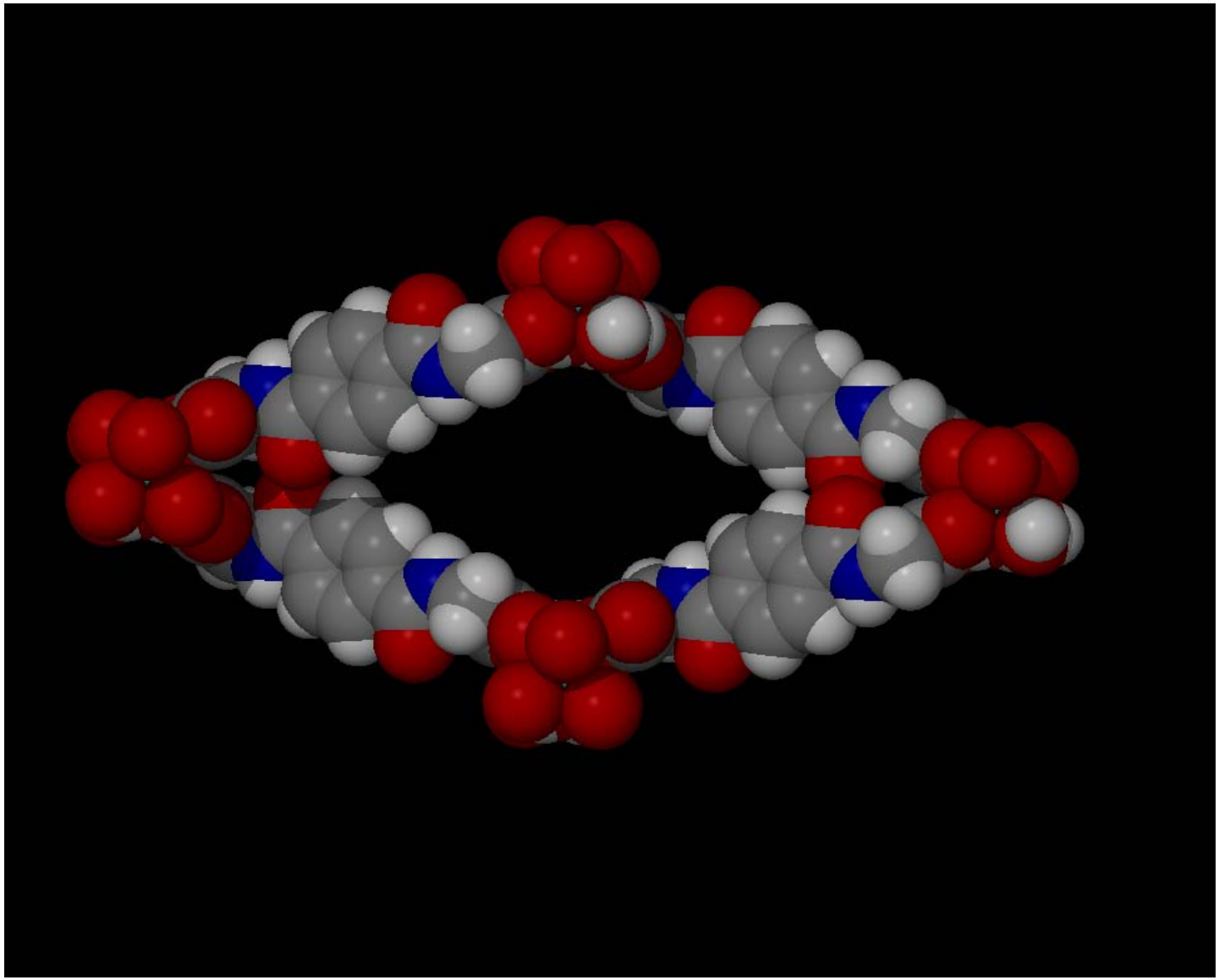


Fig. S1. The rhombic channels formed in the cds net, in the structures of **1** and **2**.

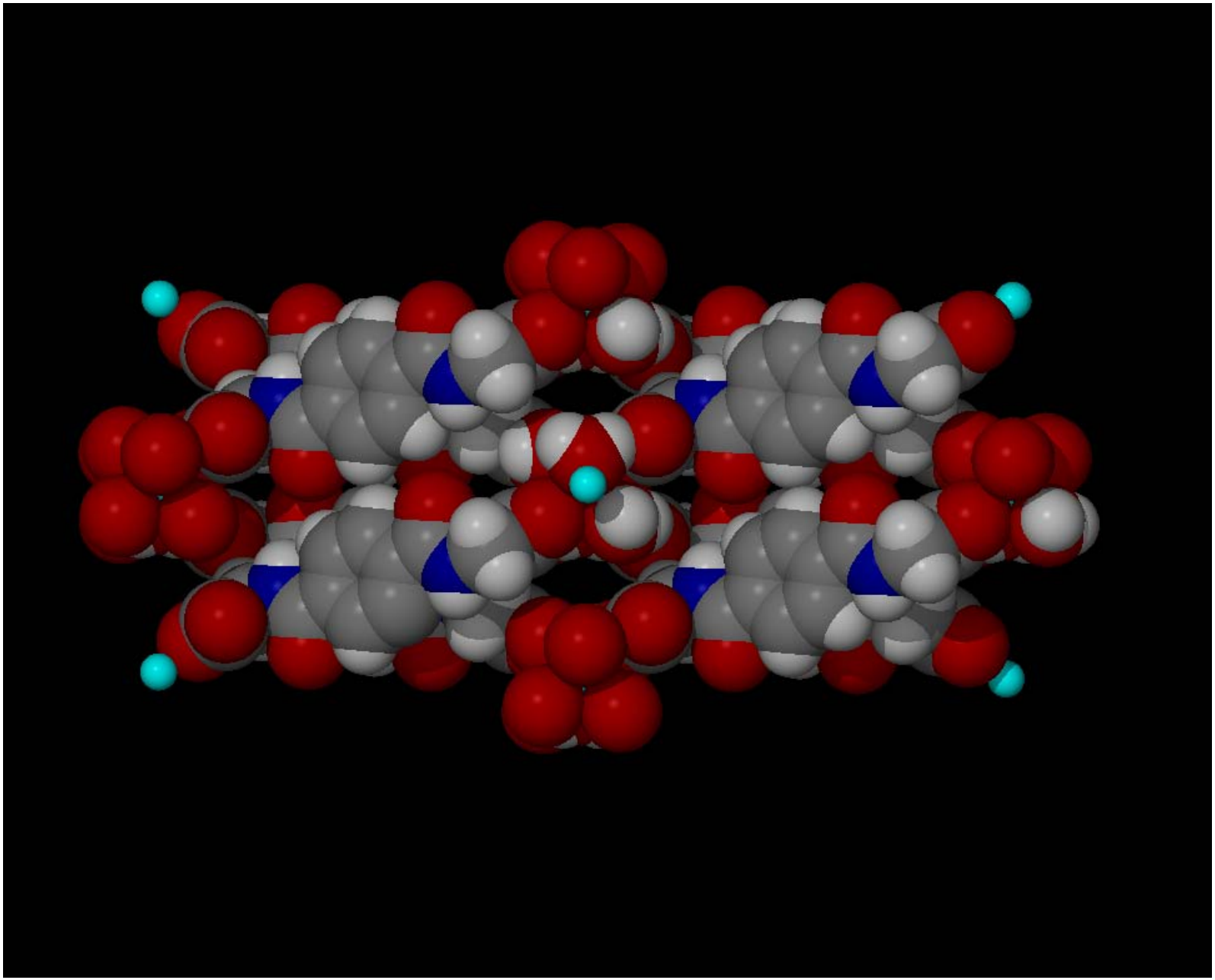


Fig. S2. The rhombic channels formed in the cds net, in the structures of **1** and **2** are filed with the metal columns of the interpenetrated network..

Fig. S3. TG (lines) and DTA (dashed lines) curves for **1**(red) and **2**(blue)

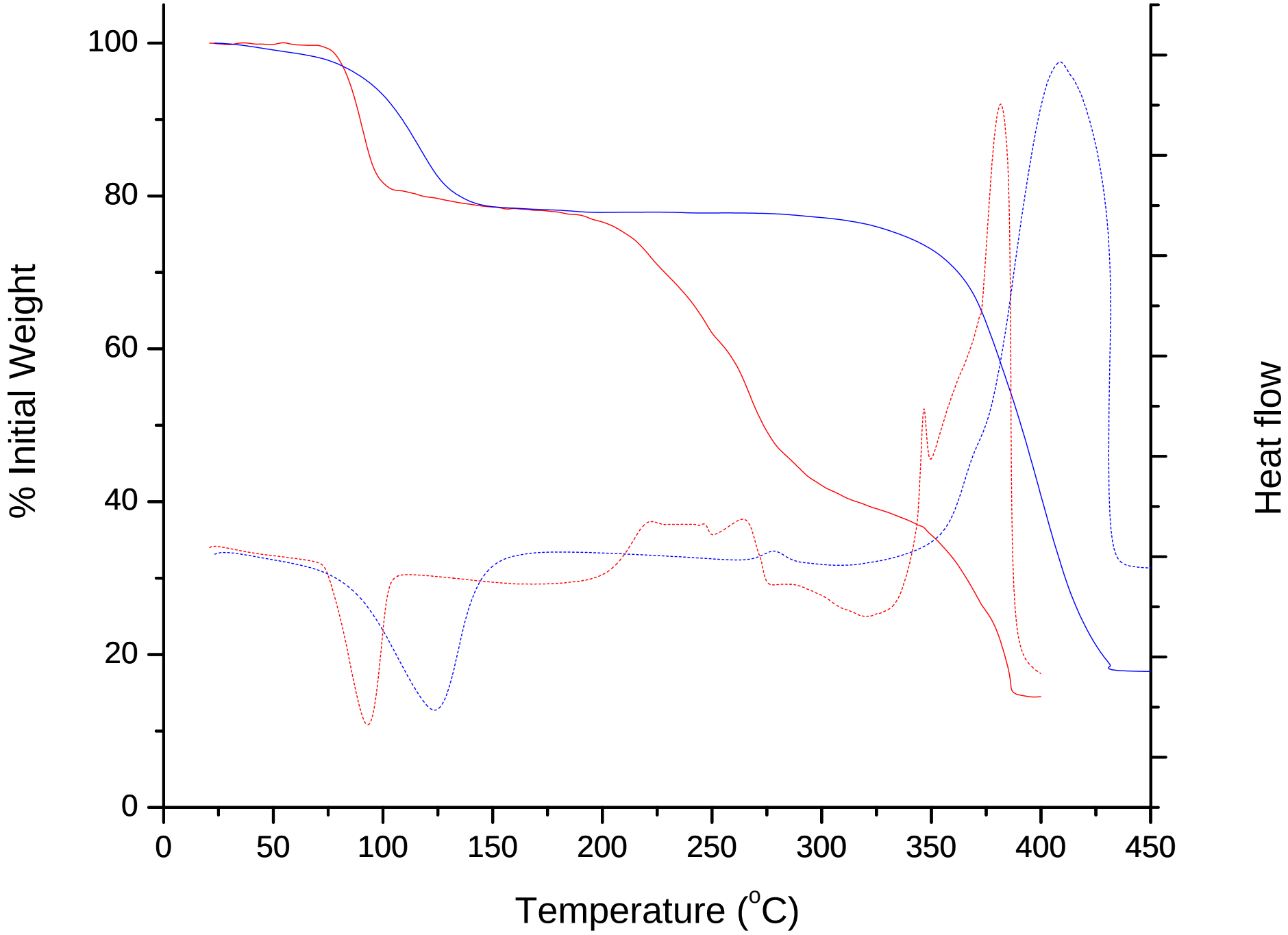


Fig. S4a. XRPD patterns for the $[CuL(H_2O)_2]_n.nH_2O$ system

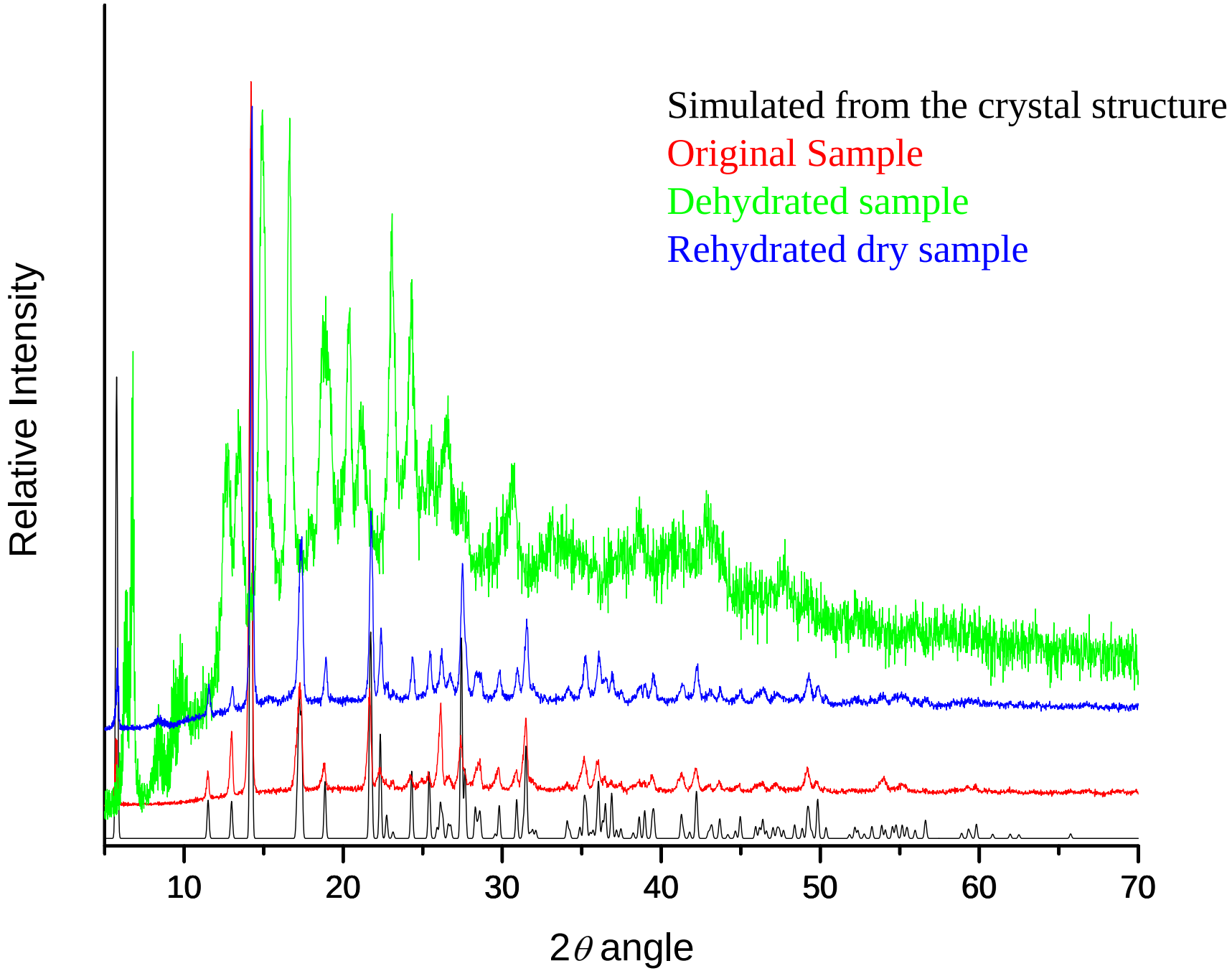


Fig. S4b. XRPD patterns for the $[CoL(H_2O)_2]_n.nH_2O$ system

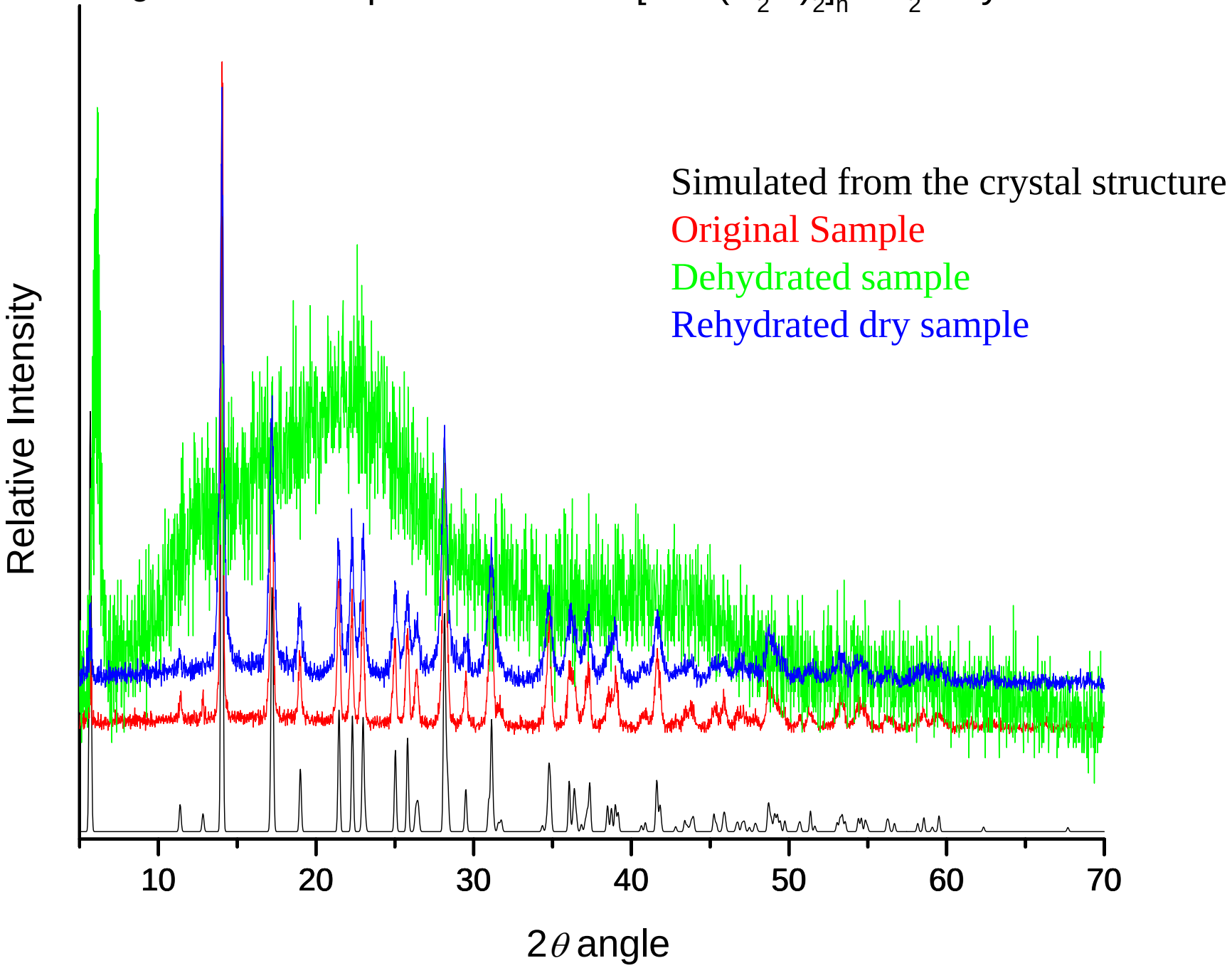


Fig.S5a. UV-Vis Diffuse Reflectance Spectra (DRS) for the $[CuL(H_2O)_3]_n.nH_2O$ system

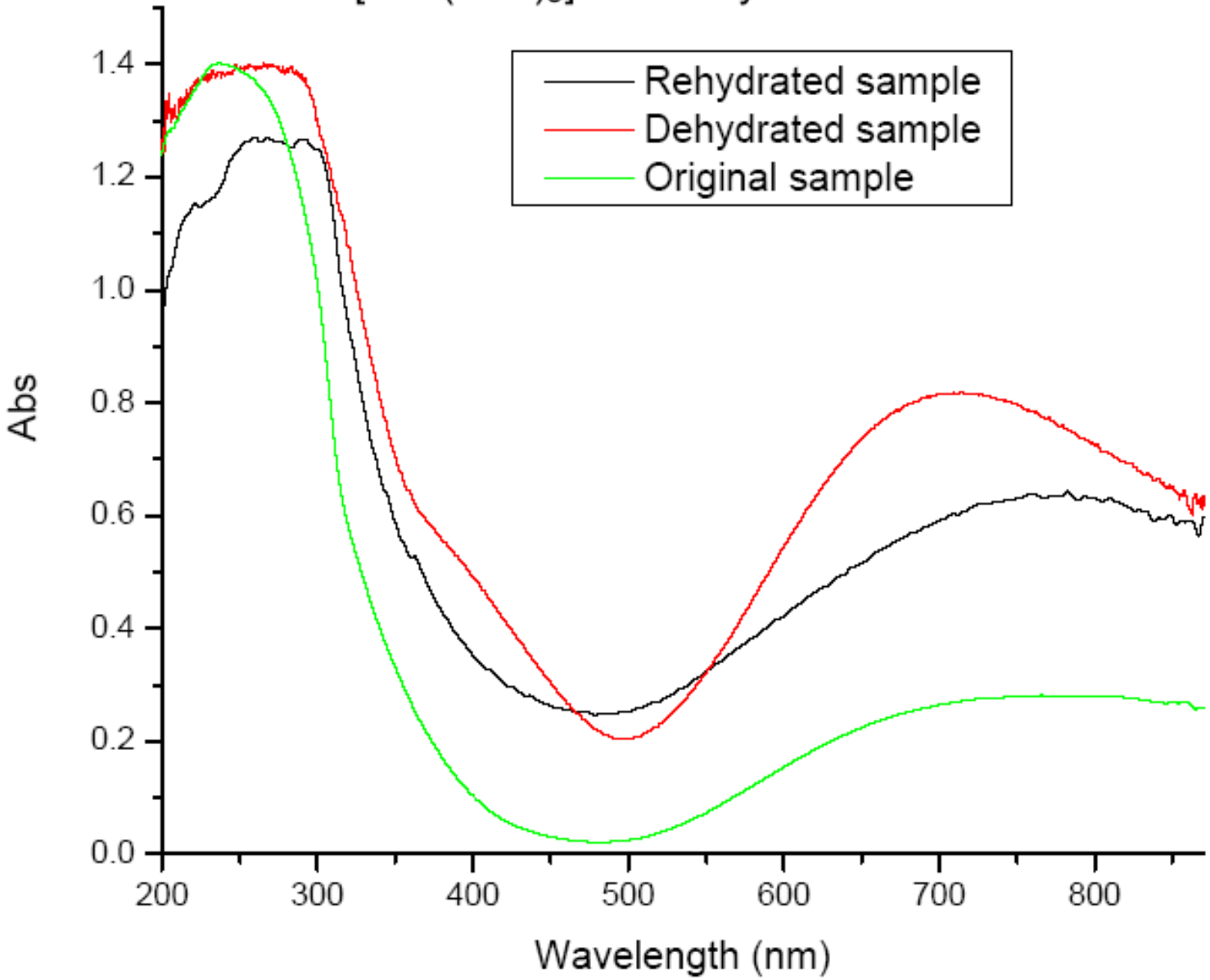
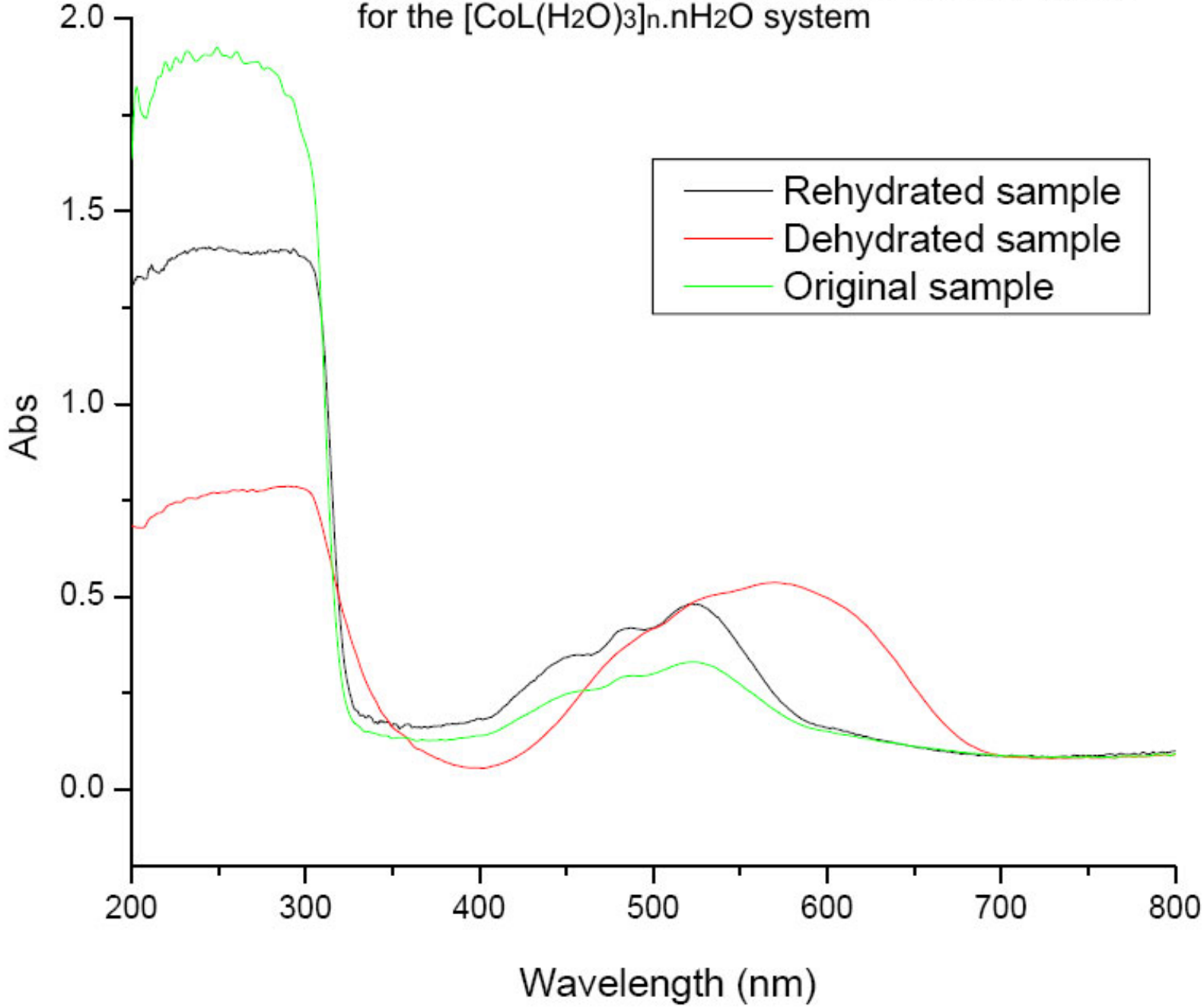


Fig.S5b. UV-Vis Diffuse Reflectance Spectra (DRS) for the $[CoL(H_2O)_3]_n.nH_2O$ system



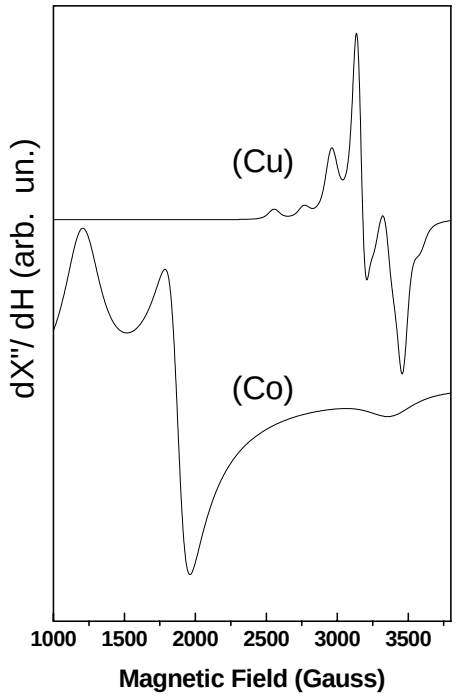


Fig. S6. Powder EPR spectrum of **1** (top) and **2** (bottom). Experimental conditions: Temperature 4.3K, microwave frequency, 9.45 GHz, Mod. Ampl. 12.5 Gpp, microwave power 32mW, mod. Frequency 100KHz.

Table S1. Hydrogen bonding parameters (Å, °) for [Cu(μ-TBG)(μ-H_2O)(H_2O)$_2$]·2H_2O (**1**).

D-H	d(D-H)	d(H..A)	DHA	d(D..A)	A
N1-H1	0.785	2.150	156.75	2.888	O6 [x, y+1, z]
O4-H41	0.814	1.921	153.47	2.675	O2 [x-1/2, -y, z]
O5-H51	0.829	1.963	175.95	2.790	O6 [-x+2, -y, -z+2]
O5-H52	0.802	1.925	170.72	2.719	O1 [-x+3/2, y, -z+2]
O6-H61	0.780	1.949	169.78	2.719	O3
O6-H62	0.717	2.251	150.22	2.896	O2 [x-1/2, -y, z]

Table S2. Hydrogen bonding parameters (Å, °) for [Co(μ-TBG)(μ-H_2O)(H_2O)$_2$]·2H_2O (**2**).

D-H	d(D-H)	d(H..A)	DHA	d(D..A)	A
N1-H1	0.922	2.064	149.44	2.896	O6 [x, y-1, z]
O4-H41	0.888	1.799	160.08	2.651	O2
O5-H51	0.859	1.928	172.01	2.781	O6 [-x, -y, -z]
O5-H52	0.917	1.820	169.88	2.727	O1 [-x-1/2, y, -z]
O6-H61	0.891	1.881	156.90	2.723	O3
O6-H62	0.887	2.197	137.87	2.916	O2 [x-1/2, -y, z]

Table S3. Diagnostic IR data for the ligand, its potassium salt and the prepared complexes.

	ν(N-H)	ν(O-H)	$\nu_{as}(CO_2)$	ν(C=O)$_{amide}$	δ(N-H)	$\nu_s(CO_2)$
H_2TBG	3363-3307	2637	1711	1639	1554	1229
K_2TBG	3341	-	1603	1638	1566	1308
1	3336	-	1607	1645	1559	1310
1 – dehydrated	3380-3322	-	1607	1627	1550	1308
1 – rehydrated	3339	-	1609	1644	1562	1313
2	3327	-	1605	1643	1559	1318
2 – dehydrated	3396	-	1619	1639	1561	1293
2 – rehydrated	3326	-	1606	1643	1560	1319