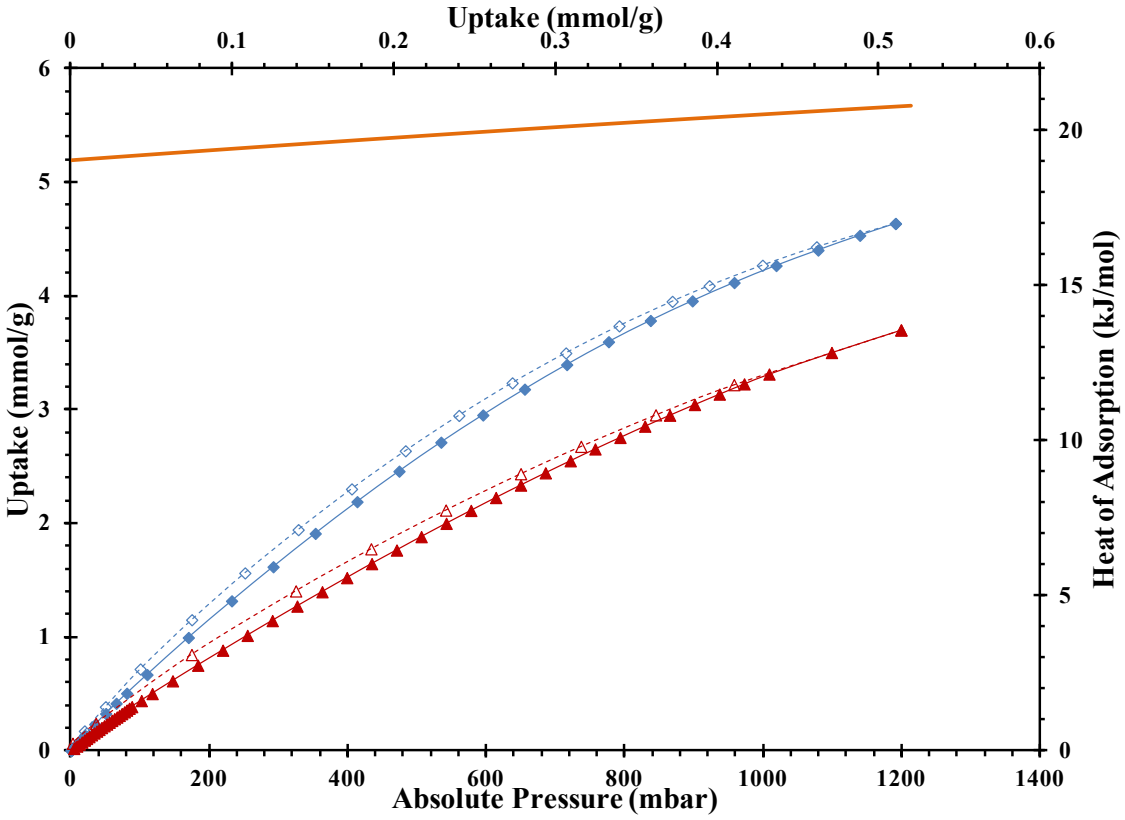
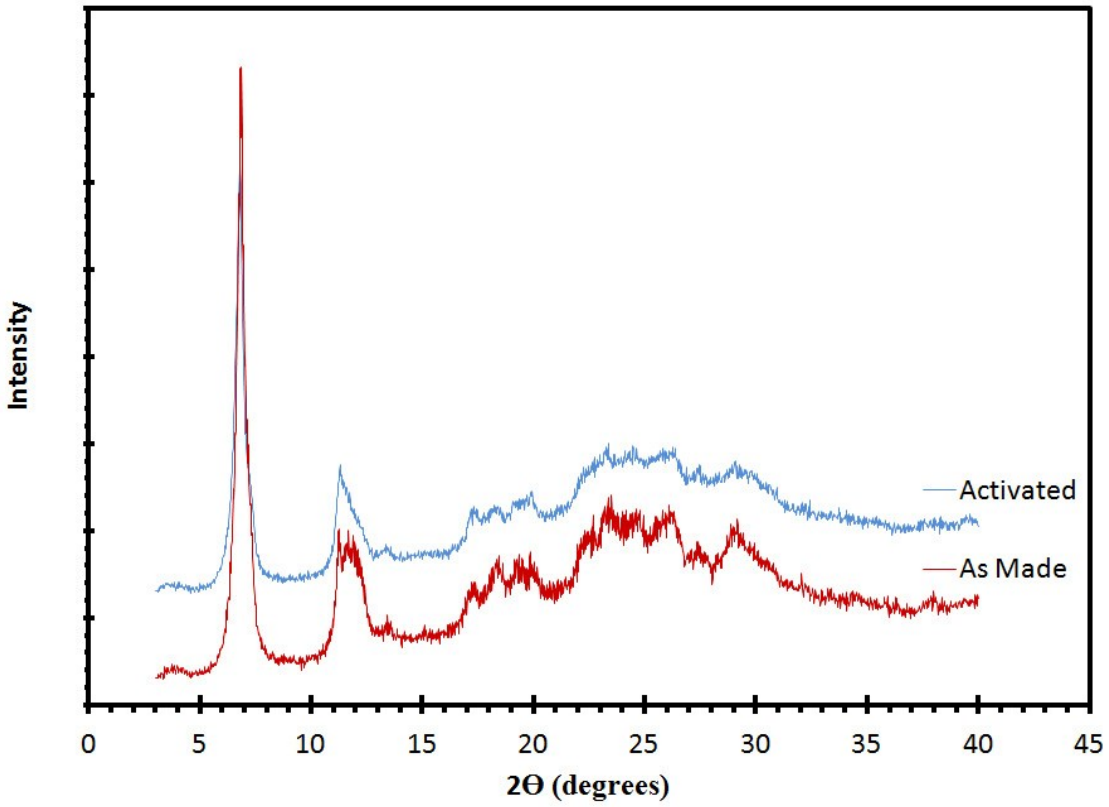


Figure 10: CO_2 isotherms of CALF-31after 24 hours of humidity exposure at 263 K (blue) and 273 K (red) with the



HOA (orange) on a secondary axis.

Figure 11: PXRD of CALF-31 before and after degassing at 150 °C for 48 hours.

Internal versus External Surface Analysis

t-plot analysis performed using Harkins and Jura equation: $t = [\ 13.99 / (\ 0.034 - \log(P/P_o)\ )\ ]^{0.5}$

ZrH_2L:

t-Plot Micropore Area: 92.9195 m²/g
t-Plot External Surface Area: 160.1453 m²/g
Slope: 0.461911 ± 0.005776 mmol/g·Å
Y-Intercept: 1.114356 ± 0.023726 mmol/g
Correlation Coefficient: 0.999531

Fitted Points		
Relative Pressure (P/P_o)	Statistical Thickness (Å)	Quantity Adsorbed (mmol/g)
0.089101	3.5923	2.76319
0.100101	3.6791	2.81
0.111396	3.7646	2.85447
0.122599	3.8466	2.89666
0.144433	4.0001	2.97075
0.18861	4.2949	3.10416
0.236632	4.6043	3.24033
0.281181	4.8902	3.36687

ZrH_2L – 48 hour humidity exposure:

t-Plot Micropore Area: 105.8431 m²/g
t-Plot External Surface Area: 146.7134 m²/g

Slope: 0.423170 ± 0.008456 mmol/g·Å
Y-Intercept: 1.264180 ± 0.034201 mmol/g
Correlation Coefficient: 0.998605

Fitted Points		
Relative Pressure (P/P_o)	Statistical Thickness (Å)	Quantity Adsorbed (mmol/g)
0.078002	3.5002	2.728
0.088957	3.5911	2.77586
0.100163	3.6796	2.8215
0.111438	3.7649	2.86319
0.12268	3.8472	2.90275
0.145028	4.0042	2.97188
0.189004	4.2974	3.09142
0.235816	4.5991	3.20959
0.281044	4.8893	3.32074

ZrH_2L – 72 hour humidity exposure:

t-Plot Micropore Area: 106.1502 m²/g
t-Plot External Surface Area: 138.0564 m²/g

Slope: 0.398200 ± 0.007672 mmol/g·Å
Y-Intercept: 1.255296 ± 0.031505 mmol/g
Correlation Coefficient: 0.998888

Fitted Points		
Relative Pressure (P/P_o)	Statistical Thickness (Å)	Quantity Adsorbed (mmol/g)
0.089144	3.5926	2.67218
0.100086	3.679	2.71563
0.111342	3.7642	2.75512
0.122534	3.8461	2.7942
0.144954	4.0037	2.8608
0.189096	4.298	2.97481
0.235404	4.5964	3.08547
0.280738	4.8873	3.19232

48% HF Hydrothermal:

t-Plot Micropore Area: 720.3167 m²/g
t-Plot External Surface Area: 96.4667 m²/g

Slope: 0.278242 ± 0.015344 mmol/g·Å
Y-Intercept: 8.109626 ± 0.062065 mmol/g
Correlation Coefficient: 0.989523

Fitted Points		
Relative Pressure (P/P_o)	Statistical Thickness (Å)	Quantity Adsorbed (mmol/g)
0.078354	3.5032	9.05444
0.089453	3.5951	9.09705
0.100955	3.6857	9.13466
0.112031	3.7693	9.16746
0.122923	3.8489	9.19626
0.144734	4.0022	9.24601
0.189226	4.2989	9.32559
0.235132	4.5947	9.38974
0.279994	4.8825	9.44236

CALF-31:

t-Plot Micropore Area: 694.1552 m²/g
t-Plot External Surface Area: 98.6113 m²/g

Slope: 0.284427 ± 0.014389 mmol/g·Å
Y-Intercept: 7.817890 ± 0.058199 mmol/g
Correlation Coefficient: 0.991161

Fitted Points		
Relative Pressure (P/P_o)	Statistical Thickness (Å)	Quantity Adsorbed (mmol/g)
0.078492	3.5044	8.78519
0.089311	3.594	8.8283
0.100824	3.6847	8.86758
0.111752	3.7673	8.90183
0.123023	3.8496	8.92388
0.144787	4.0025	8.97535
0.189366	4.2998	9.05988
0.235104	4.5945	9.12725
0.279904	4.882	9.18198

CALF-31 – 24 hour humidity exposure:

t-Plot Micropore Area: 686.6969 m²/g
t-Plot External Surface Area: 99.7908 m²/g

Slope: 0.287829 ± 0.016082 mmol/g·Å
Y-Intercept: 7.860992 ± 0.065009 mmol/g
Correlation Coefficient: 0.989250

Fitted Points		
Relative Pressure (P/P_o)	Statistical Thickness (Å)	Quantity Adsorbed (mmol/g)
0.078089	3.501	8.83792
0.089172	3.5929	8.88133
0.100582	3.6828	8.91995
0.111465	3.7651	8.95523
0.122632	3.8468	8.9839
0.144758	4.0023	9.03656
0.189475	4.3005	9.11991
0.234412	4.5901	9.18438
0.279181	4.8773	9.2373

BET Model Fitting:

ZrH_2L:

Slope: 0.384338 ± 0.001799 g/mmol
Y-Intercept: 0.001228 ± 0.000124 g/mmol
Correlation Coefficient: 0.9998795

Fitted Points		
Relative Pressure (P/P_o)	Quantity Adsorbed (mmol/g)	$1/[Q(P_o/P -1)]$
0.003248	1.68046	0.00194
0.006278	1.87477	0.00337
0.010907	2.03283	0.00542
0.022343	2.26477	0.01009
0.030965	2.38069	0.01342
0.043275	2.49233	0.01815
0.054415	2.57329	0.02236
0.060133	2.61392	0.02448
0.077934	2.71021	0.03119
0.089101	2.76319	0.0354
0.100101	2.81	0.03959
0.111396	2.85447	0.04392
0.122599	2.89666	0.048

ZrH_2L – 48 hour humidity exposure:

Slope: 0.385356 ± 0.001785 g/mmol
Y-Intercept: 0.000985 ± 0.000107 g/mmol
Correlation Coefficient: 0.9998820

Fitted Points		
Relative Pressure (P/P_o)	Quantity Adsorbed (mmol/g)	$1/[Q(P_o/P -1)]$
0.00227	1.6713	0.00136
0.004829	1.86886	0.0026
0.008559	2.02694	0.00426
0.013469	2.16112	0.00632
0.020849	2.29648	0.00927
0.032274	2.43597	0.01369
0.043779	2.52853	0.01811
0.05476	2.6043	0.02225
0.06038	2.64106	0.02433
0.078002	2.728	0.03101
0.088957	2.77586	0.03518
0.100163	2.8215	0.03945
0.111438	2.86319	0.0438

ZrH_2L – 72 hour humidity exposure:

Slope: 0.398371 ± 0.001226 g/mmol
Y-Intercept: 0.001181 ± 0.000085 g/mmol
Correlation Coefficient: 0.9999479

Fitted Points		
Relative Pressure (P/P_o)	Quantity Adsorbed (mmol/g)	$1/[Q(P_o/P -1)]$
0.005352	1.83814	0.00293
0.008983	1.96126	0.00462
0.013514	2.07731	0.00659
0.021693	2.22207	0.00998
0.032684	2.3428	0.01442
0.043414	2.4307	0.01867
0.055026	2.50526	0.02324
0.06042	2.54138	0.0253
0.077941	2.62548	0.0322
0.089144	2.67218	0.03662
0.100086	2.71563	0.04095
0.111342	2.75512	0.04548
0.122534	2.7942	0.04998

48% HF Hydrothermal:

Slope: 0.119455 ± 0.000424 g/mmol
Y-Intercept: 0.000005 ± 0.000017 g/mmol
Correlation Coefficient: 0.9999181

Fitted Points		
Relative Pressure (P/P_o)	Quantity Adsorbed (mmol/g)	$1/[Q(P_o/P -1)]$
0.000811	6.98532	0.00012
0.001123	7.22812	0.00016
0.001611	7.4639	0.00022
0.002385	7.68762	0.00031
0.003607	7.89952	0.00046
0.005424	8.08903	0.00067
0.008139	8.25857	0.00099
0.011414	8.39374	0.00138
0.021357	8.62316	0.00253
0.03149	8.75626	0.00371
0.042926	8.85921	0.00506
0.054902	8.94014	0.0065
0.061299	8.97655	0.00727
0.078354	9.05444	0.00939
0.089453	9.09705	0.0108

CALF-31:

Slope: 0.123069 ± 0.000349 g/mmol
Y-Intercept: 0.000010 ± 0.000013 g/mmol
Correlation Coefficient: 0.9999356

Fitted Points		
Relative Pressure (P/P_o)	Quantity Adsorbed (mmol/g)	$1/[Q(P_o/P -1)]$
0.000331	5.97472	0.00006
0.000426	6.22536	0.00007
0.000561	6.4746	0.00009
0.000761	6.72142	0.00011
0.001068	6.96381	0.00015
0.001549	7.19866	0.00022
0.002318	7.42001	0.00031
0.003514	7.6255	0.00046
0.005258	7.80805	0.00068
0.008077	7.98316	0.00102
0.011127	8.10904	0.00139
0.021424	8.348	0.00262
0.031715	8.48299	0.00386
0.043302	8.58934	0.00527
0.055053	8.66793	0.00672
0.061212	8.70412	0.00749
0.078492	8.78519	0.0097
0.089311	8.8283	0.01111

CALF-31 – 24 hour humidity exposure:

Slope: 0.124083 ± 0.000578 g/mmol
Y-Intercept: -0.000022 ± 0.000030 g/mmol
Correlation Coefficient: 0.9998372

Fitted Points		
Relative Pressure (P/P_o)	Quantity Adsorbed (mmol/g)	$1/[Q(P_o/P -1)]$
0.000921	6.92642	0.00013
0.001324	7.16388	0.00019
0.001959	7.38954	0.00027
0.002927	7.59685	0.00039
0.004345	7.78333	0.00056
0.006273	7.94438	0.00079
0.008955	8.05825	0.00112
0.011933	8.17727	0.00148
0.021272	8.39197	0.00259
0.031872	8.53704	0.00386
0.043603	8.64313	0.00527
0.054893	8.72038	0.00666
0.061089	8.75819	0.00743
0.078089	8.83792	0.00958
0.089172	8.88133	0.01102
0.100582	8.91995	0.01254
0.111465	8.95523	0.01401