Supporting Information for:

Investigation of the Synthesis, Activation, and Isosteric Heats of CO_2 Adsorption of the Isostructural Series of Metal-Organic Frameworks $M_3(BTC)_2$ (M = Cr, Fe, Ni, Cu, Mo, Ru)

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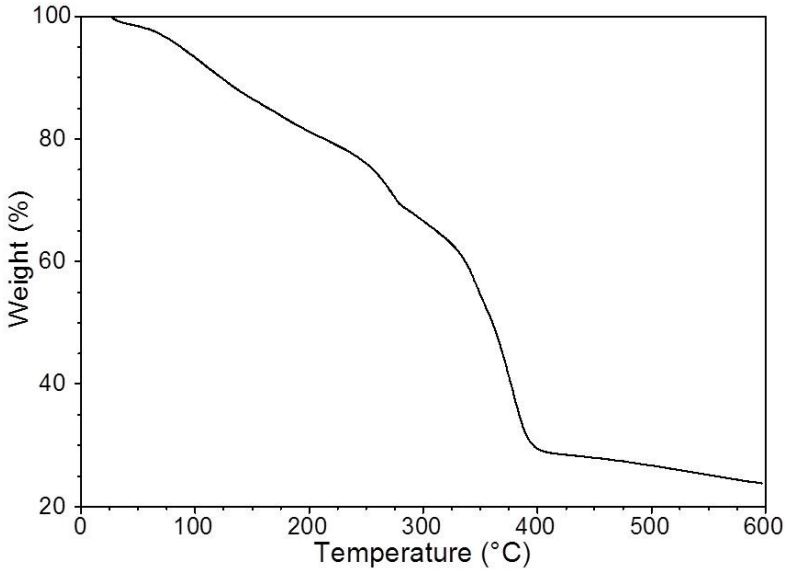

Figure S1. Thermogravimetric analysis data for as-synthesized $Ni_3(BTC)_2$ measured using a ramp rate of 1.0 ˚C/min.

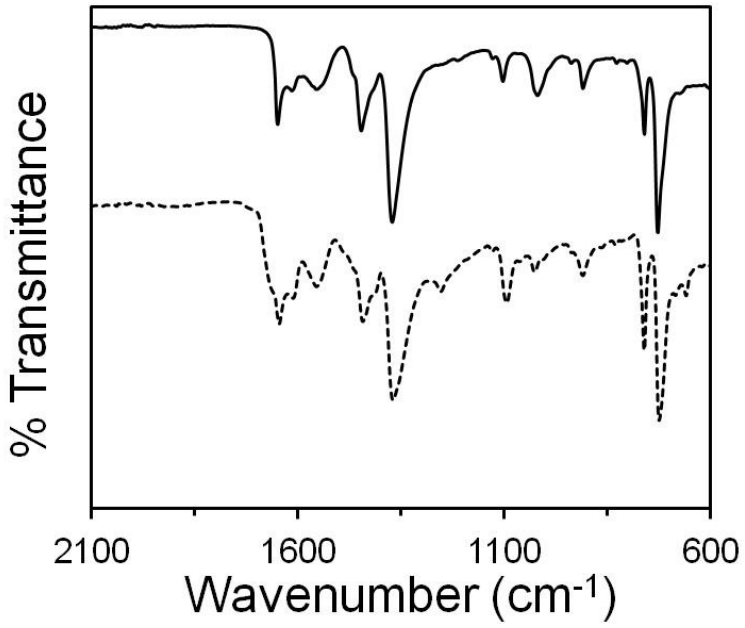

Figure S2. FT-IR spectra of as-synthesized (- - -) and methanol exchanged (—) samples of $Ni_3(BTC)_2$.

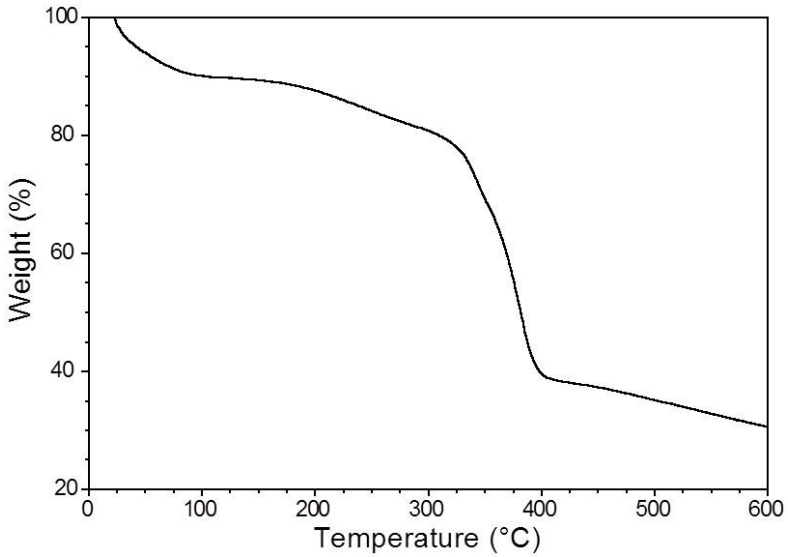

Figure S3. Thermogravimetric analysis data for methanol-exchanged $Ni_3(BTC)_2$ measured using a ramp rate of 1.0 ˚C/min.

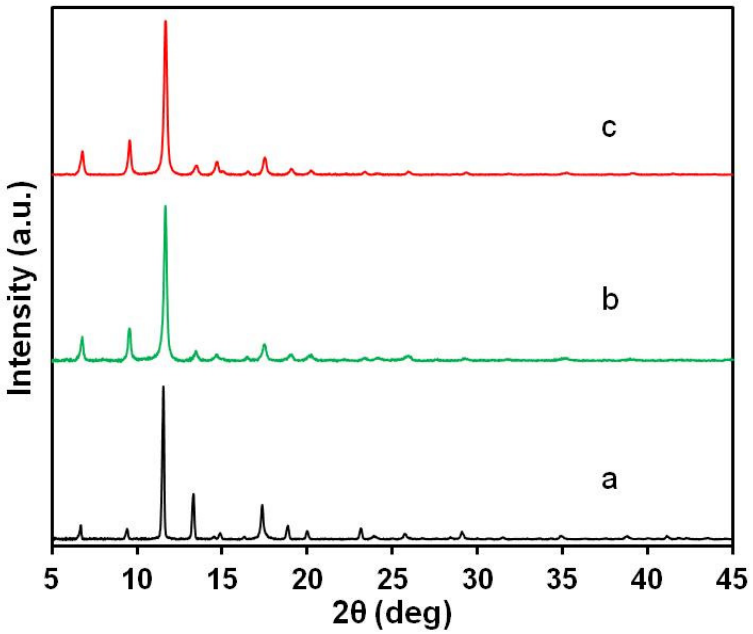

Figure S4. Powder X-ray diffraction patterns of (a) as-synthesized, (b) methanol-exchanged, and (c) activated samples of $Ni_3(BTC)_2$.

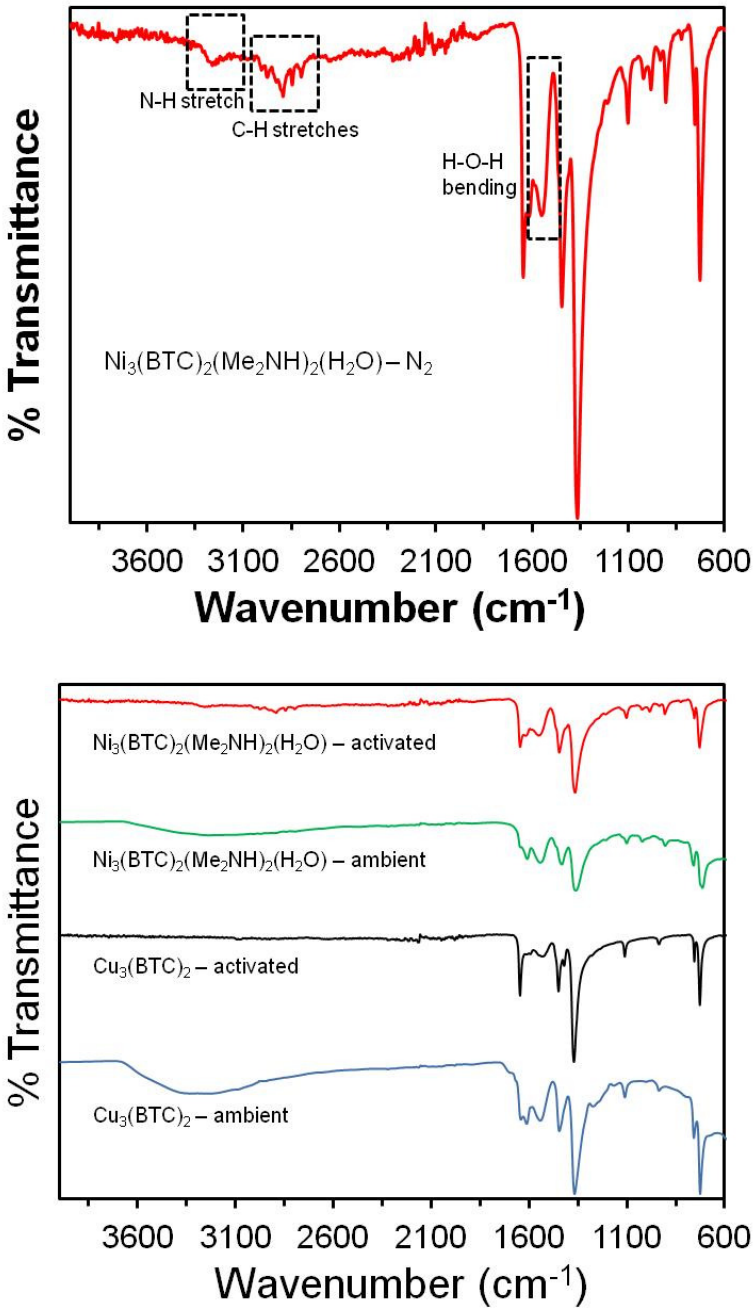

Figure S5. FT-IR spectra of activated samples of $Ni_3(BTC)_2(Me_2NH)_2(H_2O)$ and $Cu_3(BTC)_2$ collected in a dry N_2 atmosphere and under ambient conditions. While no clear O-H stretching (3000-3600 cm^{-1}) band is observed in the spectrum of $Ni_3(BTC)_2(Me_2NH)_2(H_2O)$ under N_2, the H-O-H bending mode in the 1600 cm^{-1} region supports the presence of residual H_2O while the aliphatic C-H stretches below 3000 cm^{-1} and weak N-H stretch at 3260 cm^{-1} indicate the presence of residual Me_2NH in the activated sample. The spectra collected under ambient conditions show the appearance of the O-H stretching and H-O-H bending modes for both $Ni_3(BTC)_2(Me_2NH)_2(H_2O)$ and $Cu_3(BTC)_2$.

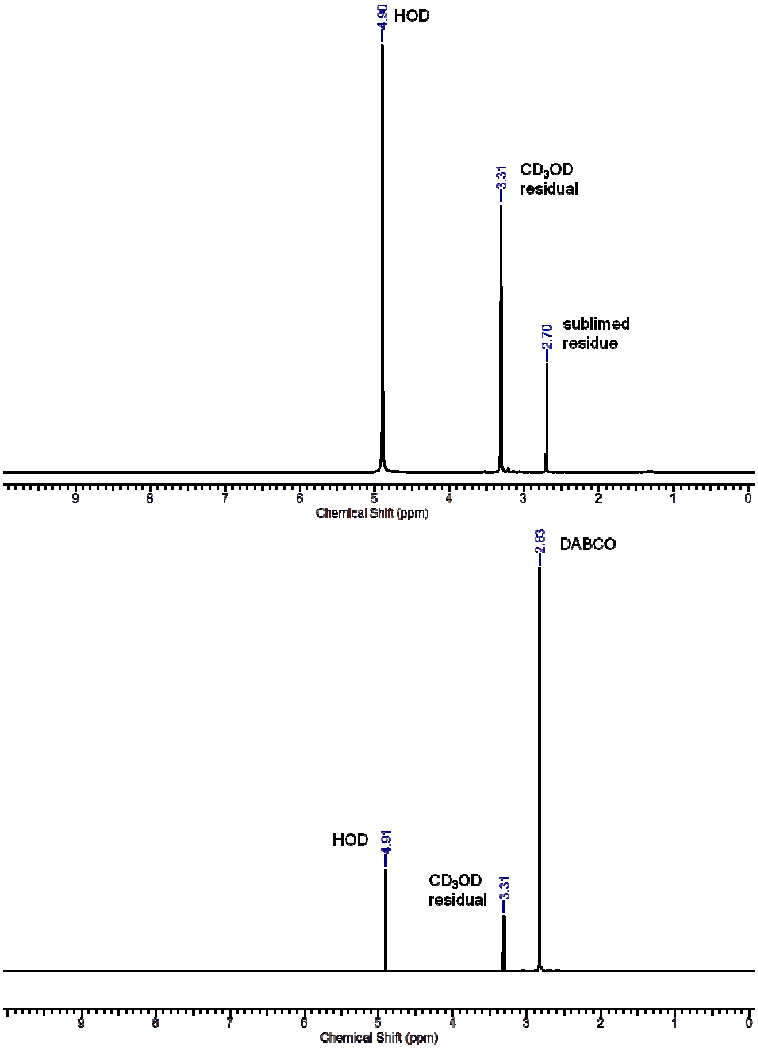

Figure S6. ^{1}H NMR spectra (CD_3OD) of sublimed residue from the attempted activation of as-synthesized $Fe_3(BTC)_2Cl$ (top) and DABCO (bottom).

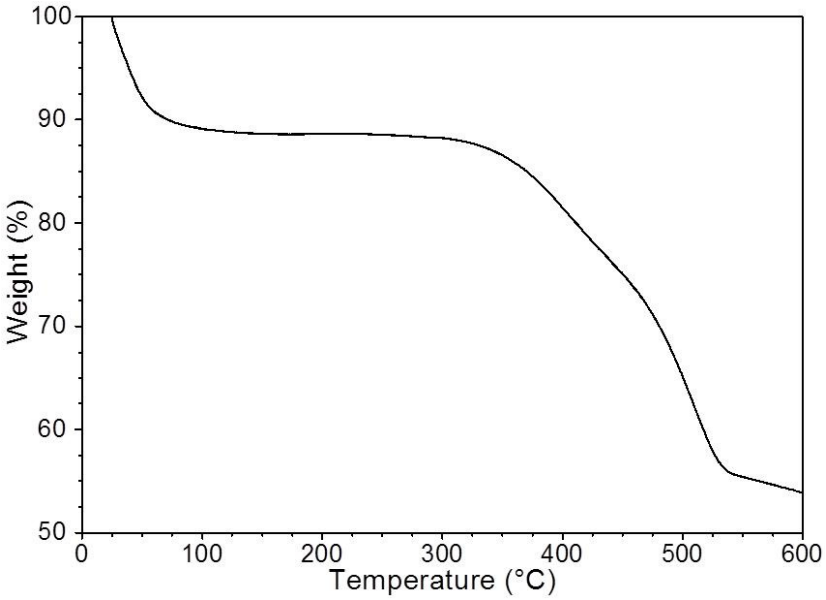

Figure S7. Thermogravimetric analysis data for methanol-exchanged $Mo_3(BTC)_2$ measured using a ramp rate of 1.0 ˚C/min.

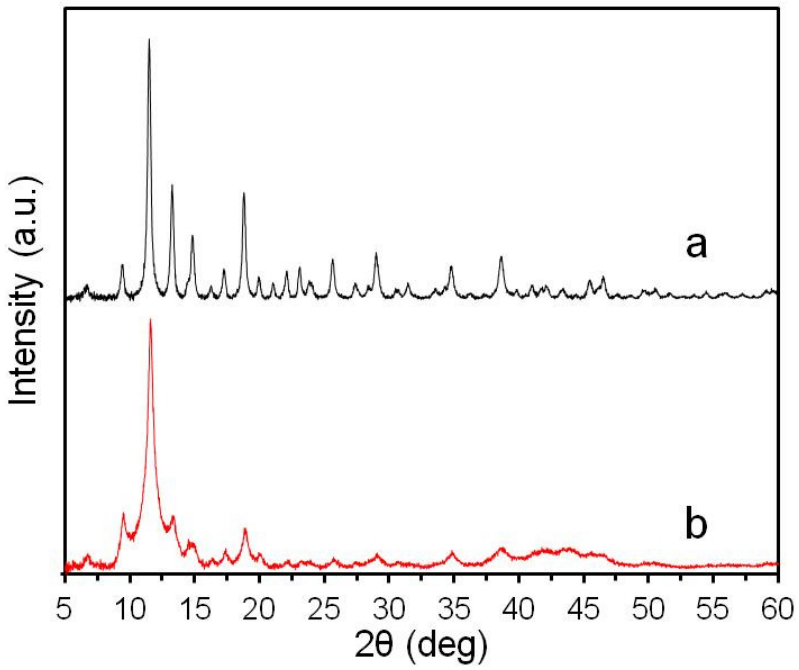

Figure S8. Powder X-ray diffraction patterns of as-synthesized samples of $Ru_3(BTC)_2$ obtained using (a) $Ru_2Cl(\mu\text{-}OPiv)_4$ and (b) $Ru_2Cl(\mu\text{-}OAc)_4$ as the ruthenium source.

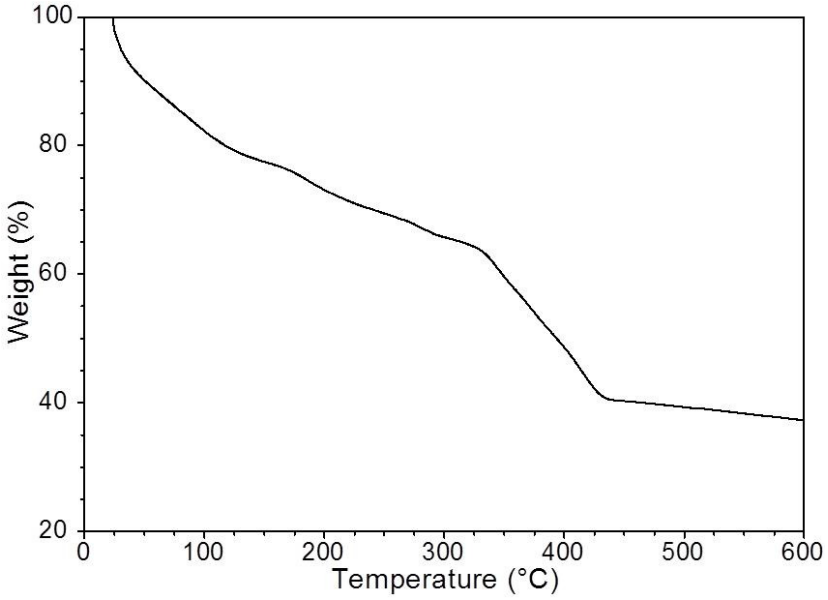

Figure S9. Thermogravimetric analysis data for as synthesized $Ru_3(BTC)_2$ measured using a ramp rate of 1.0 ˚C/min.

Table S1. Virial coefficients calculated from fitting of the CO_2 adsorption isotherms.

	$Cu_3(BTC)_2$	$Cr_3(BTC)_2$	$Ni_3(BTC)_2(Me_2NH)_2(H_2O)$	$Mo_3(BTC)_2(DMF)_{0.5}$	$[Ru_3(BTC)_2][BTC]_{0.5}$
a_0	-3586 ± 29	-3214 ± 28	-4430 ± 46	-3084 ± 51	-3921 ± 46
a_1	15.2 ± 0.8	14.5 ± 0.8	136.4 ± 1.6	42.7 ± 2.5	74.61 ± 1.6
b_0	16.8 ± 0.1	15.7 ± 0.1	19.0 ± 0.14	15.7 ± 0.15	17.73 ± 0.14

Table S2. Adsorption Data for CO_2 uptake in $Cu_3(BTC)_2$.

315 K		325 K		333 K	
Pressure (Torr)	Quantity Adsorbed (cm^3/g STP)	Pressure (Torr)	Quantity Adsorbed (cm^3/g STP)	Pressure (Torr)	Quantity Adsorbed (cm^3/g STP)
2.02	0.185	2.16	0.136	2.26	0.105
3.28	0.302	3.73	0.242	3.75	0.183
3.40	0.315	4.41	0.287	4.41	0.215
4.42	0.411	8.08	0.544	8.10	0.413
7.97	0.756	13.29	0.911	13.52	0.696
13.30	1.254	17.10	1.160	17.07	0.885
17.07	1.615	21.06	1.421	21.09	1.083
21.31	2.020	25.41	1.710	25.05	1.298
25.07	2.371	36.97	2.466	36.81	1.893
37.07	3.479	49.57	3.275	49.63	2.558
49.58	4.633	74.57	4.878	75.17	3.832
74.48	6.861	99.74	6.507	99.79	5.048
99.90	9.115	149.15	9.630	149.85	7.540
149.27	13.536	200.37	12.811	200.34	10.057
199.76	17.957	250.31	15.852	250.51	12.501
250.28	22.316	300.34	18.902	300.29	14.840
300.34	26.604	350.28	21.996	349.77	17.101
350.68	30.666	400.45	25.020	400.20	19.452
400.09	34.702	450.54	27.866	450.32	21.932
450.38	38.917	500.26	30.724	500.47	24.328
500.64	43.007	550.11	33.659	550.44	26.612
550.49	46.903	600.51	36.613	600.33	28.768
600.41	50.586	650.60	39.390	650.32	30.846
650.06	54.376	700.14	41.983	700.19	33.098
700.34	58.383	749.95	44.814	750.48	35.478
750.37	62.185	800.27	47.729	800.55	37.724
800.10	65.757				

Table S3. Adsorption Data for CO_2 uptake in $Cr_3(BTC)_2$.

314 K		324 K		333 K	
Pressure (Torr)	Quantity Adsorbed (cm^3/g STP)	Pressure (Torr)	Quantity Adsorbed (cm^3/g STP)	Pressure (Torr)	Quantity Adsorbed (cm^3/g STP)
2.37	0.229	2.56	0.164	2.67	0.133
3.68	0.353	5.21	0.346	5.27	0.270
4.39	0.419	8.19	0.549	8.17	0.423
7.99	0.758	13.34	0.899	13.20	0.692
13.29	1.223	17.10	1.143	17.09	0.891
17.04	1.554	21.38	1.436	21.07	1.099
21.08	1.921	25.41	1.702	25.10	1.291
25.28	2.303	37.33	2.500	37.19	1.915
36.99	3.312	49.96	3.319	50.29	2.582
49.91	4.456	74.49	4.891	74.70	3.798
74.49	6.568	100.26	6.545	99.85	5.054
99.85	8.735	149.59	9.733	149.04	7.456
149.02	12.871	200.44	12.965	200.25	9.913
200.24	17.135	250.41	16.080	250.35	12.287
250.26	21.377	300.37	19.132	299.76	14.652
300.06	25.543	350.27	22.223	350.25	17.089
350.30	29.683	400.22	25.403	400.20	19.513
400.35	33.653	450.41	28.490	450.30	21.890
450.11	37.678	500.45	31.451	500.22	24.265
500.33	41.854	550.25	34.398	550.47	26.580
550.39	45.934	600.10	37.477	600.24	28.807
600.41	49.819	650.49	40.548	650.27	31.093
650.28	53.562	700.35	43.539	700.37	33.392
699.60	57.567	750.38	46.387	750.22	35.735
750.71	61.612	800.03	49.166	800.45	38.086
800.34	65.434				

Table S4. Adsorption Data for CO_2 uptake in $Ni_3(BTC)_2(Me_2NH)_2(H_2O)$.

313 K		323 K		333 K	
Pressure (Torr)	Quantity Adsorbed (cm^3/g STP)	Pressure (Torr)	Quantity Adsorbed (cm^3/g STP)	Pressure (Torr)	Quantity Adsorbed (cm^3/g STP)
1.53	0.272	1.76	0.180	1.81	0.125
2.39	0.429	2.86	0.302	2.89	0.205
3.40	0.612	3.41	0.362	3.40	0.243
4.40	0.793	4.39	0.469	4.40	0.318
8.16	1.466	7.95	0.884	8.01	0.613
13.26	2.355	13.30	1.478	13.61	1.040
17.23	3.024	17.05	1.905	17.07	1.300
21.32	3.691	21.12	2.333	21.07	1.597
25.07	4.268	25.03	2.768	25.40	1.922
36.84	6.058	37.38	4.014	36.90	2.754
50.42	7.933	49.91	5.285	50.34	3.691
75.15	11.030	74.64	7.534	75.26	5.334
100.36	13.823	100.27	9.653	99.95	6.871
150.07	18.542	149.31	13.318	149.38	9.721
200.24	22.629	200.14	16.747	200.30	12.377
250.18	26.229	250.22	19.769	250.32	14.745
300.34	29.375	300.33	22.486	299.82	16.917
350.24	32.271	350.11	24.888	350.47	18.952
400.34	35.067	400.13	27.141	400.35	20.903
450.36	37.679	450.19	29.396	450.23	22.779
500.27	40.005	500.33	31.570	500.27	24.581
550.13	42.170	550.35	33.538	550.35	26.260
600.12	44.373	600.23	35.290	600.21	27.903
650.27	46.590	650.18	37.003	650.46	29.501
700.36	48.667	700.10	38.812	700.27	31.038
750.55	50.448	750.30	40.612	750.14	32.459
799.93	52.224	800.45	42.275	800.30	33.821

Table S5. Adsorption Data for CO_2 uptake in $Mo_3(BTC)_2(DMF)_{0.5}$.

314 K		324 K		334 K	
Pressure (Torr)	Quantity Adsorbed (cm^3/g STP)	Pressure (Torr)	Quantity Adsorbed (cm^3/g STP)	Pressure (Torr)	Quantity Adsorbed (cm^3/g STP)
2.38	0.154	2.54	0.103	2.63	0.081
3.73	0.244	5.28	0.236	5.32	0.182
4.40	0.289	8.18	0.382	8.19	0.295
8.03	0.550	13.24	0.616	13.48	0.496
13.58	0.904	17.05	0.805	17.42	0.647
17.02	1.131	21.38	1.014	21.11	0.778
21.10	1.396	25.07	1.193	25.08	0.915
25.39	1.667	37.27	1.742	36.82	1.339
37.18	2.417	50.02	2.350	49.62	1.801
50.24	3.211	75.19	3.467	74.78	2.693
74.67	4.672	100.31	4.556	100.32	3.578
100.21	6.200	149.11	6.652	149.93	5.243
149.14	8.997	200.38	8.841	200.07	6.910
200.42	11.797	250.45	10.889	250.29	8.574
250.26	14.440	300.41	12.851	299.95	10.195
300.30	17.136	350.27	14.819	350.37	11.787
350.36	19.756	400.15	16.825	400.38	13.356
400.37	22.249	450.34	18.799	450.31	14.908
450.40	24.632	500.31	20.654	500.35	16.484
500.14	27.038	550.31	22.414	550.43	18.029
550.35	29.505	599.92	24.227	600.40	19.525
600.33	31.909	650.16	26.147	650.18	21.088
650.38	34.184	700.48	28.018	700.36	22.629
700.15	36.357	750.20	29.732	750.31	23.968
750.20	38.630	800.28	31.342	800.25	25.201
800.40	40.979				

Table S6. Adsorption Data for CO_2 uptake in $[Ru_3(BTC)_2][BTC]_{0.5}$.

313 K		323 K		333 K	
Pressure (Torr)	Quantity Adsorbed (cm^3/g STP)	Pressure (Torr)	Quantity Adsorbed (cm^3/g STP)	Pressure (Torr)	Quantity Adsorbed (cm^3/g STP)
1.92	0.236	2.17	0.170	2.33	0.115
3.24	0.403	3.71	0.301	3.75	0.196
3.40	0.424	4.41	0.358	4.41	0.232
4.40	0.550	8.07	0.683	8.08	0.462
8.07	1.007	13.31	1.128	13.31	0.765
13.26	1.661	17.07	1.440	17.27	1.013
17.38	2.153	21.39	1.811	21.11	1.254
21.31	2.612	25.12	2.103	25.11	1.481
25.06	3.064	37.49	3.101	36.89	2.179
36.91	4.416	50.06	4.112	49.76	2.917
50.03	5.842	74.59	5.960	75.07	4.334
74.91	8.411	100.35	7.814	99.87	5.676
99.60	10.882	149.11	11.104	150.00	8.249
149.53	15.492	200.37	14.392	200.44	10.665
200.35	19.778	250.36	17.430	250.37	12.956
250.28	23.646	299.96	20.283	300.40	15.179
300.22	27.321	350.36	23.049	350.39	17.368
350.41	30.805	400.35	25.673	400.41	19.503
400.41	33.979	450.27	28.151	450.49	21.548
450.19	36.985	500.39	30.492	500.51	23.446
500.35	39.892	550.42	32.705	550.14	25.214
550.23	42.718	600.10	34.808	600.31	26.976
600.34	45.516	650.33	36.979	650.37	28.795
650.31	48.193	700.46	39.088	700.28	30.597
700.20	50.715	750.17	41.149	750.29	32.380
750.11	53.119	800.43	43.162	800.32	34.063
800.50	55.375				