

Syntheses, structures, properties and DFT study of hybrid inorganic–organic architectures constructed from trinuclear lanthanide frameworks and Keggin-type polyoxometalates

Masoud Mirzaei,^{*,a} Hossein Eshtiagh-Hosseini,^a Nahid Lotfian,^a Alireza Salimi,^a Antonio Bauzá,^b
Rik Van Deun,^c Roel Decadt,^c Miquel Barceló-Oliver,^b and Antonio Frontera^{*,b}

^a*Department of Chemistry, Ferdowsi University of Mashhad, 917751436 Mashhad, Iran. E-mail: mirzaeesh@um.ac.ir*

^b*Department of Chemistry, Universitat de les IllesBalears, Crta de Valldemossa km 7.5, 07122 Palma (Balears), Spain. E-mail: toni.frontera@uib.es*

^c*L³ – Luminescent Lanthanide Lab, f-element coordination chemistry, Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 – S3, B-9000 Gent, Belgium*

Supplementary Material

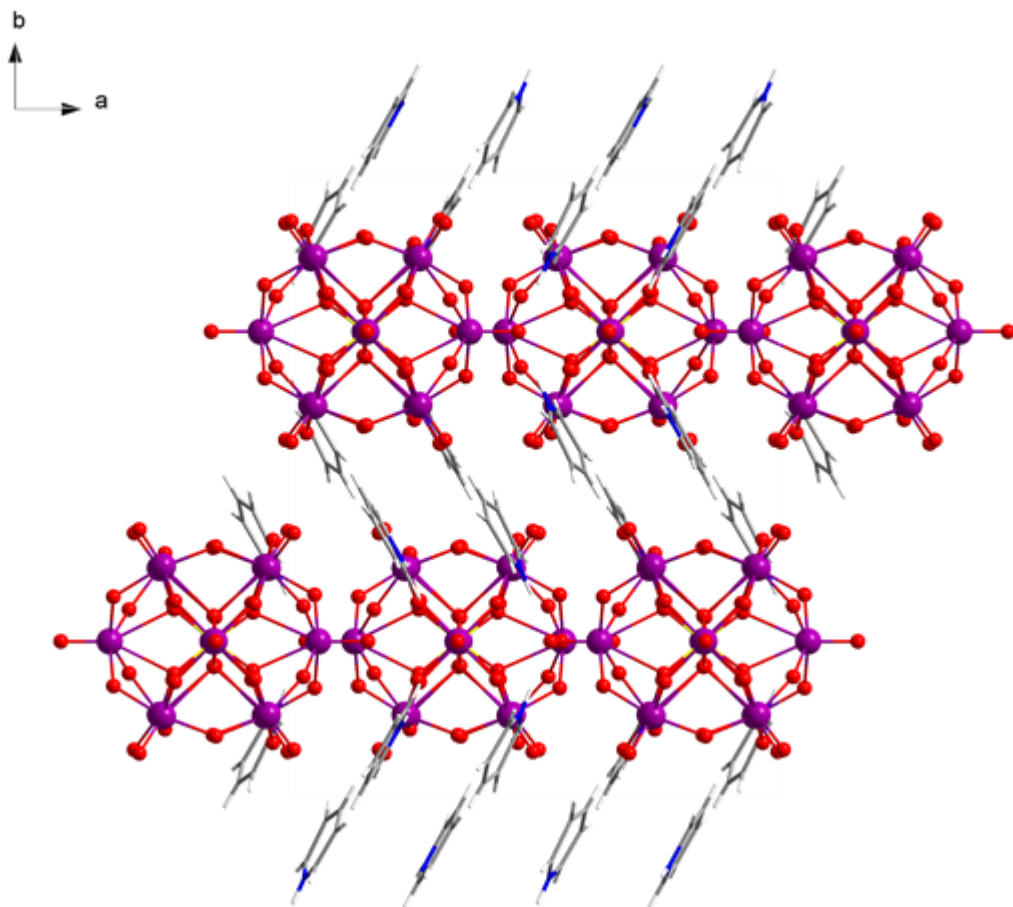
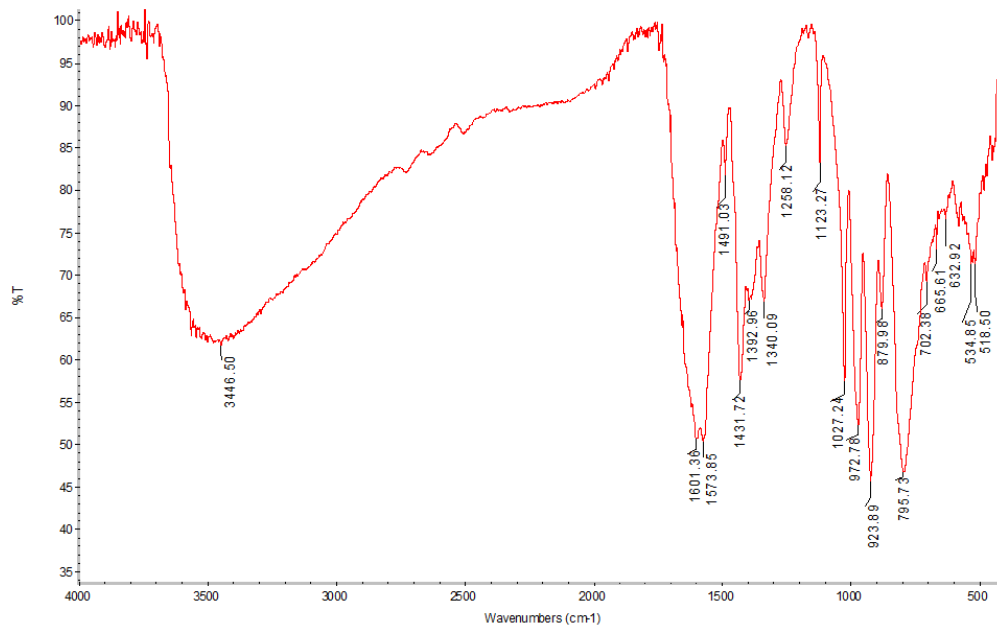
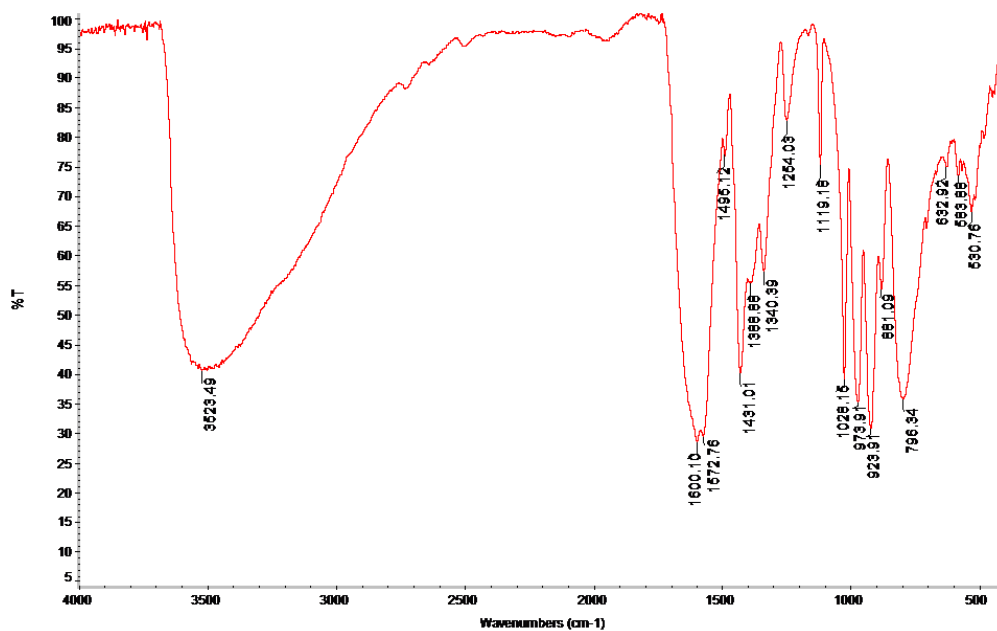


Figure S1. Crystal structure of $[\text{C}_5\text{H}_5\text{NH}]_4[\text{SiW}_{12}\text{O}_{40}]\cdot\text{H}_2\text{O}$. Packing cell viewed along the c -axis.

Compound 1



Compound 2



Compound 3

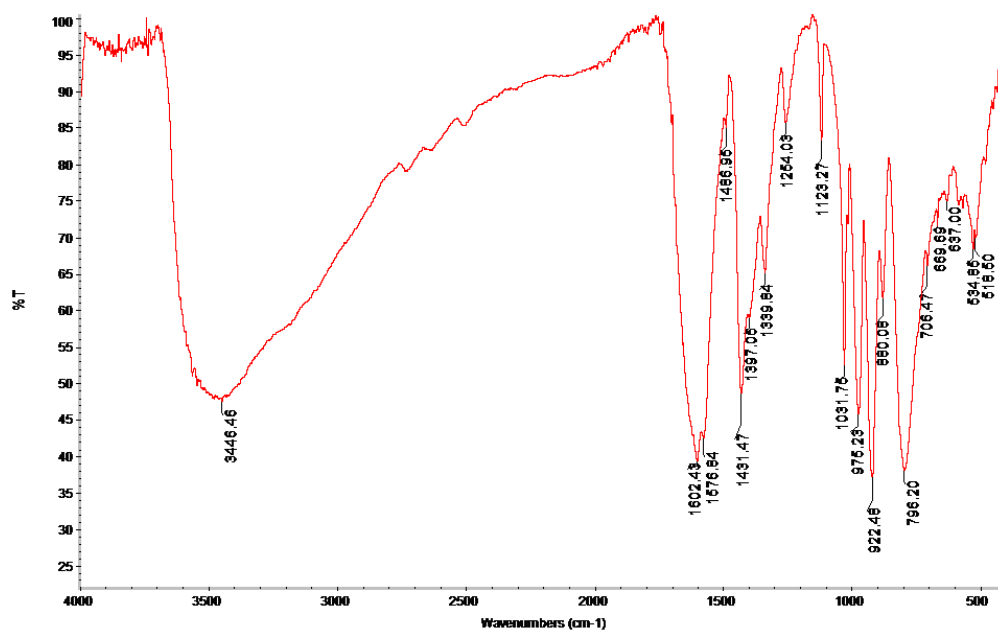


Figure S2. FTIR spectra of compound 1-3.

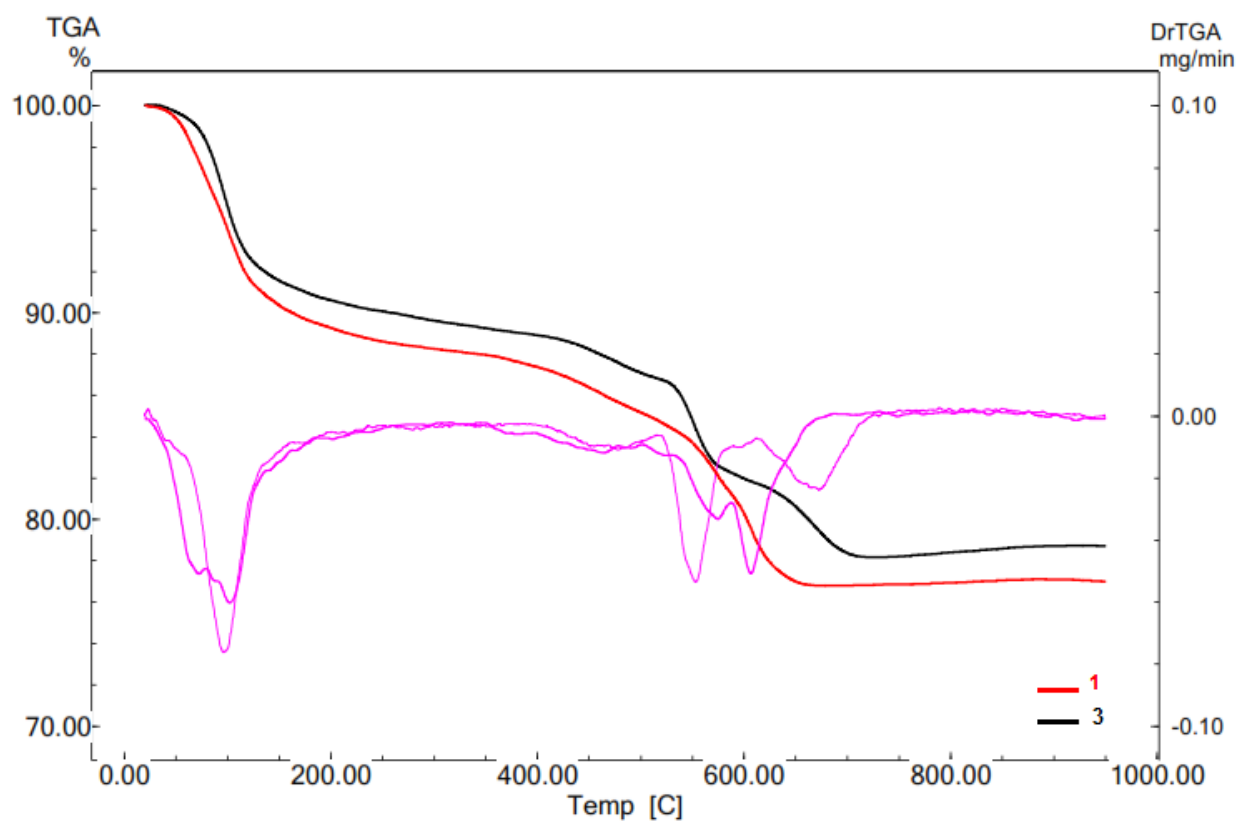


Figure S3. TG/DTG curves of compounds **1** and **3**.

Luminescence of complex **1**

In contrast to Eu^{3+} (**3**), La^{3+} is “spectroscopically silent”. Hence, the excitation and emission spectra do not show any narrow line emission typical for trivalent lanthanides. Instead, both emission and excitation spectra show broad band emission. This emission is likely due to the 4-hydroxypyridine-2,6-dicarboxylic acid (OHpydc) present in the material. Even though OHpydc is also present in the Eu^{3+} compound, the emission of the Eu^{3+} ion is several orders of magnitude stronger than that of OHpydc, so the broad band emission is not observable in **3**. Upon excitation at 365 nm, **1** shows a broad band emission with a maximum at 440 nm. Monitoring the emission at 440 nm, the wavelength of the excitation light is varied between 250 and 385 nm in order to record an excitation spectrum. **1** shows a broad excitation band with a maximum at 365 nm. The excitation and emission spectra are shown in Figure S4. No evidence of O→W charge transfer can be found in either the excitation or the emission spectrum.

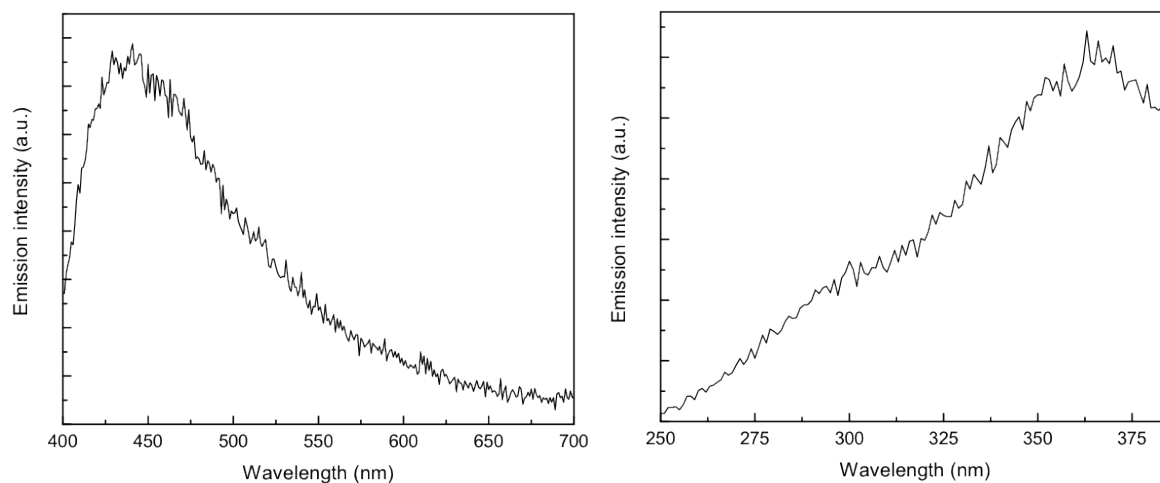


Figure S4. Left: Emission spectrum of **1**, excited at 365 nm. Right: Excitation spectrum of **1**, monitoring the emission at 440 nm.

Table S1. Crystallographic Data and Structure Refinement for **4**

empirical formula	C ₂₀ H ₂₆ N ₄ O ₄₁ SiW ₁₂
formula weight	3212.62
temperature (K)	120(2)
crystal size (mm ³)	0.32 × 0.32 × 0.27
crystal system	orthorhombic
space group	<i>P n m a</i>
<i>a</i> (Å)	16.5140(4)
<i>b</i> (Å)	20.8786(7)
<i>c</i> (Å)	14.0532(4)
α, β, γ (°)	90
<i>V</i> (Å ³)	4845.4(2)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	4.401
θ Range (°)	2.47- 25.68
μ (mm ⁻¹)	28.494
<i>F</i> (000)	5608
reflections collected	4740
independent reflections	3927
<i>R</i> _{int}	0.1507
final <i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.1011, 0.2018
GOOF	1.238

^a $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$. ^b $wR_2 = \frac{\{\sum w(F_o^2 - F_c^2)^2\}}{\sum w(F_o^2)^2}^{1/2}$.