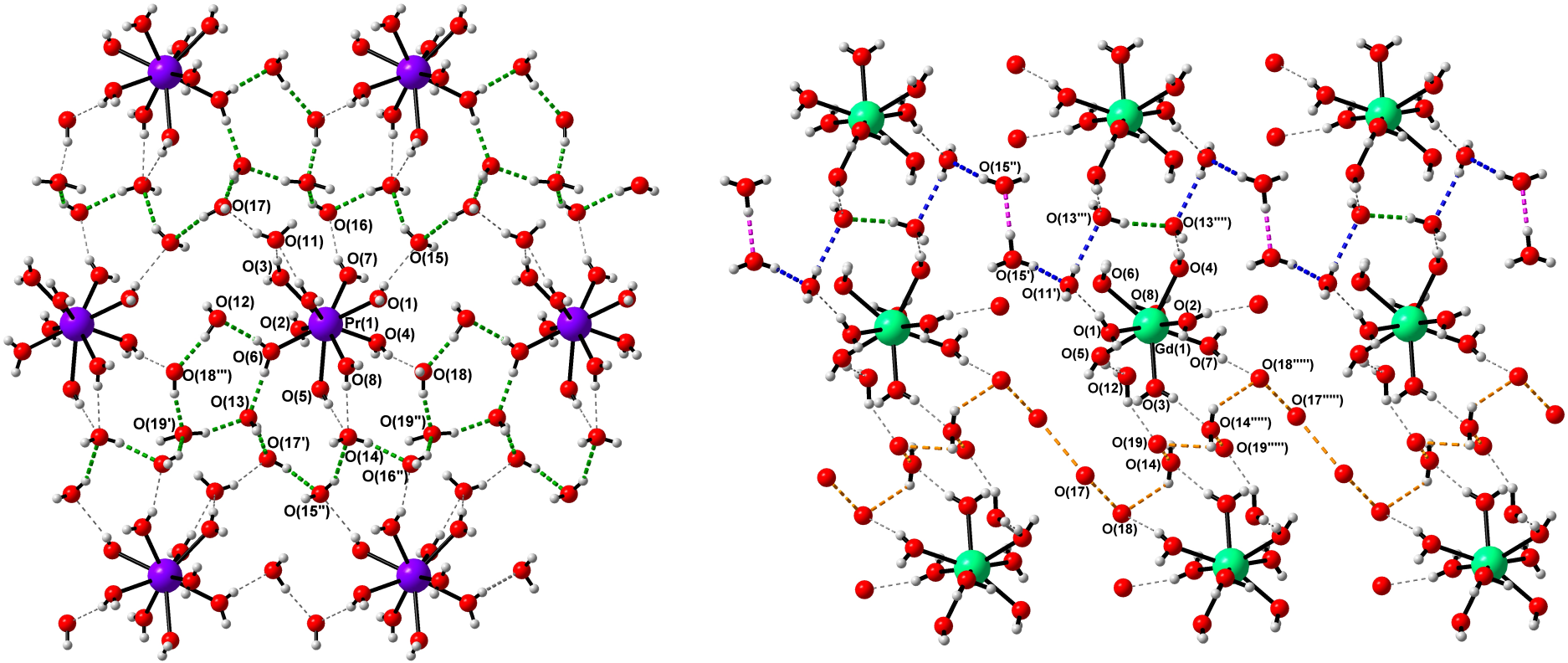

Fig. S1 (Left) A hydrogen-bonded layer in the structure of **1** showing the lattice waters between the $[Pr(OH_2)_9]^{3+}$ cationic pillars. Pr purple, O red, H pale grey. Hydrogen bonds defining the helices and cyclic pentamers of water molecules are highlighted in green.(Right) A hydrogen-bonded layer in the structure of **5** showing the lattice waters between the $[Gd(OH_2)_9]^{3+}$ cationic pillars. Gd green, O red, H pale grey. In the structure of **5**, crystal waters also associate to form two independent helical chains. One of these can best be described as $\cdot\cdot(H_2O)\cdot\cdot(H_5O_2)^{+}\cdot\cdot(H_2O)\cdot\cdot(H_3O_2)^{-}\cdot\cdot(H_2O)\cdot\cdot$ in which hydrogen bonds highlighted in blue and pink, while the second water infinite tape is highlighted in orange

Table S1 Parameters for hydrogen bonding in **1**.

D–H ··A	D ··H/Å	H ··A/Å	D ··A/Å	D–H ··A(º)
N1–H1 ··N7[a]	0.96(5)	1.82(5)	2.772(6)	177(3)
O1–H11 ··N21	0.81(4)	1.97(5)	2.765(5)	167(5)
O1–H12 ··O15	0.66(6)	2.27(6)	2.890(6)	157(7)
N13–H13 ··N11[a]	0.77(5)	2.00(5)	2.757(6)	172(4)
N17–H17 ··N23[a]	0.82(5)	1.87(5)	2.682(5)	173(5)
O2–H21 ··N6[b]	0.67(6)	2.15(6)	2.803(5)	166(6)
O2–H22 ··N24[b]	0.75(5)	2.12(5)	2.830(5)	159(6)
O3–H31 ··O11	0.88(5)	1.95(5)	2.770(5)	155(5)
O3–H32 ··N18[c]	0.73(5)	2.27(6)	2.932(5)	151(6)
O4–H41 ··O18	0.82(5)	1.90(5)	2.695(5)	162(5)
O4–H42 ··N5[b]	0.81(5)	2.06(5)	2.861(5)	167(6)
O5–H52 ··O14	0.79(6)	2.18(6)	2.942(5)	165(6)
O6–H61 ··O12	0.74(6)	1.96(6)	2.689(6)	170(6)
O6–H62 ··O13	0.89(6)	1.89(6)	2.767(5)	171(5)
O7–H71 ··N20[b]	0.78(6)	2.06(6)	2.832(6)	177(6)
O7–H72 ··O16	0.77(6)	2.03(6)	2.770(5)	161(6)
O8–H81 ··O14	0.78(6)	2.04(6)	2.822(5)	176(7)
O8–H82 ··N10	0.74(5)	2.11(5)	2.840(5)	165(6)
O9–H91 ··O11	0.79(6)	1.94(6)	2.724(5)	173(4)
O9–H92 ··N22	0.67(5)	2.22(5)	2.877(5)	166(5)
O11–H111 ··O17	0.83(5)	1.98(5)	2.778(6)	161(5)
O11–H112 ··N4	0.91(5)	1.94(5)	2.810(6)	157(4)
O12–H121 ··O18[e]	0.87(5)	1.87(5)	2.730(6)	168(5)
O12–H122 ··N19[c]	0.85(5)	2.12(5)	2.960(5)	169(5)
O13–H131 ··O17[f]	0.99(5)	1.85(5)	2.794(5)	161(5)
O13–H132 ··N15[d]	0.92(5)	1.91(5)	2.808(5)	167(5)
O14–H141 ··O16[g]	0.81(4)	1.99(5)	2.761(6)	159(5)
O14–H142 ··N16[d]	0.82(5)	2.03(5)	2.854(6)	175(3)
O15–H151 ··N19[b]	0.85(5)	2.33(5)	3.010(5)	138(5)
O15–H152 ··O14[h]	0.85(5)	2.18(5)	2.969(5)	154(5)
O16–H161 ··N12[a]	0.79(4)	2.05(4)	2.833(5)	175(3)
O16–H162 ··O19	0.82(5)	2.20(5)	2.830(5)	134(4)
O17–H171 ··O15[e]	0.85(5)	2.10(5)	2.878(5)	153(4)
O17–H172 ··N8[e]	0.88(4)	2.03(4)	2.898(5)	171(6)
O18–H181 ··O19[g]	0.92(4)	1.73(4)	2.635(6)	168(5)
O18–H182 ··N9	0.86(5)	1.97(5)	2.804(5)	166(6)
O19–H191 ··O13[e]	1.05(6)	1.88(5)	2.873(6)	158(5)
O19–H192 ··N3[e]	1.06(5)	1.82(5)	2.840(6)	160(4)

[a] 1+*x*, *y*, *z* [b] –1/2+*x*, 1/2–*y*, –1/2+*z*, [c] –3/2+*x*, 1/2–*y*,–1/2+*z*, [d] 1–*x*, –*y*, 1–*z*, [e] –1+*x*, *y*, *z* [f] –1/2–*x*, 1/2+*y*, 1/2–*z* [g] 1/2–*x*, –1/2 + *y*, 1/2–*z* [h] 1/2–*x*, 1/2+*y*, 1/2–*z*

Table S2 Parameters for hydrogen bonding in **5**.

D–H ··A	D ··H/Å	H ··A/Å	D ··A/Å	D–H ··A(º)
N(4)–H(4) ··N(6)[a]	0.88	1.87	2.7500	172
O(1)–H(11) ··O(11)[b]	0.81	1.96	2.7527	168
O(1)–H(12) ··N(10)[c]	0.84	1.98	2.8208	177
N(16)–H(16) ··N(11)[d]	0.75	2.00	2.7484	173
O(2)–H(21) ··O(16)[e]	0.78	1.97	2.7179	163
O(2)–H(22) ··N(9)[c]	0.83	1.92	2.7482	177
N(24)–H(24) ··N(19)[f]	0.86	1.90	2.7495	170
O(3)–H(31) ··O(14)[e]	0.83	1.90	2.7174	168
O(3)–H(32) ··N(13)	0.82	2.00	2.8207	175
O(4)–H(41) ··N(7)[g]	0.89	1.95	2.7842	156
O(4)–H(41) ··N(8)[g]	0.89	2.62	3.2580	129
O(4)–H(42) ··O(13)[e]	0.91	1.80	2.7040	170
O(5)–H(51) ··O(12)[h]	0.85	1.82	2.6517	165
O(5)–H(52) ··N(14)	0.85	1.94	2.7860	172
O(6)–H(62) ··N(8)[g]	0.96	1.80	2.7452	168
O(7)–H(71) ··O(18)[e]	0.82	1.93	2.7321	168
O(7)–H(72) ··N(1)[e]	0.83	2.11	2.8828	154
O(8)–H(81) ··N(5)[e]	0.84	2.08	2.8308	149
O(8)–H(82) ··N(3)[h]	0.98	2.53	3.4648	161
O(11)–H(111) ··N(20)	0.85	2.13	2.9826	177
O(11)–H(112) ··O(13)[i]	0.66	2.17	2.8089	164
O(12)–H(121) ··O(19)[h]	0.96	1.95	2.7986	146
O(12)–H(122) ··N(17)	0.97	2.57	3.4391	150
O(12)–H(122) ··N(18)	0.97	1.79	2.7509	176
O(13)–H(131) ··N(22)[j]	0.82	2.05	2.8047	153
O(13)–H(132) ··O(13)[k]	0.82	2.07	2.8674	163
O(14)–H(141) ··N(12)[e]	0.92	1.94	2.8409	164
O(14)–H(142) ··O(18)	0.86	2.40	2.7364	104
O(15)–H(151) ··N(21)	0.88	1.92	2.7931	175
O(15)–H(151) ··N(22)	0.88	2.58	3.3354	145
O(15)–H(152) ··O(11)	0.80	2.12	2.7924	141
O(16)–H(161) ··N(2)	0.91	2.05	2.9007	157
O(16)–H(162) ··O(15)[j]	1.20	2.04	2.8163	118

[a] x, –1+ y, z, [b] 1– x, – y, [c] – x, – y,1– z, 1 – z, [d]. 1+ x, y, z, [e]. – x, 1– y, 1– z, [f] –1+ x, y, z, [g] x, y, 1 + z, [h] 1– x, 1– y, 1– z, [i] 1– x, 1– y, – z, [j] x, 1+ y, z, [k] – x, 2– y, – z

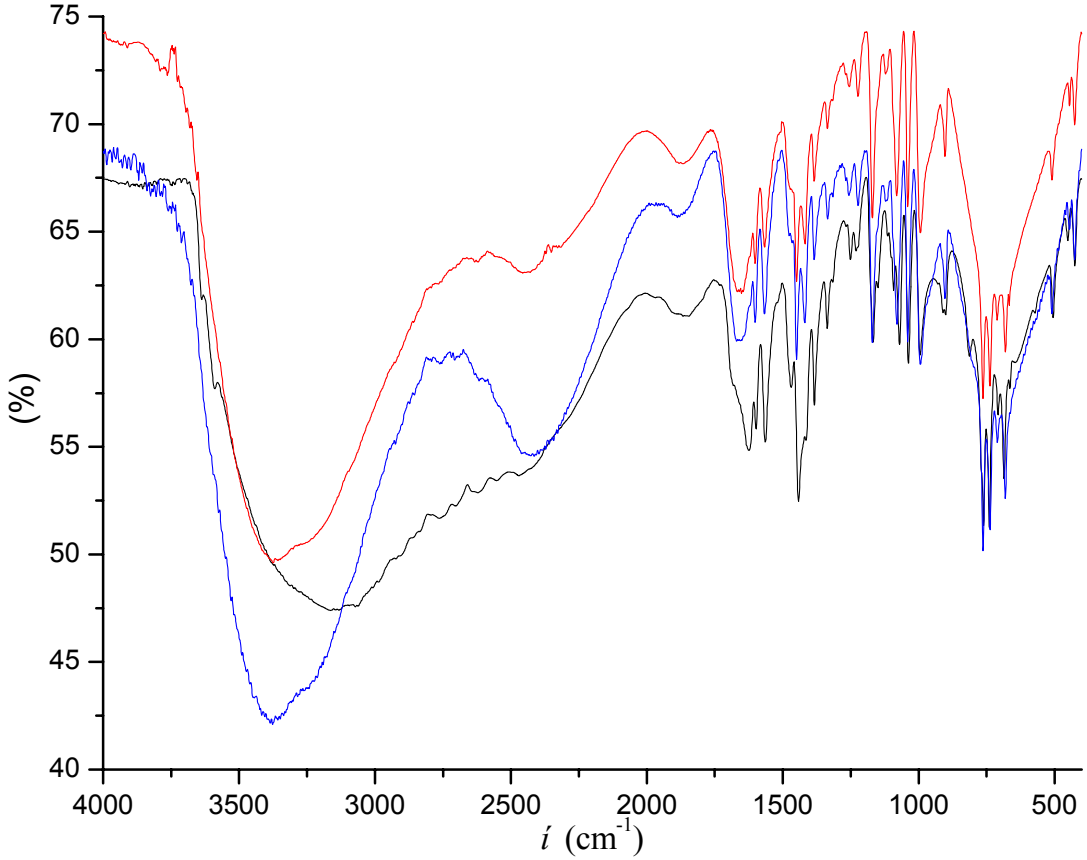

Fig. S2 IR spectra's of compound **1** (blue) heated sample (black) and rehydrated sample (red)

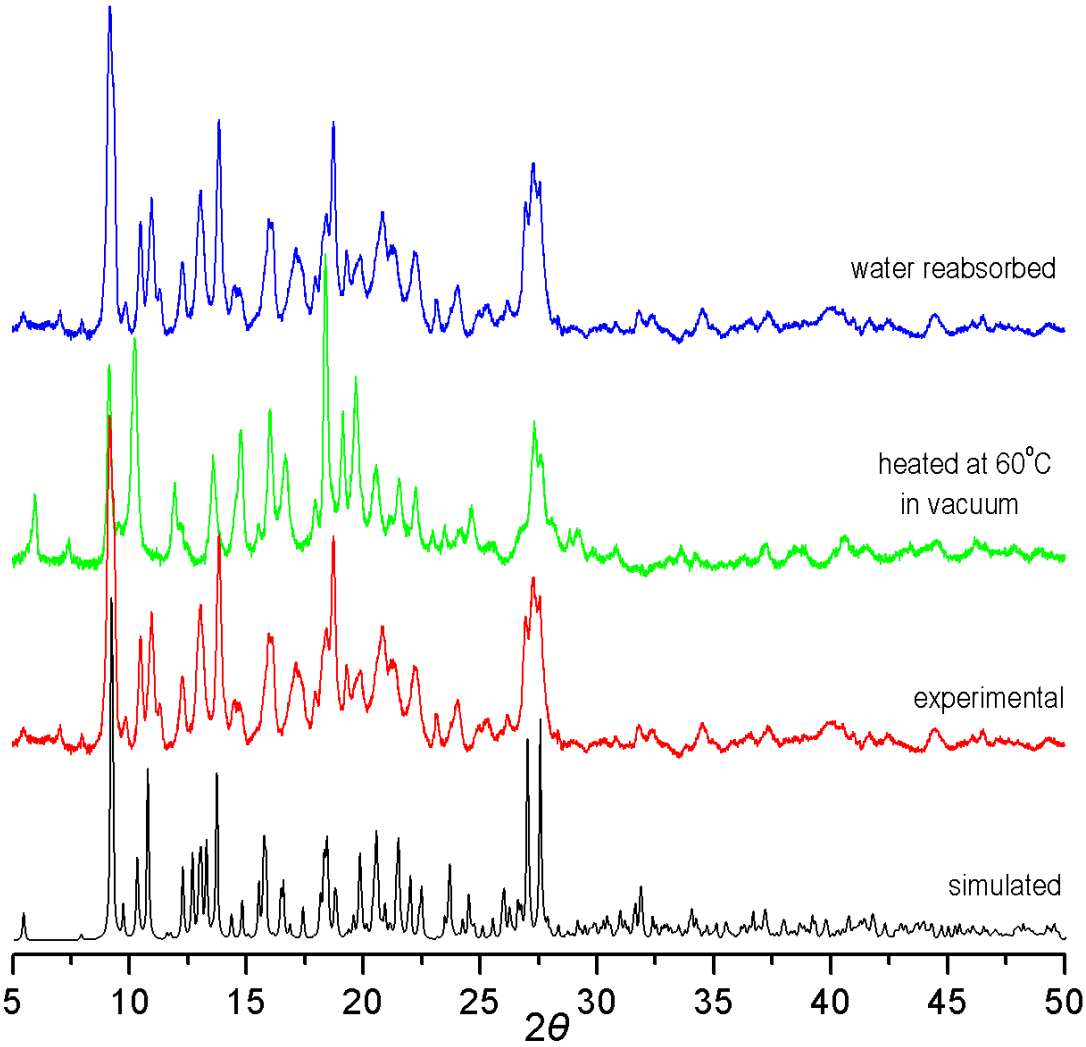

Fig.S3 XRPD patterns for the $[Gd(H_2O)_8](m\text{–}BDTH)_3\cdot 9(H_2O)$ **5** simulated (black), experimental (red), heated at 60°C in vacuum (green) and water reabsorbed (blue).