Luminescence thermometry using sprayed films of metal complexes

Riccardo Marin,a† Nathalie Catherine Millan,a Laura Kelly,a Nan Liu,a Emille Martinazzo Rodrigues,a Muralee Murugesu*a and Eva Hemmer*a

a Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada.
† Present address: Nanomaterials for Bioimaging Group (nanoBIG), Departamento de Física de Materiales, Facultad de Ciencias, Universidad Autónoma de Madrid, C/ Francisco Tomás y Valiente 7, Madrid 28049, Spain.
E-mail:  ehemmer@uottawa.ca  
M.Murugesu@uottawa.ca

TABLE OF CONTENT

1. Characterization of the complexes
2. Appearance of the sprayed films
3. Emission spectra as a function of temperature
4. Uncertainty and repeatability of LIR-based thermometry for the 20% Eu film
5. Comparison of the performance of selected Tb3+/Eu3+-based thermometers
6. Photoluminescence decay curves as a function of temperature
7. Additional analysis of the photoluminescence decay curves
8. Relative thermal sensitivity from the average lifetime
9. Chromaticity diagrams for all the mixed films
10. Repeatability of CIE-based thermometry
References
1. Characterization of the complexes

**Figure S1.** Fourier-transform infrared (FTIR) spectra of Tb and Eu complexes, along with the spectra of the ligands. The similarity between Tb and Eu spectra, along with the presence of signals characteristic of the ligands, is evidence of the nature of the two compounds.

**Figure S2.** Powder X-ray diffraction (PXRD) patterns of Tb and Eu complexes along with a simulated pattern of Dy(tfac)phen (CCDC #1037819). The position of the reflections of the synthesized complexes matches well with the one of the reflections of the simulated pattern. This is definitive evidence of the nature of Tb and Eu.

**Figure S3.** Photostability study performed on three films: 100% Tb (green), 20% Eu (orange), and 100% Eu (red). For all films, the excitation wavelength was 327 nm. The monitored emission wavelength was 542 nm for 100% Tb and 612 nm for 20% Eu and 100% Eu. The samples were excited during three periods of 60 min intercut by two 10-min dark periods. The intensity decrease was 10, 5, and 4% respectively. Two spectra were recorded at time 0 and 200 min for the 20% Eu sample. The ratio between the integrated Tb$^{3+}$ (538-555 nm) and Eu$^{3+}$ (608-612 nm) emission was stable within a 4% variability: this stability is of utmost importance to ensure reliable thermal readout based on the Tb$^{3+}$/Eu$^{3+}$ luminescence intensity ratio.
2. Appearance of the sprayed films

Figure S4. Sprayed films with different Eu content under daylight (a) and under UV excitation (b; 350 nm). c) Brightfield and fluorescence image under UV illumination (390 nm) of the 20% Eu film taken with a microscope. d) Emission spectrum extracted at the centre of the area shown in (c). e) Value of the intensity ratio between the Tb$^{3+}$ and Eu$^{3+}$ transitions indicated with an arrow in (d), calculated for ten different spots. The integration ranges used for the Eu$^{3+}$ and Tb$^{3+}$ transitions are 610-614 nm and 537-558 nm. Five spots were taken from the area in (c) and five more from a different region of the film. The consistency of the value found for the intensity ratio (0.138 ± 0.003) is a good indication of the compositional homogeneity of the film.
3. Emission spectra as a function of temperature

**Figure S5.** Temperature-dependent emission spectra of mixed films with 0.5 (a), 1 (b), 2.5 (c), 5 (d), and 10% (e) Eu recorded under 327 nm excitation. All the spectra are normalized to the $^5D_0 \rightarrow ^7F_2$ emission of Eu$^{3+}$ to better visualize the relative trend of the Tb$^{3+}$ and Eu$^{3+}$ emissions. The spectra of the 20% Eu film are reported in Figure 3a of the main manuscript.

**Mott-Seitz function**

Equation 5 in the main manuscript is a Mott-Seitz function, which is reproduced below as Eq. S1.

$$LIR(T) = \frac{LIR_0}{1 + \alpha_1 \exp \left(-\Delta_1/k_BT\right) + \alpha_2 \exp \left(-\Delta_2/k_BT\right)} \quad (S1)$$

This is an expression that considers two thermally activated de-excitation pathways to describe the trend of, in this case, the Tb$^{3+}$-to-Eu$^{3+}$ luminescence intensity ratio ($LIR$).

Here, $LIR_0$ stands for the initial ratio found at low temperature. $\alpha_{1,2}$ and $\Delta_{1,2}$ are respectively pre-exponential factors (approximating the relative weight of non-radiative and radiative decay) and activation energies for the two de-excitation pathways. $k_B$ is the Boltzmann constant. Despite the physical meaning of this function, herein it is simply used as a phenomenological description of the experimental trend of $LIR$. The fitting parameters for the six $LIR$ vs $T$ datasets are reported below in Table S1.

**Table S1.** Summary of the fitting parameters for the curves reported in Figure 3b of the main manuscript.

<table>
<thead>
<tr>
<th>Film</th>
<th>$LIR_0$</th>
<th>$\alpha_1$</th>
<th>$\Delta_1$</th>
<th>$\alpha_2$</th>
<th>$\Delta_2$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% Eu</td>
<td>203</td>
<td>23</td>
<td>380</td>
<td>74180</td>
<td>1780</td>
<td>0.9997</td>
</tr>
<tr>
<td>1% Eu</td>
<td>138</td>
<td>31</td>
<td>403</td>
<td>175590</td>
<td>1920</td>
<td>0.9994</td>
</tr>
<tr>
<td>2.5% Eu</td>
<td>52.2</td>
<td>64</td>
<td>535</td>
<td>492400</td>
<td>2120</td>
<td>0.9998</td>
</tr>
<tr>
<td>5% Eu</td>
<td>18.5</td>
<td>72</td>
<td>516</td>
<td>2490000</td>
<td>2450</td>
<td>0.9941</td>
</tr>
<tr>
<td>10% Eu</td>
<td>10.6</td>
<td>240</td>
<td>711</td>
<td>6950000</td>
<td>2610</td>
<td>0.9991</td>
</tr>
<tr>
<td>20% Eu</td>
<td>5.29</td>
<td>143</td>
<td>614</td>
<td>33670000</td>
<td>2850</td>
<td>0.9986</td>
</tr>
</tbody>
</table>
4. Uncertainty and repeatability of LIR-based thermometry for the 20% Eu film

Figure S6. Uncertainty for the LIR-based approach using the 20% Eu film. The shadowed red line is a guide for the eye.

Figure S7. Study of the repeatability of the LIR-based approach using the 20% Eu film. Three separate cycles of measurements were performed.
5. Comparison of the performance of selected Tb$^{3+}$/Eu$^{3+}$-based thermometers

Table S2. Comparison of the performance of selected Tb$^{3+}$/Eu$^{3+}$-based luminescent thermometers.

<table>
<thead>
<tr>
<th>Material</th>
<th>T range, K</th>
<th>max $S_r$, %·K$^{-1}$ [@ T]</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>{Tb$_x$Eu$<em>y$Gd$</em>{20-x-y}$} molecular cluster-aggregate</td>
<td>268-338</td>
<td>4.17 [309 K]</td>
<td>1</td>
</tr>
<tr>
<td>pdms-eddpo(1%)-[Tb$<em>{0.90}$Eu$</em>{0.10}$(bzac)$_3$]</td>
<td>80-250</td>
<td>11.05 [203 K]</td>
<td>2</td>
</tr>
<tr>
<td>Eu,TbPOM@MOF</td>
<td>60-360</td>
<td>0.71 [60 K]</td>
<td>3</td>
</tr>
<tr>
<td>Eu,Tb 2D sheets</td>
<td>110-360</td>
<td>1.08 [360 K]</td>
<td>3</td>
</tr>
<tr>
<td>Tb$<em>{0.95}$Eu$</em>{0.05}$HY</td>
<td>4-300</td>
<td>31 [4 K]</td>
<td>4</td>
</tr>
<tr>
<td>cycEu-phTb</td>
<td>10-298</td>
<td>1.86 [constant]</td>
<td>5</td>
</tr>
<tr>
<td>[Tb$<em>{0.95}$Eu$</em>{0.05}$(hfa)$_3$(dpbp)$_n$]</td>
<td>200-300</td>
<td>0.83 [constant]</td>
<td>6</td>
</tr>
<tr>
<td>Tb$<em>{0.95}$Eu$</em>{0.05}$(BDC)$_2$(H$_2$O)$_2$</td>
<td>298-320</td>
<td>0.31 [318 K]</td>
<td>7</td>
</tr>
<tr>
<td>[Eu$<em>{0.53}$Tb$</em>{0.47}$(tfa)$_2$]$_2^+$Na$_2^+$</td>
<td>273-373</td>
<td>2.7 [353 K]</td>
<td>8</td>
</tr>
</tbody>
</table>

pdms = polydimethylsiloxane
eddpo = ethyl phenyl (diethoxymethyl)phosphonate
bzac = benzoylacetonate
POM = polyoxometalate
MOF = metal organic framework
H$_4$L = 5-hydroxy-1,2,4-benzenetricarboxylic acid
cyc-phen = cyclen 1,10-phenanthroline; cycLn$_1$-phLn$_2$ is the complex obtained from the two lanthanides, cyc-phen and pyrrolidine-1-carbodithioate
hfa = hexafluoro acetylacetonate
dpbp = 4,4’-bis(diphenylphosphoryl)biphenyl
BDC = 1,4-benzendicarboxylate
tfa = trifluoro acetylacetonate
6. Photoluminescence decay curves as a function of temperature

![Photoluminescence decay curves](image)

**Figure S8.** Photoluminescence decay curves of the Tb^{3+}:5D_4 level for mixed films with 0.5, 1, 2.5, 5, 10, and 20% Eu, as well as the pure Tb film (0% Eu), and films with 1 and 10% Gd. The measurements were performed monitoring the emission at 542 nm under 327 nm excitation. All the curves are normalized at 0 s. The fitting curves (stretched exponential) for the decays recorded at 30 (blue curve) and 330 K (red curve) are reported as black lines for all film compositions.

**Table S3.** Summary of the fitting parameters for the decay curves for the 10% Eu film. The results for this film are representative for the results of the fitting procedure followed for all the films.

<table>
<thead>
<tr>
<th>T, K</th>
<th>I_0</th>
<th>τ</th>
<th>β</th>
<th>R^2</th>
<th>T, K</th>
<th>I_0</th>
<th>τ</th>
<th>β</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.989</td>
<td>968</td>
<td>0.956</td>
<td>0.9998</td>
<td>190</td>
<td>0.992</td>
<td>835</td>
<td>0.920</td>
<td>0.9998</td>
</tr>
<tr>
<td>50</td>
<td>0.998</td>
<td>970</td>
<td>0.956</td>
<td>0.9998</td>
<td>210</td>
<td>0.980</td>
<td>754</td>
<td>0.890</td>
<td>0.9998</td>
</tr>
<tr>
<td>70</td>
<td>1.007</td>
<td>981</td>
<td>0.962</td>
<td>0.9998</td>
<td>230</td>
<td>0.990</td>
<td>620</td>
<td>0.857</td>
<td>0.9998</td>
</tr>
<tr>
<td>90</td>
<td>1.003</td>
<td>985</td>
<td>0.964</td>
<td>0.9999</td>
<td>250</td>
<td>0.998</td>
<td>444</td>
<td>0.808</td>
<td>0.9997</td>
</tr>
<tr>
<td>110</td>
<td>1.004</td>
<td>988</td>
<td>0.964</td>
<td>0.9998</td>
<td>270</td>
<td>1.055</td>
<td>250.0</td>
<td>0.746</td>
<td>0.9997</td>
</tr>
<tr>
<td>130</td>
<td>0.982</td>
<td>983</td>
<td>0.961</td>
<td>0.9998</td>
<td>290</td>
<td>1.063</td>
<td>129.5</td>
<td>0.727</td>
<td>0.9996</td>
</tr>
<tr>
<td>150</td>
<td>1.008</td>
<td>963</td>
<td>0.965</td>
<td>0.9999</td>
<td>310</td>
<td>1.074</td>
<td>67.7</td>
<td>0.768</td>
<td>0.9992</td>
</tr>
<tr>
<td>170</td>
<td>1.000</td>
<td>917</td>
<td>0.955</td>
<td>0.9999</td>
<td>330</td>
<td>1.060</td>
<td>34.3</td>
<td>0.863</td>
<td>0.9989</td>
</tr>
</tbody>
</table>
7. Additional analysis of the photoluminescence decay curves

**Figure S9.** Fit of the lifetime vs temperature dataset for the pure Tb film using a Mott-Seitz function with a single de-excitation pathway, wherein the activation energy (Δ) has been fixed to 1620 cm⁻¹, i.e., the energy difference between the Tb³⁺: ⁵D₄ emitting state and the lowest triplet state of the ligand system (i.e., phen). Symbols are experimental points and the solid line is the fitting curve.

**Figure S10.** Comparison of the lifetime vs temperature datasets for films of 100% Tb, 1% Eu, and 1% Gd. Symbols are experimental points and solid lines are fitting curves using Equation 5 in the main manuscript.
8. Relative thermal sensitivity from the average lifetime

Figure S11. Relative thermal sensitivity based on the lifetime of the Tb$^{3+}$ excited state for selected film compositions that illustrate the effect of increasing the Eu content. The trend is similar to the one observed for the LIR-based thermometry, with higher percentages of Eu pushing the sensitivity to higher values, reaching a maximum of approximately 3.8 %·K$^{-1}$ for the 20% Eu film.
9. Chromaticity diagrams for all the mixed films

Figure S12. CIE coordinates as a function of temperature superimposed to the chromaticity diagram for all the mixed films.
10. Repeatability of CIE-based thermometry

![Graph showing repeatability of CIE-based thermometry for 2.5% Eu and 20% Eu films.]

**Figure S13.** Repeatability for the CIE-based thermometric approaches explored. Top: 2.5% Eu film x, y, and y/x. Bottom: 20% Eu film x, y, and y/x.

**References**