Supplementary material (ESI) for Journal of Materials Chemistry

Independent verification of the saturation hydrogen uptake in MOF-177 and establishment of a benchmark for hydrogen adsorption in metal-organic frameworks

(Supplementary information: 10 pages)

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Synthesis of 4,4',4''-benzene-1,3,5-triyl-tribenzoic acid (H_3BTB)

1. 1,3,5-Tri(4',4',4''-acetylphenyl)benzene

$AlCl_3$ (33 g) was dissolved in 180 mL acetyl chloride in a 1 L round bottom flask with a ice/water bath. 1,3,5-Triphenylbenzene (10 g) was dissolved in 200 mL CH_2Cl_2, which was transferred to a dropping funnel and gradually added to the cold $AlCl_3$/acetyl chloride solution. The color of the solution turned deep red very fast. After stirring the mixture for 2 hours at room temperature, the red suspension was poured into a 2 L Erlenmeyer flask with at least 1800 mL ice in it VERY SLOWLY. The mixture was stirred overnight and light yellow slurry form was obtained.

The organic phase was separated and the water phase was washed with CH_2Cl_2 (3 × 200 mL). Two CH_2Cl_2 portions were combined and were washed with 5% NaOH aqueous solution (2 × 200 mL). The resulted CH_2Cl_2 was dried over anhydrous $MgSO_4$ and then filtered. The clear solution is then evaporated to remove the solvent and white solid is yielded. The solid is then stirred with 1 L boiled ethanol for 30 min. The ethanol which turns yellow is removed by hot filtration. Repeat the purification one more time. Dry the filter cake in air over night to yield 11 g solid.

2. 4,4',4''-benzene-1,3,5-triyl-tribenzoic acid

1,3,5-tri(4',4',4"-acetylphenyl)benzene (11 g) was suspended in 500 mL of 1,4-dioxane in 1 L round bottom flask. NaOH (35 g) was dissolved in 240 mL of water and cooled in the freezer for one hour. Bromine (16 mL) was added slowly to the cold solution with stirring until a deep yellow solution was yielded. The prepared NaOBr solution was added slowly to the dioxane suspension. The suspension was turned into a yellowish cloudy solution. The reaction mixture was stirring at 60 °C for 2 hours and then cooled to room temperature. $Na_2S_2O_3 \cdot 5H_2O$ aqueous solution (5%) was added to the reaction mixture to quench NaOBr and stirred for 10 min. The reaction mixture was filtered while it was warm, and the filtrate was acidified with 50 mL conc. HCl.

Powder X-ray diffraction patterns

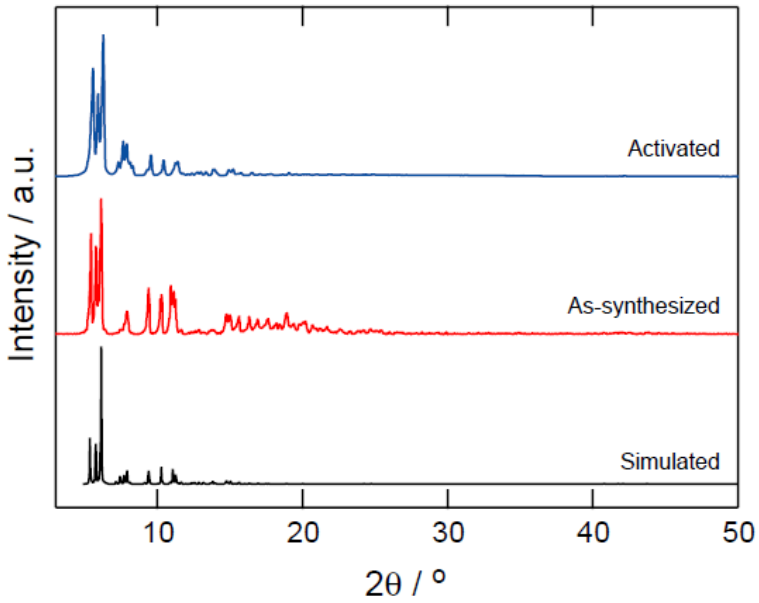

Fig. S1 Powder X-ray diffraction patterns for MOF-177; activated (blue) and as-synthesized materials (red) and simulated pattern (black).

Thermogravimetric Analysis Curves

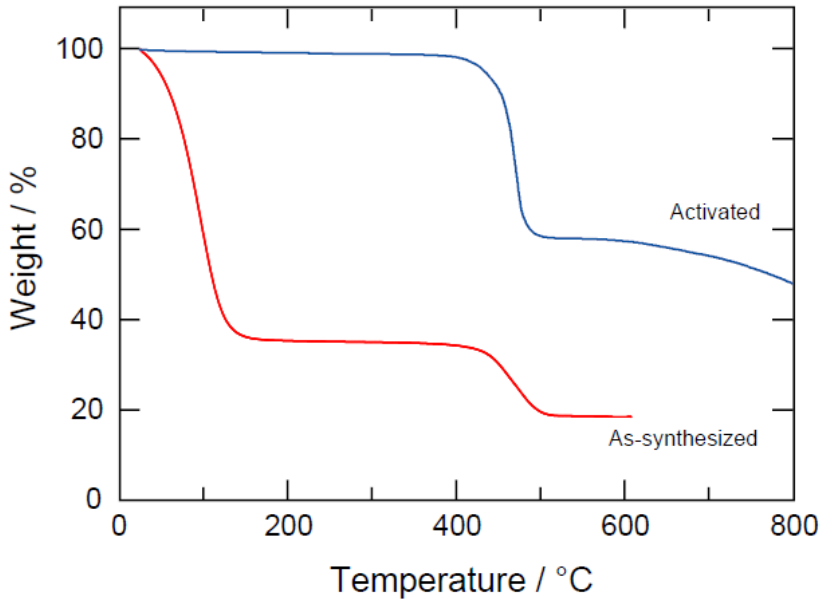

Fig. S2 Thermogravimetric analysis curves for as-synthesized and activated MOF-177.

Low-pressure N_2 sorption data

Table S1 Low-pressure N_2 sorption data for MOF-177 at 77 K.

P/P_0	N_2 uptake / $cm^3\ g^{-1}$	P/P_0	N_2 uptake / $cm^3\ g^{-1}$
1.97E-05	8.50446	0.0785	1139.6
2.03E-05	8.79798	0.0897	1147.25
2.91E-05	12.0131	0.101	1153.88
3.00E-05	12.2558	0.148	1173.31
3.90E-05	14.8749	0.202	1187.97
5.47E-05	19.6731	0.247	1197.01
6.44E-05	22.3109	0.298	1205.2
6.75E-05	23.1541	0.35	1212.04
8.12E-05	26.4227	0.401	1217.76
8.39E-05	27.0762	0.452	1222.73
0.000186	44.5113	0.503	1226.95
0.000287	56.2828	0.554	1230.78
0.000391	65.2749	0.604	1234.3
0.000491	72.4889	0.655	1237.48
0.000592	78.678	0.705	1240.41
0.00069	84.4185	0.755	1243.14
0.000794	89.9793	0.806	1245.74
0.000894	95.0021	0.855	1248.2
0.000996	100.204	0.905	1250.66
0.002	146.558	0.955	1253.31
0.003	195.661	0.996	1258.96
0.004	251.891	0.892	1250.39
0.005	318.398	0.791	1245.02
0.00601	396.272	0.69	1239.56
0.00701	481.54	0.59	1233.33
0.00801	564.128	0.491	1226.02
0.00901	633.959	0.393	1216.91
0.00901	643.571	0.295	1204.84
0.0162	935.309	0.199	1187.24
0.0276	1055.61	0.0997	1153.23
0.037	1086.22	0.0487	1108.26
0.0471	1106		
0.0596	1122.47		
0.0683	1131.14		

Low-pressure H_2 sorption data

Table S2 Low-pressure H_2 sorption data for MOF-177 at 77 and 87 K.

P / Torr	H_2 uptake at 77 K / cm^3 g^{-1}	P / Torr	H_2 uptake at 87 K / cm^3 g^{-1}
0.10466	0.0316	0.099306	0.0141
0.168206	0.0451	0.154595	0.0185
0.23908	0.0627	0.252117	0.0289
0.320887	0.0844	0.328293	0.038
0.411869	0.1093	0.408907	0.0482
0.479111	0.1279	0.511365	0.0613
0.575258	0.1555	0.561018	0.0673
0.643525	0.1746	0.715879	0.0877
0.734499	0.1996	0.783919	0.0948
0.820898	0.2218	0.823667	0.0991
1.687388	0.4748	1.681423	0.2148
2.514661	0.7133	2.50718	0.3246
3.231867	0.9191	3.326747	0.4334
4.093354	1.1521	4.04413	0.526
4.858896	1.3658	4.831056	0.6263
5.713444	1.5915	5.803538	0.7516
6.502145	1.8115	6.459497	0.8352
7.298593	2.0329	7.38969	0.9556
12.10084	3.4065	14.95063	1.9716
19.10184	5.303	21.10421	2.7565
26.83311	7.3565	28.76524	3.7225
34.85004	9.4484	36.72455	4.7174
42.93798	11.5204	44.77872	5.7121
51.06384	13.5714	52.84173	6.7144
59.20101	15.5988	60.87339	7.7035
67.3067	17.5895	68.9348	8.6818
75.4253	19.5552	76.96324	9.6597
83.54229	21.4941	85.06003	10.6455
123.3728	30.6497	118.7303	14.6285
163.8972	39.4072	165.5374	20.0051
204.4458	47.7246	199.4891	23.8004
245.0913	55.6665	246.047	28.9187
285.5592	63.209	280.1514	32.5612
326.1079	70.561	326.5324	37.4648
366.4709	77.5969	360.7253	41.0301
406.9308	84.2624	407.0822	45.6283
447.3503	90.8379	441.4599	49.0168
487.7617	97.1797	480.6856	52.8124
528.3346	103.4646	520.8922	56.6804
568.6976	109.5588	567.9485	61.1235
609.1091	115.4013	602.5514	64.2878

Table S2 Continued.

P / Torr	H_2 uptake at 77 K / cm^3 g^{-1}	P / Torr	H_2 uptake at 87 K / cm^3 g^{-1}
690.1579	126.6408	682.2168	71.4667
730.8034	132.2545	722.4555	75.0167
771.118	137.5811	762.662	78.6369
806.4538	142.2847	799.6848	81.7527
720.8942	130.8185	719.923	74.8455
646.0426	120.4113	639.8797	67.8308
559.7325	107.9638	559.3702	60.4121
477.901	95.4854	479.0857	52.8372
405.3976	83.6883	398.7932	44.9053
319.0471	68.9426	318.5168	36.7782
237.5868	53.8156	238.3932	28.1649
157.135	37.6388	158.2374	19.2092
77.46443	19.8488	78.17322	9.8109
37.53472	10.0282	41.61188	5.2618
9.234598	2.5574	8.789	1.1269

High-pressure H_2 sorption data

Table S3 High-pressure H_2 sorption data for MOF-177 at 77 K (volumetric #1).

P / bar	Ex / mg g^{-1}	Abs / mg g^{-1}	Ex / g L^{-1}	Abs / g L^{-1}
0.00	0.0	0.0	0.00	0.00
1.81	18.2	19.3	7.75	8.22
3.48	26.7	28.7	11.42	12.25
6.68	39.4	43.0	16.83	18.35
12.75	52.6	59.2	22.47	25.29
18.14	59.3	68.6	25.33	29.30
23.85	64.2	76.4	27.43	32.63
32.08	68.0	84.3	29.03	36.00
39.50	70.8	90.8	30.21	38.77
48.42	73.0	97.5	31.16	41.63
54.98	75.7	103.5	32.33	44.21
61.49	76.5	107.6	32.67	45.95
66.20	77.1	110.6	32.93	47.22
71.95	75.5	111.8	32.23	47.76

Table S4 High-pressure H_2 sorption data for MOF-177 at 77 K (volumetric #2).

P / bar	Ex / mg g^{-1}	Abs / mg g^{-1}	Ex / g L^{-1}	Abs / g L^{-1}
0.00	0.0	0.0	0.00	0.00
0.69	9.8	10.4	4.19	4.42
1.94	19.5	20.7	8.32	8.822
4.22	30.9	33.2	13.19	14.17
7.66	42.7	46.7	18.23	19.95
14.76	54.6	62.2	23.31	26.55
23.69	63.3	75.4	27.01	32.18
29.83	67.8	83.0	28.95	35.43
35.96	70.6	88.8	30.14	37.94
42.21	72.7	94.1	31.02	40.16
48.55	74.3	98.9	31.74	42.24
57.07	74.3	103.2	31.73	44.06
65.64	75.2	108.4	32.11	46.28
69.68	77.6	112.8	33.13	48.17
72.37	78.2	114.7	33.37	48.98

Table S5 High-pressure H_2 sorption data for MOF-177 at 77 K (gravimetric).

P / bar	Ex / mg g^{-1}	Abs / mg g^{-1}	Ex / g L^{-1}	Abs / g L^{-1}
0.00	0.0	0.0	0.00	0.00
0.26	3.8	4.2	1.63	1.78
1.36	14.1	15.1	6.03	6.44
2.62	22.9	24.5	9.77	10.47
6.66	40.5	44.3	17.28	18.92
13.24	55.5	62.9	23.70	26.86
26.71	68.2	83.0	29.13	35.43
39.65	72.2	94.0	30.82	40.13
52.44	73.0	101.7	31.15	43.43
65.48	72.5	108.3	30.95	46.26
75.46	72.1	113.4	30.78	48.41
71.99	71.9	111.3	30.71	47.54
60.20	72.6	105.6	31.00	45.09
46.81	72.8	98.5	31.09	42.06
33.67	71.0	89.5	30.30	38.22
19.79	63.5	74.5	27.13	31.82
10.08	49.7	55.4	21.21	23.64
4.06	30.6	33.0	13.06	14.09
1.34	14.2	15.1	6.06	6.46

Curve fittings for low-pressure H_2 isotherms

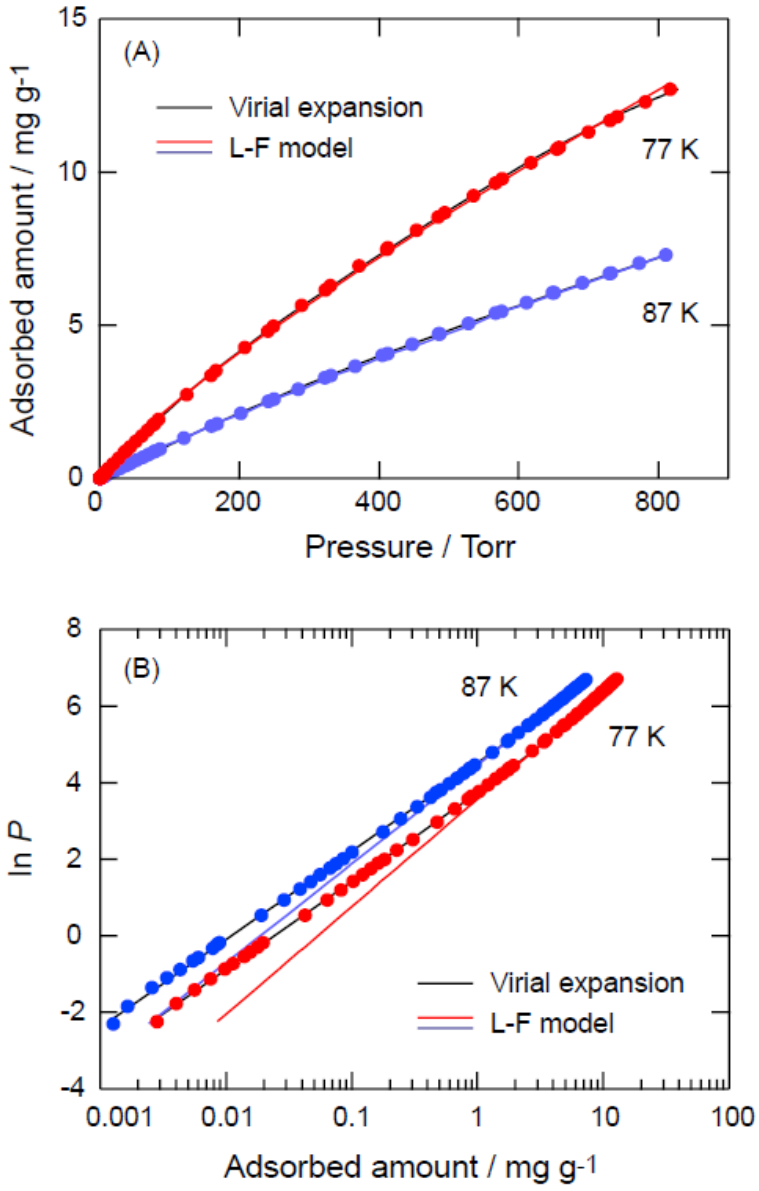

Fig. S3 Fitted H_2 adsorption isotherms of MOF-177 measured at 77 K (red) and 87 K (blue); colored curves for the Langmuir-Freundlich model, black curves for viral expansion. Although curve fitting based on the Langmuir-Freundlich model looks reasonable in the high-pressure region (A), their fitting curves in the low coverage region are not suitable for the calculation of the adsorption enthalpy (B) due to poor fitting.

High-pressure H_2 isotherms for MOF-177

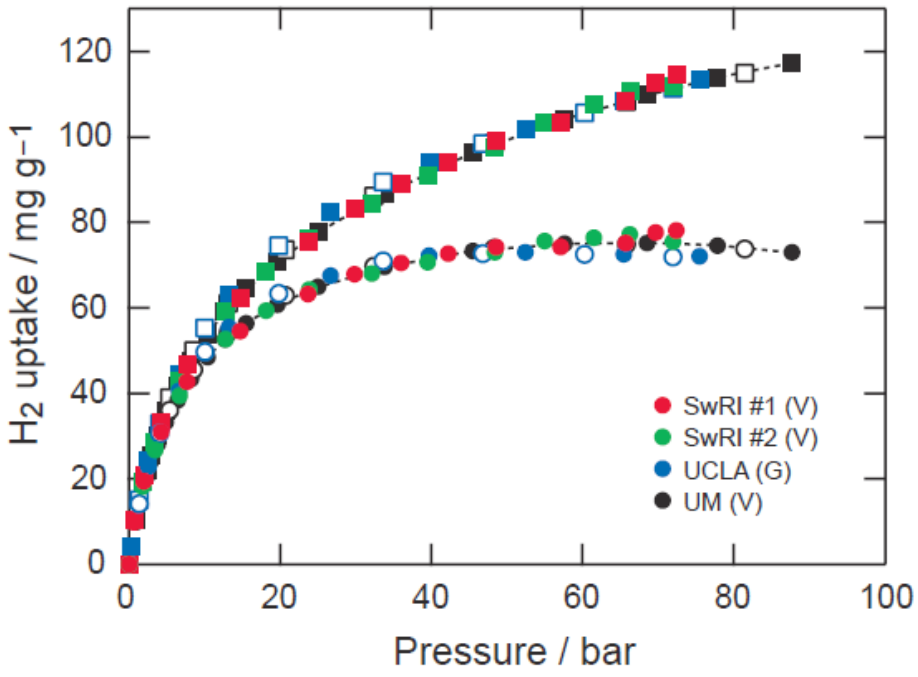

Fig. S4 High-pressure H_2 isotherms for MOF-177. Circle and square symbols represent surface excess and absolute adsorbed amounts, respectively.