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Supporting information

Ratiometric mixed Eu-Tb Metal-Organic Framework as a new cryogenic luminescent thermometer

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Experimental section

All chemicals and reagents were purchased from major chemical suppliers and used as received.

Synthesis of [Tb_2(1,3-bdc)$_3$(H_2O)$_2$]·H_2O ***(1)***. 1,3-H_2bdc (223 mg, 1.34 mmol) was dissolved in 10 ml of a NaOH solution (0.3 M) while $TbCl_3\cdot6H_2O$ (250 mg, 0.67 mmol) was dissolved in 2 ml dezionized water. The two solutions was mixed and a white precipitate was formed. The pH of the mixture was adjusted at 5 by addition of small amount of a NaOH solution (1.5 M). Then, the above mixture was placed in a sealed 21 ml Teflon-lined stainless vessel, which was heated at 180°C for 72h under autogenous pressure and cooled down to room temperature. Colorless block crystals were obtained. Yield: 0.143 g (37.06%). Anal. Calcd for $C_{24}H_{18}Tb_2O_{15}$ (%): C, 33.4; H, 2.08. Found: C, 32.9; H, 1.96. IR (KBr pellet, cm^{-1}): 1616 (vs), 1603 (vs), 1551 (sh), 1529 (vs), 1481 (vs), 1456 (vs), 1391 (vs), 833 (m), 746 (s), 717 (s), 683 (m), 656 (m), 542 (m) and 420 (m).

Synthesis of [Eu_2(1,3-bdc)$_3$(H_2O)$_2$]·H_2O ***(2)***. 1,3-H_2bdc (582 mg, 3.50 mmol) was dissolved in 10 ml of a NaOH solution (0.3 M) while $Eu(NO_3)_3\cdot5H_2O$ (300 mg, 0.70 mmol) was dissolved in 2 ml dezionized water. The two solutions was mixed and a white precipitate was formed. The pH of the mixture was adjusted at 5 by addition of small amount of a NaOH solution (1.5 M). Then, the above mixture was placed in a sealed 21 ml Teflon-lined stainless vessel, which was heated at 150°C for 48h under autogenous pressure and cooled down to room temperature. Colorless block crystals were obtained. Yield: 0.121 g (40.67%). Anal. Calcd for $C_{24}H_{18}Eu_2O_{15}$ (%): C, 33.9; H, 2.1. Found: C, 34.4; H, 1.97. IR (KBr pellet, cm^{-1}): 16146 (vs), 1601 (vs), 1547 (sh), 1528 (vs), 1479 (vs), 1454 (vs), 1389 (vs), 833 (m), 746 (s), 716 (s), 683 (m), 656 (m), 538 (m) and 424 (m).

Synthesis of [$Tb_{0.90}Eu_{0.1}$(1,3-bdc)$_3$(H_2O)$_2$]·H_2O ***(3)***. The mixed-lanthanide compound was synthesized purely as a white microcrystalline powder using the same procedure as (***1)*** except using mixtures of $TbCl_3\cdot6H_2O$ and $Eu(NO_3)_3\cdot5H_2O$ with the corresponding molar ratio of Tb^{3+} and Eu^{3+} ions equal to 20:1 ($TbCl_3\cdot$6H2O: 285 mg, $Eu(NO_3)_3\cdot5H_2O$: 17 mg). After filtration, the powder was washed with water, then ethanol, and dried in air. Yield: 0.185 g (47.95 %). IR (KBr pellet, cm-1): 1616 (vs), 1603 (vs), 1551 (sh), 1529 (vs), 1481 (vs), 1456 (vs), 1391 (vs), 833 (m), 746 (s), 716 (s), 681 (m), 656 (m), 540 (m) and 420 (m). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was performed to assess the content of Tb and Eu and the final composition was determined as [$Tb_{0.87}Eu_{0.13}$(1,3-bdc)$_3$(H_2O)$_2$]·H_2O.

Physical measurements. FT-IR spectra were recorded in the 4000-400 cm^{-1} range on a BRUKER Vertex equipped with a computer control using the OPUS software. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed by flowing dry argon with a heating and cooling rate of 5°C/min on a SETARAM TG-DSC 111 between 20 and 1000°C. Powder X-ray Diffraction spectra were monitored using a D8 Bruker diffractometer in the Bragg-Brentano geometry, equipped with a front germanium monochromator, a copper anode (Cu*K*-L3 radiation λ=1.540598 Å) and a LynxEye PSD detector.

Photoluminescence. Room-temperature Photoluminescence spectra were recorded on a Jobin-Yvon Fluorolog 3 fluorometer equipped with a CCD camera (excitation source: 450 W Xe arc lamp). The temperature-dependent photoluminescence measurements were recorded with a modular double grating excitation spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog–3® 2-Triax, Horiba Scientific) coupled to a R928 Hamamatsu photomultiplier, using the front face acquisition mode. The excitation source was a 450 W Xe arc lamp. The emission spectra were corrected for detection and optical spectral response of the spectrofluorimeter and the excitation spectra were weighed for the spectral distribution of the lamp intensity using a photodiode reference detector. The temperature was controlled by a helium−closed cycle cryostat with vacuum system measuring ca. 5×10−6 mbar and a Lakeshore 330 auto−tuning temperature controller with a resistance heater. The temperature can be adjusted from ca. 12 to 450 K with a maximum accuracy of 0.1 K. The sample temperature was fixed to a particular value using the auto−tuning temperature controller; after waiting 5 min to thermalize the sample, four consecutive steady−state emission spectra were measured for each temperature; the maximum temperature difference detected during the acquisitions was 0.1 K, the temperature accuracy of the controller. To prevent the dehydration of the sample under high vacuum, the vacuum system was only initialized at a temperature below 260 K, to allow to frozen the sample. At the very low pressure the hydrated phase is only stable up to 230 K, at 250 K it starts to have some phase transformation. Consequently, the temperature dependence measurements of the $[Tb_{0.87}Eu_{0.13}(1,3\text{-}bdc)_3(H_2O)_2]\cdot H_2O$ emission, including the temperature cycling, were recorded in the 12-230 K range.

Computational details. All calculations have been performed at the DFT level of theory employing the G09D01 suite of programs.[S1] The functional used to perform the calculations has been B3LYP, in conjunction of the Def2TZVP basis set.[S2–S4]All the GS and ES geometries have been optimized and checked to be true minima on the Potential Energy Surface (PES) by diagonalizing their Hessians. Calculations on the triplet excited state have been performed using the unrestricted formalism.[S5] In order to plot the phosphorescence spectra, vibronic contributions to electronic emission have been considered using the Vertical Hessian (VH) approach as implemented in the used version of the Gaussian Package.[S6,S7] The VH model includes frequency changes and mode mixing between the two electronic states. In all cases, the Franck−Condon approximation was enforced, the transition moment is barely affected by (small) geometry modifications. The simulated phosphorescence spectrum has been plotted with the VMS programs.[S8]

Table S1. Lattice parameters of compounds ***(1)*** and ***(2)*** obtained by structural refinement of PXRD patterns by the Le Bail method.

	(1)	***(2)***
Chemical composition	$[Tb_2(1,3\text{-bdc})_3(H_2O)_2]\cdot H_2O$	$[Eu_2(1,3\text{-bdc})_3(H_2O)_2]\cdot H_2O$
Space group	$P2_1/c$	$P2_1/c$
a (Å)	10.6061 (9)	10.6431 (8)
b (Å)	14.2204 (4)	14.2360 (7)
c (Å)	17.140 (18)	17.1814 (10)
β (°)	97.904 (10)	97.958 (5)

Figure S1. Simulated XRD pattern of the compound [Y_2(1,3-bdc)$_3$(H_2O)$_2$]·H_2O reported in reference 10 (black line) and room-temperature experimental PXRD diffractograms of compounds ***(1)*** in red line, ***(2)*** in blue line and ***(3)*** in purple line.

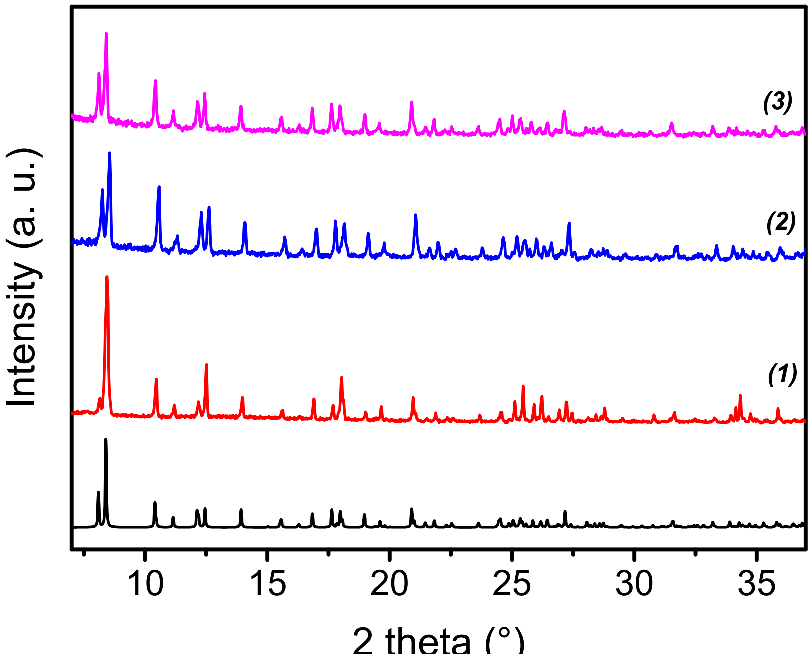


Figure S2. Crystal structure of the coordination polymer [Ln_2(1,3-bdc)$_3$(H_2O)$_2$]·H_2O (Ln = Tb or Eu) a) along the b axis and b) along the c axis.

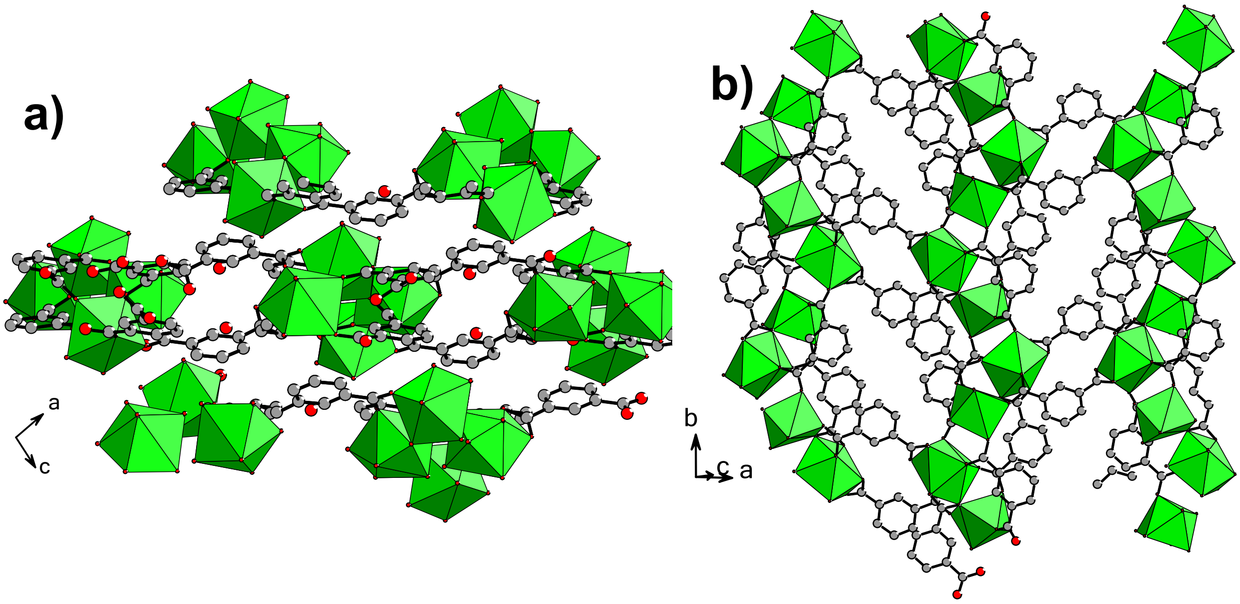


Figure S3. TGA measurements of compounds ***(1)*** (black line) and ***(2)*** (red line).

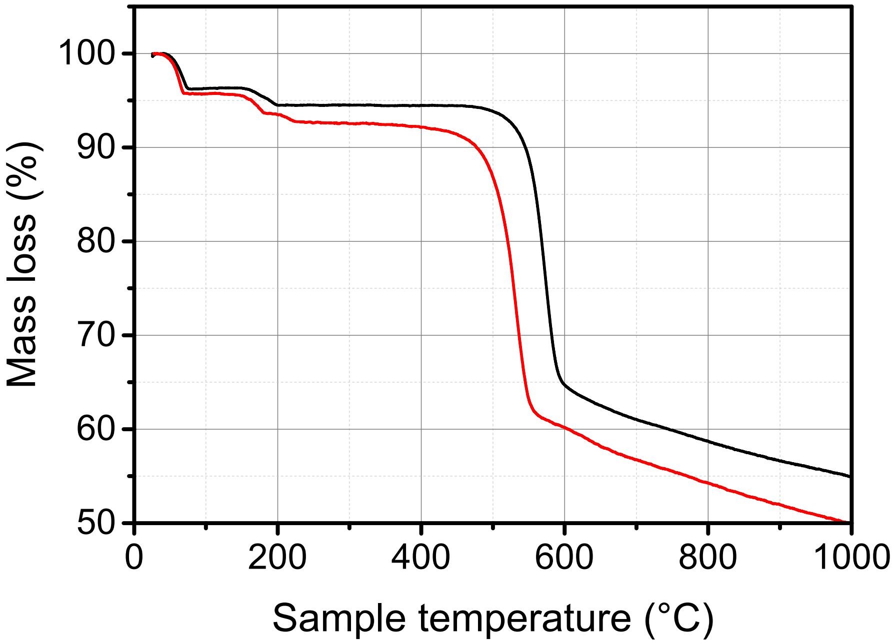


Figure S4. Room-temperature FT-IR spectra of 1,3-H_2bdc (isophtalic acid) and the compounds ***(1)-(3)***.

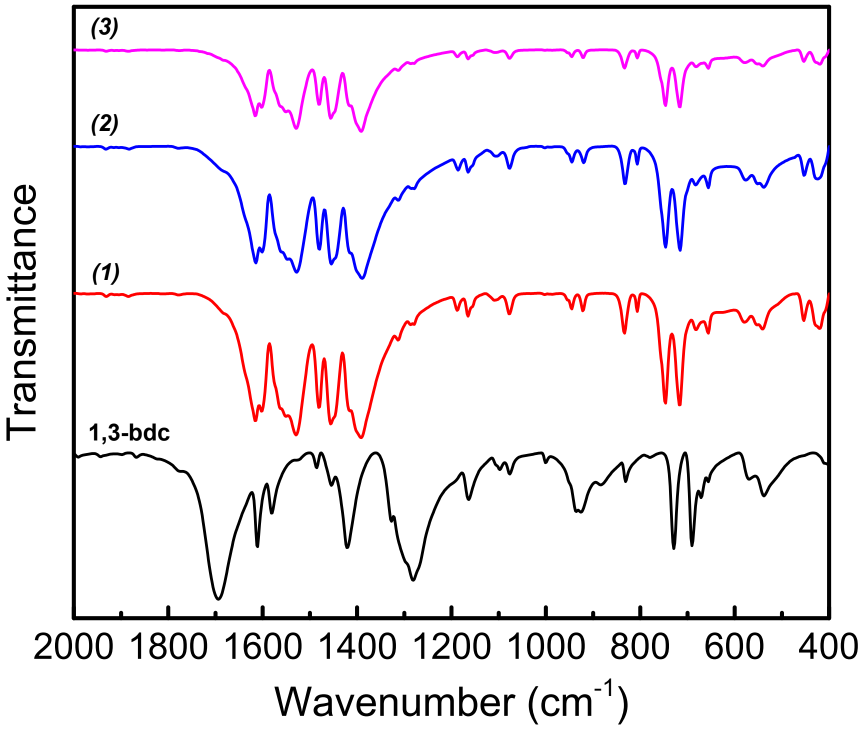


Figure S5. Room-temperature PL spectrum of 1,3-H_2bdc under UV excitation at 305 nm (black line) and simulated spectrum obtained by DFT calculations (red line).

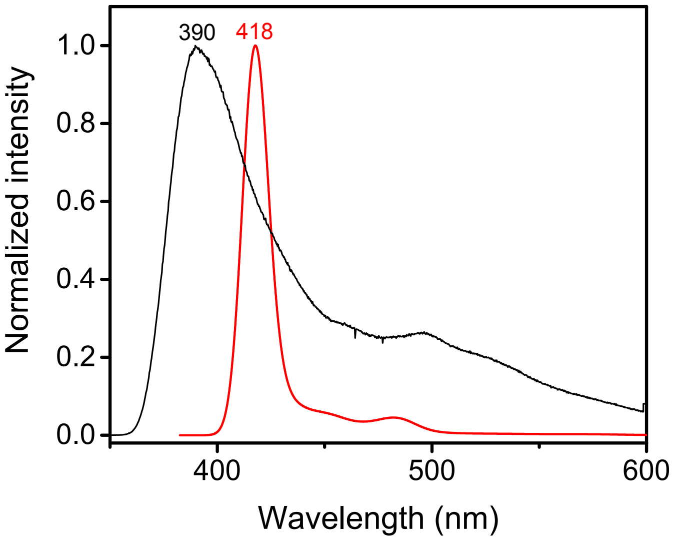


Figure S6. Room-temperature PL spectra of compounds a) ***(1)***, and b) ***(2)*** (UV excitation at 305 nm).

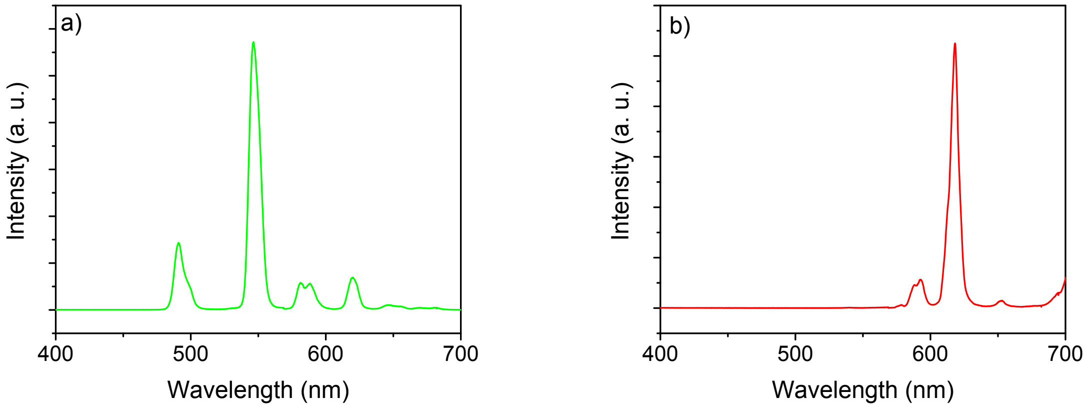


Figure S7. Excitation spectra of compound ***(3)*** monitoring the emission at 619 nm (Eu^{3+}, red lines) and 542 nm (Tb^{3+}, green lines) recorded at a) room temperature and b) 12 K. The $^7F_6$ ❸ $^5H_7$, $^5D_{0,1}$, Tb^{3+} lines signed at 315-317 nm are resonant with the $^7F_{0,1}$ ❸ $^5H_{3\text{-}7}$ Eu^{3+} transitions (not signed in the figure). The assignment of the Eu^{3+} and Tb^{3+} levels follows references S9 and S10, respectively.

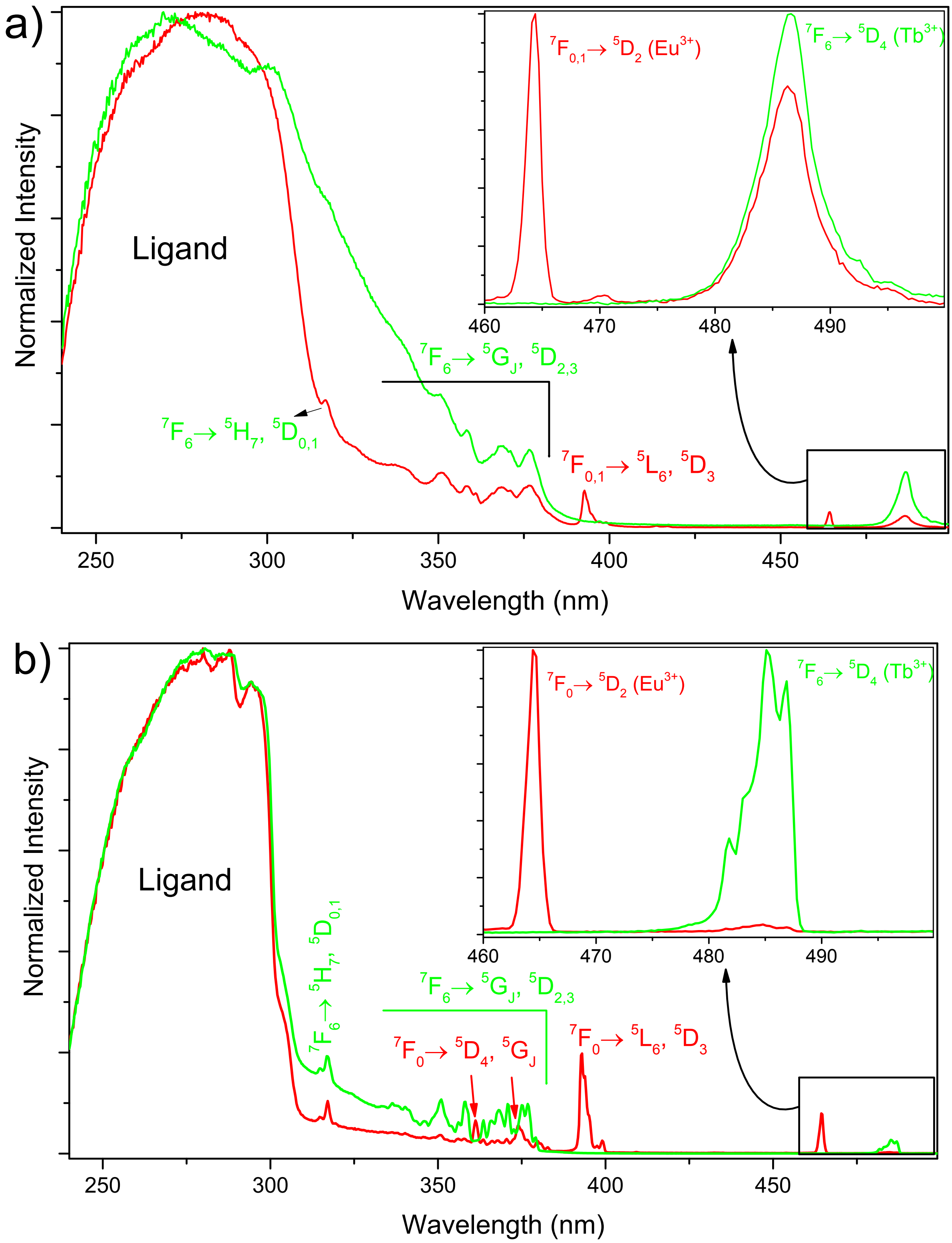


Figure S8. Energy diagram of Tb^{3+} and Eu^{3+} ions, including non-radiative (dot arrows) and radiative (full arrows) transitions and Tb^{3+}-to-Eu^{3+} energy transfer process, accordingly to the excitation spectra of ***(3)*** recorded at 12 K (Figure S7b). The assignment of the excited states follows reference 17a.

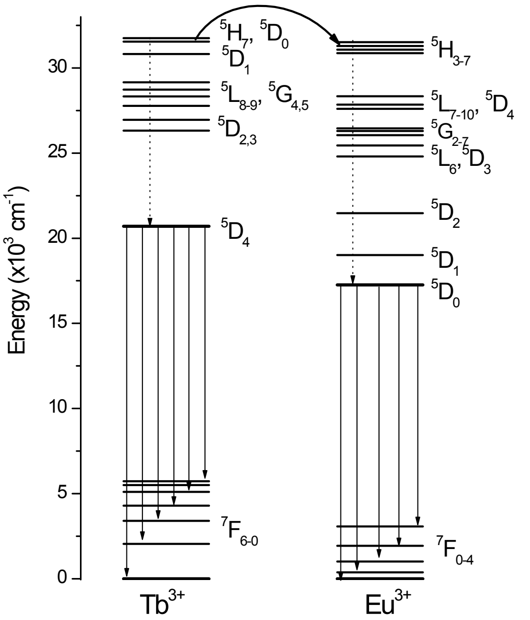


Figure S9. Temperature uncertainty ($\delta T = {}^{1}/_{S_r} \times \delta\Delta/\Delta$), in the 12 – 230 K range, in the determination of the thermometric parameters Δ obtained for the luminescent thermometer defined with compound ***(3)***. $\delta\Delta/\Delta$ was estimated by the average relative errors in the same temperature range (0.2%).

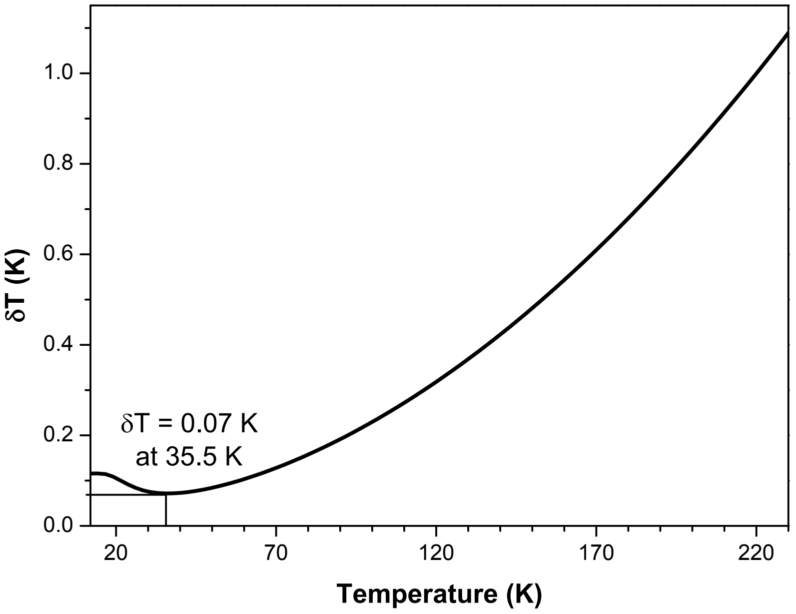
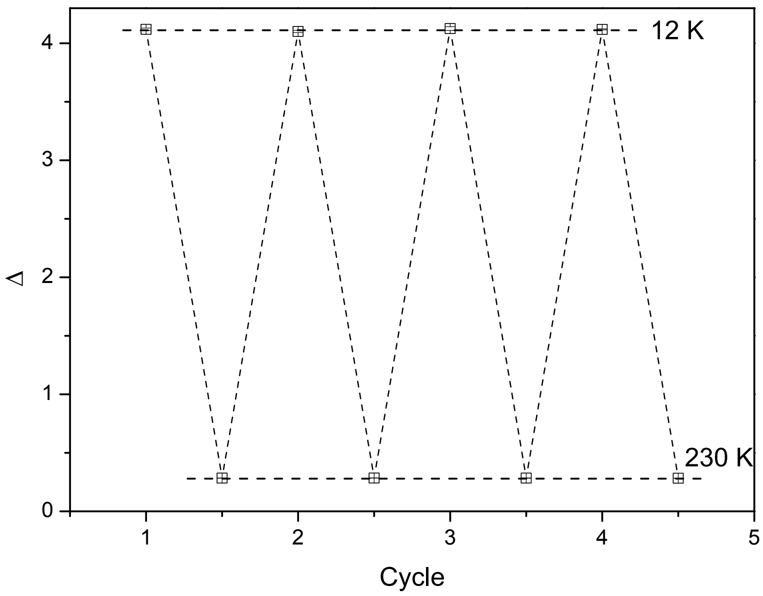


Figure S10. Temperature cycling between 12 and 230 K revealing a repeatability > 99% for the luminescent thermometer.



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