Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Six new 3*d*-4*f* heterometallic coordination polymers constructed from pyrazole-bridged $Cu^{II}Ln^{III}$ dinuclear units

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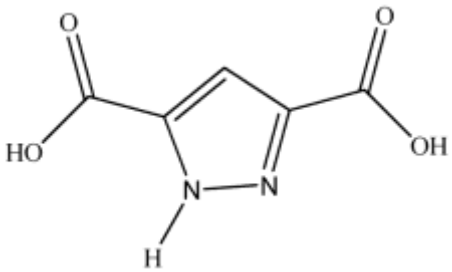

Scheme S1: the molecular structure of H_3pdc ligand

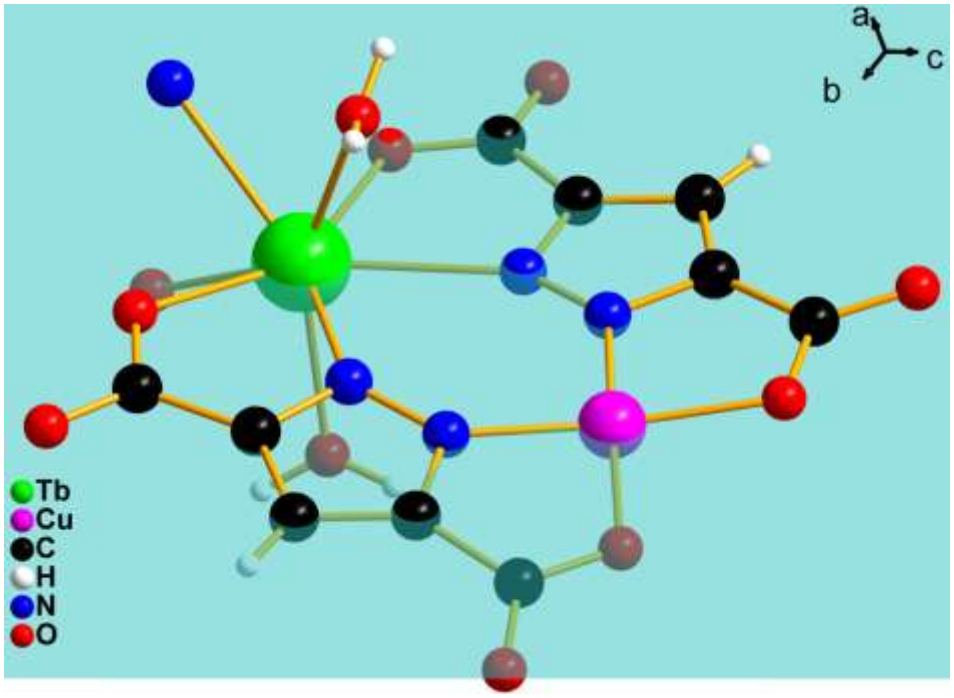

Fig. S1: The cyan plane was drawn through two aromatic rings showing that the two metal atoms (Cu(1) and Tb(1)) re roughly located in this plane together with the pdc^{3-} ligand.

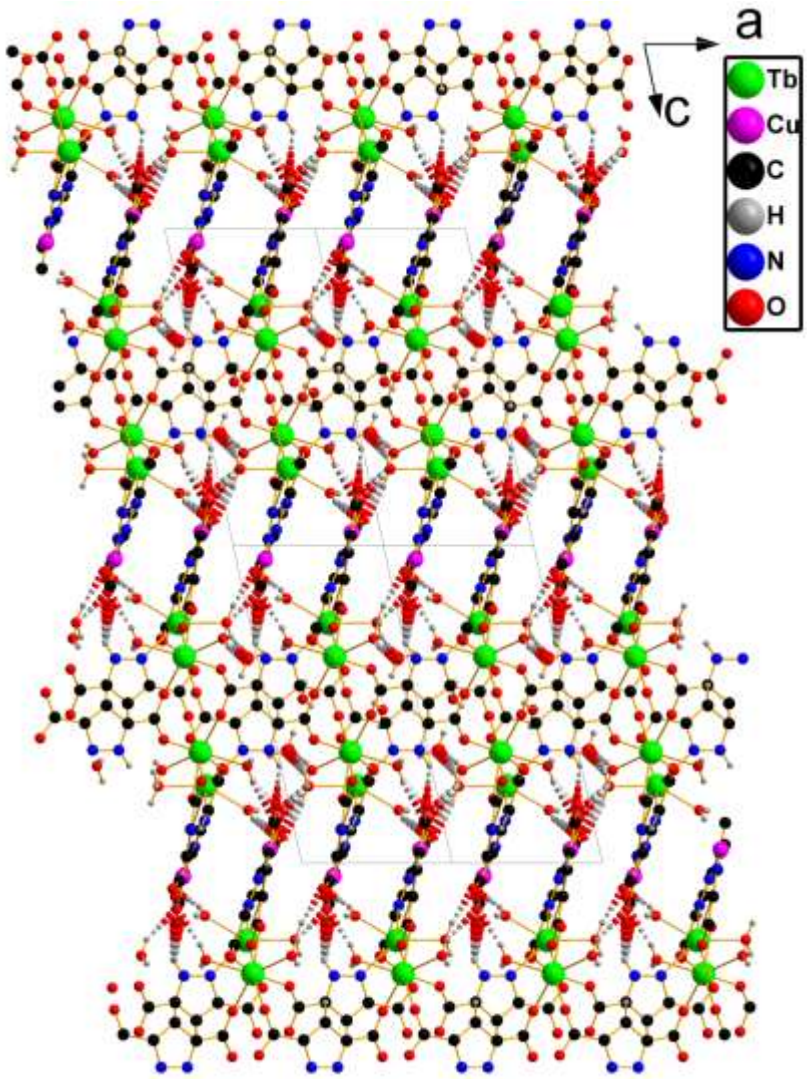

Fig. S2: Packing structure of **1** view down the *b*-axis. The hydrogen bonding interactions between layers are highlighted in two colors leading the 2-D network to the formation of a 3-D supramolecular framework. There are H-bonds in the pores via the guest water molecules not highlighted.

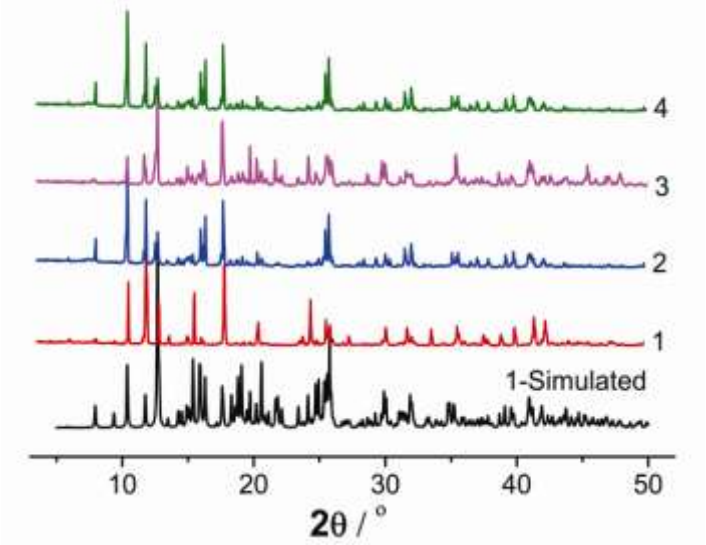

Fig. S3: PXRD patterns for compounds **1-4** and simulated from single crystal data.

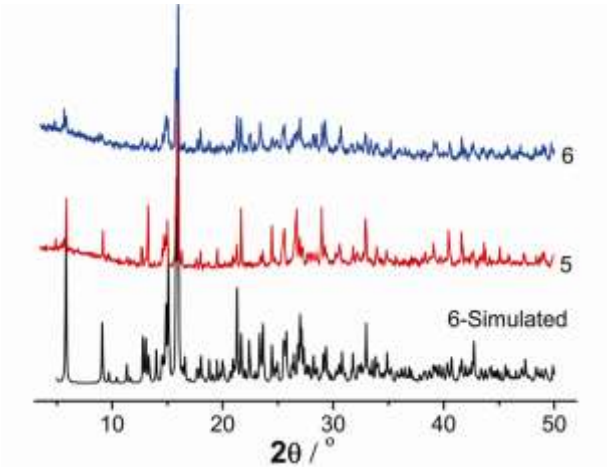

Fig. S4: PXRD patterns for compounds **5** and **6** and simulated from single crystal data.

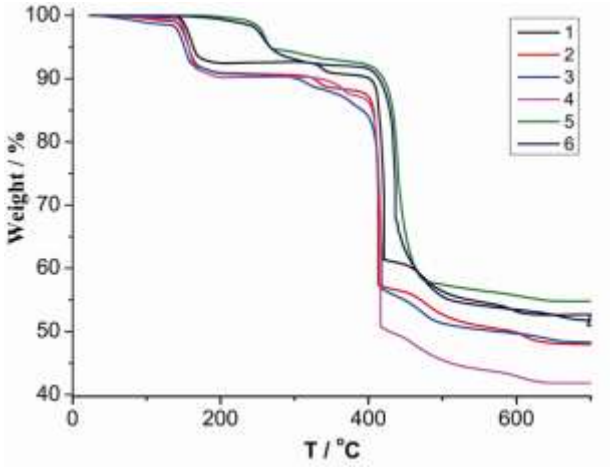

Fig. S5 TG curves of complexes **1–6** (heating rate of 10 ºC/min in air).

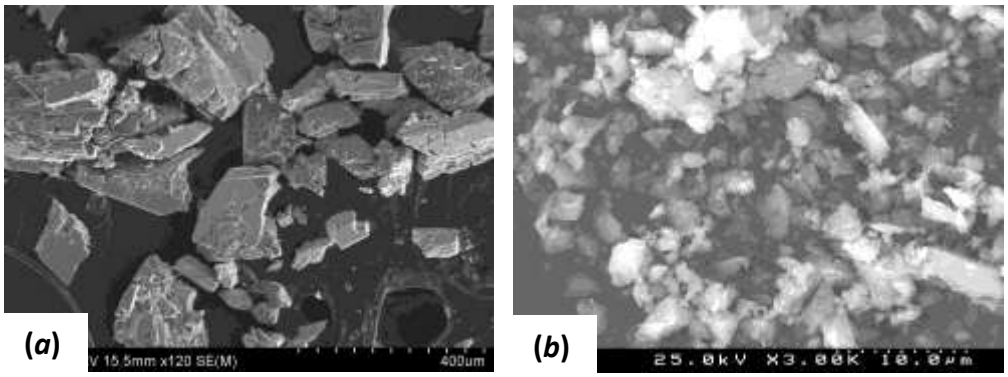

Fig. S6: The SEM images of **3** in the different stages (***a***) as-synthesized; (***b***) after 2nd cycle.

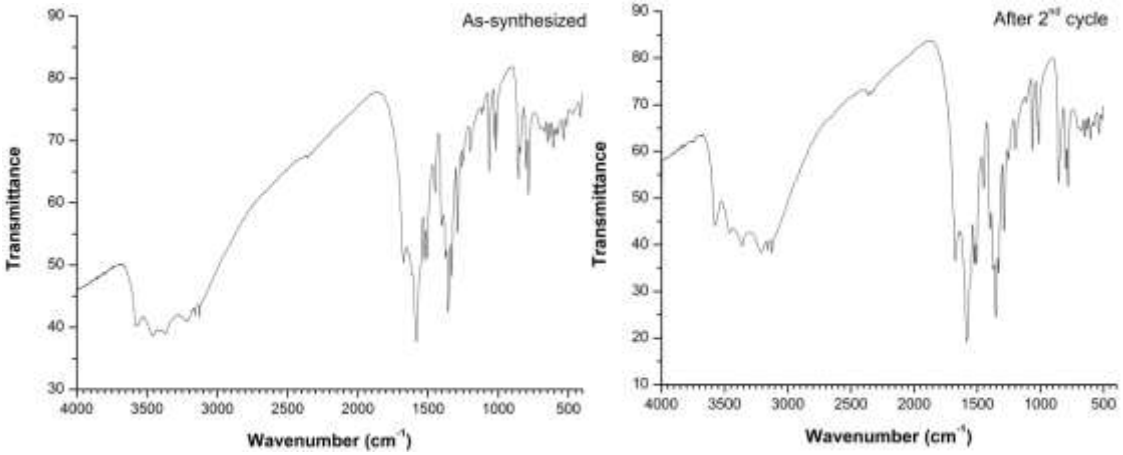

Fig. S7: The FT-IR spectra of **3** in the different stages (***Left***) as-synthesized; (***Right***) after 2nd cycle.

Table S1. Hydrogen bonds for **1** (35CuTb2) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6N)...O(3)#6	0.88	2.21	2.915(3)	137.3
O(13)-H(13A)...O(18)#3	0.86	2.00	2.819(3)	160.1
O(13)-H(13B)...O(7)#9	0.87	1.90	2.760(3)	170.0
O(14)-H(14A)...O(3)#6	0.86	1.78	2.630(3)	169.4
O(14)-H(14B)...O(7)#10	0.86	1.86	2.651(3)	151.7
O(15)-H(15A)...O(4)#7	0.86	2.05	2.807(3)	146.5
O(15)-H(15B)...N(6)#4	0.87	2.57	3.424(3)	170.6
O(16)-H(16A)...O(18)	0.87	1.91	2.769(3)	168.4
O(16)-H(16B)...O(4)#11	0.87	2.12	2.930(2)	155.2
O(17)-H(17A)...O(5)#3	0.86	2.03	2.850(3)	159.0
O(17)-H(17B)...O(9)	0.86	2.32	3.104(3)	150.8
O(17)-H(17B)...O(10)	0.86	2.32	3.019(3)	138.2
O(18)-H(18A)...O(17)#3	0.86	1.85	2.696(3)	164.2
O(18)-H(18B)...O(6)#8	0.86	2.51	3.349(3)	165.0

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+2,-y+1,-z+1 #3 -x+1,-y+2,-z+1

#4 -x+1,-y+1,-z+1 #5 x+1,y,z #6 -x+1,-y+1,-z+2

#7 x,y,z-1 #8 -x+2,-y+2,-z+1 #9 -x,-y+2,-z+2

#10 -x+1,-y+2,-z+2 #11 x+1,y,z-1

Table S2. Hydrogen bonds for **2** (35CuDy2) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6N)...O(3)#6	0.88	2.21	2.911(4)	136.6
O(13)-H(13A)...O(18)#3	0.86	2.00	2.821(4)	159.6
O(13)-H(13B)...O(7)#9	0.86	1.91	2.761(4)	170.0
O(14)-H(14A)...O(3)#6	0.86	1.77	2.630(3)	169.8
O(14)-H(14B)...O(7)#10	0.86	1.85	2.641(3)	151.3
O(15)-H(15A)...O(4)#7	0.86	2.05	2.807(3)	146.6
O(15)-H(15B)...N(6)#4	0.87	2.58	3.431(4)	170.0
O(16)-H(16A)...O(18)	0.87	1.90	2.757(4)	168.0
O(16)-H(16B)...O(4)#11	0.86	2.13	2.936(3)	154.9
O(17)-H(17A)...O(5)#3	0.86	2.03	2.847(4)	158.8
O(17)-H(17B)...O(9)	0.86	2.31	3.088(4)	150.7
O(17)-H(17B)...O(10)	0.86	2.33	3.021(4)	137.9
O(18)-H(18A)...O(17)#3	0.86	1.85	2.689(4)	164.0
O(18)-H(18B)...O(6)#8	0.86	2.50	3.336(4)	165.0

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+2,-y+1,-z+1 #3 -x+1,-y+2,-z+1

#4 -x+1,-y+1,-z+1 #5 x+1,y,z #6 -x+1,-y+1,-z+2

#7 x,y,z-1 #8 -x+2,-y+2,-z+1 #9 -x,-y+2,-z+2

#10 -x+1,-y+2,-z+2 #11 x+1,y,z-1

Table S3. Hydrogen bonds for **3** (35CuEr2) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6N)...O(3)#6	0.88	2.22	2.908(3)	134.8
O(13)-H(13A)...O(18)#3	0.85	2.01	2.822(3)	159.1
O(13)-H(13B)...O(7)#9	0.86	1.91	2.766(2)	169.7
O(14)-H(14A)...O(3)#6	0.86	1.77	2.623(2)	170.5
O(14)-H(14B)...O(7)#10	0.86	1.85	2.640(2)	150.7
O(15)-H(15A)...O(4)#7	0.85	2.06	2.811(2)	146.7
O(15)-H(15B)...N(6)#4	0.86	2.61	3.458(3)	169.0
O(16)-H(16A)...O(18)	0.86	1.90	2.751(2)	167.4
O(16)-H(16B)...O(4)#11	0.86	2.14	2.946(2)	154.5
O(17)-H(17A)...O(5)#3	0.86	2.03	2.846(3)	158.7
O(17)-H(17B)...O(9)	0.86	2.30	3.077(3)	150.2
O(17)-H(17B)...O(10)	0.86	2.32	3.010(2)	137.9
O(18)-H(18A)...O(17)#3	0.86	1.84	2.679(3)	163.6
O(18)-H(18B)...O(6)#8	0.86	2.49	3.324(2)	164.9

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+2,-y+1,-z+1 #3 -x+1,-y+2,-z+1

#4 -x+1,-y+1,-z+1 #5 x+1,y,z #6 -x+1,-y+1,-z+2

#7 x,y,z-1 #8 -x+2,-y+2,-z+1 #9 -x,-y+2,-z+2

#10 -x+1,-y+2,-z+2 #11 x+1,y,z-1

Table S4. Hydrogen bonds for **4** (35CuY2) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6N)...O(3)#6	0.88	2.21	2.908(4)	136.0
O(13)-H(13A)...O(18)#3	0.86	2.01	2.827(4)	159.6
O(13)-H(13B)...O(7)#9	0.86	1.91	2.765(3)	169.7
O(14)-H(14A)...O(3)#6	0.86	1.77	2.626(3)	170.1
O(14)-H(14B)...O(7)#10	0.86	1.86	2.652(3)	150.9
O(15)-H(15A)...O(4)#7	0.86	2.06	2.810(3)	146.5
O(15)-H(15B)...N(6)#4	0.87	2.59	3.443(4)	169.4
O(16)-H(16A)...O(18)	0.87	1.91	2.768(3)	168.0
O(16)-H(16B)...O(4)#11	0.86	2.14	2.939(3)	154.6
O(17)-H(17A)...O(5)#3	0.86	2.04	2.856(4)	158.7
O(17)-H(17B)...O(9)	0.86	2.31	3.089(4)	150.3
O(17)-H(17B)...O(10)	0.86	2.33	3.018(4)	137.9
O(18)-H(18A)...O(17)#3	0.86	1.84	2.679(4)	163.7
O(18)-H(18B)...O(6)#8	0.86	2.51	3.348(3)	165.0

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+2,-y+1,-z+1 #3 -x+1,-y+2,-z+1

#4 -x+1,-y+1,-z+1 #5 x+1,y,z #6 -x+1,-y+1,-z+2

#7 x,y,z-1 #8 -x+2,-y+2,-z+1 #9 -x,-y+2,-z+2

#10 -x+1,-y+2,-z+2 #11 x+1,y,z-1

Table S5. Hydrogen bonds for **5** (35CuEu) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(25)-H(25A)...O(6)#2	0.85	1.97	2.789(9)	163.6
O(25)-H(25B)...O(24)#3	0.84	1.98	2.795(9)	163.0
O(26)-H(26A)...O(22)#4	0.85	2.47	3.041(9)	125.3
O(26)-H(26C)...O(15)#4	0.85	1.95	2.645(9)	137.9
O(26)-H(26C)...O(16)#4	0.85	2.41	3.223(8)	159.5
O(27)-H(27A)...O(2)#10	0.79	2.29	3.059(9)	165.1
O(27)-H(27B)...O(20)#6	0.91	2.52	3.158(9)	127.1
O(27)-H(27B)...O(19)#6	0.91	1.90	2.762(8)	156.5
O(28)-H(28A)...O(20)#6	0.85	1.91	2.670(8)	148.9
O(28)-H(28C)...O(7)#2	0.85	1.89	2.736(9)	175.2
O(29)-H(29A)...O(23)	0.84	1.90	2.650(9)	148.3
O(29)-H(29B)...O(1)#5	0.85	1.91	2.697(9)	153.1
O(30)-H(30A)...O(3)#6	0.84	2.07	2.774(9)	140.3
O(30)-H(30A)...O(18)#6	0.84	2.36	3.073(8)	142.0
O(30)-H(30B)...O(14)#3	0.83	1.92	2.724(9)	165.1
O(31)-H(31A)...O(6)#9	0.84	2.58	3.287(11)	142.4
O(31)-H(31B)...O(13)#3	0.84	1.80	2.636(9)	171.7
O(32)-H(32A)...O(6)#5	0.85	1.92	2.730(10)	158.1
O(32)-H(32B)...O(9)#4	0.85	2.03	2.833(8)	158.3

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z+1 #2 x-1,y,z #3 -x,-y+1,-z

#4 -x+1,-y+1,-z #5 x,y,z-1 #6 -x+1,-y,-z

#7 x,y,z+1 #8 x+1,y,z #9 x-1,y,z-1 #10 -x+1,-y,-z+1

Table S6. Hydrogen bonds for **6** (35CuGd) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(25)-H(25A)...O(6)#2	0.85	1.98	2.796(5)	163.4
O(25)-H(25B)...O(24)#3	0.84	1.97	2.785(5)	163.5
O(26)-H(26A)...O(22)#4	0.85	2.50	3.063(5)	124.9
O(26)-H(26C)...O(15)#4	0.85	1.95	2.648(5)	138.1
O(26)-H(26C)...O(16)#4	0.85	2.41	3.219(5)	159.6
O(27)-H(27A)...O(2)#10	0.79	2.30	3.065(5)	164.5
O(27)-H(27B)...O(19)#6	0.91	1.89	2.751(5)	156.1
O(27)-H(27B)...O(20)#6	0.91	2.53	3.170(5)	127.6
O(28)-H(28A)...O(20)#6	0.85	1.91	2.678(5)	149.9
O(28)-H(28C)...O(7)#2	0.85	1.89	2.741(5)	175.3
O(29)-H(29A)...O(23)	0.84	1.89	2.645(5)	149.1
O(29)-H(29B)...O(1)#5	0.85	1.92	2.707(5)	153.6
O(30)-H(30A)...O(3)#6	0.84	2.09	2.788(5)	140.5
O(30)-H(30A)...O(18)#6	0.84	2.38	3.093(5)	142.6
O(30)-H(30B)...O(14)#3	0.83	1.92	2.724(5)	164.7
O(31)-H(31A)...O(6)#9	0.84	2.59	3.296(6)	142.6
O(31)-H(31B)...O(13)#3	0.84	1.79	2.627(5)	172.1
O(32)-H(32A)...O(6)#5	0.85	1.93	2.739(5)	158.8
O(32)-H(32B)...O(9)#4	0.85	2.06	2.860(5)	157.1

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z+1 #2 x-1,y,z #3 -x,-y+1,-z

#4 -x+1,-y+1,-z #5 x,y,z-1 #6 -x+1,-y,-z

#7 x,y,z+1 #8 x+1,y,z #9 x-1,y,z-1 #10 -x+1,-y,-z+1