Supporting Information for:

Screening and evaluating aminated cationic functional moieties for potential CO_2 capture applications using an anionic MOF scaffold

Tao Li,[b] and Nathaniel L. Rosi[ab*]

[a] United States Department of Energy, National Energy Technology Laboratory, 626 Cochrans Mill Road, Pittsburgh, Pennsylvania 15236

[b] Department of Chemistry, University of Pittsburgh, 219 Parkman Ave, Pittsburgh, Pennsylvania 15260. E-mail: nrosi@pitt.edu

Table of Contents

1. General procedures and instrumentation

N,N'-dimethylformamide (DMF) was purchased from Fisher Scientific; all other chemicals were purchased from Aldrich Chemical Co. All chemicals were used directly without further purification. Nanopure water (18.2 MΩ) was obtained using a Barnstead DiamondTM System. Powder X-ray diffraction (PXRD) patterns were collected using a Bruker AXS D8 Discover powder diffractometer equipped with a Cu Kα X-ray source at 40 kV, 40 mA. Scan speed and step size were set at 0.2 sec/step and 0.02 °/step, respectively. Generally, MOF samples were first spread evenly onto a glass slide. Sample height was aligned with a laser and data were collected for the desired range. Elemental microanalyses (EA) were performed by the University of Illinois Department of Chemistry Microanalytical Laboratory using a Perkin-Elmer 240 Elemental Analyzer and an Exeter Analytical CE440. Thermogravimetric analysis (TGA) was conducted on a TGA Q500 thermal analysis system. Prior to analysis, samples were dried under argon flow (UHP) to remove excess solvent. Approximately 5 mg of sample were loaded into a platinum pan and heated under a constant N_2 (UHP) flow from room temperature to 600 °C at a rate of 5 °C/min. Scanning electron microscopy (SEM) images were obtained using a Philips XL-30 field emission scanning electron microscope under BSE mode.

Gas adsorption isotherms were collected on a Quantachrome Autosorb-1 instrument. Approximately ~55-60 mg of each sample was added into a pre-weighed sample analysis tube. The samples were degassed at room temperature under vacuum for ~24 hours until the pressure change rate was no more than 3.5 mTorr/min. A liquid N_2 bath was used for the N_2 adsorption experiments at 77 K. A water/ethylene glycol bath was used for isotherms collected at 273 K. UHP grade N_2 and CO_2 gas adsorbates (99.999 %) were used in this study.

2. Syntheses of materials

Preparation of I

Bio-MOF-1 was synthesized according to the reported method.[1] Stock solutions of $Zn(OAc)_2 \cdot 6H_2O$ (0.05 M), adenine (0.05 M), H_2BPDC (0.1 M), and HNO_3 (1 M) in DMF were first prepared. To a 20 ml glass vial was added $Zn(OAc)_2$ (7.5 ml), adenine (2.5 ml), H_2BPDC (2.5 ml), HNO_3 (1 ml), and nanopure water (1 ml). The vial was then capped and place in a 130°C oven for 24 h. Rod shaped crystals were then collected and washed with DMF (3X) and dry ethanol (3X) followed by soaking in dry ethanol for 3 days. During this process, ethanol was replaced with fresh ethanol after 10 min, 20 min, and then every 24 h. Finally, the crystals were dried under UHP argon flow until they can move around freely.

Preparation of II, III, and IV

Three samples of **I** (~200 mg) were soaked in ethanolic solutions of GND^+Cl^- (0.1 M, 5 ml), $AmGND^+Cl^-$ (0.05 M, 5 ml), and $DiAmGND^+Cl^-$ (0.02 M, 5 ml) over the course of 7, 7, and 15 days during which the solutions were refreshed every day. The crystals were then washed with dry ethanol (3X) and dried under argon flow to yield **II**, **III**, and **IV**, respectively.

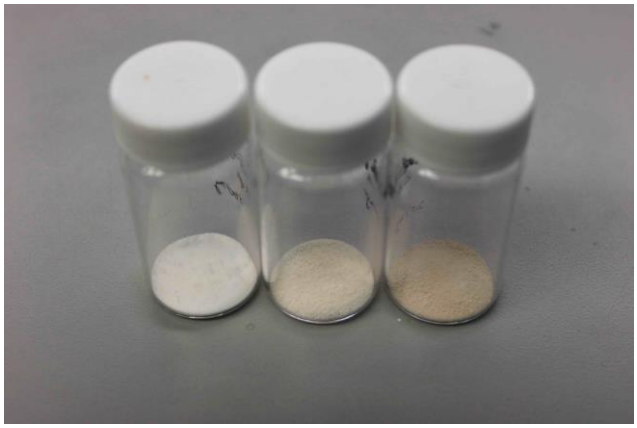

Figure S1. Samples of **II** (left), **III** (middle), and **IV** (right).

3. ^{1}H-NMR analysis

Proton nuclear magnetic resonance spectra (^{1}H-NMR) were collected on a Bruker Avance 300 MHz spectrometers. Chemical shifts are in parts per million using the residual solvent peak as the reference value. The value used for proton spectra is 2.5 ppm for d_6-DMSO. Approximately 5 mg of each MOF sample was first thoroughly washed with DMF and then dried under argon flow. d_6-DMSO (0.65 ml) and concentrated DCl (3 µl) were added to dissolve the MOF. ^{1}H-NMR of **I-IV** were collected at room temperature. The integration for one set of the BPDC aromatic hydrogens was set as 24 (for the $[Zn_8(Ad)_4(BPDC)_6O_1]$ unit). We then integrated the methyl peak for each cation to determine the number of cations per material. We expect 2 cations per $[Zn_8(Ad)_4(BPDC)_6O_1]$ unit. The data are consistent with this expectation and are summarized below.

I: $NH_2(C\mathbf{H_3})_2^+$, δ 2.54 (singlet, 11.65 H)

II: $NH_2(C\mathbf{H_3})_2^+$, no peak observed for methyl protons at δ=2.54

III: $NH_2(C\mathbf{H_3})_2^+$, no peak observed for methyl protons at δ=2.54

IV: $NH_2(C\mathbf{H_3})_2^+$, no peak observed for methyl protons at δ=2.54

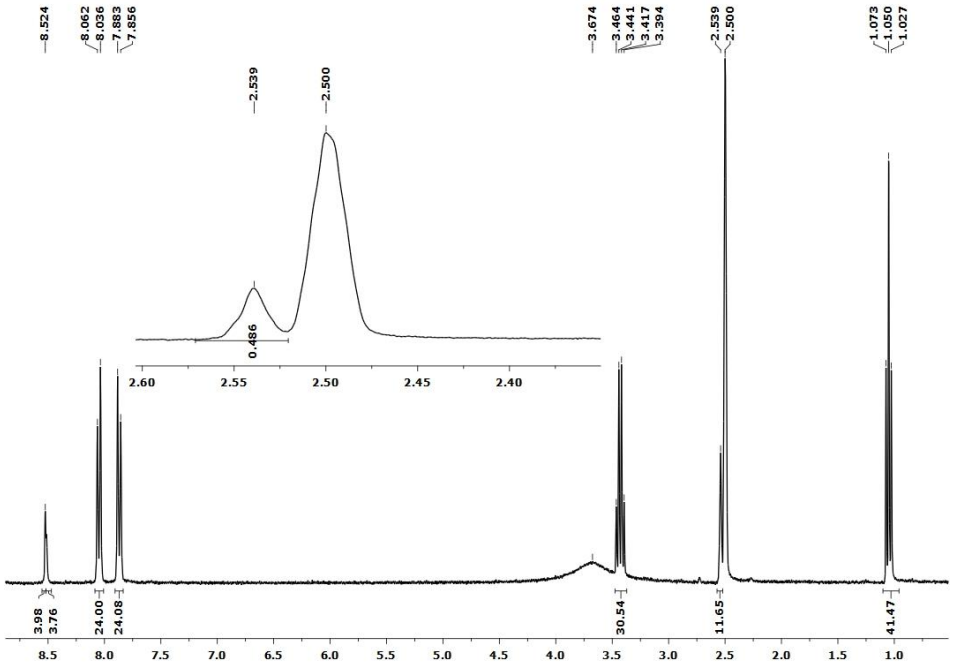

Figure S2. ^{1}H NMR of **I** (300 MHz, d_6-DMSO) δ 8.52 (s, 4H), 8.51 (s, 4H), 8.05 (d, J = 7.8 Hz, 24H), 7.87 (d, J = 8.1 Hz, 24H), 2.54 (s, 12H). Peaks at δ = 3.43 and 1.05 are from ethanol. Peaks at δ = 8.52-8.51 are from adenine. Peaks at δ = 8.05 and 7.87 are from BPDC.

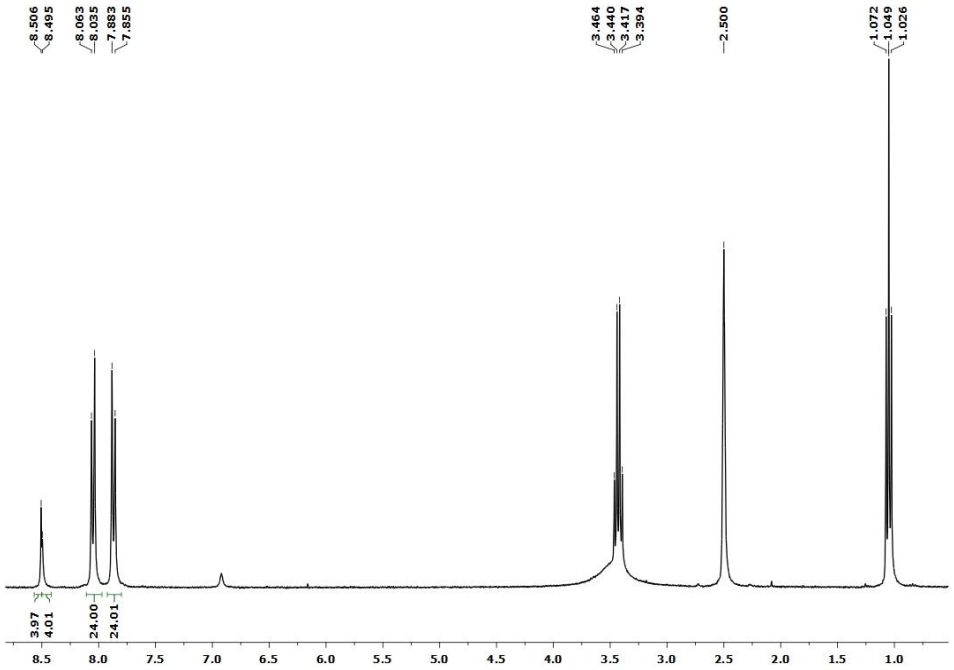

Figure S3. ^{1}H NMR of **II** (300 MHz, d_6-DMSO) δ 8.51 (s, 4H), 8.50 (s, 4H), 8.05 (d, J = 7.8 Hz, 24H), 7.87 (d, J = 8.1 Hz, 24H). Peaks at δ = 3.43 and 1.05 are from ethanol. Peaks at δ = 8.50-8.51 are from adenine. Peaks at δ = 8.05 and 7.87 are from BPDC.

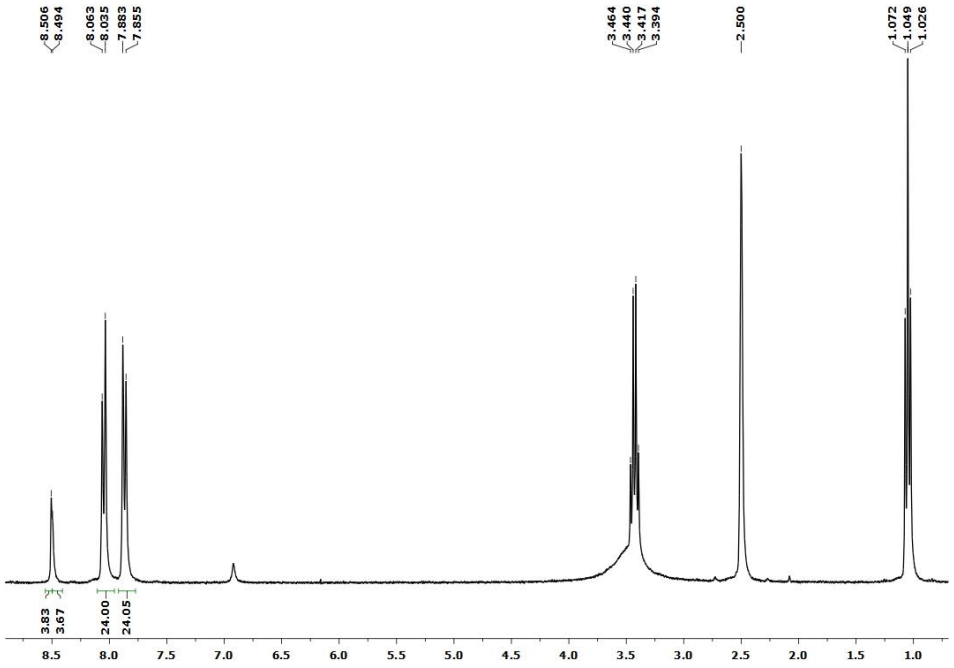

Figure S4. ^{1}H NMR of **III** (300 MHz, d_6-DMSO) δ 8.51 (s, 4H), 8.50 (s, 4H), 8.05 (d, J = 7.8 Hz, 24H), 7.87 (d, J = 8.1 Hz, 24H). Peaks at δ = 3.43 and 1.05 are from ethanol. Peaks at δ = 8.50-8.51 are from adenine. Peaks at δ = 8.05 and 7.87 are from BPDC.

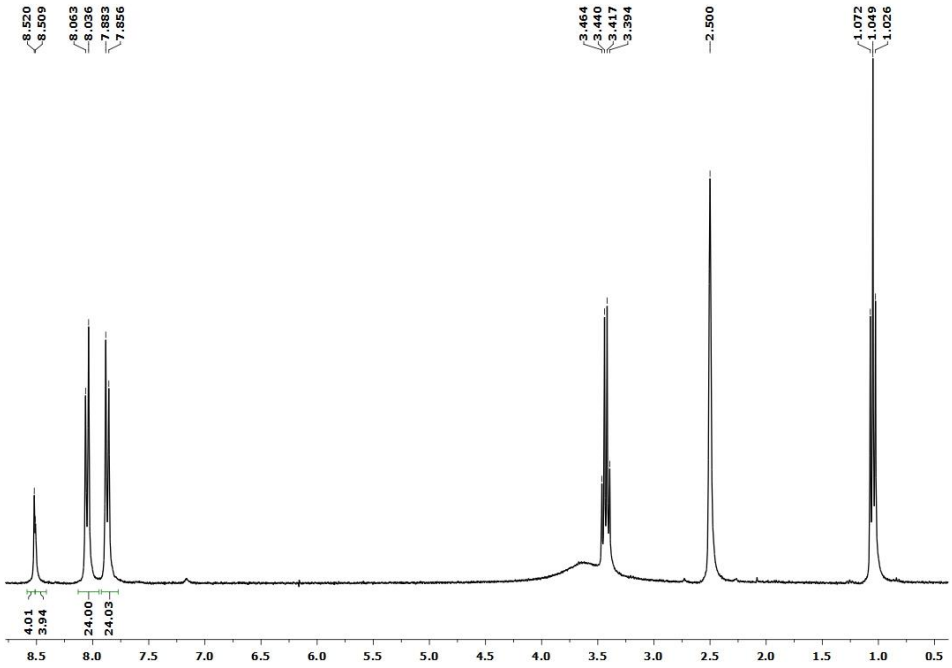

Figure S5. ^{1}H NMR of **IV** (300 MHz, d_6-DMSO) δ 8.52 (s, 4H), 8.51 (s, 4H), 8.05 (d, J = 7.8 Hz, 24H), 7.87 (d, J = 8.1 Hz, 24H). Peaks at δ = 3.43 and 1.05 are from ethanol. Peaks at δ = 8.52-8.51 are from adenine. Peaks at δ = 8.05 and 7.87 are from BPDC.

4. LC-MS analysis of digested II-IV

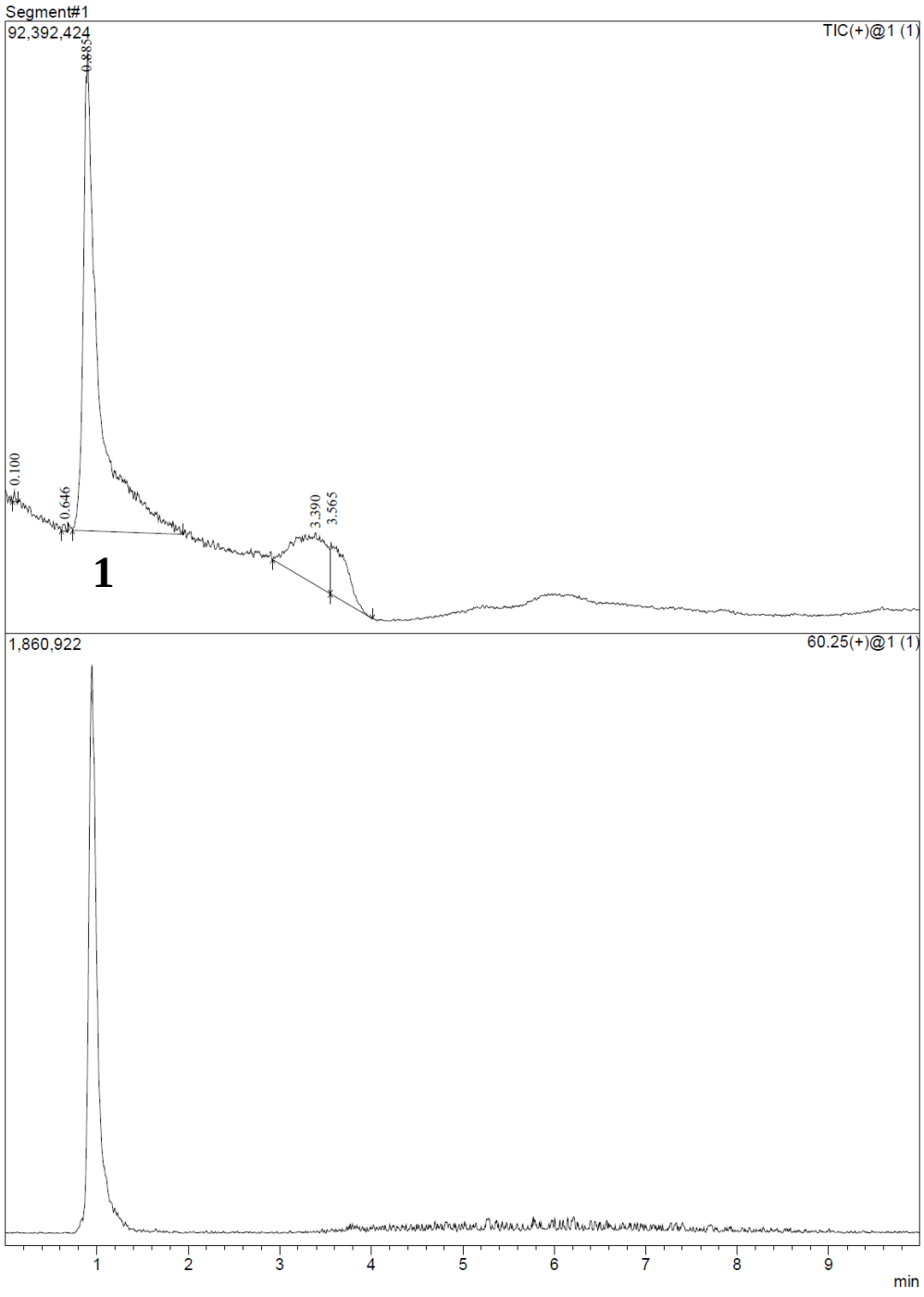

Figure S6. TIC chromatogram for **II** digested in HCl/DMF (top: all ions; bottom: m/z=60.25)

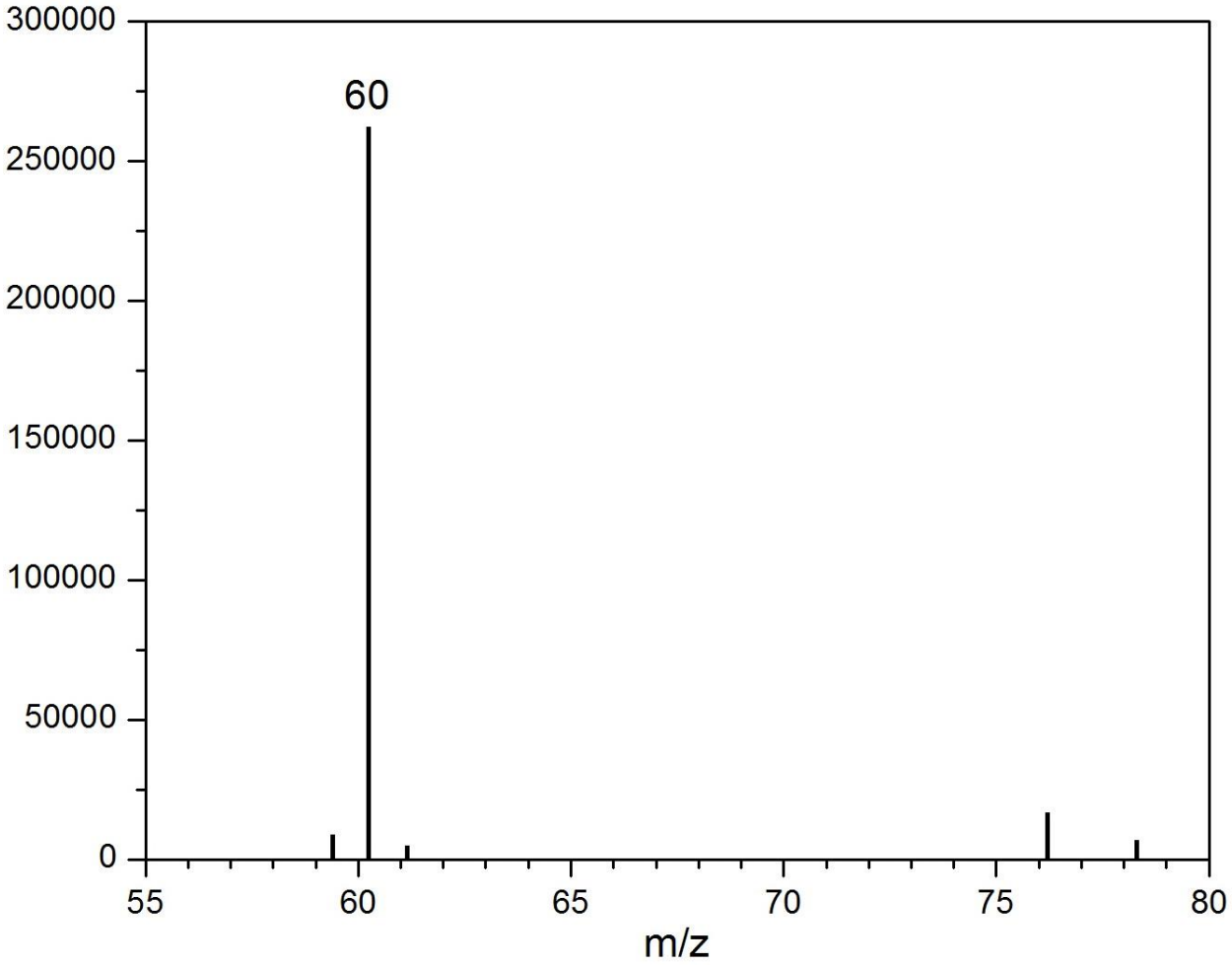

Figure S7. MS spectrum for the first integral (**1**) of **II** digested in HCl/DMF. The peak at 60m/z corresponds to the guanadinium cation.

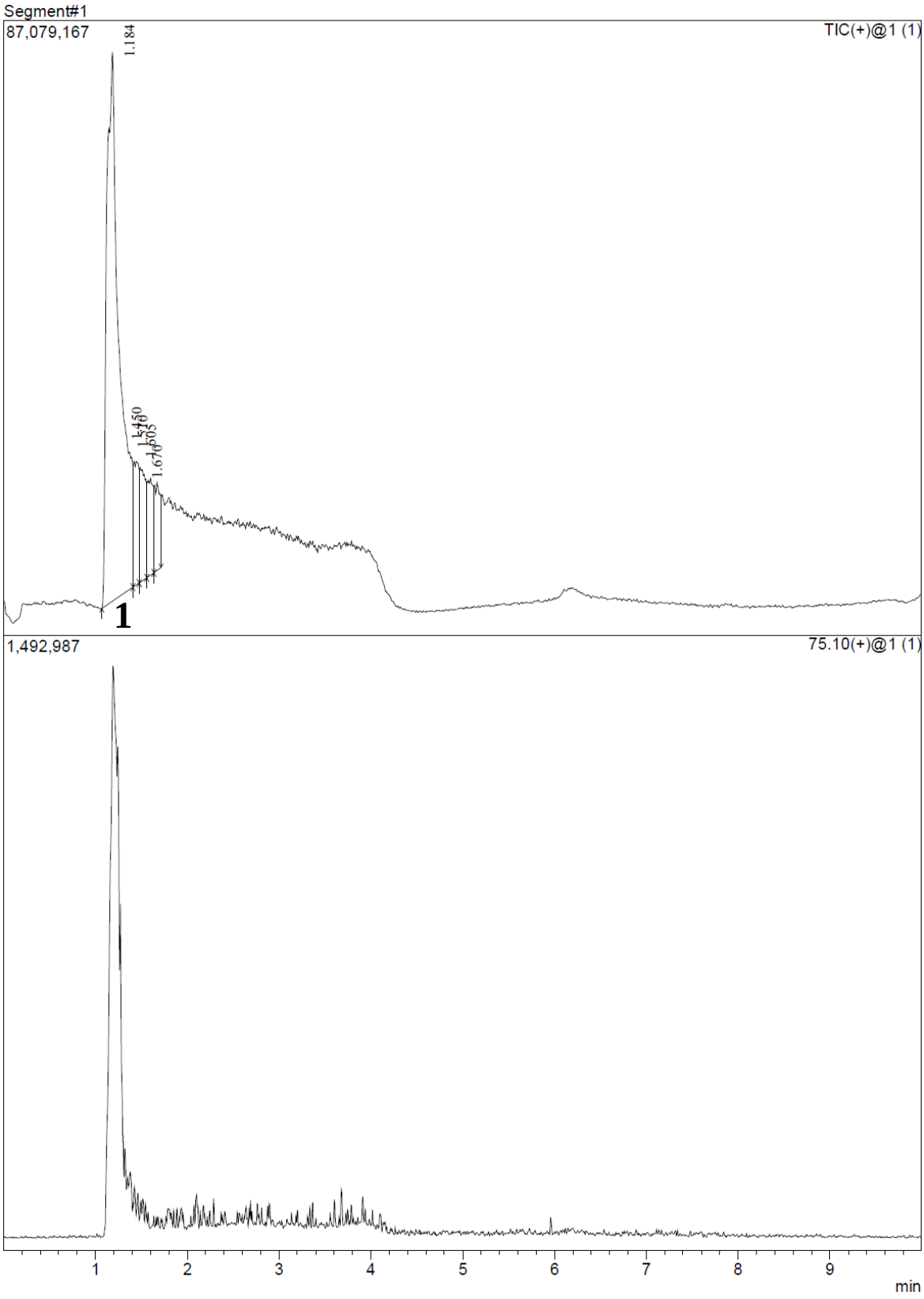

Figure S8. TIC chromatogram for **III** digested in HCl/DMF (top: all ions; bottom: m/z=75.10)

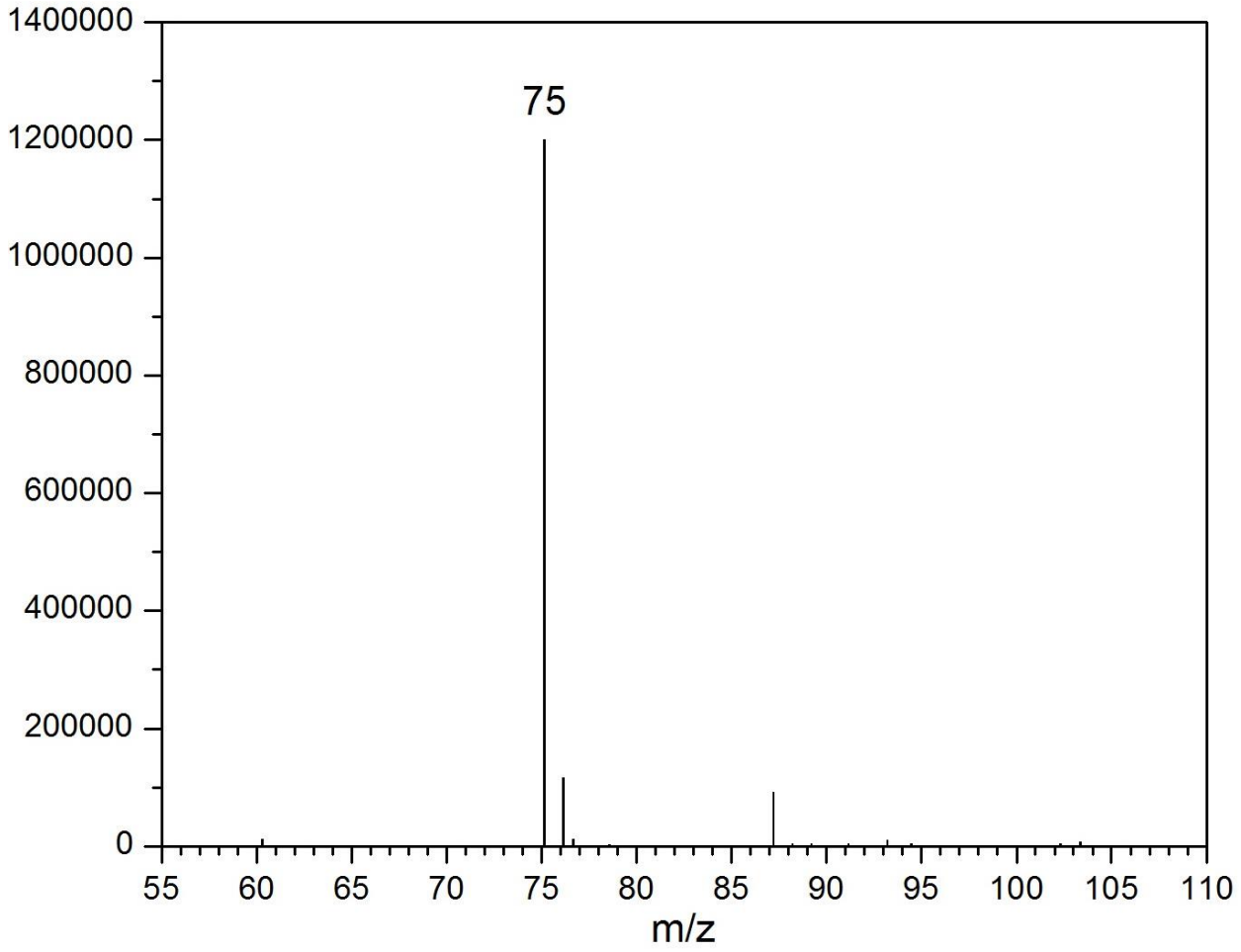

Figure S9. MS spectrum for the first integral (**1**) of **III** digested in HCl/DMF. The peak at 75m/z corresponds to the aminoguanidinium cation.

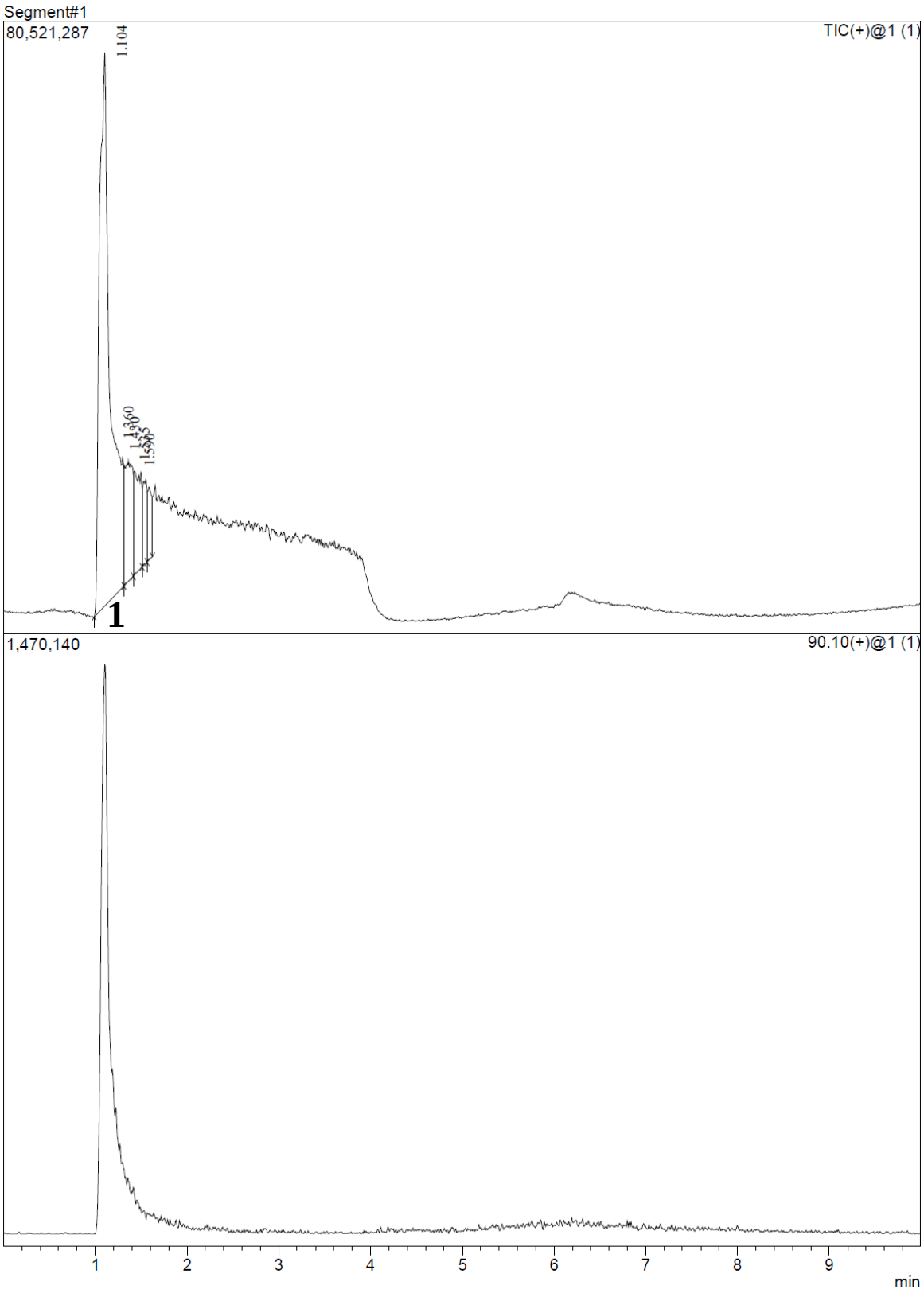

Figure S10. TIC chromatogram for **IV** digested in HCl/DMF (top: all ions; bottom: m/z=90.10)

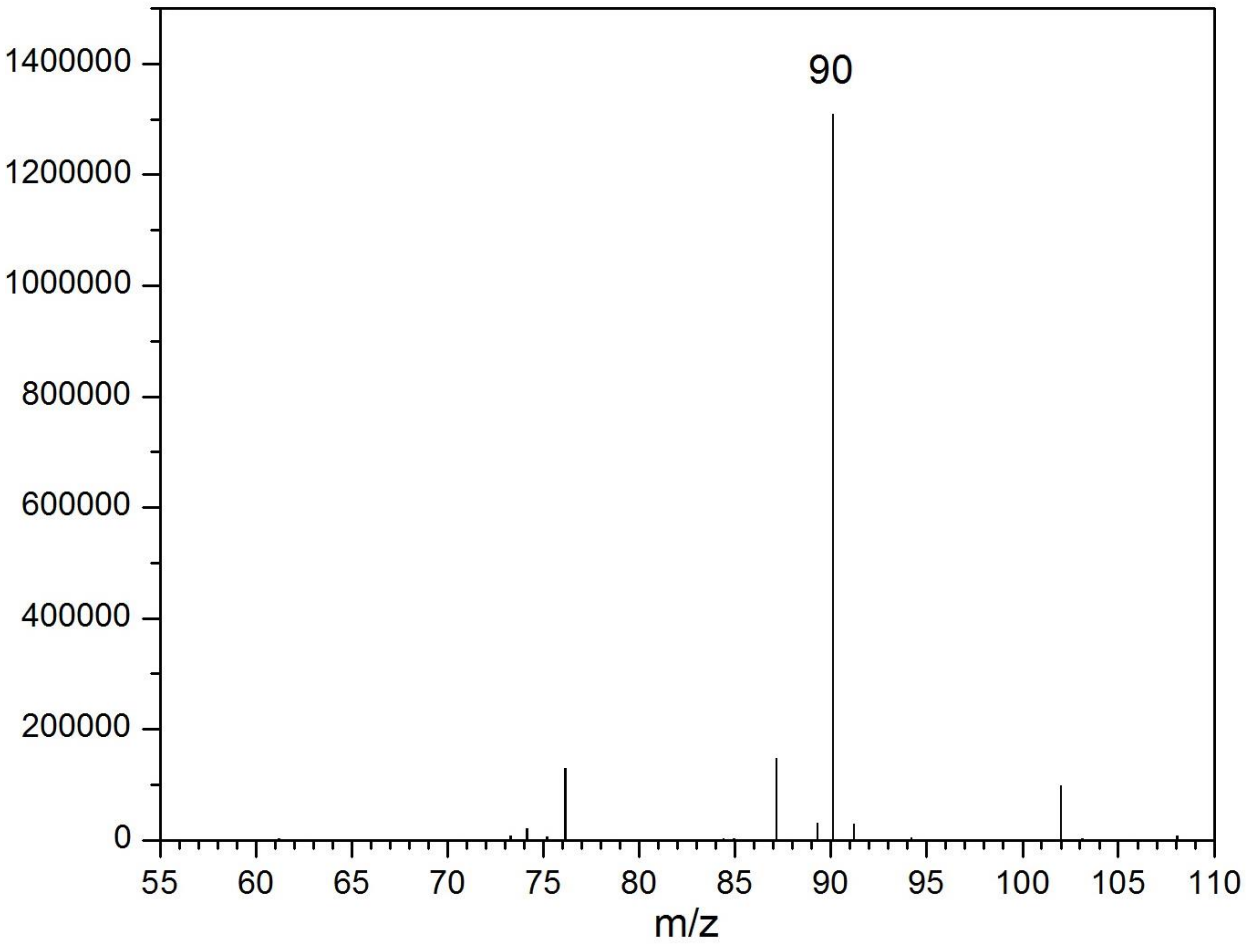

Figure S11. MS spectrum for the first integral (**1**) of **IV** digested in HCl/DMF. The peak at 75m/z corresponds to the diaminoguanidinium cation.

5. Elemental analysis

I:

$Zn_8(Ad)_4(BPDC)_6O \bullet 1.8(DMA+)$**,** $0.2(H+)$**,** $12(CH_3CH_2OH)$**,** $7H_2O$

Calcd.: C, 48.21; H, 5.06; N, 9.31. Found: C, 48.21; H, 4.72; N, 9.21.

II:

$Zn_8(Ad)_4(BPDC)_6O \bullet 1.75(GND^+)$**,** $0.25(H^+)$**,** $12(CH_3CH_2OH)$**,** $7.25H_2O$

Calcd.: C, 47.14; H, 4.92; N, 10.70. Found: C, 47.13; H, 4.56; N, 10.65.

III:

$Zn_8(Ad)_4(BPDC)_6O \bullet 1.85(AmGND^+)$**,** $0.15(H^+)$**,** $11.5(CH_3CH_2OH)$ **,** $6.75H_2O$

Calcd.: C, 46.79; H, 4.86; N, 11.60. Found: C, 46.79; H, 4.53; N, 11.55.

IV:

$Zn_8(Ad)_4(BPDC)_6O \bullet 1.85(DiAmGND^+)$**,** $0.15(H^+)$**,** $11.25(CH_3CH_2OH)$ **,** $6.75H_2O$

Calcd.: C, 46.38; H, 4.85; N, 12.33. Found: C, 46.38; H, 4.43; N, 12.25.

I after activation at 100^oC:

$Zn_8(Ad)_4(BPDC)_6O \bullet 1.8(DMA^+)$**,** $0.3(H^+)$**,** $4H_2O$

Calcd.: C, 48.36; H, 3.25; N, 11.39. Found: C, 48.45; H, 2.90; N, 11.23.

II after activation at 100^oC:

$Zn_8(Ad)_4(BPDC)_6O \bullet 1.75(GND^+)$**,** $0.25(H^+)$**,** $2.75H_2O$

Calcd.: C, 47.54; H, 3.03; N, 13.24. Found: C, 47.48; H, 2.72; N, 13.25.

III after activation at 100^oC:

$Zn_8(Ad)_4(BPDC)_6O \bullet 1.85(AmGND^+)$**,** $0.15(H^+)$**,** $2.5H_2O$

Calcd.: C, 47.07; H, 3.06; N, 14.21. Found: C, 47.02; H, 2.67; N, 14.14.

IV after activation at 100^oC:

$Zn_8(Ad)_4(BPDC)_6O \bullet 1.05(DiAmGND^+)$**,** $0.95(H^+)$**,** $1.25H_2O$

Calcd.: C, 47.88; H, 2.90; N, 13.42. Found: C, 47.87; H, 2.72; N, 13.40.

IV after activation at room temperature:

$Zn_8(Ad)_4(BPDC)_6O \bullet 1.85(DiAmGND^+)$**,** $0.15(H^+)$**,** $1.50H_2O$

Calcd.: C, 46.90; H, 3.05; N, 15.11. Found: C, 46.88; H, 2.74; N, 15.05.

6. Scanning electron microscope (SEM) images

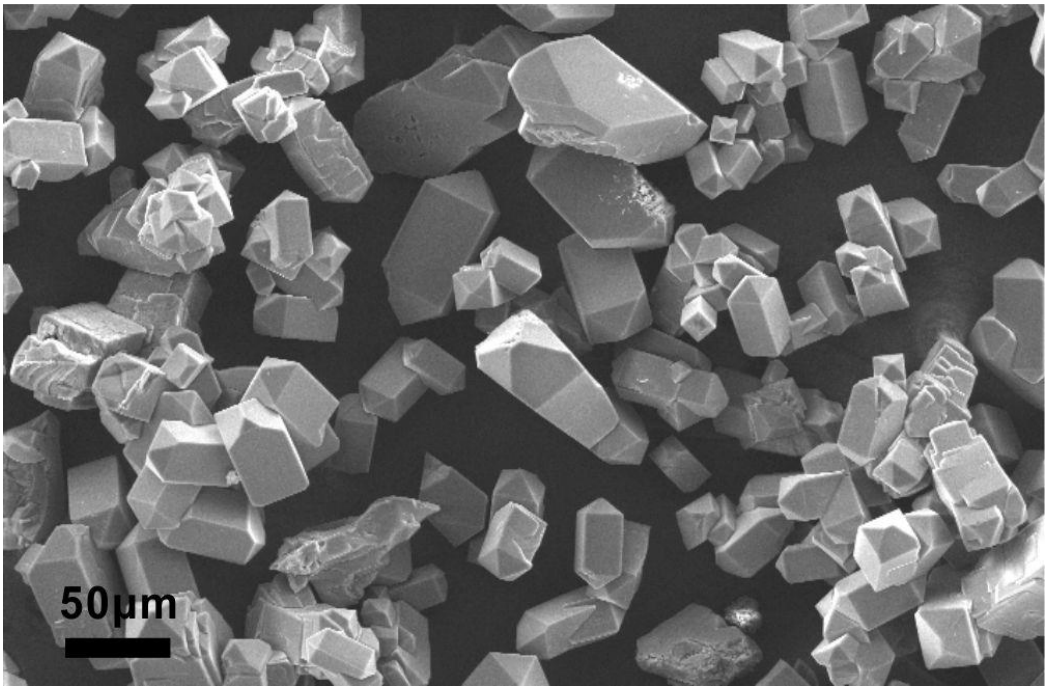

Figure S12. SEM image of **I**.

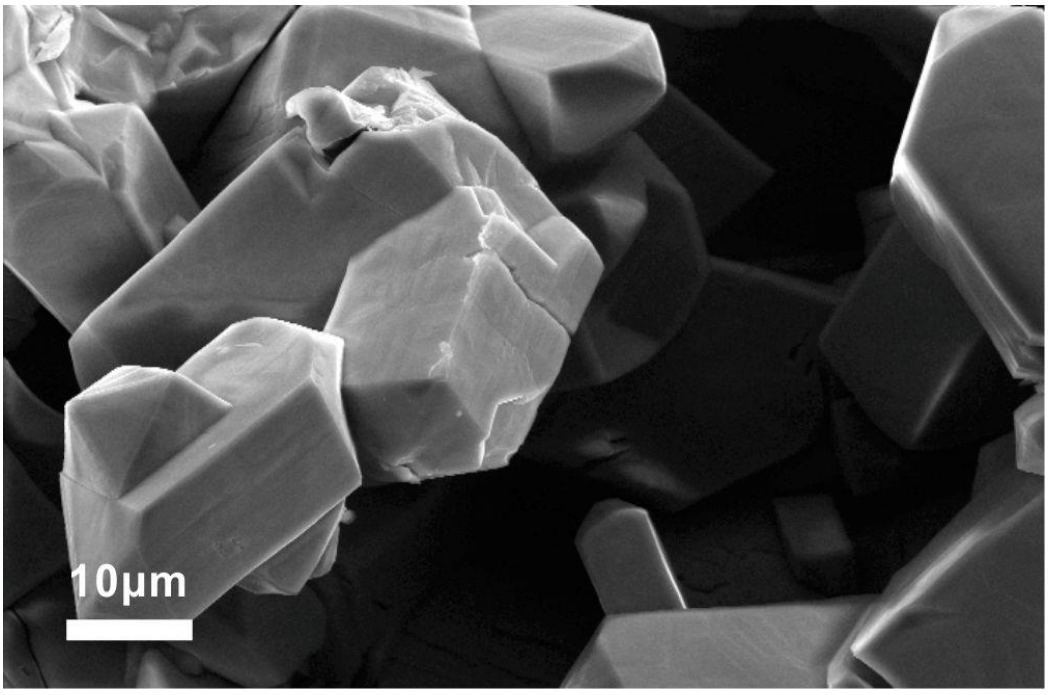

Figure S13. SEM image of **II**.

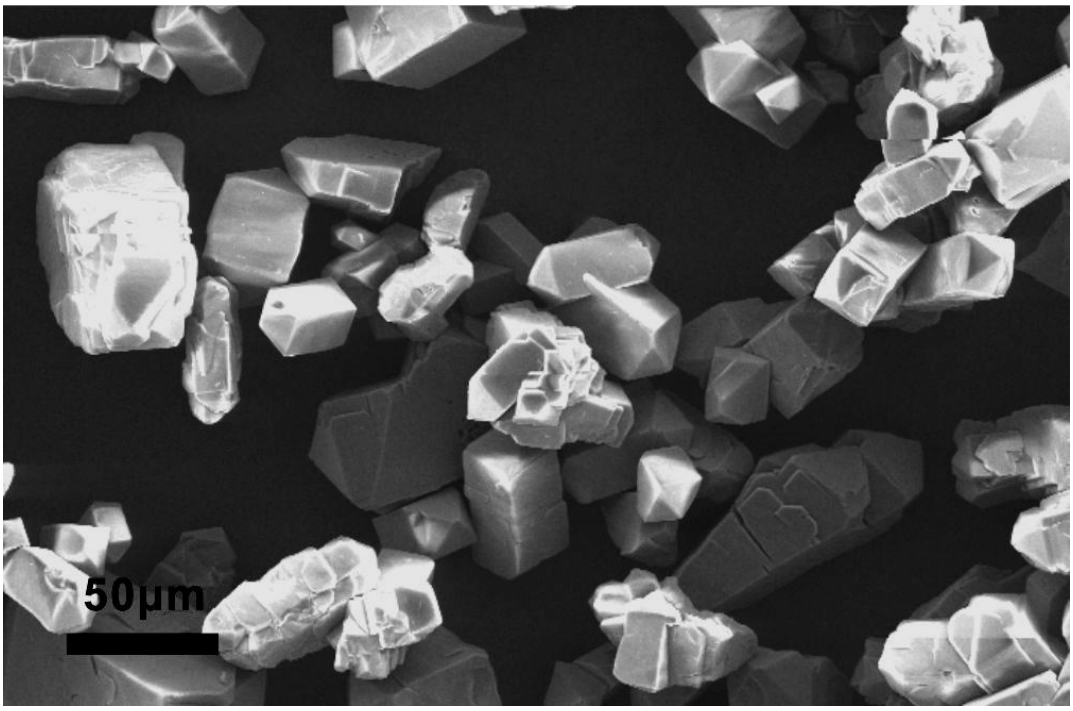

Figure S14. SEM image of **III**.

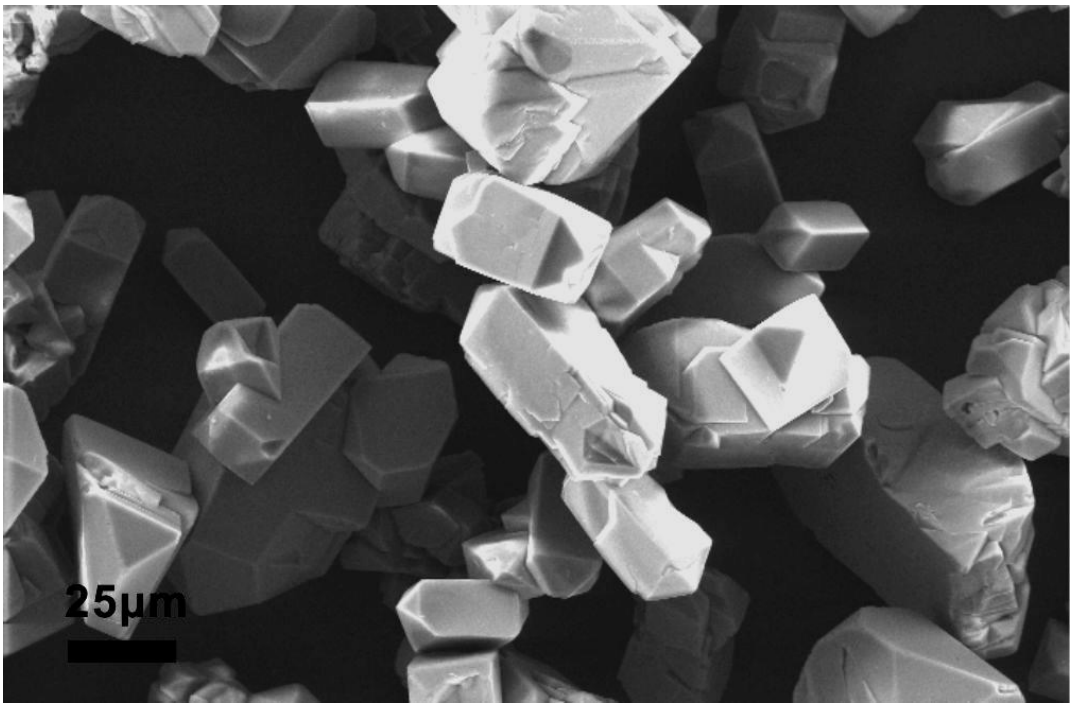

Figure S15. SEM image of **IV**.

7. Thermogravimetric analysis (TGA)

The TGA data for each MOF (**I-IV**) is given below. We compared the weight loss steps to the chemical formulas calculated from the EA data (Section 5) and found that they were in good agreement with one another. Small discrepancies between the EA and TGA data for MOF samples are commonly observed, especially when solvent is included in the pores.

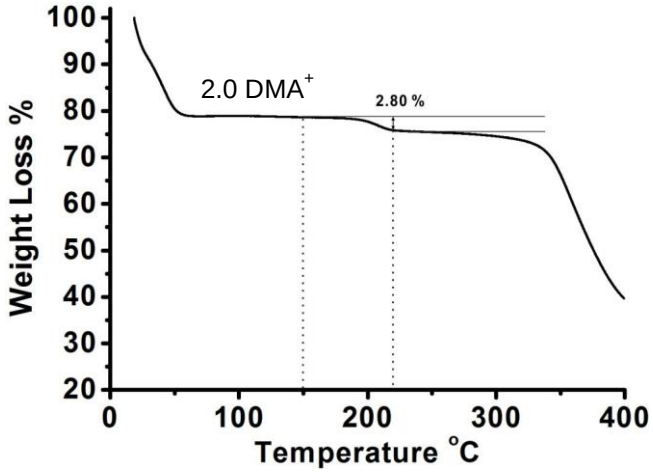

Figure S16. TGA of **I**. The first 21.4% weight loss step (0-150 ^{o}C) corresponds to evaporation of ethanol and water guest molecules (calcd 20.7% based on EA data). The second 2.8% weight loss step (150-220 ^{o}C) corresponds to the loss of 2 DMA (1.8 calcd from EA).

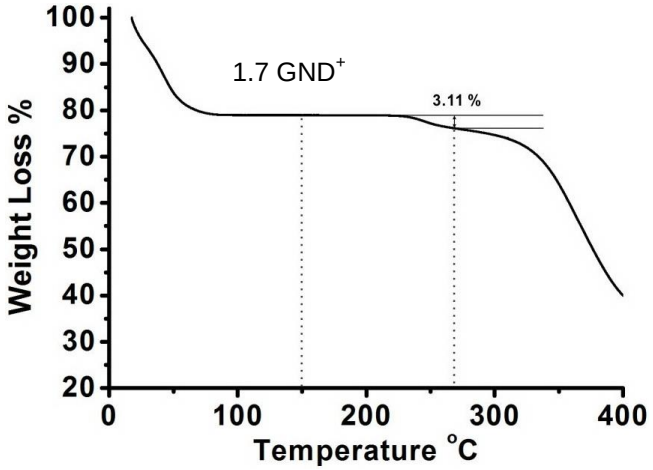

Figure S17. TGA of **II**. The first 21.0% weight loss step (0-150 ^{o}C) corresponds to evaporation of ethanol and water guest molecules (calcd 20.7% based on EA data). The second 3.11% weight loss step (150-275 ^{o}C) corresponds to the loss of 1.75 GND (1.75 calcd from EA).

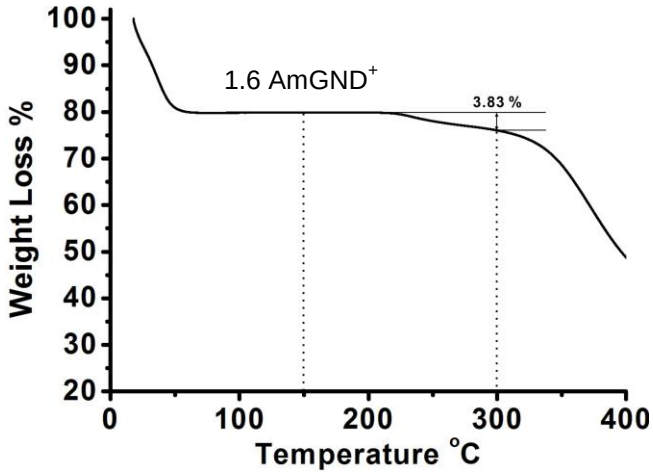

Figure S18. TGA of **III**. The first 20.1% weight loss step (0-150 °C) corresponds to evaporation of ethanol and water guest molecules (calcd 19.7% based on EA data). The second 3.83% weight loss step (150-300 °C) corresponds to the loss of 1.72 AmGND (1.85 calcd from EA).

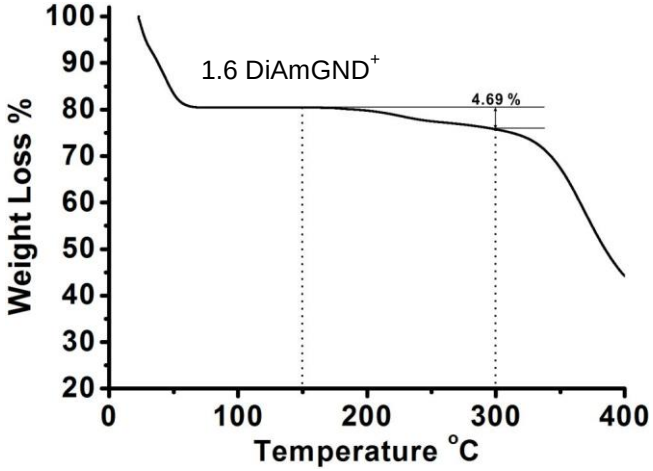

Figure S19. TGA of **IV**. The first 19.6% weight loss step (0-150 °C) corresponds to evaporation of ethanol and water guest molecules (calcd 18.8% based on EA data). The second 4.69% weight loss step (150-300 °C) corresponds to the loss of 1.76 DiAmGND (1.85 calcd from EA).

8. CO_2 adsorption data tables

Table S1. CO_2 adsorption data of **I** at various temperatures. The measurement errors for CO_2 isotherm at 273 K are ±0.06 mmol/g at 1 bar and ±0.06 mmol/g at 0.5 bar, as calculated from three independent measurements.

CO_2 adsorption of **I** at various temperature									
273K		298K		303K		308K		313K	
Pressure (bar)	CO_2 adsorbed (mmol/g)	Pressure (bar)	CO_2 adsorbed (mmol/g)	Pressure (bar)	CO_2 adsorbed (mmol /g)	Pressure (bar)	CO_2 adsorbed (mmol /g)	Pressure (bar)	CO_2 adsorbed (mmol /g)
0.021789	0.131986	0.022627	0.020236	0.010602	0.004988	0.022821	5.29E-05	0.022814	0.011059
0.032067	0.195472	0.032855	0.045327	0.022819	0.026632	0.033018	0.018274	0.033037	0.027694
0.042169	0.256383	0.042959	0.070719	0.03301	0.047345	0.043134	0.036686	0.043127	0.044087
0.052429	0.314931	0.053157	0.094605	0.043162	0.068464	0.053265	0.054879	0.053323	0.059182
0.062535	0.373789	0.063244	0.118905	0.053265	0.089687	0.063406	0.07323	0.063382	0.076075
0.072675	0.431604	0.073411	0.143794	0.063389	0.110811	0.073501	0.091628	0.07362	0.090436
0.082756	0.487961	0.083452	0.169893	0.073534	0.131931	0.083657	0.109408	0.083699	0.105612
0.092939	0.543076	0.093651	0.194086	0.083649	0.152459	0.093799	0.127028	0.093849	0.121626
0.103072	0.597106	0.10377	0.218601	0.093816	0.172531	0.103924	0.145334	0.103973	0.137126
0.154066	0.853645	0.152324	0.330351	0.10396	0.192905	0.153013	0.22614	0.153177	0.210096
0.204802	1.089543	0.202986	0.442415	0.152759	0.28742	0.20375	0.30614	0.203877	0.28325
0.255463	1.315118	0.253551	0.554902	0.203438	0.381265	0.2543	0.38868	0.254479	0.355675
0.306115	1.529982	0.304289	0.663624	0.253976	0.47613	0.305001	0.468905	0.30519	0.426572
0.356812	1.736543	0.354941	0.771382	0.304748	0.566297	0.355685	0.547905	0.355727	0.499463
0.407462	1.934206	0.405641	0.875661	0.355386	0.656012	0.406344	0.626076	0.406429	0.568417
0.45821	2.125479	0.456393	0.978124	0.406065	0.744165	0.456908	0.704319	0.457046	0.637776
0.508962	2.309417	0.506981	1.081154	0.456679	0.831054	0.507651	0.780091	0.507769	0.705957
0.559512	2.492186	0.557699	1.180718	0.507425	0.915631	0.558337	0.85433	0.558375	0.773167
0.610236	2.668818	0.608415	1.279126	0.558138	0.998509	0.608946	0.928958	0.609006	0.839585
0.660856	2.841353	0.658912	1.379559	0.608847	1.078765	0.659671	1.000982	0.659748	0.904425
0.711516	3.009622	0.709732	1.474953	0.659494	1.159126	0.71035	1.072021	0.710299	0.971495
0.762222	3.172162	0.760402	1.569864	0.710079	1.240327	0.760973	1.143266	0.761131	1.033625
0.81286	3.333802	0.811002	1.665451	0.760804	1.317489	0.81163	1.213384	0.811717	1.097443
0.86352	3.490936	0.861742	1.758982	0.811439	1.394751	0.862395	1.281778	0.86253	1.156402
0.914147	3.64776	0.912444	1.851754	0.862159	1.468927	0.913115	1.347666	0.913035	1.220587
0.964758	3.801009	0.963145	1.940992	0.912779	1.543919	0.963808	1.413701	0.963863	1.279671
1.010472	3.938139	1.008918	2.021699	0.963578	1.61525	1.009421	1.475741	1.009673	1.333035
				1.00919	1.682485				

Table S2. CO_2 adsorption data of **II** at various temperatures. The measurement errors for CO_2 isotherm at 273 K are ±0.07 mmol/g at 1 bar and ±0.05 mmol/g at 0.5 bar, as calculated from three independent measurements.

CO_2 adsorption of **II** at various temperature									
273K		298K		303K		308K		313K	
Pressure (bar)	CO_2 adsorbed (mmol/g)	Pressure (bar)	CO_2 adsorbed (mmol/g)	Pressure (bar)	CO_2 adsorbed (mmol /g)	Pressure (bar)	CO_2 adsorbed (mmol /g)	Pressure (bar)	CO_2 adsorbed (mmol /g)
0.001028	0.006043	0.00213	0.00401	0.00214	0.00183	0.03307	0.01579	0.02288	0.00883
0.002038	0.014013	0.00314	0.00672	0.00314	0.0038	0.04318	0.03794	0.03316	0.02688
0.003165	0.022424	0.00422	0.00956	0.0042	0.00605	0.05331	0.06012	0.04334	0.04536
0.004236	0.030363	0.00529	0.0118	0.00532	0.00505	0.06347	0.08165	0.05337	0.06531
0.005187	0.034444	0.00635	0.01422	0.00639	0.00431	0.07356	0.10332	0.06356	0.08248
0.006153	0.041723	0.00739	0.01654	0.00745	0.00346	0.08377	0.12354	0.07365	0.10189
0.007225	0.049707	0.00846	0.01912	0.00851	0.00299	0.09382	0.14585	0.08378	0.1213
0.008287	0.057639	0.00954	0.02175	0.00958	0.00225	0.10399	0.16711	0.09394	0.14007
0.009386	0.065843	0.01059	0.02424	0.01065	0.00209	0.15318	0.26417	0.10406	0.15829
0.010448	0.073753	0.02268	0.05791	0.02271	0.03071	0.20389	0.36038	0.15337	0.2445
0.021709	0.157328	0.03288	0.08795	0.03292	0.05673	0.2545	0.45828	0.20413	0.32769
0.032047	0.237734	0.04301	0.11755	0.04315	0.08079	0.30519	0.55323	0.25469	0.41453
0.04226	0.313107	0.05317	0.1463	0.05323	0.10657	0.35576	0.64863	0.30544	0.49709
0.052457	0.385983	0.06334	0.17413	0.06338	0.13193	0.40662	0.73846	0.35595	0.58046
0.062563	0.457884	0.07348	0.20282	0.07349	0.15753	0.45708	0.83131	0.40674	0.65979
0.072746	0.529635	0.08358	0.23249	0.08361	0.18206	0.50795	0.9179	0.45731	0.7435
0.082867	0.59883	0.09368	0.26196	0.09376	0.20714	0.55853	1.00616	0.50808	0.81897
0.093006	0.667341	0.10377	0.29121	0.10385	0.23221	0.60914	1.09394	0.55871	0.89717
0.1032	0.73345	0.1526	0.41982	0.1528	0.34578	0.65988	1.17863	0.60946	0.97114
0.154267	1.049626	0.20324	0.54874	0.20351	0.45833	0.71048	1.26314	0.66006	1.05091
0.204928	1.340782	0.25388	0.67632	0.25415	0.57071	0.76128	1.34151	0.71069	1.12478
0.255563	1.617255	0.30469	0.79783	0.3049	0.67868	0.81196	1.42036	0.76135	1.19975
0.306241	1.879017	0.35528	0.9198	0.35551	0.78559	0.86259	1.50006	0.81209	1.27228
0.356939	2.13048	0.406	1.03812	0.40624	0.88954	0.91326	1.57904	0.86277	1.34294
0.407727	2.370428	0.45665	1.15483	0.4568	0.99451	0.96404	1.65329	0.9134	1.41393
0.45843	2.603586	0.50747	1.2668	0.50755	1.09419	1.00972	1.72196	0.96411	1.4833
0.509125	2.829078	0.55804	1.37984	0.55823	1.19242			1.00974	1.54638
0.559741	3.050143	0.60876	1.49034	0.60894	1.28918				
0.610429	3.264663	0.65942	1.59895	0.65951	1.38672				
0.661079	3.473425	0.71019	1.70406	0.71024	1.48029				
0.711762	3.677707	0.76078	1.81103	0.76092	1.5722				
0.762357	3.877947	0.81155	1.91338	0.81155	1.66338				
0.812999	4.076069	0.8622	2.01754	0.86227	1.75065				
0.863627	4.269763	0.91281	2.12035	0.91288	1.8387				
0.914266	4.461375	0.96357	2.21783	0.96361	1.92292				
0.964972	4.648279	1.00931	2.30781	1.00934	2.00089				
1.00774	4.803193								

Table S3. CO_2 adsorption data of **III** at various temperatures. The measurement errors for CO_2 isotherm at 273 K are ±0.10 mmol/g at 1 bar and ±0.06 mmol/g at 0.5 bar, as calculated from three independent measurements.

CO_2 adsorption of **III** at various temperature									
273K		298K		303K		308K		313K	
Pressure (bar)	CO_2 adsorbed (mmol/g)	Pressure (bar)	CO_2 adsorbed (mmol/g)	Pressure (bar)	CO_2 adsorbed (mmol /g)	Pressure (bar)	CO_2 adsorbed (mmol /g)	Pressure (bar)	CO_2 adsorbed (mmol /g)
0.0218698	0.1162368	0.022655	0.036331	0.022711	0.028371	0.043256	0.012947	0.022736	0.01952
0.0321319	0.1940817	0.03289	0.067655	0.032938	0.053285	0.05339	0.034425	0.033035	0.037389
0.042286	0.2690496	0.043024	0.098406	0.043113	0.078309	0.063572	0.055278	0.04318	0.054306
0.052449	0.3415998	0.053168	0.128552	0.053222	0.103361	0.073815	0.073688	0.053336	0.072757
0.0626153	0.4142667	0.063225	0.160321	0.063348	0.127651	0.083827	0.096271	0.063475	0.090219
0.072704	0.4861334	0.073478	0.188913	0.07346	0.15382	0.093917	0.119961	0.073585	0.108256
0.0828743	0.5559289	0.083555	0.219227	0.083624	0.178749	0.104083	0.141914	0.083686	0.126446
0.0930182	0.6247169	0.093698	0.249237	0.093727	0.205157	0.153201	0.241856	0.093883	0.142213
0.1031549	0.6922057	0.103836	0.279325	0.103991	0.22831	0.203964	0.339429	0.10401	0.160541
0.1541376	1.0130064	0.152516	0.415594	0.152855	0.344965	0.254585	0.439208	0.153377	0.243232
0.204792	1.3087544	0.20317	0.55292	0.203604	0.457364	0.30521	0.537854	0.204129	0.324924
0.2553836	1.5929015	0.253699	0.691505	0.254212	0.569533	0.355784	0.636832	0.25468	0.409627
0.3061069	1.8616536	0.304521	0.82373	0.304936	0.678119	0.406541	0.730469	0.305207	0.494573
0.3569173	2.119735	0.355209	0.953917	0.355481	0.789553	0.457155	0.825169	0.355863	0.578206
0.4075251	2.3706574	0.405835	1.085832	0.406233	0.894947	0.507922	0.916411	0.406635	0.656789
0.4583143	2.608964	0.456491	1.214718	0.456871	1.000671	0.558469	1.010009	0.457172	0.738214
0.5088937	2.8437118	0.507207	1.340629	0.507544	1.102558	0.609183	1.099502	0.507833	0.819002
0.5595197	3.070909	0.557808	1.466015	0.558251	1.201831	0.659821	1.190189	0.558553	0.896849
0.6102947	3.2883901	0.608499	1.588123	0.608912	1.299825	0.710656	1.274852	0.609172	0.975918
0.6608954	3.5050051	0.659147	1.709999	0.659379	1.397255	0.76123	1.361729	0.659703	1.055687
0.7115153	3.7173458	0.709738	1.831926	0.709918	1.497613	0.811892	1.448667	0.710777	1.127366
0.7621089	3.9265419	0.760612	1.947539	0.760632	1.593994	0.86257	1.532894	0.761576	1.197206
0.8127471	4.1296185	0.811091	2.067106	0.811298	1.688797	0.913318	1.614601	0.812219	1.270498
0.8634248	4.3263871	0.861808	2.182324	0.861943	1.783694	0.963743	1.700539	0.862927	1.341132
0.9140538	4.5214046	0.912536	2.29436	0.912629	1.876199	1.009599	1.773479	0.913484	1.413872
0.9647548	4.7118842	0.963336	2.406415	0.963369	1.966481			0.964198	1.482852
1.0104261	4.8827246	1.009258	2.500016	1.009048	2.049896			1.009767	1.548929

Table S4. CO_2 adsorption data of **IV** at various temperatures. The measurement errors for CO_2 isotherm at 273 K are ±0.05 mmol/g at 1 bar, ±0.06 mmol/g at 0.5 bar, as calculated from three independent measurements.

CO_2 adsorption of **IV** at various temperature									
273K		298K		303K		308K		313K	
Pressure (bar)	CO_2 adsorbed (mmol/g)	Pressure (bar)	CO_2 adsorbed (mmol/g)	Pressure (bar)	CO_2 adsorbed (mmol /g)	Pressure (bar)	CO_2 adsorbed (mmol /g)	Pressure (bar)	CO_2 adsorbed (mmol /g)
0.021553	0.1624	0.0226	0.0233	0.03307	0.02169	0.04335	0.0113	0.04323	0.01239
0.0319	0.2405	0.0329	0.057	0.04319	0.04863	0.05347	0.0354	0.05338	0.03255
0.042072	0.3163	0.043	0.0911	0.05332	0.07442	0.06362	0.0587	0.06352	0.05338
0.052169	0.3908	0.0531	0.1251	0.06348	0.1003	0.07372	0.0828	0.07359	0.07448
0.062496	0.461	0.0633	0.159	0.07354	0.12768	0.08388	0.1062	0.08375	0.09554
0.07247	0.5343	0.0734	0.1935	0.08364	0.15465	0.09402	0.1301	0.09387	0.11572
0.082672	0.6054	0.0835	0.228	0.09384	0.18069	0.10412	0.1531	0.10405	0.13535
0.092809	0.6746	0.0936	0.2613	0.10398	0.20543	0.15325	0.2624	0.15329	0.22965
0.102988	0.7433	0.1038	0.2949	0.15292	0.32175	0.20389	0.3705	0.20401	0.32363
0.154061	1.0686	0.1523	0.4474	0.2037	0.43604	0.25455	0.479	0.25461	0.41901
0.204738	1.3703	0.2029	0.6013	0.25432	0.55124	0.30523	0.5851	0.30533	0.51041
0.255346	1.6606	0.2536	0.7535	0.30502	0.662	0.35587	0.6903	0.35593	0.60384
0.306014	1.9357	0.3044	0.9013	0.35568	0.77298	0.40658	0.7936	0.40665	0.69324
0.35663	2.2026	0.355	1.0488	0.40637	0.88185	0.45728	0.8949	0.45726	0.78469
0.407307	2.4594	0.4057	1.1919	0.45696	0.98801	0.50789	0.9957	0.50797	0.87251
0.457995	2.7086	0.4564	1.3336	0.50768	1.09263	0.55856	1.0948	0.5586	0.96117
0.508665	2.9504	0.5071	1.471	0.55836	1.19706	0.60915	1.1946	0.60921	1.05042
0.559361	3.1873	0.5578	1.6086	0.60906	1.29722	0.65992	1.2904	0.65993	1.1364
0.610144	3.4191	0.6085	1.7435	0.65965	1.39994	0.71057	1.386	0.7106	1.22208
0.660776	3.6471	0.6591	1.8791	0.71037	1.49782	0.76118	1.4804	0.76123	1.3063
0.711394	3.872	0.7098	2.0095	0.76109	1.59552	0.81197	1.5722	0.81203	1.38798
0.762137	4.0917	0.7606	2.1375	0.81181	1.69025	0.86264	1.6615	0.86266	1.46845
0.81285	4.3073	0.8112	2.2668	0.86244	1.78406	0.91326	1.7525	0.91329	1.55127
0.86352	4.5212	0.8619	2.393	0.91302	1.87967	0.9639	1.8416	0.96405	1.62852
0.914151	4.7309	0.9126	2.5183	0.96381	1.97075	1.00959	1.9236	1.00972	1.70332
0.964821	4.9385	0.9633	2.641	1.0095	2.05454				
1.01051	5.1233	1.0091	2.7514						

9. CO_2 isotherms fitting details

Table S5. Fitting equations and constants for isosteric heats of adsorption calculations.

Sample	Temp. K	Constants			
		a	*b*	*c*	*d*
I	298	10.03303	8.83801	9.77169	8.83933
	303	1.08324	6.15394	10.87888	6.1534
	308	8.84595	16.47001	16.90994	16.46993
	313	9.32528	12.85033	9.09477	12.85026
II	298	843.9469	587.5734	2.14619	1.50846
	303	7.39312	5.77474	6.08989	5.77304
	308	12.6257	13.38018	12.15632	13.37319
	313	9.6757	12.92324	11.79441	12.92291
III	298	19.48741	8.05225	3.06392	8.0554
	303	7.07399	7.55536	10.34733	7.55615
	308	204305.4	230147	204300.8	230136.8
	313	10.65716	12.79185	10.60953	12.79188
IV	298	13.83048	8.94252	13.40006	8.93489
	303	14.06428	12.51262	13.64335	12.50879
	308	18161.66	18848.88	18156.45	18853.28
	313	38075.03	44810.75	38072.77	44810.99

CO_2 adsorption isotherms of **I-IV** at different temperatures (298 K, 303 K, 308 K, and 313 K) were fit to the dual site Langmuir model.[2] This model is particularly useful for fitting isotherms of materials that exhibit both strong and weak adsorbate binding sites.[3]

$$C = \frac{a \times P}{b + P} + \frac{c \times P}{d + P}$$

(*C*, moles adsorbed; *P*, pressure; *a*, *b*, *c*, and *d*, constants.)

Isosteric heats were computed by first plotting adsorption isosteres, plots of *ln(P)* versus *1/T* at constant loading of CO_2, by interpolating data within the experimental range from the dual site Langmuir model. Points on the adsorption isosteres were computed at 298, 303, 308, and 313 K. The isostere data were then fitted to a line, with the slope of the line being proportional to the isosteric heat at that loading.

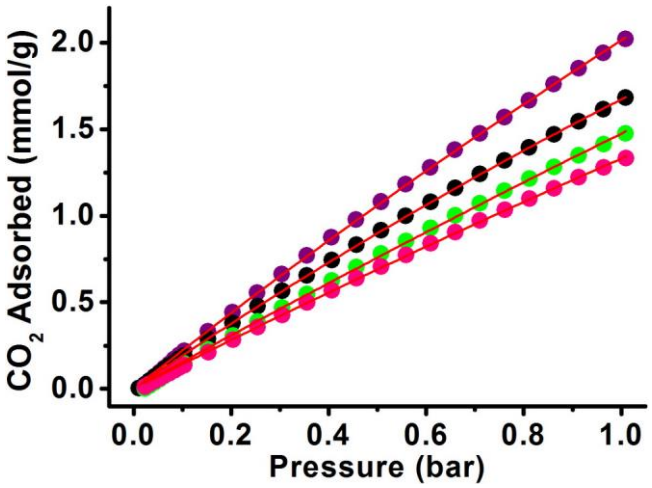

Figure S20. Dual site Langmuir fits of **I** CO_2 adsorption isotherms at 298 K (purple), 303 K (black), 308 K (green), and 313 K (pink). (Spheres: experimental data; lines: Langmuir fits)

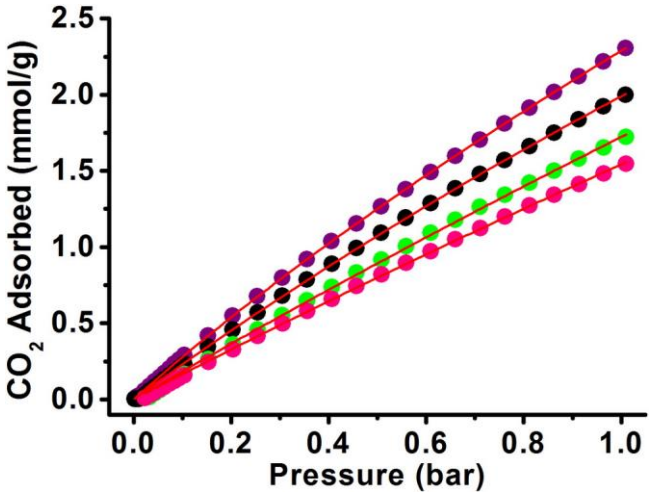

Figure S21. Dual site Langmuir fits of **II** CO_2 adsorption isotherms at 298 K (purple), 303 K (black), 308 K (green), and 313 K (pink). (Spheres: experimental data; lines: Langmuir fits)

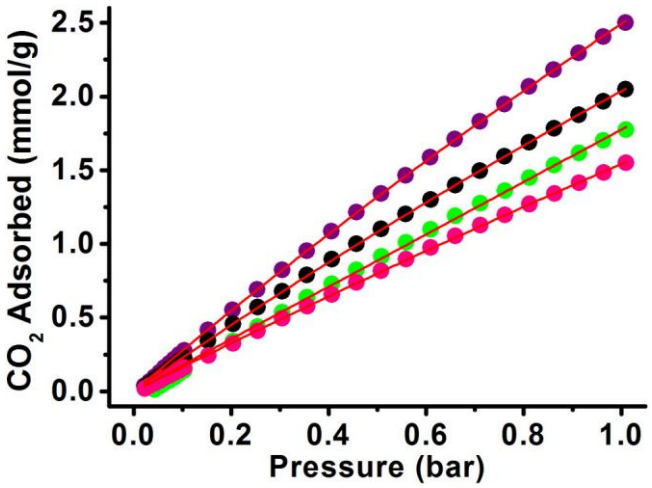

Figure S22. Dual site Langmuir fits of **III** CO_2 adsorption isotherms at 298 K (purple), 303 K (black), 308 K (green), and 313 K (pink). (Spheres: experimental data; lines: Langmuir fits)

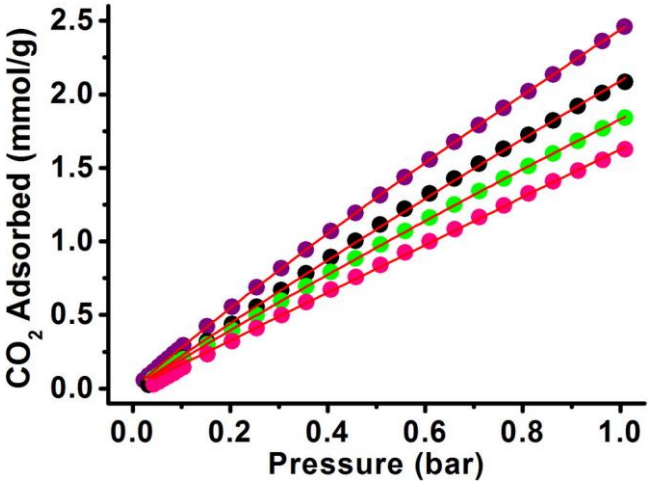

Figure S23. Dual site Langmuir fits of **IV** CO_2 adsorption isotherms at 298 K (purple), 303 K (black), 308 K (green), and 313 K (pink). (Spheres: experimental data; lines: Langmuir fits)

10. References

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