Synthesis, crystal structures and properties of new lanthanide benzene-1,2,3-triyltris-methylenephosphonates

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Introduction

Metal phosphonates are acidic solids with tunable functionalities. These features together with the presence of both coordinated and lattice water molecules favor the formation of hydrogen-bonding networks, providing them with proton conduction properties, adjustable by synthesis conditions [1–3].

This study describes the synthesis and structural analysis of a series of compounds resulting from the combination of benzene-1,2,3-triyltris(methylene) phosphonic acid (BTTMP) with lanthanide ions. Four structural series have been isolated under hydrothermal conditions, and their crystal structures have been solved *ab initio* from X-ray powder diffraction data by employing both laboratory and synchrotron radiation. All compounds are hydrated layered structures with luminescent and proton conductivity properties as described below.

Synthesis & Structural Studies

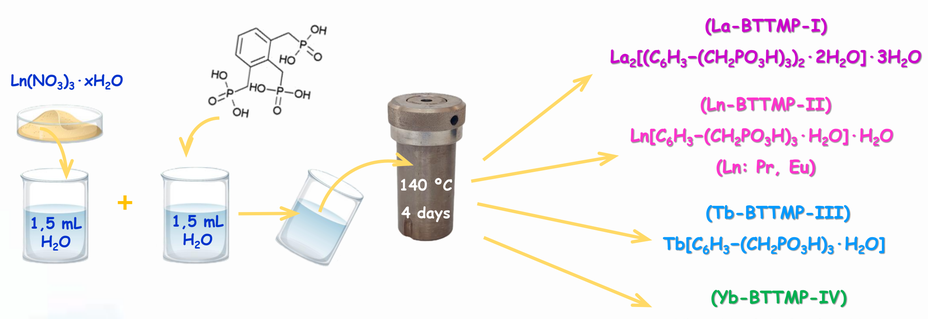

Figure 1. Preparation of Ln-BTTMP.

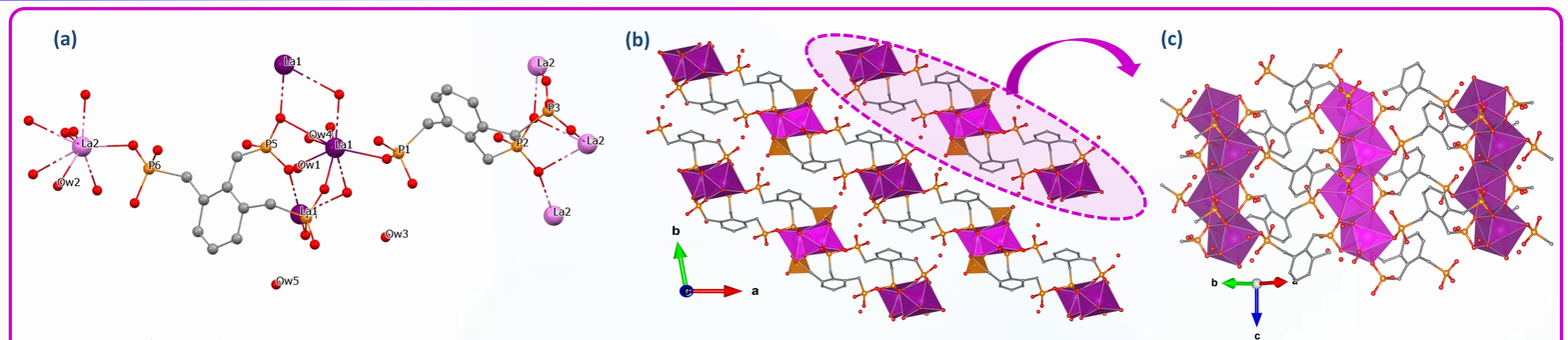

Figure 2. **(a)** Coordination environments of La1 and La2; **(b)** Packing of the layers and **(c)** Chains of edge-sharing LaO_8 polyhedral in **La-BTTMP** (Series-I).

Table 1. Crystallography data of selected compounds.

	Serie-I	Serie-II		Serie-III	Serie-IV
	La-BTTMP	Pr-BTTMP	Eu-BTTMP	Tb-BTTMP	Yb-BTTMP
Space Group	*P -1*	*$P2_1/n$*	*$P2_1/n$*	*$P2_1/a$*	*$P2_1/c$*
Crystal System	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
λ (Å)	0.6188	0.7093	0.41318	0.7093	0.6199
a (Å)	18.0814(2)	18.1535(9)	18.1956(2)	14.7518(6)	11.2631(2)
b (Å)	12.1357(1)	7.1190(3)	7.0235(6)	18.2221(23)	13.1109(2)
c (Å)	7.1985(7)	12.0430(7)	11.9912(1)	5.5648(2)	10.2696(1)
α (°)	90.804(8)	90.0	90.0	90.0	90.0
β (°)	92.799(10)	98.532(3)	97.974(6)	94.7860(27)	98.911(6)
γ (°)	99.3705(7)	90.0	90.0	90.0	90.0
V (Å^3)	1556.3(3)	1539.2(2)	1517.6(3)	1490.6(2)	1498.2(3)
Z	2	4	4	4	4
Range data (°)	2.5 - 43.2	3.6 - 42.0	2.0 - 42.0	3.5 – 42.0	3.5 – 45.0
Indep. reflections	5501	976	8280	949	2960
Data / restrains / parameters	7138/114/198	3300/65/115	7020/57/122	3300/64/45	10704/57/124
R_{WP}	0.080	0.119	0.055	0.119	0.050
R_P	0.056	0.092	0.039	0.088	0.036
R_F	0.027	0.103	0.020	0.102	0.017

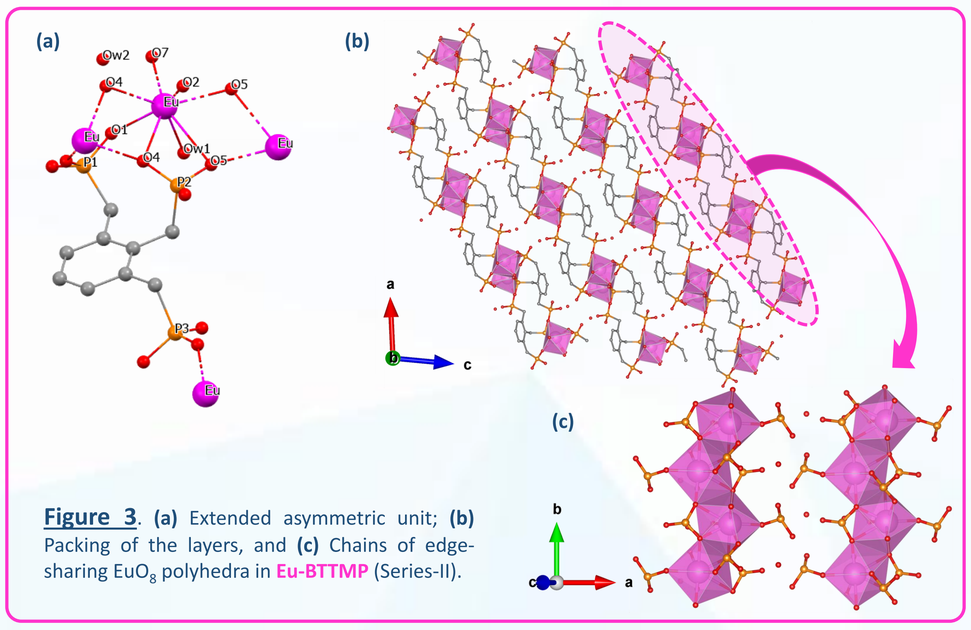

Figure 3. **(a)** Extended asymmetric unit; **(b)** Packing of the layers, and **(c)** Chains of edge-sharing EuO_8 polyhedra in **Eu-BTTMP** (Series-II).

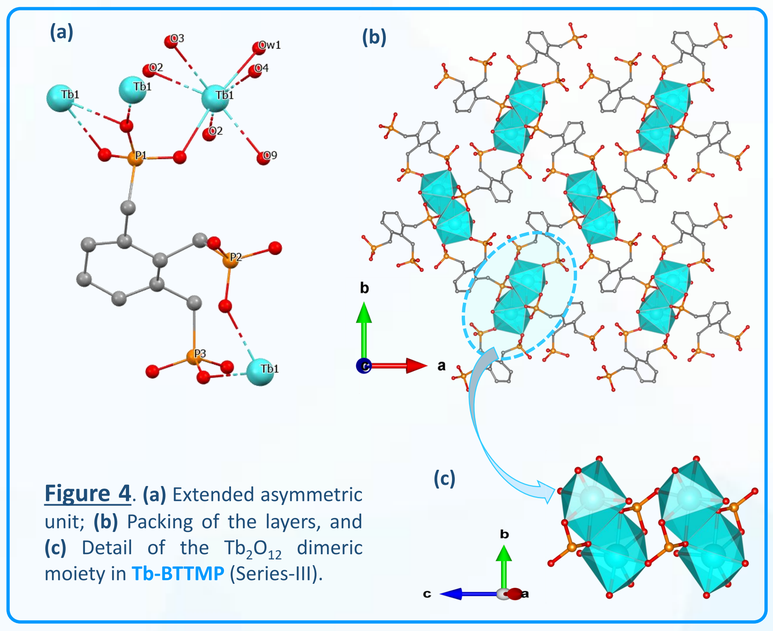

Figure 4. **(a)** Extended asymmetric unit; **(b)** Packing of the layers, and **(c)** Detail of the Tb_2O_{12} dimeric moiety in **Tb-BTTMP** (Series-III).

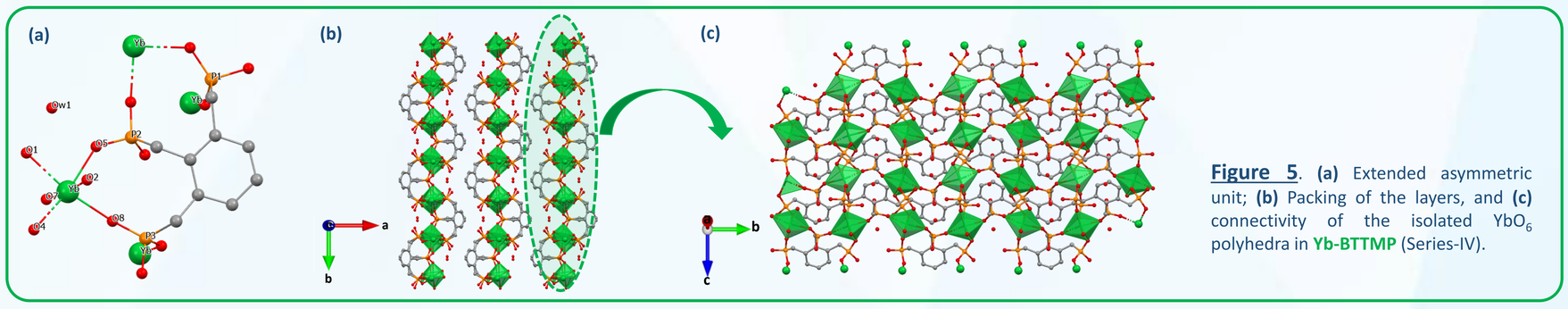

Figure 5. **(a)** Extended asymmetric unit; **(b)** Packing of the layers, and **(c)** connectivity of the isolated YbO_6 polyhedra in **Yb-BTTMP** (Series-IV).

Proton conductivity properties

Humidity chamber (Espec SH-222) for proton conductivity measurements (UMA).

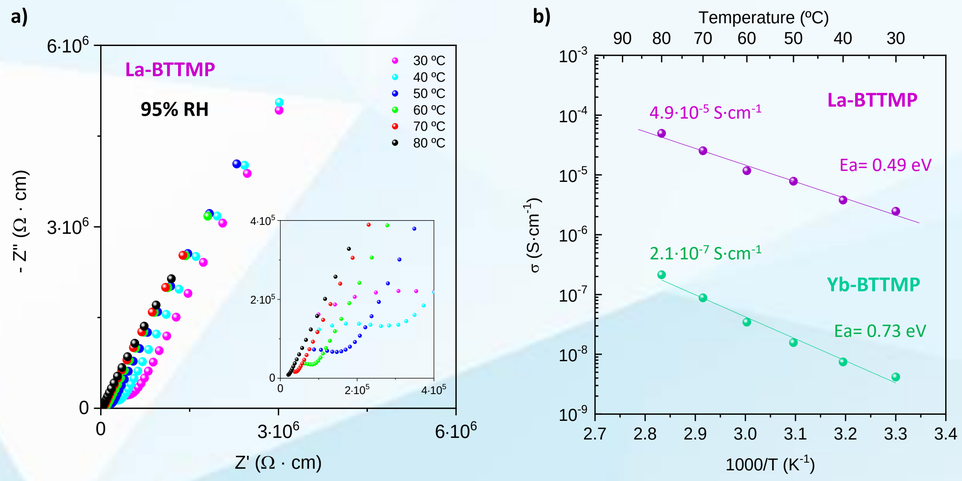

Figure 6. **(a)** Nyquist plot for **La-BTTMP** (Series-I) at selected temperatures and 95% RH; **(b)** Plot of conductivity (σ, S · cm^{-1}) vs temperature (°C) at 95% RH for selected compounds .

Luminescent properties

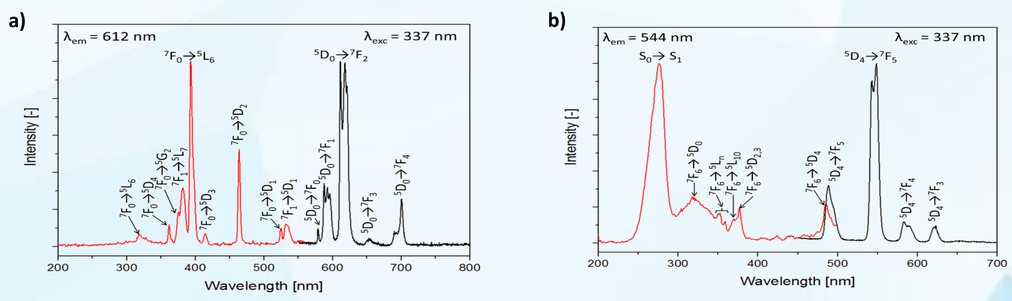

Figure 7. Excitation (red trace) and emission (black trace) spectrum for **Eu-BTTMP** **(a)**, and **Tb-BTTMP** **(b)** along with transition assignments.

Figure 8. Emission spectra of **Eu-BTTMP** **(a)**, and **Tb-BTTMP** **(b)** excited at 337 nm at different temperatures.

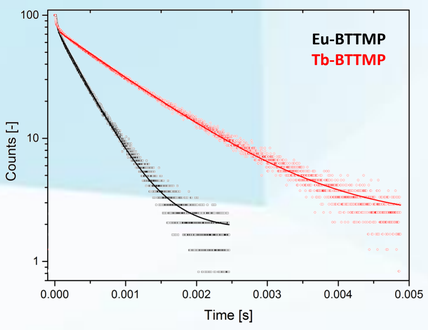

Figure 9. Emission decay spectra (λ=337 nm) of **Eu-BTTMP** (black) and **Tb-BTTMP** (red), registered at 612 nm and 545 nm, respectively.

Conclusions

- Lanthanide ions exhibit variable connectivity with ligand benzene-1,2,3-triyltris(methylene) phosphonate (BTTMP).
- **Ln-BTTMP** present a moderate to low proton conductivities attributed to the absence of extended H-bond network. In order to further enhance proton conductivity properties of these materials, post-synthesis modifications are underway.
- These materials present moderate photoluminescence properties attribute to f-f transitions of the lanthanide ions, with the luminescence lifetimes of 1.05 ms for **Tb-BTTMP** (Series-III) and 396 μs for **Eu-BTTMP** (Serie-II).

References

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[2] M. Boone, F. Artizzu, J. Goura, D. Mara, R. Van Deun, M. D'hooghe, Coordination Chemistry Reviews, 501, 215525 (2024).
[3] I.R. Salcedo, M. Bazaga-García, R.M.P. Colodrero, A. Vílchez-Cózar, F. Cañamero-Cebrián, P. Olivera-Pastor, J.K. Zaręba, A. Cabeza. Cryst. Growth Des. 24, 7910–7918 (2024).

Acknowledgments

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