Supporting Information

Two series of novel 3D potentially porous heterometallic Cu–Ln coordination frameworks assembled by 3,4-Pyridinedicarboxylic acid with different topologies and channels: syntheses, structures, luminescence and magnetic properties

Xuan-Wen Liu,[a] Rui Guo,[a] He Liu,[a] Ye-Qi Yu,[a] Xi-Wei Qi,[a] Jing-Yuan Xu[b] and Cheng-Zhi Xie*[b]

[a]*Key Laboratory of Electronic Information and Energy Materials of Qinhuangdao, Northeastern University at Qinhuangdao, Qinhuangdao,066004, P. R. China.*

[b]*Tianjin Key Laboratory on Technologies Enabling Development of Clinical Therapeutics and Diagnostics (Theranostics), School of Pharmacy, Tianjin Medical University, Tianjin 300070, P. R. China.*

** E-mail: xiechengzhi@tmu.edu.cn*

Table of Contents

Contents **Page No**

Table S1. Selected bond lengths (Å) and angles (º) for complexes **1**–**5**

Complex **1**			
Eu(1)-O(29)	2.415(2)	Eu(1)-O(30)	2.420(2)
Eu(1)-O(28)	2.427(3)	Eu(1)-O(27)	2.440(2)
Eu(1)-O(26)	2.431(3)	Eu(1)-O(20)#1	2.436(2)
Eu(1)-O(6)	2.482(2)	Eu(1)-O(5)	2.528(2)
Eu(1)-O(19)#1	2.541(2)	Eu(2)-O(16)	2.363(2)
Eu(2)-O(32)	2.406(2)	Eu(2)-O(35)	2.439(2)
Eu(2)-O(4)#2	2.443(2)	Eu(2)-O(34)	2.452(2)
Eu(2)-O(33)	2.460(2)	Eu(2)-O(22)	2.514(2)
Eu(2)-O(21)	2.514(2)	Eu(2)-O(3)#2	2.544(2)
Cu(1)-O(2)	1.979(2)	Cu(1)-O(11)#3	1.985(2)
Cu(1)-N(2)	2.013(3)	Cu(1)-N(6)#4	2.023(3)
Cu(1)-O(31)	2.294(3)	Cu(2)-N(4)	1.987(2)
Cu(2)-N(3)	1.999(3)	Cu(2)-O(8)	2.009(2)
Cu(2)-O(24)#5	2.026(2)	Cu(2)-O(25)	2.237(3)
Cu(3)-O(13)	1.985(2)	Cu(3)-N(5)#6	1.990(2)
Cu(3)-O(17)	1.990(2)	Cu(3)-N(1)#7	2.008(2)
Cu(3)-O(36)	2.247(4)	Cu(3)-O(36A)	2.249(6)
O(29)-Eu(1)-O(28)	70.73(9)	O(29)-Eu(1)-O(30)	76.65(8)
O(28)-Eu(1)-O(30)	139.49(9)	O(29)-Eu(1)-O(26)	78.12(9)
O(28)-Eu(1)-O(26)	74.86(10)	O(30)-Eu(1)-O(26)	75.48(8)
O(29)-Eu(1)-O(27)	137.66(8)	O(28)-Eu(1)-O(27)	68.01(9)
O(30)-Eu(1)-O(27)	144.50(8)	O(26)-Eu(1)-O(27)	99.69(9)
O(16)-Eu(2)-O(32)	77.37(8)	O(16)-Eu(2)-O(35)	73.32(8)
O(32)-Eu(2)-O(35)	72.99(9)	O(16)-Eu(2)-O(4)#2	140.15(7)
O(32)-Eu(2)-O(4)#2	100.06(8)	O(35)-Eu(2)-O(4)#2	68.11(8)
O(16)-Eu(2)-O(34)	82.15(8)	O(32)-Eu(2)-O(34)	144.96(8)
O(35)-Eu(2)-O(34)	74.04(9)	O(4)#2-Eu(2)-O(34)	78.16(7)
O(16)-Eu(2)-O(33)	95.59(8)	O(32)-Eu(2)-O(33)	70.11(8)
O(11)#3-Cu(1)-N(2)	92.26(9)	O(2)-Cu(1)-N(6)#4	89.53(9)
O(11)#3-Cu(1)-N(6)#4	89.64(9)	N(2)-Cu(1)-N(6)#4	177.30(11)
O(2)-Cu(1)-O(31)	94.36(10)	O(11)#3-Cu(1)-O(31)	89.70(10)
N(2)-Cu(1)-O(31)	91.30(11)	N(6)#4-Cu(1)-O(31)	90.64(11)
N(4)-Cu(2)-N(3)	170.08(11)	N(4)-Cu(2)-O(8)	87.61(9)
N(3)-Cu(2)-O(8)	93.53(9)	N(4)-Cu(2)-O(24)#5	91.62(9)
N(3)-Cu(2)-O(24)#5	86.43(9)	O(8)-Cu(2)-O(24)#5	175.19(10)
Complex **2**			
Gd(1)-O(28)	2.409(6)	Gd(1)-O(30)	2.410(5)
Gd(1)-O(27)	2.412(5)	Gd(1)-O(29)	2.416(5)

Gd(1)-O(20)#1	2.416(5)	Gd(1)-O(26)	2.434(6)
Gd(1)-O(6)	2.479(5)	Gd(1)-O(5)	2.505(5)
Gd(1)-O(19)#1	2.538(5)	Gd(2)-O(16)	2.348(5)
Gd(2)-O(32)	2.399(5)	Gd(2)-O(4)#2	2.439(4)
Gd(2)-O(34)	2.441(5)	Gd(2)-O(33)	2.444(5)
Gd(2)-O(35)	2.446(5)	Gd(2)-O(21)	2.500(5)
Gd(2)-O(22)	2.514(5)	Gd(2)-O(3)#2	2.541(5)
Cu(1)-O(11)#3	1.974(4)	Cu(1)-O(2)	1.978(4)
Cu(1)-N(2)	2.016(5)	Cu(1)-N(6)#4	2.021(5)
Cu(1)-O(31)	2.292(7)	Cu(2)-N(4)	1.988(5)
Cu(2)-N(3)	1.994(5)	Cu(2)-O(8)	2.013(4)
Cu(2)-O(24)#5	2.022(4)	Cu(2)-O(25)	2.229(5)
Cu(3)-O(13)	1.990(4)	Cu(3)-O(17)	1.994(4)
Cu(3)-N(5)#6	1.997(5)	Cu(3)-N(1)#7	2.006(5)
Cu(3)-O(36A)	2.219(16)	Cu(3)-O(36)	2.255(7)
O(28)-Gd(1)-O(30)	139.9(2)	O(28)-Gd(1)-O(27)	69.2(2)
O(30)-Gd(1)-O(27)	143.20(18)	O(28)-Gd(1)-O(20)#1	76.9(3)
O(30)-Gd(1)-O(20)#1	122.17(18)	O(16)-Gd(2)-O(32)	77.50(19)
O(16)-Gd(2)-O(4)#2	140.29(16)	O(32)-Gd(2)-O(4)#2	100.08(17)
O(16)-Gd(2)-O(34)	82.09(19)	O(32)-Gd(2)-O(34)	144.62(19)
O(11)#3-Cu(1)-O(2)	176.1(2)	O(11)#3-Cu(1)-N(2)	92.2(2)
O(2)-Cu(1)-N(2)	88.48(19)	O(11)#3-Cu(1)-N(6)#4	89.7(2)
O(2)-Cu(1)-N(6)#4	89.5(2)	N(2)-Cu(1)-N(6)#4	177.2(2)
O(11)#3-Cu(1)-O(31)	89.6(2)	O(2)-Cu(1)-O(31)	94.3(2)
N(2)-Cu(1)-O(31)	91.2(2)	N(6)#4-Cu(1)-O(31)	91.0(2)
N(4)-Cu(2)-N(3)	170.3(2)	N(4)-Cu(2)-O(8)	87.59(19)
N(3)-Cu(2)-O(8)	93.54(19)	N(4)-Cu(2)-O(24)#5	91.27(19)
N(3)-Cu(2)-O(24)#5	86.73(19)	O(8)-Cu(2)-O(24)#5	174.70(19)
N(4)-Cu(2)-O(25)	96.8(2)	N(3)-Cu(2)-O(25)	92.8(2)
O(8)-Cu(2)-O(25)	90.7(2)	O(24)#5-Cu(2)-O(25)	94.6(2)
O(13)-Cu(3)-O(17)	166.7(2)	O(13)-Cu(3)-N(5)#6	90.7(2)
O(17)-Cu(3)-N(5)#6	88.1(2)	O(13)-Cu(3)-N(1)#7	90.81(19)
O(17)-Cu(3)-N(1)#7	90.47(19)	N(5)#6-Cu(3)-N(1)#7	178.5(2)
O(13)-Cu(3)-O(36)	103.7(3)	O(17)-Cu(3)-O(36)	89.6(3)
N(5)#6-Cu(3)-O(36)	92.7(3)	N(1)#7-Cu(3)-O(36)	86.7(2)
O(28)-Gd(1)-O(30)	139.9(2)	O(28)-Gd(1)-O(27)	69.2(2)
Complex **3**			
Tb(1)-O(29)	2.419(6)	Tb(1)-O(2)	2.426(5)
Tb(1)-O(27)	2.432(6)	Tb(1)-O(28)	2.436(6)
Tb(1)-O(6)	2.485(5)	Tb(1)-O(7)	2.493(5)
Tb(1)-O(3)	2.537(5)	Tb(2)-O(36)	2.395(7)
Tb(2)-O(33)	2.406(6)	Tb(2)-O(34)	2.398(5)

Tb(2)-O(22)	2.398(5)	Tb(2)-O(35)	2.400(5)
Tb(2)-O(31)	2.402(6)	Tb(2)-O(21)	2.458(5)
Tb(2)-O(20)	2.501(5)	Tb(2)-O(23)	2.527(5)
Cu(1)-O(16)#2	1.987(5)	Cu(1)-O(24)#3	1.996(5)
Cu(1)-N(2)	1.994(6)	Cu(1)-N(1)#2	2.007(6)
Cu(1)-O(1)	2.216(7)	Cu(2)-N(4)	1.986(6)
Cu(2)-N(3)	1.992(6)	Cu(2)-O(18)	2.011(5)
Cu(2)-O(9)	2.025(5)	Cu(2)-O(30)	2.229(6)
Cu(3)-O(12)#4	1.978(5)	Cu(3)-O(4)#5	1.986(5)
Cu(3)-N(5)	2.009(6)	Cu(3)-N(6)#4	2.022(6)
Cu(3)-O(32)	2.285(7)		
O(26)-Tb(1)-O(29)	73.4(2)	O(14)#1-Tb(1)-O(2)	140.79(18)
O(26)-Tb(1)-O(2)	99.95(19)	O(29)-Tb(1)-O(2)	68.03(18)
O(14)#1-Tb(1)-O(27)	94.8(2)	O(26)-Tb(1)-O(27)	70.1(2)
O(36)-Tb(2)-O(34)	139.4(2)	O(36)-Tb(2)-O(22)	77.4(3)
O(34)-Tb(2)-O(22)	122.46(19)	O(36)-Tb(2)-O(35)	70.7(3)
O(34)-Tb(2)-O(35)	75.9(2)	O(22)-Tb(2)-O(35)	85.2(2)
O(16)#2-Cu(1)-N(2)	90.3(2)	O(16)#2-Cu(1)-O(24)#3	166.2(2)
N(2)-Cu(1)-O(24)#3	88.3(2)	O(16)#2-Cu(1)-N(1)#2	91.2(2)
N(2)-Cu(1)-N(1)#2	178.4(2)	O(24)#3-Cu(1)-N(1)#2	90.2(2)
O(16)#2-Cu(1)-O(1)	100.4(3)	N(2)-Cu(1)-O(1)	91.7(3)
O(24)#3-Cu(1)-O(1)	93.4(3)	N(1)#2-Cu(1)-O(1)	87.7(3)
N(4)-Cu(2)-N(3)	170.4(2)	N(4)-Cu(2)-O(18)	87.7(2)
N(3)-Cu(2)-O(18)	93.3(2)	N(4)-Cu(2)-O(9)	91.4(2)
N(3)-Cu(2)-O(9)	86.7(2)	O(18)-Cu(2)-O(9)	174.9(2)
N(4)-Cu(2)-O(30)	96.4(2)	N(3)-Cu(2)-O(30)	93.1(2)
O(18)-Cu(2)-O(30)	90.3(2)	O(9)-Cu(2)-O(30)	94.7(2)
O(12)#4-Cu(3)-O(4)#5	175.9(2)	O(12)#4-Cu(3)-N(5)	92.1(2)
O(4)#5-Cu(3)-N(5)	88.4(2)	O(12)#4-Cu(3)-N(6)#4	89.6(2)
O(4)#5-Cu(3)-N(6)#4	89.7(2)	N(5)-Cu(3)-N(6)#4	177.4(3)

Complex **4**

Cu(1)-N(1)	2.004(6)	Cu(1)-O(7)#2	2.002(5)
Cu(1)-O(3)#1	1.981(5)	Cu(1)-N(2)	1.997(5)
Cu(1)-O(5)	2.301(7)	Ho(1)-O(14)	2.337(5)
Ho(1)-O(13)	2.340(5)	Ho(1)-O(10)#3	2.369(5)
Ho(1)-O(9)	2.412(5)	Ho(1)-O(11)	2.425(5)
Ho(1)-O(8)	2.435(5)	Ho(1)-O(2)#4	2.437(5)
Ho(1)-O(1)#4	2.478(5)	Ho(1)-O(10)	2.504(5)
O(3)#1-Cu(1)-N(2)	88.6(2)	O(3)#1-Cu(1)-O(7)#2	174.4(2)
N(2)-Cu(1)-O(7)#2	90.7(2)	O(3)#1-Cu(1)-N(1)	91.2(2)
N(2)-Cu(1)-N(1)	177.4(2)	O(7)#2-Cu(1)-N(1)	89.3(2)
O(3)#1-Cu(1)-O(5)	90.4(2)	N(2)-Cu(1)-O(5)	90.8(2)
O(7)#2-Cu(1)-O(5)	95.2(2)	N(1)-Cu(1)-O(5)	91.8(2)

O(13)-Ho(1)-O(14)	79.6(2)	O(13)-Ho(1)-O(10)#3	76.04(18)
O(14)-Ho(1)-O(10)#3	84.74(19)	O(13)-Ho(1)-O(9)	143.14(18)
O(14)-Ho(1)-O(9)	76.54(18)	O(10)#3-Ho(1)-O(9)	74.17(17)
O(13)-Ho(1)-O(11)	82.89(19)	O(14)-Ho(1)-O(11)	148.45(19)
O(10)#3-Ho(1)-O(11)	116.16(17)	O(9)-Ho(1)-O(11)	130.04(18)
O(13)-Ho(1)-O(8)	150.20(18)	O(14)-Ho(1)-O(8)	128.25(18)
O(10)#3-Ho(1)-O(8)	94.39(17)	O(9)-Ho(1)-O(8)	53.97(16)
O(11)-Ho(1)-O(8)	76.13(17)	O(13)-Ho(1)-O(2)#4	124.80(18)
O(14)-Ho(1)-O(2)#4	81.62(19)	O(10)#3-Ho(1)-O(2)#4	151.95(17)
O(9)-Ho(1)-O(2)#4	78.86(16)	O(11)-Ho(1)-O(2)#4	87.20(17)
O(8)-Ho(1)-O(2)#4	75.48(17)	O(13)-Ho(1)-O(1)#4	71.96(18)
O(14)-Ho(1)-O(1)#4	77.3(2)	O(10)#3-Ho(1)-O(1)#4	145.51(18)
O(9)-Ho(1)-O(1)#4	127.97(17)	O(11)-Ho(1)-O(1)#4	72.43(18)
O(8)-Ho(1)-O(1)#4	119.87(17)	O(2)#4-Ho(1)-O(1)#4	53.35(17)
O(13)-Ho(1)-O(10)	79.81(19)	O(14)-Ho(1)-O(10)	146.45(18)
O(10)#3-Ho(1)-O(10)	64.7(2)	O(9)-Ho(1)-O(10)	105.99(17)
O(11)-Ho(1)-O(10)	52.43(16)	O(8)-Ho(1)-O(10)	70.66(17)
O(2)#4-Ho(1)-O(10)	131.92(18)	O(1)#4-Ho(1)-O(10)	120.37(17)

Complex **5**

Er(1)-O(12)	2.313(4)	Er(1)-O(13)	2.318(4)
Er(1)-O(9)#2	2.346(3)	Er(1)-O(1)#3	2.391(3)
Er(1)-O(10)	2.415(3)	Er(1)-O(2)#3	2.418(3)
Er(1)-O(5)	2.422(4)	Er(1)-O(6)	2.472(4)
Er(1)-O(9)	2.476(3)	Cu(1)-O(7)	1.973(3)
Cu(1)-N(2)#3	1.993(4)	Cu(1)-O(4)#4	1.997(3)
Cu(1)-N(1)	2.001(4)	Cu(1)-O(11)	2.246(5)
C(6)-O(1)-Er(1)#1	91.1(3)	O(12)-Er(1)-O(13)	80.56(14)
O(12)-Er(1)-O(9)#2	84.98(13)	O(13)-Er(1)-O(9)#2	76.04(13)
O(12)-Er(1)-O(1)#3	75.52(13)	O(13)-Er(1)-O(1)#3	143.30(13)
O(9)#2-Er(1)-O(1)#3	74.52(12)	O(12)-Er(1)-O(10)	147.94(13)
O(13)-Er(1)-O(10)	82.39(13)	O(9)#2-Er(1)-O(10)	116.79(11)
O(1)#3-Er(1)-O(10)	130.83(12)	O(12)-Er(1)-O(2)#3	128.13(13)
O(13)-Er(1)-O(2)#3	149.40(13)	O(9)#2-Er(1)-O(2)#3	94.29(12)
O(1)#3-Er(1)-O(2)#3	54.77(11)	O(10)-Er(1)-O(2)#3	76.22(12)
O(12)-Er(1)-O(5)	81.62(13)	O(13)-Er(1)-O(5)	124.81(13)
O(9)#2-Er(1)-O(5)	152.40(11)	O(1)#3-Er(1)-O(5)	78.81(12)
O(10)-Er(1)-O(5)	86.18(11)	O(2)#3-Er(1)-O(5)	75.66(12)
O(12)-Er(1)-O(6)	76.15(13)	O(13)-Er(1)-O(6)	71.31(13)
O(9)#2-Er(1)-O(6)	144.40(13)	O(1)#3-Er(1)-O(6)	127.34(12)
O(10)-Er(1)-O(6)	72.73(11)	O(2)#3-Er(1)-O(6)	121.13(12)
O(5)-Er(1)-O(6)	53.77(12)	O(12)-Er(1)-O(9)	146.72(13)
O(13)-Er(1)-O(9)	78.98(13)	O(9)#2-Er(1)-O(9)	64.76(13)
O(1)#3-Er(1)-O(9)	107.13(11)	O(10)-Er(1)-O(9)	52.99(11)

O(2)#3-Er(1)-O(9)	70.72(12)	O(5)-Er(1)-O(9)	131.66(12)
O(6)-Er(1)-O(9)	120.68(11)	O(7)-Cu(1)-N(2)#3	91.47(15)
O(7)-Cu(1)-O(4)#4	172.57(15)	N(2)#3-Cu(1)-O(4)#4	88.86(15)
O(7)-Cu(1)-N(1)	88.80(15)	N(2)#3-Cu(1)-N(1)	177.05(18)
O(4)#4-Cu(1)-N(1)	90.50(15)	O(7)-Cu(1)-O(11)	91.15(17)
N(2)#3-Cu(1)-O(11)	92.33(17)	O(4)#4-Cu(1)-O(11)	96.25(17)
N(1)-Cu(1)-O(11)	90.61(17)		

Symmetry transformations used to generate equivalent atoms for **1**: #1 -x+3/2, y-1/2, -z+1/2; #2 -x+2, -y, -z+1; #3 x+1, y, z; #4 -x+5/2, y-1/2, -z+1/2; #5 x-1/2, -y+1/2, z-1/2; #6 x+1/2, -y+1/2, z-1/2; #7 -x+3/2, y+1/2, -z+1/2. For **2**: #1 -x+3/2, y-1/2, -z+1/2; #2 -x+2, -y, -z+1; #3 x+1, y, z; #4 -x+5/2, y-1/2, -z+1/2; #5 x-1/2, -y+1/2, z-1/2; #6 x+1/2, -y+1/2, z-1/2; #7 -x+3/2, y+1/2, -z+1/2. For **3**: #1 x+1/2, -y+1/2, z+1/2; #2 x+1, y, z; #3 -x+1/2, y+1/2, -z+3/2; #4 x-1, y, z; #5 -x-1/2, y-1/2, -z+3/2. For **4**: #1 -x+1, y+1/2, -z+1/2; #2 -x, y-1/2, -z+1/2; #3 -x, -y+1, -z; #4 x, y+1, z. For **5**: #1 -x, -y, -z+1; #2 -x+1, y-1/2, -z+3/2; #3 -x+2, y-1/2, -z+3/2.

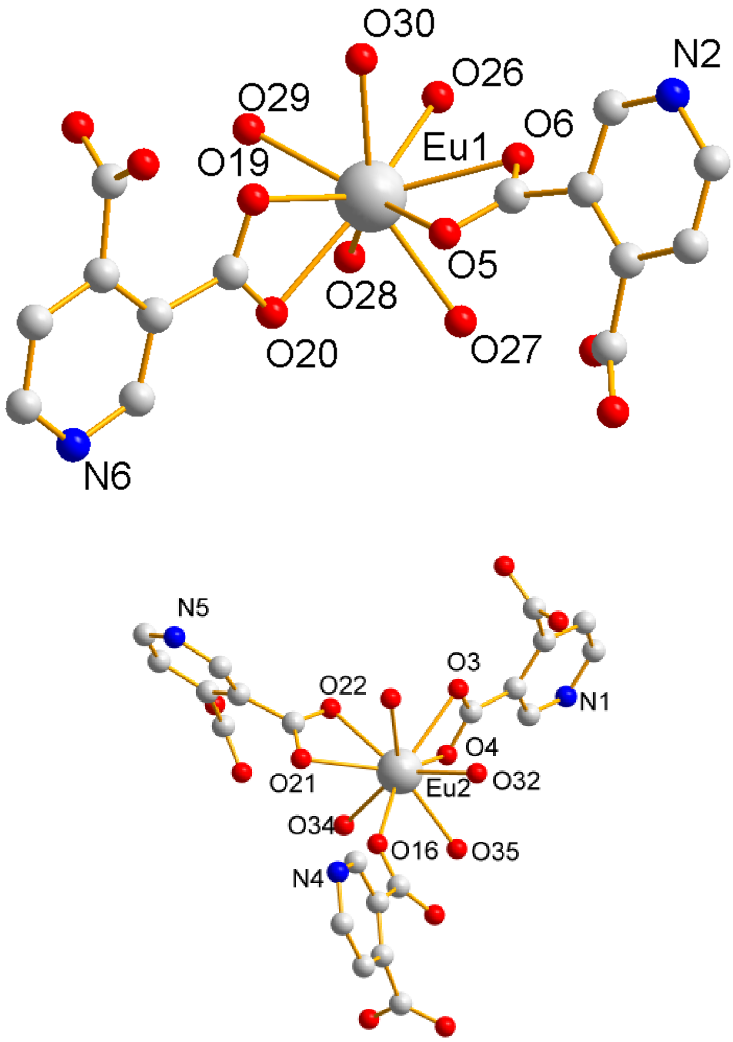

Fig. S1 The coordination environments of Eu(III) ions in **1**, all hydrogen atoms are omitted for clarity

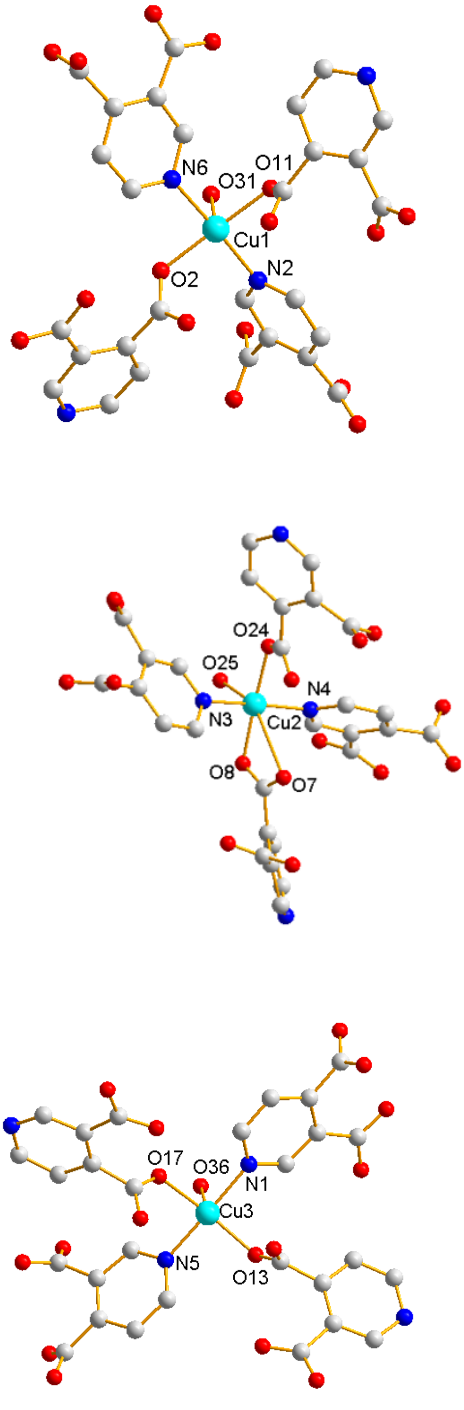

Fig. S2 The coordination environments of Cu(II) ions in **1**, all hydrogen atoms are omitted for clarity.

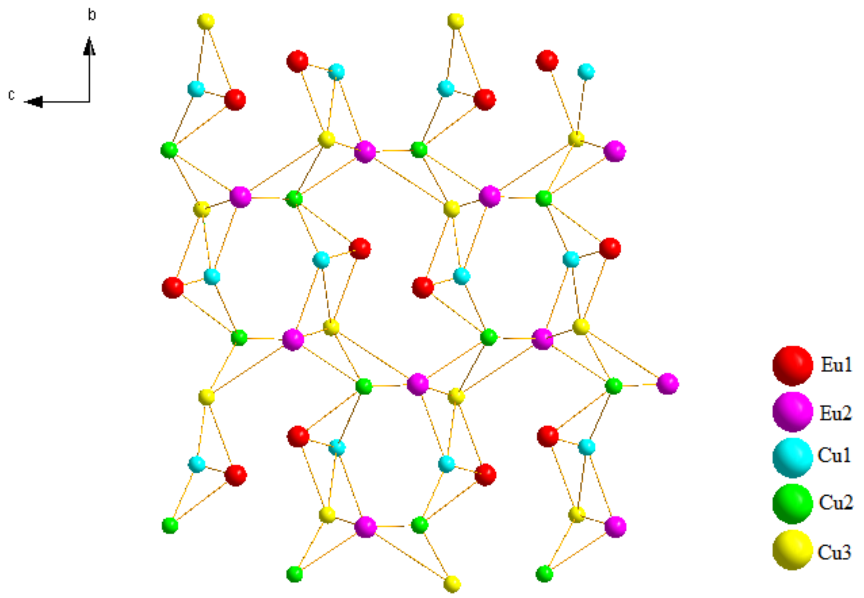

Fig. S3 View of the 5-nodal points with 4,6,7,7,8-connected topologic network of **1**.

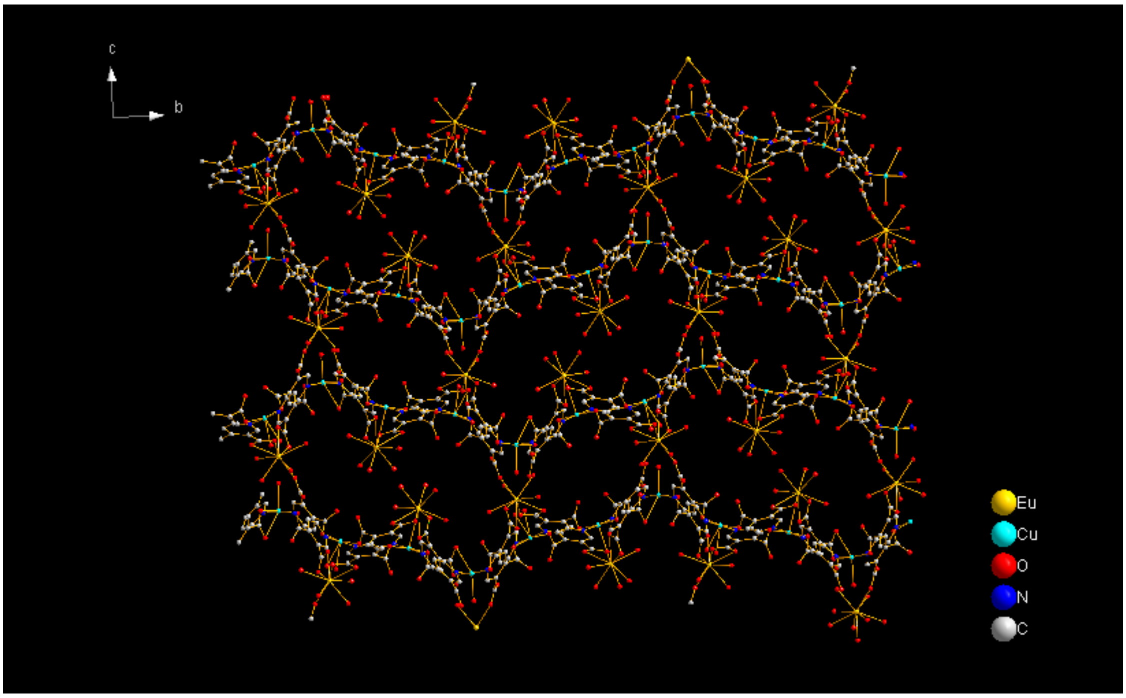

Fig. S4 Projection of the 3D framework showing the 1D channels in **1**; the H atoms and lattice water molecules are omitted for clarity.

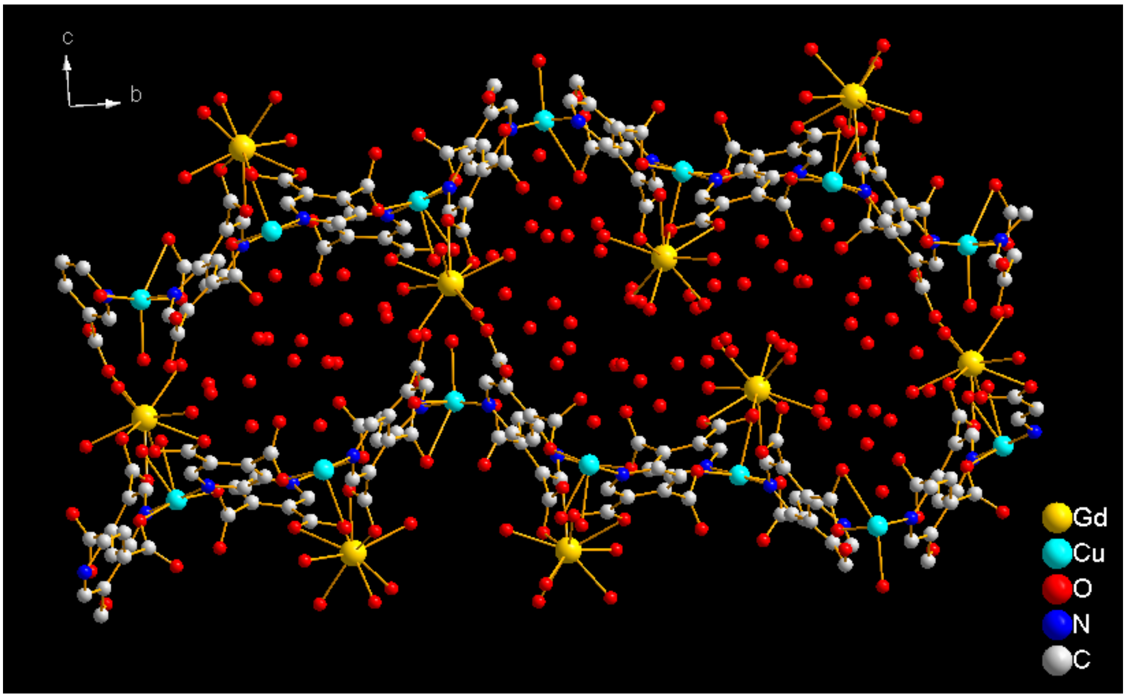

Fig. S5 View of S-shape channel and smaller hexagonal channel which are all filled with guest water molecules in **2**; the H atoms are omitted for clarity.

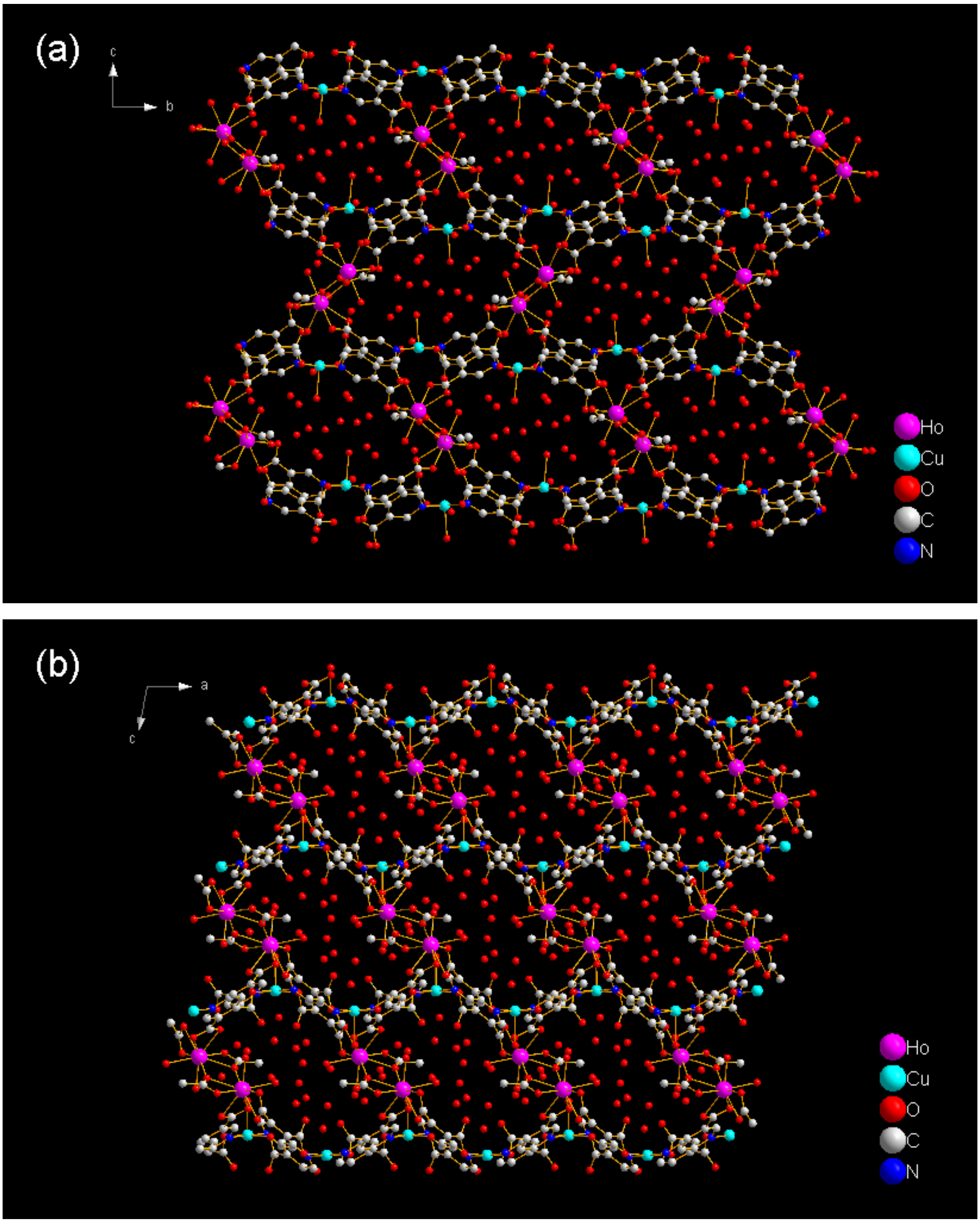

Fig. S6 Projection of the 3D framework viewed along the *a* axis (a) and *b* axis (b) showing 1D channels in **4**; the H atoms are omitted for clarity.

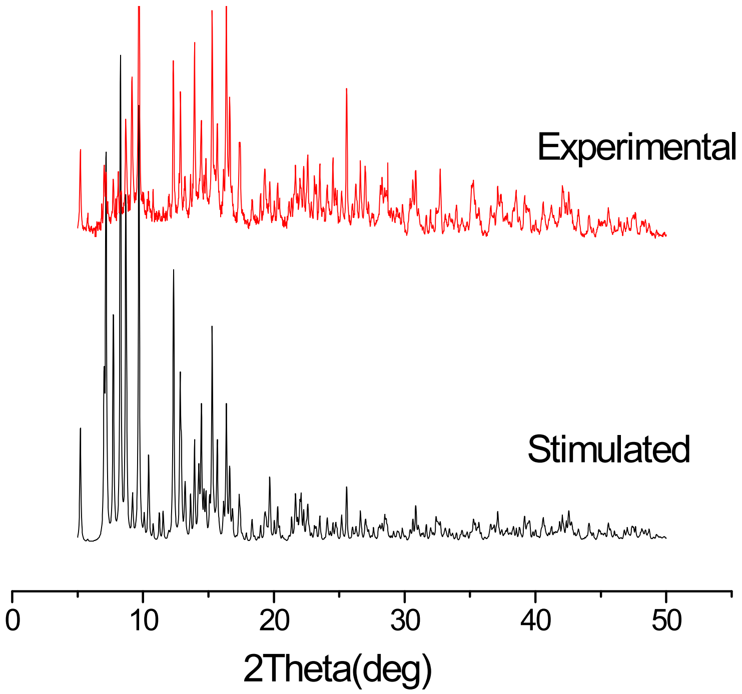

Fig. S7 Simulated and experimental X-ray powder diffraction patterns of complex **1**.

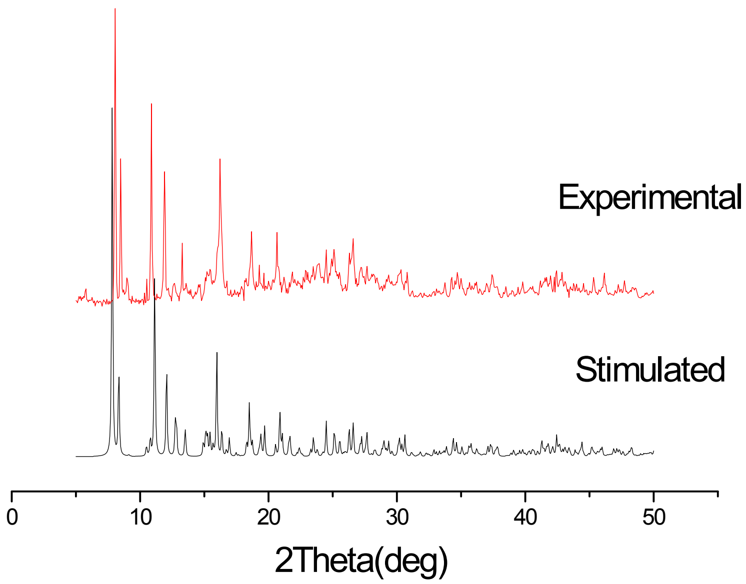

Fig. S8 Simulated and experimental X-ray powder diffraction patterns of complex **4**.

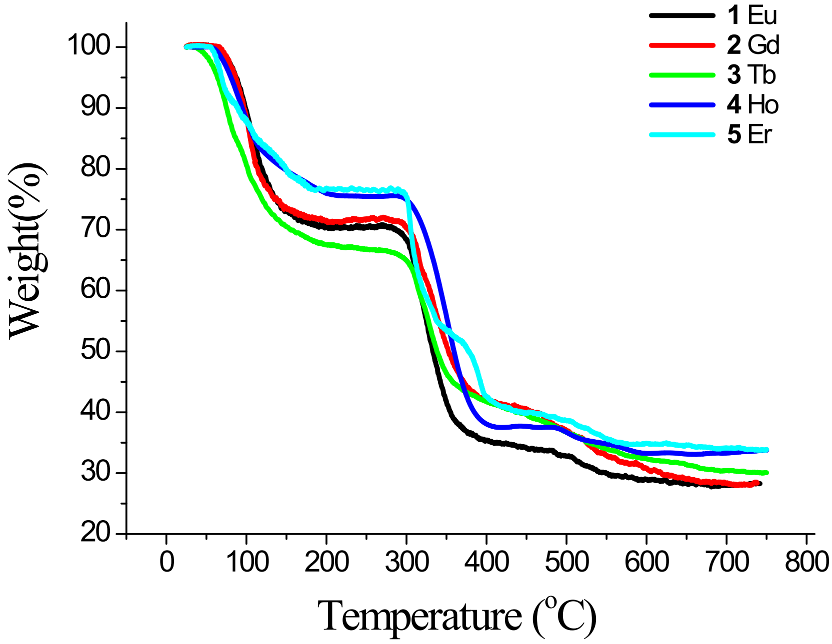

Fig. S9 Thermal gravimetric analysis (TGA) curves of complexes **1**–**5**.

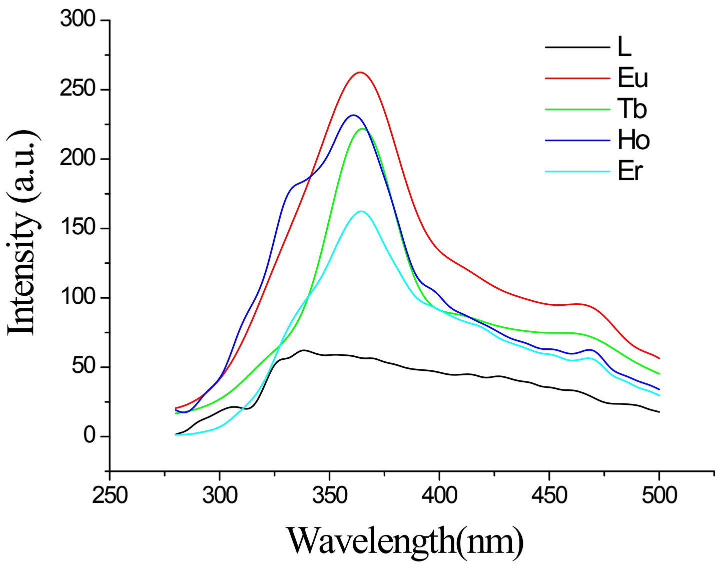

Fig. S10 Photoemission spectra of free 3,4-pdcH_2 ligand and complexes **1**, **3**, **4**, **5** in the solid state at room temperature

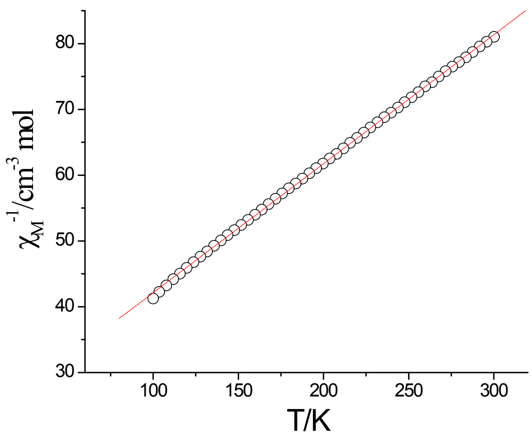

Fig. S11 The χ_M^{-1} versus T curve for **1**. The solid line represents the Curie-Weiss fitting result.

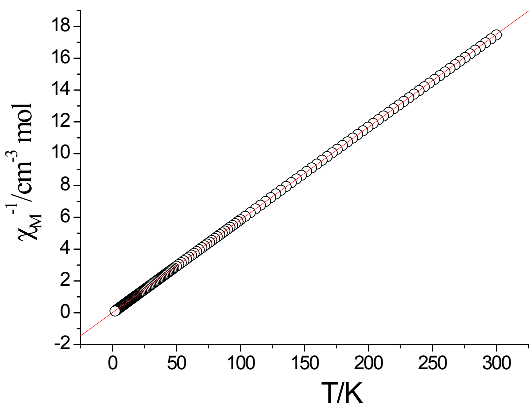

Fig. S12 The χ_M^{-1} versus T curve for **2**. The solid line represents the Curie-Weiss fitting result.