Supporting information for

Synthesis of diamondoid lanthanide-polyoxometalate solids as tunable photoluminescent materials

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Single crystal X-ray data collections and structure determinations

The unit cell determinations and data collections for the crystals of **Ln-POMs** (Ln = La, Eu and Tb) were performed on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector. The data were collected using graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å) at 293 K. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.[S1] The structures were solved by direct methods and refined by full-matrix least-square methods with the SHELX-97 program package.[S2] Because the diffraction ability of the light atoms of C, N and O is very poor compared with the heavy atoms of W and Ln, the disordered DMF ligands can not be well-positioned from difference Fourier maps. The distances between C, N and O atoms of DMF ligands were fixed to the reasonable values, and were refined isotropically. The four disordered lattice DMF molecules could not be located successfully from Fourier maps in the refinement cycles. The four lattice DMF molecules were removed using the SQUEEZE procedure implemented in the PLATON package.[S3] The resulting new files were used to further refine the structures. The compositions of the three Ln-POMs were based on the elemental analyses, thermogravimetric analyses (TGA) and single crystal structures. The four lattice DMF molecules were added to account for the formulae in the cif files. The poor crystal data suggest that only the gross connectivities and partial structures were obtained. The relative high Flack parameter for Tb-POM suggests that the crystal is

partially twined.

References

S1. *CrysAlisPro*, version 1.171.34.44, Oxford Diffraction Ltd.: Oxfordshire, U.K., 2010.

S2. G. M. Sheldrick, *Program for Structure Refinement*: University of Göttingen, Germany, 1997.

S3. A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7.

Figures

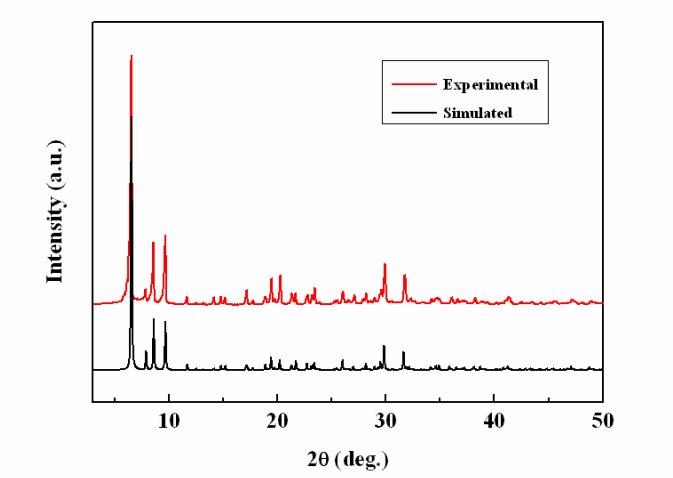

Fig. S1. PXRD for **La-POM**.

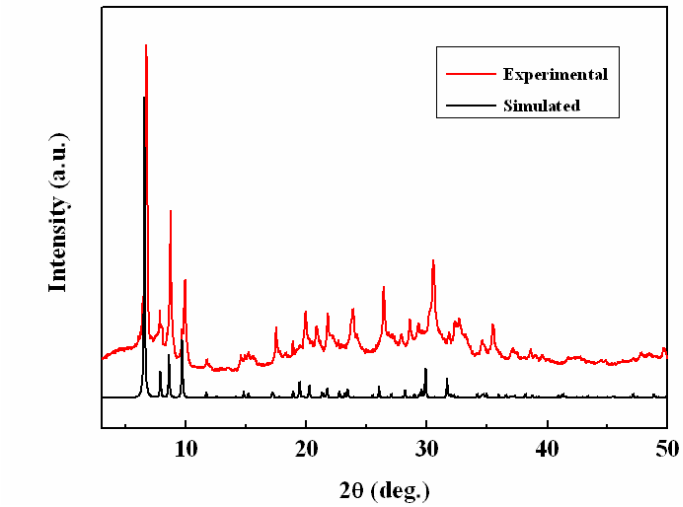

Fig. S2. PXRD for **Eu-POM**.

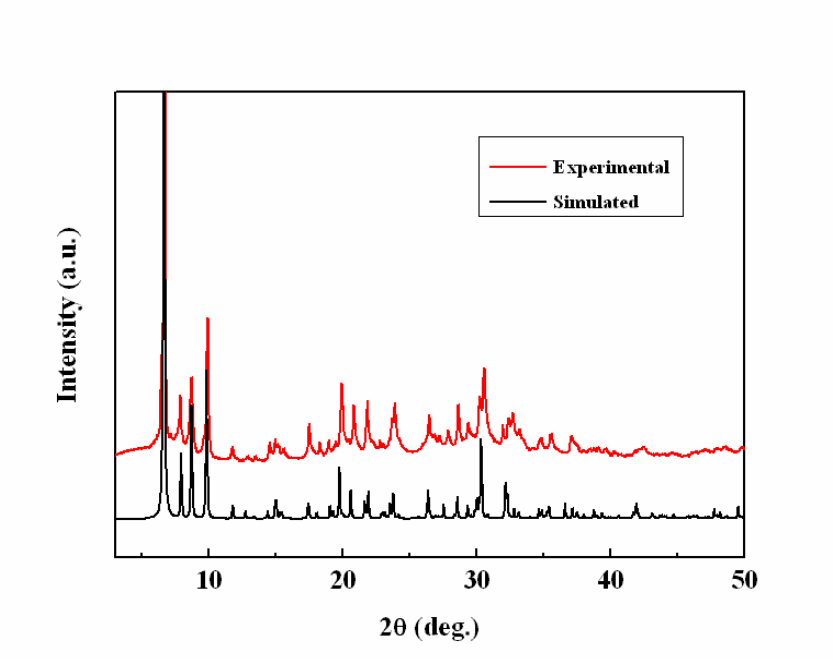

Fig. S3. PXRD for **Tb-POM**.

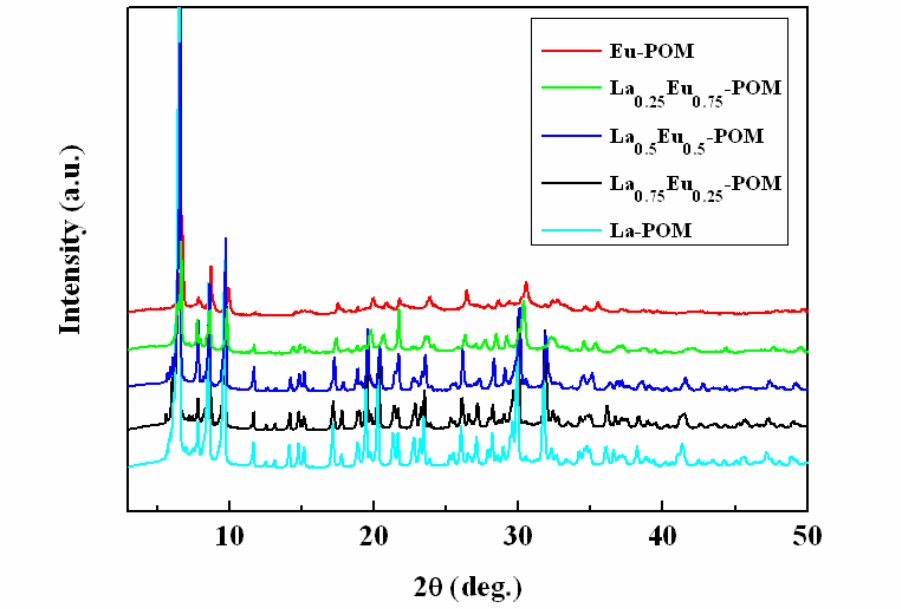

Fig. S4. PXRD for **$La_{1-x}Eu_x$-POM**.

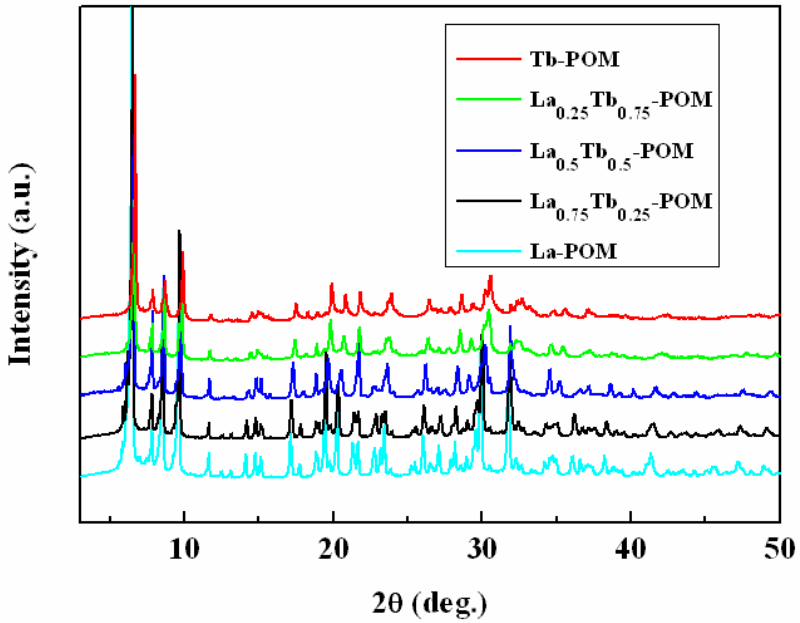

Fig. S5. PXRD for **$La_{1-x}Tb_x$-POM**.

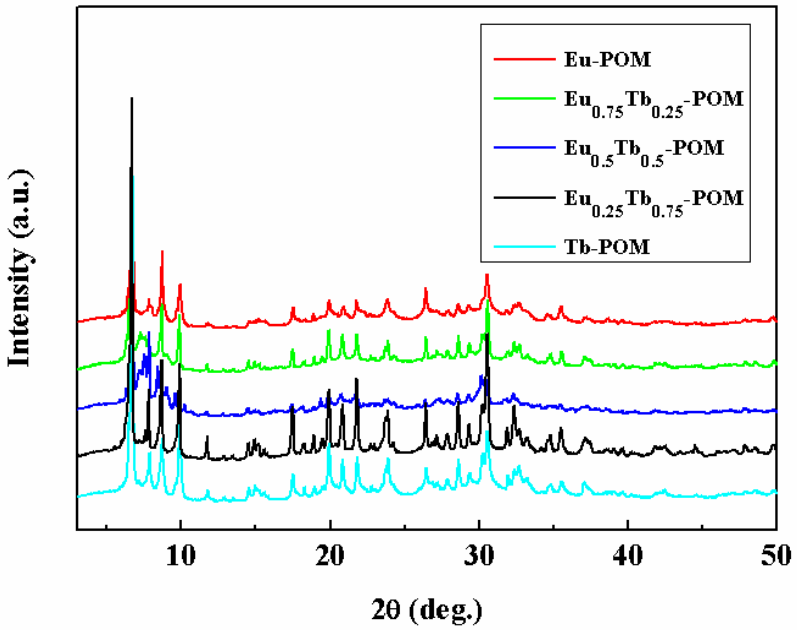

Fig. S6. PXRD for **Eu_xTb_{1-x}-POM**.

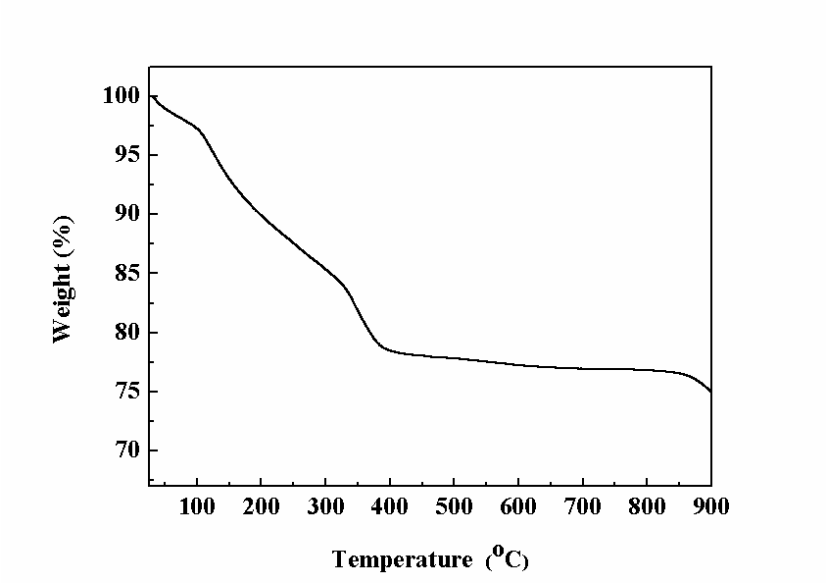

Fig. S7. TGA curve for **La-POM**.

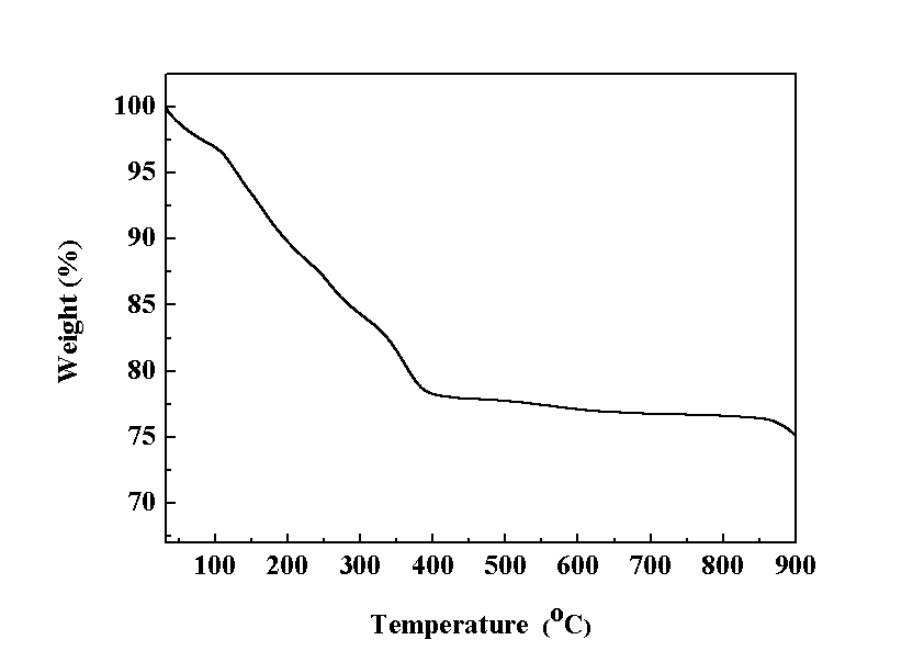

Fig. S8. TGA curve for **Eu-POM**.

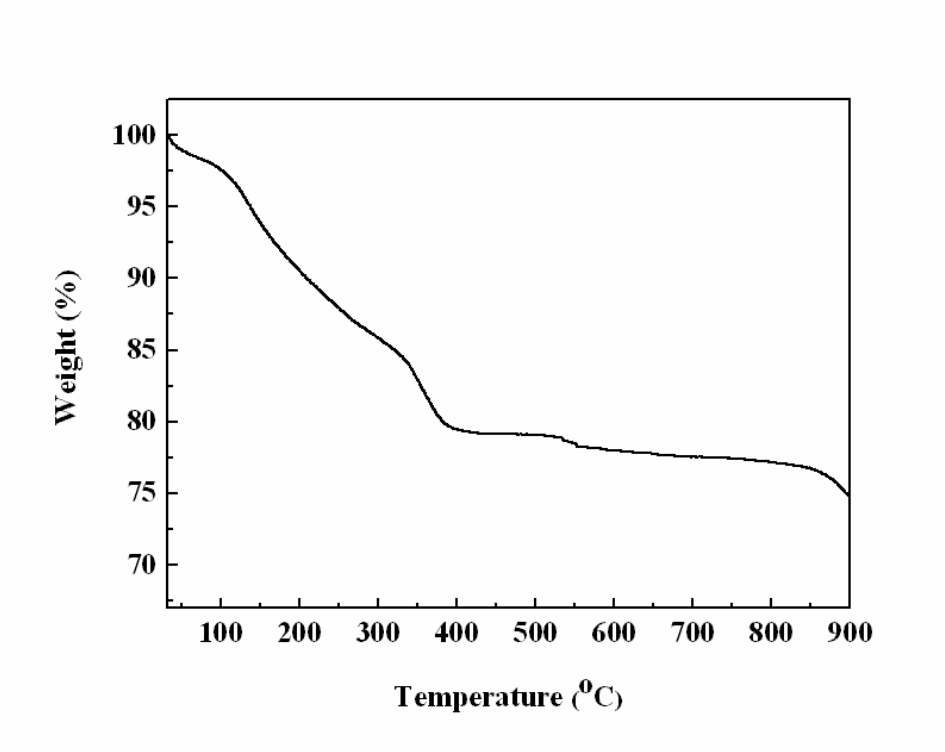

Fig. S9. TGA curve for **Tb-POM**.

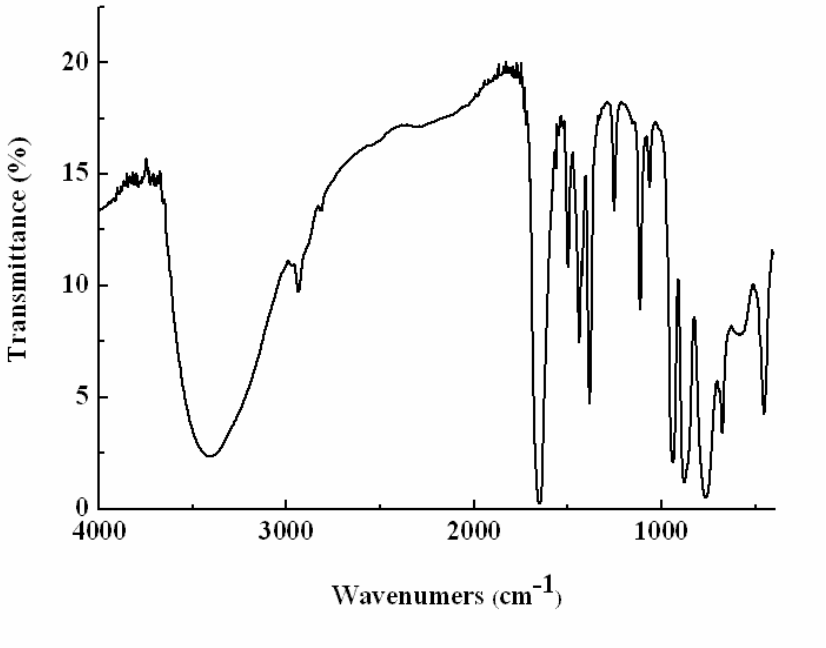

Fig. S10. IR spectrum of **La-POM**.

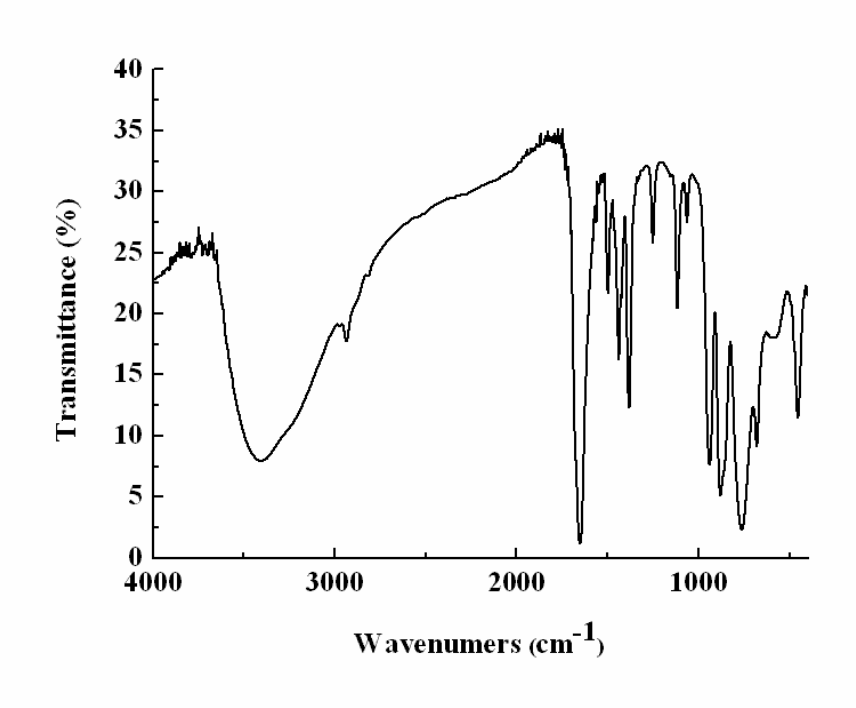

Fig. S11. IR spectrum of **Eu-POM**.

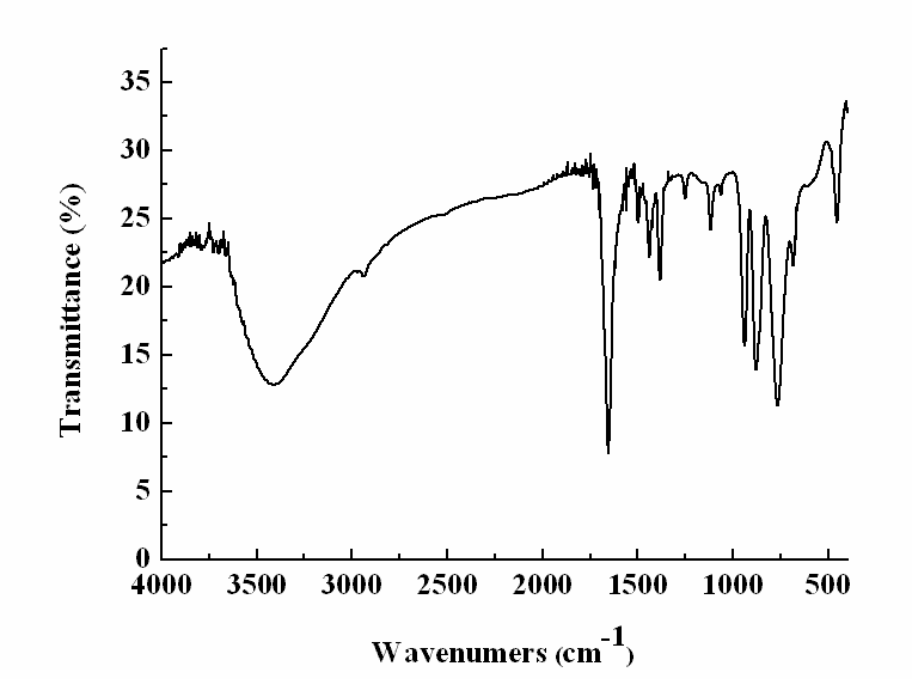

Fig. S12. IR spectrum of **Tb-POM**.

Tables

Table S1. Selected bond lengths (Å) and angles (°) for **La-POM**.

Bond length	(Å)	Bond angle	(°)	Bond angle	(°)
W(1)-O(2)	1.712(16)	O(2)-W(1)-O(5)	100.4(7)	O(7)^{iii}-W(3)-O(8)	89.0(5)
W(1)-O(5)	1.833(12)	O(2)-W(1)-O(10)	101.2(7)	O(9)-W(3)-O(8)	73.8(5)
W(1)-O(10)	1.899(13)	O(5)-W(1)-O(10)	91.4(6)	O(5)-W(3)-O(8)	71.7(5)
W(1)-O(1)	1.938(14)	O(2)-W(1)-O(1)	97.1(7)	O(13)^{iv}-La(1)-O(13)	94.3(13)
W(1)-O(7)	1.957(14)	O(5)-W(1)-O(1)	91.1(6)	O(13)^{iv}-La(1)-O(12)^{iv}	138.9(7)
W(1)-O(8)	2.175(13)	O(10)-W(1)-O(1)	160.8(6)	O(13)-La(1)-O(12)^{iv}	72.4(8)
W(2)-O(4)	1.715(15)	O(2)-W(1)-O(7)	100.6(7)	O(12)^{iv}-La(1)-O(12)	141.3(10)
W(2)-O(9)	1.924(15)	O(5)-W(1)-O(7)	158.9(6)	O(13)^{iv}-La(1)-O(3)	132.9(6)
W(2)-O(1)	1.940(14)	O(10)-W(1)-O(7)	83.6(5)	O(12)^{iv}-La(1)-O(3)	70.6(5)
W(2)-O(10)^{i}	1.945(12)	O(1)-W(1)-O(7)	87.2(6)	O(13)^{iv}-La(1)-O(11)	139.4(7)
W(2)-O(6)	2.018(14)	O(2)-W(1)-O(8)	169.3(6)	O(13)-La(1)-O(11)	77.2(7)
W(2)-O(8)	2.190(13)	O(5)-W(1)-O(8)	73.2(5)	O(12)^{iv}-La(1)-O(11)	76.6(6)
W(3)-O(11)	1.735(15)	O(10)-W(1)-O(8)	87.8(5)	O(12)-La(1)-O(11)	88.2(6)
W(3)-O(6)^{ii}	1.827(14)	O(1)-W(1)-O(8)	74.7(6)	O(3)-La(1)-O(11)	66.7(3)
W(3)-O(7)^{iii}	1.871(14)	O(7)-W(1)-O(8)	86.1(5)	O(11)-La(1)-O(11)^{iv}	133.4(6)
W(3)-O(9)	1.982(12)	O(4)-W(2)-O(9)	98.8(6)	O(13)^{iv}-La(1)-O(14)	72.1(8)
W(3)-O(5)	1.984(13)	O(4)-W(2)-O(1)	99.4(7)	O(13)-La(1)-O(14)	68.0(9)
W(3)-O(8)	2.119(12)	O(9)-W(2)-O(1)	91.5(6)	O(12)^{iv}-La(1)-O(14)	131.2(7)
La(1)-O(13)^{iv}	2.50(3)	O(4)-W(2)-O(10)^{i}	100.4(6)	O(12)-La(1)-O(14)	70.9(7)
La(1)-O(12)^{iv}	2.50(2)	O(9)-W(2)-O(10)^{i}	160.3(5)	O(3)-La(1)-O(14)	120.1(5)
La(1)-O(3)	2.55(3)	O(1)-W(2)-O(10)^{i}	90.0(6)	O(11)-La(1)-O(14)	67.9(6)
La(1)-O(11)^{iv}	2.558(14)	O(4)-W(2)-O(6)	100.2(6)	O(11)^{iv}-La(1)-O(14)	140.6(6)
La(1)-O(14)^{iv}	2.64(2)	O(9)-W(2)-O(6)	87.9(6)	O(14)-La(1)-O(14)^{iv}	119.9(11)
Zn(1)-O(8)	1.883(12)	O(1)-W(2)-O(6)	160.3(6)	O(8)^{iii}-Zn(1)-O(8)^{ii}	109.4(4)
		O(10)^{i}-W(2)-O(6)	84.2(6)	O(8)^{ii}-Zn(1)-O(8)	109.5(7)
		O(4)-W(2)-O(8)	169.5(6)	O(8)^{ii}-Zn(1)-O(8)^{i}	109.4(4)
		O(9)-W(2)-O(8)	73.3(4)	O(8)-Zn(1)-O(8)^{i}	109.4(3)
		O(1)-W(2)-O(8)	74.3(6)	W(1)-O(1)-W(2)	114.4(8)
		O(10)^{i}-W(2)-O(8)	88.2(5)	W(1)-O(5)-W(3)	116.5(7)
		O(6)-W(2)-O(8)	86.7(5)	W(3)^{ii}-O(6)-W(2)	149.0(7)
		O(11)-W(3)-O(6)^{ii}	101.3(6)	W(3)^{i}-O(7)-W(1)	151.8(7)
		O(11)-W(3)-O(7)^{iii}	103.5(6)	Zn(1)-O(8)-W(3)	118.5(6)
		O(6)^{ii}-W(3)-O(7)^{iii}	89.0(6)	Zn(1)-O(8)-W(1)	120.3(5)
		O(11)-W(3)-O(9)	93.9(6)	W(3)-O(8)-W(1)	98.3(5)
		O(6)^{ii}-W(3)-O(9)	88.8(6)	Zn(1)-O(8)-W(2)	119.5(7)
		O(7)^{iii}-W(3)-O(9)	162.6(5)	W(3)-O(8)-W(2)	98.9(4)
		O(11)-W(3)-O(5)	96.2(6)	W(1)-O(8)-W(2)	96.6(5)
		O(6)^{ii}-W(3)-O(5)	162.3(5)	W(2)-O(9)-W(3)	113.9(5)
		O(7)^{iii}-W(3)-O(5)	90.2(6)	W(1)-O(10)-W(2)^{iii}	154.7(8)
		O(9)-W(3)-O(5)	86.8(6)	W(3)-O(11)-La(1)	162.0(8)
		O(11)-W(3)-O(8)	162.9(6)	C(4)-O(12)-La(1)	135.4(19)
		O(6)^{ii}-W(3)-O(8)	90.6(5)	C(1)-O(14)-La(1)	127(2)

Symmetry transformations used to generate equivalent atoms: i) -y+1/2, x+1/2, -z+3/2; ii) -x, -y+1, z; iii) y-1/2, -x+1/2, -z+3/2; iv) x, -y+3/2, -z+5/4.

Table S2. Selected bond lengths (Å) and angles (°) for **Eu-POM**.

Bond length	(Å)	Bond angle	(°)	Bond angle	(°)
W(1)-O(2)	1.751(13)	O(2)-W(1)-O(1)	101.2(5)	O(7)-W(3)-O(6)	73.6(4)
W(1)-O(1)	1.820(11)	O(2)-W(1)-O(8)	103.4(5)	O(10)^{ii}-W(3)-O(6)	87.8(4)
W(1)-O(8)	1.862(10)	O(1)-W(1)-O(8)	89.1(5)	O(9)-W(3)-O(6)	73.9(4)
W(1)-O(11)	1.991(10)	O(2)-W(1)-O(11)	93.6(5)	O(8)^{iii}-W(3)-O(6)	87.2(4)
W(1)-O(7)	2.010(11)	O(1)-W(1)-O(11)	88.0(5)	O(5)-Eu(1)-O(5)^{iv}	145.4(8)
W(1)-O(6)	2.097(9)	O(8)-W(1)-O(11)	163.0(4)	O(5)-Eu(1)-O(2)	89.5(5)
W(2)-O(3)	1.661(12)	O(2)-W(1)-O(7)	96.5(6)	O(5)^{iv}-Eu(1)-O(2)	76.9(4)
W(2)-O(11)	1.910(11)	O(1)-W(1)-O(7)	162.2(5)	O(2)-Eu(1)-O(2)^{iv}	133.2(6)
W(2)-O(9)	1.918(12)	O(8)-W(1)-O(7)	89.6(5)	O(5)-Eu(1)-O(14)	138.2(8)
W(2)-O(10)	1.924(10)	O(11)-W(1)-O(7)	88.1(5)	O(5)^{iv}-Eu(1)-O(14)	69.7(9)
W(2)-O(1)^{i}	2.015(11)	O(2)-W(1)-O(6)	162.4(5)	O(2)-Eu(1)-O(14)	76.8(8)
W(2)-O(6)	2.174(9)	O(1)-W(1)-O(6)	90.2(4)	O(2)^{iv}-Eu(1)-O(14)	139.6(6)
W(3)-O(12)	1.711(13)	O(8)-W(1)-O(6)	90.0(4)	O(14)-Eu(1)-O(14)^{iv}	95.7(17)
W(3)-O(7)	1.820(14)	O(11)-W(1)-O(6)	73.3(4)	O(5)-Eu(1)-O(13)	72.7(4)
W(3)-O(10)^{ii}	1.905(11)	O(7)-W(1)-O(6)	72.0(5)	O(2)-Eu(1)-O(13)	66.6(3)
W(3)-O(9)	1.952(11)	O(3)-W(2)-O(11)	98.0(5)	O(14)-Eu(1)-O(13)	132.2(8)
W(3)-O(8)^{iii}	1.969(10)	O(3)-W(2)-O(9)	99.0(5)	O(5)-Eu(1)-O(4)	70.0(7)
W(3)-O(6)	2.179(9)	O(11)-W(2)-O(9)	92.3(5)	O(5)^{iv}-Eu(1)-O(4)	130.4(7)
Eu(1)-O(5)^{iv}	2.505(13)	O(3)-W(2)-O(10)	101.4(6)	O(2)-Eu(1)-O(4)	69.1(5)
Eu(1)-O(2)	2.533(13)	O(11)-W(2)-O(10)	159.6(4)	O(2)^{iv}-Eu(1)-O(4)	140.1(6)
Eu(1)-O(14)	2.56(3)	O(9)-W(2)-O(10)	90.5(5)	O(14)-Eu(1)-O(4)	68.2(9)
Eu(1)-O(13)	2.58(2)	O(3)-W(2)-O(1)^{i}	100.6(5)	O(14)^{iv}-Eu(1)-O(4)	71.3(7)
Eu(1)-O(4)	2.584(19)	O(11)-W(2)-O(1)^{i}	87.2(4)	O(13)-Eu(1)-O(4)	121.1(4)
Zn(1)-O(6)	1.898(8)	O(9)-W(2)-O(1)^{i}	160.2(4)	O(4)-Eu(1)-O(4)^{iv}	117.9(8)
		O(10)-W(2)-O(1)^{i}	83.5(5)	O(6)^{ii}-Zn(1)-O(6)^{iii}	108.3(5)
		O(3)-W(2)-O(6)	168.6(5)	O(6)^{ii}-Zn(1)-O(6)	110.0(3)
		O(11)-W(2)-O(6)	73.1(4)	W(1)-O(1)-W(2)^{i}	149.3(6)
		O(9)-W(2)-O(6)	74.6(4)	W(1)-O(2)-Eu(1)	162.3(7)
		O(10)-W(2)-O(6)	88.3(4)	C(1)-O(4)-Eu(1)	127.3(18)
		O(1)^{i}-W(2)-O(6)	86.3(4)	C(4)-O(5)-Eu(1)	134.5(13)
		O(12)-W(3)-O(7)	98.7(6)	Zn(1)-O(6)-W(1)	118.6(5)
		O(12)-W(3)-O(10)^{ii}	101.8(6)	Zn(1)-O(6)-W(2)	119.4(5)
		O(7)-W(3)-O(10)^{ii}	91.7(5)	W(1)-O(6)-W(2)	99.8(3)
		O(12)-W(3)-O(9)	97.6(6)	Zn(1)-O(6)-W(3)	119.1(4)
		O(7)-W(3)-O(9)	91.7(5)	W(1)-O(6)-W(3)	98.6(4)
		O(10)^{ii}-W(3)-O(9)	159.6(5)	W(2)-O(6)-W(3)	96.9(4)
		O(12)-W(3)-O(8)^{iii}	101.1(6)	W(3)-O(7)-W(1)	115.6(7)
		O(7)-W(3)-O(8)^{iii}	160.2(5)	W(1)-O(8)-W(3)^{ii}	151.2(6)
		O(10)^{ii}-W(3)-O(8)^{iii}	82.6(4)	W(2)-O(9)-W(3)	114.6(6)
		O(9)-W(3)-O(8)^{iii}	87.4(5)	W(3)^{iii}-O(10)-W(2)	156.5(7)
		O(12)-W(3)-O(6)	168.0(5)	W(2)-O(11)-W(1)	113.8(4)

Symmetry transformations used to generate equivalent atoms: i) -x+2, -y, z; ii) -y+1, x-1, -z; iii) y+1, -x+1, -z; iv) x, -y+1/2, -z+1/4.

Table S3. Selected bond lengths (Å) and angles (°) for **Tb-POM**.

Bond length	(Å)	Bond angle	(°)	Bond angle	(°)
W(1)-O(2)	1.65(4)	O(2)-W(1)-O(1)	105.0(12)	O(10)^{ii}-W(3)-O(6)	86.3(8)
W(1)-O(1)	1.92(3)	O(2)-W(1)-O(8)	102.4(12)	O(7)-W(3)-O(6)	74.1(7)
W(1)-O(8)	1.93(3)	O(1)-W(1)-O(8)	88.1(10)	O(9)-W(3)-O(6)	74.7(11)
W(1)-O(7)	1.988(17)	O(2)-W(1)-O(7)	93.4(13)	O(8)^{iii}-W(3)-O(6)	86.3(7)
W(1)-O(11)	2.03(2)	O(1)-W(1)-O(7)	161.6(8)	O(5)^{iv}-Tb(1)-O(5)	141.5(18)
W(1)-O(6)	2.075(17)	O(8)-W(1)-O(7)	88.6(10)	O(5)^{iv}-Tb(1)-O(4)	133.7(11)
W(2)-O(11)	1.78(3)	O(2)-W(1)-O(11)	98.8(14)	O(5)-Tb(1)-O(4)	74.4(9)
W(2)-O(3)	1.78(2)	O(1)-W(1)-O(11)	87.8(7)	O(4)-Tb(1)-O(4)^{iv}	100.3(14)
W(2)-O(1)^{i}	1.87(3)	O(8)-W(1)-O(11)	158.8(10)	O(5)^{iv}-Tb(1)-O(14)^{iv}	137(2)
W(2)-O(9)	1.95(3)	O(7)-W(1)-O(11)	88.8(8)	O(5)-Tb(1)-O(14)^{iv}	72(2)
W(2)-O(10)	1.98(2)	O(2)-W(1)-O(6)	164.3(12)	O(4)-Tb(1)-O(14)^{iv}	68.7(19)
W(2)-O(6)	2.20(2)	O(1)-W(1)-O(6)	86.6(6)	O(4)-Tb(1)-O(14)	64(2)
W(3)-O(12)	1.59(3)	O(8)-W(1)-O(6)	88.3(7)	O(14)^{iv}-Tb(1)-O(14)	103(3)
W(3)-O(10)^{ii}	1.86(2)	O(7)-W(1)-O(6)	75.2(8)	O(5)-Tb(1)-O(13)	70.7(9)
W(3)-O(7)	1.90(2)	O(11)-W(1)-O(6)	70.7(9)	O(4)-Tb(1)-O(13)	129.9(7)
W(3)-O(9)	1.91(3)	O(11)-W(2)-O(3)	96.8(11)	O(14)-Tb(1)-O(13)	128.7(13)
W(3)-O(8)^{iii}	1.92(3)	O(11)-W(2)-O(1)^{i}	87.4(8)	O(5)^{iv}-Tb(1)-O(2)^{iv}	82.0(10)
W(3)-O(6)	2.199(15)	O(3)-W(2)-O(1)^{i}	99.7(9)	O(5)-Tb(1)-O(2)^{iv}	82.9(10)
Tb(1)-O(5)^{iv}	2.26(3)	O(11)-W(2)-O(9)	95.3(12)	O(4)-Tb(1)-O(2)^{iv}	141.9(10)
Tb(1)-O(4)	2.40(3)	O(3)-W(2)-O(9)	103.7(12)	O(4)^{iv}-Tb(1)-O(2)^{iv}	73.9(12)
Tb(1)-O(14)	2.42(6)	O(1)^{i}-W(2)-O(9)	156.0(9)	O(14)^{iv}-Tb(1)-O(2)^{iv}	75.3(17)
Tb(1)-O(13)	2.45(5)	O(11)-W(2)-O(10)	157.2(8)	O(14)-Tb(1)-O(2)^{iv}	139(2)
Tb(1)-O(2)	2.47(3)	O(3)-W(2)-O(10)	104.0(11)	O(13)-Tb(1)-O(2)	66.6(8)
Zn(1)-O(6)	1.881(14)	O(1)^{i}-W(2)-O(10)	80.0(7)	O(2)^{iv}-Tb(1)-O(2)	133.2(16)
		O(9)-W(2)-O(10)	88.9(11)	O(6)-Zn(1)-O(6)^{i}	107.7(8)
		O(11)-W(2)-O(6)	72.4(7)	O(6)-Zn(1)-O(6)^{ii}	110.3(4)
		O(3)-W(2)-O(6)	168.5(10)	W(2)^{i}-O(1)-W(1)	155.9(8)
		O(1)^{i}-W(2)-O(6)	84.1(6)	W(1)-O(2)-Tb(1)	164.7(19)
		O(9)-W(2)-O(6)	74.1(10)	C(1)-O(4)-Tb(1)	116.7(19)
		O(10)-W(2)-O(6)	87.3(7)	C(4)-O(5)-Tb(1)	144(2)
		O(12)-W(3)-O(10)^{ii}	100.4(10)	Zn(1)-O(6)-W(1)	120.3(10)
		O(12)-W(3)-O(7)	87.8(11)	Zn(1)-O(6)-W(3)	119.1(6)
		O(10)^{ii}-W(3)-O(7)	93.1(8)	W(1)-O(6)-W(3)	98.1(7)
		O(12)-W(3)-O(9)	101.4(13)	Zn(1)-O(6)-W(2)	119.1(10)
		O(10)^{ii}-W(3)-O(9)	157.5(12)	W(1)-O(6)-W(2)	99.5(5)
		O(7)-W(3)-O(9)	93.2(9)	W(3)-O(6)-W(2)	95.8(7)
		O(12)-W(3)-O(8)^{iii}	111.8(11)	W(3)-O(7)-W(1)	112.4(10)
		O(10)^{ii}-W(3)-O(8)^{iii}	84.7(9)	W(3)^{ii}-O(8)-W(1)	147.5(15)
		O(7)-W(3)-O(8)^{iii}	160.4(7)	W(3)-O(9)-W(2)	115.4(16)
		O(9)-W(3)-O(8)^{iii}	82.2(13)	W(3)^{iii}-O(10)-W(2)	159.0(12)
		O(12)-W(3)-O(6)	161.1(10)	W(2)-O(11)-W(1)	117.4(10)

Symmetry transformations used to generate equivalent atoms: i) -x, -y+1, z; ii) –y+1/2, x+1/2, -z+1/2; iii) y-1/2, -x+1/2, -z+1/2; iv) x, -y+1/2, -z+1/4.

Table S4. Luminescent color coordinates of **Ln-POM**s.

Samples	**$La_{1-x}Eu_x$-POM**	**$La_{1-x}Tb_x$-POM**	**Eu_xTb_{1-x}-POM**
x=0.25	(0.612, 0.328)	(0.273, 0.424)	(0.452, 0.323)
x=0. 5	(0.617, 0.330)	(0.278, 0.465)	(0.395, 0.326)
x=0.75	(0.635, 0.333)	(0.289, 0.505)	(0.342, 0.362)
x=1	(0.632, 0.333)	(0.292, 0.517)	(0.632, 0.333)

Table S5. ICP-MS analysis for **Ln-POM**s.

x	**$La_{1-x}Eu_x$-POM** **La : Eu**	**$La_{1-x}Tb_x$-POM** **La : Tb**	**Eu_xTb_{1-x}-POM** **Eu : Tb**
x = 0.25	0.73 : 0.27	0.74 : 0.26	0.28 : 0.72
x = 0.5	0.46 : 0.54	0.47 : 0.53	0.49 : 0.51
x = 0.75	0.24 : 0.76	0.27 : 0.73	0.74 : 0.26