Electronic Supplementary Material (ESI) for CrystEngComm.

Structural chemistry and selective CO_2 uptake of a piperazine-derived porous coordination polymer

Chris S. Hawes, Keith F. White, Brendan F. Abrahams, Gregory P. Knowles, Alan L. Chaffee, Stuart R. Batten and David R. Turner

Supporting Information

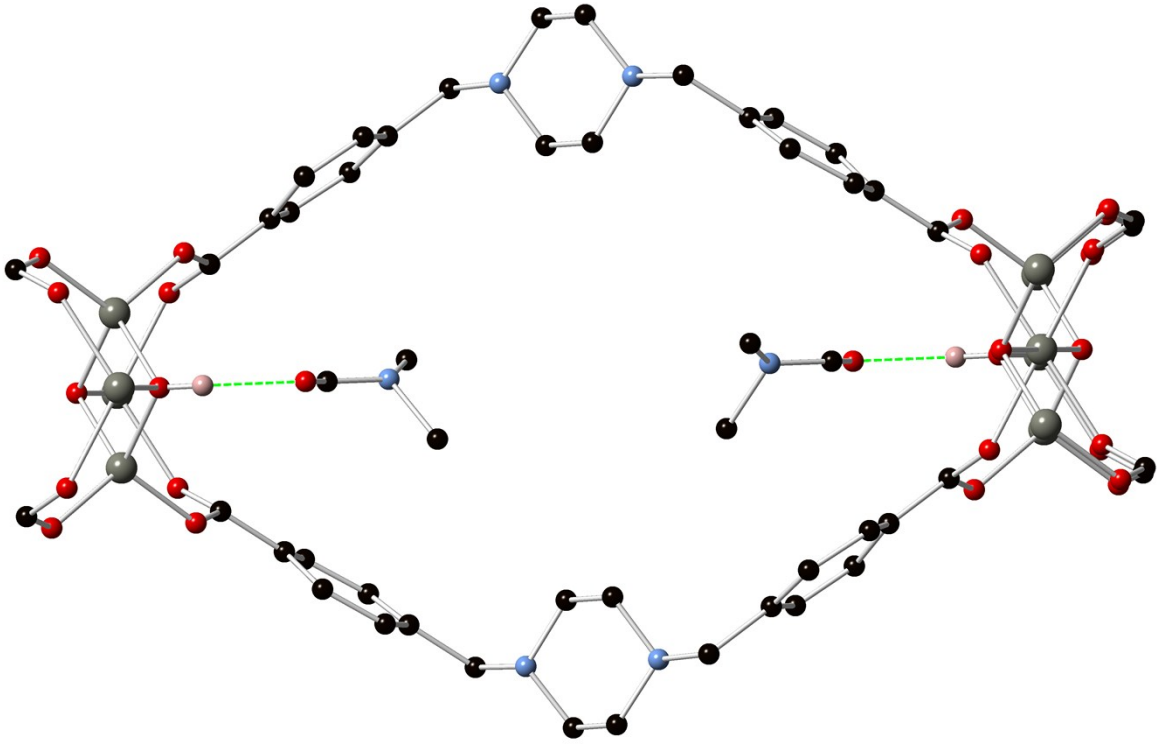

Figure S1 Hydrogen bonding between DMF guest molecules and hydroxido ligands within the structure of **1**. Hydrogen atoms not involved in hydrogen bonding, and disorder omitted for clarity.

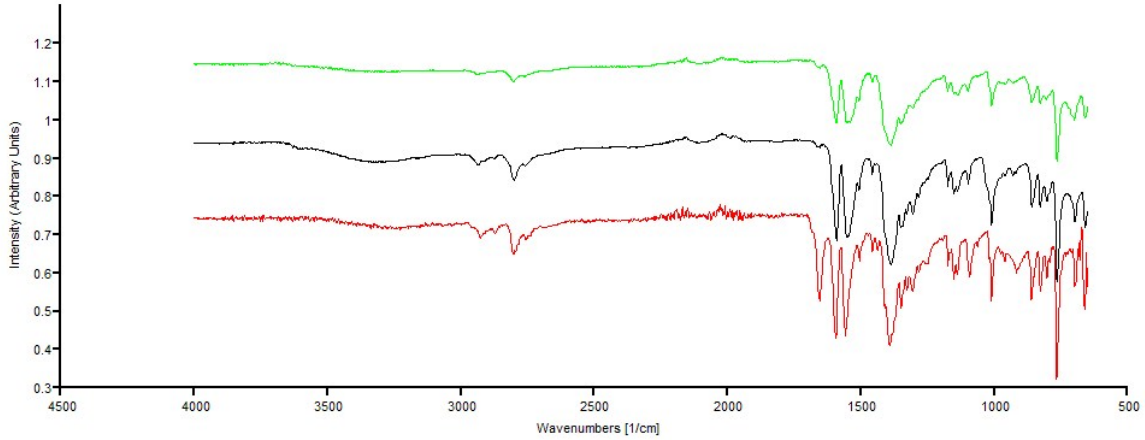

Figure S2 Overlaid infrared spectra of complex **1**, freshly isolated (red), after soaking in methanol for 24 hours (black), and following vacuum activation and gas sorption experiments (green). Figure compiled with Spekwin32.[1]

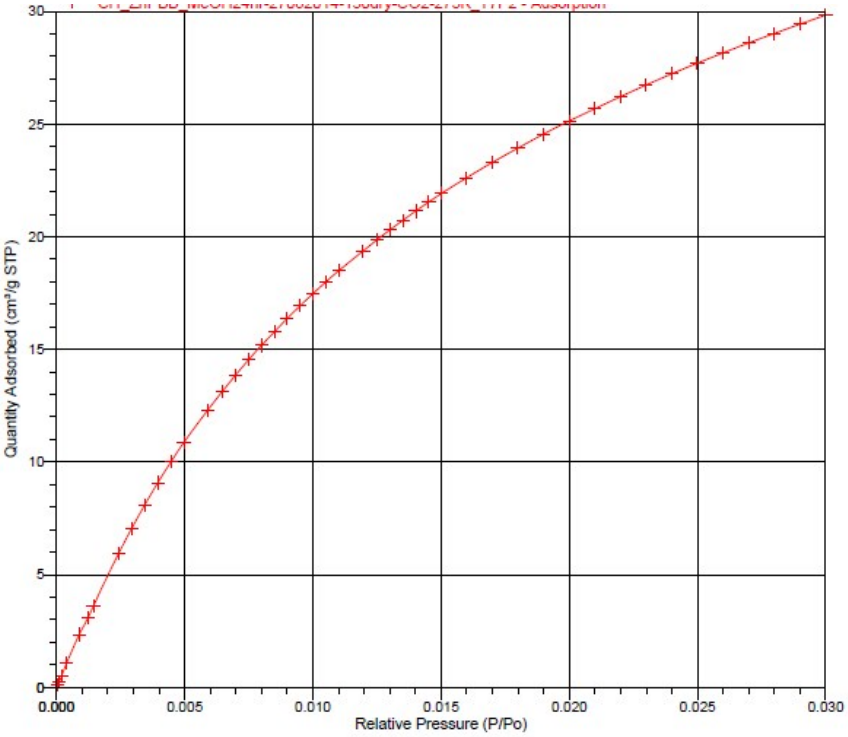

Figure S3 CO_2 sorption isotherm in the pressure range 0 – 1 atm, recorded at 273K.

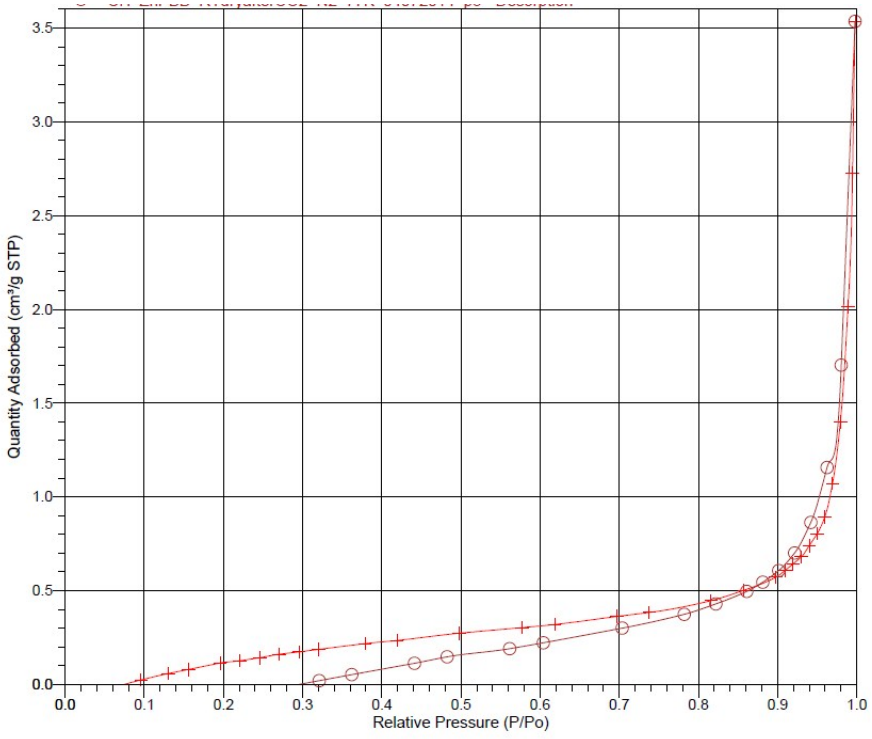

Figure S4 N_2 sorption isotherm in the pressure range 0 – 1atm, recorded at 77K. Crosses represent adsorption path, circles represent desorption path. Apparent negative values of adsorption at low pressures are most likely due to small uncertainties in the free space measurement which only become significant at very low uptakes.

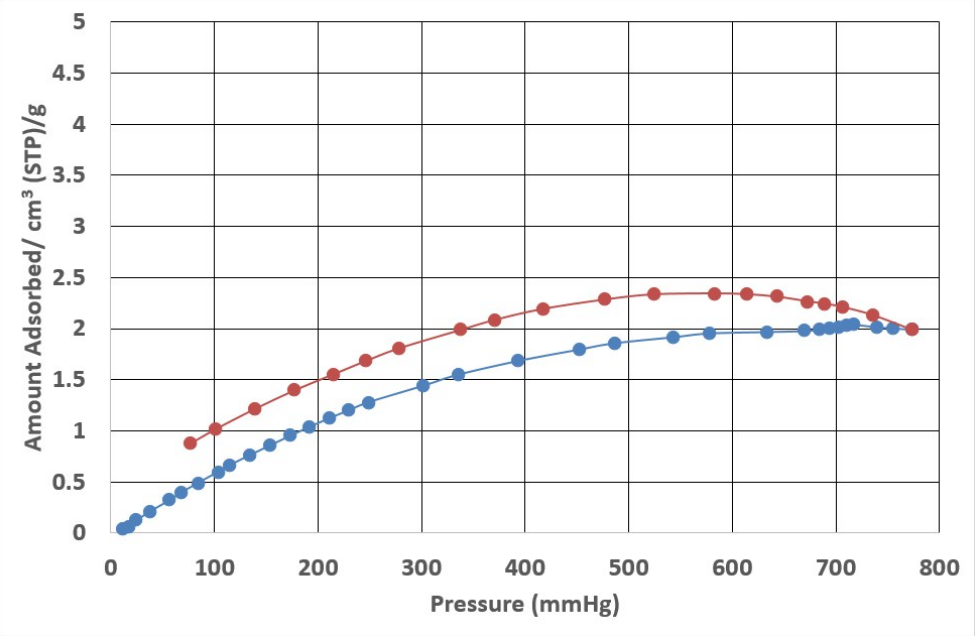

Figure S5 N_2 adsorption isotherm measured at 273K in the pressure range 0 – 1atm. Blue trace represents adsorption path, red trace represents desorption path.

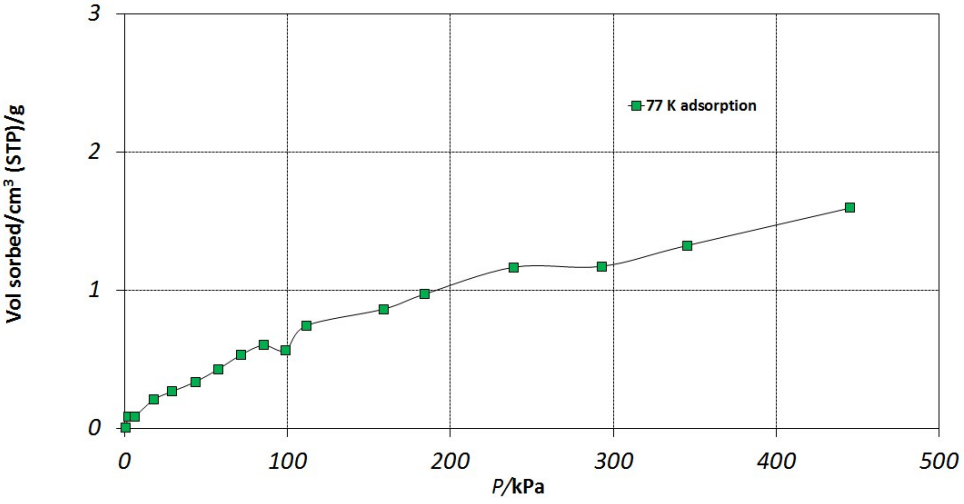

Figure S6 H_2 sorption isotherm in the pressure range 0 – 4.5 atm, recorded at 77K.

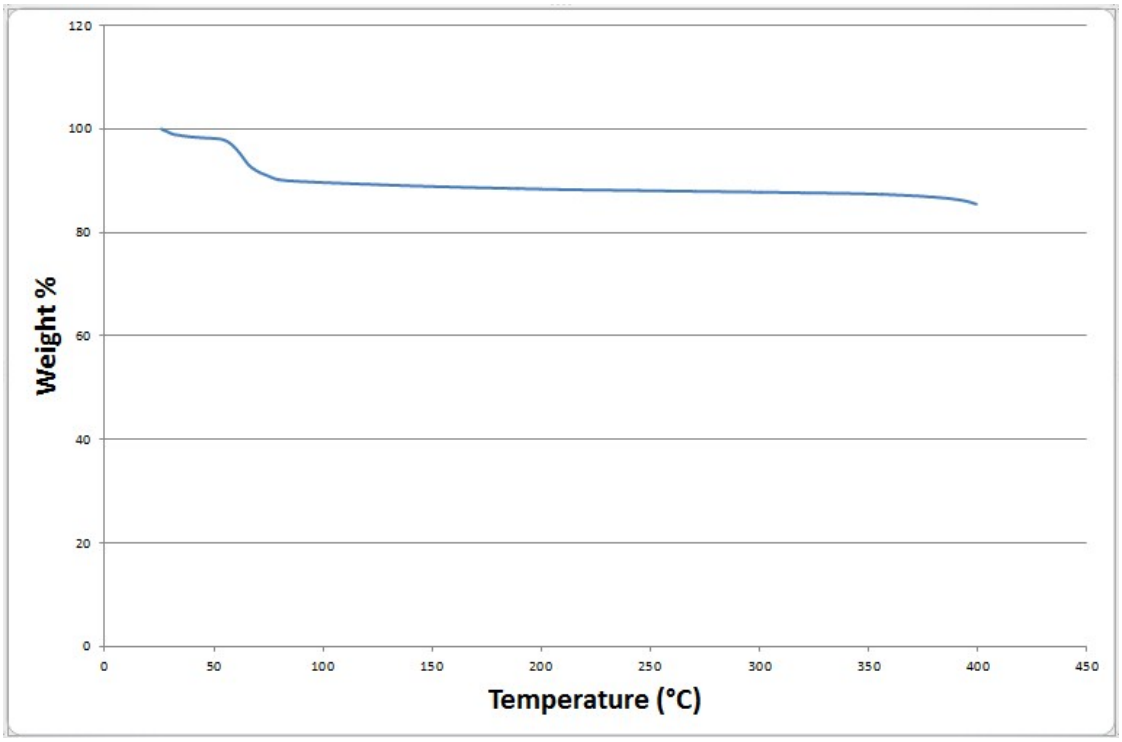

Figure S7 Thermogravimetric analysis plot for $\mathbf{K_2L1{\bullet}2H_2O}$

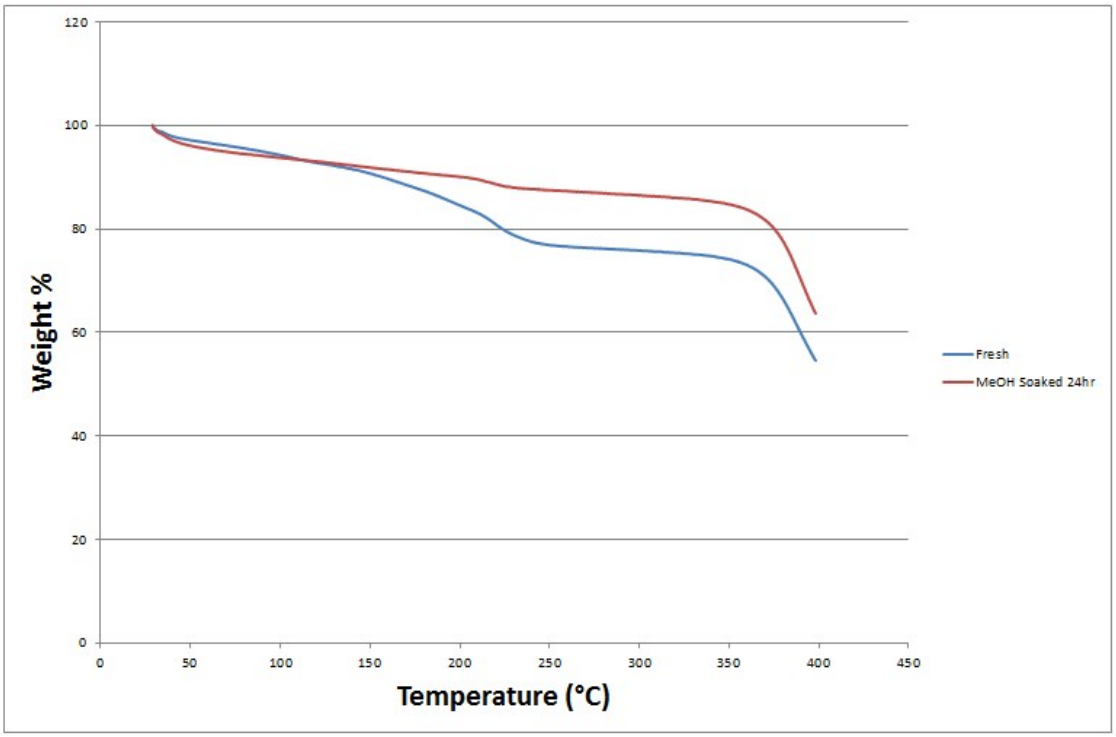

Figure S8 Thermogravimetric analysis plot for compound **1**, freshly isolated from DMF solution (Blue) and following 24 hours of soaking in methanol (red)

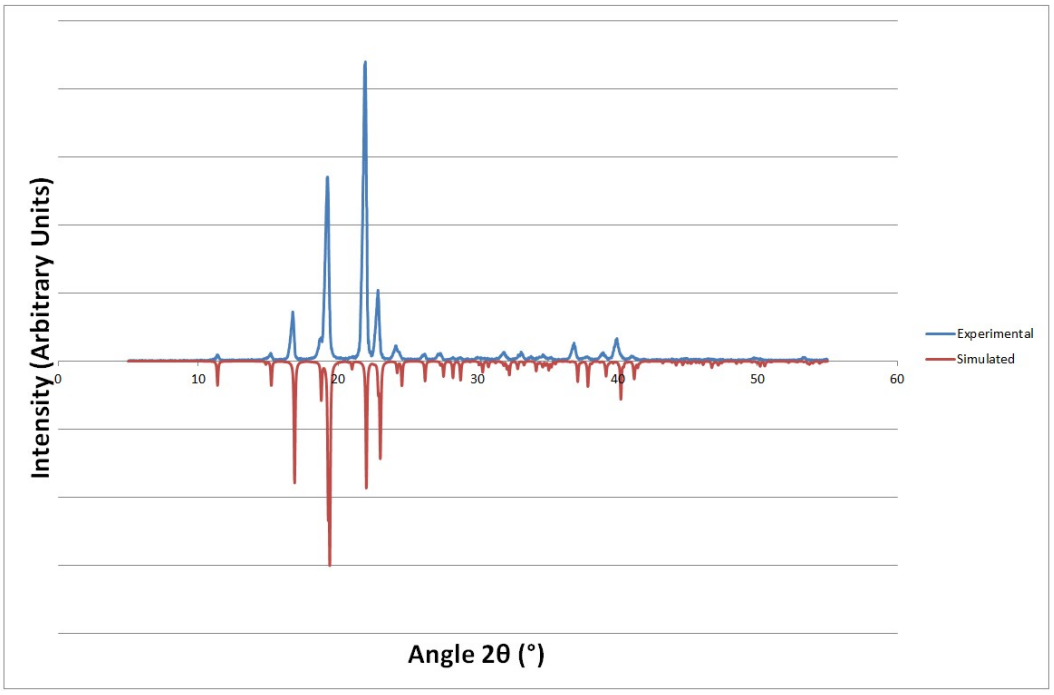

Figure S9 X-ray powder diffraction plot for ligand **H_2L1** (blue) compared with pattern simulated from the single crystal data (red).

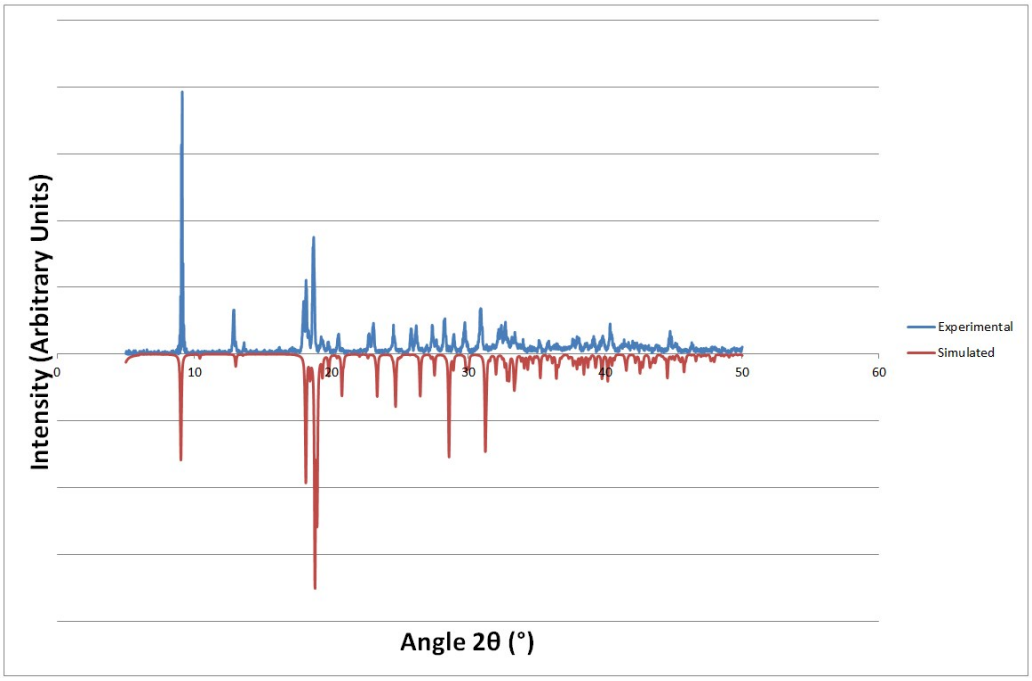

Figure S10 X-ray powder diffraction plot for ligand **K_2L1•2H_2O** (blue) compared with pattern simulated from the single crystal data (red).

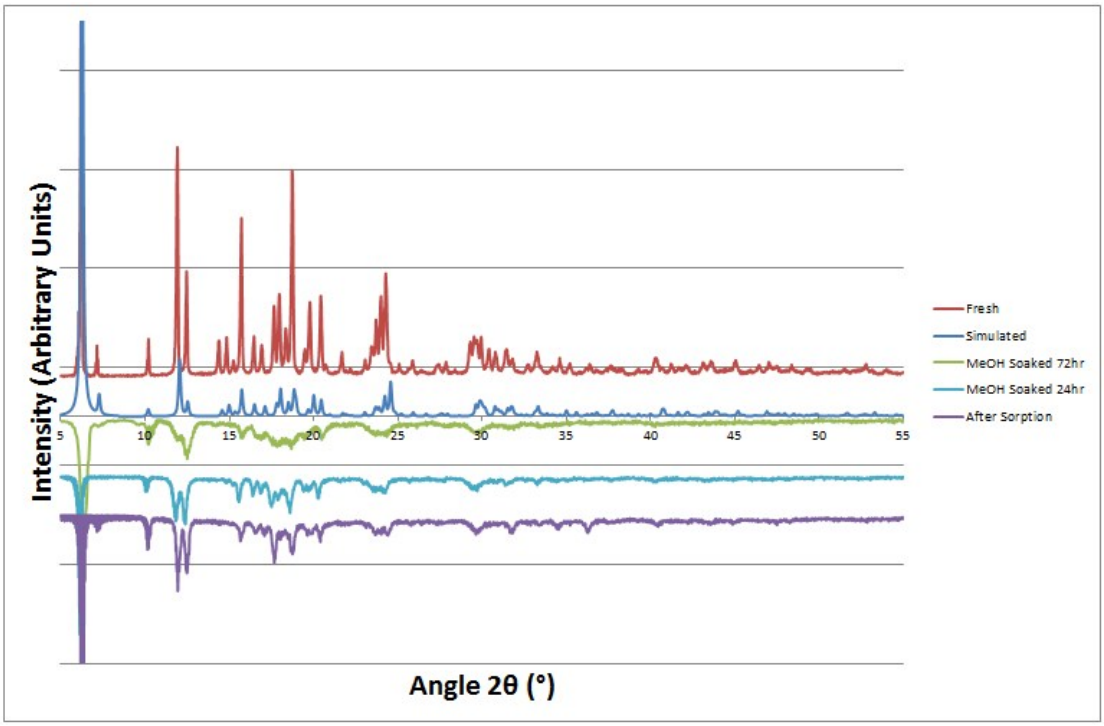

Figure S11 X-ray powder diffraction plot for ligand **1** showing pattern simulated from single crystal data (blue), pattern from a freshly isolated sample (red), and following soaking in methanol for 72 hours and 24 hours, (green and cyan, respectively), showing the extent of peak broadening on extended exposure to methanol. Shown in purple is the diffraction pattern obtained on a sample following solvent exchange, evacuation and gas sorption analysis.

Enthalpy of Sorption Calculation

The isosteric heat of CO_2 sorption was calculated using a least-squares fitting of a virial-type thermal adsorption equation that modelled ln(P) as a function of the amount of surface excess of gas sorbed over the measurement temperatures 258, 273 and 298 K.[2] Optimised virial coefficients and R^2 values are given in the table below.

Table S1: Optimised virial coefficients and R^2 value for the least squares fitting of the modelled ln(P) as a function of the amount of surface excess of gas sorbed over the measurement temperatures.

Gas	CO_2
Temps (K)	258, 273, 298
a0	-3304.57
a1	6.122947
a2	132.0977
a3	-62.6307
a4	32.81609
a5	-5.73031
b	15.42647
R^2	0.99661295

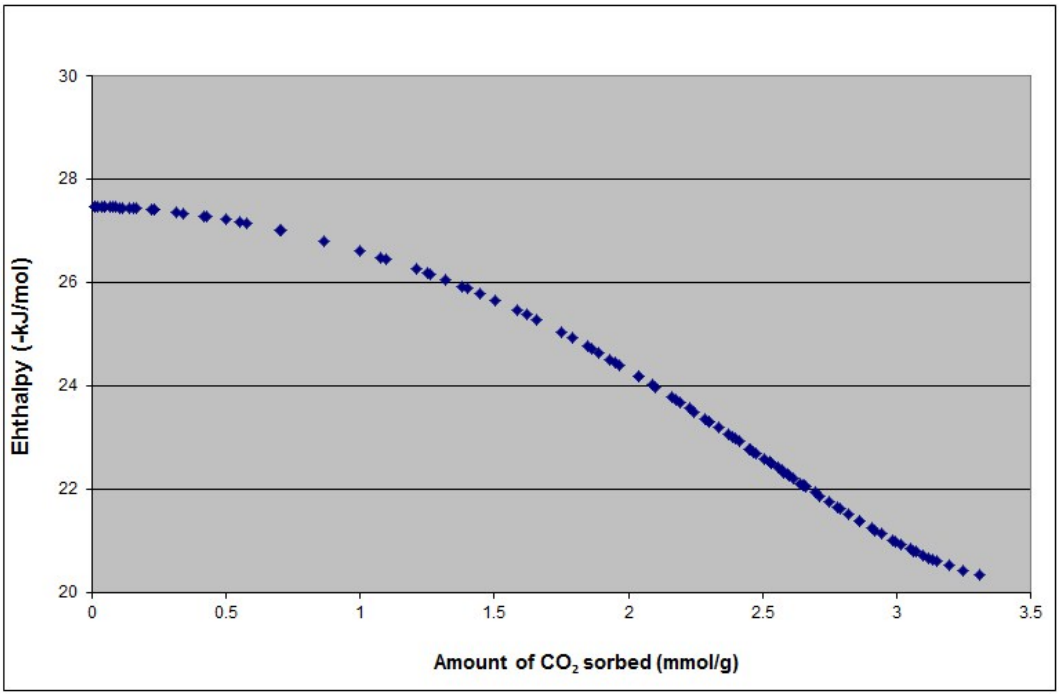

Figure S12 CO_2 adsorption enthalpy plotted against amount of CO_2 adsorbed for compound **1**

Crystallographic Parameters

Table S2: Hydrogen bonding parameters for compounds **H_2L1**, **$K_2L1 \cdot H_2O$** and complex **1**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
H_2L1						
O1	H1	N11[1]	0.914(16)	1.668(17)	2.579(2)	173(2)
$K_2L1 \cdot H_2O$						
O15	H15A	O4[2]	0.851(17)	1.96(2)	2.755(3)	155(3)
O15	H15B	O4[3]	0.863(17)	1.940(19)	2.764(3)	159(3)
1						
O3	H3	O17[4]	0.83(2)	2.03(5)	2.781(6)	149(8)

[1]-1+x,+y,-1+z; [2]1-x,1-y,1-z; [3]1-x,1/2+y,3/2-z; [4]1-x,+y,1-z

References

[1] F. Menges, *SpekWin32 – Optical Spectroscopy Software,* **Version 1.71.6.1**, 2013

[2] L.Czepirski and J. Jagiello, *Chem. Eng. Sci*. 1989, **44**, 797-801