Electronic Supporting Information for

A Multi-Responsive Luminescent Sensor for Organic Small-Molecule Pollutants and Metal Ions Based on a 4d-4f Metal-Organic Framework

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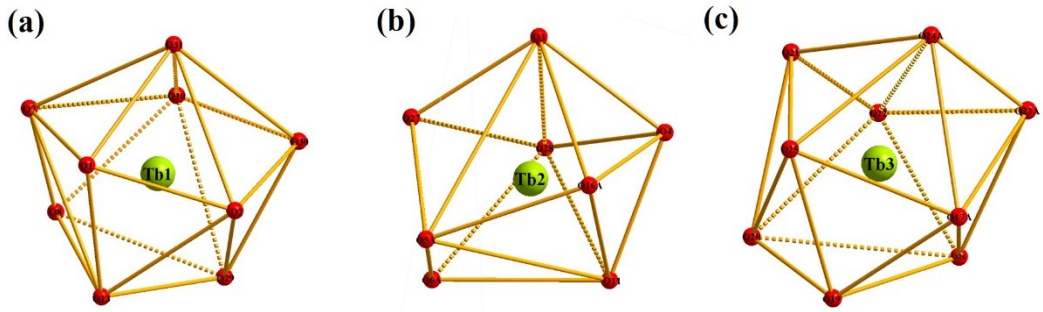

Fig. S1 Coordination polyhedron around Tb^{3+} ions in HMOF **1**.

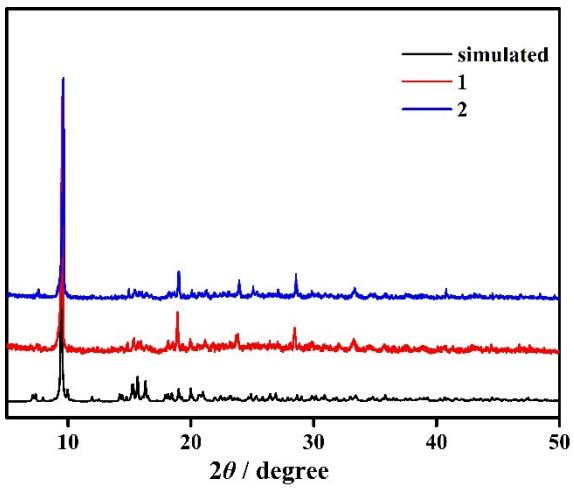

Fig. S2 Simulated and experimental PXRD patterns of HMOFs **1** and **2**.

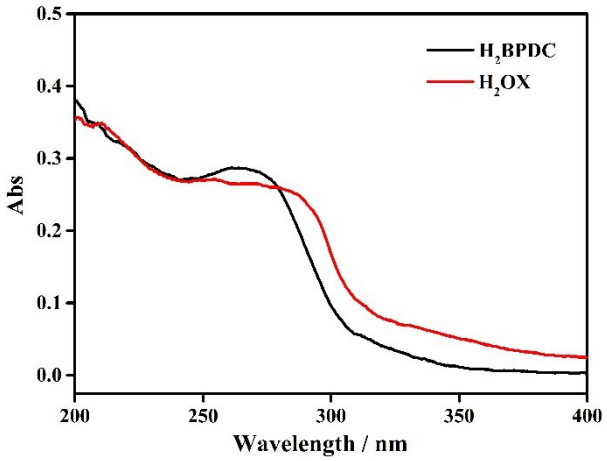

Fig. S3 UV-vis spectra of H_2BPDC and H_2OX.

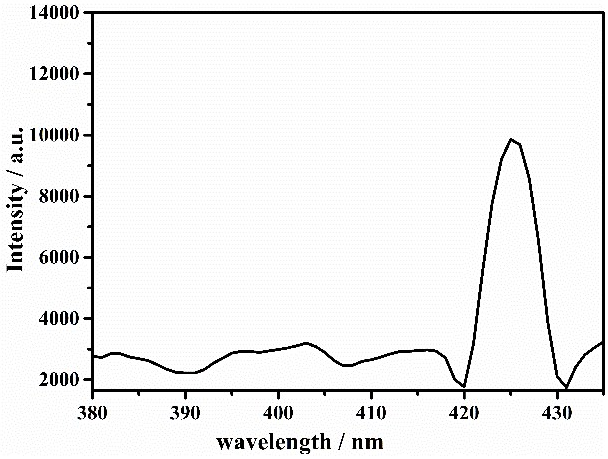

Fig. S4 The phosphorescence spectrum of HMOF **2** (Gd-MOF) at 77K.

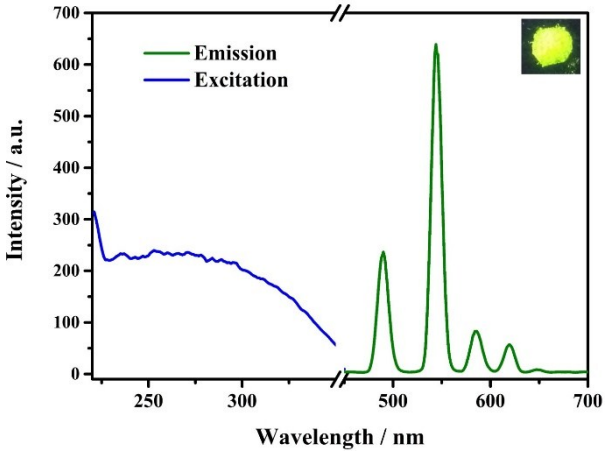

Fig. S5 The solid-state excitation spectrum and emission spectrum with the excitation wavelength of 290 nm for HMOF **1** at room temperature.

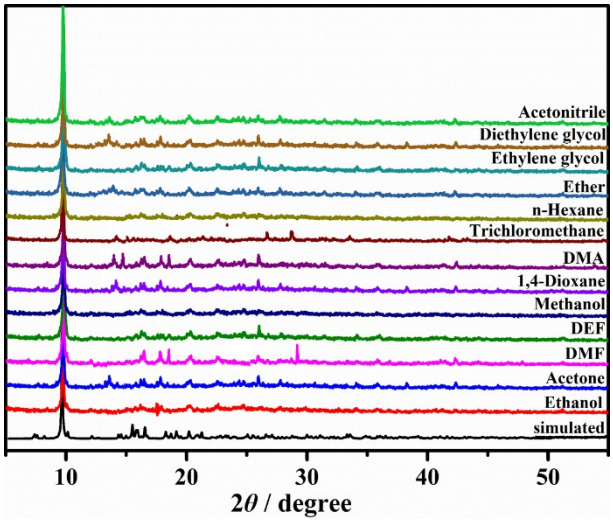

Fig. S6 PXRD patterns of HMOF **1** after immersing in different solvents for 24 hours.

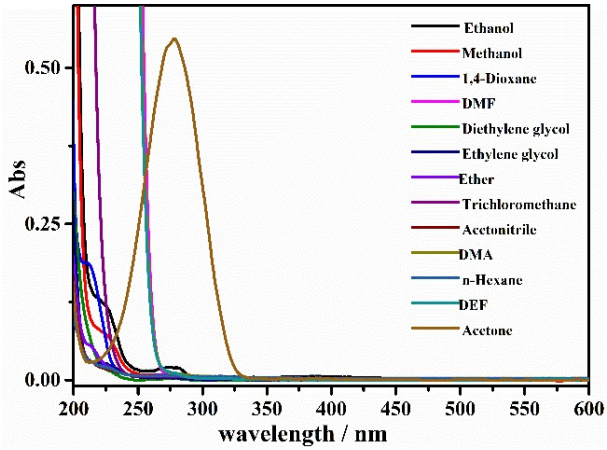

Fig. S7 UV-vis spectra of different solvents.

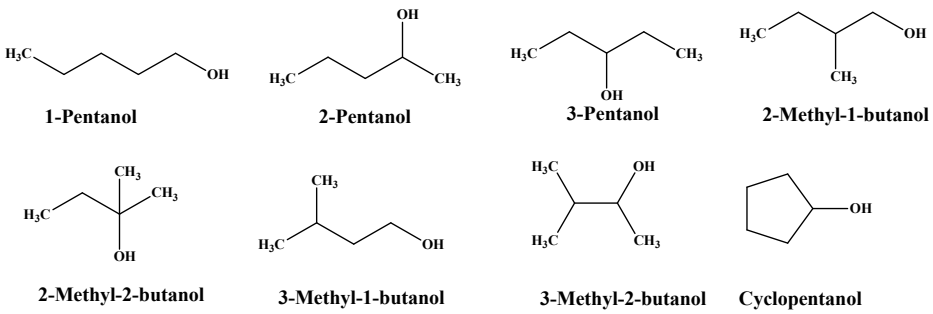

Fig. S8 Eight kinds of alcohols isomers of $C_5H_{12}O$.

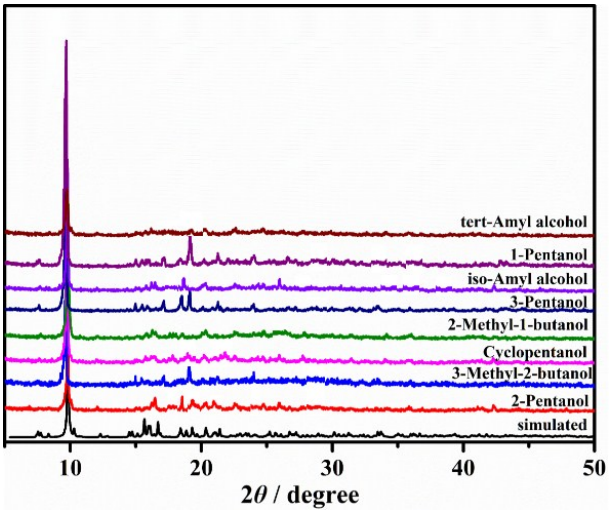

Fig. S9 PXRD of HMOF **1** after immersing in different $C_5H_{12}O$ isomers.

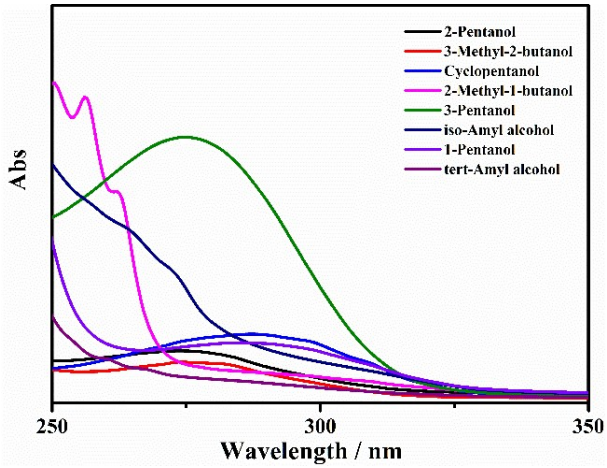

Fig. S10 UV-vis spectra of $C_5H_{12}O$ isomers.

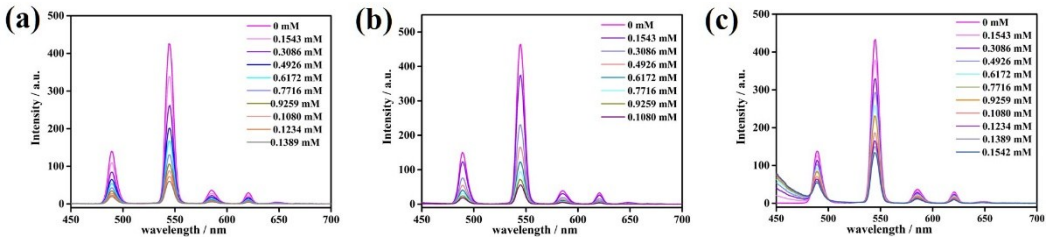

Fig. S11 Emission spectra of HMOF **1** with the addition of 1,3-benzendiamine (a), 1,2-benzendiamine (b) and 1,4-benzendiamine (c) in ethanol.

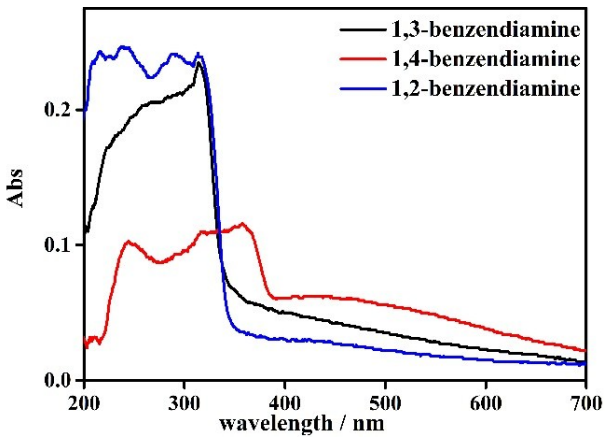

Fig. S12 UV-vis spectra of 1,2-benzendiamine, 1,3-benzendiamine and 1,4-benzendiamine.

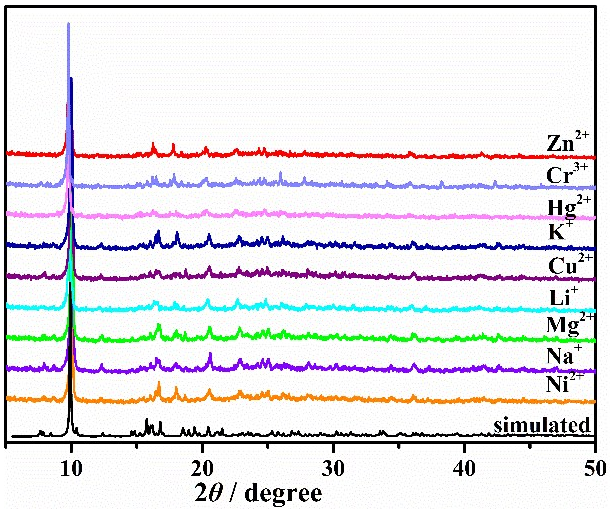

Fig. S13 PXRD of HMOF **1** after immersing in different solutions containing various metal ions.

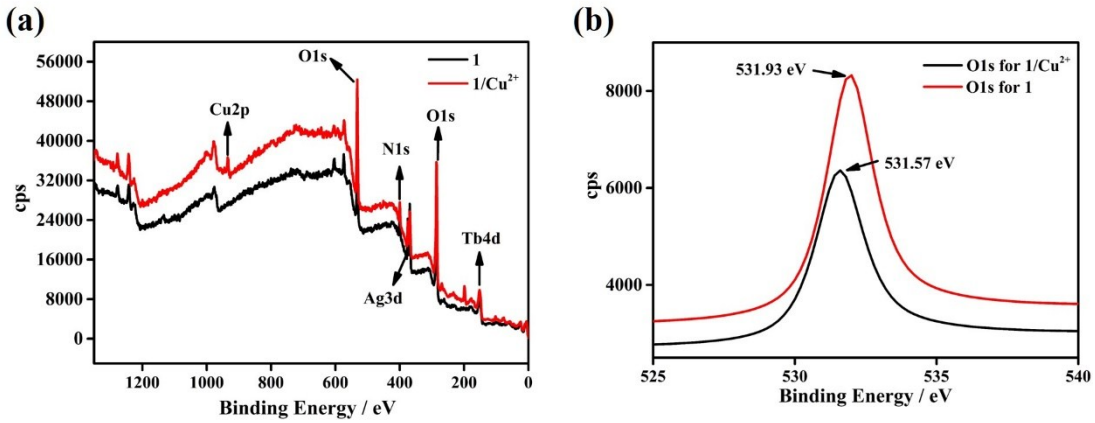

Fig. S14 (a) XPS for HMOF **1** and **1**/$Cu^{2+}$and (b) O1s XPS for HMOF **1** and **1**/Cu^{2+}.

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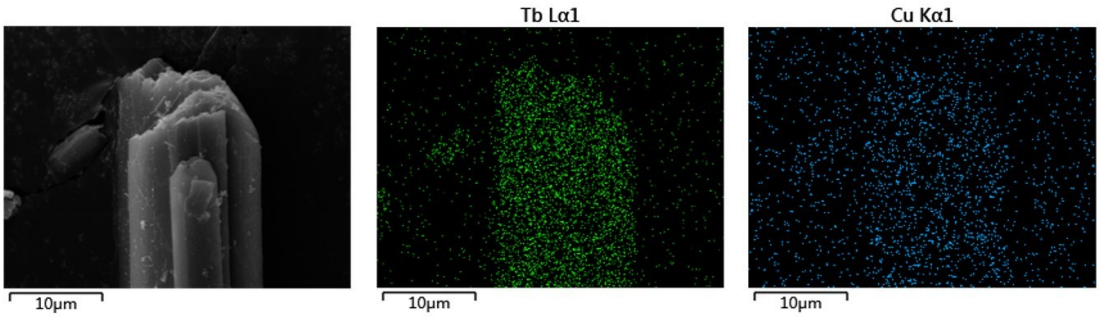

Fig. S15 SEM image of **1**/Cu^{2+} (left) and the corresponding elemental distributions of Tb^{3+} (middle) and Cu^{2+} (right).

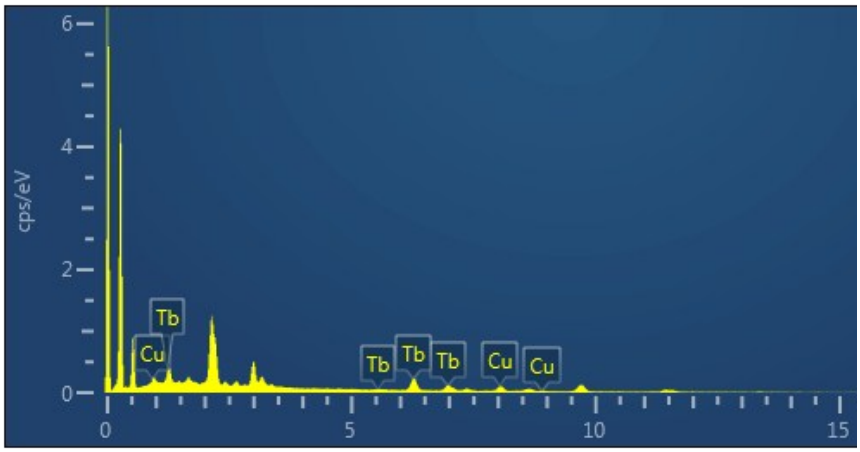

Fig. S16 The EDS of the solid sample of **1**/Cu^{2+}.

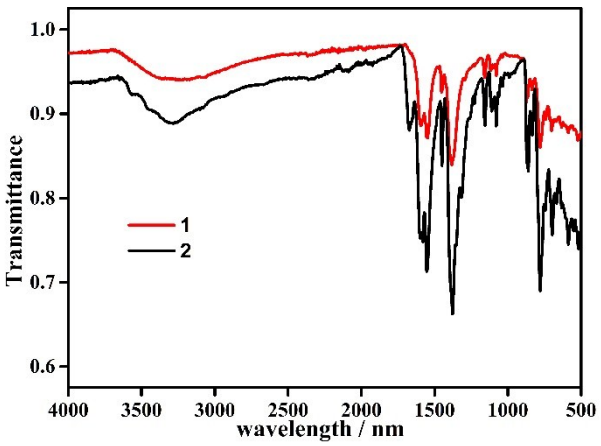

Fig. S17 FT-IR spectra of HMOFs **1** and **2**.

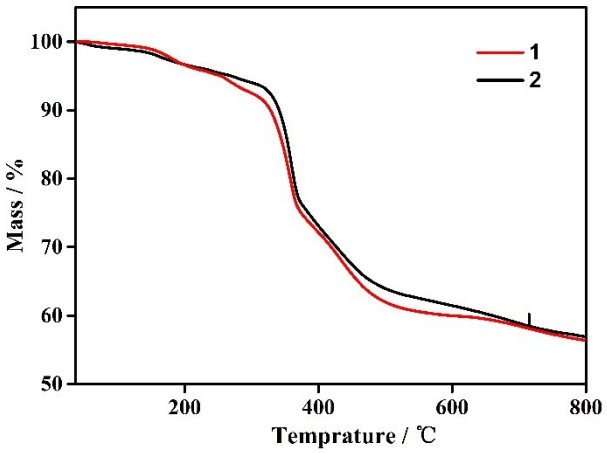

Fig. S18 The TGA of HMOFs **1** and **2**.

Table S1 Crystal Data and Structural Refinement Parameters for HMOFs **1** and **2**

	HMOF **1**	HMOF **2**
formula	$C_{62}H_{58}Ag_3Tb_3N_{10}O_{38}$	$C_{62}H_{58}Ag_3Gd_3N_{10}O_{38}$
fw	2351.44	2346.43
λ / Å	0.71073	0.71073
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	12.69(4)	12.69(3)
b (Å)	12.97(4)	12.95(3)
c (Å)	23.51(7)	23.50(6)
α (deg)	104.00(10)	103.97(4)
β (deg)	102.15(10)	101.91(5)
γ (deg)	91.67(10)	91.81(3)
V / Å^3	3659.89(2)	3653.7(14)
Z	2	2
ρ_{calc} / mg mm^{-3}	2.019	2.018
μ / mm^{-1}	3.739	3.565
reflns collected / unique	56122	29820
R(int)	0.0759	0.0658
2θ range / deg	5.682 to 50.018	6.04 to 50.02
F(000)	2140.0	2134.0
GOF on F^2	1.045	0.918
R_1 / wR_2[$I > 2\sigma(I)$]	0.0426 / 0.0876	0.0471 / 0.1114
R_1 / wR_2 (all data)	0.0656 / 0.0944	0.0638 / 0.1187
largest diff. peak / hole / e Å^{-3}	1.70 / -2.05	2.86 / -1.84

Table S2 Selected bond lengths (Å) and angles (°) for HMOF **1**

HMOF **1**					
Tb1-O25	2.438(5)	O25-Tb1-O27	144.22(16)	O24^{3}-Tb2-O29	79.47(19)
Tb1-O27	2.449(5)	O25-Tb1-O4	71.53(16)	O5^{1}-Tb2-O12	108.1(2)
Tb1-O4	2.467(5)	O25-Tb1-O10	131.98(16)	O5^{1}-Tb2-O24^{3}	69.11(18)
Tb1-O10	2.555(5)	O25-Tb1-O9	80.58(17)	O5^{1}-Tb2-O13	90.6(3)
Tb1-O21	2.413(5)	O25-Tb1-O26	71.62(16)	O5^{1}-Tb2-O11	79.29(18)
Tb1-O9	2.492(5)	O25-Tb1-O22	134.09(16)	O5^{1}-Tb2-O23^{3}	130.1(2)
Tb1-O26	2.471(5)	O27-Tb1-O4	136.20(17)	O5^{1}-Tb2-O29	75.4(2)
Tb1-O7	2.395(5)	O27-Tb1-O10	75.23(16)	O5^{1}-Tb2-O28	139.3(2)
Tb1-O22	2.516(5)	O27-Tb1-O9	125.21(16)	O1^{3}-Tb2-O12	78.51(19)
Tb2-O12	2.501(5)	O27-Tb1-O26	72.80(16)	O1^{3}-Tb2-O24^{3}	69.98(19)
Tb2-O24^{3}	2.423(5)	O27-Tb1-O22	70.27(16)	O1^{3}-Tb2-O11	121.9(2)
Tb2-O5^{2}	2.330(6)	O4-Tb1-O10	96.30(16)	O1^{3}-Tb2-O23^{3}	94.8(2)
Tb2-O1^{3}	2.337(6)	O4-Tb1-O9	70.80(17)	O1^{3}-Tb2-O29	149.3(2)
Tb2-O11	2.502(5)	O4-Tb1-O26	126.49(17)	O1^{3}-Tb2-O28	127.2(3)
Tb2-O23^{3}	2.462(5)	O4-Tb1-O22	66.37(17)	O23^{3}-Tb2-O12	121.65(18)
Tb2-O29	2.457(6)	O21-Tb1-O25	87.08(16)	O23^{3}-Tb2-O11	134.59(16)
Tb2-O28	2.402(6)	O21-Tb1-O27	81.35(16)	O29-Tb2-O12	131.60(19)
Tb3-O31	2.424(5)	O21-Tb1-O4	75.88(17)	O29-Tb2-O11	82.76(19)
Tb3-O18^{1}	2.415(4)	O21-Tb1-O10	136.16(15)	O29-Tb2-O23^{3}	75.12(18)
Tb3-O30	2.363(5)	O21-Tb1-O9	146.61(16)	O28-Tb2-O12	71.2(2)
Tb3-O19	2.417(5)	O21-Tb1-O26	64.83(16)	O28-Tb2-O24^{3}	132.5(2)
Tb3-O14^{2}	2.409(4)	O21-Tb1-O22	65.94(16)	O28-Tb2-O11	68.52(18)
Tb3-O13^{2}	2.526(5)	O9-Tb1-O10	52.04(16)	O28-Tb2-O23^{3}	67.98(18)
Tb3-O20	2.620(5)	O9-Tb1-O22	101.56(17)	O28-Tb2-O29	76.5(3)
Tb3-O15^{1}	2.451(5)	O26-Tb1-O10	137.20(16)	O31-Tb3-O13^{1}	127.23(15)
Tb3-O16^{1}	2.578(5)	O26-Tb1-O9	136.97(16)	O31-Tb3-O20	88.31(17)
Ag1-N4^{4}	2.233(6)	O26-Tb1-O22	121.41(16)	O31-Tb3-O15^{2}	122.50(18)
Ag1-N2	2.409(6)	O7-Tb1-O25	86.50(16)	O31-Tb3-O16^{2}	71.03(17)
Ag1-N10^{5}	2.558(6)	O7-Tb1-O27	78.74(16)	O18^{2}-Tb3-O31	81.55(16)
Ag1-N1	2.272(6)	O7-Tb1-O4	141.48(17)	O18^{2}-Tb3-O19	71.67(16)
Ag2-N7	2.255(6)	O7-Tb1-O10	75.01(16)	O18^{2}-Tb3-O13^{1}	148.75(15)
Ag2-N3	2.243(6)	O7-Tb1-O21	135.60(16)	O18^{2}-Tb3-O20	122.92(15)
Ag2-N5	2.235(6)	O7-Tb1-O9	74.73(16)	O18^{2}-Tb3-O15^{2}	82.31(16)
Ag3-N6	2.246(6)	O7-Tb1-O26	71.46(16)	O18^{2}-Tb3-O16^{2}	69.45(15)
Ag3-N8	2.217(6)	O7-Tb1-O22	138.82(16)	O30-Tb3-O31	144.42(17)
Ag3-N9	2.280(6)	O22-Tb1-O10	71.40(15)	O30-Tb3-O18^{2}	78.41(16)
		O12-Tb2-O11	52.37(16)	O30-Tb3-O19	74.25(17)
		O24^{3}-Tb2-O12	148.22(17)	O30-Tb3-O14^{1}	132.81(16)
		O24^{3}-Tb2-O11	146.71(16)	O30-Tb3-O13^{1}	81.27(16)
		O24^{3}-Tb2-O23^{3}	66.51(16)	O30-Tb3-O20	78.54(16)
		O30-Tb3-O15^{2}	83.53(18)	O30-Tb3-O16^{2}	126.68(16)

O19-Tb3-O31	71.66(17)	O13[1]-Tb3-O16[2]	105.59(16)	N5-Ag2-N3	123.0(2)
O19-Tb3-O13[1]	124.65(16)	O15[2]-Tb3-O13[1]	71.99(17)	N6-Ag3-N9	106.9(2)
O19-Tb3-O20	51.97(15)	O15[2]-Tb3-O20	144.45(16)	N8-Ag3-N6	125.6(2)
O19-Tb3-O15[2]	148.49(17)	O15[2]-Tb3-O16[2]	51.62(16)	N8-Ag3-N9	123.8(2)
O19-Tb3-O16[2]	128.93(16)	O16[2]-Tb3-O20	154.77(15)		
O14[1]-Tb3-O31	74.76(16)	N4[4]-Ag1-N2	139.9(2)		
O14[1]-Tb3-O18[2]	147.64(16)	N4[4]-Ag1-N10[5]	89.5(2)		
O14[1]-Tb3-O19	119.45(16)	N4[4]-Ag1-N1	134.5(2)		
O14[1]-Tb3-O13[1]	53.12(15)	N2-Ag1-N10[5]	85.4(2)		
O14[1]-Tb3-O20	78.55(16)	N1-Ag1-N2	71.1(2)		
O14[1]-Tb3-O15[2]	92.04(17)	N1-Ag1-N10[5]	132.7(2)		
O14[1]-Tb3-O16[2]	82.05(16)	N3-Ag2-N7	111.9(2)		
O13[1]-Tb3-O20	75.10(15)	N5-Ag2-N7	122.0(2)		

Symmetry transformations used to generate equivalent atoms:[1]+X,1+Y,+Z; [2]-1-X,2-Y,-Z; [3]1-X,2-Y,1-Z; [4]-X,1-Y,1-Z; [5]-X,2-Y,1-Z; [6]+X,-1+Y,+Z

Table S3 Selected bond lengths (Å) and angles (°) for HMOF 2

HMOF **2**					
Gd1-O12[1]	2.478(5)	O12[1]-Gd1-O11[1]	52.20(17)	O7-Gd3-O13	69.17(17)
Gd1-O1[2]	2.455(5)	O12[1]-Gd1-O23	102.07(18)	O25-Gd3-O14	123.26(18)
Gd1-O31	2.426(5)	O12[1]-Gd1-O30	136.56(18)	O25-Gd3-O5[3]	87.13(18)
Gd1-O11[1]	2.540(5)	O12-Gd1-O12[1]	70.74(17)	O25-Gd3-O15[4]	126.75(18)
Gd1-O29	2.425(5)	O1[2]-Gd1-O11[1]	95.80(17)	O25-Gd3-O13	71.98(18)
Gd1-O23	2.508(5)	O1[2]-Gd1-O23	66.38(18)	O6[3]-Gd3-O7	71.50(17)
Gd1-O18[1]	2.392(5)	O1[2]-Gd1-O30	126.15(17)	O6[3]-Gd3-O25	71.61(19)
Gd1-O30	2.478(5)	O31-Gd1-O12[1]	125.12(17)	O6[3]-Gd3-O14	148.1(2)
Gd1-O24	2.412(5)	O31-Gd1-O1[2]	136.09(19)	O6[3]-Gd3-O5[3]	52.17(17)
Gd2-O9[5]	2.493(6)	O31-Gd1-O11[1]	75.11(17)	O6[3]-Gd3-O15[4]	124.49(17)
Gd2-O28	2.394(7)	O31-Gd1-O23	70.08(17)	O6[3]-Gd3-O16[4]	120.03(17)
Gd2-O27	2.428(6)	O31-Gd1-O30	73.59(18)	O6[3]-Gd3-O13	129.01(17)
Gd2-O21	2.423(5)	O29-Gd1-O12[1]	80.56(17)	O26-Gd3-O7	78.41(18)
Gd2-O20	2.297(6)	O29-Gd1-O1[2]	71.88(18)	O26-Gd3-O25	144.9(2)
Gd2-O22	2.438(5)	O29-Gd1-O31	144.16(17)	O26-Gd3-O6[3]	74.62(18)
Gd2-O10[5]	2.498(5)	O29-Gd1-O11[1]	132.17(17)	O26-Gd3-O14	82.68(19)
Gd2-O4[2]	2.312(7)	O29-Gd1-O23	134.20(17)	O26-Gd3-O5[3]	79.68(17)
Gd3-O7	2.404(5)	O29-Gd1-O30	70.81(17)	O26-Gd3-O15[4]	81.03(18)
Gd3-O25	2.407(5)	O23-Gd1-O11[1]	71.36(17)	O26-Gd3-O16[4]	133.20(18)
Gd3-O6[3]	2.401(5)	O18[1]-Gd1-O12[1]	74.10(17)	O26-Gd3-O13	125.67(17)
Gd3-O26	2.341(5)	O18[1]-Gd1-O1[2]	141.20(18)	O14-Gd3-O5[3]	144.62(17)
Gd3-O14	2.442(5)	O18[1]-Gd1-O31	78.69(18)	O14-Gd3-O15[4]	72.10(18)
Gd3-O5[3]	2.607(5)	O18[1]-Gd1-O11[1]	74.67(17)	O14-Gd3-O13	51.48(17)
Gd3-O15[4]	2.531(5)	O18[1]-Gd1-O29	86.77(18)	O15[4]-Gd3-O5[3]	75.00(17)
Gd3-O16[4]	2.406(5)	O18[1]-Gd1-O23	138.44(17)	O15[4]-Gd3-O13	105.79(17)
Gd3-O13	2.576(5)	O181-Gd1-O30	72.37(17)	O16[4]-Gd3-O25	74.20(19)
Ag2-N7	2.215(6)	O18[1]-Gd1-O24	136.24(17)	O16[4]-Gd3-O14	91.8(2)
Ag2-N3	2.283(6)	O30-Gd1-O11[1]	138.04(17)	O16[4]-Gd3-O5[3]	78.68(17)
Ag2-N5	2.246(6)	O30-Gd1-O23	121.33(18)	O16[4]-Gd3-O15[4]	53.42(17)
Ag3-N8	2.238(6)	O24-Gd1-O12[1]	146.31(17)	O16[4]-Gd3-O13	81.82(17)
Ag3-N9	2.256(6)	O24-Gd1-O1[2]	75.70(17)	O13-Gd3-O5[3]	154.64(16)
Ag3-N6	2.240(7)	O24-Gd1-O31	82.12(18)	O9[5]-Gd2-O10[5]	52.15(19)
Ag1-N2	2.285(7)	O24-Gd1O11[1]	136.48(18)	O28-Gd2-O9[5]	72.4(3)
Ag1-N10[6]	2.230(7)	O24-Gd1-O29	86.37(17)	O28-Gd2-O27	74.9(3)
Ag1-N1	2.418(7)	O24-Gd1-O23	66.13(17)	O28-Gd2-O21	131.9(2)
Ag1-N4	2.555(6)	O24-Gd1-O30	64.56(17)	O28-Gd2-O22	68.1(2)
		O7-Gd3-O25	82.02(18)	O28-Gd2-O10[5]	68.4(2)
		O7-Gd3-O14	82.36(19)	O27-Gd2-O9[5]	132.7(2)
		O7-Gd3-O5[3]	123.10(17)	O27-Gd2-O22	75.94(19)
		O7-Gd3-O15[4]	148.95(17)	O27-Gd2-O10[5]	84.4(2)
		O7-Gd3-O16[4]	147.05(17)	O21-Gd2-O9[5]	148.1(2)

O21-Gd2-O27	78.6(2)	O4[2]-Gd2-O28	128.5(3)	N10[6]-Ag1-N2	134.7(2)
O21-Gd2-O22	66.91(17)	O4[2]-Gd2-O27	148.5(2)	N10[6]-Ag1-N1	139.4(2)
O21-Gd2-O10[5]	146.87(17)	O4[2]Gd2-O21	70.0(2)	N10[6]-Ag1-N4	89.0(2)
O20-Gd2-O9[5]	106.4(2)	O4[2]-Gd2-O22	92.8(2)	N1-Ag1-N4	85.4(2)
O20-Gd2-O28	138.7(3)	O4[2]-Gd2-O10[5]	121.8(2)		
O20-Gd2-O27	77.8(2)	N7-Ag2-N3	123.2(2)		
O20-Gd2-O21	70.06(19)	N7-Ag2-N5	125.5(2)		
O20-Gd2-O22	132.9(2)	N5-Ag2-N3	107.2(2)		
O20-Gd2-O10[5]	78.69(19)	N8-Ag3-N9	112.5(2)		
O20-Gd2-O4[2]	89.8(3)	N8-Ag3-N6	122.0(2)		
O22-Gd2-O9[5]	120.1(2)	N6-Ag3-N9	122.5(2)		
O22-Gd2-O10[5]	135.52(17)	N2-Ag1-N1	71.4(2)		
O4[2]-Gd2-O9[5]	78.4(2)	N2-Ag1-N4	133.0(2)		

Symmetry transformations used to generate equivalent atoms:[1]2-X,-Y,2-Z; [2]1+X,-1+Y,+Z; [3]-X,1-Y,1-Z; [4]-X,-Y,1-Z; [5]+X,-1+Y,+Z; [6]+X,1+Y,+Z; [7]-1+X,1+Y,+Z