Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

p-Xylylenediamine derived ligands as flexible connectors in the design of porous coordination polymers

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References

S1. Special Crystallographic Refinement Information

(H_6*P_4pxy*)Cl_2

All carboxylic acid and ammonium hydrogen atoms were located from the Fourier difference map and were refined to standard bond lengths using SHELX DFIX commands. Five reflections with large error/esd values were omitted, all of which were of low angle and likely obstructed by the beam stop.

[Cu_4(***M_4pxy***)$_2$(DMF)$_2$(OH_2)] (**1**)

The crystal was weakly diffracting, giving low intensity data and a large R_{int} value.

The ***M_4pxy*** ligand is disordered over two positions. A series of SADI, SIMU and ISOR restraints were used to help model the disorder. The disorder was only able to be sensibly modelled for half of the M_4pxy ligand present in the asymmetric unit.

The crystallographic inversion centre lies at the centre of the cage complex, with the residual electron density within the cavity modelled as a disordered aqua ligand, split equally across both positions. There is insufficient volume within the cavity for any other sensible ligands to be modelled across these positions. The hydrogen atoms on the O10 aqua ligand were placed in calculated positions and refined with AFIX restraints.

Poly-[Cu_2(***M_4pxy***)(OH_2)$_2$] (**2**)

Crystals did not diffract past 0.9 Å and this resolution was used as a cut-off value during refinement. The crystals also suffered from radiation damage from use of the synchrotron source. The data has slightly low completeness and a large R_{int} (and subsequently R_1) value as a result of this poor diffraction and radiation damage.

Two SHELX DFIX commands and one DANG command were used in the refinement of the hydrogen atoms on the aqua ligand (H5A and H5B).

There were significant regions of disordered electron density detected in the residual Fourier difference map after the refinement of all framework atoms. None of these lattice solvent molecules could be reasonably modelled, and the remaining electron density had its contribution to the diffraction data accounted for with the SQUEEZE routine within PLATON.[1] Analysis of the voids from SQUEEZE results in a total electron count of 289 e^- within the voids per unit cell, with a void volume of 1504 $Å^3$. An estimation of the nature of the solvent was unable to be determined as a pure phase of ***2*** was not isolated, and thus microanalysis and thermogravimetric analysis data was not obtained.

Poly-[Cu_2(***P*$_4$*pxy***)(DMF)(OH_2)]·2DMF·3H_2O (***3*·2DMF·3H_2O**)

The hydrogen atoms on the aqua ligand (O10) were located from the Fourier difference map and were refined using SHELX DFIX commands. A restraint was also used to model this ligand in a chemically appropriate orientation.

ISOR commands were used on the carbon and nitrogen atoms of the DMF ligand in order to model the ellipsoids more sensibly. There are some weak residual electron density peaks in the Fourier map nearby indicating possible disorder however these small peaks could not be modelled satisfactorily, and the large displacement parameters accurately model the situation.

There were significant regions of disordered electron density detected in the residual Fourier difference map after the refinement of all framework atoms. Only one lattice DMF molecule could be reasonably modelled, and the remaining electron density had its contribution to the diffraction data accounted for with the SQUEEZE routine within PLATON.[1] Analysis of the voids from SQUEEZE results in a total electron count of 835 e^- within the voids per unit cell, with a void volume of 3786 $Å^3$. These values equate to 104 e^- in 473 $Å^3$ per asymmetric unit (containing one formula unit). This electron density is accounted for as one DMF and three waters per ASU (8 DMF and 24 H_2O molecules per cell, total electron count of 560 e^-, 1152 $Å^3$ using 18 $Å^3$ per non-H atom).

The total amount of solvent (ligands, refined DMF and SQUEEZED) also reasonably matches the 17 % mass loss observed in TGA up to 215 °C (Fig. S9), with a calculated mass of 19 % (3 DMF and 4 H_2O molecules per [Cu_2(***P*$_4$*pxy***)]), in addition to matching the elemental percentages found with microanalysis (see main text).

Poly-[Mn_2(***P*$_4$*pxy***)($DMA)_2$] (**4**)

ISOR commands were used on the carbon and nitrogen atoms of the DMA ligand in order to model the ellipsoids more reasonably. There are some residual electron density peaks on the Fourier map nearby indicating potential disorder of this ligand. Attempts to model were not satisfactory, thus the slightly large displacement parameters are a good model of this ligand.

Poly-[Co_4(***P*$_4$*pxy***)$_2$($DMF)_2$(μ-$OH_2)_2$($OH_2)_2$]·6DMF·4H_2O (***5*·6DMF·4H_2O**)

The hydrogen atoms of the aqua ligands were located from the Fourier difference map and refined using SHELX DFIX restraints. DFIX and DANG restraints were also utilised on the aqua ligands to ensure chemically sensible orientations with respect to neighbouring groups.

The largest unassigned electron density peak on the Fourier map is located in the centre of the cobalt cluster and lies on a special position, and is likely an adsorption artefact from the data collection.

There were significant regions of disordered electron density detected in the residual Fourier difference map after the refinement of all framework atoms. Only one lattice DMF molecule could be reasonably modelled, and the remaining electron density had its contribution to the diffraction data accounted for with the SQUEEZE routine within PLATON.[1] Analysis of the voids from SQUEEZE results in a total electron count of 276 e^- within the voids per unit cell, with a void volume of 880 $Å^3$. These values equate to 138 e^- in 441 $Å^3$ per asymmetric unit (containing one formula unit). This electron density is accounted for as 5.5 DMF (as one is modelled per asymmetric unit) and four waters per ASU

(11 DMF and 8 H_2O molecules per cell, total electron count of 440 e^-, 1134 $Å^3$ using 18 $Å^3$ per non-H atom).

The total amount of solvent (ligands, refined DMF and SQUEEZED) also reasonably matches the 22 % mass loss observed in TGA up to 210 °C (Fig. S11), with a calculated mass of 23 % (6 DMF and 6 H_2O molecules per $[Co_4(\boldsymbol{P_4pxy})_2(DMF)_2(\mu\text{-}OH_2)]$), in addition to matching the elemental percentages found with microanalysis (see main text).

Poly-$[Cd_2(\boldsymbol{P_4pxy})(OH_2)_2]\cdot DMA\cdot 3H_2O$ (***6*·DMA·3H$_2$O**)

Several low angle reflections, which had large error/esd values and are assumed to have been obstructed by the beam stop during data collection, were omitted. The two largest residual electron density peaks on the Fourier difference map are in close proximity to the cadmium cations, and are assumed to be adsorption artefacts.

The hydrogen atoms on the aqua ligands were placed in calculated positions and refined using SHELX DFIX commands. DFIX and DANG commands were also used to ensure chemically sensible orientations with respect to neighbouring groups in some instances.

There were significant regions of disordered electron density detected in the residual Fourier difference map after the refinement of all framework atoms. None of the lattice solvent molecules could be reasonably modelled, and the remaining electron density had its contribution to the diffraction data accounted for with the SQUEEZE routine within PLATON.[1] Analysis of the voids from SQUEEZE results in a total electron count of 254 e^- within the voids per unit cell, with a void volume of 1648 $Å^3$. These values equate to 64 e^- in 412 $Å^3$ per asymmetric unit (containing one formula unit). This electron density is accounted for as one DMA and three waters per ASU (4 DMA and 12 H_2O molecules per cell, total electron count of 312 e^-, 864 $Å^3$ using 18 $Å^3$ per non-H atom).

The total amount of solvent (ligands and SQUEEZED) also reasonably matches the 16 % mass loss observed in TGA up to 250 °C (Fig. S12), with a calculated mass of 16 % (1 DMA and 5 H_2O molecules per $[Cd_2(\boldsymbol{P_4pxy})]$), in addition to matching the elemental percentages found with microanalysis (see main text).

S2. Powder X-Ray Diffraction

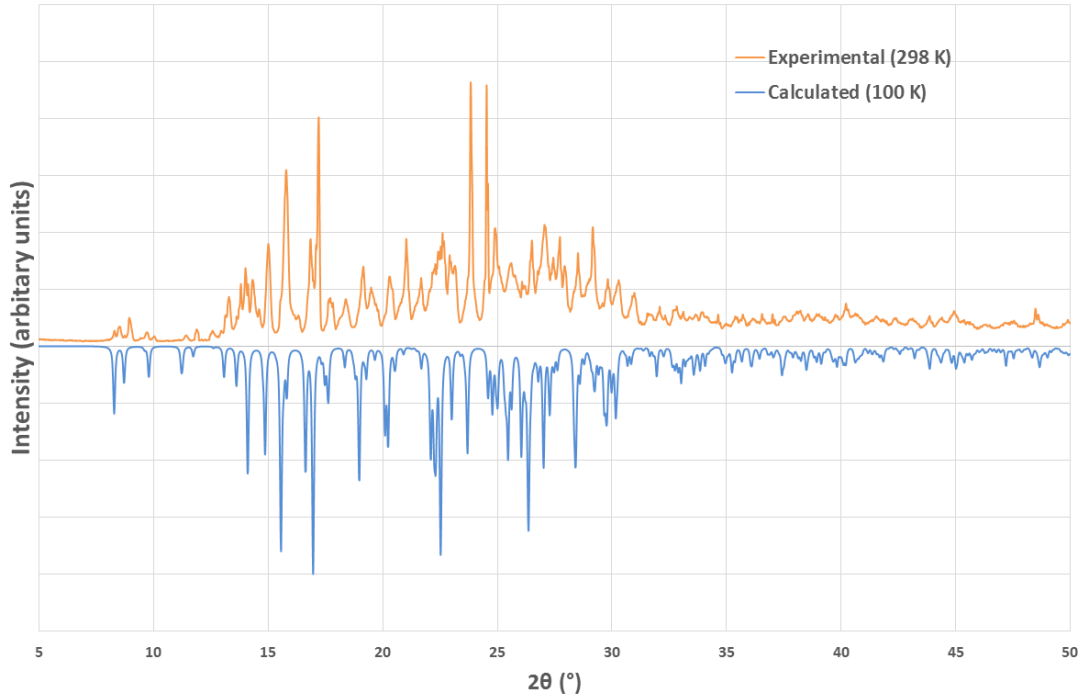

Figure S1. Bulk PXRD on a sample of **(H_6*P_4pxy*)Cl_2**, with the calculated pattern from single crystal XRD shown inverted (blue), and the as synthesised experimental pattern shown positive (orange).

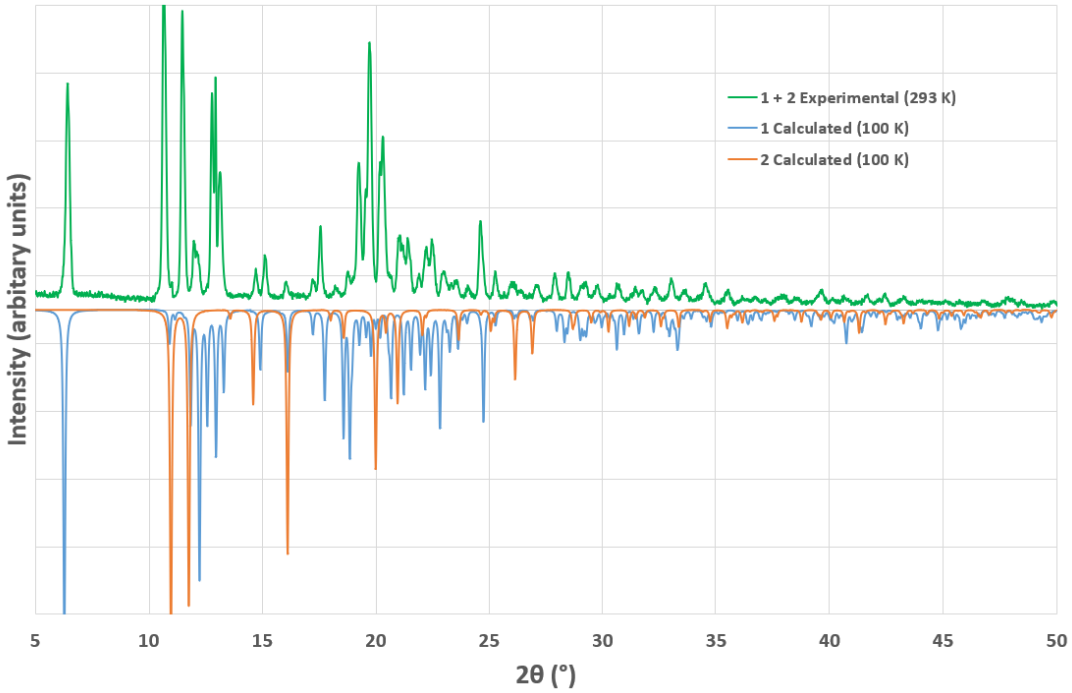

Figure S2. Bulk PXRD on a sample of ***1*** and ***2***, with the calculated patterns from single crystal XRD of ***1*** and ***2*** shown inverted (blue and orange respectively), and the as synthesised experimental pattern shown positive (green).

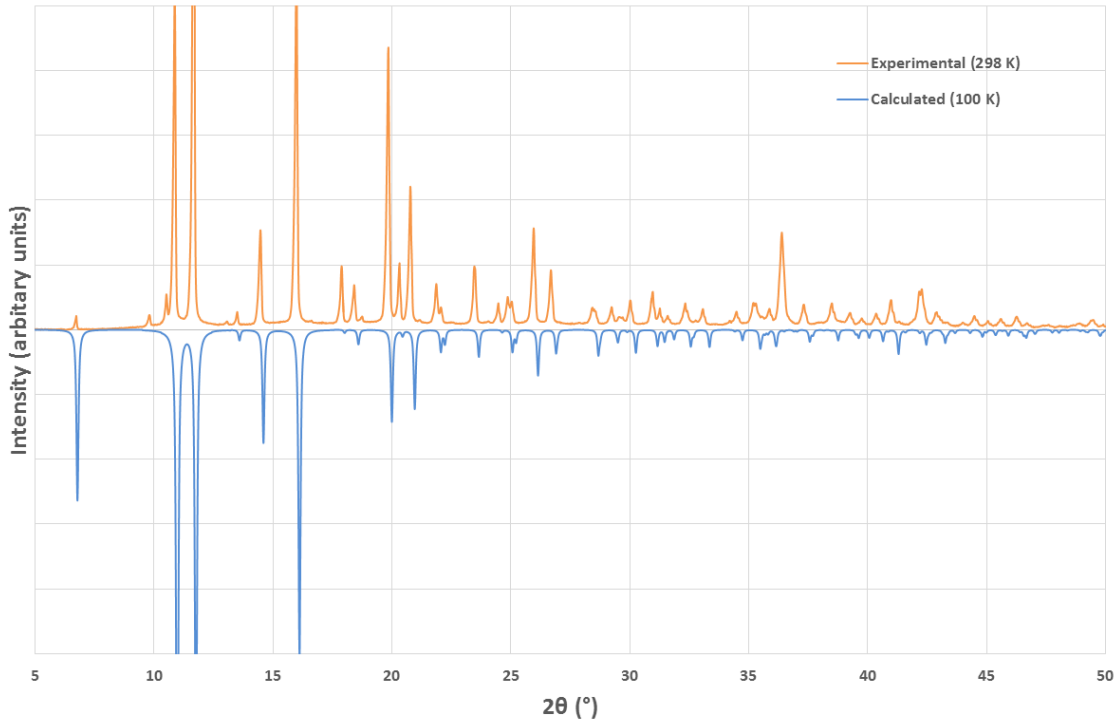

Figure S3. Bulk PXRD on a sample of ***3*·2DMF·3H$_2$O**, with the calculated pattern from single crystal XRD shown inverted (blue), and the as synthesised experimental pattern shown positive (orange).

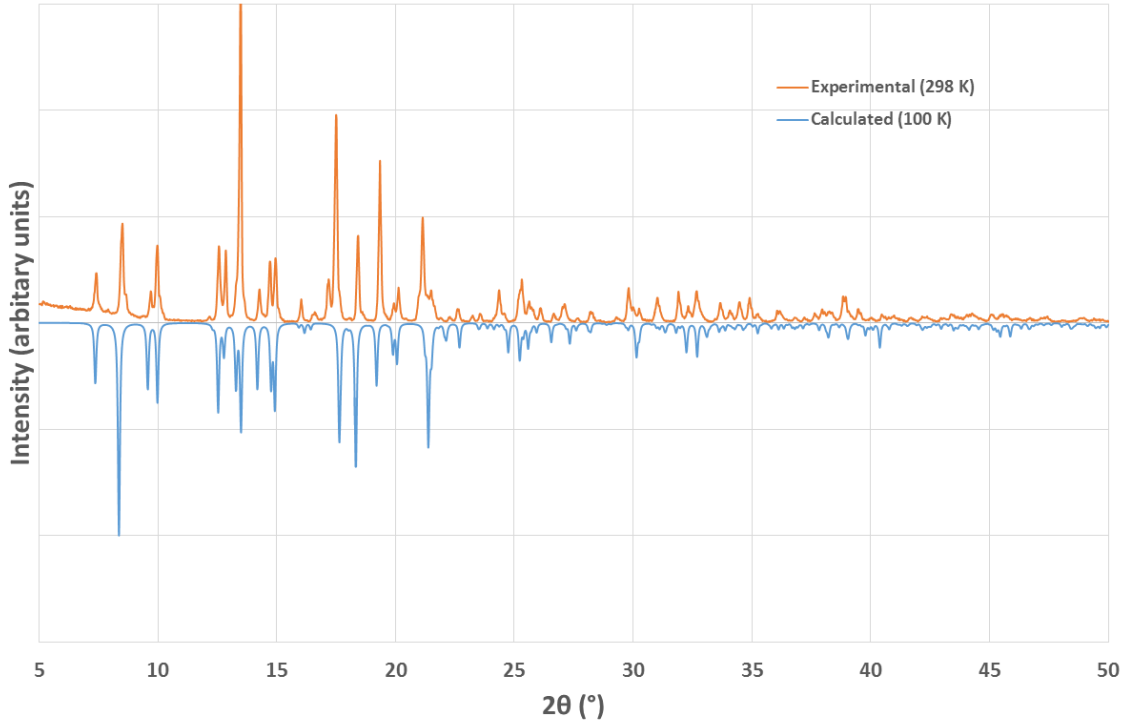

Figure S4. Bulk PXRD on a sample of ***4***, with the calculated pattern from single crystal XRD shown inverted (blue), and the as synthesised experimental pattern shown positive (orange).

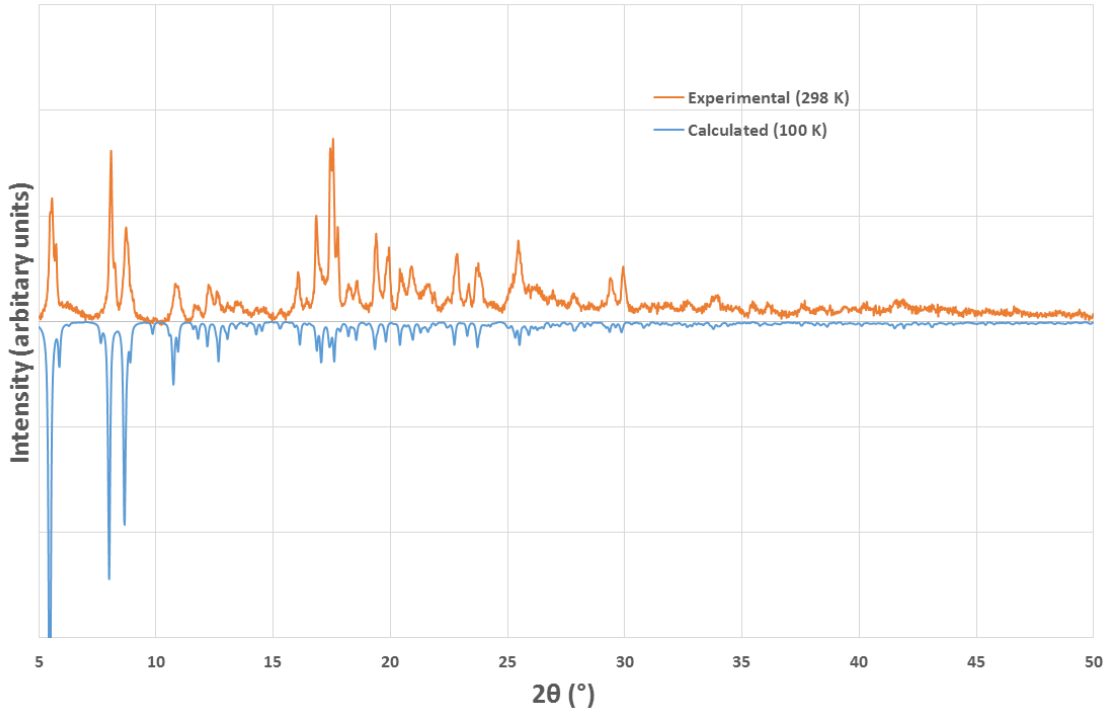

Figure S5. Bulk PXRD on a sample of ***5*·6DMF·4H$_2$O**, with the calculated pattern from single crystal XRD shown inverted (blue), and the as synthesised experimental pattern shown positive (orange).

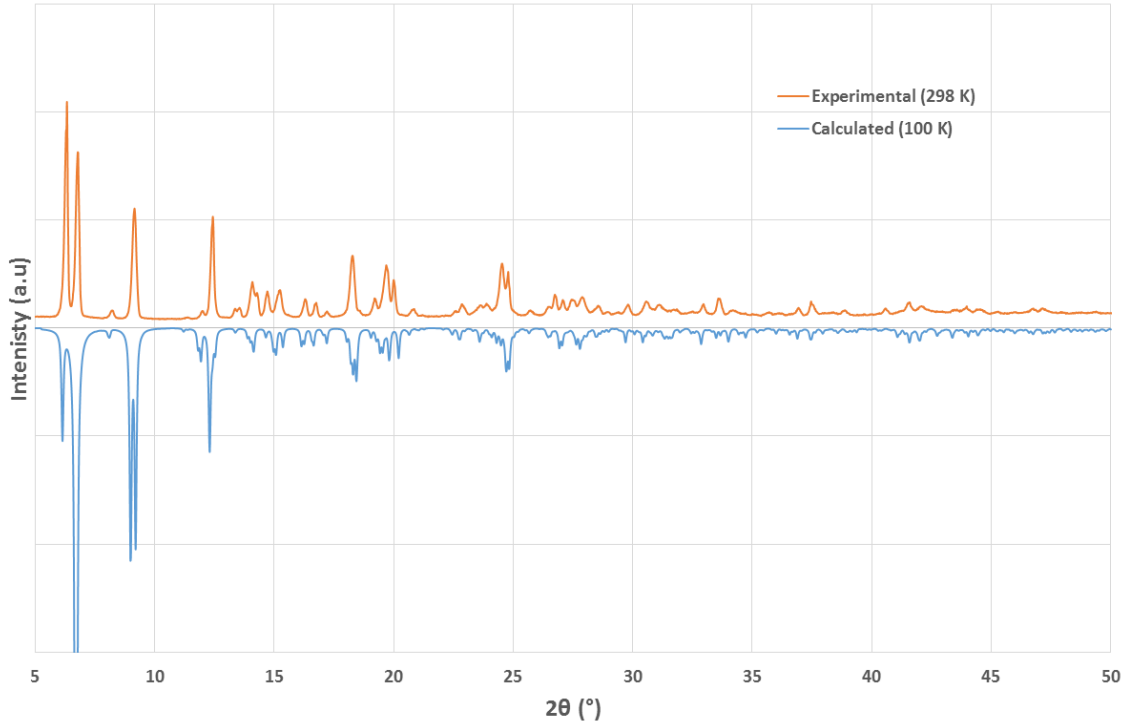

Figure S6. Bulk PXRD on a sample of ***6*·DMA·3H$_2$O**, with the calculated pattern from single crystal XRD shown inverted (blue), and the as synthesised experimental pattern shown positive (orange).

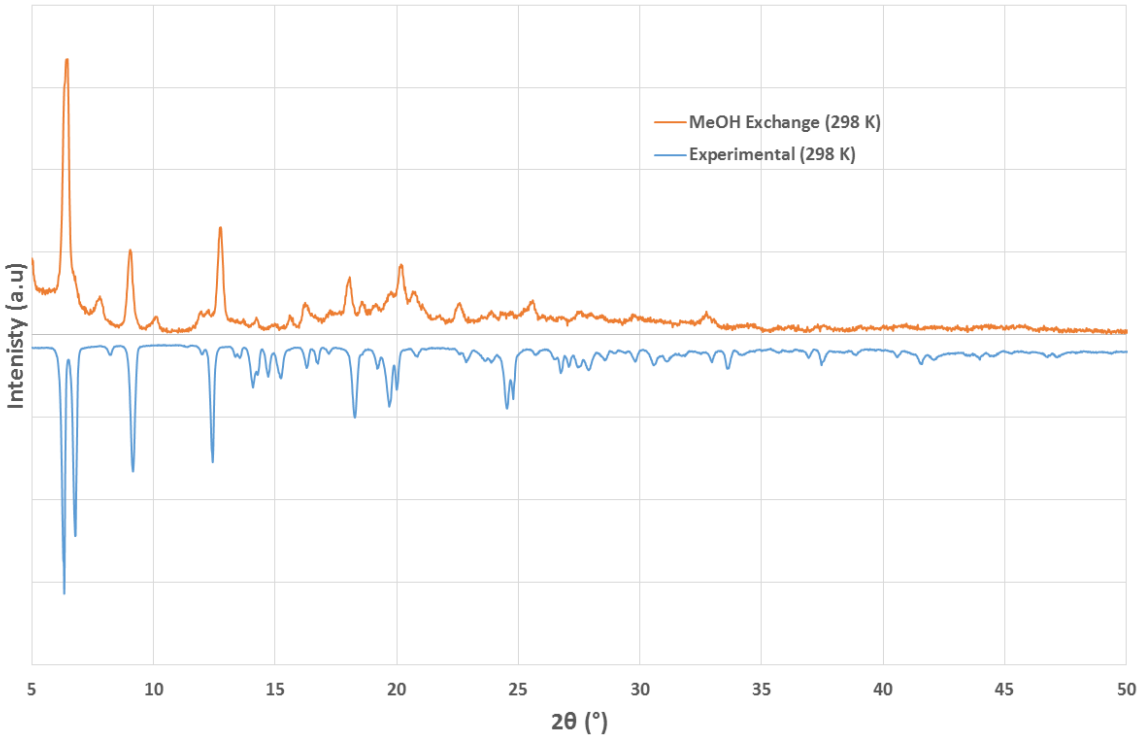

Figure S7. Bulk PXRD on a sample of ***6*·DMA·3H$_2$O**, with the as synthesised experimental pattern shown inverted (blue), and the MeOH exchanged experimental pattern shown positive (orange).

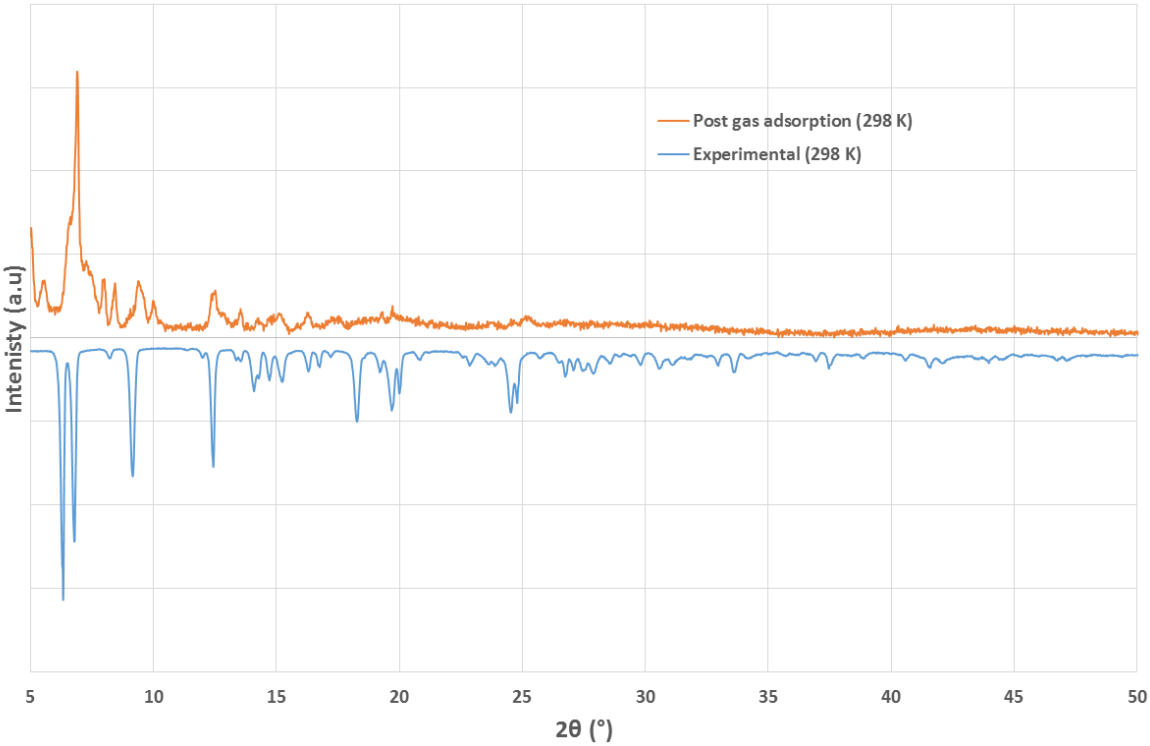

Figure S8. Bulk PXRD on a sample of ***6*·DMA·3H$_2$O**, with the as synthesised experimental pattern shown inverted (blue), and the experimental pattern after the gas adsorption experiment shown positive (orange).

S3. Thermogravimetric Analysis

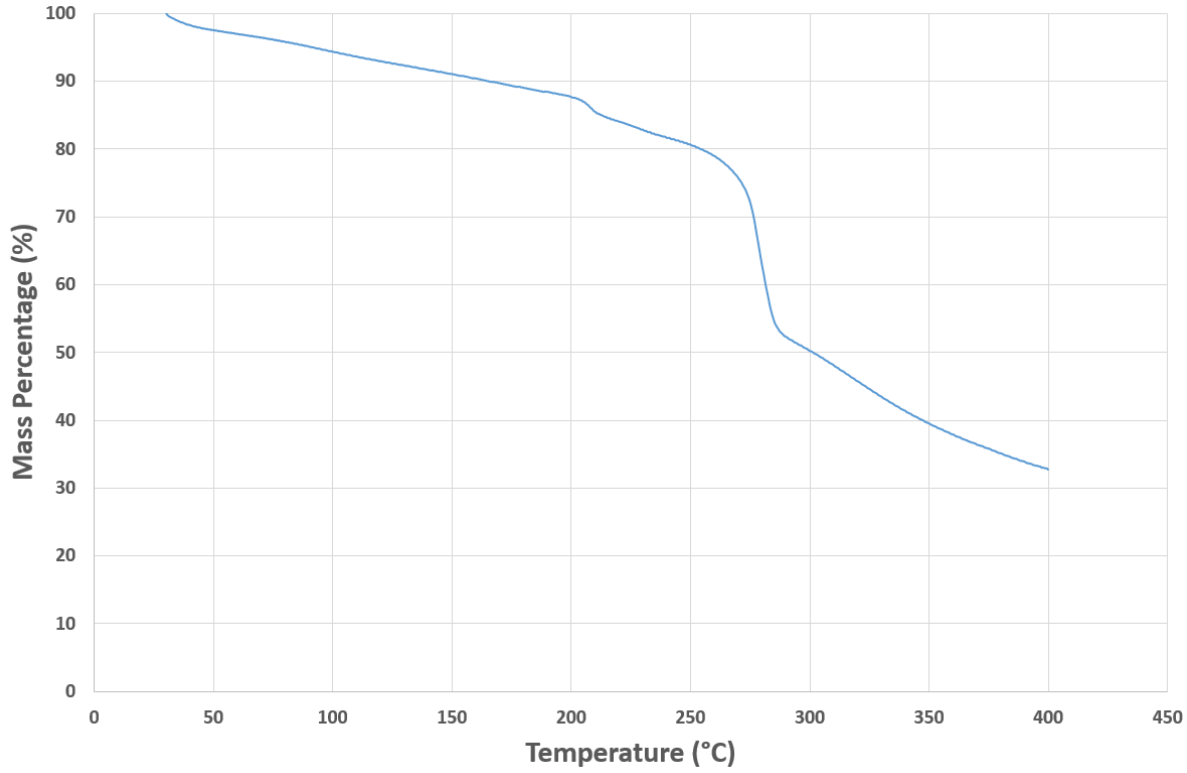

Figure S9. Thermogravimetric analysis of the as synthesised sample of ***3*·3DMF·3H$_2$O**.

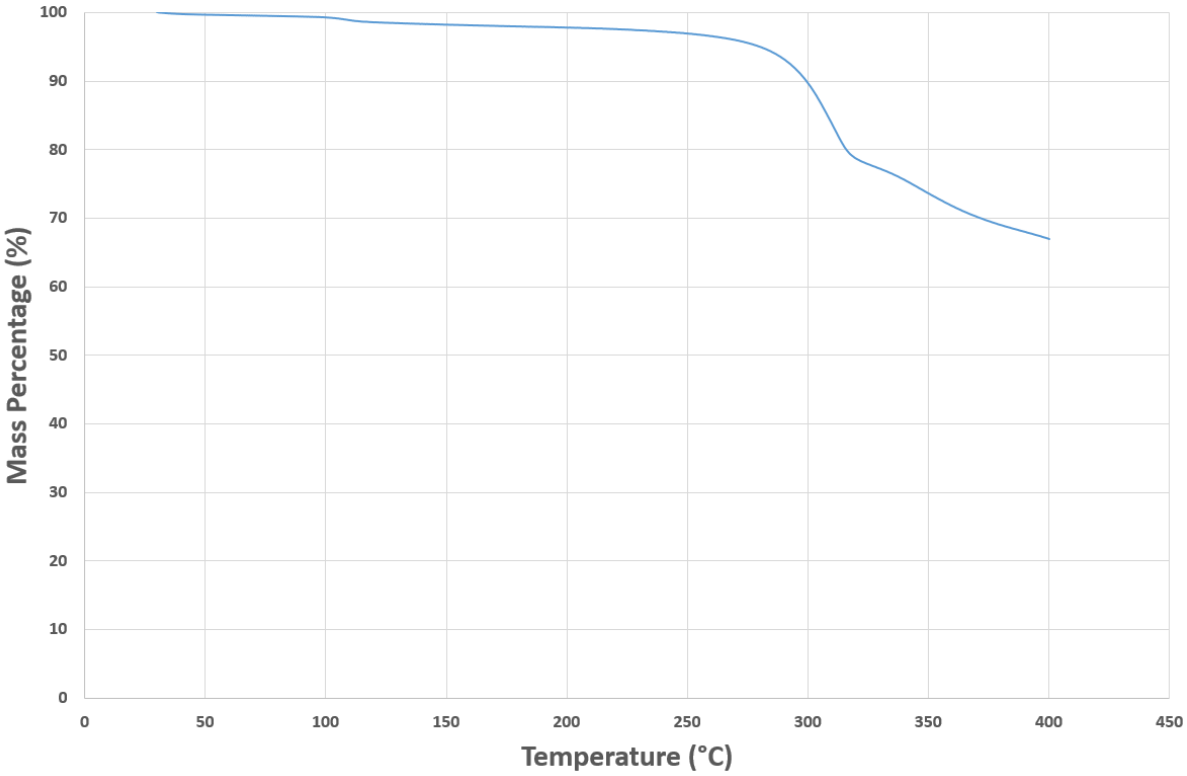

Figure S10. Thermogravimetric analysis of the as synthesised sample of ***4***.

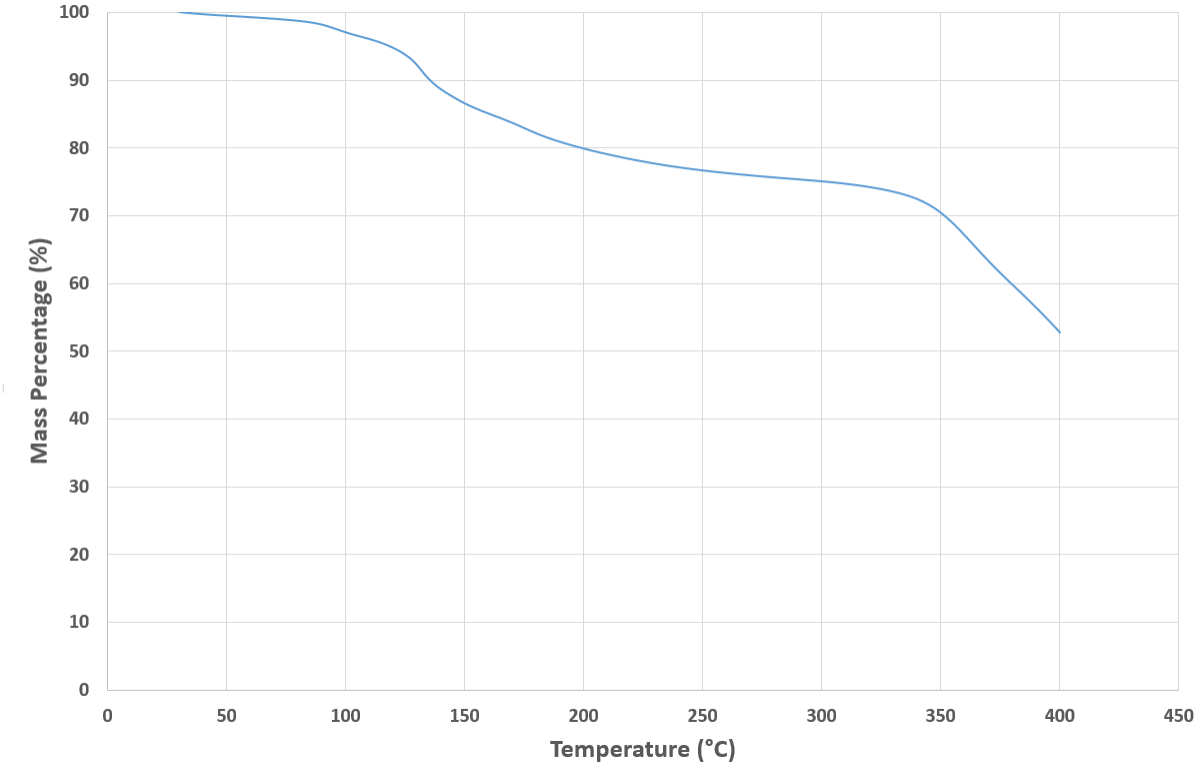

Figure S11. Thermogravimetric analysis of the as synthesised sample of ***5*·6DMF·4H$_2$O**.

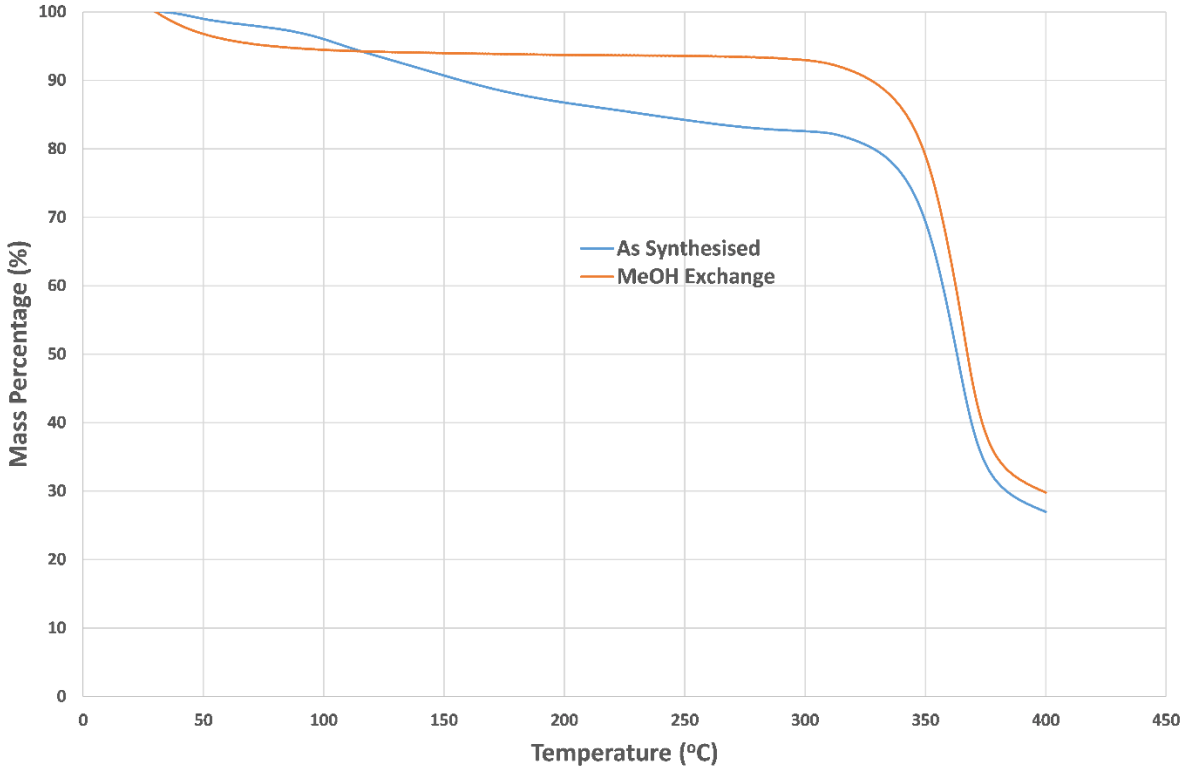

Figure S12. Thermogravimetric analysis of the as synthesised sample of ***6*·DMA·3H$_2$O** (blue) and the methanol exchanged sample of ***6*** (orange).

S4. Gas Adsorption Data

Table S1. Data for N_2 adsorption into ***6*** at 77 K with 10 second equilibration time up to 0.05 partial pressure, then to 40 second equilibration time for the rest of the isotherm

Relative Pressure (P/P_o)	Absolute Pressure (mbar)	Quantity Adsorbed (cm^3/g STP)	Elapsed Time (h:min)	Saturation Pressure (mbar)
			03:33	993.2047647
0.007277787	7.294000104	18.31318037	12:15	1002.227788
0.012097171	12.13142854	20.09557783	14:26	1002.831905
0.028535188	28.64917798	21.74413512	15:42	1003.994733
0.063149211	63.4120768	22.6816417	15:59	1004.162606
0.086837324	87.41553031	28.79934215	26:12	1006.658495
0.091192874	91.8032727	29.07003024	26:36	1006.693486
0.117317231	118.1196571	29.59496488	27:00	1006.839796
0.136356455	137.3374719	29.91696033	27:15	1007.194503
0.151669484	152.7339754	30.15397379	27:26	1007.018492
0.176026682	177.2713919	30.43140582	27:37	1007.071141
0.200984676	202.4066191	30.66584635	27:47	1007.074884
0.225990926	227.5762876	30.88942678	27:56	1007.015156
0.250888551	252.6656607	31.07274403	28:03	1007.083265
0.275853525	277.7787136	31.24345211	28:10	1006.979026
0.300669743	302.7840279	31.40170323	28:18	1007.031919
0.320768966	323.0383687	31.54315603	28:25	1007.074884
0.378804827	381.5042772	31.73142776	28:32	1007.12623
0.437971536	441.1254458	31.90771687	28:39	1007.201176
0.498269641	501.8689589	32.05630827	28:46	1007.223635
0.577376684	581.5717327	32.20332576	28:53	1007.265705
0.618263029	622.8235174	32.32715565	29:00	1007.376291
0.6968622	702.0225889	32.47498107	29:07	1007.405179
0.756789414	762.4547262	32.63058153	29:14	1007.485983
0.816948247	823.1600344	32.79988963	29:21	1007.603649
0.857607032	864.1629382	33.02385163	29:28	1007.644417
0.897614344	904.6762174	33.2982898	29:35	1007.867381
0.909764602	917.0347416	33.47712405	29:43	1007.991231
0.920198175	927.570336	33.66860353	29:50	1008.011493
0.930185246	937.6661064	33.85249489	29:57	1008.042334
0.939965978	947.6276104	34.0683717	30:04	1008.150967
0.950026444	957.8642384	34.31162806	30:11	1008.25008
0.95993049	967.8773333	34.62492881	30:18	1008.278561
0.969999409	978.038528	35.0158412	30:25	1008.287756
0.979629184	987.8465616	35.58382021	30:32	1008.388253
0.988914722	997.6616746	36.57140255	30:40	1008.845002
0.994877849	1003.378735	37.77099507	30:49	1008.544653
0.998187441	1006.856314	38.96283372	31:00	1008.684615
0.980975097	989.6723396	36.5446468	31:09	1008.865915
0.963319606	971.890025	35.69311765	31:16	1008.896756
0.942376594	950.8690438	35.28542125	31:23	1009.011737
0.921953666	930.2493155	35.08848623	31:30	1008.997903
0.901821494	909.9012121	34.95840364	31:37	1008.959332
0.881578179	889.5031453	34.88538329	31:45	1008.989522
0.861226381	869.0639848	34.83729941	31:52	1009.100515
0.822242579	829.7562545	34.75022674	31:59	1009.138028
0.782024825	789.2253987	34.69920718	32:06	1009.207603
0.703716663	710.2709359	34.65554262	32:13	1009.313795
0.604270429	609.9708116	34.64259315	32:20	1009.433496
0.561748867	567.0816286	34.66515587	32:27	1009.493143
0.48280971	487.4284114	34.64646309	32:34	1009.566297
0.460680676	465.1021173	34.64545338	32:41	1009.597626
0.36271848	366.2111385	34.64028405	32:49	1009.629118

0.340538985	343.8297138	34.64153795	32:56	1009.663295
0.281412247	284.1368144	34.62097799	33:03	1009.681766
0.25053936	252.969835	34.60056354	33:10	1009.700971
0.200782295	202.7575424	34.53969456	33:17	1009.837759
0.150696535	152.1807066	34.42674129	33:24	1009.848745
0.100242586	101.2290337	34.23279591	33:35	1009.840608

Table S2. Data for N_2 adsorption into ***6*** at 77 K with 20 second equilibration time up to 0.15 partial pressure

Relative Pressure (P/P_o)	Absolute Pressure (mbar)	Quantity Adsorbed (cm^3/g STP)	Elapsed Time (h:min)	Saturation Pressure (mbar)
			03:34	1009.514137
0.00828333	8.314288825	23.11880494	20:54	1003.73743
0.007762647	7.743572357	24.48438864	26:44	997.5427879
0.013079508	13.04066845	25.87307033	28:54	997.0305415
0.016565448	16.52312518	26.98353729	31:19	997.4451396
0.017767947	17.71997349	27.5093339	32:23	997.2999693
0.020926547	20.85721316	28.19284777	33:34	996.6868197
0.030926543	30.80135287	28.96138556	34:10	995.9520166
0.043878826	43.69399269	29.67525467	34:48	995.7876421
0.057436562	57.16996886	30.16175972	35:06	995.3584781
0.059896916	59.61194797	30.32902835	35:17	995.242358
0.065350531	65.03512282	30.52527316	35:25	995.1735974
0.070155406	69.81351921	30.69870854	35:32	995.1267263
0.074968113	74.5960809	30.87538316	35:40	995.0374595
0.080005907	79.61610075	31.05194143	35:49	995.1277841
0.085130286	84.6966981	31.21657041	35:57	994.9067736
0.090210285	89.77926876	31.34853534	36:03	995.222096
0.095324664	94.86227681	31.48398392	36:09	995.1493481
0.100346762	99.8449818	31.62245318	36:16	994.9995394
0.105443216	104.8983699	31.74278963	36:21	994.832805
0.110478888	109.9179473	31.84946488	36:25	994.9226414
0.115469199	114.8738905	31.96232847	36:31	994.8444415
0.120457303	119.8599013	32.06828608	36:35	995.0405517
0.125513243	124.896384	32.16669066	36:39	995.0853071
0.130542304	129.8951196	32.26093074	36:44	995.0423419
0.135543638	134.8716809	32.35023277	36:48	995.0425046
0.140514725	139.8407863	32.44214389	36:52	995.203787
0.145565968	144.855105	32.53163139	36:56	995.1165546
0.150613161	149.8569124	32.61572354	36:59	994.9788705

Table S3. Data for CO_2 adsorption into ***6*** at 273 K with 40 second equilibration time

Relative Pressure (P/P_o)	Absolute Pressure (mbar)	Quantity Adsorbed (cm^3/g STP)	Elapsed Time (h:min)	Saturation Pressure (mbar)
				34852.76851
5.13228E-05	1.788742401	0.050540912	04:22	
0.000108196	3.770942436	0.128610871	04:31	
0.00019691	6.862862772	0.261701228	04:43	
0.000402645	14.03330479	0.58302699	05:12	
0.000896054	31.22996508	1.374197029	06:03	
0.001231911	42.93552522	1.92458562	06:46	
0.001487584	51.84642573	2.349014156	07:21	
0.002402963	83.74992719	3.742687993	08:13	
0.002967159	103.4136894	4.581793642	08:45	
0.003479228	121.2607365	5.327068703	09:12	
0.003977533	138.6280359	6.058779288	09:40	
0.00448483	156.308725	6.769066018	10:02	
0.004977983	173.496494	7.459099639	10:24	
0.00593246	206.7626461	8.749766963	10:48	
0.006474679	225.6604901	9.488313219	11:07	
0.006982227	243.3499574	10.17045823	11:23	
0.00748057	260.7185689	10.83746686	11:40	
0.007984346	278.2765772	11.48698483	11:54	
0.008479364	295.5293128	12.1220697	12:07	
0.008980924	313.010057	12.76481667	12:21	
0.009484241	330.5520551	13.39446284	12:33	
0.009983338	347.9469706	14.0077223	12:45	
0.010482764	365.3533394	14.61612552	12:57	
0.010983871	382.8182971	15.21322625	13:08	
0.011938914	416.104223	16.32829589	13:21	
0.012481845	435.0268656	16.95251228	13:32	
0.01298445	452.5440244	17.51320667	13:42	
0.013485053	469.9914461	18.05658359	13:52	
0.013985719	487.4410243	18.59077656	14:01	
0.014487254	504.9209141	19.1148964	14:11	
0.014984589	522.2544128	19.6233504	14:20	
0.015932713	555.2991476	20.64242529	14:31	
0.016963136	591.2122588	21.75402818	14:41	
0.017961552	626.0098202	22.81130131	14:51	
0.018971165	661.1976084	23.77854613	15:01	
0.01995856	695.6110867	24.69339457	15:10	
0.020963821	730.6471946	25.59041005	15:20	
0.021963289	765.4814148	26.45094558	15:29	
0.022964855	800.3887898	27.27796768	15:39	
0.023965362	835.2592212	28.06554664	15:47	
0.024966541	870.1530882	28.82760677	15:56	
0.025968914	905.0885371	29.55999677	16:05	
0.026968311	939.920316	30.26378307	16:13	
0.0279671	974.7308565	30.94145078	16:22	
0.028970252	1009.693484	31.59398154	16:31	
0.029970042	1044.538934	32.22559577	16:39	
0.000927306	32.31916764	1.642435157	21:16	

S5. Partial Pressure vs. Quantity Adsorbed

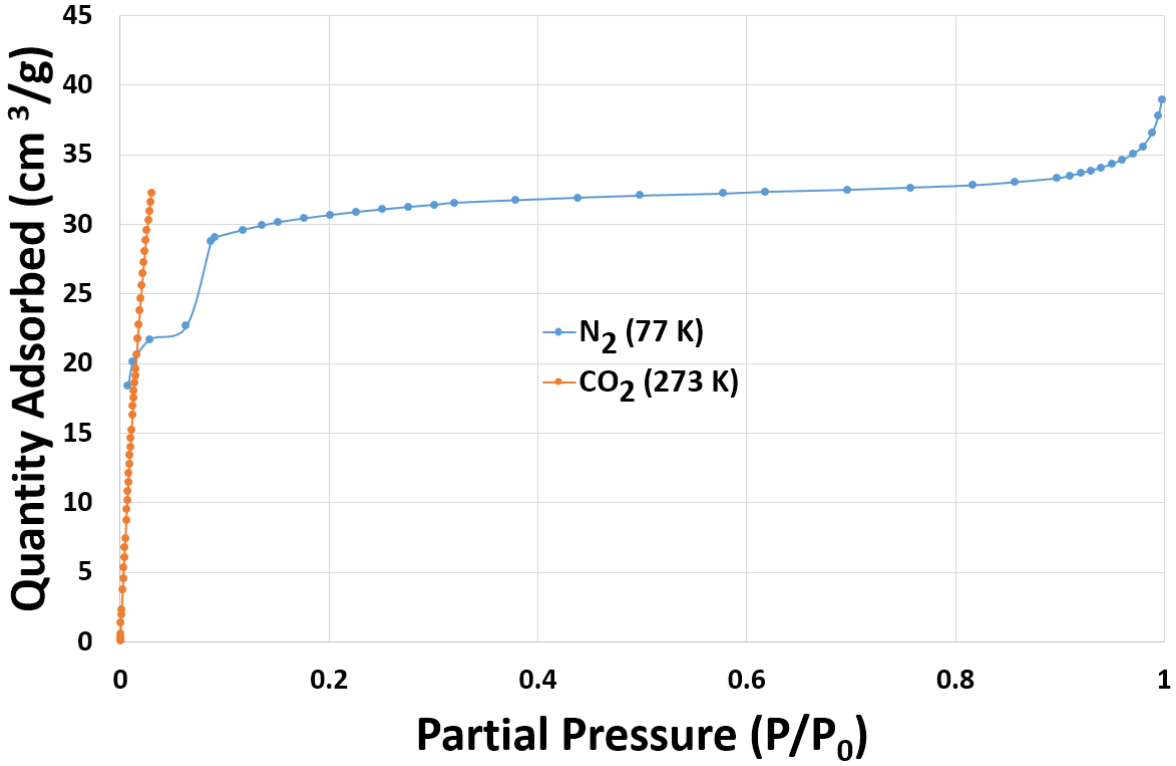

Figure S13. The quantity of N_2 (blue) and CO_2 (orange) adsorbed by **6** *vs.* partial pressure, demonstrating similar uptake between the two gasses at equivalent partial pressures.

S6. Catenane Motif Present Within poly-[$Co_4(P4pxy)_2(DMF)_2(\mu\text{-}OH_2)_2(OH_2)_2$] (5)

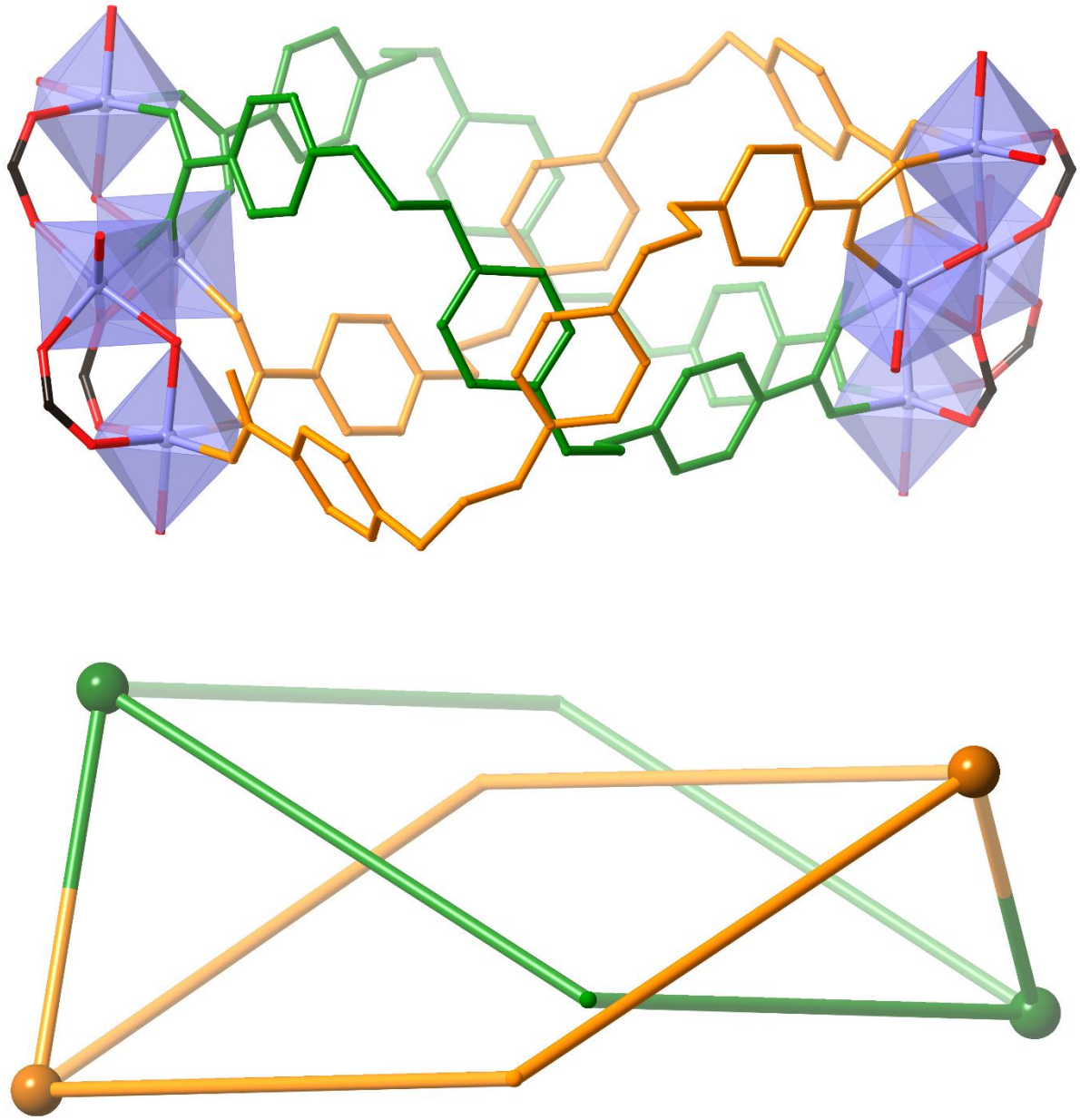

Figure S14. *Top:* The self-penetrating motif present within the structure of **5**, which share the same set of metal nodes. *Bottom:* A schematic representation of the catenane motif.

References

1. A. L. Spek, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2015, **71**, 9-18.