Supporting Information for:

Metal-Organic Frameworks from Divalent Metals and 1,4-Benzenedicarboxylate with Bidentate Pyridine-*N*-oxide Co-ligands

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S1: Details of Crystal Structure Solutions

S1.1: $Co_3(BDC)_3(DPNO)_2$ at 100 K

After initial structure solution of the MOF, the R-factor was rather high at 13% with 2 DMF molecules and 4 waters located but still electron density unaccounted for. Therefore the SQUEEZE routine was used in PLATON to model possible solvent in the voids: this calculates a void of 1013.8 Å^3 and an electron count of 213. DMF has 40 electrons and water has 10 electrons so that crudely works out at 4 DMF molecules and 5 waters. ((4 x 40) + (5 x 10) = 210). This lowered R1 to 9 %. SIMU restraints were used to give some of the cigar shaped thermal parameters of terephthalate ligand C ellipsoids more in line with chemically similar ligands. The higher symmetry monoclinic C-centred cell was also investigated. $a = 33.001$ Å $b = 9.584$ Å $c = 18.144$ Å $\beta = 99.26$ but refinement using Squeeze gave an Rint of about 12% with many problematic thermal parameters so the refinement was completed in the triclinic cell.

In the asymmetric unit there are two fully occupied cobalts (Co3 and Co4), two half occupied cobalts on special positions (Co1 and Co2) two bipy N-oxides (A and B), two full occupied terephthalates (ligands C and D) and two terephthalates on

inversion centres (E and F). The structure has four cobalts, Co1 and Co2 sit on inversion centres at half occupancy. The cobalts come as trimers, for example, Co1 sits on the inversion centre with Co4 and a symmetry related Co4 as the other parts of the trimer. Co1 to Co4 is bridged by the carboxylates of terephthalate ligands C and D and the oxygen of the bipy N-oxide ligand A. The Co4 cobalt has these two bridging terephtahlates but also a terephthalate that binds by both oxygens of the carboxylate (this ligand (terephthalate E) lies on an inversion centre and the other half spans to a symmetry related Co4) and the nitrogen of the bipy N-oxide. A similar situation exists for Co2 (on inversion centre) and Co3 with terephthalates C and F and bipy N-oxide B and terephthalate F spanning to a symmetry related Co3.

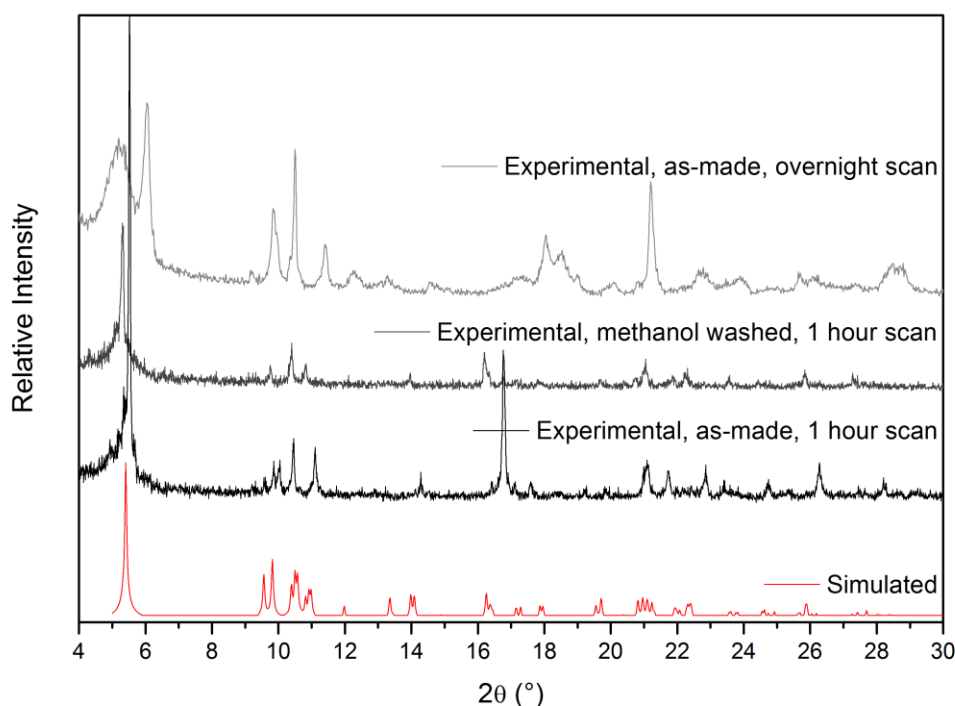### S1.2: $Co_2(BDC)_2(DPNDO)$ at 293 K

The crystal was twinned and the structure refined on HKLF5 with twin ratio 0.46:54. The asymmetric unit contains cobalts on special positions (2 fold axis and so are refined at half occupancy), two terephthalates sitting on special positions (inversion centre in the centre of the ring) and a 2,2'bipyridly di-*N*-oxides where the centre of the bipyridyl bond sits on a two- fold axis. Although there is diffuse residual electron density, with Q peaks as large as 1.5 $Å^3$, no solvent could be modelled in the pores of the structure, so it is assumed that this is highly disordered.

### S1.3: $Co_2(BDC)_2(DPNDO)[CH_3OH]_{2.5}[H_2O]_{1.5}$ at 150 K

All crystals examined were twinned to some extent; the specimens were taken from the same batch as the sample above but immersed in methanol before being studied. The twin ratio refined to 56:44. The asymmetric unit contains a cobalt on a general position (Co1) and two cobalts on inversion centres (Co2 and Co3) The oxygens of

the DPNDO bridge between the three cobalts. There are 4 molecules of terephthalate that all lie on inversion centres (so only half of each molecule in the asymmetric unit) The diffuse electron density in the cavities of the structure was modelled as MeOH and water. The occupancies were chosen so as to give the solvents reasonable thermal parameters, which were refined isotropically. No hydrogens were located for these solvents but were included in the formula so as to calculate correct density etc. This was modelled as two half occupied methanols (O35A-C35A and O36-C36), one quarter occupied methanol (O36A-C36A), one half occupied water (O35) and one quarter occupied water (O37). These were refined under various PARTs instructions so as to prevent any steric clashes between partially occupied solvent.

S2: Powder X-ray diffraction

Figure S2.1: Measured and experimental powder XRD patterns for Co$_3$(BDC)$_3$(DPNO)$_2$ at room temperature showing the instability of the structure.
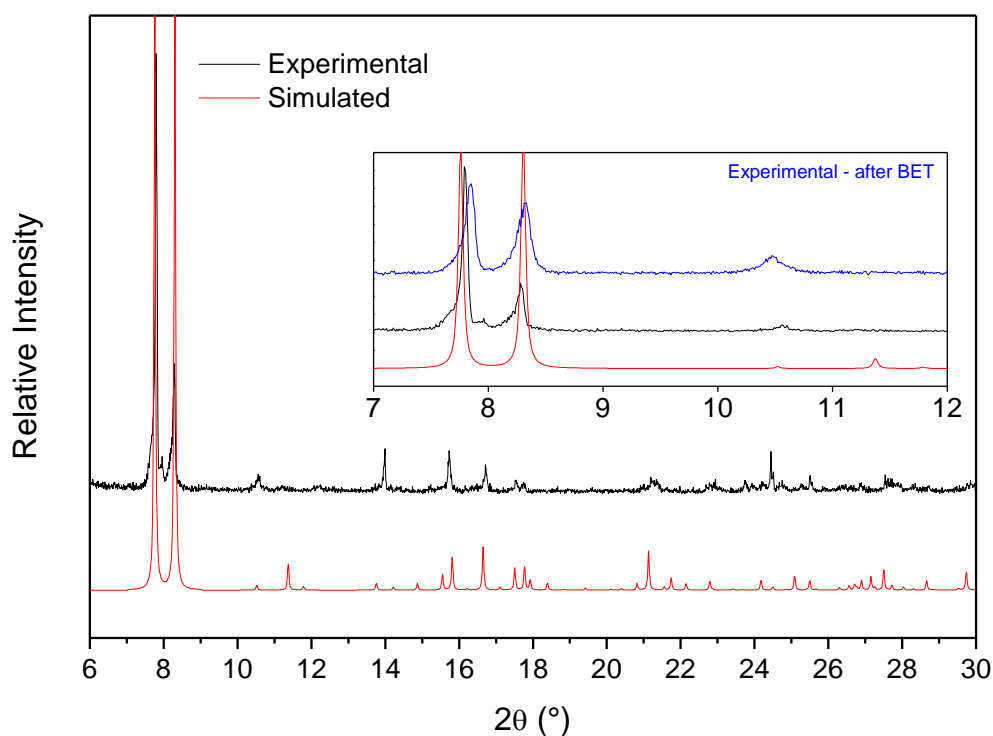
Figure S2.2: Measured powder XRD pattern for Co₂(BDC)₂(DPNDO) at room temperature with simulated pattern from room temperature single crystal structure. The inset shows the powder pattern measured from the sample after nitrogen adsorption experiments that show the framework remains intact.
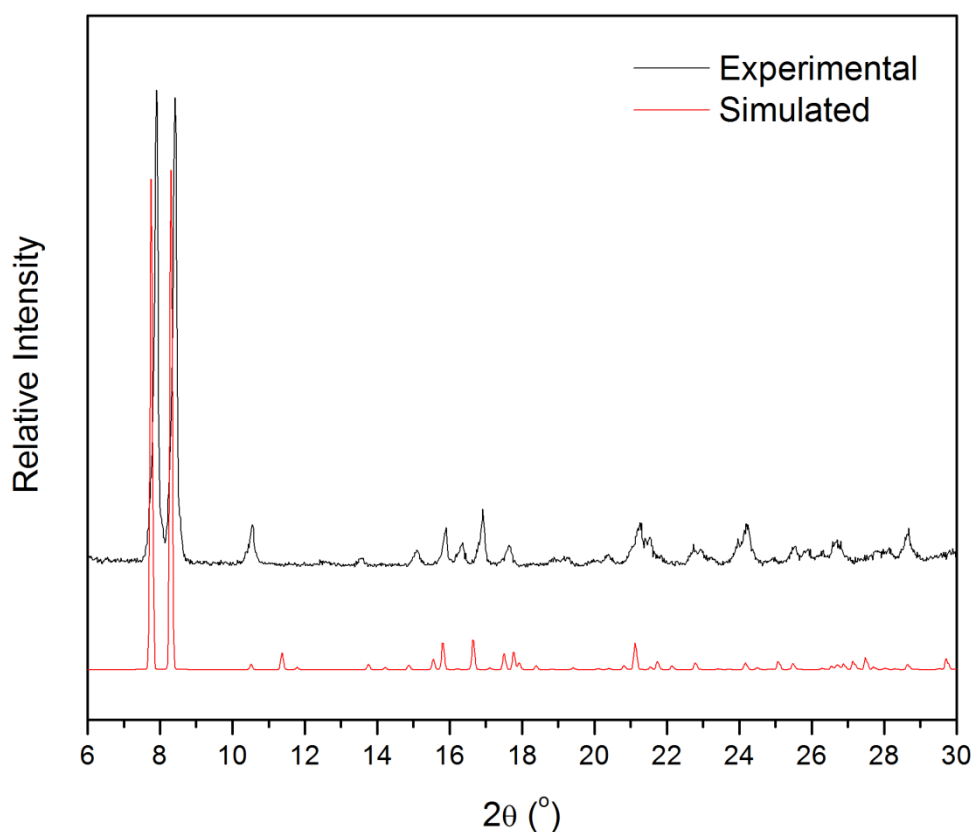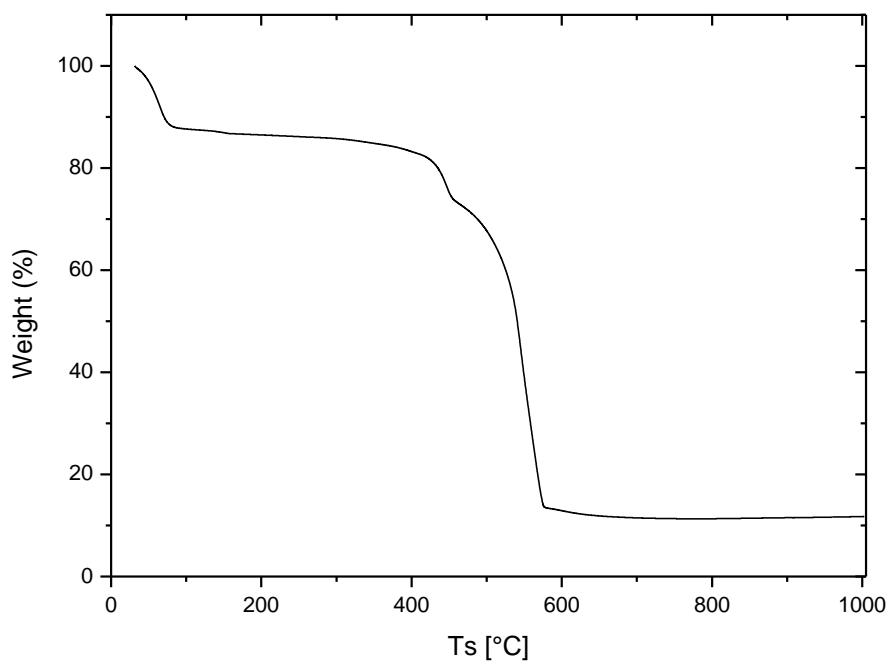

Figure S2.3: Measured powder XRD pattern for Mg₂(BDC)₂(DPNDO) at room temperature with simulated pattern from room temperature single crystal structure of Co₂(BDC)₂(DPNDO).
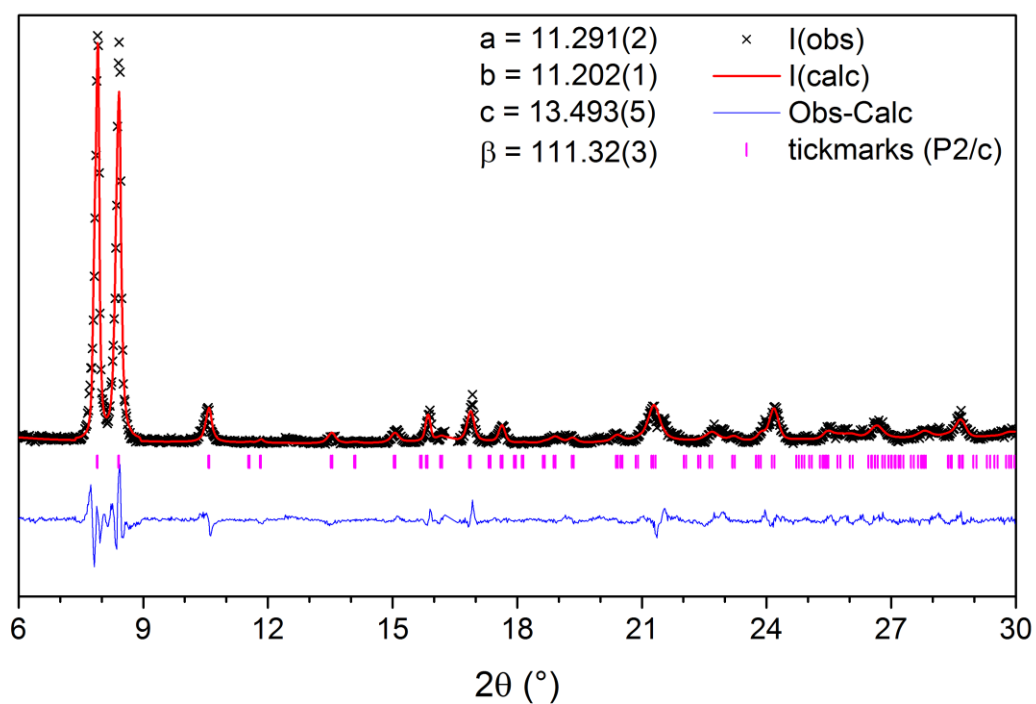
Figure S2.4: Full fit (Le Bail method) for Mg$_2$(BDC)$_2$(DPNDO) in space group *P*2/*c*. (Cu Kα1/2 radiation)

S3: Thermogravimetry and Thermodiffraction

Figure S3.1: Thermogravimetric analysis of Mg$_2$(BDC)$_2$(DPNDO) after methanol washing (static air, heated at 10 °C min^{-1})

Figure S3.2: Thermodiffraction of Mg$_2$(BDC)$_2$(DPNDO) after methanol washing.

S4: BET analysis

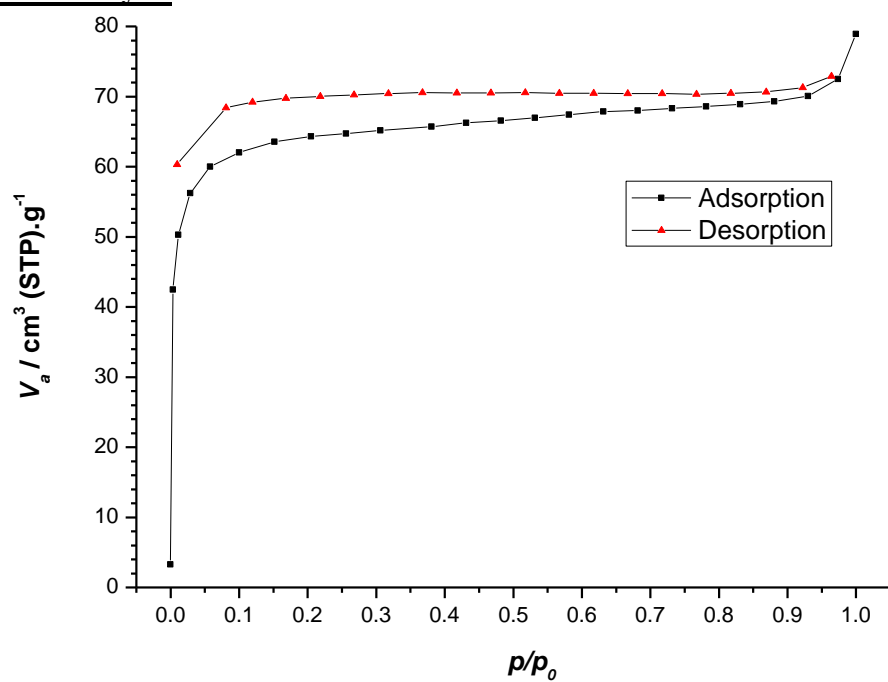**Figure S4.1: Nitrogen Adsorption/Desorption isotherms of Co$_2$(BDC)$_2$(DPNDO) at 77 K**

BET = 4.35*(1/B) = 252 m^2/g

Parameter	Value	Error
A	2.73886E-5	5.13696E-6
B	0.01725	1.56829E-4

R	SD	N	P
0.99992	6.53301E-6	4	<0.0001
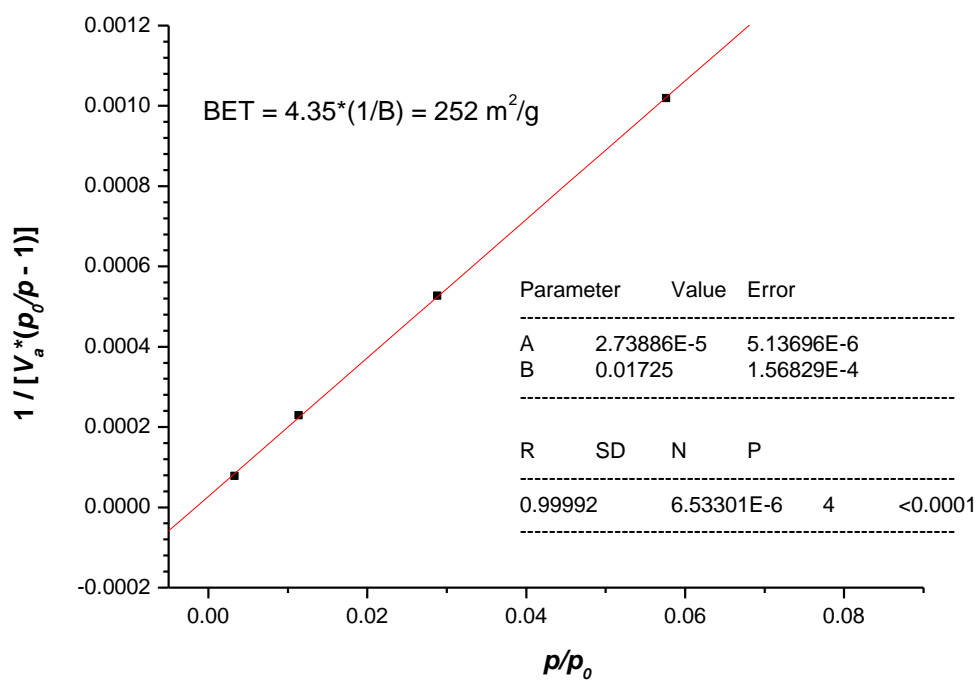
Figure S4.2: BET analysis of Co$_2$(BDC)$_2$(DPNDO)
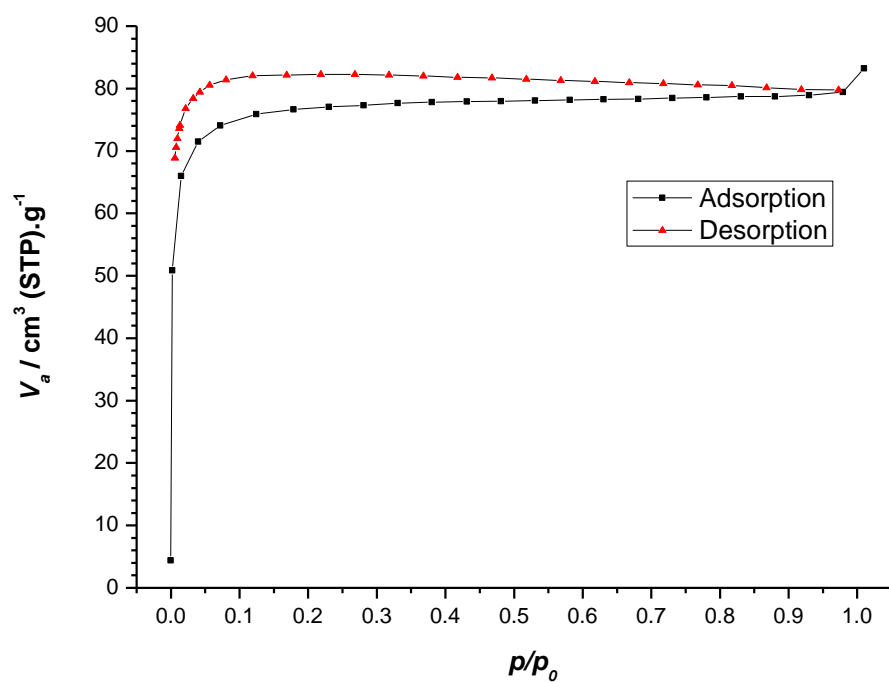
Figure S4.3: Nitrogen Adsorption/Desorption isotherms of Mg$_2$(BDC)$_2$(DPNDO) at 77K

$$BET = 4.35*(1/B) = 303 \text{ m}^2/\text{g}$$

Parameter	Value	Error
A	1.14622E-5	3.13815E-6
B	0.01436	7.53352E-5

R	SD	N	P
0.99997	4.00893E-6	4	<0.0001
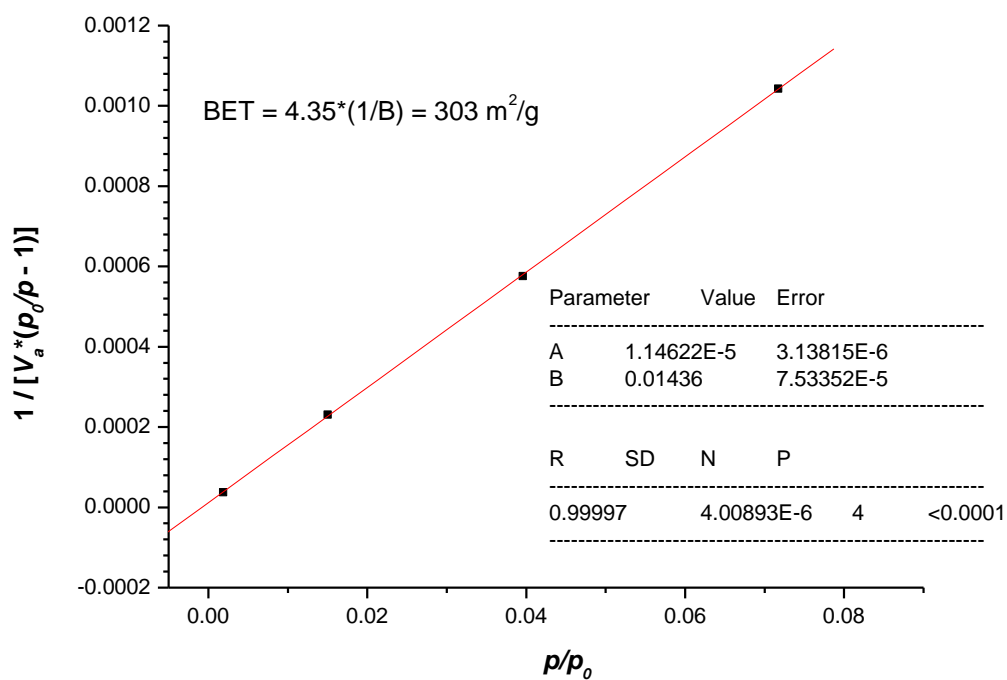
Figure S4.4: BET analysis of Mg$_2$(BDC)$_2$(DPNDO)

S5: Simulations

Table S5.1 – Computational characterisation of Co(BDC)(DPNO) and Co(BDC)(DPNDO)

Structure	Acc. SA (m^2/g)	Sim. BET SA (m^2/g)[†]	He pore volume @ 298 K (cm^3/g)	Pore Diameter(s) (Å)
Co$_3$(BDC)$_3$(DPNO)$_2$	525	729	0.28	6.0, 6.7
Co$_2$(BDC)$_2$(DPNDO)	113	458	0.21	3.9, 4.9

† - Surface area determined from application of the BET equation (and appropriate consistency criteria) to N$_2$ isotherm at 77 K obtained from GCMC simulations.
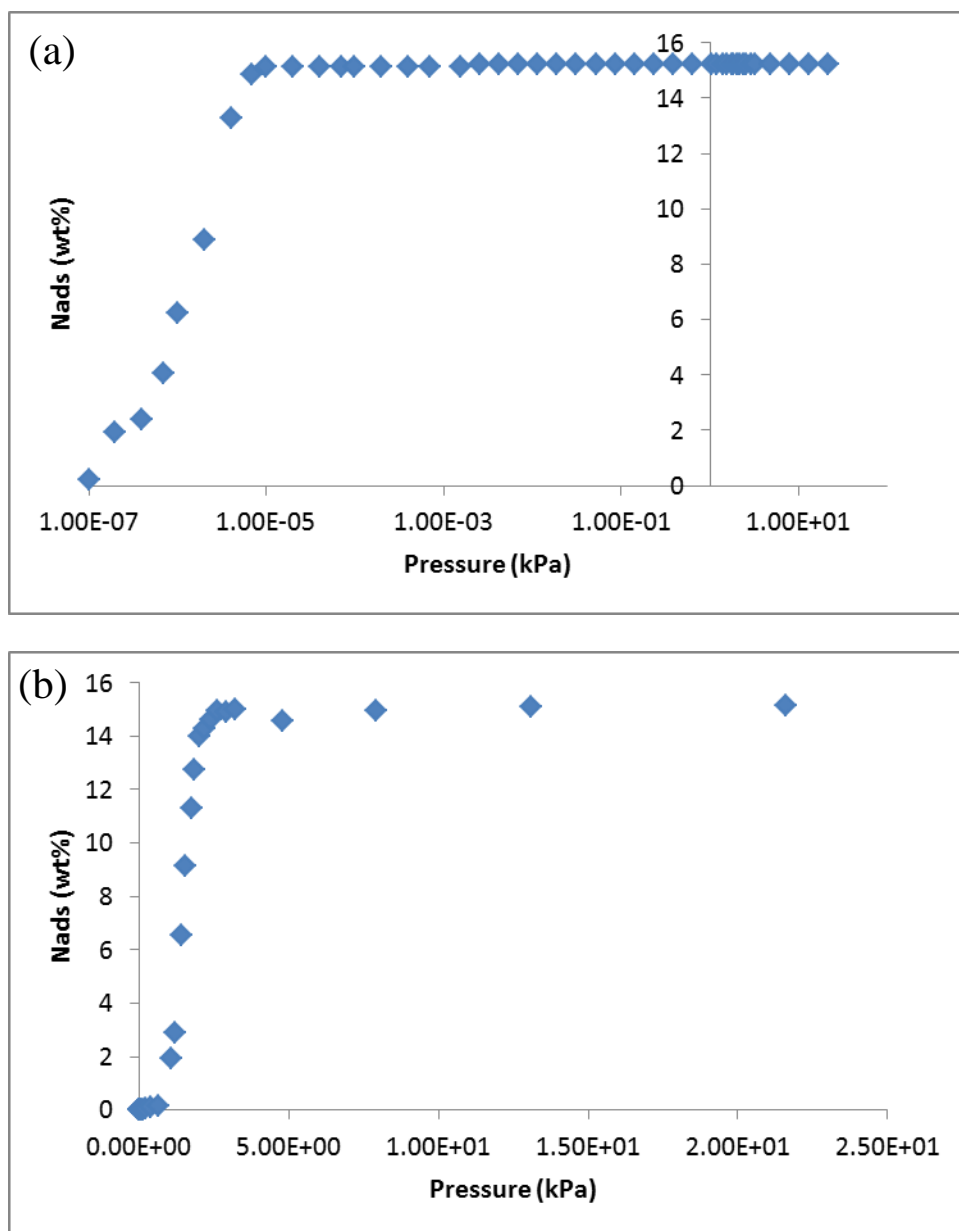
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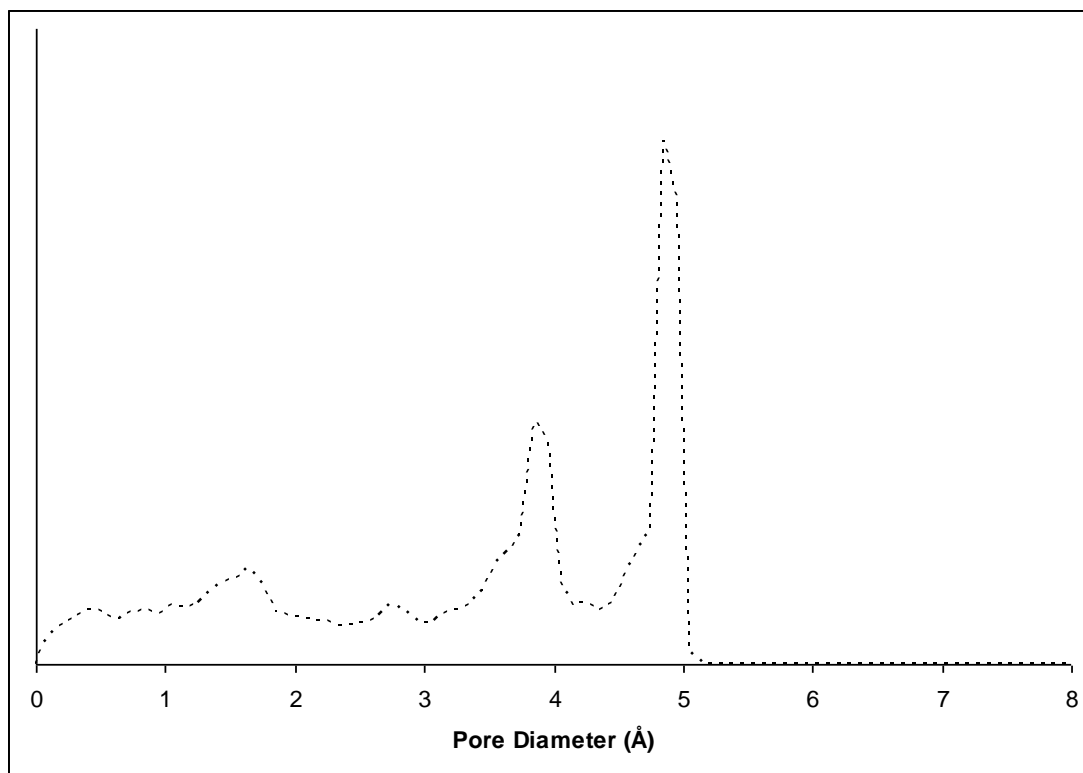
Figure S5.1: Simulated pore size distribution of Co$_2$(BDC)$_2$(DPNDO)
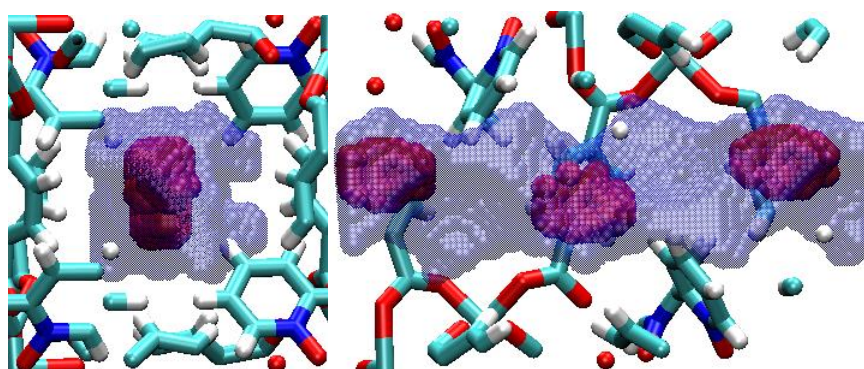
Figure S5.2: Regions of the pore volume of Co$_2$(BDC)$_2$(DPNDO) corresponding to the channel windows (red) and voids near the DPNDO linkers (blue). The channel cross-section is shown on the left (corresponding to Figure 4), while the view running along the channel is on the right (corresponding to Figure 3(b)).

Figure S5.3: Simulated methanol adsorption isotherms for Co$_2$(BDC)$_2$(DPNDO) at (a) 150 K and (b) 303 K.