Supplementary Material (ESI) for Dalton Transactions

Unique two-fold interpenetration of 3D microporous 3d-4f heterometal-organic frameworks (HMOF) based on a rigid ligand

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Electronic Supporting Information

Table S1 Selected bond lengths and angles

1					
Gd(1)-O(4)	2.256(2)	O(4)-Gd(1)-O(12)#1	80.12(9)	O(12)#1-Gd(1)-O(5)	77.99(8)
Gd(1)-O(12)#1	2.315(2)	O(4)-Gd(1)-O(5)	157.72(9)	O(12)#1-Gd(1)-O(13)	81.39(9)
Gd(1)-O(5)	2.356(2)	O(4)-Gd(1)-O(13)	104.70(9)	O(12)#1-Gd(1)-O(7)#2	147.60(7)
Gd(1)-O(13)	2.453(3)	O(4)-Gd(1)-O(7)#2	128.19(8)	O(12)#1-Gd(1)-O(10)	131.64(8)
Gd(1)-O(7)#2	2.472(2)	O(4)-Gd(1)-O(10)	81.99(9)	O(12)#1-Gd(1)-O(9)	81.83(9)
Gd(1)-O(10)	2.476(2)	O(4)-Gd(1)-O(9)	88.03(9)	O(12)#1-Gd(1)-O(8)#2	140.10(8)
Gd(1)-O(9)	2.477(2)	O(4)-Gd(1)-O(8)#2	77.70(8)		
Gd(1)-O(8)#2	2.502(2)				
Cu(1)-O(1)#3	1.949(2)	O(1)#3-Cu(1)-N(1)	90.13(10)	N(1)-Cu(1)-N(6)#4	167.34(10)
Cu(1)-N(1)	1.995(3)	O(1)#3-Cu(1)-N(6)#4	92.99(10)	N(1)-Cu(1)-N(5)#4	92.49(11)
Cu(1)-N(6)#4	1.996(3)	O(1)#3-Cu(1)-N(5)#4	163.33(9)	N(1)-Cu(1)-N(2)	78.12(10)
Cu(1)-N(5)#4	2.029(3)	O(1)#3-Cu(1)-N(2)	94.53(10)	N(4)#5-Cu(2)-N(4)	103.94(16)
Cu(1)-N(2)	2.187(3)	N(3)#5-Cu(2)-N(4)#5	79.69(10)	N(4)#5-Cu(2)-O(14)#5	164.94(16)
Cu(2)-N(3)#5	1.974(2)	N(3)#5-Cu(2)-N(4)	96.96(10)	N(4)#5-Cu(2)-O(14)	90.34(15)
Cu(2)-N(4)#5	2.123(3)	N(3)#5-Cu(2)-O(14)#5	94.07(14)	N(3)-Cu(2)-N(4)#5	96.96(10)
Cu(2)-N(4)	2.123(3)	N(3)#5-Cu(2)-O(14)	90.18(15)		
Cu(2)-O(14)	2.290(5)	N(3)#5-Cu(2)-N(3)	174.61(17)		
2					
Tb(1)-O(11)	2.247(3)	O(11)-Tb(1)-O(6)	80.20(11)	O(6)-Tb(1)-O(4)	77.90(11)
Tb(1)-O(6)	2.300(3)	O(11)-Tb(1)-O(4)	157.79(12)	O(6)-Tb(1)-O(10)	81.49(13)
Tb(1)-O(4)	2.337(3)	O(11)-Tb(1)-O(10)	104.19(12)	O(6)-Tb(1)-O(8)#1	131.39(12)
Tb(1)-O(10)	2.430(4)	O(11)-Tb(1)-O(8)#1	81.65(12)	O(6)-Tb(1)-O(2)#2	147.38(10)
Tb(1)-O(8)#1	2.455(3)	O(11)-Tb(1)-O(2)#2	128.40(11)	O(6)-Tb(1)-O(9)#1	81.26(11)
Tb(1)-O(2)#2	2.456(3)	O(11)-Tb(1)-O(9)#1	87.62(12)	O(6)-Tb(1)-O(1)#2	140.34(11)
Tb(1)-O(9)#1	2.457(3)	O(11)-Tb(1)-O(1)#2	77.39(11)		

Tb(1)-O(1)#2	2.489(3)				
Cu(1)-O(14)#3	1.947(3)	O(14)#3-Cu(1)-N(5)#4	93.09(14)	N(5)#4-Cu(1)-N(1)	167.31(13)
Cu(1)-N(5)#4	1.989(4)	O(14)#3-Cu(1)-N(1)	89.94(14)	N(5)#4-Cu(1)-N(6)#4	81.19(15)
Cu(1)-N(1)	1.992(4)	O(14)#3-Cu(1)-N(6)#4	163.08(12)	N(5)#4-Cu(1)-N(2)	113.74(13)
Cu(1)-N(6)#4	2.025(4)	O(14)#3-Cu(1)-N(2)	94.72(12)	N(4)-Cu(2)-N(3)#5	96.97(14)
Cu(1)-N(2)	2.177(3)	N(4)#5-Cu(2)-N(4)	175.1(2)	N(4)-Cu(2)-N(3)	79.96(14)
Cu(2)-N(4)#5	1.970(3)	N(4)#5-Cu(2)-N(3)#5	79.96(14)	N(4)-Cu(2)-O(5)#5	90.37(18)
Cu(2)-N(4)	1.970(3)	N(4)#5-Cu(2)-N(3)	96.97(14)	N(4)-Cu(2)-O(5)	93.47(18)
Cu(2)-N(3)#5	2.114(4)	N(4)#5-Cu(2)-O(5)#5	93.47(18)		
Cu(2)-O(5)	2.289(7)	N(4)#5-Cu(2)-O(5)	90.37(18)		
3					
Eu(1)-O(4)	2.260(3)	O(4)-Eu(1)-O(8)#1	80.34(11)	O(8)#1-Eu(1)-O(10)	78.20(10)
Eu(1)-O(8)#1	2.318(3)	O(4)-Eu(1)-O(10)	157.92(12)	O(8)#1-Eu(1)-O(6)#2	132.03(11)
Eu(1)-O(10)	2.369(3)	O(4)-Eu(1)-O(6)#2	81.70(11)	O(8)#1-Eu(1)-O(13)#3	147.49(9)
Eu(1)-O(6)#2	2.478(3)	O(4)-Eu(1)-O(13)#3	127.79(11)	O(8)#1-Eu(1)-O(9)	80.75(11)
Eu(1)-O(13)#3	2.480(3)	O(4)-Eu(1)-O(9)	105.79(12)	O(8)#1-Eu(1)-O(5)#2	82.13(11)
Eu(1)-O(9)	2.481(3)	O(4)-Eu(1)-O(5)#2	87.01(12)	O(8)#1-Eu(1)-O(12)#3	139.33(11)
Eu(1)-O(5)#2	2.486(3)	O(4)-Eu(1)-O(12)#3	77.51(11)		
Eu(1)-O(12)#3	2.514(3)				
Cu(1)-O(1)#4	1.943(3)	O(1)#4-Cu(1)-N(3)	92.88(14)	N(3)-Cu(1)-N(2)	167.41(15)
Cu(1)-N(3)	1.987(4)	O(1)#4-Cu(1)-N(2)	90.32(13)	N(3)-Cu(1)-N(4)	81.22(15)
Cu(1)-N(2)	2.000(3)	O(1)#4-Cu(1)-N(4)	163.40(13)	N(3)-Cu(1)-N(1)	113.83(13)
Cu(1)-N(4)	2.026(4)	O(1)#4-Cu(1)-N(1)	94.18(13)	N(6)#5-Cu(2)-N(6)	102.8(2)
Cu(1)-N(1)	2.179(4)	N(5)#5-Cu(2)-N(6)#5	96.62(14)	N(6)#5-Cu(2)-O(14)	165.9(2)
Cu(2)-N(5)#5	1.965(4)	N(5)#5-Cu(2)-N(6)	79.75(14)	N(6)#5-Cu(2)-O(14)#5	90.52(19)
Cu(2)-N(5)	1.965(4)	N(5)#5-Cu(2)-O(14)	90.26(18)	N(5)-Cu(2)-N(6)#5	79.75(14)
Cu(2)-N(6)#5	2.123(4)	N(5)#5-Cu(2)-O(14)#5	94.26(18)		
Cu(2)-O(14)	2.281(7)	N(5)#5-Cu(2)-N(5)	174.2(2)		
4					
Ho(1)-O(4)#1	2.189(6)	O(4)#1-Ho(1)-O(5)#2	80.2(3)	O(5)#2-Ho(1)-O(9)	76.8(2)
Ho(1)-O(5)#2	2.277(8)	O(4)#1-Ho(1)-O(9)	156.8(3)	O(5)#2-Ho(1)-O(13)	81.2(3)
Ho(1)-O(9)	2.304(5)	O(4)#1-Ho(1)-O(13)	101.5(3)	O(5)#2-Ho(1)-O(8)	79.3(3)
Ho(1)-O(13)	2.354(9)	O(4)#1-Ho(1)-O(8)	87.8(2)	O(5)#2-Ho(1)-O(12)	147.4(2)
Ho(1)-O(8)	2.407(7)	O(4)#1-Ho(1)-O(12)	129.4(2)	O(5)#2-Ho(1)-O(7)	129.9(3)
Ho(1)-O(12)	2.412(6)	O(4)#1-Ho(1)-O(7)	82.0(2)	O(5)#2-Ho(1)-O(11)	142.9(3)
Ho(1)-O(7)	2.421(7)	O(4)#1-Ho(1)-O(11)	78.8(2)		
Ho(1)-O(11)	2.464(7)				
Cu(1)-O(1)#3	1.937(7)	O(1)#3-Cu(1)-N(4)	89.6(3)	N(4)-Cu(1)-N(2)	169.1(3)
Cu(1)-N(4)	1.977(8)	O(1)#3-Cu(1)-N(2)	92.4(3)	N(4)-Cu(1)-N(1)	93.8(3)
Cu(1)-N(2)	1.999(8)	O(1)#3-Cu(1)-N(1)	163.3(3)	N(4)-Cu(1)-N(3)	76.9(3)
Cu(1)-N(1)	2.037(8)	O(1)#3-Cu(1)-N(3)	94.6(3)	N(6)#5-Cu(2)-N(5)	97.9(3)
Cu(1)-N(3)	2.196(7)	N(6)#4-Cu(2)-N(6)#5	176.5(5)	N(6)#5-Cu(2)-N(5)#6	80.0(3)
Cu(2)-N(6)#4	1.965(7)	N(6)#4-Cu(2)-N(5)	80.0(3)	N(6)#5-Cu(2)-O(16)	94.8(6)

Cu(2)-N(6)#5	1.965(7)	N(6)#4-Cu(2)-N(5)#6	97.9(3)	N(6)#5-Cu(2)-O(16)#6	87.9(6)
Cu(2)-N(5)	2.084(8)	N(6)#4-Cu(2)-O(16)	87.9(6)		
Cu(2)-O(16)	2.35(2)	N(6)#4-Cu(2)-O(16)#6	94.8(6)		
5					
Yb(1)-O(8)	1.944(3)	O(8)-Yb(1)-O(10)	153.11(14)	O(10)-Yb(1)-O(1)#1	78.47(13)
Yb(1)-O(10)	1.984(3)	O(8)-Yb(1)-O(1)#1	74.77(14)	O(10)-Yb(1)-O(3)#2	110.20(13)
Yb(1)-O(1)#1	2.310(3)	O(8)-Yb(1)-O(3)#2	82.65(14)	O(10)-Yb(1)-O(12)#3	76.02(12)
Yb(1)-O(3)#2	2.463(3)	O(8)-Yb(1)-O(12)#3	130.54(13)	O(10)-Yb(1)-O(13)#3	116.31(12)
Yb(1)-O(12)#3	2.504(3)	O(8)-Yb(1)-O(13)#3	87.82(13)	O(10)-Yb(1)-O(9)	79.19(15)
Yb(1)-O(13)#3	2.542(3)	O(8)-Yb(1)-O(9)	102.19(16)	O(10)-Yb(1)-O(4)#2	88.17(12)
Yb(1)-O(9)	2.580(5)	O(8)-Yb(1)-O(4)#2	81.95(13)		
Yb(1)-O(4)#2	2.714(3)				
Cu(1)-N(5)	1.818(4)	N(5)#4-Cu(1)-N(5)	176.1(3)	N(5)-Cu(1)-O(14)	91.93(13)
Cu(1)-O(14)	1.967(10)	N(5)#4-Cu(1)-O(14)	91.93(13)	N(5)-Cu(1)-N(6)	73.96(15)
Cu(1)-N(6)	2.302(4)	N(5)#4-Cu(1)-N(6)	103.85(15)	N(5)-Cu(1)-N(6)#4	103.85(15)
Cu(1)-N(6)#4	2.302(4)	N(5)#4-Cu(1)-N(6)#4	73.96(15)	N(5)-Cu(1)-O(15)	99.3(3)
Cu(1)-O(15)	2.396(14)	N(5)#4-Cu(1)-O(15)	83.5(3)	N(5)-Cu(1)-O(15)#4	83.5(3)
Cu(2)-N(3)	1.996(4)	N(5)#4-Cu(1)-O(15)#4	99.3(3)	O(5)#5-Cu(2)-N(1)	165.36(14)
Cu(2)-O(5)#5	2.022(3)	N(3)-Cu(2)-O(5)#5	88.11(14)	O(5)#5-Cu(2)-N(4)	82.95(13)
Cu(2)-N(1)	2.147(4)	N(3)-Cu(2)-N(1)	106.50(15)	O(5)#5-Cu(2)-N(2)	100.46(13)
Cu(2)-N(4)	2.183(4)	N(3)-Cu(2)-N(4)	70.61(15)		
Cu(2)-N(2)	2.203(4)	N(3)-Cu(2)-N(2)	118.58(14)		
6					
Lu(1)-O(5)	2.151(4)	O(5)-Lu(1)-O(9)	80.38(16)	O(9)-Lu(1)-O(7)	77.21(15)
Lu(1)-O(9)	2.246(4)	O(5)-Lu(1)-O(7)	157.44(16)	O(9)-Lu(1)-O(8)	80.00(19)
Lu(1)-O(7)	2.269(4)	O(5)-Lu(1)-O(8)	98.20(18)	O(9)-Lu(1)-O(2)	147.33(14)
Lu(1)-O(8)	2.313(5)	O(5)-Lu(1)-O(2)	129.41(16)	O(9)-Lu(1)-O(3)	78.02(16)
Lu(1)-O(2)	2.383(4)	O(5)-Lu(1)-O(3)	88.12(16)	O(9)-Lu(1)-O(4)	129.42(15)
Lu(1)-O(3)	2.385(4)	O(5)-Lu(1)-O(4)	82.20(15)	O(9)-Lu(1)-O(1)	143.68(17)
Lu(1)-O(4)	2.410(3)	O(5)-Lu(1)-O(1)	77.91(15)		
Lu(1)-O(1)	2.433(4)				
Cu(1)-O(12)#1	1.942(4)	O(12)#1-Cu(1)-N(5)#2	93.37(18)	N(5)#2-Cu(1)-N(2)	167.66(19)
Cu(1)-N(5)#2	1.987(5)	O(12)#1-Cu(1)-N(2)	89.83(17)	N(5)#2-Cu(1)-N(6)#2	80.65(18)
Cu(1)-N(2)	2.013(5)	O(12)#1-Cu(1)-N(6)#2	162.46(18)	N(5)#2-Cu(1)-N(1)	113.16(18)
Cu(1)-N(6)#2	2.038(4)	O(12)#1-Cu(1)-N(1)	94.54(17)	N(4)-Cu(2)-O(13)	91.81(14)
Cu(1)-N(1)	2.197(5)	N(4)#3-Cu(2)-N(4)	176.4(3)	N(4)-Cu(2)-N(3)	79.67(18)
Cu(2)-N(4)#3	1.979(5)	N(4)#3-Cu(2)-O(13)	91.81(14)	N(4)-Cu(2)-N(3)#3	98.15(19)
Cu(2)-O(13)	1.995(10)	N(4)#3-Cu(2)-N(3)	98.15(19)		
Cu(2)-N(3)	2.112(5)	N(4)#3-Cu(2)-N(3)#3	79.67(19)		

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

-x+2,y,-z+3/2; #6 -x, y, -z+5/2. **5**: #1 x-1/2, y+1/2, z; #2 x-1/2, y-1/2, z; #3 -x+1/2, y-1/2, -z+1/2; #4 -x, y, -z+1/2; #5 -x+1/2, y-1/2, -z-1/2. **6**: #1 -x+3/2, y-1/2, -z+1/2; #2 x+1/2, y+1/2, z; #3 -x+1, y, -z-1/2.

Drawings

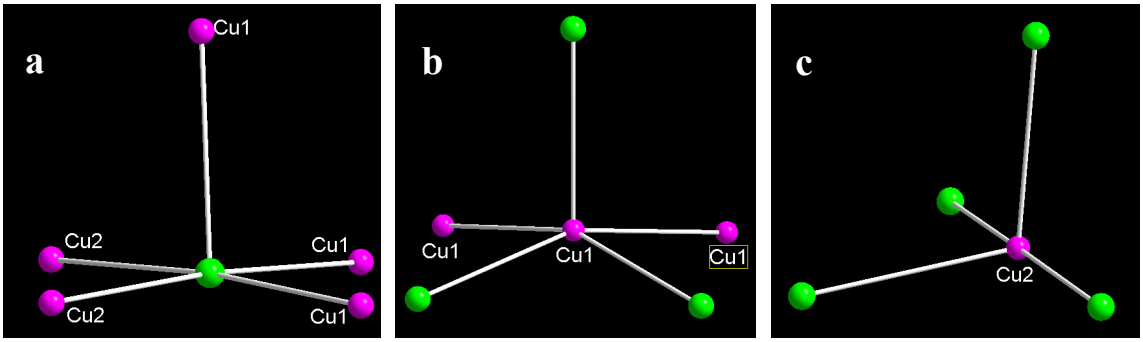

Figure S1 (a) Three Cu1 ions and two Cu2 ions around Gd ions; (b) the metal ions around Cu1 ions; and (c) four Gd ions around Cu2 ions connected by the ligands. All the ligands were omitted. Color codes: green, Gd, purple, Cu.

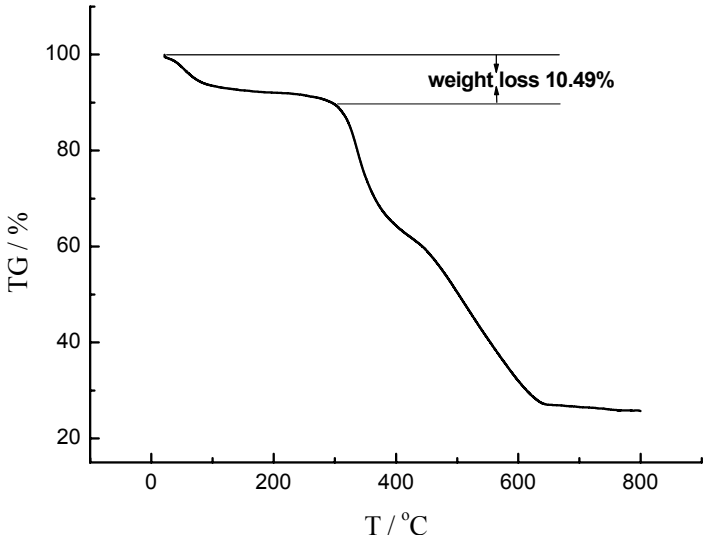

Figure S2 TGA diagram of compound **1**.

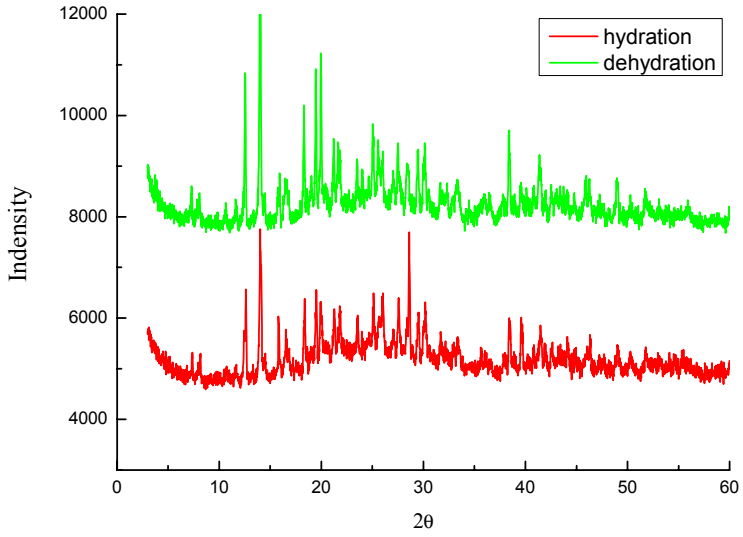

Figure S3 The PXRD spectra of compound **1**. red: hydrated, green: dehydrated.