

Constructing lanthanide polyanions with various size with Vis and NIR luminescence for potential biological applications

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Introduction & research goal

Polyoxometalates (POMs) are discrete anionic metal-oxygen clusters of early transition metals usually W, Mo, or V in a high oxidation state.¹ One of the most fascination lanthanide POMs (LnPOMs) is the $(\text{NH}_4)_{12}\text{H}_2(\text{Eu}_4(\text{MoO}_4)(\text{H}_2\text{O})_{16}(\text{Mo}_7\text{O}_{24})_4) \times 13\text{H}_2\text{O}$ cluster reported by Nakamura et al.² This LnPOM showed very good anti-HIV-1 activity, anti-bacterial activity on several different cell lines, as well as very good luminescence properties.

A series of **tetranuclear LnPOMs** built from $[\text{Mo}_7\text{O}_{24}]^{6-}$ heptamolybdate polyanions with La^{3+} , Eu^{3+} , Tb^{3+} , Sm^{3+} , Dy^{3+} , and Nd^{3+} were synthesized and a detailed analysis revealed that the tetranuclear clusters formed **monomers or dimers linked through oxygen bridges**. The smaller lanthanide ions - Er^{3+} and Yb^{3+} did not form tetranuclear clusters, but instead mononuclear sandwich type POMs were obtained. A rare case of **low percentage trivalent lanthanide doping in multinuclear LnPOMs** has been investigated using the $[\text{La}_4(\text{MoO}_4)(\text{H}_2\text{O})_{16}(\text{Mo}_7\text{O}_{24})_4]^{14-}$ polyanion as the host material. The tetranuclear LnPOM was doped with 5% of Eu^{3+} , Tb^{3+} , Sm^{3+} , Dy^{3+} , Nd^{3+} , Er^{3+} and Yb^{3+} and the structures and luminescence properties of the 5% Ln^{3+} POMs were investigated and compared with the appropriate 100% LnPOMs.

Polyoxometalates

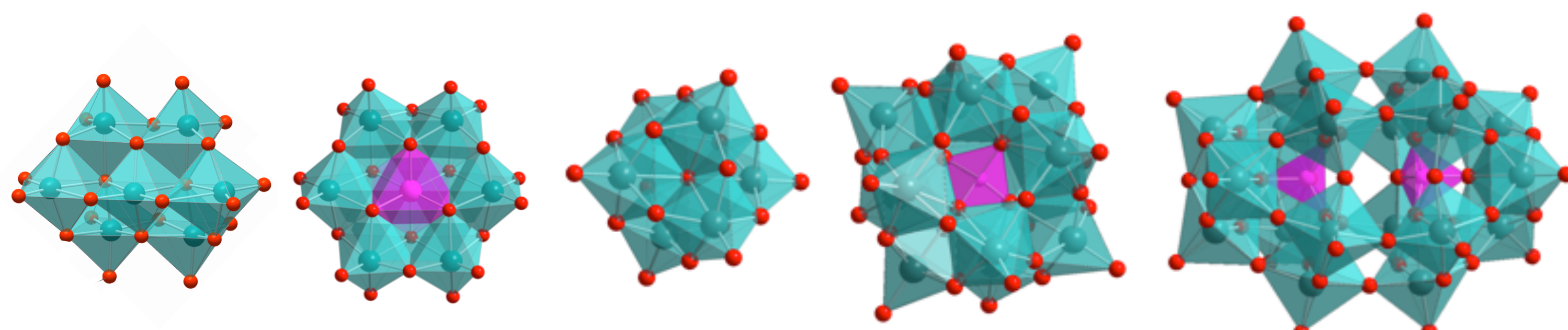


Fig. 1: POMs exhibit a huge variety in their size, shape and nuclearities. From left to right structures of some common POMs: heptamolybdate, Anderson-Evans, Lindqvist, Keggin and Wells-Dawson POMs.²

Crystal structures of $[\text{La}_4(\text{MoO}_4)(\text{H}_2\text{O})_{16}(\text{Mo}_7\text{O}_{24})_4]^{14-}$ (LaPOM1 and LaPOM2)

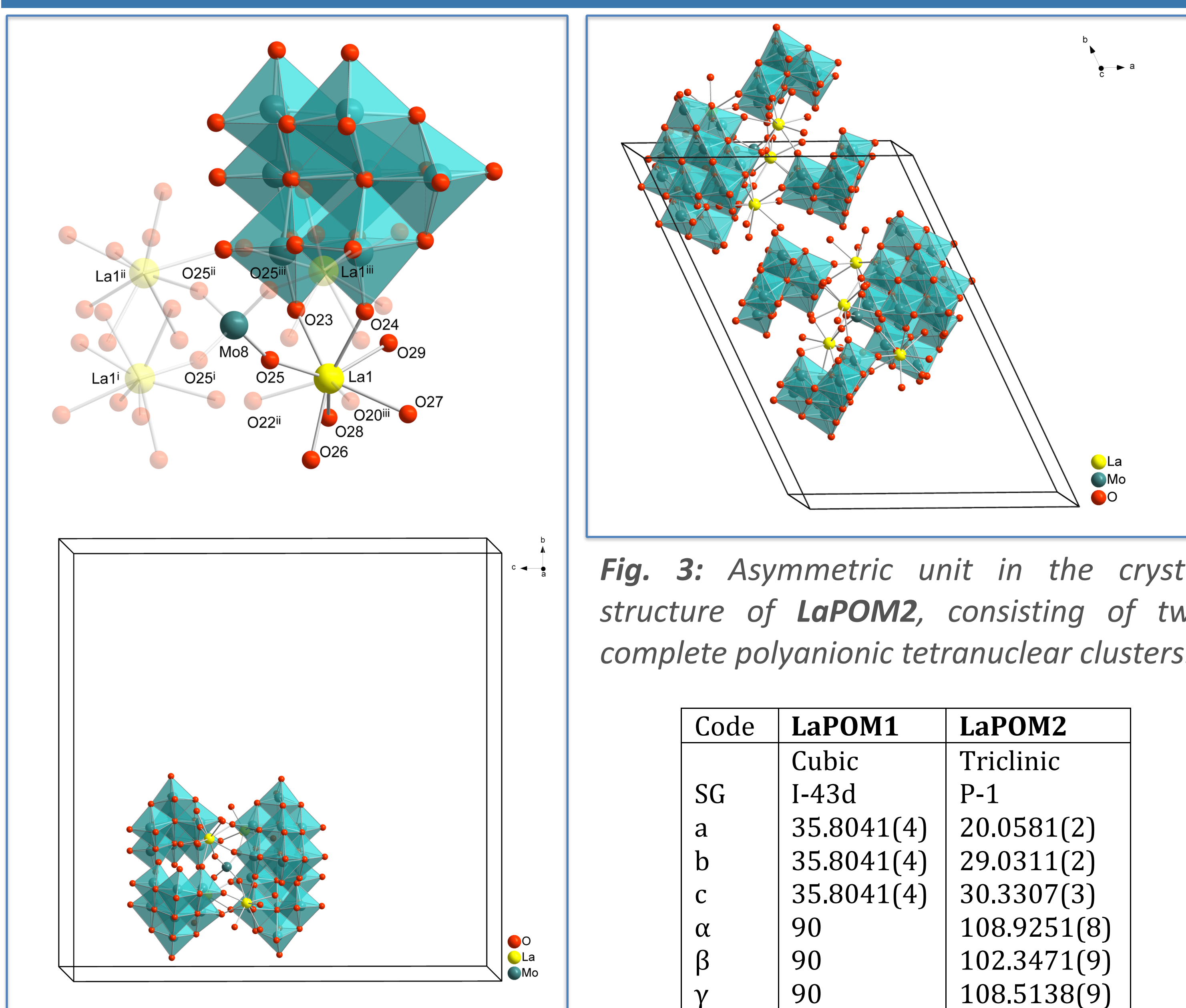


Fig. 2: Top - coordination environment of the MoO_4 and LaO units in the **LaPOM1** structure. Symmetry codes: (i) $1-x, 0.5-y, z$; (ii) $0.25+y, 0.75-x, 1.25-z$; (iii) $0.75-y, -0.25+x, 1.25+z$. The asymmetric unit is highlighted. Bottom - molecular structure of the **LaPOM1** tetranuclear polyanionic cluster in the cubic unit cell.

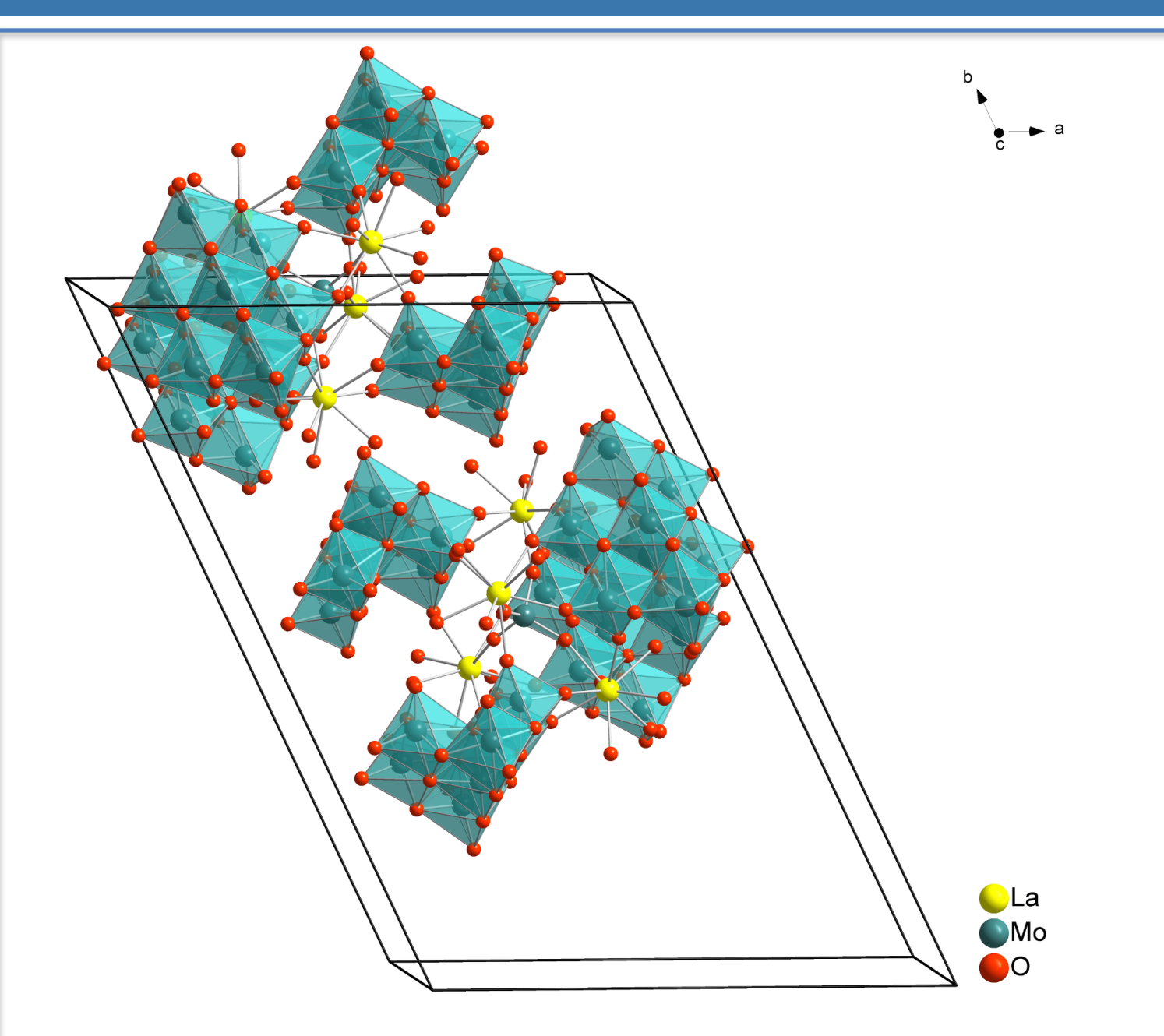


Fig. 3: Asymmetric unit in the crystal structure of **LaPOM2**, consisting of two complete polyanionic tetranuclear clusters.

Code	LaPOM1	LaPOM2
SG	Cubic	Triclinic
	I-43d	P-1
a	35.8041(4)	20.0581(2)
b	35.8041(4)	29.0311(2)
c	35.8041(4)	30.3307(3)
α	90	108.9251(8)
β	90	102.3471(9)
γ	90	108.5138(9)

References

- Pope, M. T.; Müller, A., *Angew. Chem. Int. Ed.*, **1991**, 30, 34-48.
- Ma, X.; Yang, W.; Chen, L.; Zhao, J. *CrystEngComm*, **2015**, 17, 8175-8197.

Crystal structures of LnPOMs

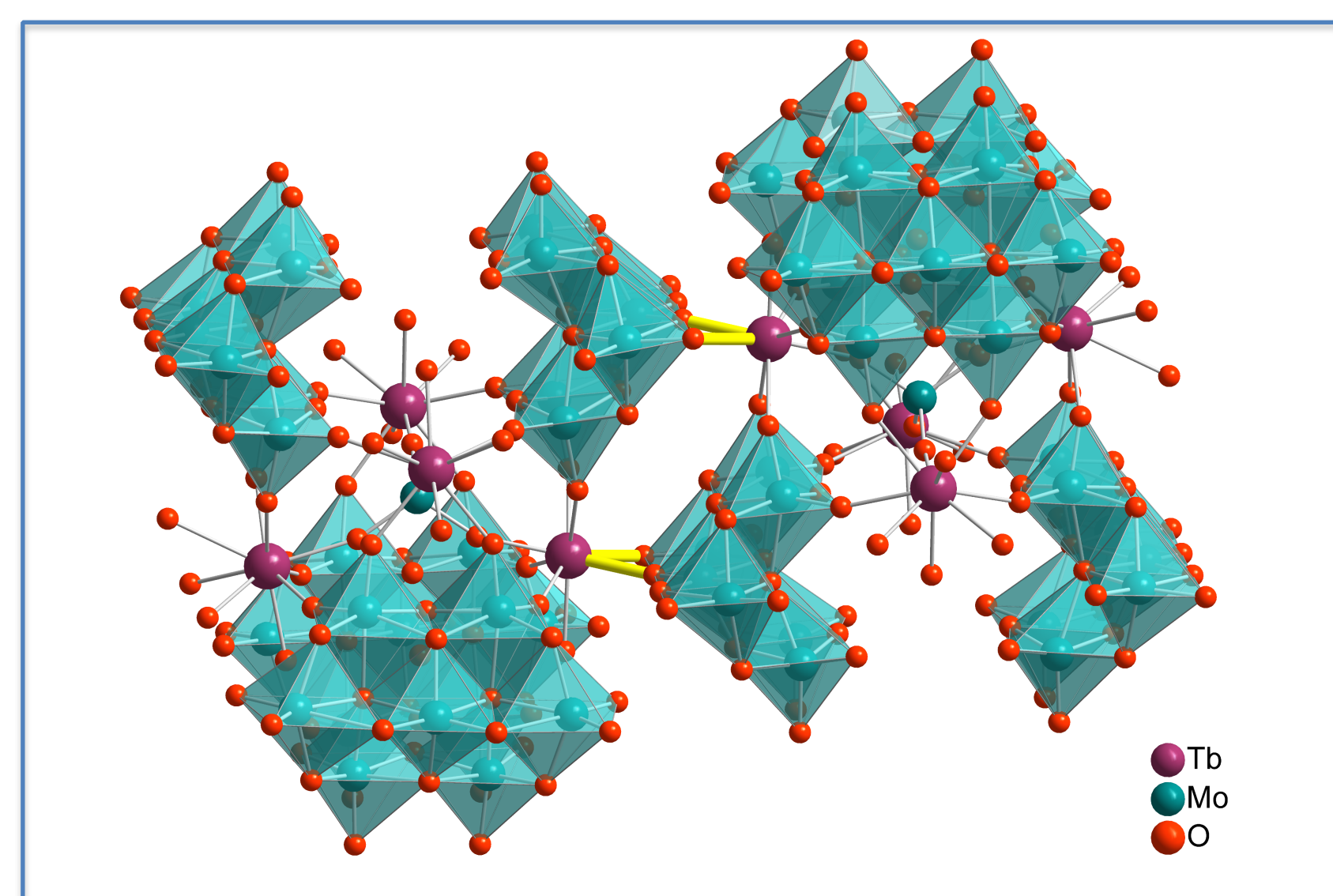


Fig. 4: Polyanionic dimer in the crystal structure of $[\text{Tb}_8(\text{MoO}_4)_2(\text{H}_2\text{O})_{26}(\text{Mo}_7\text{O}_{24})_8]^{28-}$ (**TbPOM**). The four Tb-O bridges are highlighted in yellow. The **TbPOM** and **DyPOM** are isomorphous and crystallized in the triclinic centro-symmetric space group *P*-1.

Fig. 5: Polyanionic dimer in the crystal structure of $[\text{Nd}_8(\text{MoO}_4)_2(\text{H}_2\text{O})_{28}(\text{Mo}_7\text{O}_{24})_8]^{42-}$ (**NdPOM**). The two Nd-O bridges are highlighted in yellow. **NdPOM** crystallized in the triclinic centro-symmetric space group *P*-1.

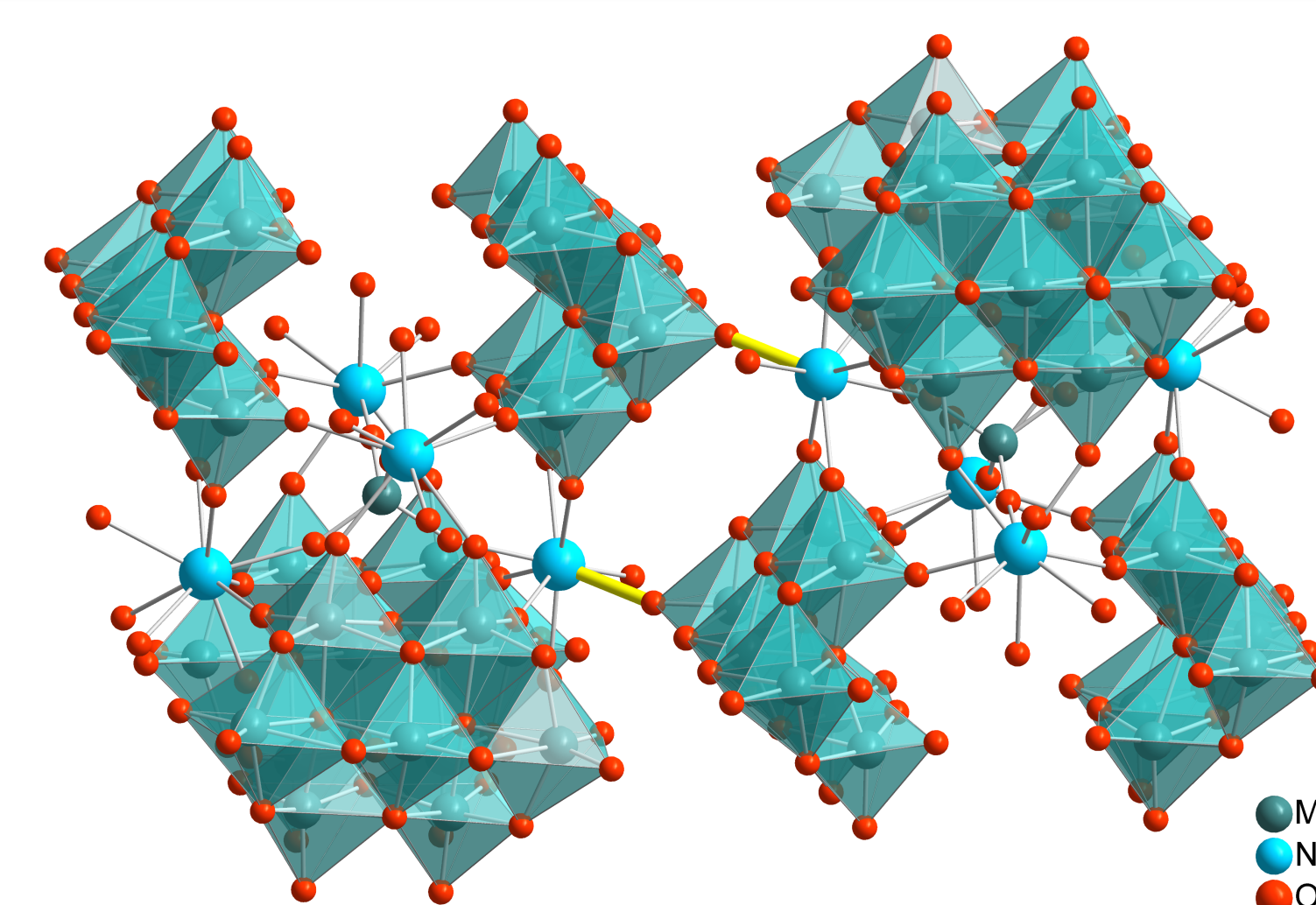


Fig. 6: Molecular structure of $[\text{Yb}(\text{H}_2\text{O})_4(\text{Mo}_7\text{O}_{24})_2]^{18-}$ (**YbPOM**), showing a mononuclear 2:1 sandwich type POM. The compounds **YbPOM** and **ErPOM** are isostructural and crystallized in the triclinic centro-symmetric space group *P*-1.

Luminescence properties

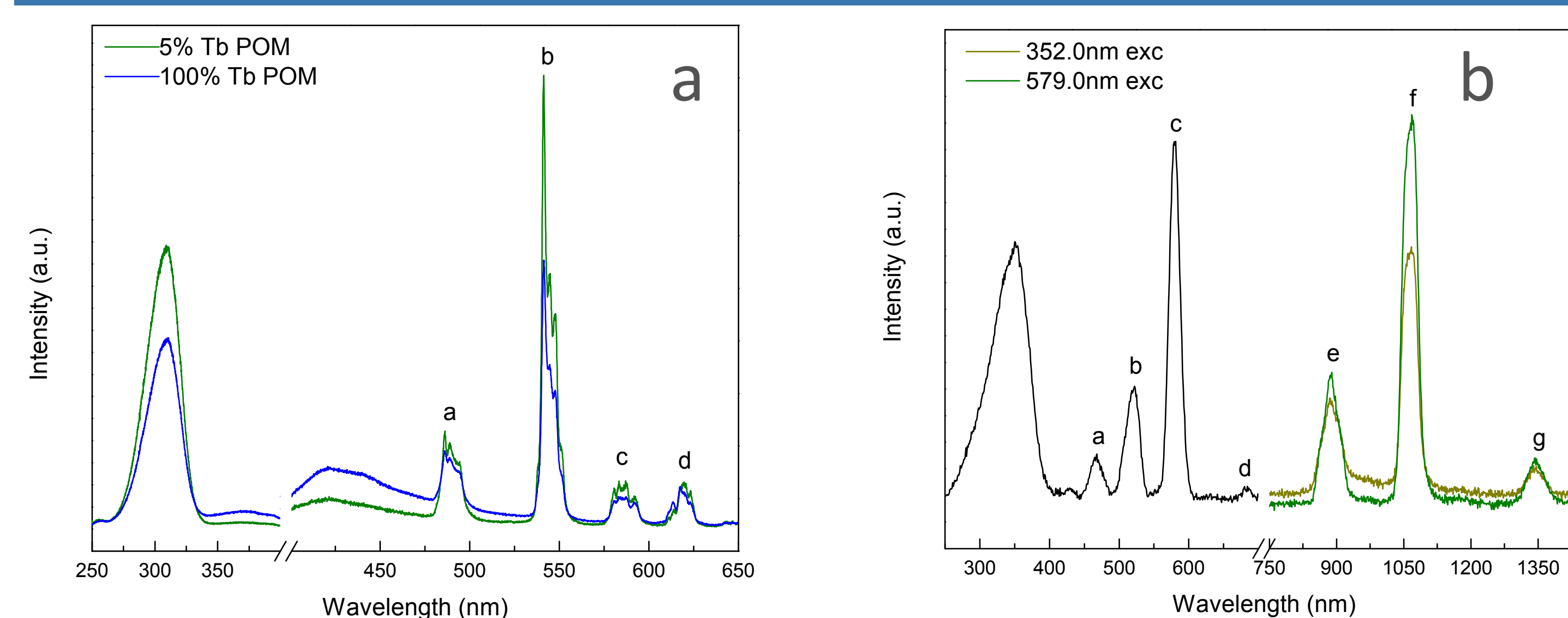


Fig. 7: Examples of the luminescence properties observed for the 100% LnPOM samples and 5%Ln: LaPOM1 samples: a) **TbPOM** and 5%**Tb**:LaPOM1, b) 5%**Nd**:LaPOM1.

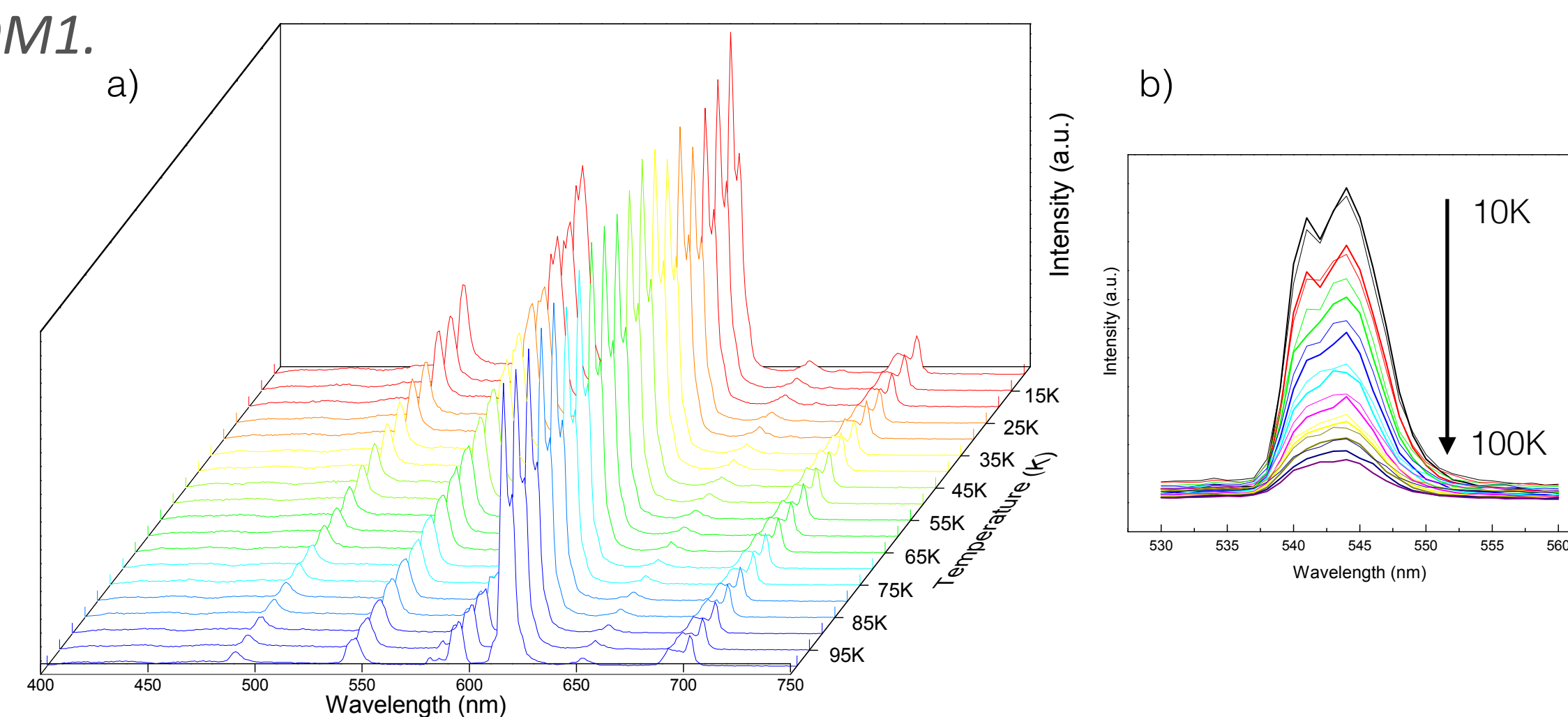


Fig. 8: a) Emission map of 5%**Eu**:**TbPOM** spectra recorded in the 10 – 100 K range, b) zoom in on the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ (Tb^{3+}) transition peak, which gradually decreases in intensity with temperature increase.

Conclusion

The biologically active $(\text{NH}_4)_{12}\text{H}_2(\text{Eu}_4(\text{MoO}_4)(\text{H}_2\text{O})_{16}(\text{Mo}_7\text{O}_{24})_4) \times 13\text{H}_2\text{O}$ POM was the inspiration of this work. We have investigated the formation of $[\text{Mo}_7\text{O}_{24}]^{6-}$ clusters with several other Ln^{3+} ions ($\text{Ln} = \text{La}^{3+}$, Tb^{3+} , Sm^{3+} , Dy^{3+} , Nd^{3+} , Er^{3+} , Yb^{3+}). Interesting, novel crystal structures were obtained and good Vis and NIR luminescence was observed for all of the compounds with emissive lanthanides. The **TbPOM** shows interesting temperature dependent luminescence properties after diluting with low percentages of Eu^{3+} ions (5-10%).