Electronic Supplementary Material (ESI) for CrystEngComm

Dryness Sensitive Porous 3*d*-4*f* Metal–Organic Framework with Unusual Dynamic Behaviour

Oscar Fabelo,[a,b,c]* Laura Cañadillas-Delgado,[a,b,c] Jorge Pasán,[a] Pau Díaz-Gallifa,[a] Ana Labrador,[d] and Catalina Ruiz-Pérez.[a]*

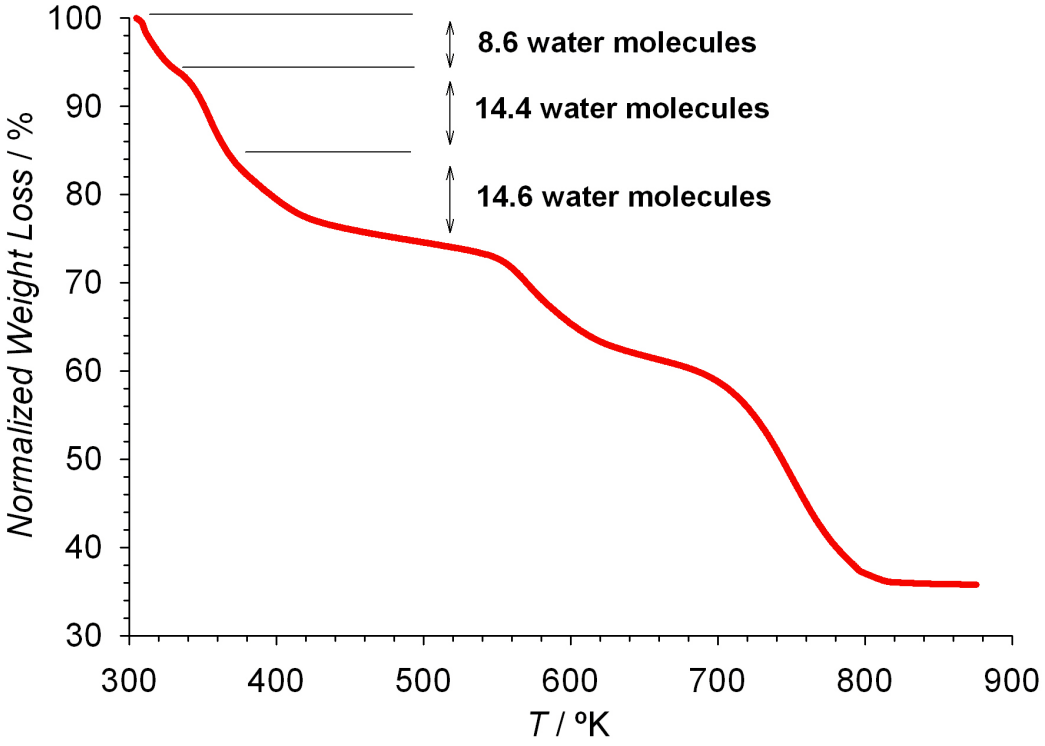

Figure S1. TG measurement for **1a**, the measurement was made in dry-nitrogen atmosphere after thermal stabilization at 300K at ambient conditions. The number of water molecules lost at the different steps is also indicated. The total loss of water molecules is *ca*. 38, which is very close to those values obtained through X-ray diffraction. The final value of the weight, *ca.* 35% of the original mass, corresponds with the final CuO and Pr_2O_3 oxides.

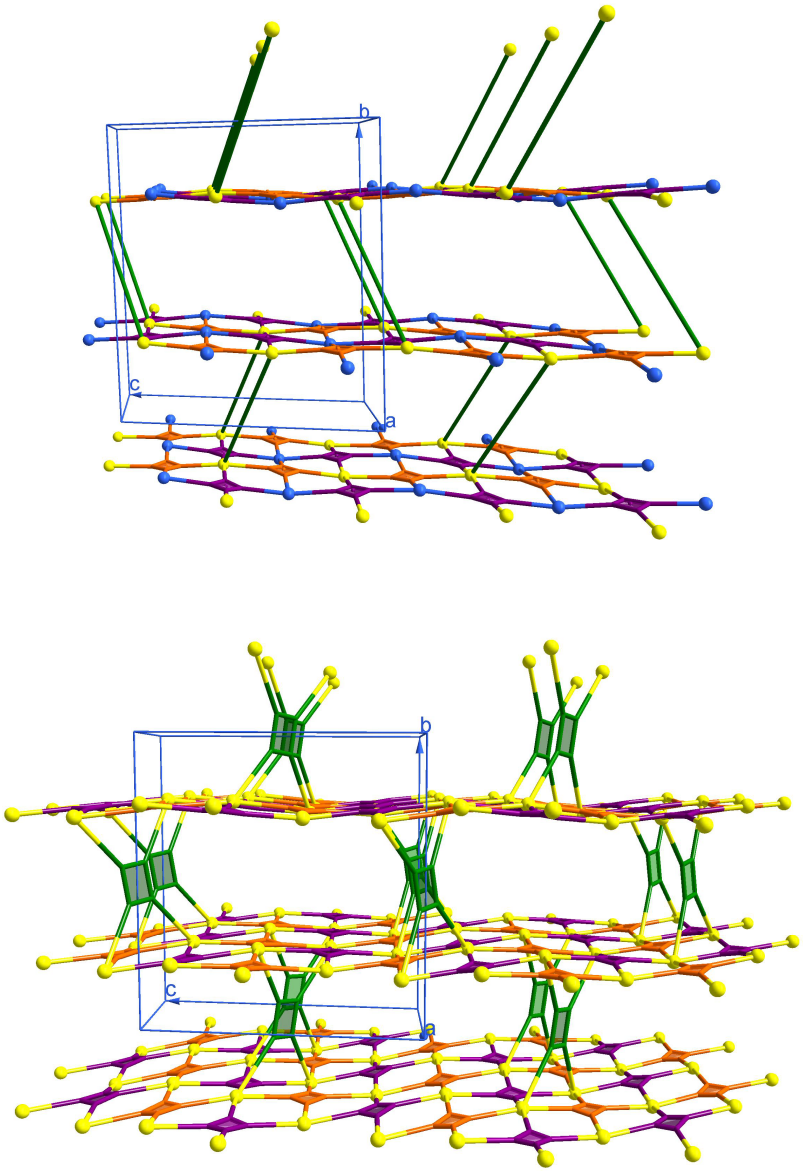

Figure S2. Topographic representation of **1a** (top) and **1b** (bottom) compounds. The four-fold nodes built up from bta^{4-} ligands are represented by squares while the metal nodes five- and four-fold are represented in spheres, yellow and blue, respectively.

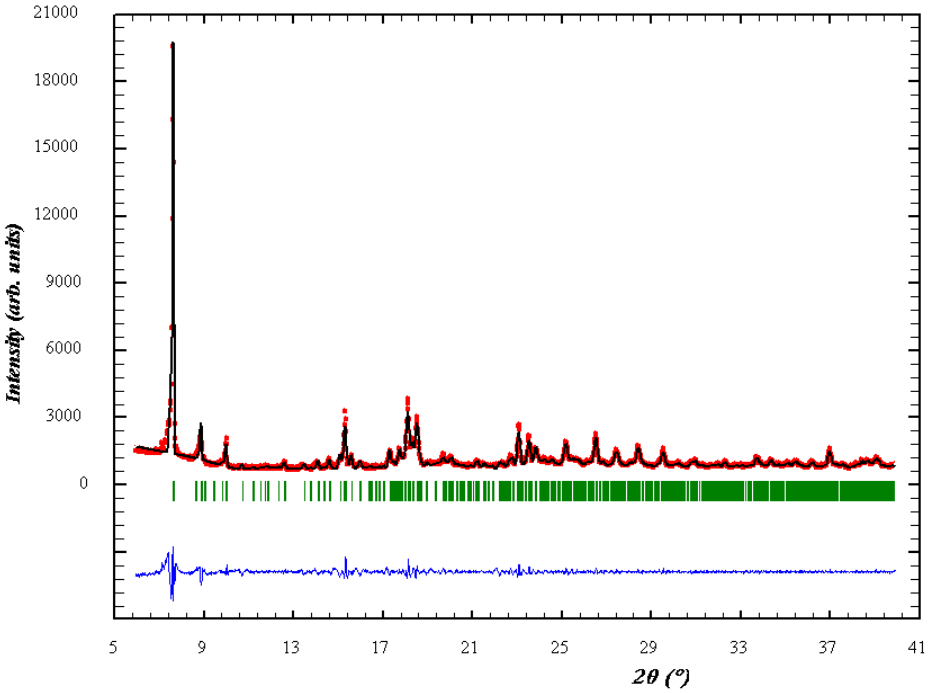

Figure S3. Le Bail fit of the powder X-ray diffraction pattern of $[Pr_4(H_2O)_{18}Cu_4(H_2O)_8bta_5]_n \cdot 14nH_2O$ compound collected on a Philips X´Pert diffractometer with Cu $K\alpha_1$ = 1.54060 Å and Cu $K\alpha_2$ = 1.54443 Å.

Table 1S. Experimental parameters and main crystallographic data for the studied compound collected at RT, with and without dry-nitrogen atmosphere, and 100K with dry-nitrogen atmosphere.

Data	***[Pr$_4$(H$_2$O)$_{18}$Cu$_4$(H$_2$O)$_8$bta$_5$]$_n$·14nH$_2$O (1a)***	***[Pr$_4$(H$_2$O)$_{18}$Cu$_4$(H$_2$O)$_6$bta$_5$]$_n$·16nH$_2$O (1b)***	
Empirical Formula	C_{25} H_{45} Cu_2 O_{40} Pr_2	C_{25} H_{45} Cu_2 O_{40} Pr_2	
Mr (g·mol^{-1})	1394.51	1394.51	
Crystal system	Monoclinic	Monoclinic	
Space group (No.)	$P2_1/n$ (14)	$P2_1/n$ (14)	
λ (Å)	0.7513	0.7388	0.7513
Crystal size (mm)	0.1 × 0.07 × 0.05	0.08 × 0.05 × 0.04	0.1 × 0.07 × 0.05
Dry-nitrogen	off	on	on
Temperature (K)	293(2)	293(2)	100(2)
a (Å)	10.953(2)	10.920(2)	10.906(2)
b (Å)	23.056(5)	20.369(4)	20.212(4)
c (Å)	19.811(4)	19.792(4)	19.769(4)
β (º)	99.88(3)	99.59(3)	99.22(3)
V (Å^3)	4929.0(17)	4340.8(15)	4301.4(15)
Z	4	4	4
D_c (g·cm^{-3})	1.879	2.134	2.156
μ (mm^{-1})	3.194	3.633	3.835
F(000)	2764	2764	2772
Reflection collected	90569	36832	264668
Reflections with I > 2σ(I)	9974	8815	8857
Goodness of fit	1.033	1.033	1.093
Final R indices [I > 2σ(I)]: R1 / wR2	0.0494/0.154	0.0453/0.130	0.0476/0.137
R indices (all data): R1 / wR2	0.0557/0.163	0.0472/0.133	0.0500/0.139

Table 2S. Comparative between atomic positions of compound **1b** collected at two different temperatures.

	100K			**293K**		
Atoms	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Pr(1)	-0.46760(2)	0.126313(13)	0.345064(13)	-0.46276(2)	0.12753(1)	0.34516(1)
Pr(2)	0.83304(3)	0.123936(13)	1.082800(13)	0.83938(2)	0.12635(1)	1.08124(1)
Cu(1)	0.28846(5)	0.17465(3)	0.58907(3)	0.29507(4)	0.17310(2)	0.58911(2)
Cu(2)	0.07202(6)	0.17265(3)	0.83172(3)	0.07855(4)	0.17338(2)	0.83025(2)
C(1)	-0.2618(5)	0.2610(3)	0.5215(2)	-0.2559(3)	0.26067(19)	0.51998(17)
C(2)	-0.2938(5)	0.2972(3)	0.5764(3)	-0.2879(3)	0.29665(18)	0.57495(18)
C(3)	-0.2196(5)	0.2935(3)	0.6407(2)	-0.2139(3)	0.29288(19)	0.63881(18)
C(4)	-0.1179(5)	0.2512(3)	0.6514(2)	-0.1118(3)	0.25086(19)	0.64974(16)
C(5)	-0.0859(5)	0.2144(3)	0.5969(2)	-0.0798(3)	0.21468(19)	0.59537(18)
C(6)	-0.1577(5)	0.2199(3)	0.5318(3)	-0.1524(3)	0.2202(2)	0.53054(18)
C(7)	-0.3321(4)	0.2683(3)	0.4500(2)	-0.3266(3)	0.26787(18)	0.44879(18)
C(8)	-0.4160(5)	0.3329(3)	0.5716(2)	-0.4104(3)	0.33130(19)	0.56951(18)
C(9)	-0.0515(4)	0.2412(3)	0.7227(2)	-0.0445(3)	0.2414(2)	0.72115(17)
C(10)	0.0299(5)	0.1722(3)	0.6059(2)	0.0344(3)	0.17169(19)	0.60493(18)
C(11)	-0.1264(5)	-0.0139(3)	0.4871(3)	-0.1270(3)	-0.01263(18)	0.48738(19)
C(12)	-0.0776(4)	0.0340(2)	0.4478(2)	-0.0773(3)	0.03424(19)	0.44890(19)
C(13)	0.0490(5)	0.0470(3)	0.4607(3)	0.0494(3)	0.04653(19)	0.46142(19)
C(14)	-0.2617(5)	-0.0320(3)	0.4751(3)	-0.2622(3)	-0.03017(18)	0.47661(19)
C(15)	-0.1598(5)	0.0741(3)	0.3942(3)	-0.1576(4)	0.0747(2)	0.3958(2)
C(20)	0.4494(5)	0.2057(3)	0.8265(2)	0.4558(3)	0.20737(19)	0.82613(17)
C(21)	0.4792(5)	0.2430(3)	0.7718(3)	0.4855(3)	0.24385(19)	0.77114(17)
C(22)	0.5816(5)	0.2857(3)	0.7830(3)	0.5879(3)	0.2860(2)	0.78210(18)
C(23)	0.6571(4)	0.2897(3)	0.8462(3)	0.6626(3)	0.29044(19)	0.84591(18)
C(24)	0.6273(4)	0.2516(3)	0.9008(2)	0.6329(3)	0.25304(19)	0.90045(17)
C(25)	0.5252(5)	0.2099(3)	0.8909(3)	0.5306(3)	0.21225(19)	0.89026(18)
C(26)	0.3318(5)	0.1648(3)	0.8231(2)	0.3401(4)	0.16653(19)	0.82229(19)
C(27)	0.4096(5)	0.2348(3)	0.7007(3)	0.4165(3)	0.23419(19)	0.70004(18)
C(28)	0.7768(5)	0.3284(3)	0.8537(2)	0.7835(3)	0.32807(19)	0.85324(19)
C(29)	0.6957(4)	0.2584(3)	0.9728(2)	0.7018(3)	0.26004(19)	0.97244(17)
O(1)	-0.3664(3)	0.21728(19)	0.41589(18)	-0.3607(3)	0.21790(15)	0.41440(14)
O(2)	-0.3465(4)	0.32689(19)	0.42729(18)	-0.3430(3)	0.32583(14)	0.42641(13)
O(3)	-0.5088(3)	0.30793(18)	0.53358(18)	-0.5032(2)	0.30586(14)	0.53162(13)
O(4)	-0.4263(4)	0.38292(19)	0.6079(2)	-0.4211(3)	0.38131(15)	0.60519(17)
O(5)	-0.0445(4)	0.28809(19)	0.76432(18)	-0.0380(3)	0.28839(16)	0.76223(14)
O(6)	-0.0091(3)	0.18401(19)	0.73727(18)	-0.0019(3)	0.18529(15)	0.73615(13)
O(7)	0.1310(3)	0.20651(19)	0.61441(18)	0.1362(2)	0.20441(14)	0.61331(14)
O(8)	0.0239(4)	0.11182(19)	0.6021(2)	0.0245(3)	0.11220(16)	0.60178(18)
O(9)	-0.3065(3)	-0.06637(19)	0.42413(19)	-0.3083(3)	-0.06429(14)	0.42520(15)
O(10)	-0.3239(3)	-0.01214(19)	0.52025(19)	-0.3236(3)	-0.01061(16)	0.52169(15)
O(11)	-0.2754(3)	0.07446(19)	0.39646(19)	-0.2738(2)	0.07505(15)	0.39640(15)
O(12)	-0.1088(4)	0.1058(2)	0.3516(2)	-0.1070(3)	0.1073(2)	0.3543(2)
O(13)	0.2315(3)	0.19662(18)	0.80321(17)	0.2392(2)	0.19737(14)	0.80368(14)
O(14)	0.3388(4)	0.1070(2)	0.8436(2)	0.3486(3)	0.10862(16)	0.84093(19)
O(15)	0.3676(3)	0.17725(19)	0.68455(18)	0.3746(3)	0.17749(14)	0.68504(13)
O(16)	0.4012(3)	0.2831(2)	0.66028(19)	0.4076(3)	0.28115(15)	0.65864(14)
O(17)	0.7851(4)	0.38107(19)	0.8212(2)	0.7922(3)	0.38029(14)	0.82240(18)
O(18)	0.8708(3)	0.30260(19)	0.89071(18)	0.8772(2)	0.30050(14)	0.88895(14)
O(19)	0.7242(3)	0.20695(19)	1.00757(18)	0.7293(3)	0.20909(14)	1.00728(14)
O(20)	0.7129(3)	0.31714(18)	0.99410(18)	0.7218(3)	0.31769(13)	0.99350(13)
O(1W)	-0.4879(3)	0.08937(19)	0.46614(19)	-0.4876(3)	0.08899(14)	0.46484(14)
O(2W)	-0.4948(4)	0.00112(19)	0.3450(2)	-0.5009(4)	0.00282(16)	0.34465(18)
O(3W)	-0.4883(5)	0.0793(2)	0.2268(2)	-0.4842(5)	0.0785(2)	0.2270(2)
O(4W)	-0.2920(3)	0.17205(18)	0.28557(18)	-0.2869(3)	0.17131(14)	0.28436(14)
O(5W)	0.6568(4)	0.1626(2)	1.14459(19)	0.6624(3)	0.16429(16)	1.14216(16)
O(6W)	0.8660(6)	0.0763(2)	1.2043(2)	0.8834(5)	0.07940(19)	1.20146(19)
O(7W)	0.8750(4)	0.00202(19)	1.0795(2)	0.8863(4)	0.00413(17)	1.07865(18)

O(8W)	0.6398(4)	0.0620(2)	1.0380(2)	0.6452(3)	0.0622(2)	1.0382(2)
O(9W)	0.8834(4)	0.0806(2)	0.9700(2)	0.8807(4)	0.08321(17)	0.96671(17)
O(10W)	-0.0919(4)	0.1738(2)	0.8664(2)	-0.0898(3)	0.17247(15)	0.86130(15)
O(11W)	0.0556(4)	0.0647(2)	0.8067(2)	0.0702(5)	0.06607(19)	0.8088(2)
O(13W)	0.4593(3)	0.18074(19)	0.55983(18)	0.4666(3)	0.17776(14)	0.56217(15)
O(1X)	0.7488(4)	-0.0257(2)	0.9138(2)	0.7484(5)	-0.0228(2)	0.9071(3)
O(2X)	0.8088(4)	0.0596(2)	0.6234(3)	0.8093(5)	0.0610(2)	0.6317(2)
O(3X)	0.6157(4)	-0.0754(2)	1.0124(2)	0.6146(4)	-0.0760(2)	1.0108(3)
O(4X)	0.5478(5)	0.0366(2)	0.8371(3)	0.5596(5)	0.0440(3)	0.8171(4)
O(5X)	0.1931(5)	0.0470(3)	0.7090(2)	0.1914(5)	0.0443(3)	0.7074(2)
O(6X)	0.6279(5)	0.1248(3)	0.6641(3)	0.6504(18)	0.1251(8)	0.6789(15)
O(7X)	0.8443(5)	-0.0035(3)	0.7430(3)	0.8632(6)	-0.0211(3)	0.7458(3)
O(8X)	0.7289(5)	0.1083(3)	0.7925(3)	0.7318(10)	0.1215(7)	0.7669(8)