Supporting Information

Highly sensitive and precise optical temperature sensors based on new luminescent Tb³⁺/Eu³⁺ *tetrakis* complexes with imidazolic counterions

Lucca B. Guimarães, Alexandre M.P. Botas, Maria C.F.C. Felinto, Rute A. S. Ferreira, Luís D. Carlos*, Oscar L. Malta, Hermi F. Brito*.

L. B. Guimarães, Prof. H. F. Brito Department of Fundamental Chemistry, Institute of Chemistry, University of São Paulo, Avenida Professor Lineu Prestes 748, 05508-008, São Paulo, Brazil E-mail: <u>hefbrito@iq.usp.br</u>

Dr. A. M. P. Botas, Prof. Rute A. S. Ferreira, Prof. L. D. Carlos Phantom-g, CICECO – Aveiro Institute of Materials, Department of Physics, Universidade de Aveiro 3810-193 Aveiro, Portugal Email: <u>lcarlos@ua.pt</u>

Dr. M. C. F. C. Felinto Institute of Energy and Nuclear Research, Avenida Professor Almeida Prado 2242, 05508-000, São Paulo, Brazil

Prof. O. L. Malta Departament of Fundamental Chemistry, Federal University of Pernambuco, Cidade Universitária, 50740-540, Recife, Brazil

The supplementary figures and tables were prepared to be an additional source of information for this article.



Figure S1: DTG curves of the $[C_4 mim][Tb_{1-x}Eu_x(btfa)_4]$ (x = 0.01, 0.05, 0.1 and 1.00) complexes recorded under synthetic air atmosphere at 10 °C min⁻¹.



Figure S2: FTIR vibrational spectra for the $[C_4mim][Tb_{1-x}Eu_x(btfa)_4]$ (x= 0.01, 0.05, 0.1 and 1.00) complexes recorded in KBr pellets.



Figure S3: Phosphorescence spectrum of the $[C_4 mim][Gd(btfa)_4]$ complex recorded at 77 K under excitation at 360 nm.



Figure S4: Luminescence decay curves for the $[C_4 mim][Tb_{1-x}Eu_x(btfa)_4]$ (x= 0.01, 0.05, 0.1 and 1.00) registered with excitation at 462 nm (Eu³⁺ ⁷F₀ \rightarrow ⁵D₂) at room temperature.



Figure S5: Spectra used to calculate the absolute quantum yield for $[C_4mim][Tb_{0.95}Eu_{0.05}(btfa)_4]$ excited at 360 nm (black line) and 465 nm (blue line). The shadow area corresponds to the diffused reflectance and was used to estimate the number of absorbed photons. Similar spectra were obtained for $[C_4mim][Tb_{0.99}Eu_{0.01}(btfa)_4]$ and $[C_4mim][Tb_{0.90}Eu_{0.10}(btfa)_4]$.



Figure S6: Emission spectra of $[C_4mim][Tb_{0.99}Eu_{0.01}(btfa)_4]$ (a) and $[C_4mim][Tb_{0.95}Eu_{0.05}(btfa)_4]$ (b) complexes recorded as a function of temperature with excitation at 360 nm. The emission spectra are normalized by the intensity at 611 nm (${}^5D_0 \rightarrow {}^7F_2$). The ${}^5D_4 \rightarrow {}^7F_5/{}^5D_0 \rightarrow {}^7F_2$ ratio of the spectra shown in a) and b) are shown in c) and d), respectively. The lines in c) and d) represent the fit with Equation 5, with parameters show in Table S2. The fit residual plots are shown on the bottom for a judgment of the fit quality. The shadowed areas mark the regions in which the thermometric parameter change within the error meaning that for these temperatures the thermometers are out of the so-called operating range.

Relative thermal sensitivity e) and temperature uncertainty f) obtained for $[C_4mim][Tb_{0.99}Eu_{0.01}(btfa)_4]$ (dashed line) and $[C_4mim][Tb_{0.95}Eu_{0.05}(btfa)_4]$ (solid line). In f), the temperature range is limited to $\delta T < 0.07$ K.



Figure S7: Intensity of the Tb³⁺ ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ (a) and the Eu³⁺ ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (b) transitions of $[C_{4}\text{mim}][Tb_{0.90}\text{Eu}_{0.10}(\text{btfa})_{4}]$ with excitation at 360 nm. The red line represents the fit to Equation 5 ($A = (2\pm1)\times10^{6}$; $E_{a} = 1965\pm179 \text{ cm}^{-1}$; $\Delta_{0} = 1.67\pm0.01$ and $R^{2} = 0.996$). The fit residual plot is shown on the bottom for a judgment of the fit quality.

Table	S1 .	CIE	(x,y)	coordinates	corresponding	to	the	emission	spectra	of	the
$[C_4 mim][Tb_{0.99}Eu_{0.01}(btfa)_4]$ complex at different temperatures.											

Temperature (K)	x	у
20	0.3920	0.6000
40	0.3904	0.6022
70	0.3901	0.6025
100	0.3883	0.6048
120	0.3867	0.6058
150	0.3864	0.6061
160	0,3870	0.6055
175	0.3869	0.6055
200	0.4015	0.5912
225	0.4942	0.5006
250	0.5930	0.4038
275	0.6404	0.3574
300	0.6616	0.3367
350	0.6745	0.3240

Table S2. Experimental parameters found fitting **Equation 5** to the ${}^{5}D_{4} \rightarrow {}^{7}F_{5}/{}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ratio of the spectra measured for $[C_{4}mim][Tb_{0.99}Eu_{0.01}(btfa)_{4}]$ and $[C_{4}mim][Tb_{0.95}Eu_{0.05}(btfa)_{4}]$ complexes with excitation at 360 nm (ligand).

Complex	Α	$E_{a \text{ (cm}^{-1})}$	Δ ₀	R ²
$[C_4 mim][Tb_{0.99}Eu_{0.01}(btfa)_4]$	$(3\pm 2) \times 10^{6}$	1712±72	49±1	0.999
$[C_4 mim][Tb_{0.95}Eu_{0.05}(btfa)_4]$	$(5\pm 2) \times 10^{5}$	1490 ± 57	11±1	0.997