

## SUPPLEMENTARY INFORMATION

### **Tunable Nd<sup>3+</sup> dimer Luminescent Molecular Thermometer via Stark Sublevels**

Yolimar Gil<sup>1\*</sup>, Julio Corredoira-Vázquez<sup>2,3</sup>, Ricardo Costa de Santana<sup>4</sup>, Carlos D. S. Brites<sup>5</sup>,  
Luís D. Carlos<sup>5</sup>, Evgenia Spodine<sup>1</sup>, Daniel Aravena<sup>6</sup>, Pablo Fuentealba<sup>1</sup>.

<sup>1</sup> *Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Olivos 1007, 8380544, Santiago, Chile. E-mail: [yolimar.gil@ciq.uchile.cl](mailto:yolimar.gil@ciq.uchile.cl)*

<sup>2</sup> *Departamento de Química Inorgánica, Facultad de Química, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain.*

<sup>3</sup> *Institute of Materials (iMATUS), Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain*

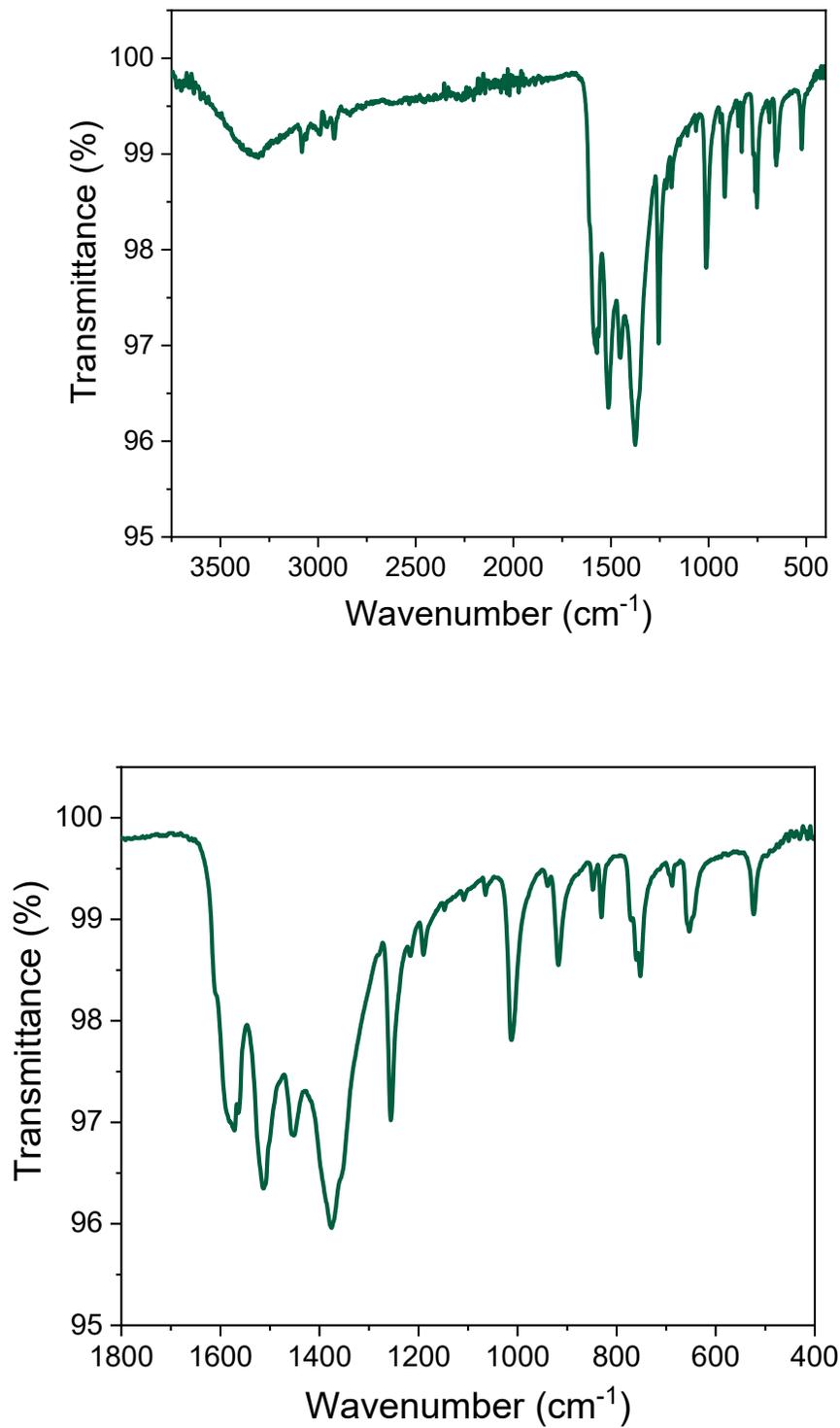
<sup>4</sup> *Instituto de Física, Universidade Federal de Goiás, Campus Samambaia, 74690-900, Goiânia, GO, Brazil.*

<sup>5</sup> *Phantom-g, CICECO – Aveiro Institute of Materials, Department of Physics, University of Aveiro, 3810-193 – Aveiro, Portugal.*

<sup>6</sup> *Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile.*

## 1. Synthesis and characterization

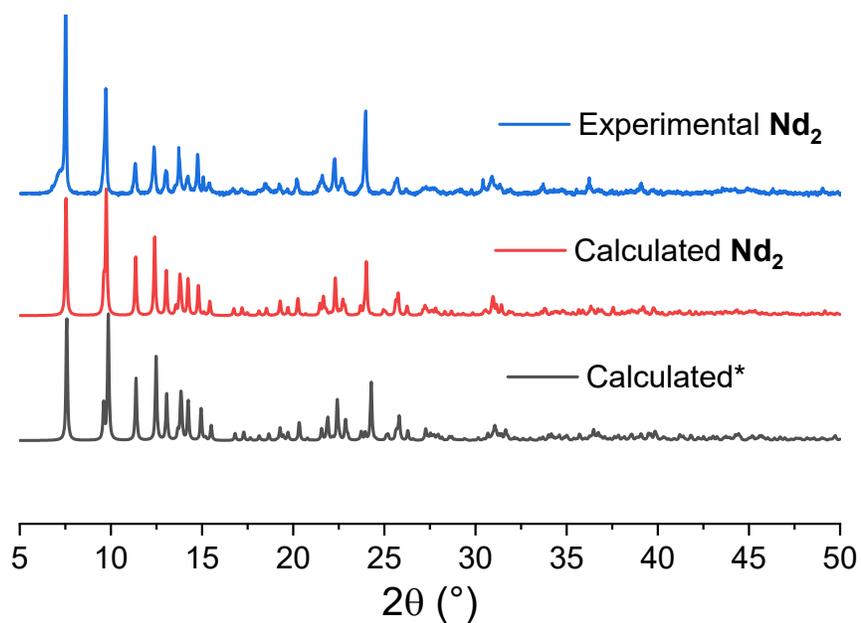
**Synthesis of  $\{[\text{Nd}(\text{acac})_3]_2(\mu\text{-bpm})\}$  ( $\text{Nd}_2$ ).** acetylacetone (132  $\mu\text{L}$ , 1.2 mmol) and triethylamine (168  $\mu\text{L}$ , 1.2 mmol) were added in a 30-mL volume microwave vial containing 15 mL of methanol: ethanol mixture (1:1). Then,  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (175 mg, 0.4 mmol) was added, and the mixture was stirred for 15 min. Finally, a solution of bpm (31.6 mg, 0.2 mmol) in 5 mL of the same solvent mixture was added, and the resulting solution was irradiated in the microwave reactor for 15 min at 100  $^\circ\text{C}$ . Purple rod crystals were obtained by slow evaporation of the reaction solution after 7 days with a yield of 116 mg (55.8 %). FTIR ( $\text{cm}^{-1}$ ): 3079, 2992, 2917 ( $\nu_{\text{C-H}}$ ), 1610 ( $\nu_{\text{C=O}}/\nu_{\text{C=C}}$ ), 1572, 1564 ( $\nu_{\text{C=N}}/\text{ring stretches}$ ), 1514 ( $\nu_{\text{C=C}}$ ), 1452, 1375 ( $\delta_{\text{CH}_3}$ ), 1256 ( $\nu_{\text{C=O}}$ ), 523 ( $\nu_{\text{Nd-O}}$ ) (Figure S1). These bands are in agreement with those described for the reported  $\{[\text{Nd}(\text{acac})_3]_2(\mu\text{-bpm})\}$  complex<sup>1</sup>.



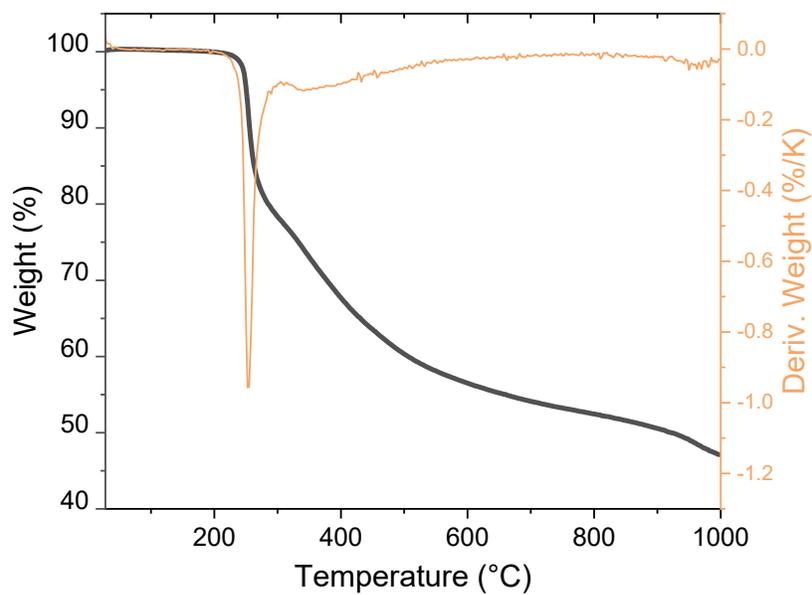
**Figure S1.** FTIR spectrum of Nd<sub>2</sub> (top) and magnified view of the 1800–400 cm<sup>-1</sup> region (bottom).

**Table S1.** Crystal data details for **Nd<sub>2</sub>**. Additional structural details have been reported elsewhere<sup>2</sup>.

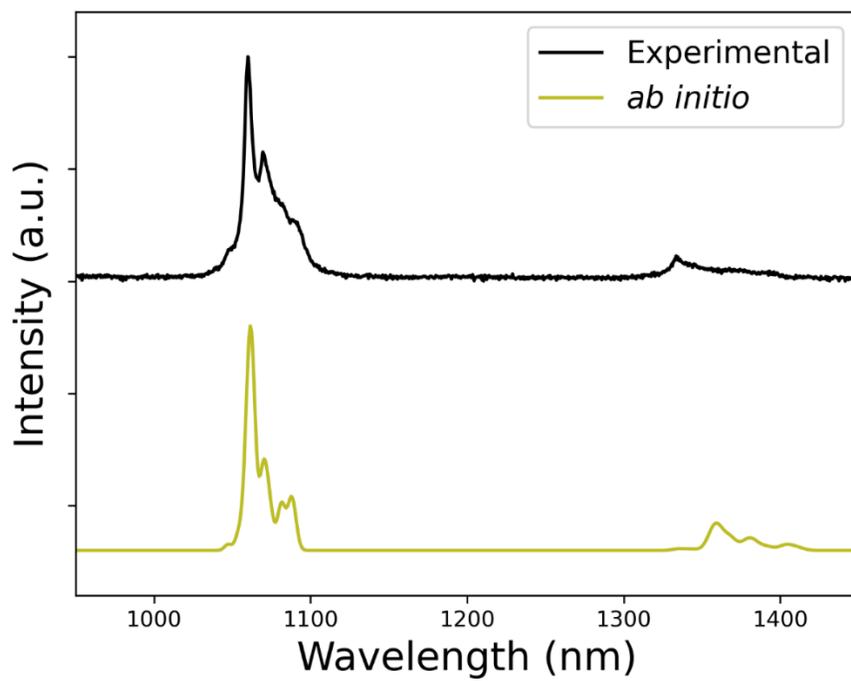
	<b>Nd<sub>2</sub></b>
FW/uma	1819.72
Formula	C <sub>38</sub> H <sub>48</sub> N <sub>4</sub> Nd <sub>2</sub> O <sub>12</sub>
T / K	296
Crystal System	Triclinic
Space Group	P-1
a (Å)	9.3290(4)
b (Å)	10.2150(4)
c (Å)	12.5246(5)
α (°)	109.028(1)
β (°)	95.809(1)
γ (°)	95.471(1)
V (Å <sup>3</sup> )	1112.03(8)
R-factor (%)	2.02



**Figure S2.** Comparison of the PXR D patterns for  $\text{Nd}_2$ : Experimental (blue), calculated (red), and simulated (black\*) based on the CIF file for  $\{[\text{Nd}(\text{acac})_3]_2(\mu\text{-bpm})\}_2$  (black).



**Figure S3.** TGA/DTGA curves for  $\text{Nd}_2$ .



**Figure S4.** Experimental (black) and ab initio calculated emission spectrum (olive) for Nd<sub>2</sub> at 300 K under 804 nm excitation.

## 2. Photoluminescence data

The integrated intensities of the  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  transition, recorded under 370 and 804 nm excitation over the 11–332 K range, were calculated using OriginLab© software. Before fitting, the wavelength scale (nm) was converted to wavenumbers ( $\text{cm}^{-1}$ ) to ensure physically meaningful integration of the spectral areas<sup>3</sup>. After subtraction of a constant baseline, the emission band was deconvoluted into six Lorentzian components for spectra recorded under 370 nm excitation and five Lorentzian components for those obtained under 804 nm excitation. The integrated intensity of each component was extracted directly from the corresponding fitted area parameter. This procedure was applied independently at each temperature, and the quality of the deconvolution was confirmed by  $R^2$  and adjusted  $R^2$  values of  $\sim 0.99$ . This procedure yielded the integrated areas ( $I_j$ ) and the associated uncertainties ( $\delta I_j$ ) for each Lorentzian component (Figures S5 and S6). These integrated intensities were subsequently used to define the thermometric parameters  $\Delta_L$  and  $\Delta_M$ , as described in the main text.

The relative thermal sensitivity ( $S_r$ ) is a figure of merit of the luminescent thermometer, determined as:<sup>4, 5</sup>

$$S_r = \frac{1}{\Delta_i} \left| \frac{\partial \Delta_i}{\partial T} \right| \quad (\text{S1})$$

where  $T$  is the measured temperature.

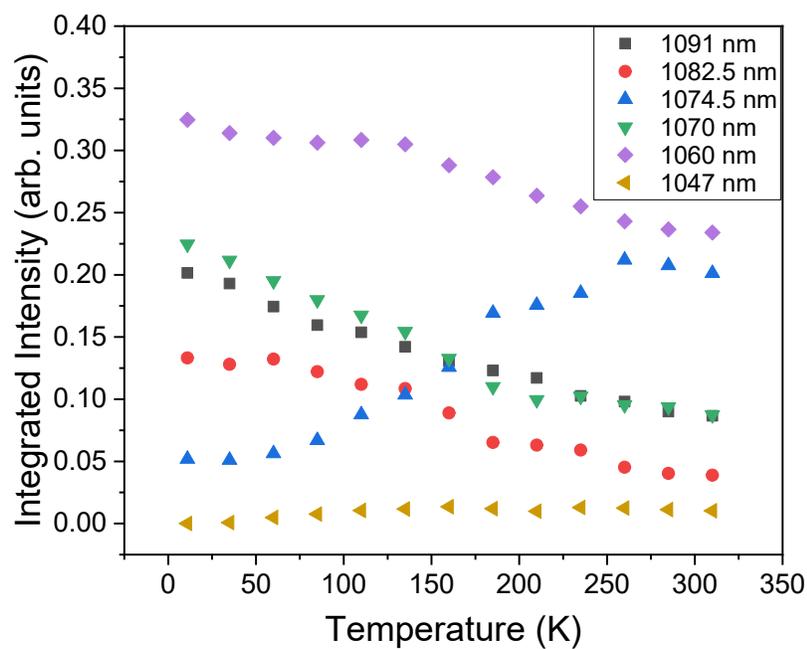
The temperature uncertainty ( $\delta T_i$ ), which quantifies the minimum temperature resolution of each luminescent thermometer, is given by:<sup>4, 5</sup>

$$\delta T_i = \frac{1}{S_r} \frac{\delta \Delta_i}{\Delta_i} \quad (\text{S2})$$

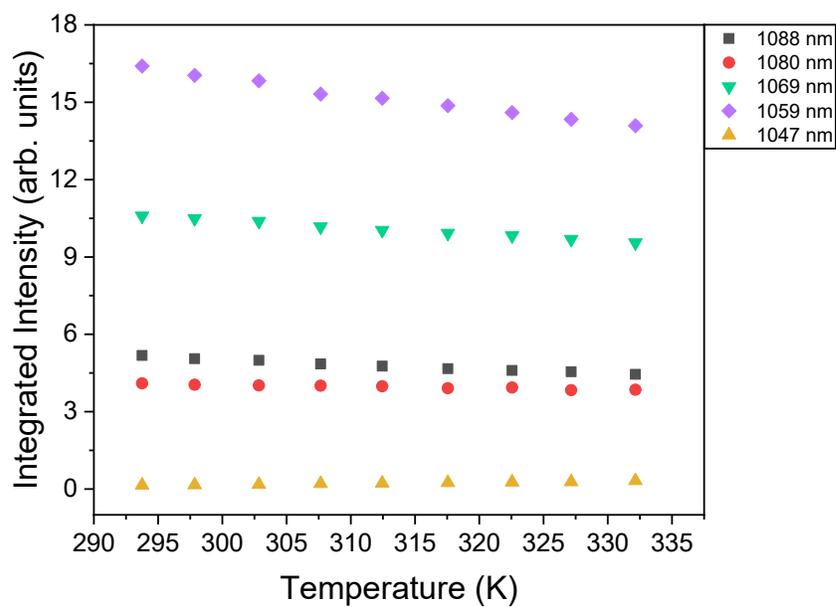
where  $\delta \Delta_i / \Delta_i$ , the relative uncertainty in  $\Delta_i$ , is estimated through error propagation as:

$$\frac{\delta \Delta_i}{\Delta_i} = \sqrt{\sum_j \left( \frac{\delta I_j}{I_j} \right)^2} \quad (\text{S3})$$

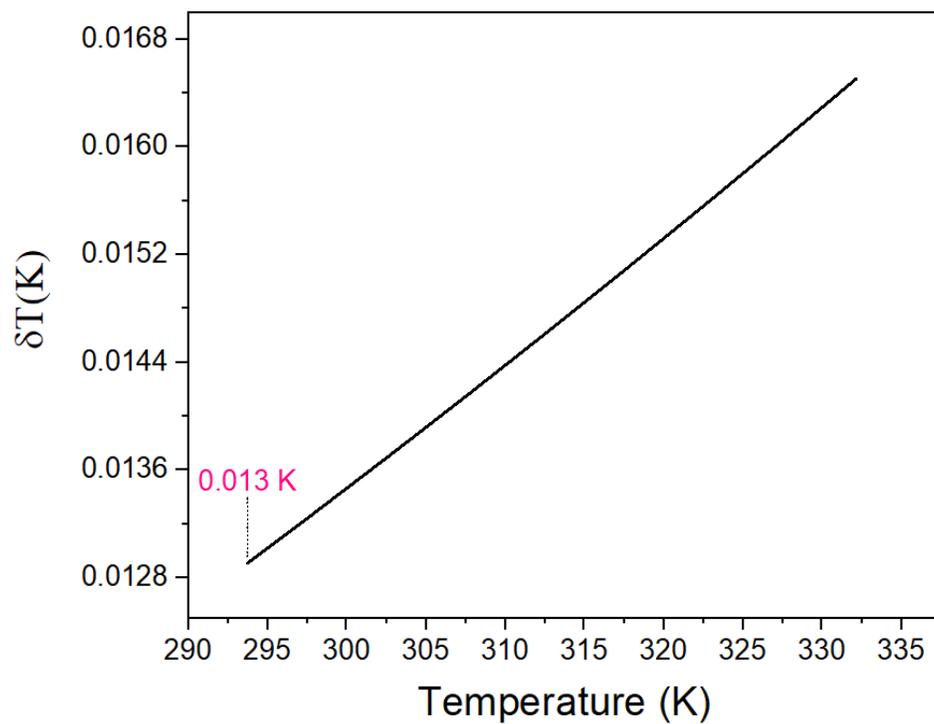
where  $\delta I_j / I_j$  quantifies the relative uncertainty on  $I_j$ .



**Figure S5.** Temperature dependence of the integrated intensities of the six deconvoluted components of the  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  transition under 370 nm excitation.



**Figure S6.** Temperature dependence of the integrated intensities of the five deconvoluted components of the  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  transition under 804 nm excitation.



**Figure S7.** Temperature dependence of  $\delta T$  values for  $\text{Nd}_2$  under metal-centred excitation, with  $\delta T$  values calculated using equation S2 and considering  $\delta\Delta/\Delta = 0.033\%$  <sup>5</sup>.

## References

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