

Electronic Supplementary Information (ESI)

Beryllium benzene dicarboxylate: the first beryllium microporous coordination polymer

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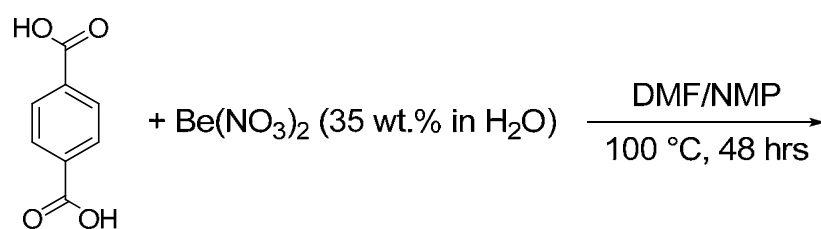
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Section I. Synthesis of Be-BDC



Terephthalic acid (0.289 g, 1.74 mmol, Fluka) was dissolved in 60 mL of a 1:1 mixture of *N,N*-dimethylformamide (DMF) and 1-methyl-2-pyrrolidinone. The solution was split into two 30 mL aliquots that were placed into a 60 mL wide-mouth jar. To each jar, Be(NO₃)₂ (35 wt.% in H₂O) (1.00 mL, 3.16 mmol, Sigma-Aldrich) was added via syringe. The jars were tightly capped and placed in a 100 °C oven for 48 hrs to yield a fine white powder. The cooled suspensions were transferred to 50 mL centrifuge tubes. The fine white powder was spun down and after decanting the mother liquor, the product was rinsed with DMF; this process was repeated twice. Finally, the product was immersed in CH₂Cl₂ for two days, during which time the solvent was decanted and replenished three times by spinning the powder down in a centrifuge. The solvent was removed under vacuum at room temperature for 12 hours, yielding the porous material. Yield of fully evacuated material is 383 mg. Elemental analysis: Be (6.29); C (44.45); O (29.92); N (0.78); H (3.22).

Section II. Powder XRD analysis of Be-BDC

Powder X-ray diffraction (PXRD) patterns were collected at ambient temperature using a Bruker D8 Advance with a LynxEye linear position sensitive detector using Cu-K α radiation (1.5406 Å) at 40 kV and 40 mA. Samples were mounted on a glass slide. Powder patterns were obtained with a 0.02° step size at a rate of 1 step/second. Powder patterns were processed in Jade Plus¹ to calculate peak positions and intensities.

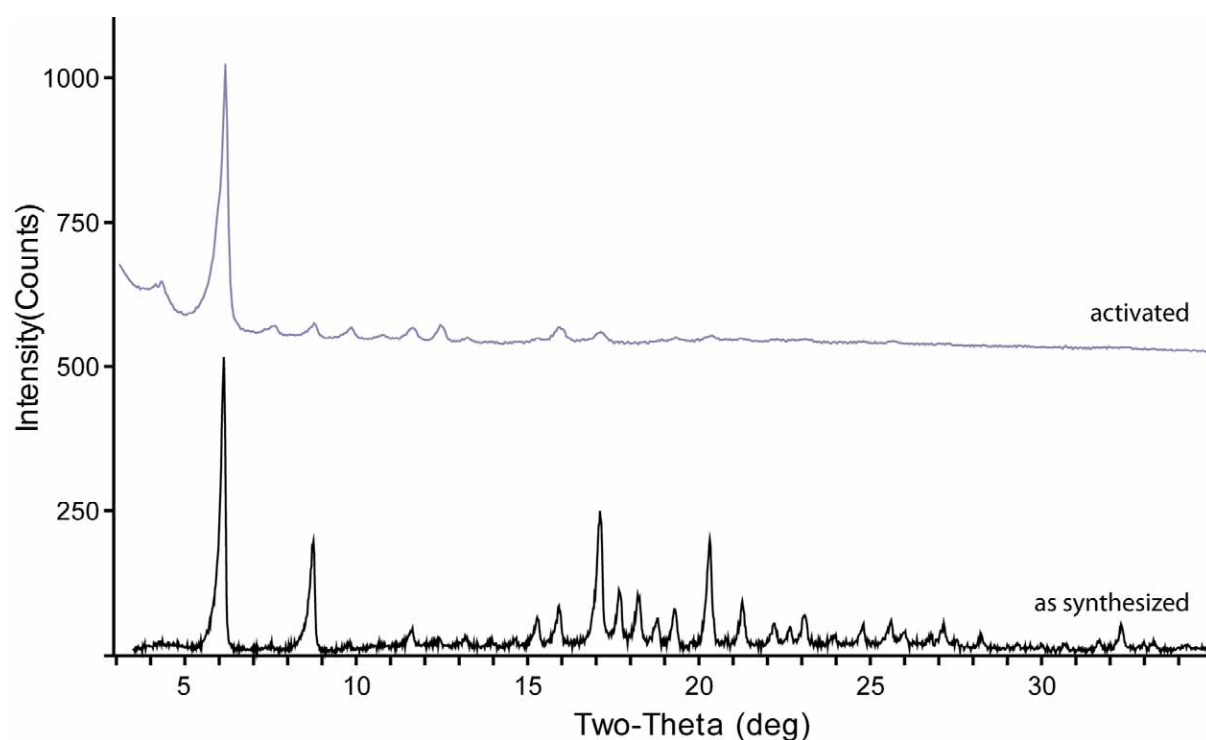


Figure S1. PXRD patterns of as synthesized Be-BDC and activated Be-BDC.

Table S1. Experimental PXRD peak positions (deg) and the relative peak intensities for as-synthesized Be-BDC.

2θ (°)	I/I_0
6.12	100.00
8.73	37.60
11.62	8.30
15.28	12.00
15.92	15.80
17.11	47.80
17.67	21.20
18.24	19.60
18.78	11.60
19.29	14.80
20.31	38.30
21.27	17.40
22.19	10.00
22.66	8.70
23.09	12.60
24.78	9.90
25.60	11.00
25.99	7.30
27.14	10.10
28.23	6.10
32.32	9.60

Section III. Gas sorption measurement on Be-BDC

Ultra-high purity He (99.999%, for void volume determination) N₂ (99.999%), Ar (99.999%), H₂ (99.999%), and CO₂ (99.999%) were purchased from Cryogenic Gasses and used as received. N₂, Ar, CO₂, and low pressure H₂ gas sorption isotherms were measured volumetrically on an Autosorb-1C outfitted with the micropore option by Quantachrome Instruments (Boynton Beach, Florida USA), running version 1.50 of the ASWin software package. In a typical sorption experiment, activated Be-BDC (26 mg) was charged into 9 mm sample cell and evacuated for 12 hrs at room temperature prior to sorption measurements. For low pressure H₂ measurements 116 mg of Be-BDC was used. N₂ sorption isotherms were measured in the range $1.00 \times 10^{-5} \leq P/P_0 \leq 1$. Ar sorption isotherms were measured in the range $1.00 \times 10^{-4} \leq P/P_0 \leq 1$. CO₂ sorption isotherms were measured in the range $1.00 \times 10^{-4} \leq P/P_0 \leq 1$. Low pressure H₂ sorption isotherms were measured in the range $0.076 \text{ torr} \leq P \leq 760$. Pore size distributions were obtained by analyzing the Ar isotherm at 87 K using non-local density functional theory (NLDFT) using a hybrid kernel based on a zeolite/silica cylindrical pore model as implemented in the ASWin software package.

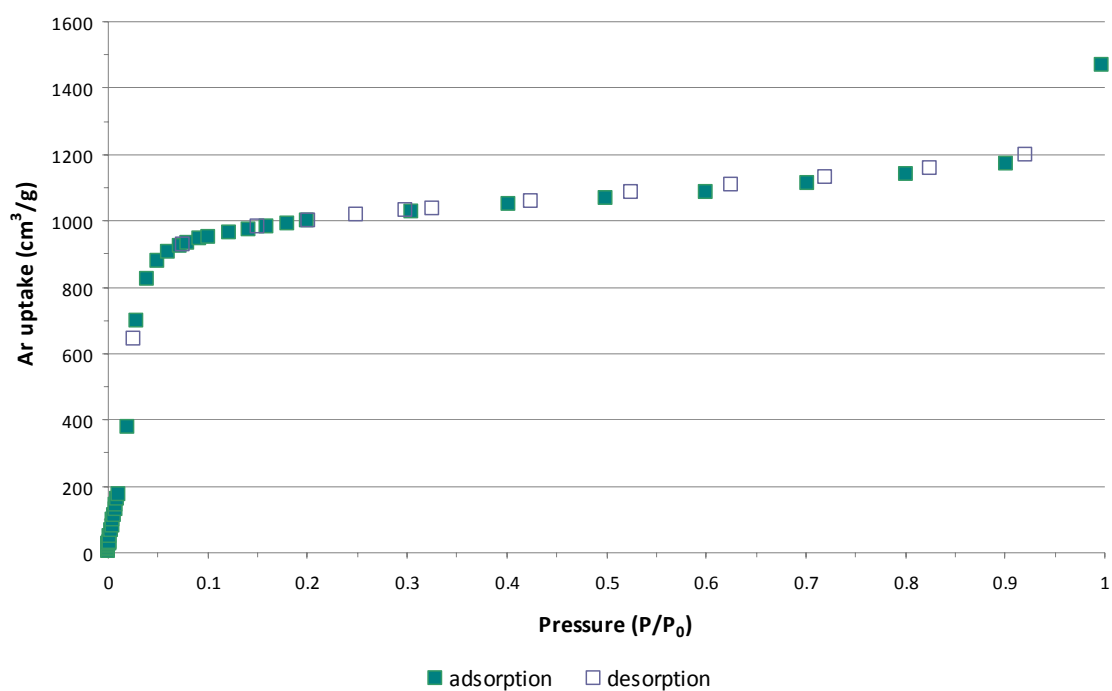


Figure S2. Ar adsorption/desorption isotherms measured at 87 K for Be-BDC.

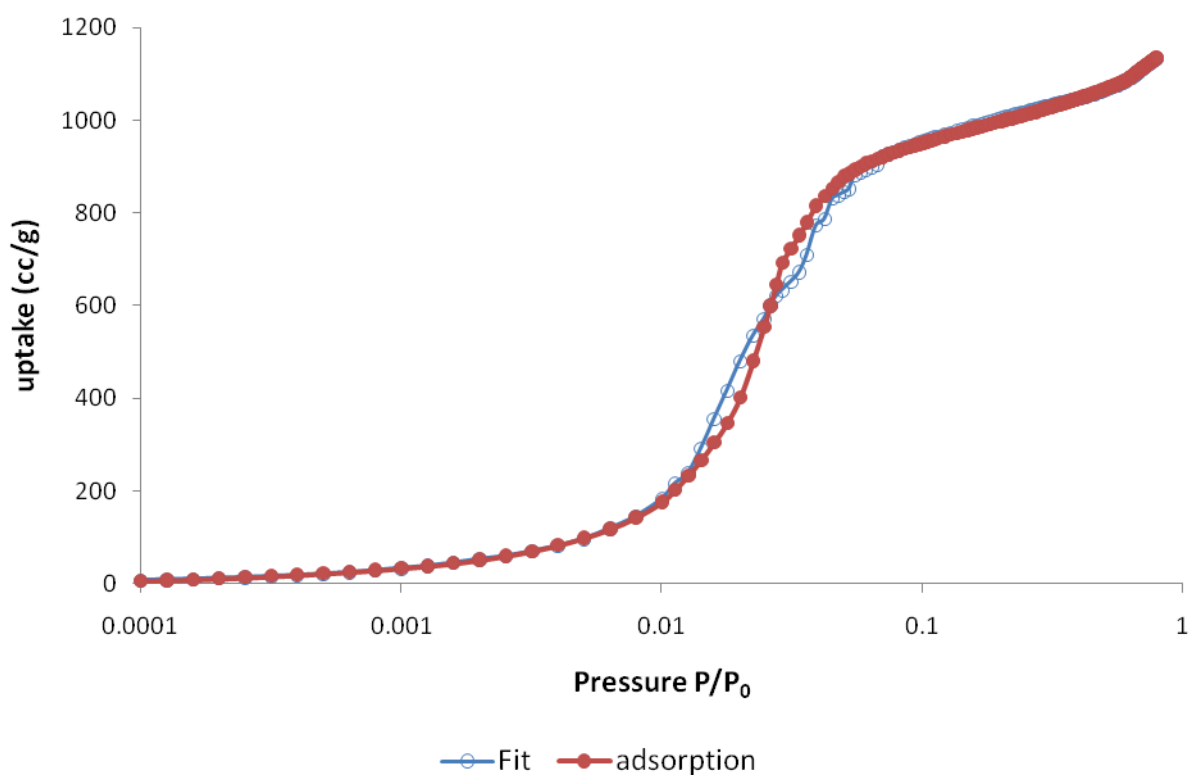


Figure S3. Calculated Ar isotherm at 87 K for Be-BDC using NLDFT (blue curve) overlaid on top of the experimental isotherm

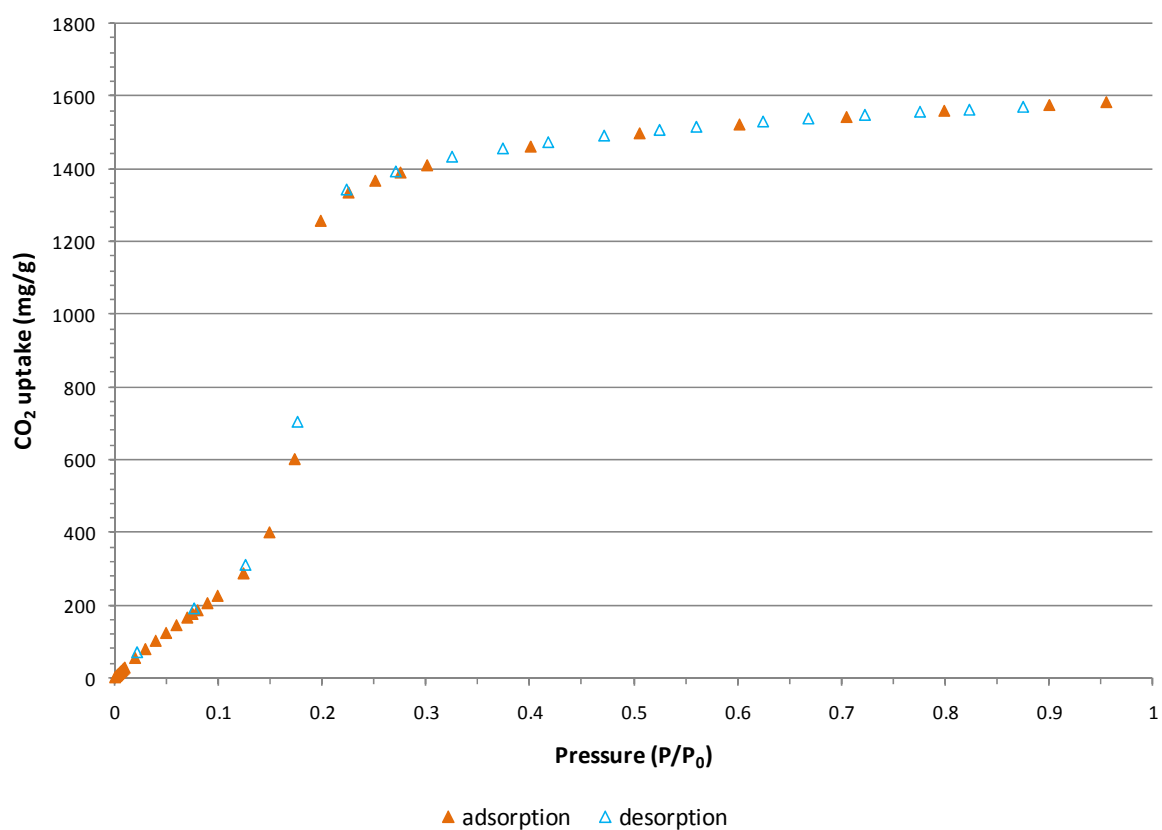


Figure S4. CO₂ adsorption/desorption isotherms measured at 195 K for Be-BDC.

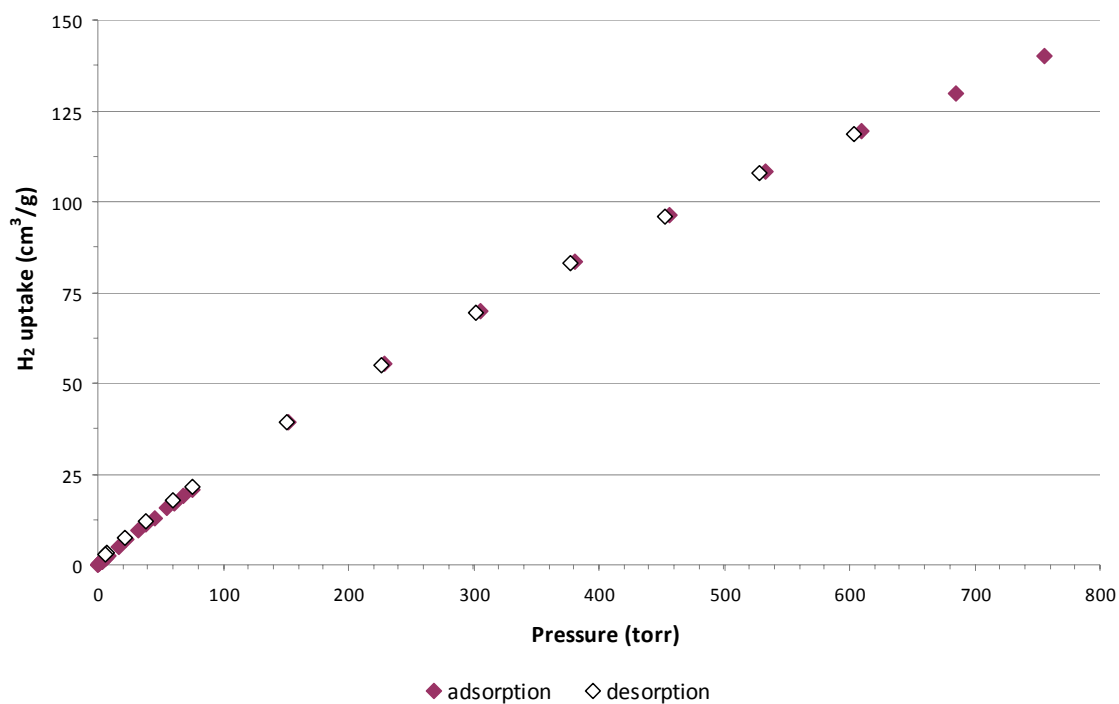


Figure S5. H₂ adsorption/desorption isotherms measured at 77 K for Be-BDC.

Section IV. High-Pressure H₂ sorption measurements on Be-BDC

High pressure volumetric measurements were performed at General Motors over the pressure range 0-70 bar using an automated Sievert's apparatus (PCT-Pro 2000 from HyEnergy LLC). The sample holder was loaded with 224 mg of Be-BDC sample under an argon atmosphere in a glove box. The sample was degassed at room temperature for 12 h. All measurements were made with ultra high purity grade (99.999%) H₂ and He. Measurements were carried out at 77 K by submerging the sample holder in a liquid nitrogen bath, the level of which was maintained constant throughout each experiment. The volume of the sample holder was determined using helium at 298 K and H₂ at 298 K and 77 K. H₂ was used to determine the dead space volume correction for a non-porous inert insert of a known geometrical volume (typically steel or aluminum); this correction accounts for the change in effective sample volume observed when cooling the sample holder from room temperature to 77 K. Also, helium was used to determine the volume occupied by a sample in the sample holder at 298 K because of its negligibly small adsorption on solid surfaces. Our volumetric analysis can be viewed as a precise application of the real gas law taking into account deviation from non-ideal behavior found at high pressures and/or low temperatures. The non-ideal gas behavior is taken into account by determining the H₂ compressibility factor, *Z*, from National Institute of Standards and Technology (NIST) data.²

Table S2. High Pressure H₂ Sorption Data for Be-BDC at 77 K.

Pressure(bar)	Excess Gravimetric H₂ Uptake (wt%)	Pressure(bar)	Excess Gravimetric H₂ Uptake (wt%)
0.757453019	0.884	65.52292026	4.280
1.83172564	1.677	61.58924835	4.416
3.028835367	2.292	57.62920111	4.507
4.292773478	2.769	53.63031745	4.614
5.577613801	3.194	49.67245527	4.698
7.162998921	3.558	45.52697344	4.771
8.764848781	3.851	41.73986731	4.845
10.66810028	4.098	37.80926771	4.927
12.57991382	4.326	33.86860331	4.977
14.50987791	4.530	29.93375888	4.972
16.44497871	4.693	26.00502901	5.013
18.37232126	4.825	22.08590187	4.978
20.21511299	4.905	18.17351207	4.807
22.40502424	4.957	14.43259725	4.481
24.58587299	4.996	10.80092207	4.106
26.74500178	5.006	8.134902871	3.770
28.90471261	4.995	6.134649227	3.353
31.05233525	4.986	4.703886545	3.014
33.17218284	4.967	3.652884246	2.629
35.28643666	4.935	2.858862107	2.255
37.39823947	4.916	2.260398382	1.924
39.51069904	4.882	1.802268781	1.624
41.46480103	4.841	1.448683631	1.358
43.84625814	4.800	1.170294293	1.124
46.18955436	4.756	0.950792973	0.923
48.51042932	4.723	0.777117093	0.749
50.81211309	4.683	0.642739378	0.598
53.11623826	4.628	0.52800971	0.460
55.4166117	4.594	0.439493314	0.349
57.71933481	4.546	0.364083095	0.246
59.45177478	4.488		
61.8153784	4.428		
64.12024083	4.366		
66.39703233	4.303		

Section V. Extended water vapor exposure to Be-BDC.

A 9 mm Nova 4200e (Quantachrome Instruments) sample cell was charged 20.9 mg Be-BDC suspended in CH_2Cl_2 . After evacuation at room temperature for 12 hrs an initial N_2 sorption isotherm was collected. The sample cell was removed and a needle was inserted to a height of approximately 3 cm above the sample. Air was then bubbled through a saturated LiCl solution to produce air with a relative humidity of approximately 10% which was passed through the needle over the sample. After 12 hours of exposure the sample was heated to 125 °C under vacuum for 16 hours. To a separate sample, air was bubbled through a saturated NaCl solution to produce air with a relative humidity of approximately 70% which was passed through the needle over the sample. After 12 hours of exposure the sample was heated to 125 °C under vacuum for 16 hours. A second N_2 sorption isotherm was collected for both samples that demonstrate loss of accessible surface area. A PXRD pattern of the resulting samples showed a dramatic loss of crystallinity

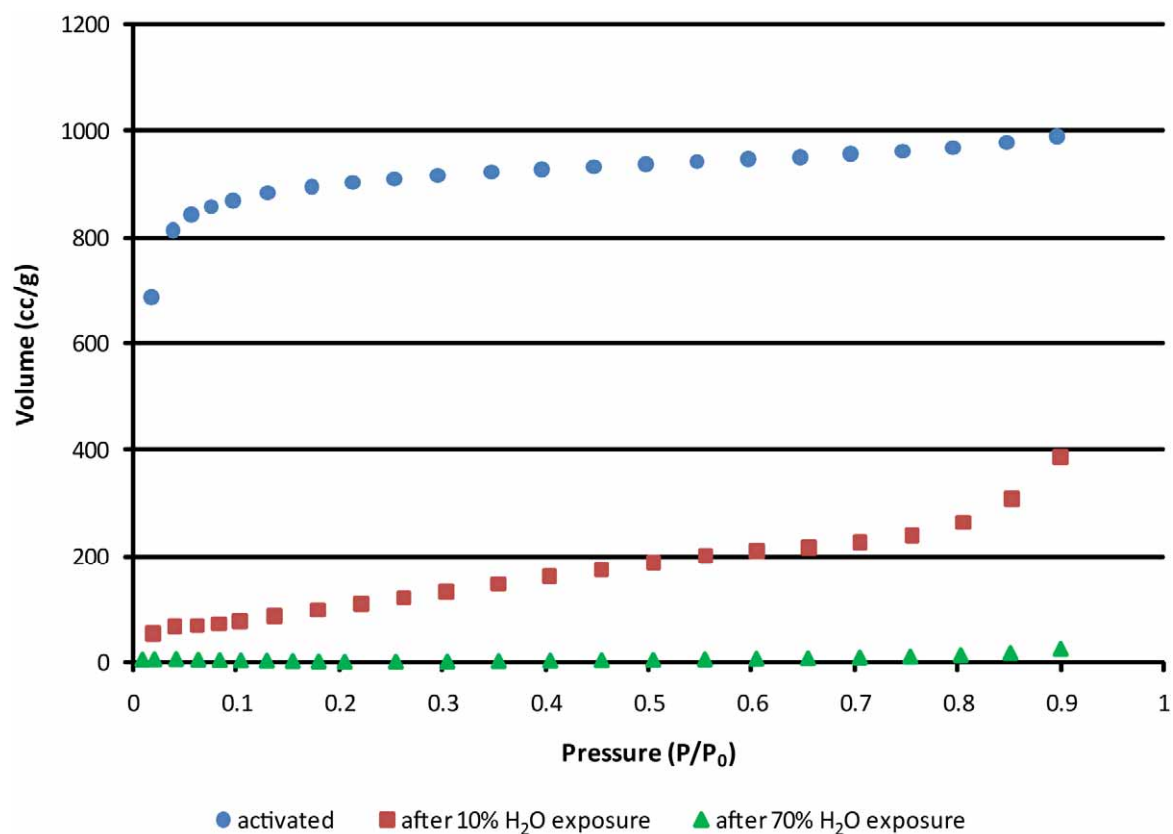


Figure S6. N₂ isotherms of Be-BDC before and after exposure to 10% and 70% humidity.

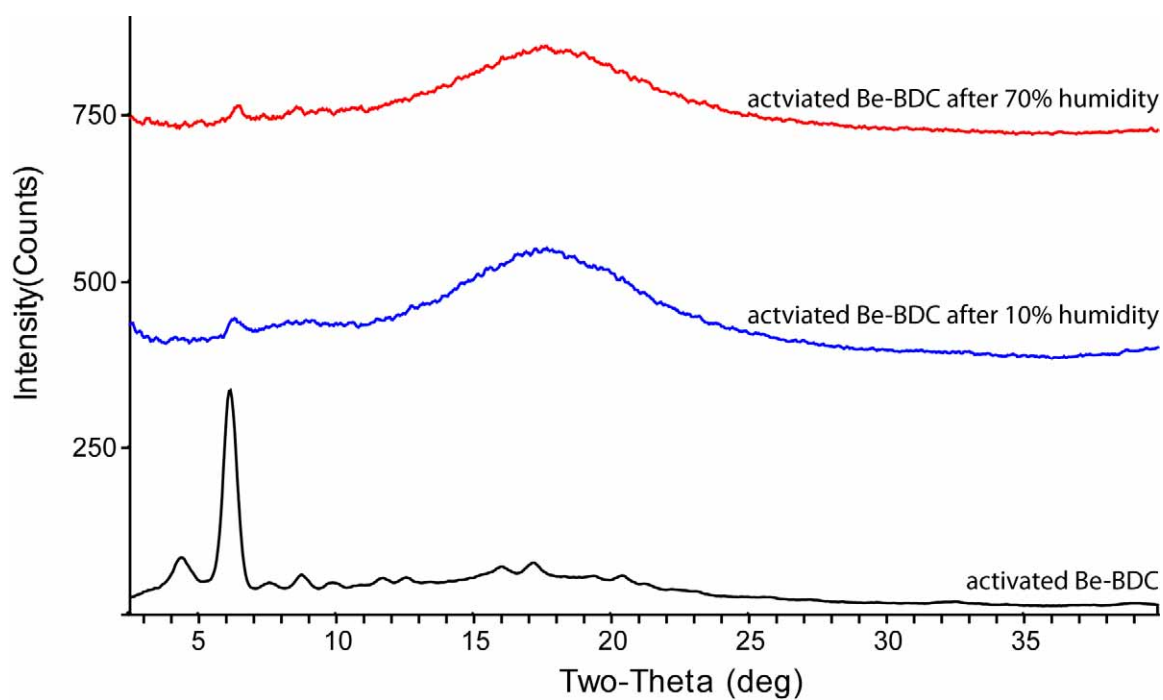


Figure S7. PXRD of Be-BDC before and after H₂O vapor exposure showing loss of crystallinity.

Section VI. Raman Spectroscopy

Raman spectra were obtained using a Renishaw inVia Raman Microscope equipped with a Leica microscope, RenCam CCD detector, 647 nm Kr ion laser, 1800 lines/mm grating, and 50 μm slit. Spectra were collected in extended scan mode in the range of 3200-100 cm^{-1} at 50% laser power and analyzed using the WiRE 3.0 software package. Calibration was performed using a silicon standard. Peaks are found at 3084, 3076, 1619, 1511, 1474, 1465, 1147, 873, and 634 cm^{-1} .

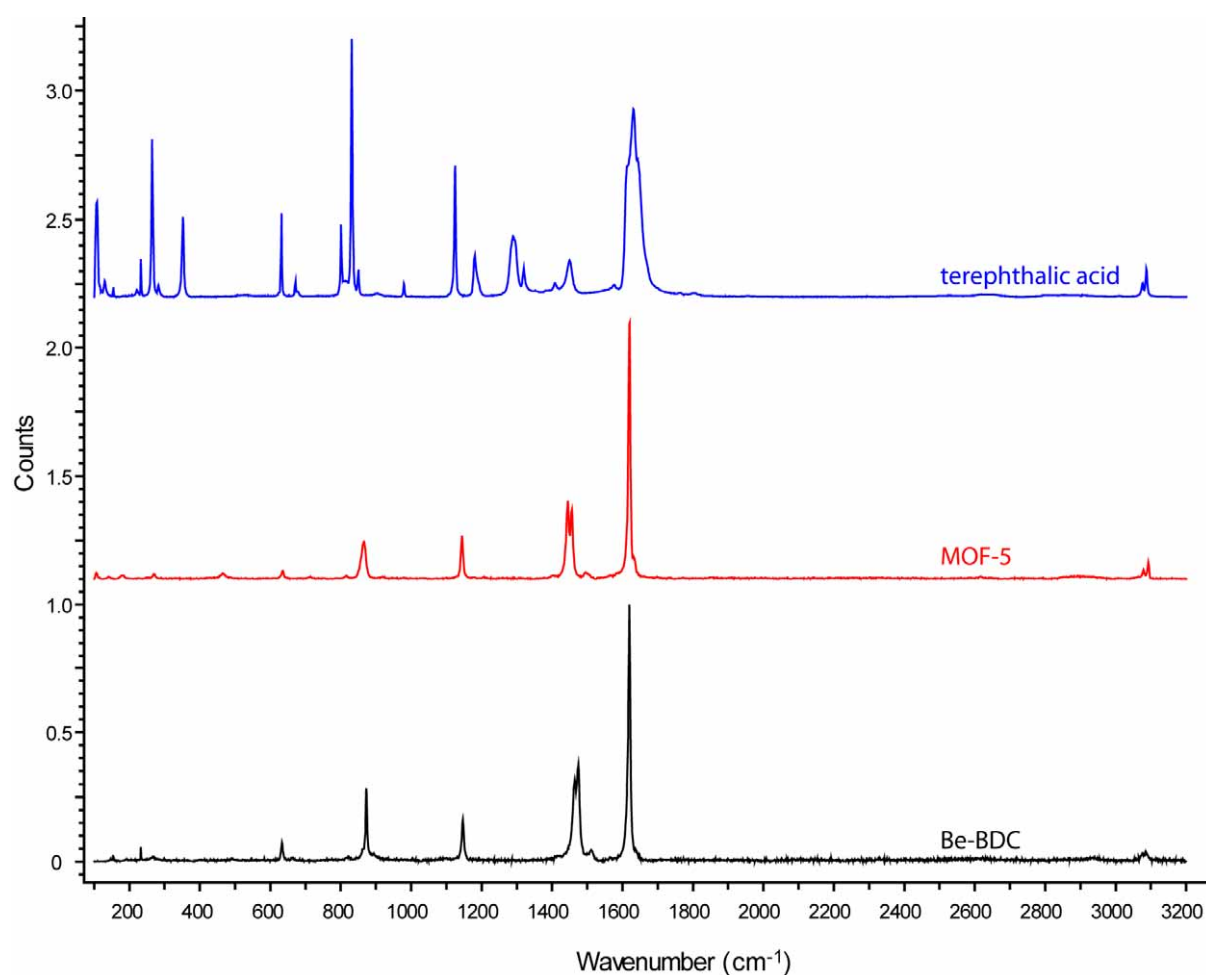


Figure S8. Raman spectra of Be-BDC, MOF-5, and terephthalic acid.

Section VII. General Procedure for SEM/EDX Experiment.

The sample (ca. 5 mg) was activated under vacuum, carbon coated and examined using a Hitachi S-3200N SEM apparatus equipped an EDAX Genesis system with a conventional Si(Li) detector with light-element capabilities (C is lightest detectible element). A typical setup consisted of a 20kV accelerating voltage, a 35 degree takeoff angle, and a working distance of 15 mm. The duration of the EDX scans on individual samples was ca. 30 s.

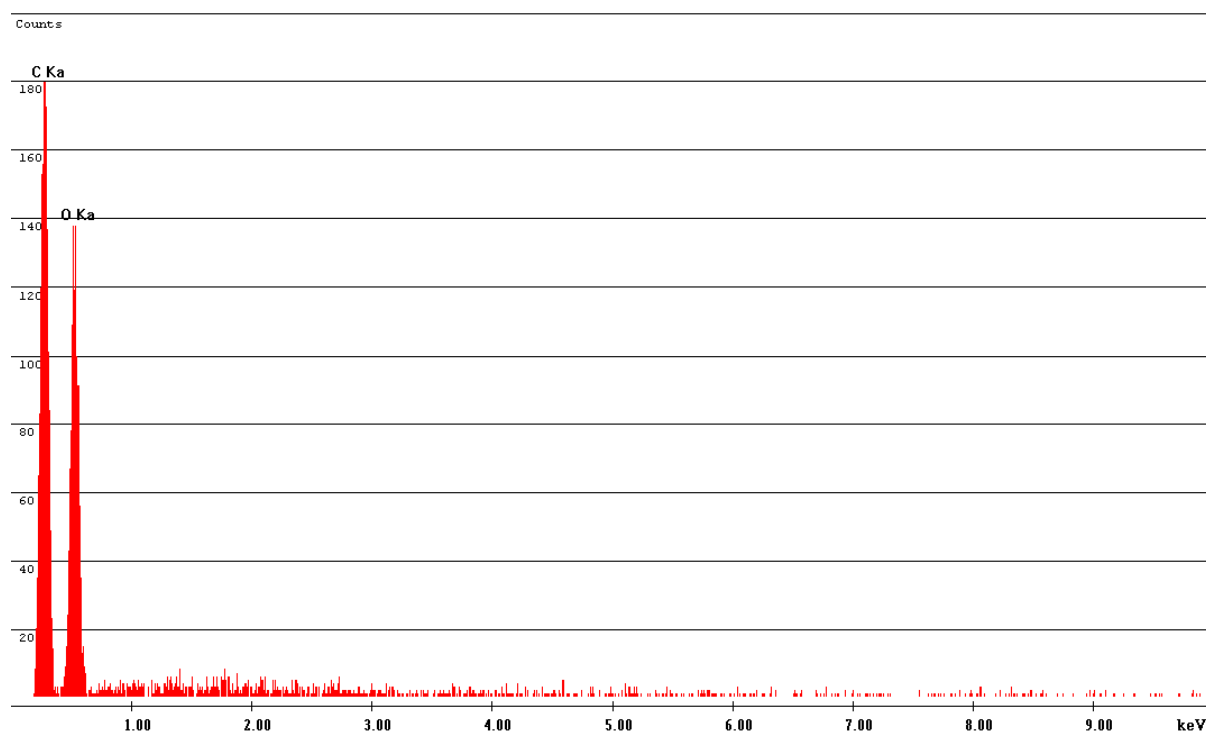


Figure S9. SEM/EDX of Be-BDC.

Section VIII. References

1. *Jade Plus 8.0*, (1995-2007) Materials Data, Inc.
2. The data of H₂ density at different pressures (from 0 - 80) at 77 K was obtained from the website of National Institute of Standards and Technology (NIST) of the USA:
<http://webbook.nist.gov/chemistry/fluid>.