Intriguing differences in hydrogen adsorption in CPO-27 materials induced by metal substitution

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1. CPO-27-Cu nitrogen isotherm

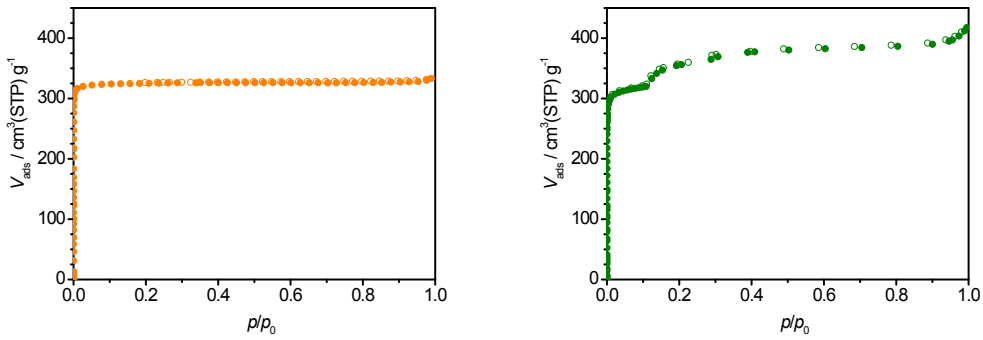


Figure S1: Nitrogen adsorption for CPO-27-Cu (left) and CPO-27-Mn (right). The adsorption branch is shown as filled symbols, whilst the desorption branch is shown as empty symbols.

2. PXRD analysis of CPO-27-Cu

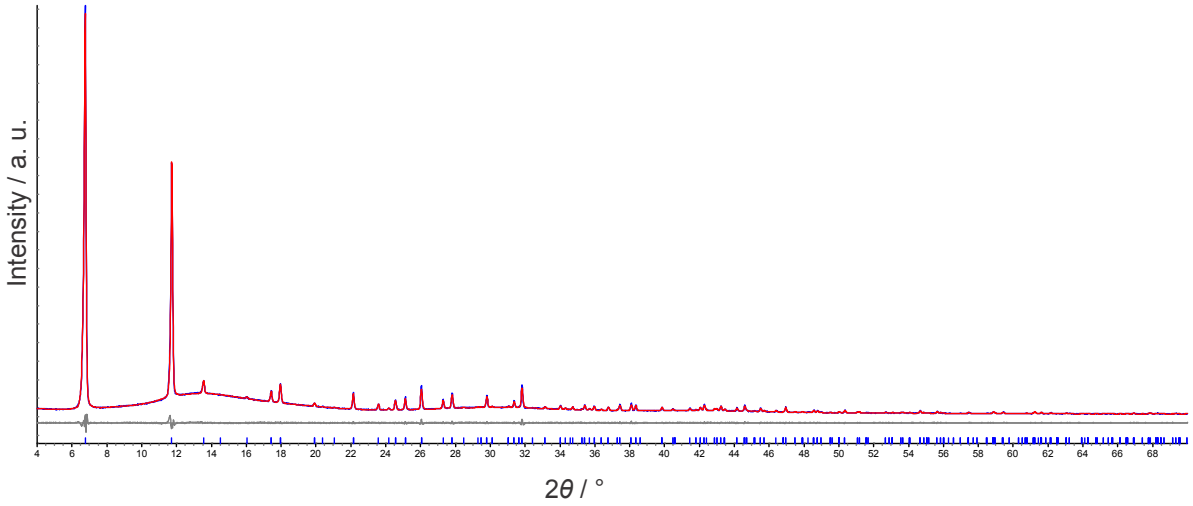


Figure S2: Pawley fit of powder XRD data of a typical sample of CPO-27-Cu synthesised according to the procedure reported herein. The broad peak in the range 10 to 20 ° is due to the experimental setup used.

3. TGA analysis of CPO-27-Cu

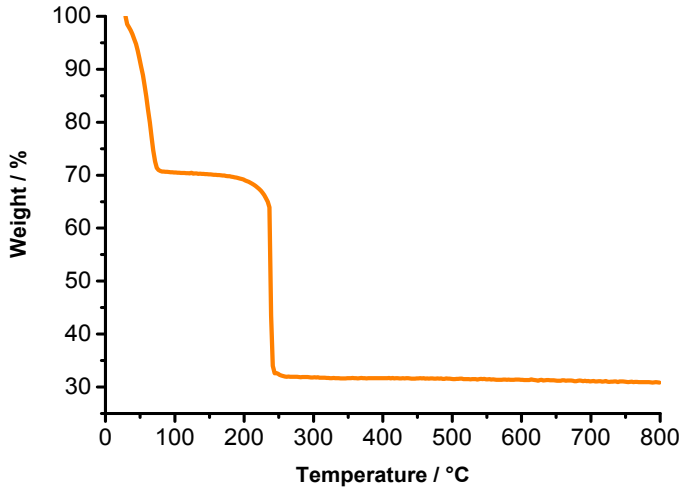


Figure S3: TGA analysis of CPO-27-Cu in air atmosphere.

4. Hydrogen adsorption / desorption data for CPO-27-Cu and -Mn

Table S1: Pressure sorption isotherm data for H_2 on CPO-27-Cu at 77 K.

Adsorption branch			Desorption branch		
p / kPa	V_{ads} / cm^3(STP) g^{-1}	n_{ads} / mol g^{-1}	p / kPa	V_{ads} / cm^3(STP) g^{-1}	n_{ads} / mol g^{-1}
0.00010897	0.00098591	4.39864E-8	99.709	164.22	0.00733
0.040493	0.4065	1.8136E-5	91.106	160.25	0.00715
0.088027	0.8944	3.99036E-5	89.858	159.65	0.00712
0.1702	1.7313	7.72419E-5	81.17	155.02	0.00692
0.2695	2.7123	1.21009E-4	79.883	154.29	0.00688
0.3774	3.7499	1.67302E-4	71.243	148.99	0.00665
0.4816	4.7269	2.10891E-4	69.918	148.13	0.00661
0.5846	5.6791	2.53373E-4	61.324	142.01	0.00634
0.6864	6.6018	2.94539E-4	59.953	141.07	0.00629
0.7885	7.5134	3.3521E-4	51.426	133.92	0.00597
0.8911	8.4167	3.75511E-4	49.998	132.48	0.00591
0.9935	9.3046	4.15125E-4	41.563	123.92	0.00553
1.0941	10.171	4.53779E-4	39.774	121.88	0.00544
1.4207	12.855	5.73526E-4	31.72	111.39	0.00497
1.5607	13.912	6.20684E-4	29.808	108.53	0.00484
1.9052	16.639	7.42349E-4	22.024	94.655	0.00422
2.0619	17.78	7.93254E-4	20.295	90.959	0.00406
2.5815	21.703	9.68279E-4	19.867	90.031	0.00402
3.0732	25.223	0.00113	12.548	69.949	0.00312
3.4416	27.744	0.00124	10.619	63.089	0.00281
3.5954	28.594	0.00128	9.8289	60.075	0.00268
4.0872	31.821	0.00142			

4.5904	34.826	0.00155			
5.1028	37.822	0.00169			
5.7624	41.49	0.00185			
6.0158	42.894	0.00191			
6.738	46.62	0.00208			
7.0257	47.894	0.00214			
7.7881	51.473	0.0023			
8.0486	52.602	0.00235			
8.7775	55.928	0.0025			
9.0455	57.083	0.00255			
9.8034	60.153	0.00268			
10.074	61.349	0.00274			
13.632	73.7	0.00329			
15.149	78.085	0.00348			
18.878	87.778	0.00392			
20.181	90.591	0.00404			
24.028	98.525	0.0044			
24.986	100.37	0.00448			
29.092	107.29	0.00479			
30.025	108.72	0.00485			
34.18	114.71	0.00512			
35.055	115.85	0.00517			
39.249	121.07	0.0054			
40.081	122.08	0.00545			
44.31	126.68	0.00565			
45.116	127.49	0.00569			
49.379	131.7	0.00588			
50.148	132.44	0.00591			
58.574	139.6	0.00623			
60.031	140.8	0.00628			
68.653	147	0.00656			
70.068	147.89	0.0066			
78.757	153.29	0.00684			
80.1	154.12	0.00688			
88.83	158.85	0.00709			
90.126	159.56	0.00712			
98.894	163.8	0.00731			
100.15	164.41	0.00734			

Table S2: Pressure sorption isotherm data for H_2 on CPO-27-Cu at 87 K.

Adsorption branch			Desorption branch		
p / kPa	V_{ads} / cm^3(STP) g^{-1}	n_{ads} / mol g^{-1}	p / kPa	V_{ads} / cm^3(STP) g^{-1}	n_{ads} / mol g^{-1}
0.00015233	0.00061182	2.72963E-8	90.292	112.64	0.00503
0.058798	0.1929	8.60623E-6	89.699	112.29	0.00501
0.1848	0.6299	2.8103E-5	80.331	106.83	0.00477
0.3143	1.0713	4.7796E-5	79.705	106.44	0.00475
0.4715	1.5973	7.12635E-5	70.401	100.36	0.00448

0.6266	2.1086	9.40752E-5	69.737	99.877	0.00446
0.7747	2.5927	1.15673E-4	60.473	93.12	0.00415
0.9282	3.0924	1.37967E-4	59.762	92.563	0.00413
1.0766	3.5694	1.59249E-4	50.575	84.679	0.00378
1.544	5.1593	2.30182E-4	49.79	83.935	0.00374
2.0502	6.6169	2.95213E-4	40.685	74.779	0.00334
2.5546	8.0544	3.59347E-4	39.823	73.766	0.00329
3.0726	9.6413	4.30146E-4	30.828	62.959	0.00281
3.5794	10.972	4.89516E-4	29.861	61.693	0.00275
4.0594	12.512	5.58223E-4	21.01	48.414	0.00216
4.5636	13.879	6.19211E-4	19.768	46.414	0.00207
5.0685	15.22	6.7904E-4	11.297	29.978	0.00134
6.1362	18.213	8.12573E-4	9.8713	26.791	0.0012
6.9863	20.255	9.03676E-4			
7.1329	20.66	9.21746E-4			
7.99	22.694	0.00101			
8.1332	23.009	0.00103			
8.9934	25.068	0.00112			
9.9991	27.432	0.00122			
14.342	36.752	0.00164			
15.054	38.156	0.0017			
19.433	46.158	0.00206			
20.076	47.269	0.00211			
24.567	54.46	0.00243			
25.177	55.252	0.00247			
29.666	61.713	0.00275			
30.196	62.613	0.00279			
34.685	68.188	0.00304			
35.208	68.995	0.00308			
39.733	74.27	0.00331			
40.217	74.648	0.00333			
44.781	79.474	0.00355			
45.235	80.026	0.00357			
49.801	84.38	0.00376			
50.243	84.791	0.00378			
59.409	92.509	0.00413			
60.229	93.162	0.00416			
69.506	100.08	0.00447			
70.247	100.58	0.00449			
79.606	106.5	0.00475			
80.276	107.04	0.00478			
89.65	112.42	0.00502			
90.274	112.63	0.00502			
99.718	117.5	0.00524			

Table S3: Pressure sorption isotherm data for H_2 on CPO-27-Mn at 77 K.

Adsorption branch			Desorption branch		
p / kPa	V_{ads} / cm^3(STP) g^{-1}	n_{ads} / mol g^{-1}	p / kPa	V_{ads} / cm^3(STP) g^{-1}	n_{ads} / mol g^{-1}
0.00009244	0.010501	4.685E-07	98.572	217.44	0.0097011
0.00087545	0.1079	4.8131E-06	90.392	213.58	0.0095289
0.0051702	0.6214	0.000027722	88.804	212.88	0.0094976
0.009509	1.1119	0.000049607	80.16	208.31	0.0092937
0.018002	2.1022	0.00009379	79.419	207.93	0.0092768
0.027102	3.118	0.00013911	70.519	202.68	0.0090426
0.040598	4.6188	0.00020607	69.114	201.8	0.0090033
0.049015	5.5673	0.00024838	60.682	196.13	0.0087503
0.061906	7.0172	0.00031307	59.274	195.12	0.0087053
0.070757	7.9997	0.00035691	50.927	188.69	0.0084184
0.079914	8.9931	0.00040123	49.429	187.43	0.0083622
0.089297	10.027	0.00044735	41.209	180.07	0.0080338
0.098991	11.071	0.00049393	39.609	178.52	0.0079647
0.1517	16.447	0.00073378	31.523	169.95	0.0075823
0.2004	21.041	0.00093874	29.788	167.9	0.0074909
0.2518	25.463	0.001136	21.926	157.55	0.0070291
0.3455	33.011	0.0014728	20.033	154.7	0.0069019
0.3979	36.64	0.0016347	19.504	153.88	0.0068654
0.4527	40.202	0.0017936	13.531	143.23	0.0063902
0.5092	43.592	0.0019449	10.783	137.14	0.0061185
0.568	46.874	0.0020913	9.895	134.88	0.0060177
0.6285	50.003	0.0022309			
0.6839	52.676	0.0023501			
0.746	55.473	0.0024749			
0.8058	57.997	0.0025875			
0.9222	62.816	0.0028025			
0.9823	64.937	0.0028972			
1.0425	66.939	0.0029865			
1.3326	74.984	0.0033454			
1.5199	79.817	0.003561			
1.9189	87.45	0.0039016			
2.1754	91.463	0.0040806			
2.6233	97.425	0.0043466			
3.0549	102.03	0.0045521			
3.7837	108.05	0.0048206			
4.94	115.41	0.005149			
7.5864	126.52	0.0056447			
10.05	133.74	0.0059668			
13.686	142.04	0.0063371			
16.141	146.77	0.0065481			
20.782	154.44	0.0068903			
26.958	163.08	0.0072758			
32.337	169.59	0.0075663			
37.451	175.19	0.0078161			
42.157	179.89	0.0080258			

47.377	184.68	0.0082395			
53.802	190.05	0.0084791			
62.25	196.4	0.0087624			
72.123	202.98	0.0090559			
82.583	209.12	0.0093299			
91.703	213.98	0.0095467			
101.08	218.5	0.0097484			

Table S4: Pressure sorption isotherm data for H_2 on CPO-27-Mn at 87 K.

Adsorption branch			Desorption branch		
p / kPa	V_{ads} / cm^3(STP) g^{-1}	n_{ads} / mol g^{-1}	p / kPa	V_{ads} / cm^3(STP) g^{-1}	n_{ads} / mol g^{-1}
0.0003091	0.0082142	3.6648E-07	98.761	175.44	0.0078273
0.0035091	0.093675	4.1793E-06	88.797	171.18	0.0076372
0.020546	0.5375	0.000023979	79.948	167.01	0.0074511
0.037332	0.974	0.000043453	69.031	161.4	0.0072009
0.052998	1.3843	0.000061761	59.226	155.76	0.0069492
0.068667	1.8088	0.0000807	50.512	150.15	0.0066989
0.086493	2.2929	0.0001023	49.302	149.34	0.0066628
0.1024	2.7162	0.00012118	40.739	142.9	0.0063755
0.1606	4.2836	0.00019111	39.46	141.84	0.0063282
0.2026	5.3879	0.00024038	31.125	134.09	0.0059824
0.3421	8.9108	0.00039756	29.631	132.54	0.0059133
0.4645	11.847	0.00052855	21.682	122.53	0.0054667
0.5962	14.848	0.00066244	19.943	119.9	0.0053493
0.7252	17.646	0.00078728	13.933	108.15	0.0048251
0.8514	20.284	0.00090497	11.119	100.54	0.0044856
0.9673	22.596	0.0010081	9.7225	95.876	0.0042775
1.0734	24.659	0.0011002			
1.4725	31.673	0.0014131			
1.5417	32.794	0.0014631			
1.8797	38.198	0.0017042			
2.2096	42.788	0.001909			
2.5557	47.349	0.0021125			
3.0932	53.608	0.0023917			
4.042	62.786	0.0028012			
6.3997	79.323	0.003539			
8.79	90.753	0.0040489			
11.026	98.75	0.0044057			
15.252	109.78	0.0048978			
21.035	120.33	0.0053685			
26.609	127.94	0.005708			
31.247	133.2	0.0059427			
37.249	138.98	0.0062006			
41.158	142.39	0.0063527			
46.444	146.58	0.0065397			
51.721	150.39	0.0067096			
61.759	156.79	0.0069952			
71.609	162.4	0.0072455			
82.192	167.8	0.0074864			

91.835	172.32	0.0076881			
102.34	176.84	0.0078897			

5. Neutron diffraction on CPO-27-Mn

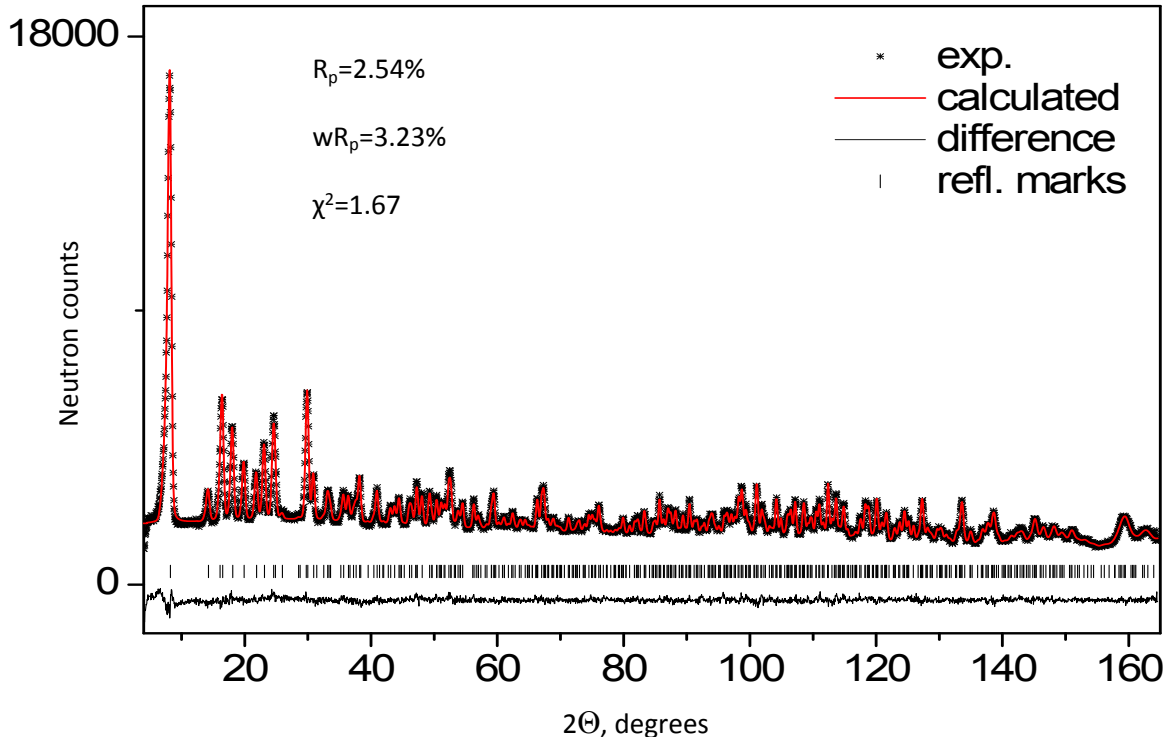


Figure S4: Refinement plot of the desolvated CPO-27-Mn material data, taken on HRPT, at 20 K. Data refined in the S.G. $R\bar{3}$, No. 148 with *a* = 26.2958(6) Å and *c* = 7.05164(19) Å.

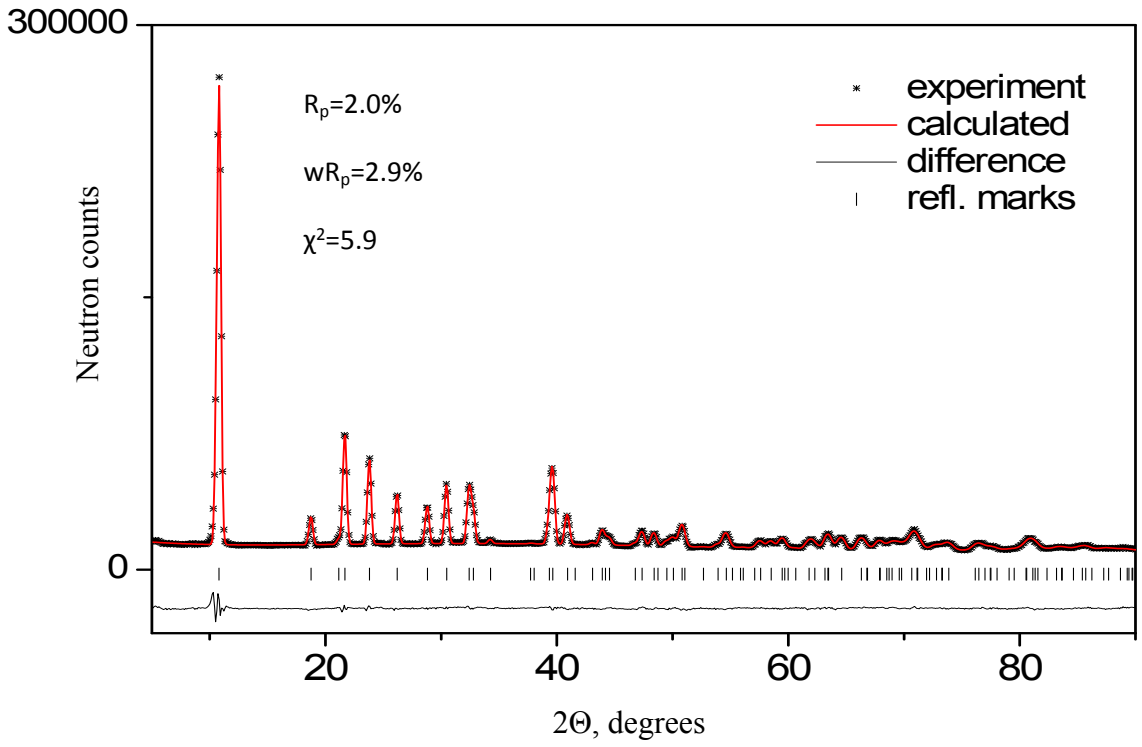


Figure S5: Refinement plot of the desolvated CPO-27-Mn material data, taken on DMC, at 20 K. Resulting lattice parameters: *a* = 26.2950(8) Å and *c* = 7.0514(3) Å.

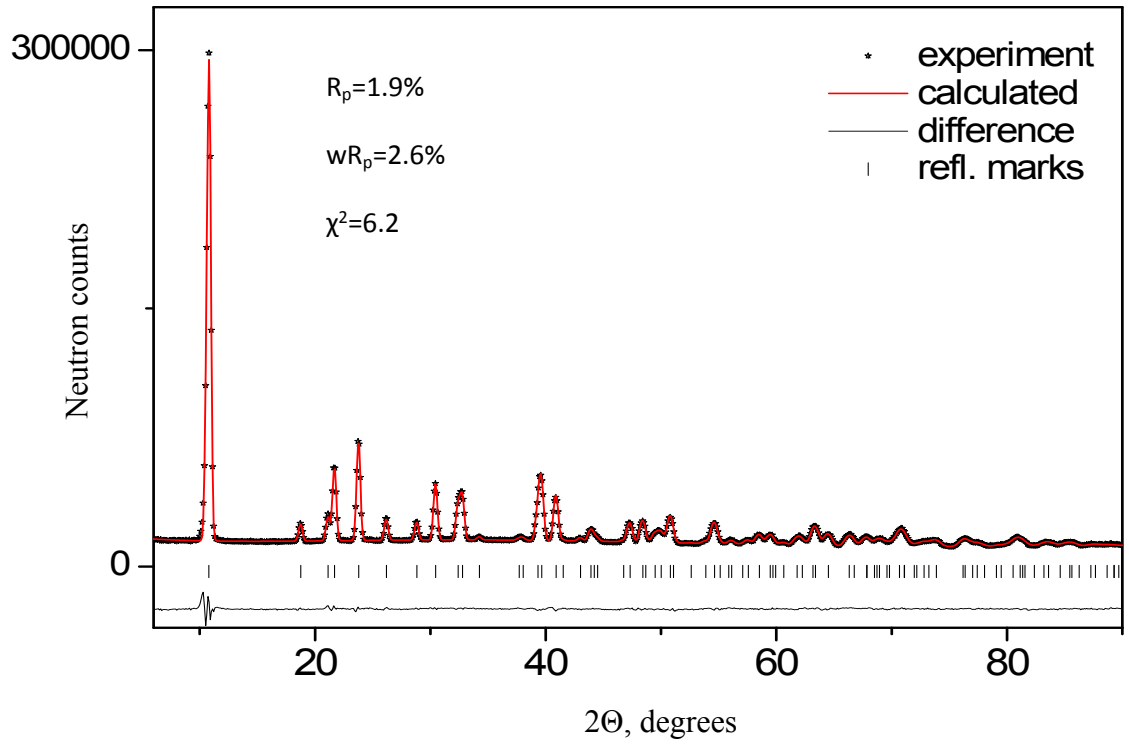


Figure S6: Refinement plot of the CPO-27-Mn material, dosed with 0.5 D_2 per Mn data, taken on DMC, at 20 K.

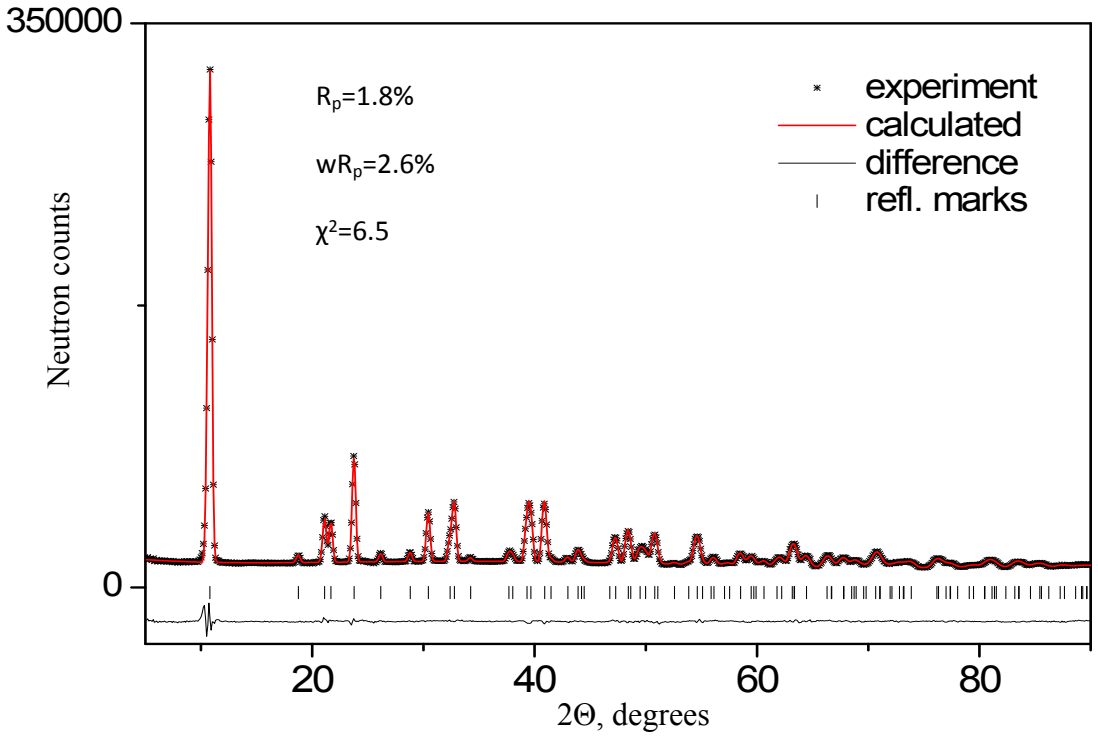


Figure S7: Refinement plot of the CPO-27-Mn material, dosed with 1 D_2 per Mn data, taken on DMC, at 20 K.

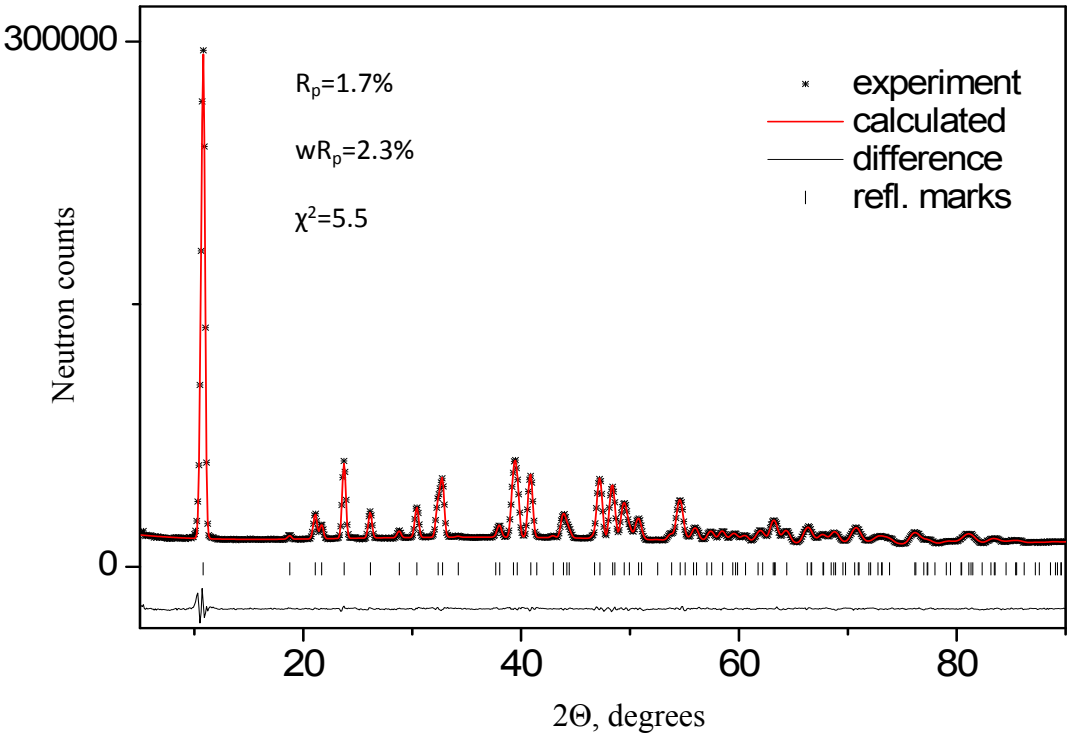


Figure S8: Refinement plot of the CPO-27-Mn material, dosed with 2 D_2 per Mn data taken on DMC, at 20 K.

6. Neutron diffraction on CPO-27-Cu

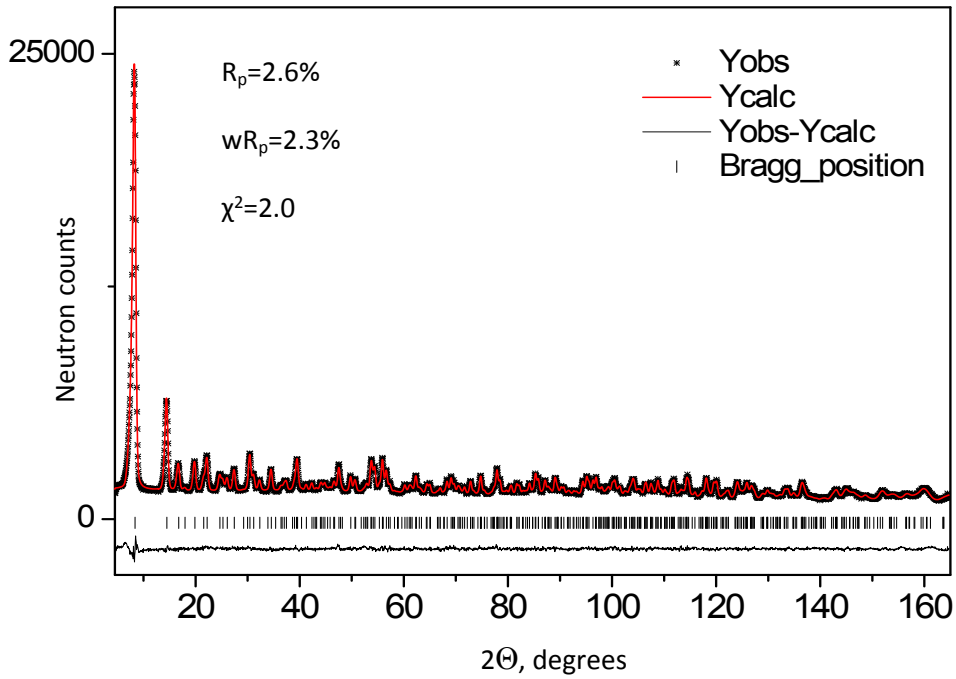


Figure S9: Refinement plot of the empty CPO-27-Cu material. HRPT Data, taken at 1.5 K.

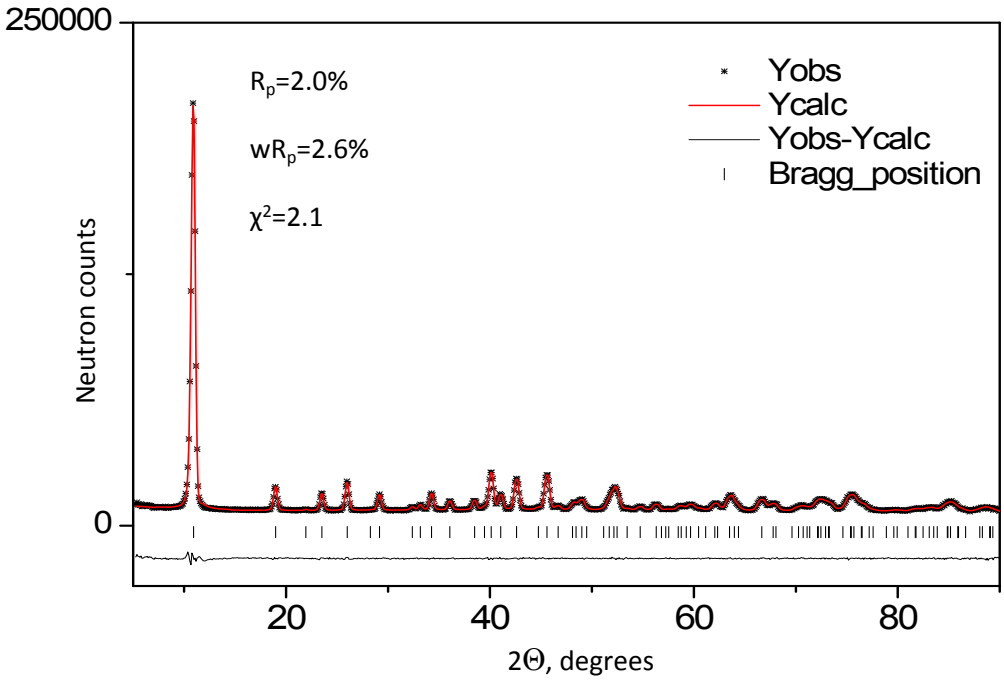


Figure S10: Refinement plot of the empty CPO-27-Cu material. DMC Data, taken at 20 K.

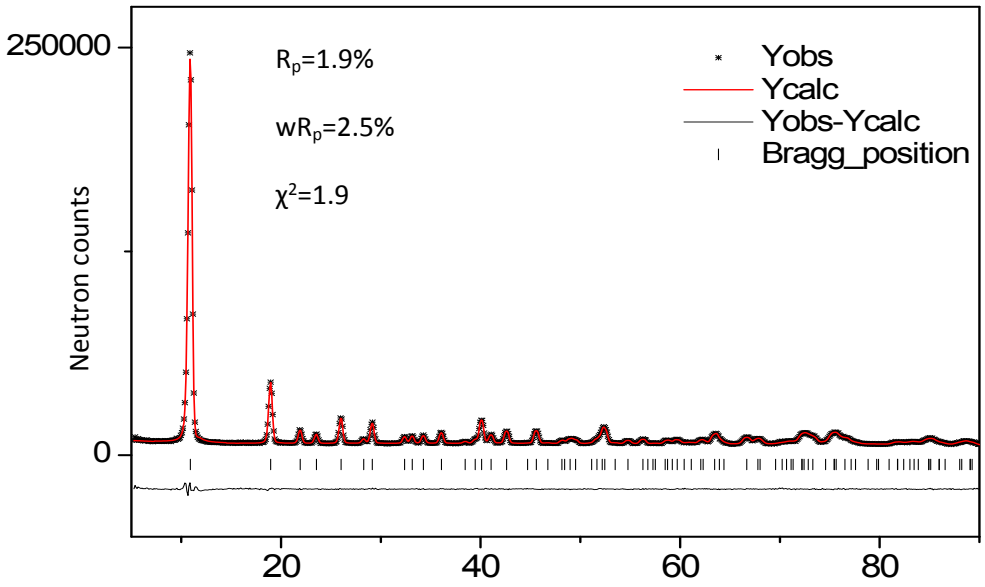


Figure S11: Refinement plot of the CPO-27-Cu material, dosed with 0.5 D_2 per Cu data taken on DMC at 20 K.

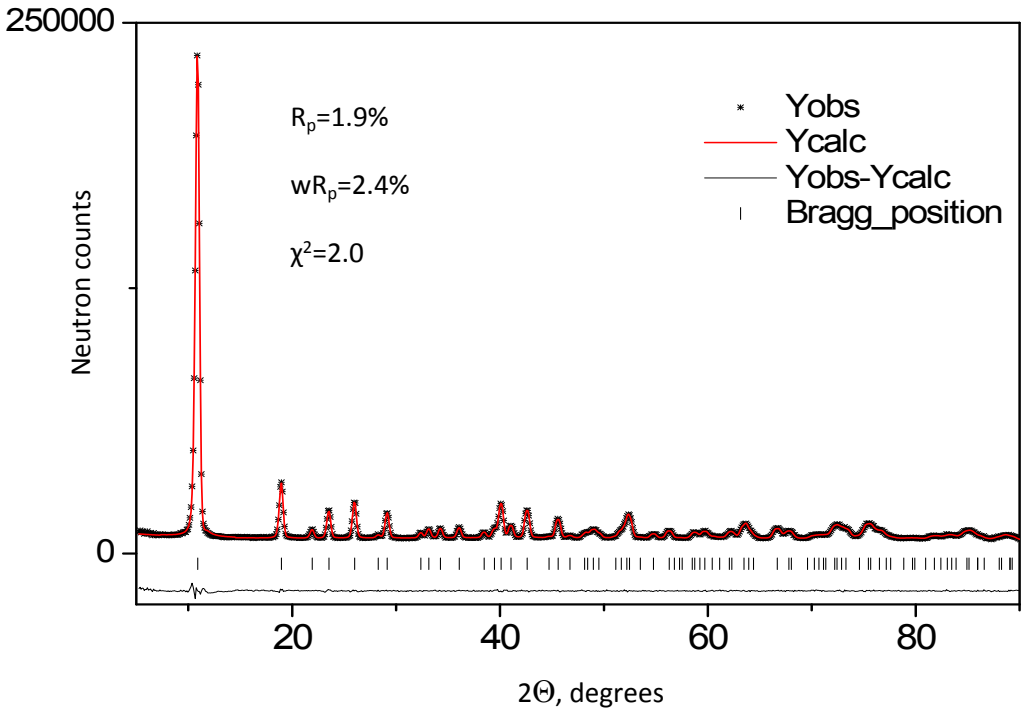


Figure S12: Refinement plot of the CPO-27-Cu material, dosed with 1 D_2 per Cu data taken on DMC at 20 K.

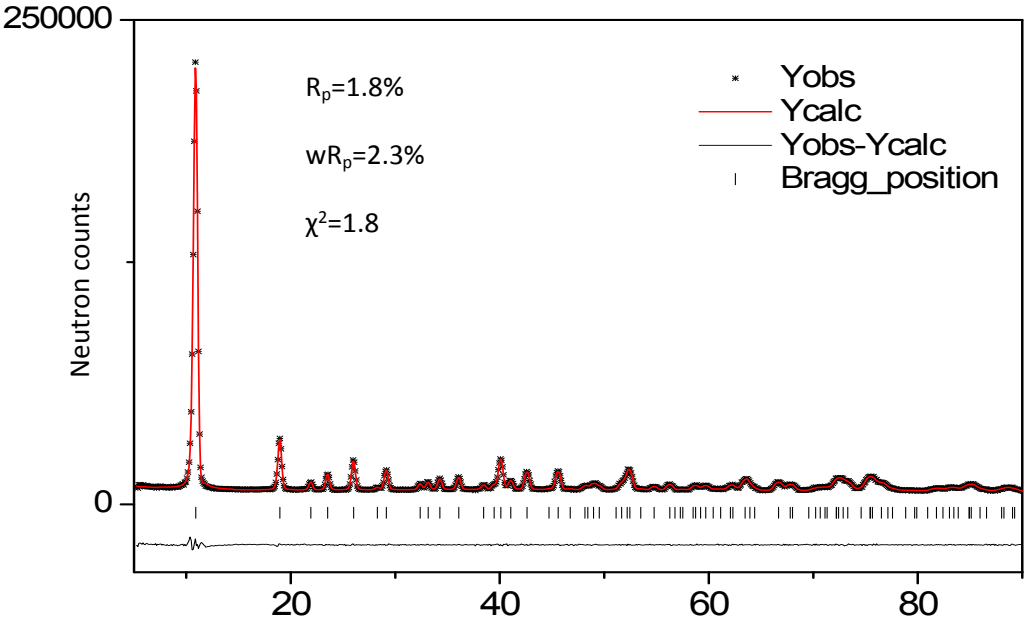


Figure S13: Refinement plot of the CPO-27-Cu material, dosed with 1 D_2 per Cu data taken on DMC at 55 K.

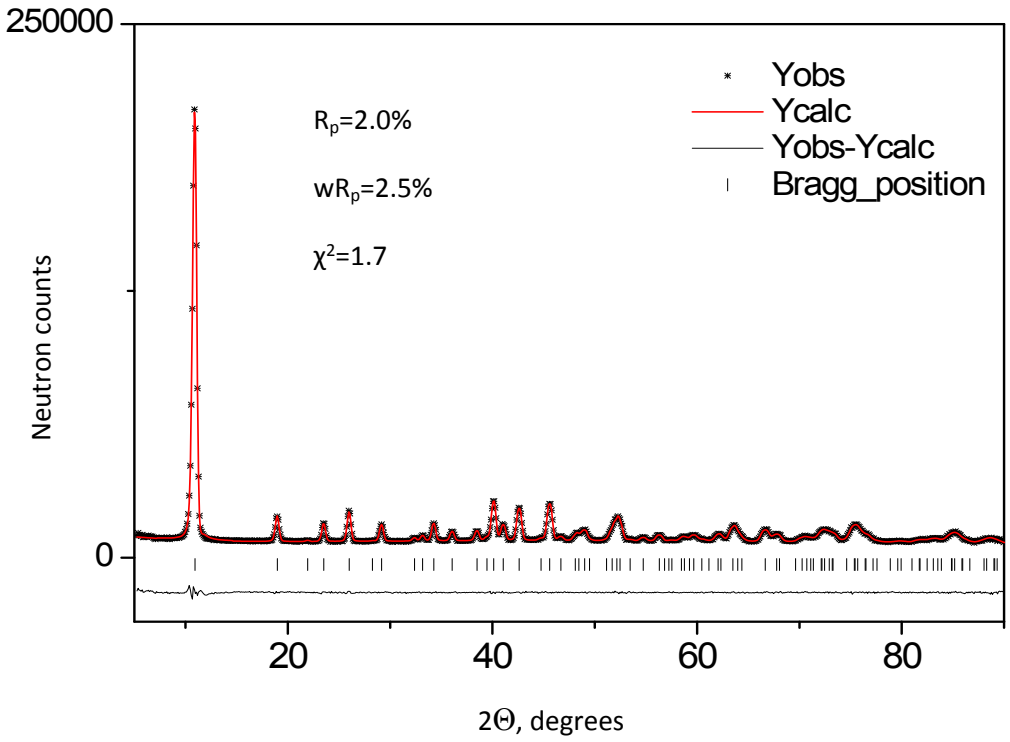


Figure S14: Refinement plot of the CPO-27-Cu material, dosed with 2 D_2 per Cu data taken on DMC, at 20 K.

Table S5: Summary of the unit cell parameters from the Rietveld refinements against CPO-27-Mn and Cu-datashown in Figures S5-S14. HRPT results are marked with asterisks.

CPO-27-Mn	*a*, Å	*c*, Å	*V*, Å^3
empty	26.2964(6)* 26.2950(8)	7.0518(2)* 7.0514(3)	4223.0(2)* 4222.3(3)
+0.5D_2/Mn	26.2885(8)	7.0608(3)	4225.9(3)
+1D_2/Mn	26.2904(7)	7.0676(3)	4230.6(2)
+2 D_2/Mn	26.2978(7)	7.0741(2)	4236.8(2)

CPO-27-Cu	*a*, Å	*c*, Å	*V*, Å^3
empty	25.8868(3)* 25.8810(16)	6.2643(1)* 6.2626(4)	3635.49(8)* 3632.8(4)
+0.5D_2/Cu	25.8776(7)	6.2623(3)	3631.7(2)
+1D_2/Cu	25.8717(6)	6.2631(3)	3630.5(2)
+2 D_2/Cu	25.8592(7)	6.2696(3)	3630.8(2)

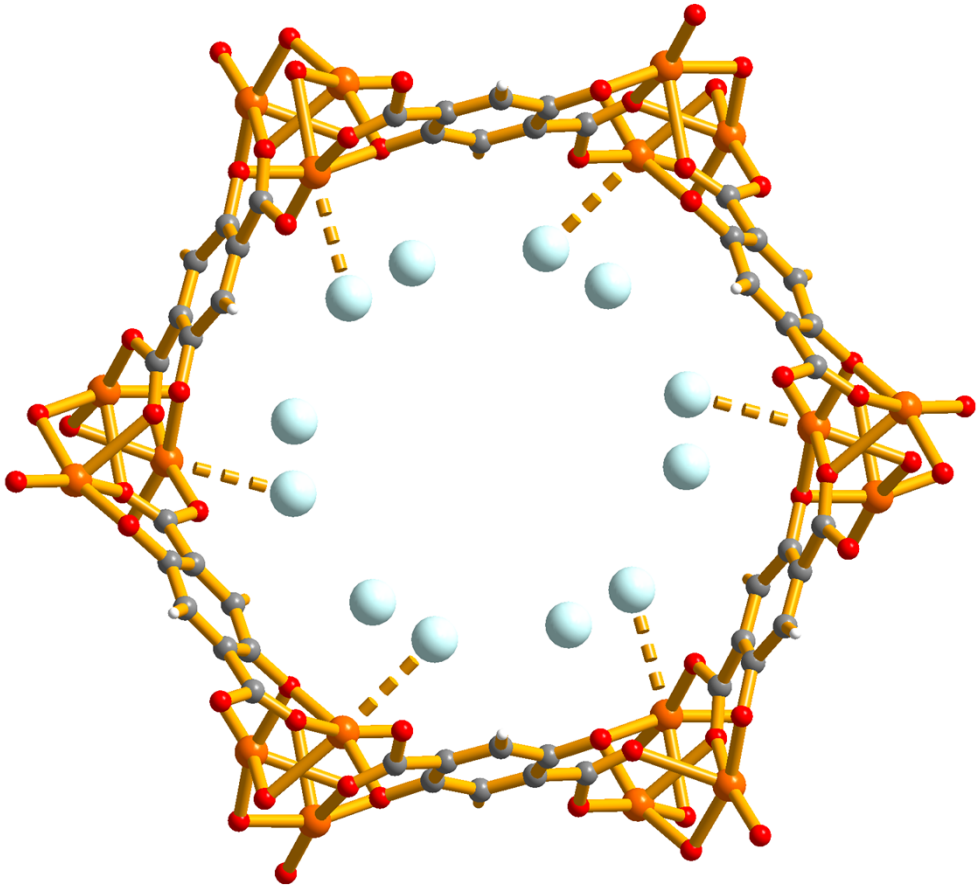


Figure S15: Crystal structure of CPO-27-Cu + 1.8 D_2 at 20 K showing the two first adsorption sites for D_2, viewed along [001].

7. Results of DFT calculations

Table S6: Comparison of DFT, PBE stereochemical data of the MnO_5 and CuO_5 square pyramidal units in the corresponding geometry optimized desolvated CPO-27 structures with 0, 1 and 2 H_2 molecules loaded with bond distances from refinements of the neutron diffraction data of the desolvated and corresponding deuterium loaded compounds. The apical M(II)–O distances are marked with asterisk.

Structure	Mn–O, Å	Cu–O, Å
CPO-27-M	Calculated: 2.117, 2.086, 2.085, 2.200, 2.130* Experimental: 2.10(2), 2.08(2), 2.05(2), 2.20(2), 2.18(2)*	Calculated: 2.109, 2.041, 2.133, 2.051, 2.553* Experimental: 1.971(7), 1.939(8), 1.985(9), 1.951(8), 2.444(9)*
+1 H_2 / M	Calculated: 2.120, 2.090, 2.088, 2.208, 2.140* Experimental: 2.17(4), 2.16(4), 1.97(4), 2.22(4), 2.08(5)*	Calculated: 2.108, 2.045, 2.132, 2.053, 2.563* Experimental: 1.92(4), 1.87(3), 1.99(3), 1.90(3), 2.43(3)*
+2 H_2 / M	Calculated: 2.122, 2.089, 2.091, 2.200, 2.144* Experimental: 2.18(5), 2.14(5), 2.16(6), 2.27(5), 2.15(6)*	Calculated: 2.109, 2.046, 2.132, 2.053, 2.564* Experimental: 1.99(4), 1.92(4), 2.02(4), 1.91(4), 2.42(3)*

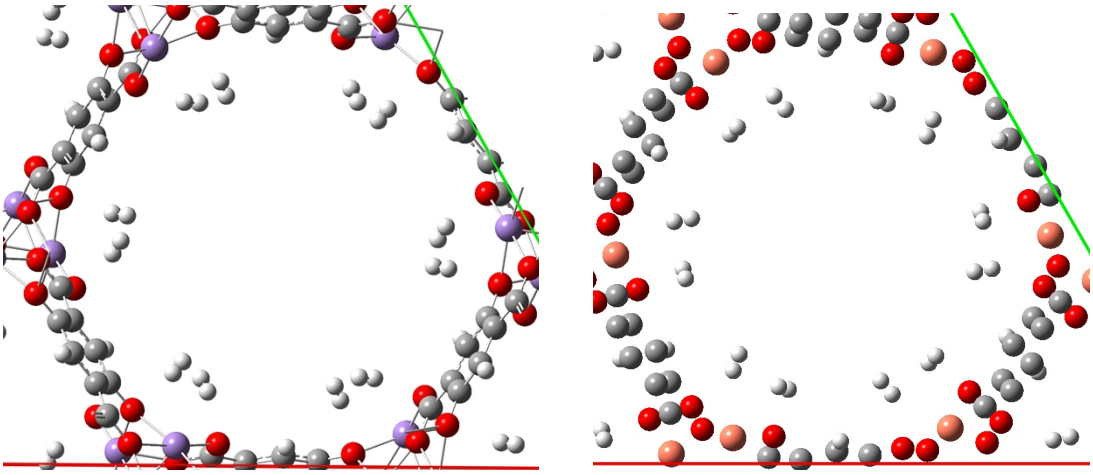
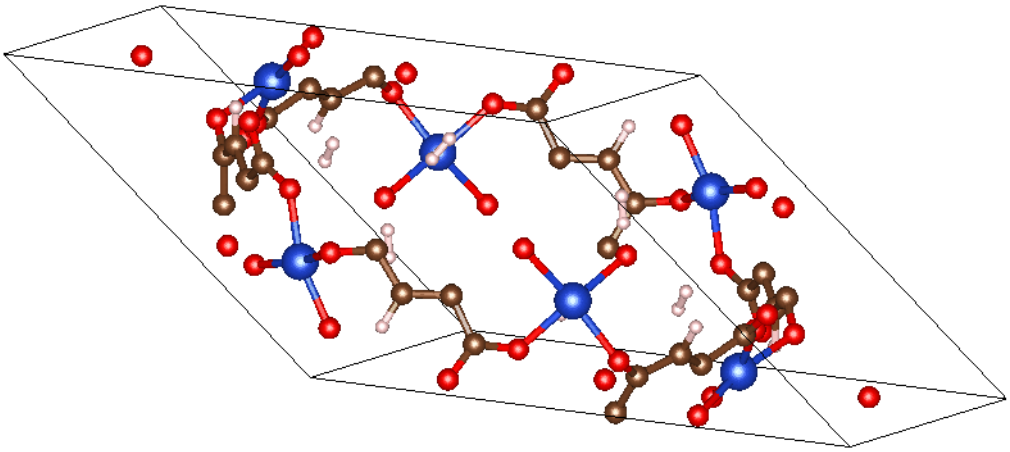


Figure S16: DFT, PBE optimised unit cell of CPO-27-Mn, on the left, and -Cu on the right, loaded with 2 H_2 per metal.

a)



b)

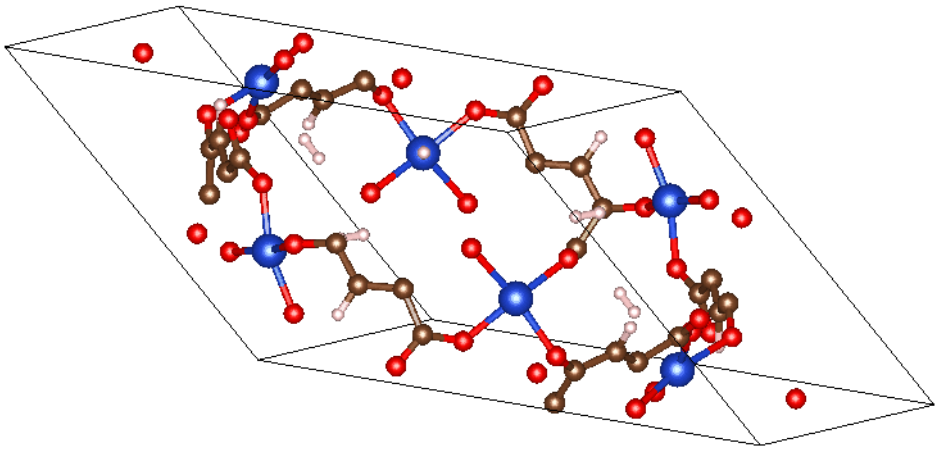


Figure S17: The primitive unit cells of the CPO-27-M with 1 H_2 in its optimised equilibrium position in a) - side-on position; b) – with the H_2 in its transition state with respect to reorientation in the direction perpendicular to the square pyramid basal plane – the side-on position. The corresponding rotational barrier, V_2, is estimated as the difference between the total energies of the two primitive unit cells and then divided by 6 to account for the presence of six H_2 molecules in the unit cells.