Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Evaluation of Brønsted Acidity and Proton Topology in Zr- and Hf-based Metal–Organic Frameworks Using Potentiometric Acid–Base Titration

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Zr-UiO-66

Hf-UiO-66

NU-1000

Zr-UiO-67(HCl)

MOF-808

Materials and Methods.

NU-1000,[1] Zr-UiO-66,[2] Zr-UiO-67(HCl),[2] Zr-PCN-57,[3] and Hf-UiO-66[4] were synthesized according to methods reported in the literature.

Instrumentation.

Activation of MOF samples was performed on a Micromeritics SmartVacPrep (Micromeritics, Norcross, GA, USA). N_2 adsorption isotherms were collected on a Tristar II 3020 (Micromeritics) at 77 K. All pore size distributions were obtained using a carbon slit pore model with a N_2 kernel (Micromeritics). Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Smartlab instrument. Thermogravimetric analyses (TGA) were carried out on a TA Instruments Q500 thermogravimetric analyzer with an evolved gas analysis furnace. Samples were heated from 20 °C to 800 °C at a rate of 10 °C/minute under flowing O_2.

MOF Ligands.

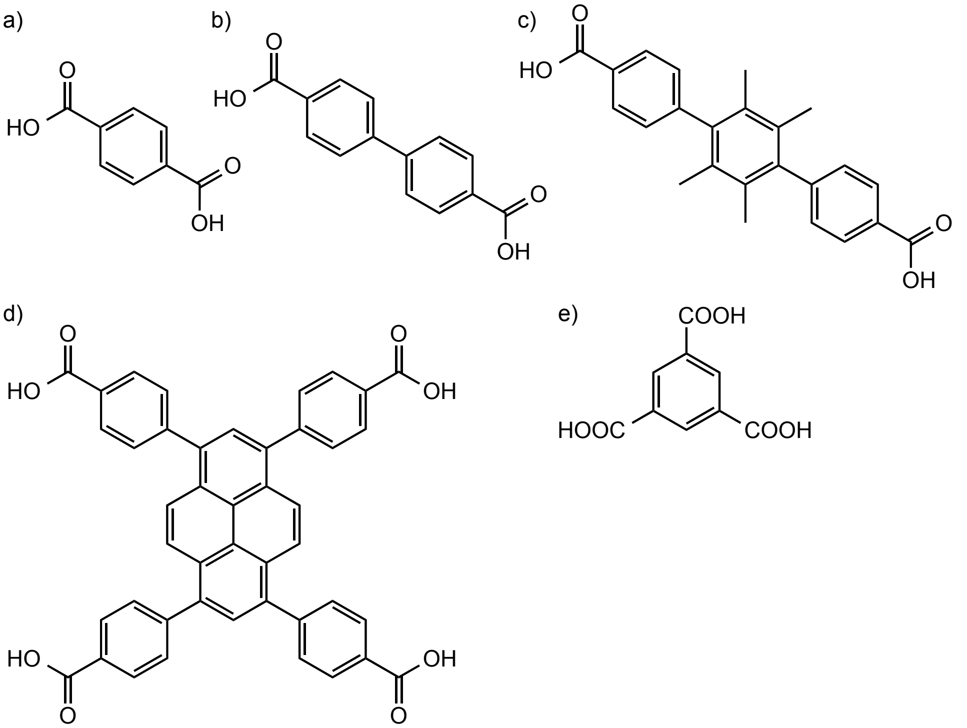

Figure S1. Ligands used for a) UiO-66, terephthalic acid, b) UiO-67, biphenyl-4,4’-dicarboxylic acid, c) PCN-57, 2′,3′,5′,6′-tetramethyl-terphenyl-4,4″-dicarboxylic acid, d) NU-1000, 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene, and e) MOF-808, benzene-1,3,5-tricarboxylic acid.

Synthesis of Hf-UiO-67. $HfCl_4$ (120 mg, 0.374 mmol), biphenyl-4,4′-dicarboxylic acid (BPDC) (100 mg, 0.413 mmol), 1.5 g benzoic acid (1.5 g, 12.3 mmol), and *N,N'*-dimethylformamide (DMF) (18 mL) were added to an 8-dram vial. The mixture was sonicated for 30 min, then incubated in an oven at 100 °C for 48 h. The resulting white solid was washed with fresh DMF (3 × 20 mL) and then with acetone (3 × 20 mL). After drying the sample in a vacuum oven, the sample was activated on a SmartVacPrep port by heating at 120 °C under vacuum for 12 h. Yield: 65% white microcrystalline powder.

Synthesis of Zr-UiO-67 (Benzoic Acid). The same procedure as Hf-UiO-67 was followed except $ZrCl_4$ (120 mg, 0.515 mmol) was used instead of $HfCl_4$. Yield: 27% white microcrystalline powder.

Synthesis of Hf-PCN-57. $HfOCl_2 \cdot 8H_2O$ (120 mg, 0.293 mmol), 2′,3′,5′,6′-tetramethyl-terphenyl-4,4″-dicarboxylic acid (TPDC-$4CH_3$) (100 mg, 0.267 mmol), 1.0 g benzoic acid, and *N,N'*-dimethylformamide (DMF) (20 mL) were added to an 8-dram vial. The mixture was sonicated for 30 min, then incubated in an oven at 100 °C for 24 h. The sample was washed and activated using the same procedure as that of Hf-UiO-67. Yield: 72% white microcrystalline powder.

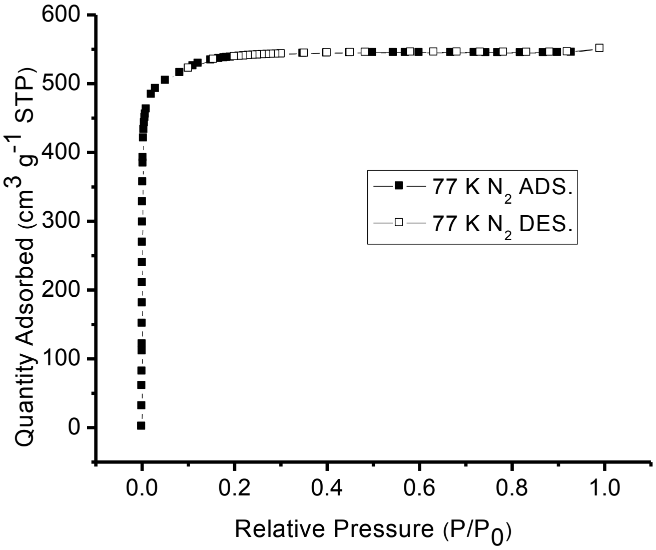

Figure S2. N_2 adsorption isotherm for Hf-UiO-67.

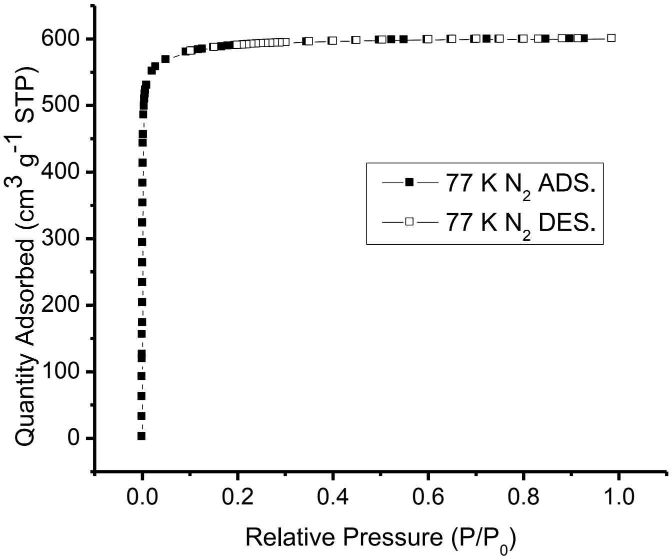

Figure S3. N_2 adsorption isotherm for Zr-UiO-67 synthesized with benzoic acid.

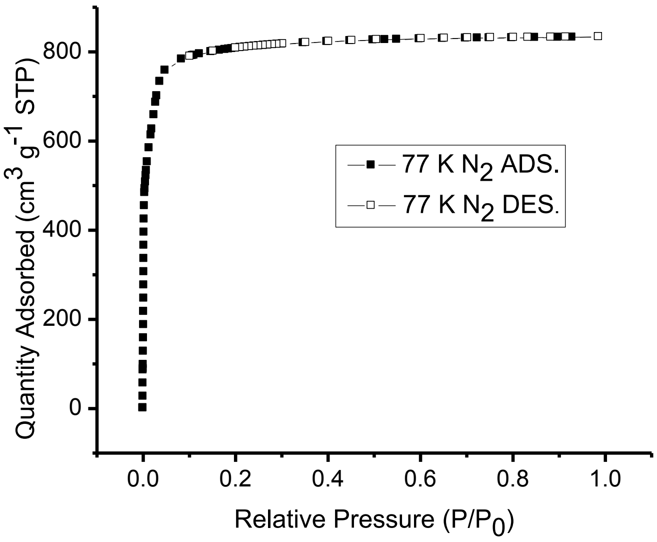

Figure S4. N_2 adsorption isotherm for Zr-PCN-57.

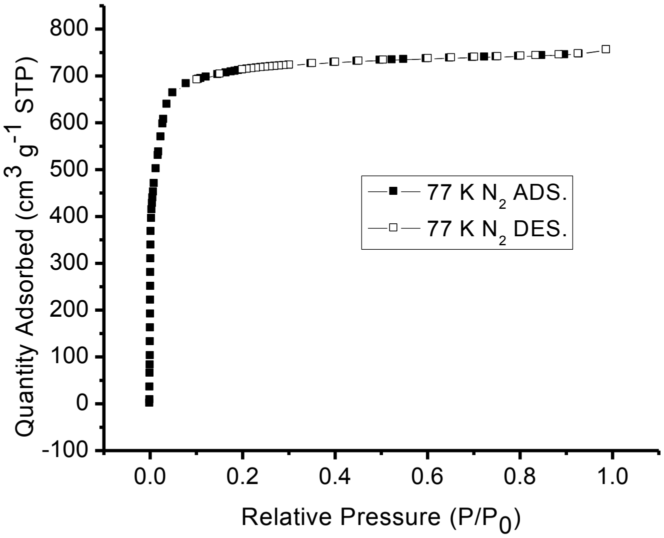

Figure S5. N_2 adsorption isotherm for Hf-PCN-57.

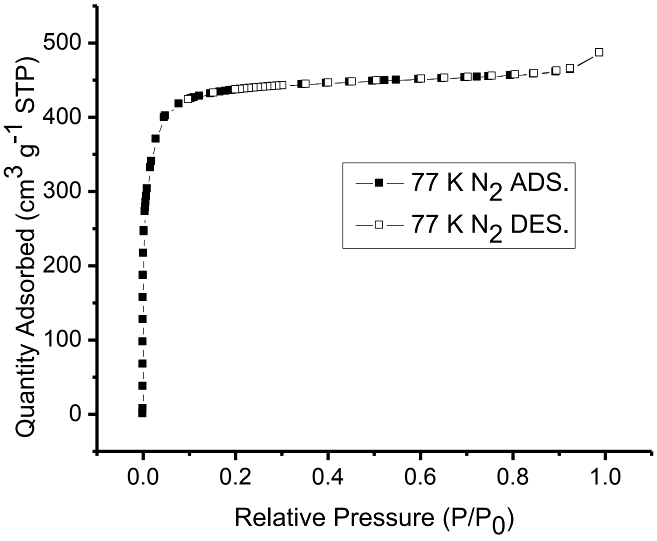

Figure S6. N_2 adsorption isotherm for Zr-UiO-66.

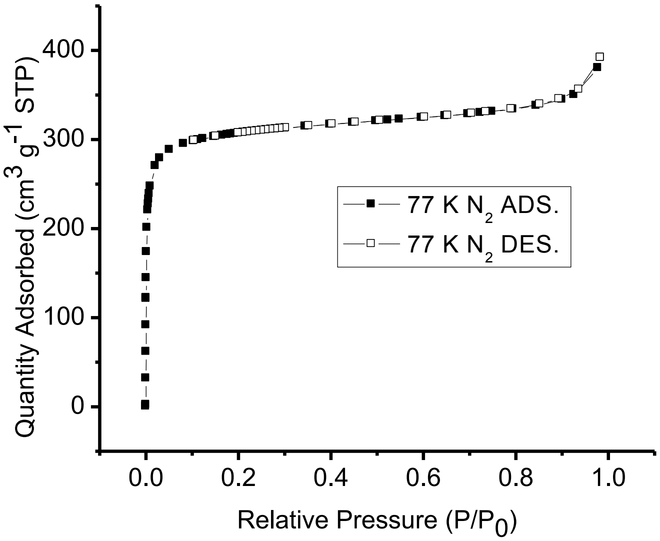

Figure S7. N_2 adsorption isotherm for Hf-UiO-66.

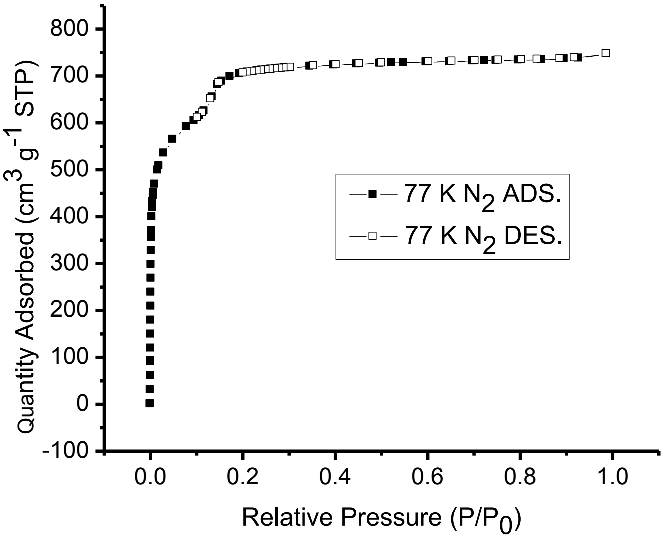

Figure S8. N_2 adsorption isotherm for Zr-UiO-67(HCl).

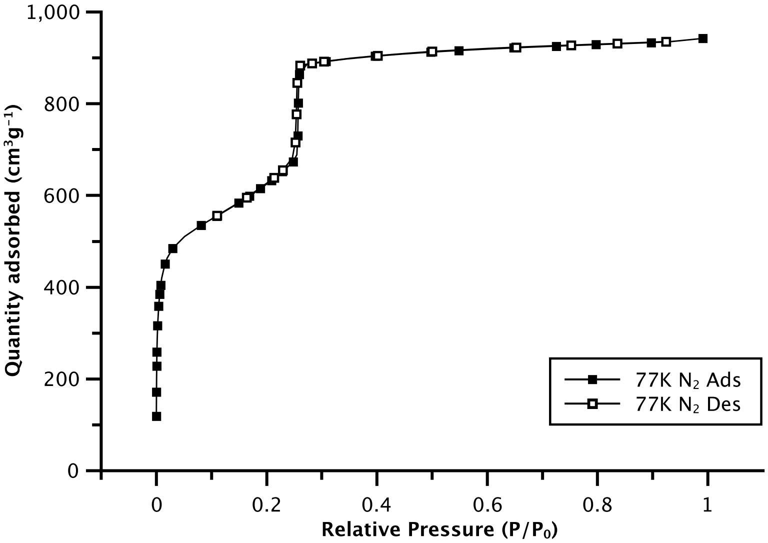

Figure S9. N_2 adsorption isotherm for NU-1000.

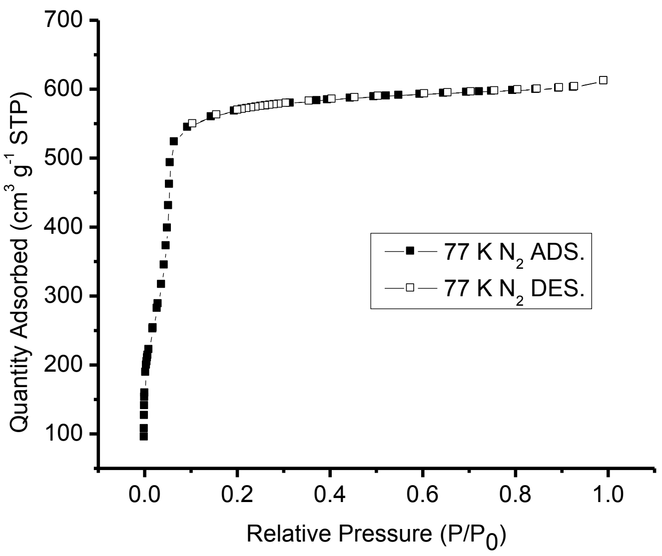

Figure S10. N_2 adsorption isotherm for MOF-808.

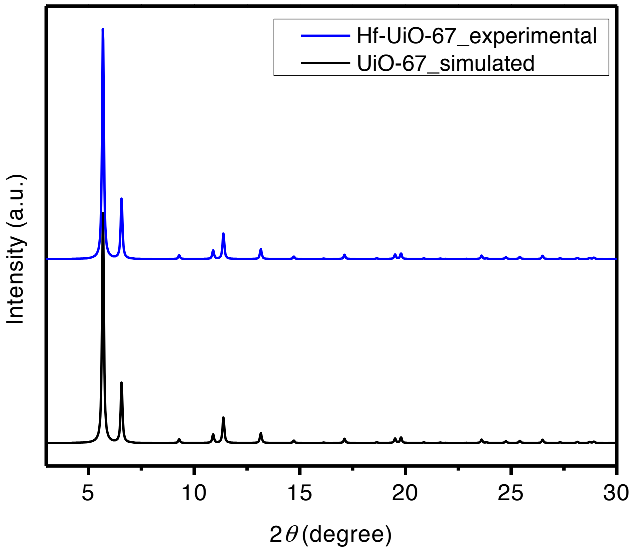

Figure S11. Simulated (black, bottom) and experimental (blue, top) PXRD patterns of Hf-UiO-67.

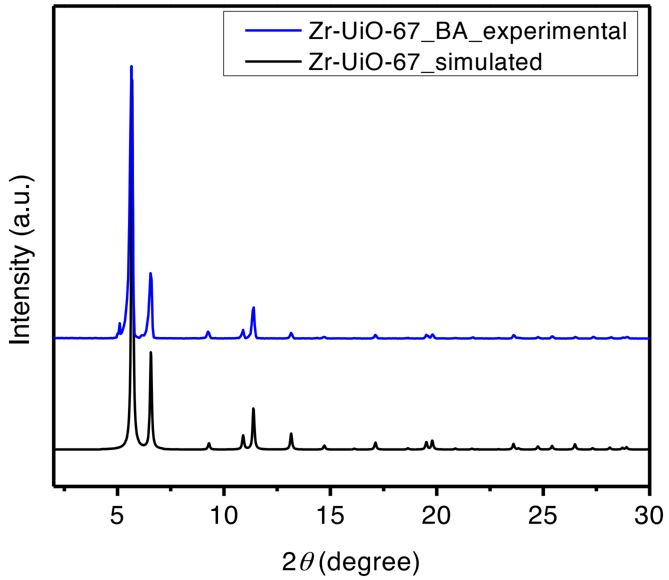

Figure S12. Simulated (black, bottom) and experimental (blue, top) PXRD patterns of Zr-UiO-67 synthesized with benzoic acid.

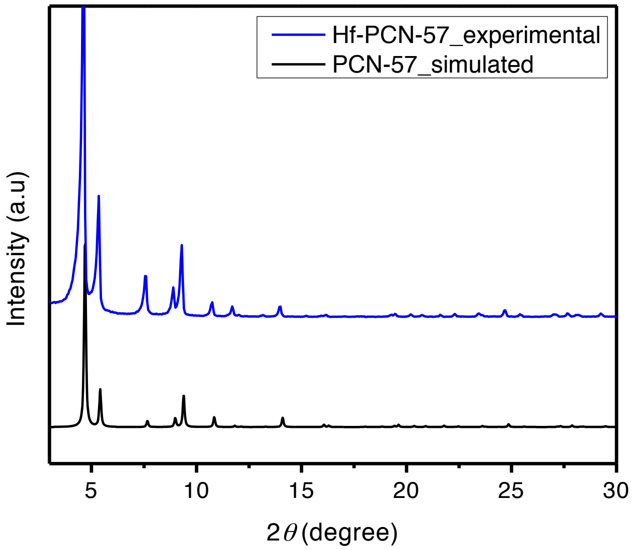

Figure S13. Simulated (black, bottom) and experimental (blue, top) PXRD patterns of Hf-PCN-57.

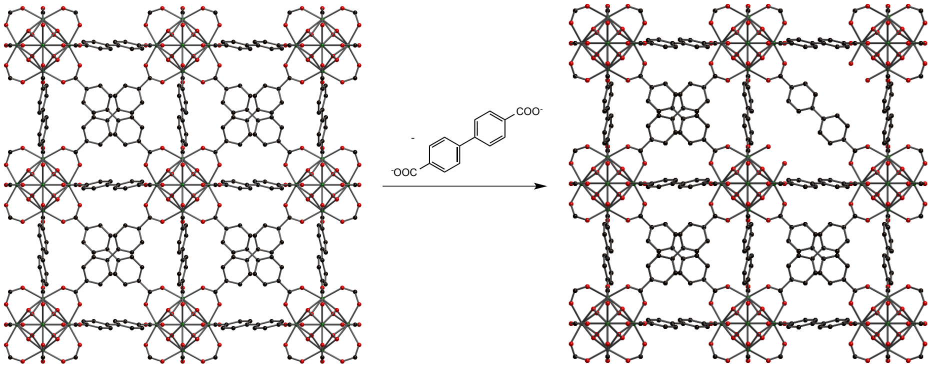

Figure S14. Representative crystal structure of UiO-67 showing a missing linker. Zr/Hf, C, and O are shown in green, black, and red, respectively. Hydrogen atoms have been omitted for clarity.

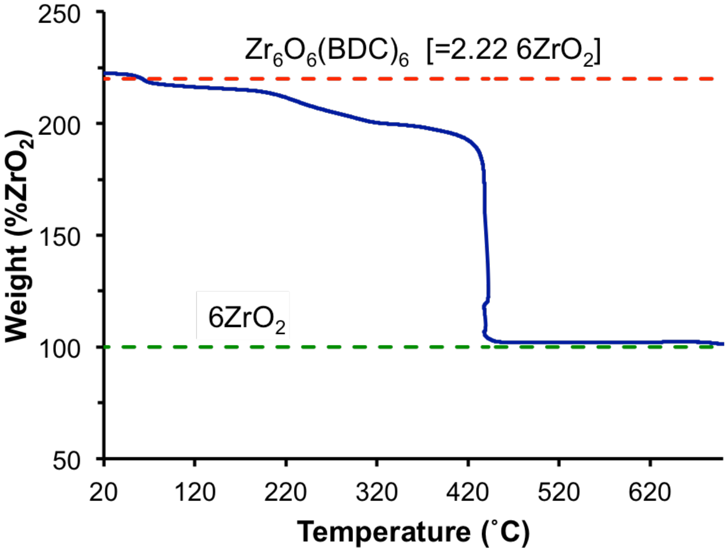

Figure S15. TGA trace of activated Zr-UiO-66.

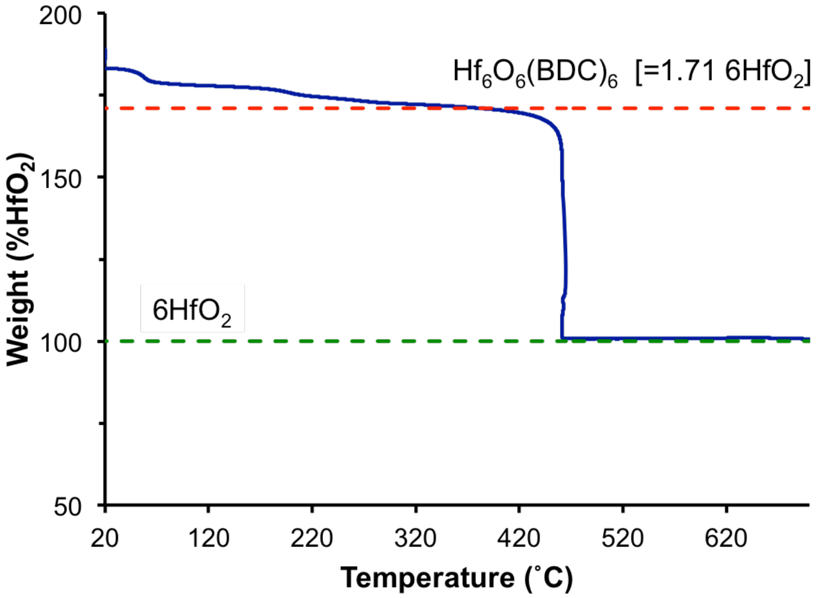

Figure S16. TGA trace of activated Hf-UiO-66.

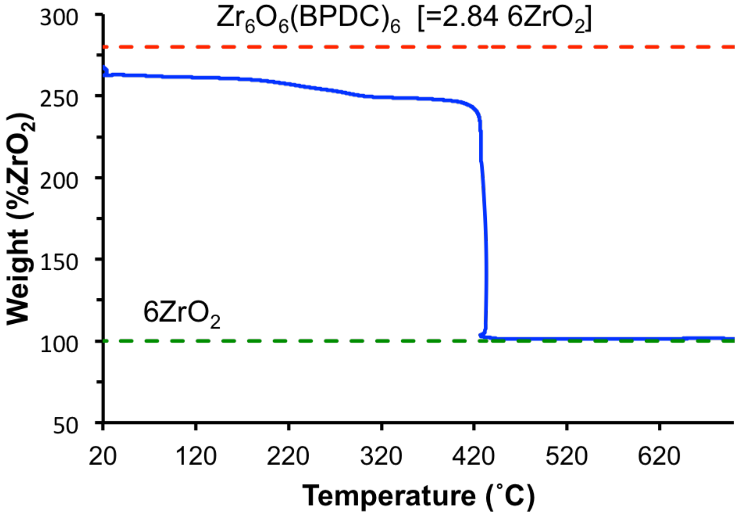

Figure S17. TGA trace of activated Zr-UiO-67(HCl) synthesized with hydrochloric acid.

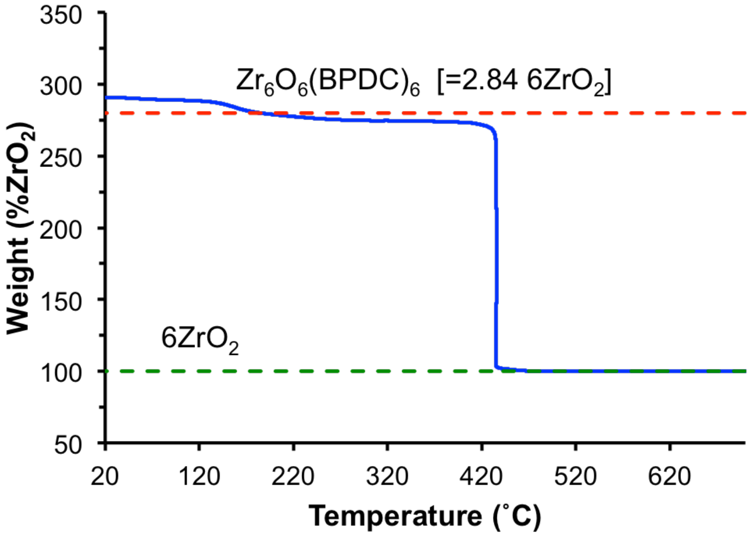

Figure S18. TGA trace of activated Zr-UiO-67 synthesized with benzoic acid.

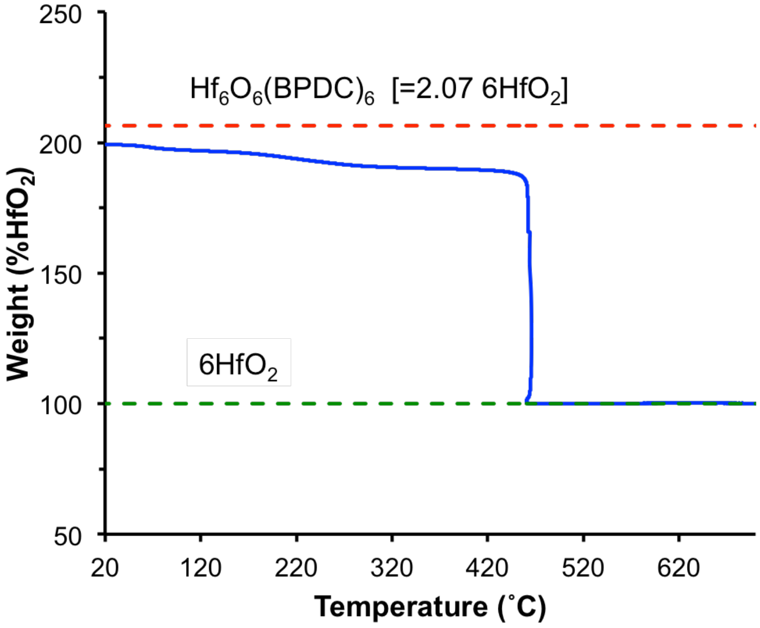

Figure S19. TGA trace of activated Hf-UiO-67.

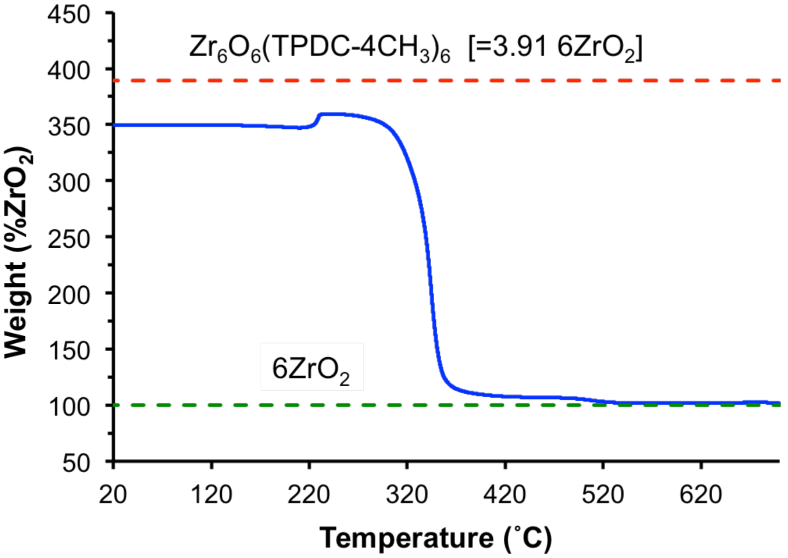

Figure S20. TGA trace of activated Zr-PCN-57. N.B.: We do not understand the weight gain observed near 220 °C for Zr-PCN-57; however, we observed similar TGA traces for multiple samples.

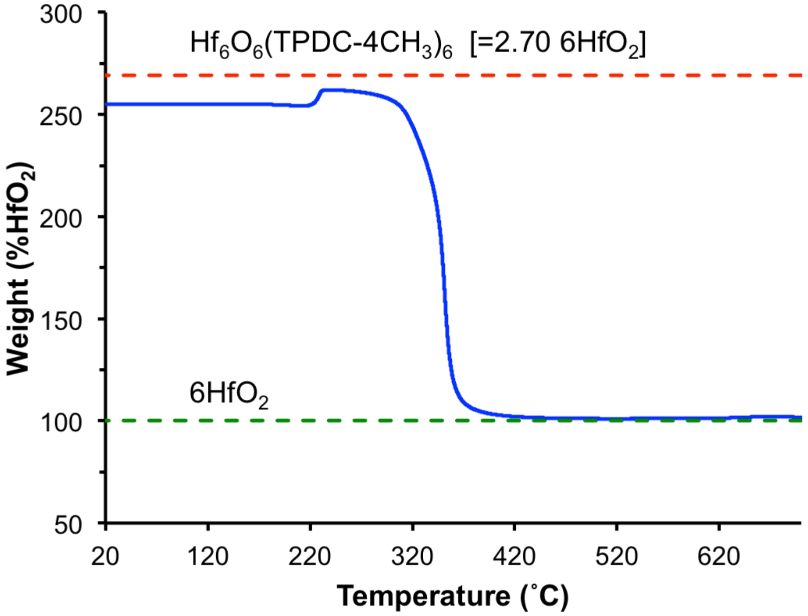

Figure S21. TGA trace of activated Hf-PCN-57. N.B.: We do not understand the weight gain observed near 220 °C for Hf-PCN-57; however, we observed similar TGA traces for multiple samples.

Table S1. Estimated Missing Linkers for UiO-type MOFs from TGA analyses.

MOF	**Decomposition Starting Point (%ZrO_2/HfO_2)**		**Estimated Missing Linkers (per M_6 cluster)**
	Experimental	**Theoretical**	
Zr-UiO-66	186	222	1.6
Zr-UiO-67(HCl)	242	284	1.3
Zr-UiO-67(BA)	271	284	0.4
Zr-PCN-57	351	391	0.8
Hf-UiO-66	160	171	0.8
Hf-UiO-67(BA)	186	207	1.1
Hf-PCN-57	257	270	0.4

Missing linker defects were calculated using the TGA analysis method described by Lillerud et al.[5]

PXRD Patterns of MOFs Post-Titration

PXRD assessment of the MOFs in this study titrated to pH = 10.5 show a complete loss of crystallinity. However, typically in the pH range during which node protons appear to be undergoing deprotonation, the MOFs seem to be stable. See below and the manuscript for more details.

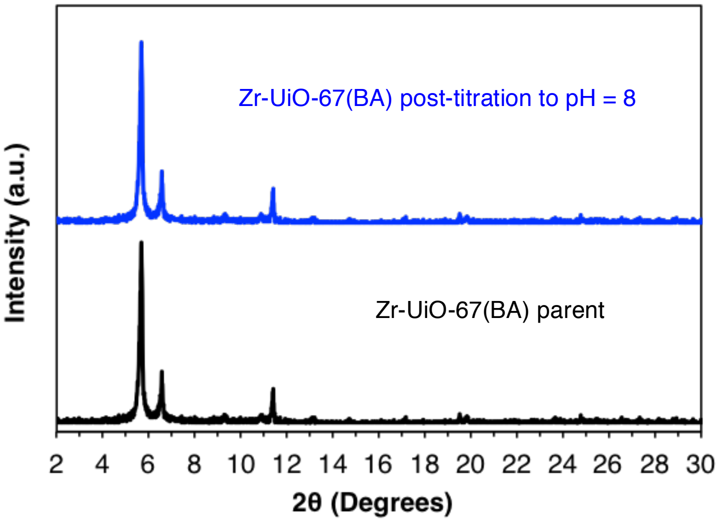

Figure S22. PXRD patterns of Zr-UiO-67(BA) parent (black, bottom) and after titration to pH = 8 (blue, top).

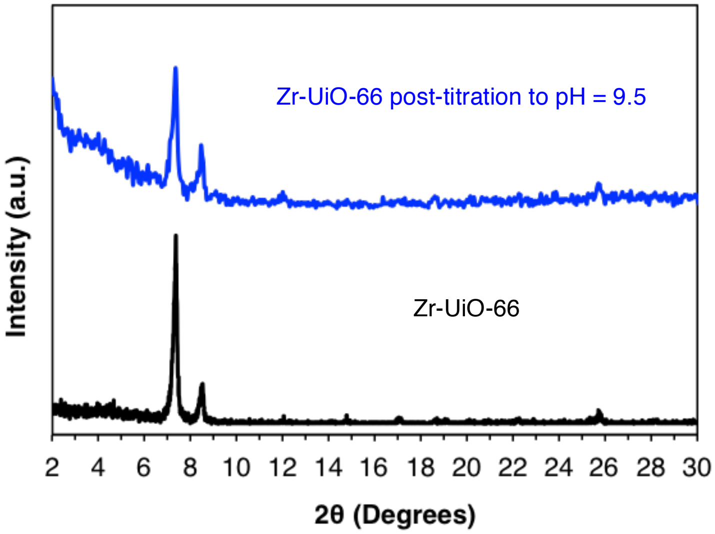

Figure S23. PXRD patterns of Zr-UiO-66 parent (black, bottom) and after titration to pH = 8 (blue, top).

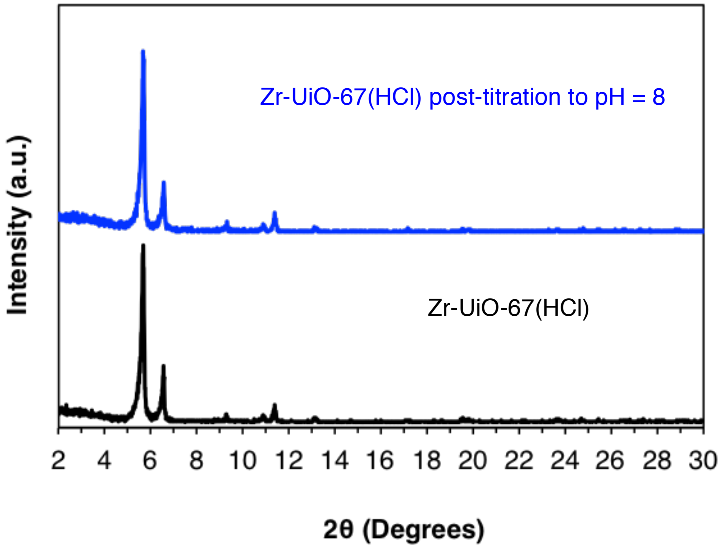

Figure S24. PXRD patterns of Zr-UiO-67(HCl) parent (black, bottom) and after titration to pH = 8 (blue, top).

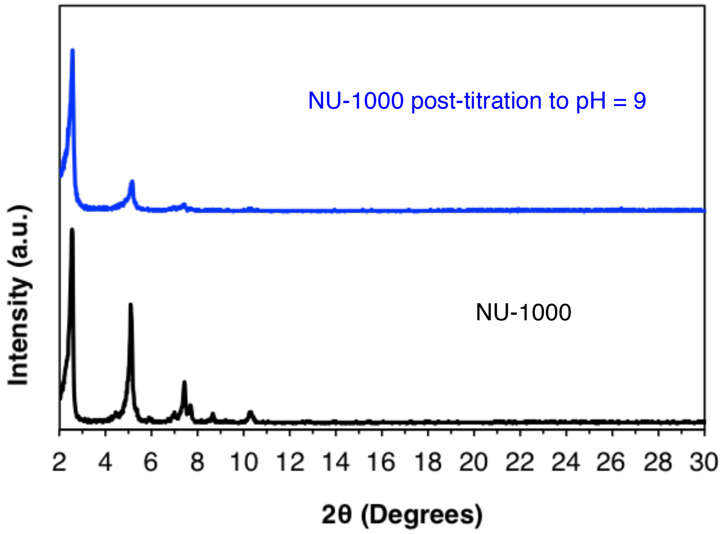

Figure S25. PXRD patterns of NU-1000 parent (black, bottom) and after titration to pH = 9 (blue, top).

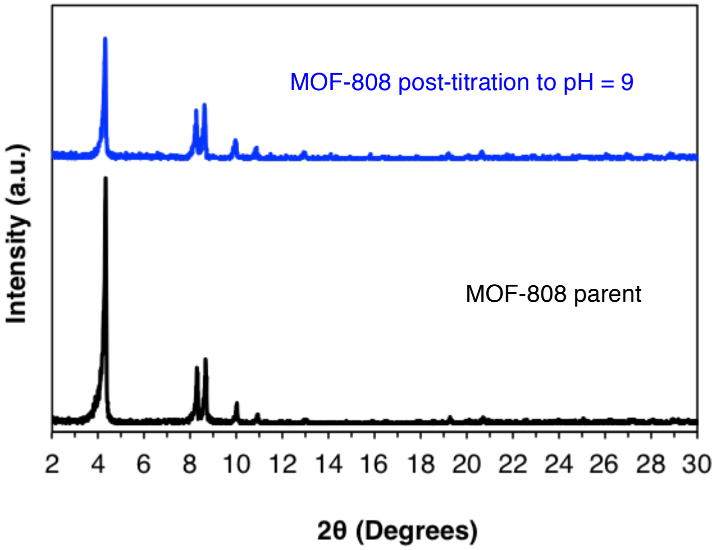

Figure S26. PXRD patterns of MOF-808 parent (black, bottom) and after titration to pH = 9 (blue, top).

Titration Data

Zr-UiO-67

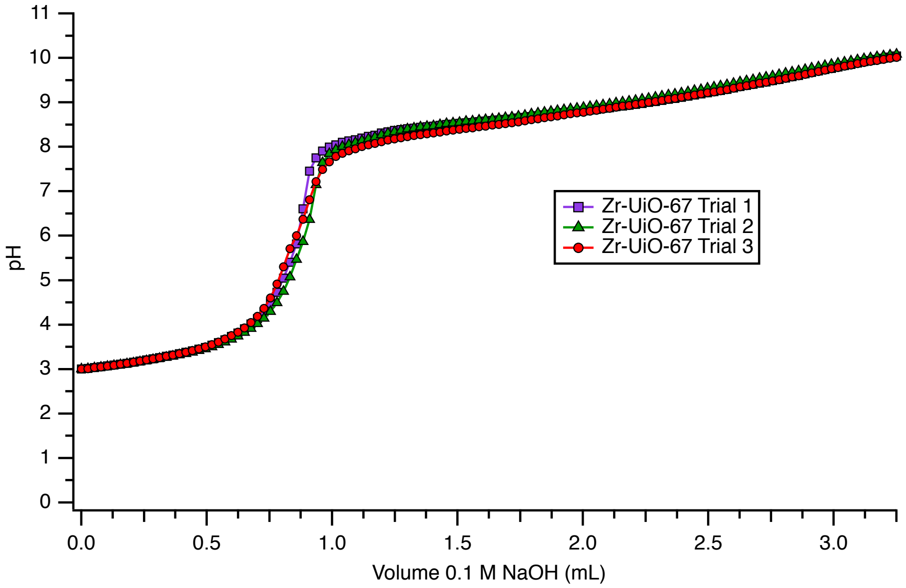

Figure S27. Overlay of three acid–base titration curves for Zr-UiO-67 showing reproducibility between samples.

Hf-UiO-67

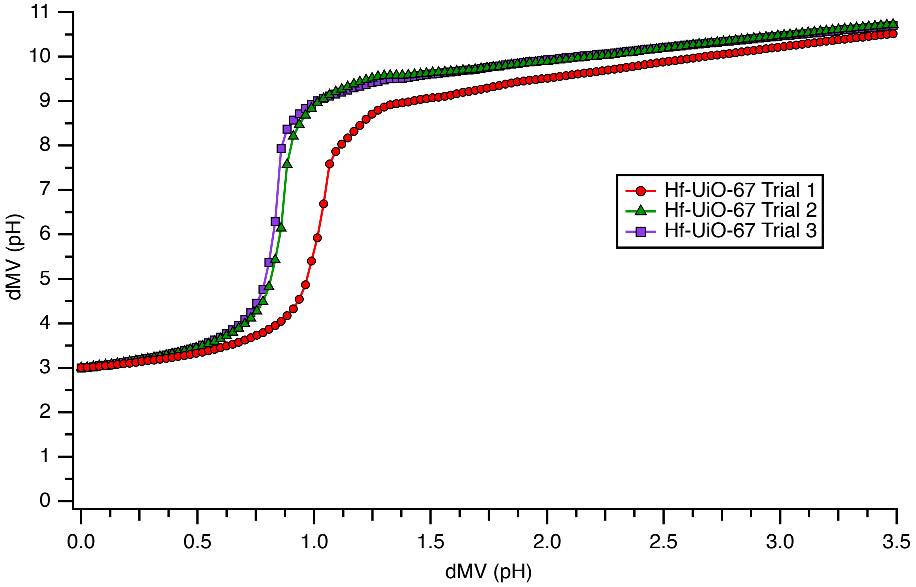

Figure S28. Overlay of three acid–base titration curves for Hf-UiO-67 showing reproducibility between samples.

Zr-PCN-57

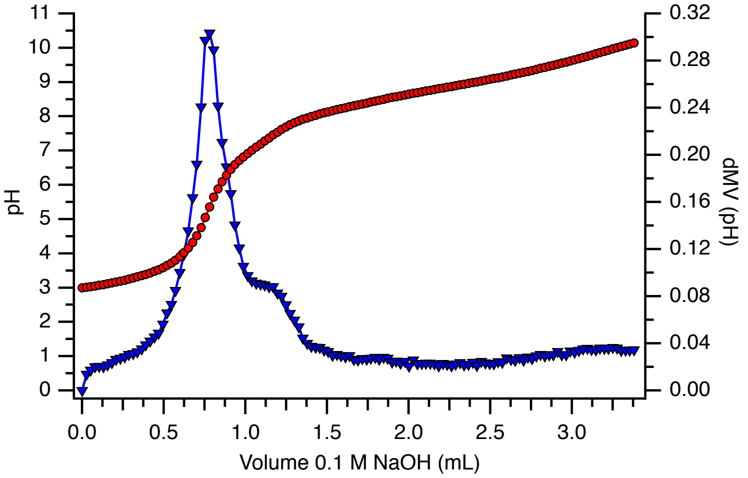

Figure S29. Acid–base titration curve of Zr-PCN-57 (red) and first derivative curve (blue).

The first derivative curve of Zr-PCN-57 may indicate a second inflection point/equivalence point around pH 7.5 suggesting the presence of some defect sites in the sample; however, due to the poor dispersion of the sample in aqueous solution we are hesitant to draw any conclusions from this data set beyond the pK_a value determined from the equivalence point at 5.4.

Hf-PCN-57

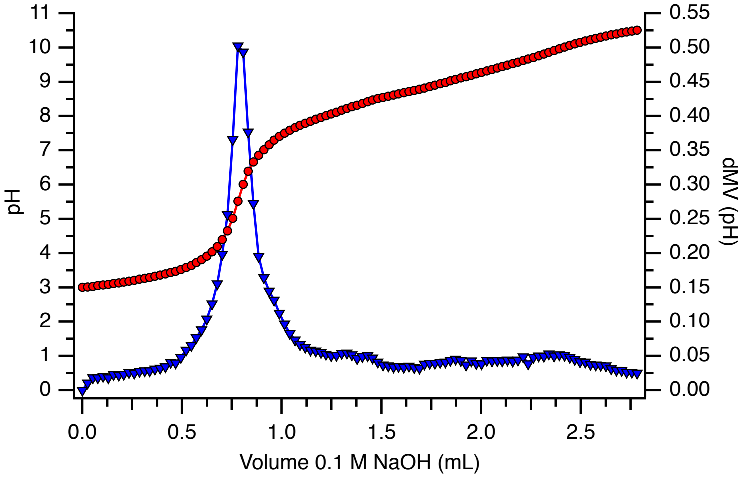

Figure S30. Acid–base titration curve of Hf-PCN-57 (red) and first derivative curve (blue).

Zr-UiO-66

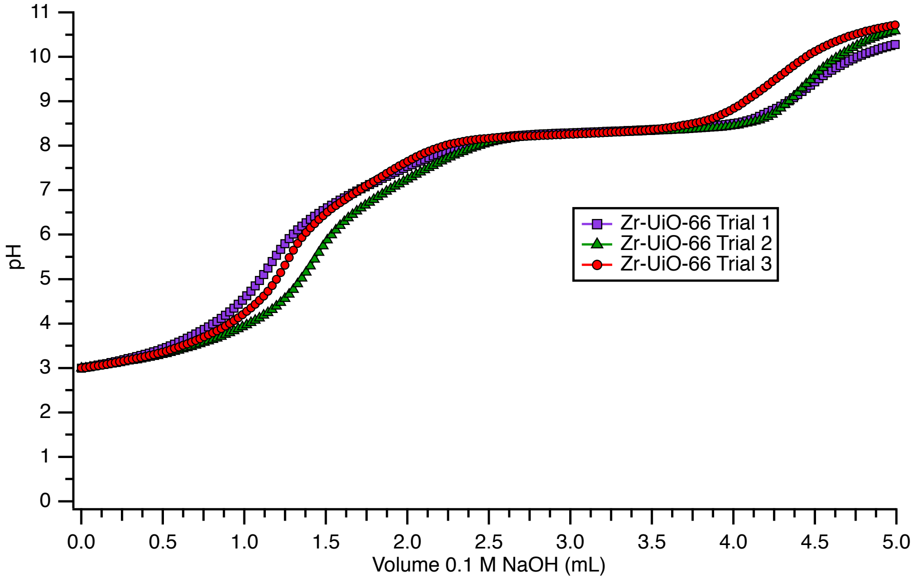

Figure S31. Overlay of three acid–base titration curves for Zr-UiO-66 showing reproducibility between samples.

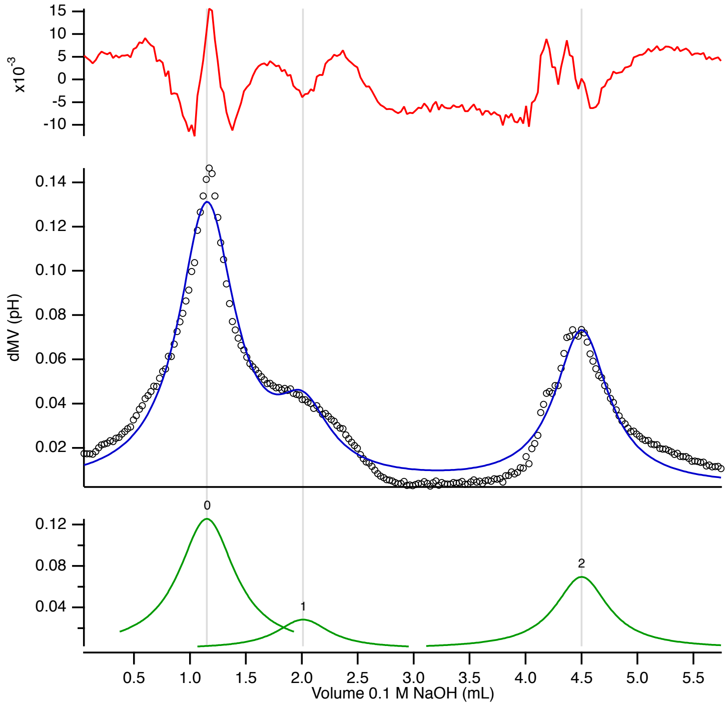

Figure S32. Representative curve fitting for the first derivative of the titration curve of pH as a function of volume of titrant added for Zr-UiO-66: Located peaks (green) (bottom); first derivative data (black circles) and fit trace (blue) (middle); residual plot (red) (top). Peaks were fit as Lorentzian functions.

```
Multipeak Fit report for Zr-UiO-66:
Chi square: 0.0075287
Total fitted points: 220
Multi-peak fit version 2.16
Total Peak Area = 0.20869 +/- 0.0060043

Baseline        Type: Constant

        y0 =    0.0023544       +/-     0.0010797

Peak 0          Type: Lorentzian

        Location =      1.15    +/-     0.0055287
        Height =        0.12558         +/-     0.0020745
        Area =          0.12024         +/-     0.0036137
        FWHM =          0.60951         +/-     0.019437

        Fit function parameters
        Location =      1.15    +/-     0.0055287
        FWHM =          0.60951         +/-     0.019437
        Area =0.12024           +/-     0.0036137

Peak 1          Type: Lorentzian

        Location =      2.0103          +/-     0.023511
        Height =        0.028322        +/-     0.0021178
        Area =          0.025549        +/-     0.0034409
        FWHM =          0.57428         +/-     0.08251

        Fit function parameters
        Location =      2.0103          +/-     0.023511
        FWHM =          0.57428         +/-     0.08251
        Area =0.025549          +/-     0.0034409

Peak 2          Type: Lorentzian

        Location =      4.5007          +/-     0.0084137
        Height =        0.069551        +/-     0.0020925
        Area =          0.06291         +/-     0.0033396
        FWHM =          0.57584         +/-     0.032298

        Fit function parameters
        Location =      4.5007          +/-     0.0084137
```

FWHM = 0.57584 +/- 0.032298
Area =0.06291 +/- 0.0033396

Table S2. Titrant consumed after the first equivalence point for Zr-UiO-66

	mmoles OH^- consumed between EP1 to EP3
Trial 1	0.333
Trial 2	0.304
Trial 3	0.302
Average	**0.313** (± 0.017)

Table S3. Defect calculations for Zr-UiO-66

Missing Linkers	**Molecular Formula**[a]	**MW**	**mmoles H^+ from defects in 0.049 g sample**
1	$Zr_6O_4(OH)_4(C_8H_4O_4)_5[(H_2O)(OH)]_2$	1570.01	0.187
2	$Zr_6O_4(OH)_4(C_8H_4O_4)_4[(H_2O)(OH)]_4$	1475.93	0.398
1.50	$Zr_6O_4(OH)_4(C_8H_4O_4)_{4.50}[(H_2O)(OH)]_{3.0}$	1522.97	0.290
1.55	$Zr_6O_4(OH)_4(C_8H_4O_4)_{4.45}[(H_2O)(OH)]_{3.09}$	1518.69	0.299
1.60	$Zr_6O_4(OH)_4(C_8H_4O_4)_{4.40}[(H_2O)(OH)]_{3.20}$	1513.56	**0.311**
1.67	$Zr_6O_4(OH)_4(C_8H_4O_4)_{4.33}[(H_2O)(OH)]_{3.33}$	1507.29	0.325
1.75	$Zr_6O_4(OH)_4(C_8H_4O_4)_{4.25}[(H_2O)(OH)]_{3.50}$	1499.45	0.343

[a] All missing linkers are assumed to be replaced with 2 H_2O molecules and 2 –OH groups.

Hf-UiO-66

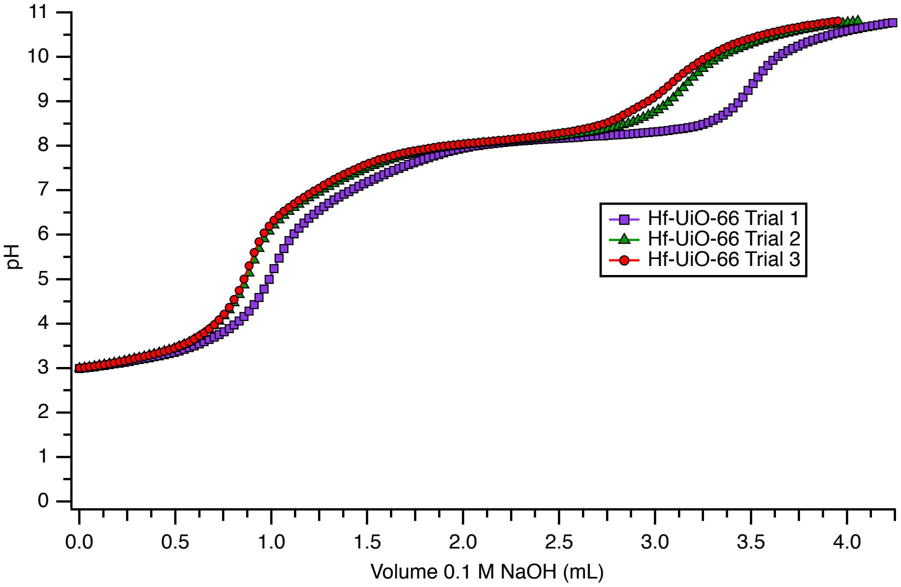

Figure S33. Overlay of three acid–base titration curves for Hf-UiO-66 showing reproducibility between samples.

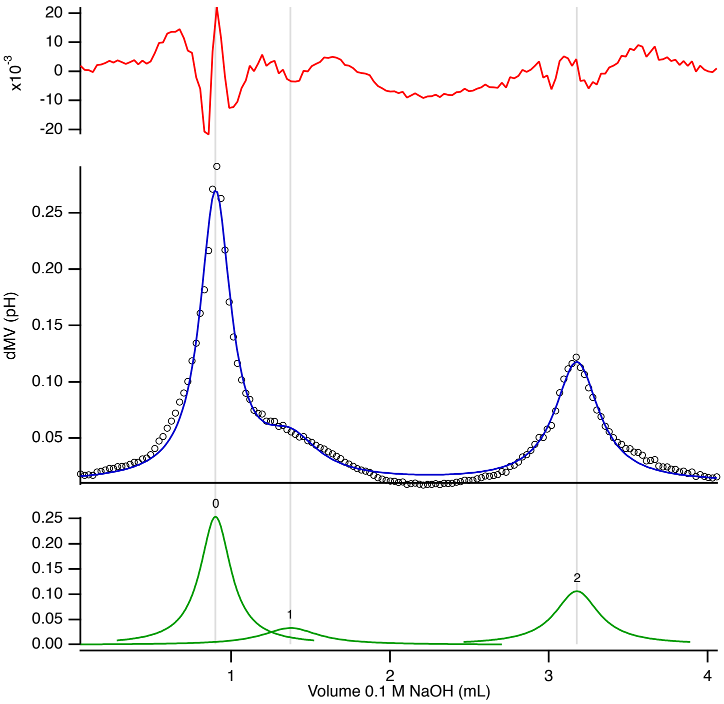

Figure S34. Representative curve fitting for the first derivative of the titration curve of pH as a function of volume of titrant added for Hf-UiO-66: Located peaks (green) (bottom); first derivative data (black circles) and fit trace (blue) (middle); residual plot (red) (top). Peaks were fit as Lorentzian functions.

```
Multipeak fit report for Hf-UiO-66:
Chi square: 0.0061373
Total fitted points: 155
Multi-peak fit version 2.16
Total Peak Area = 0.17198 +/- 0.0046317

Baseline        Type: Constant

        y0 =    0.010397        +/-     0.0011316

Peak 0          Type: Lorentzian

        Location =      0.90188         +/-     0.0017373
        Height =        0.25346         +/-     0.0035568
        Area =          0.093242        +/-     0.0021403
        FWHM =          0.2342          +/-     0.0059391

        Fit function parameters
        Location =      0.90188         +/-     0.0017373
        FWHM =          0.2342          +/-     0.0059391
        Area =0.093242        +/-     0.0021403

Peak 1          Type: Lorentzian

        Location =      1.3735          +/-     0.019753
        Height =        0.033173        +/-     0.0026263
        Area =          0.022545        +/-     0.0033673
        FWHM =          0.43265         +/-     0.069871

        Fit function parameters
        Location =      1.3735          +/-     0.019753
        FWHM =          0.43265         +/-     0.069871
        Area =0.022545        +/-     0.0033673

Peak 2          Type: Lorentzian

        Location =      3.1761          +/-     0.0045788
        Height =        0.10617         +/-     0.0029212
        Area =          0.056192        +/-     0.0023521
        FWHM =          0.33693         +/-     0.01605

        Fit function parameters
        Location =      3.1761          +/-     0.0045788
        FWHM =          0.33693         +/-     0.01605
```

Area =0.056192 +/- 0.0023521

Table S4. Titrant consumed after the first equivalence point for Hf-UiO-66

	mmoles OH^- consumed between EP1 to EP3
Trial 1	0.252
Trial 2	0.226
Trial 3	0.268
Average	**0.249** (±0.021)

Table S5. Defect calculations for Hf-UiO-66

Missing Linkers	**Molecular Formula**[a]	**MW**	**mmoles H^+ from defects in 0.049 g sample**
1	$Hf_6O_4(OH)_4(C_8H_4O_4)_5[(H_2O)(OH)]_2$	2093.60	0.140
2	$Hf_6O_4(OH)_4(C_8H_4O_4)_4[(H_2O)(OH)]_4$	1999.52	0.294
1.55	$Hf_6O_4(OH)_4(C_8H_4O_4)_{4.45}[(H_2O)(OH)]_{3.09}$	2042.28	0.222
1.60	$Hf_6O_4(OH)_4(C_8H_4O_4)_{4.40}[(H_2O)(OH)]_{3.20}$	2037.15	0.231
1.65	$Hf_6O_4(OH)_4(C_8H_4O_4)_{4.35}[(H_2O)(OH)]_{3.30}$	2032.45	0.239
1.70	$Hf_6O_4(OH)_4(C_8H_4O_4)_{4.30}[(H_2O)(OH)]_{3.40}$	2027.74	**0.246**
1.75	$Hf_6O_4(OH)_4(C_8H_4O_4)_{4.25}[(H_2O)(OH)]_{3.50}$	2023.04	0.254
1.80	$Hf_6O_4(OH)_4(C_8H_4O_4)_{4.20}[(H_2O)(OH)]_{3.60}$	2018.34	0.262
1.85	$Hf_6O_4(OH)_4(C_8H_4O_4)_{4.15}[(H_2O)(OH)]_{3.70}$	2013.6	0.270

[a] All missing linkers are assumed to be replaced with 2 H_2O molecules and 2 –OH groups.

NU-1000

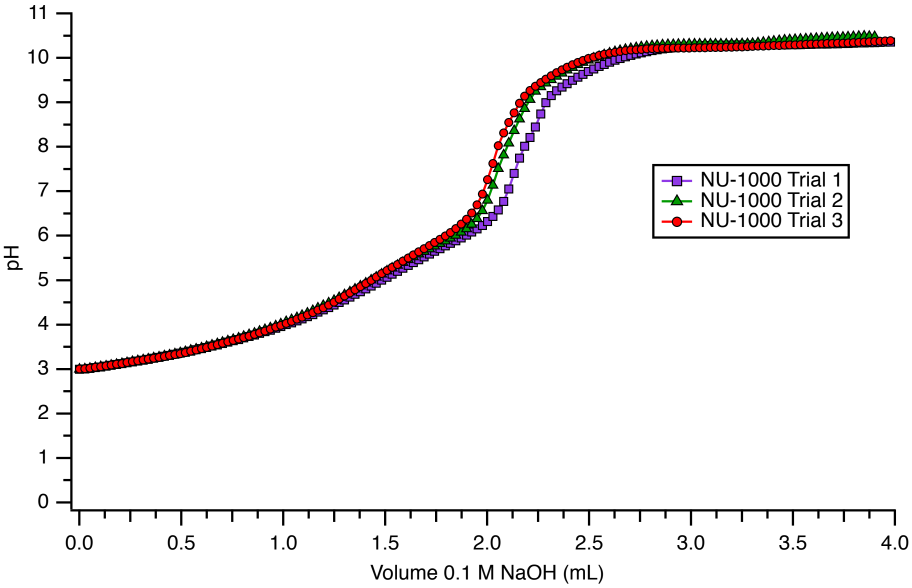

Figure S35. Overlay of three acid–base titration curves for NU-1000 showing reproducibility between samples.

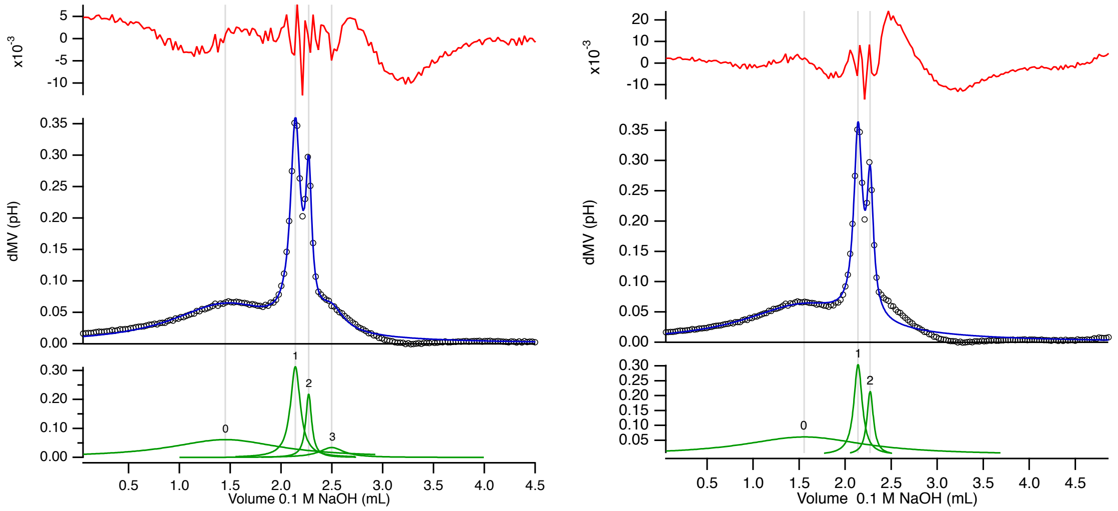

Figure S36. Representative curve fittings for the first derivative of the titration curve of pH as a function of volume of titrant added for NU-1000: Located peaks (green) (bottom); first derivative data (black circles) and fit trace (blue) (middle); residual plot (red) (top). Peaks were fit as four Lorentzian functions (left) and three Lorentzian functions (right).

Multipeak fit report for NU-1000 with 4 peaks:
Chi square: 0.0026865
Total fitted points: 172
Multi-peak fit version 2.16

```
Total Peak Area = 0.22374 +/- 0.004041

Baseline        Type: Constant

        y0 =    0        +/-     0

Peak 0          Type: Lorentzian

        Location =      1.4513          +/-     0.013591
        Height =        0.061526        +/-     0.00095128
        Area =          0.12681         +/-     0.003338
        FWHM =          1.3121          +/-     0.041091

        Fit function parameters
        Location =      1.4513          +/-     0.013591
        FWHM =          1.3121          +/-     0.041091
        Area =0.12681         +/-     0.003338

Peak 1          Type: Lorentzian

        Location =      2.1401          +/-     0.00069592
        Height =        0.31358         +/-     0.0031991
        Area =          0.057384        +/-     0.0011179
        FWHM =          0.1165          +/-     0.0024424

        Fit function parameters
        Location =      2.1401          +/-     0.00069592
        FWHM =          0.1165          +/-     0.0024424
        Area =0.057384        +/-     0.0011179

Peak 2          Type: Lorentzian

        Location =      2.2713          +/-     0.00070087
        Height =        0.21853         +/-     0.0042816
        Area =          0.023995        +/-     0.0009536
        FWHM =          0.069901        +/-     0.0029488

        Fit function parameters
        Location =      2.2713          +/-     0.00070087
        FWHM =          0.069901        +/-     0.0029488
        Area =0.023995        +/-     0.0009536

Peak 3          Type: Lorentzian
```

```
          Location =    2.4977          +/-     0.010343
          Height =      0.034356        +/-     0.0020581
          Area =        0.015556        +/-     0.0017403
          FWHM =        0.28826         +/-     0.03486

          Fit function parameters
          Location =    2.4977          +/-     0.010343
          FWHM =        0.28826         +/-     0.03486
          Area =0.015556      +/-       0.0017403

Multipeak fit report for NU-1000 with 3 peaks:
Chi square: 0.0082375
Total fitted points: 186
Multi-peak fit version 2.16
Total Peak Area = 0.23603 +/- 0.0051088

Baseline        Type: Constant

          y0 =   0        +/-     0

Peak 0          Type: Lorentzian

          Location =    1.5559          +/-     0.023391
          Height =      0.061113        +/-     0.0014903
          Area =        0.15554         +/-     0.0045733
          FWHM =        1.6203          +/-     0.059643

          Fit function parameters
          Location =    1.5559          +/-     0.023391
          FWHM =        1.6203          +/-     0.059643
          Area =0.15554        +/-      0.0045733

Peak 1          Type: Lorentzian

          Location =    2.1396          +/-     0.0011479
          Height =      0.30434         +/-     0.0054959
          Area =        0.052134        +/-     0.0017519
          FWHM =        0.10905         +/-     0.0039493

          Fit function parameters
          Location =    2.1396          +/-     0.0011479
          FWHM =        0.10905         +/-     0.0039493
          Area =0.052134      +/-       0.0017519
```

Peak 2 Type: Lorentzian

Location = 2.2716 +/- 0.0013596
Height = 0.21396 +/- 0.0063174
Area = 0.028358 +/- 0.0014543
FWHM = 0.084377 +/- 0.0047285

Fit function parameters
Location = 2.2716 +/- 0.0013596
FWHM = 0.084377 +/- 0.0047285
Area =0.028358 +/- 0.0014543

Table S6. Total moles titrant consumed for NU-1000

	Total mmoles OH^- consumed to EP3	**Total mmoles OH^- consumed to EP4**
Trial 1	0.226	0.250
Trial 2	0.216	0.247
Trial 3	0.216	0.237
Average	**0.219** (± 0.006)	**0.244** (± 0.007)

Table S7. Defect calculations for NU-1000

Occupancy of Mesopores (%)	**Molecular Formula**	**MW**	**Total mmoles H^+ in 0.049 g sample**
0	$Zr_6O_4(\mu_3\text{-}OH)_4(OH)_4(H_2O)_4(C_{44}H_{22}O_8)_2$	2176.76	0.360
20	$[Zr_6O_4(OH)_4(OH)_4(H_2O)_4(C_{44}H_{22}O_8)_2]_{0.80}$ $[(Zr_6O_4(OH)_4)_2(C_{44}H_{22}O_8)_6]_{0.20}$	2827.54	0.252
25	$[Zr_6O_4(OH)_4(OH)_4(H_2O)_4(C_{44}H_{22}O_8)_2]_{0.75}$ $[(Zr_6O_4(OH)_4)_2(C_{44}H_{22}O_8)_6]_{0.25}$	2990.23	**0.229**
30	$[Zr_6O_4(OH)_4(OH)_4(H_2O)_4(C_{44}H_{22}O_8)_2]_{0.70}$ $[(Zr_6O_4(OH)_4)_2(C_{44}H_{22}O_8)_6]_{0.30}$	2949.12	0.211

The first derivative curve of NU-1000 can be fit to three or four Lorentzian peaks to give three or four equivalence points, respectively (Fig. S30). Adding a fourth peak to the fitting does not significantly shift the peak locations of peaks 0–3 (see above). We expect that NU-1000 likely has only three real pK_a values (calculated pK_{a4} = 9.43 ± 0.09), so we calculated defects based on the position of peak 2 (EP3); however, it should be noted that using EP4 in the calculation does not significantly change the occupancy of the mesopores with an estimated value of 20% instead of 25%.[6]

Zr-UiO-67(HCl)

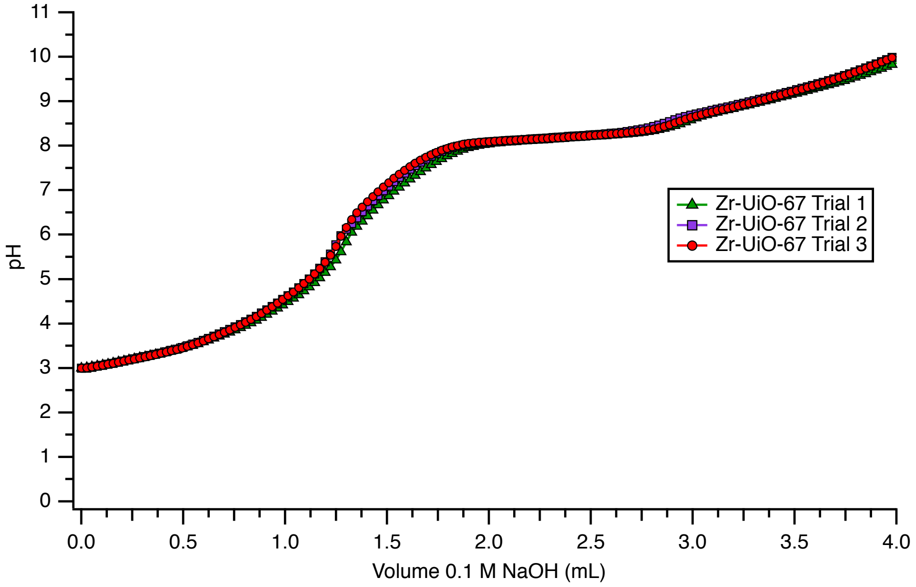

Figure S37. Overlay of three acid–base titration curves for Zr-UiO-67(HCl) showing reproducibility between samples.

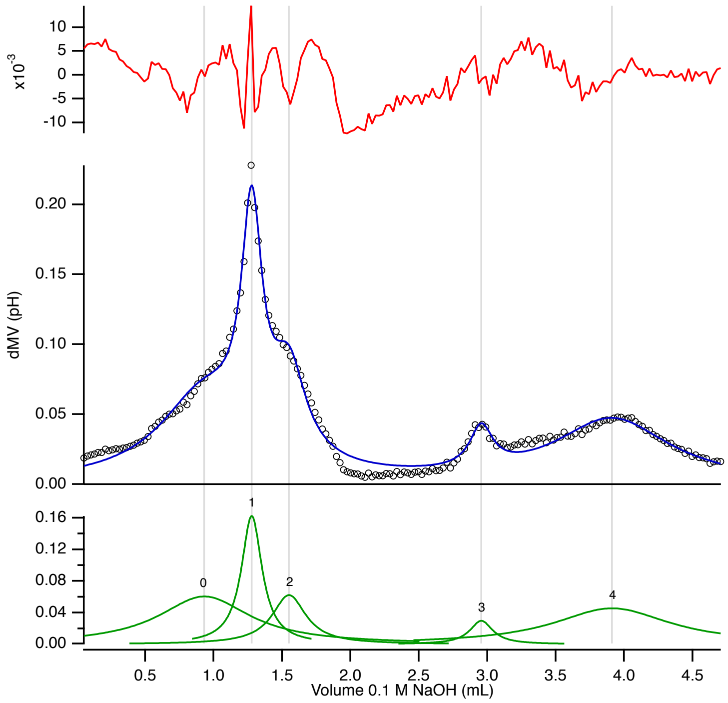

Figure S38. Representative curve fitting for the first derivative of the titration curve of pH as a function of volume of titrant added for Zr-UiO-67(HCl): Located peaks (green) (bottom); first derivative data (black circles) and fit trace (blue) (middle); residual plot (red) (top). Peaks were fit as Lorentzian functions. Peak 0 was used for fitting purposes only; calculations were done using Peak 1 as the first equivalence point.

```
Multipeak fit report for Zr-UiO-67(HCl).
Chi square: 0.0041681
Total fitted points: 180
Multi-peak fit version 2.16
Total Peak Area = 0.23759 +/- 0.0080377

Baseline      Type: Constant

     y0 =   0        +/-    0

Peak 0        Type: Lorentzian

     Location =   0.93205      +/-   0.024521
     Height =     0.060447     +/-   0.0021793
     Area =       0.077706     +/-   0.0058788
     FWHM =       0.8184       +/-   0.052022

     Fit function parameters
     Location =   0.93205     +/-    0.024521
     FWHM =       0.8184      +/-    0.052022
     Area =0.077706     +/-     0.0058788

Peak 1        Type: Lorentzian

     Location =   1.2785       +/-   0.0022141
     Height =     0.16231      +/-   0.0042786
     Area =       0.046839     +/-   0.0030097
     FWHM =       0.18372      +/-   0.0096725

     Fit function parameters
     Location =   1.2785      +/-    0.0022141
     FWHM =       0.18372     +/-    0.0096725
     Area =0.046839     +/-     0.0030097

Peak 2        Type: Lorentzian

     Location =   1.5512       +/-   0.008467
     Height =     0.062172     +/-   0.0029672
     Area =       0.029369     +/-   0.002985
     FWHM =       0.30073      +/-   0.027024

     Fit function parameters
     Location =   1.5512      +/-    0.008467
     FWHM =       0.30073     +/-    0.027024
```

```
        Area =0.029369      +/-      0.002985

Peak 3          Type: Lorentzian

        Location =    2.9567          +/-     0.0099685
        Height =      0.029641        +/-     0.0028731
        Area =        0.0095518       +/-     0.0012787
        FWHM =        0.20515         +/-     0.032995

        Fit function parameters
        Location =    2.9567         +/-      0.0099685
        FWHM =        0.20515        +/-      0.032995
        Area =0.0095518     +/-      0.0012787

Peak 4          Type: Lorentzian

        Location =    3.9125          +/-     0.015982
        Height =      0.045507        +/-     0.0013322
        Area =        0.074124        +/-     0.003231
        FWHM =        1.0369          +/-     0.059319

        Fit function parameters
        Location =    3.9125         +/-      0.015982
        FWHM =        1.0369         +/-      0.059319
        Area =0.074124      +/-      0.003231
```

Table S8. Titrant consumed after the first equivalence point for Zr-UiO-67(HCl)

	mmoles OH^- consumed between EP1 to EP4
Trial 1	0.268
Trial 2	0.270
Trial 3	0.263
Average	**0.266** (± 0.004)

Table S9. Defect calculations for Zr-UiO-67(HCl)

Missing Linkers	**Molecular Formula**[a]	**MW**	**mmoles H^+ from defects in 0.049 g sample**
1	$Zr_6O_4(OH)_4(C_{14}H_8O_4)_5[(H_2O)(OH)]_2$	1950.51	0.151
2	$Zr_6O_4(OH)_4(C_{14}H_8O_4)_4[(H_2O)(OH)]_4$	1780.33	0.330
1.60	$Zr_6O_4(OH)_4(C_{14}H_8O_4)_{4.40}[(H_2O)(OH)]_{3.20}$	1848.40	0.254
1.65	$Zr_6O_4(OH)_4(C_{14}H_8O_4)_{4.35}[(H_2O)(OH)]_{3.30}$	1839.89	**0.264**
1.70	$Zr_6O_4(OH)_4(C_{14}H_8O_4)_{4.30}[(H_2O)(OH)]_{3.40}$	1831.38	0.273
1.75	$Zr_6O_4(OH)_4(C_{14}H_8O_4)_{4.25}[(H_2O)(OH)]_{3.50}$	1822.88	0.282
1.80	$Zr_6O_4(OH)_4(C_{14}H_8O_4)_{4.20}[(H_2O)(OH)]_{3.60}$	1814.37	0.292

[a] All missing linkers are assumed to be replaced with 2 H_2O molecules and 2 –OH groups.

Note that if the third equivalence point is used for the missing linker calculation for Zr-UiO-67(HCl) instead of the fourth apparent equivalence point, 0.168 ± 0.002 mmoles of OH^- is consumed, which corresponds to approximately 1.10 missing linkers (0.167 mmoles H^+ from defects in 0.049 g sample).

MOF-808

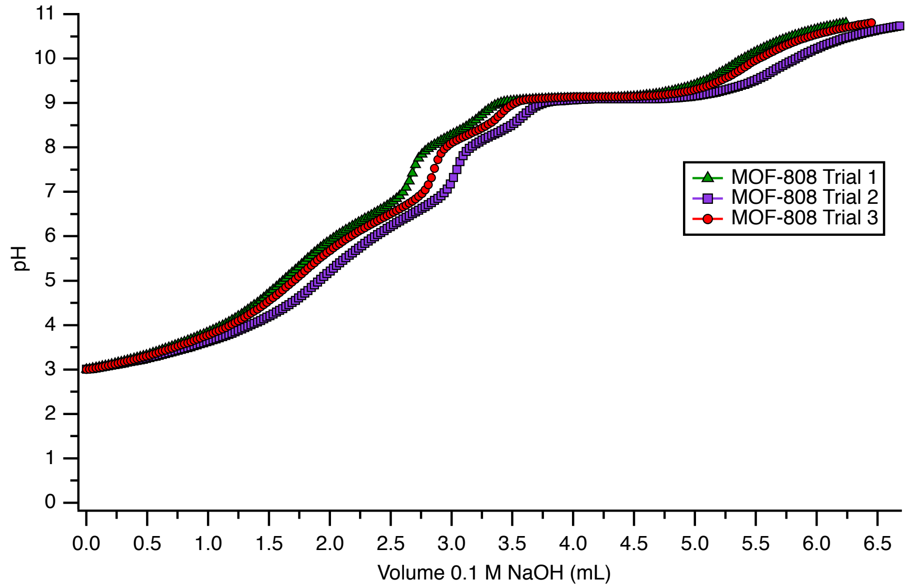

Figure S39. Overlay of three acid–base titration curves for activated MOF-808 showing reproducibility between samples.

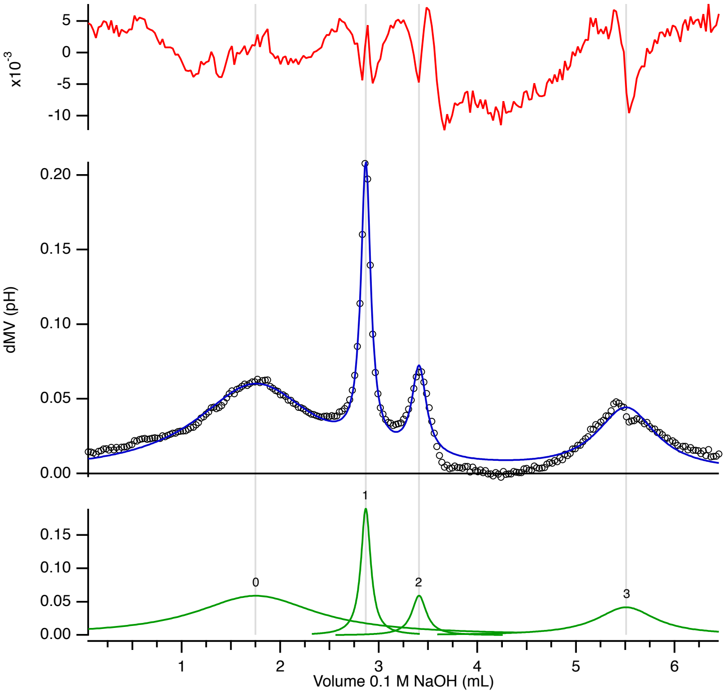

Figure S40. Representative curve fitting for the first derivative of the titration curve of pH as a function of volume of titrant added for MOF-808: Located peaks (green) (bottom); first derivative data (black circles) and fit trace (blue) (middle); residual plot (red) (top). Peaks were fit as Lorentzian functions.

```
Multipeak fit report for MOF-808
Chi square: 0.0054865
Total fitted points: 247
Multi-peak fit version 2.16
Total Peak Area = 0.23749 +/- 0.0038647

Baseline      Type: Constant

       y0 =   0       +/-    0

Peak 0        Type: Lorentzian

       Location =   1.7495        +/-    0.013917
       Height =     0.059156      +/-    0.0010558
       Area =       0.13776       +/-    0.0031872
       FWHM =       1.4825        +/-    0.046555

       Fit function parameters
       Location =   1.7495       +/-     0.013917
       FWHM =       1.4825       +/-     0.046555
       Area =0.13776       +/-     0.0031872

Peak 1        Type: Lorentzian

       Location =   2.8676        +/-    0.0011336
       Height =     0.18951       +/-    0.0036161
       Area =       0.035379      +/-    0.00081817
       FWHM =       0.11885       +/-    0.0035296

       Fit function parameters
       Location =   2.8676       +/-     0.0011336
       FWHM =       0.11885      +/-     0.0035296
       Area =0.035379      +/-     0.00081817

Peak 2        Type: Lorentzian

       Location =   3.4083        +/-    0.0044165
       Height =     0.059309      +/-    0.0029664
       Area =       0.016479      +/-    0.00092191
       FWHM =       0.17688       +/-    0.013238

       Fit function parameters
       Location =   3.4083       +/-     0.0044165
       FWHM =       0.17688      +/-     0.013238
```

```
          Area =0.016479      +/-      0.00092191

Peak 3          Type: Lorentzian

          Location =     5.5089          +/-     0.012687
          Height =       0.041943        +/-     0.001473
          Area =         0.047867        +/-     0.0018049
          FWHM =         0.72653         +/-     0.03812

          Fit function parameters
          Location =     5.5089         +/-      0.012687
          FWHM =         0.72653        +/-      0.03812
          Area =0.047867      +/-      0.0018049
```

Table S10. Total moles titrant consumed for MOF-808

	mmoles OH^- consumed
Trial 1	0.541
Trial 2	0.580
Trial 3	0.551
Average	**0.557** (±0.020)

Table S11. Proton quantification calculation for MOF-808

Molecular Formula	**MW**	**Total mmoles H^+ expected in 0.049 g sample**
$Zr_6O_4(\mu_3\text{-}OH)_4(OH)_6(H_2O)_6(C_9H_3O_6)_2$	1303.73	0.827

(0.557/0.827) × 100% = 67% of mmoles H^+ expected

References

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