Site-selective Eu(III) spectroscopy of highly efficient luminescent mixed-metal Pb(II)/Eu(III) coordination polymers

C. D. E. S. Barbosa,[a] L. L. Da Luz,[a] F. A. Almeida Paz,[b] O. L. Malta,[a,c] M. O. Rodrigues,[d] S. A. Júnior,[a] R. A. S. Ferreira,[e] and L. D. Carlos[e*]

[a] *University Federal of Pernambuco, Department of Chemistry, Laboratório de Terras Raras, 50590-470, Recife, Brazil*
[b] *Department of Chemistry, CICECO – Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal*
[c] *Departamento de Química – CCEN-UFPB, Cidade Universitária, CEP 58051-970, João Pessoa-PB, Brazil*
[d] *University of Brasília (IQ – UNB), Campus Universitário Darcy Ribeiro, LIMA – Laboratório de Inorgânica e Materiais, 70904970, Brasília, Brazil*
[e] *Department of Physics and CICECO – Aveiro Institute of Materials, University of Aveiro, 3810 – 193 Aveiro, Portugal*

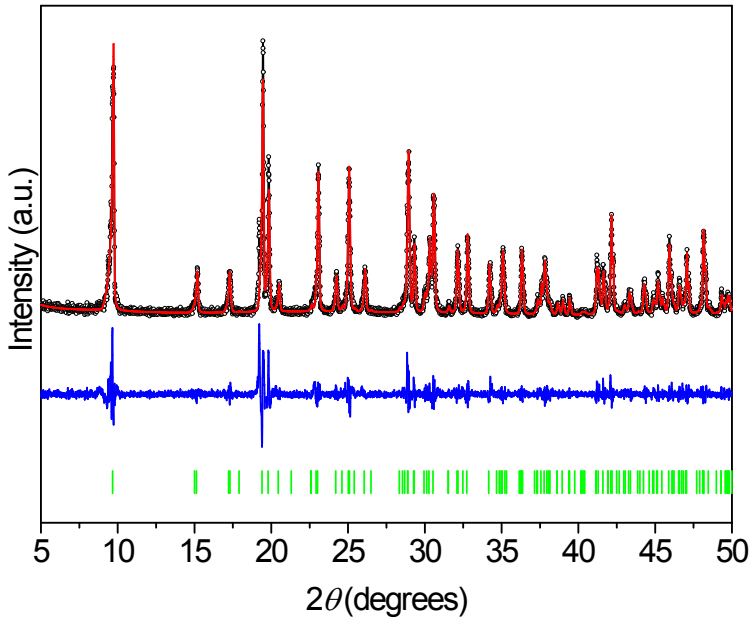

Figure S1. Rietveld plot of $Pb_{0.95}Eu_{0.05}$-BDC. The observed data points, the best fit profile, and the difference between experimental and refinement data are represented as black circles, red line and blue line, respectively. Green vertical bars represent the angular position of the allowed Bragg reflections of the $[Pb(BDC)]_n$ phase. The reliability factors of the refinement are $\chi^2 = 2.14$, $R_{wp} = 10.35$, $R_p = 6.54$, and $R_F^2 = 0.065$.

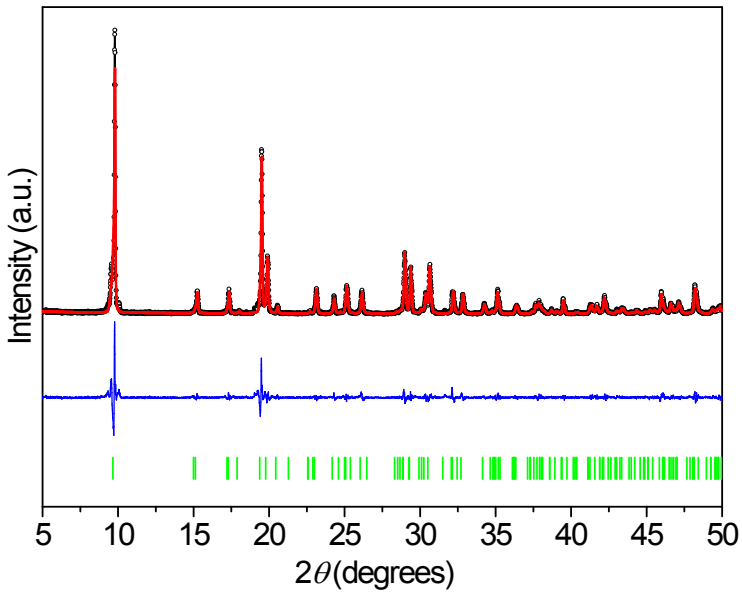

Figure S2. Rietveld plot of $Pb_{0.90}Eu_{0.10}$-BDC. The observed data points, the best fit profile, and the difference between experimental and refinement data are represented as black circles, red line and blue line, respectively. Green vertical bars represent the angular position of the allowed Bragg reflections of the $[Pb(BDC)]_n$ phase. The reliability factors of the refinement are $\chi^2 = 4.28$, $R_{wp} = 12.64$, $R_p = 9.38$, and $R_F^2 = 0.092$.

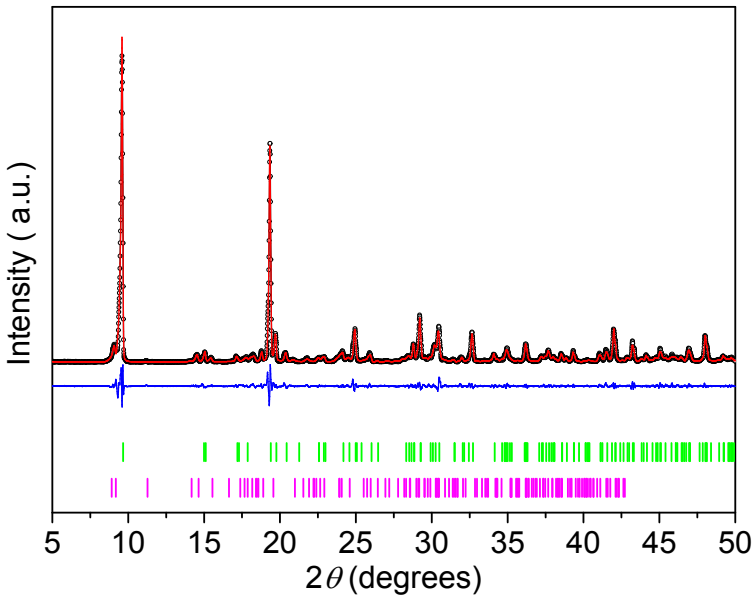

Figure S3. Rietveld plot of $Pb_{0.75}Eu_{0.25}$-BDC. The observed data points, the best fit profile, and the difference between experimental and refinement data are represented as black circles, red line and blue line, respectively. Green and magenta vertical bars represent the angular position of the allowed Bragg reflections of the $[Pb(BDC)]_n$ and $[Eu_2(BDC)_3(H_2O)_4]$ phases, respectively. The reliability factors of the refinement are χ^2=2.67, R_{wp}=8.62, R_p=6.74, and R_F^2= 0.045.

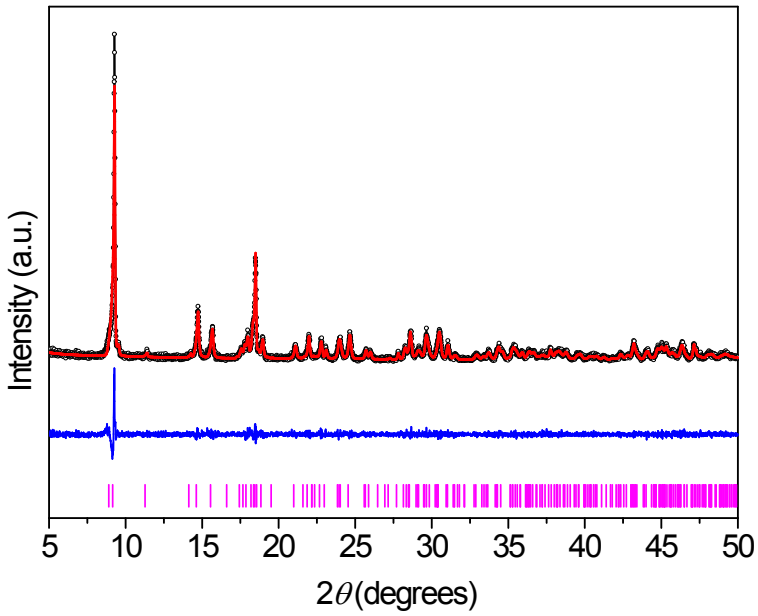

Figure S4. Rietveld plot of $Pb_{0.50}Eu_{0.50}$-BDC. The observed data points, the best fit profile, and the difference between experimental and refinement data are represented as black circles, red line and blue line, respectively. Magenta vertical bars represent the angular position of the allowed Bragg reflections of the $[Eu_2(BDC)_3(H_2O)_4]$ phase. The reliability factors of the refinement are χ^2=3.52, R_{wp}=7.33, R_p=5.28, and R_F^2= 0.041.

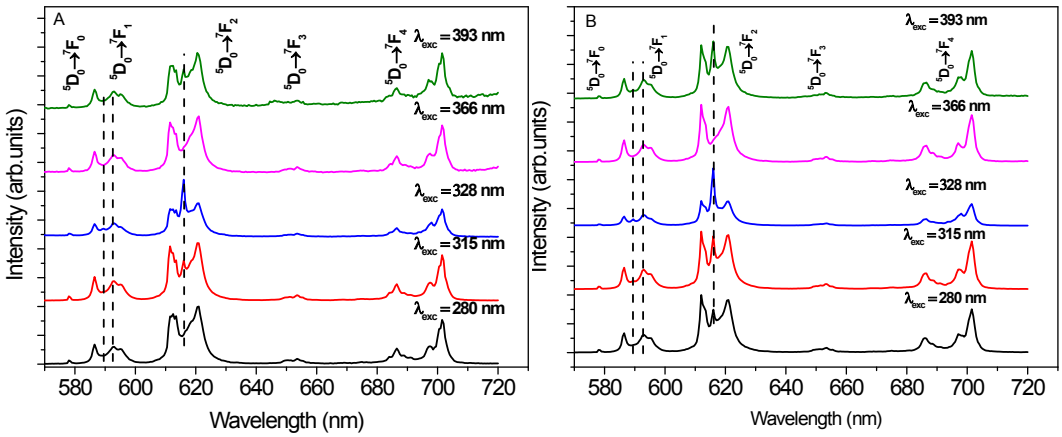

Figure S5. Emission spectra (300 K) of (A) $Pb_{0.95}Eu_{0.05}$-BDC and of (B) $Pb_{0.90}Eu_{0.10}$-BDC recorded under different excitation (280, 315, 328, 366 and 393 nm) wavelengths. The vertical lines identify the Stark components of the $[Eu_2(BDC)_3(H_2O)_4]$ phase.

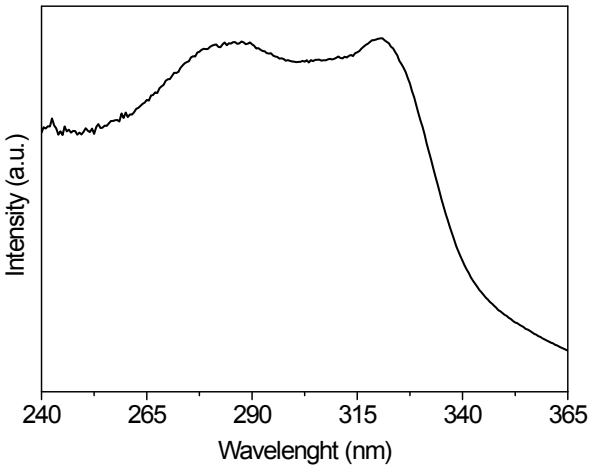

Figure S6. Excitation spectrum (300 K) of Na_2BDC monitored at 388 nm.

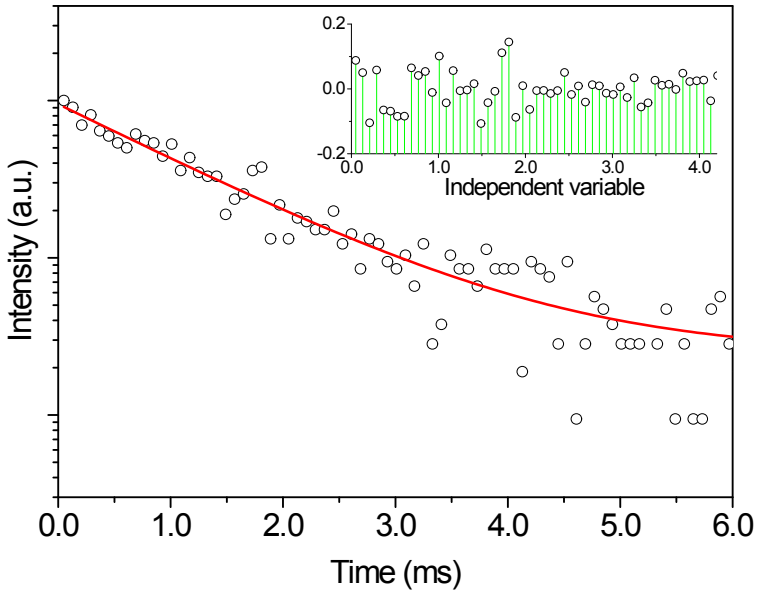

Figure S7. Emission decay curve (300 K) of $Pb_{0.95}Eu_{0.05}$ – BDC excited at 315 nm and monitored at the $^5D_0 \rightarrow {}^7F_0$ transition (578 nm). The solid line represents the data best fit ($\chi^2_{red}=2.2\times10^{-3}$) using a single exponential function. The inset shows the fit residual plot.

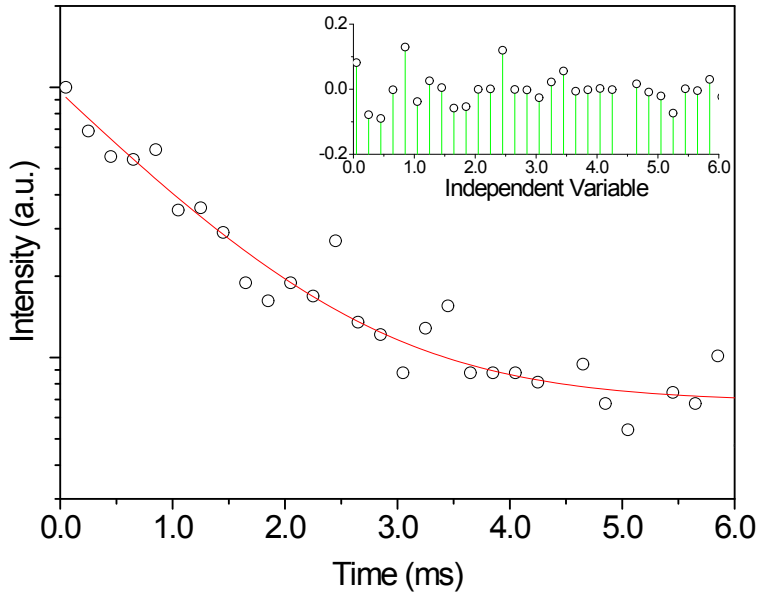

Figure S8. Emission decay curve (300 K) of $Pb_{0.90}Eu_{0.10}$-BDC excited at 315 nm and monitored at the $^5D_0 \rightarrow {}^7F_0$ transition (578 nm). The solid line represents the data best fit ($\chi^2_{red}=4.6\times10^{-3}$) using a single exponential function. The inset shows the fit residual plot.

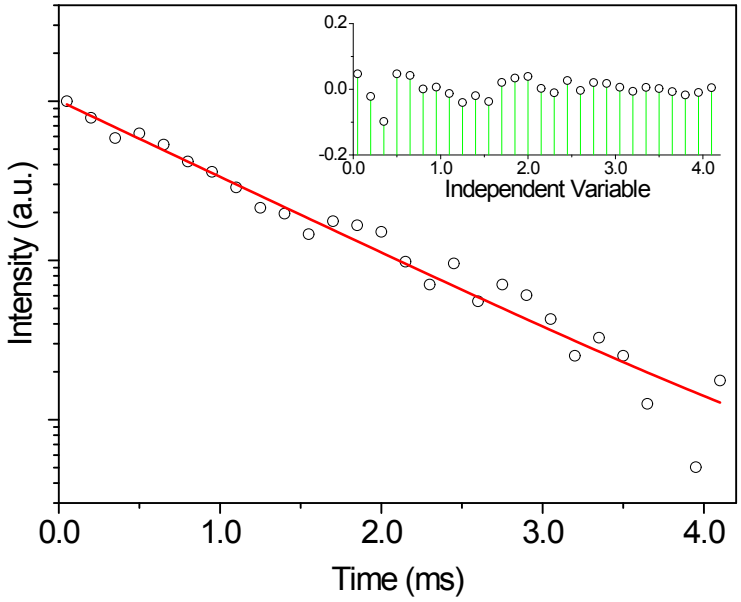

Figure S9. Emission decay curve (300 K) of $Pb_{0.75}Eu_{0.25}$-BDC excited at 315 nm and monitored at the $^5D_0 \rightarrow {}^7F_0$ transition (578 nm). The solid line represents the data best fit ($\chi^2_{red}=9.7\times10^{-4}$) using a single exponential function. The inset shows the fit residual plot.

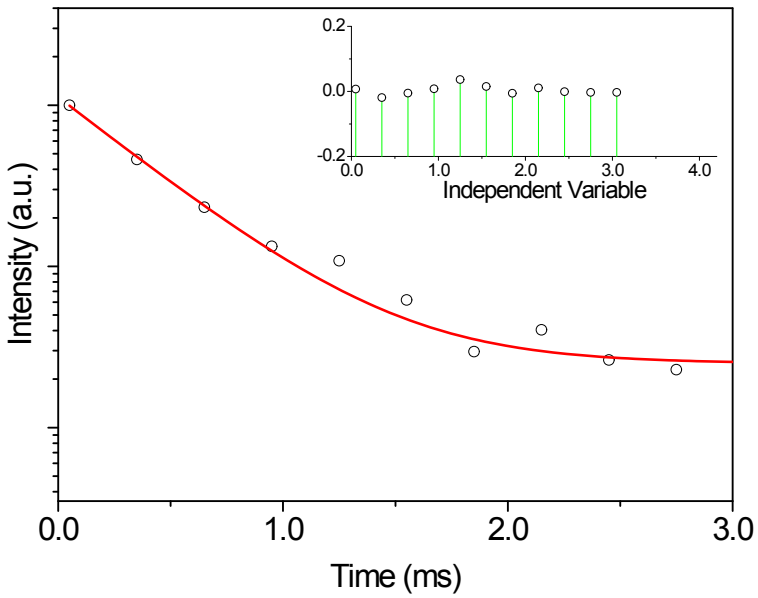

Figure S10. Emission decay curve (300 K) of $Pb_{0.75}Eu_{0.25}$-BDC excited at 315 nm and monitored at the $^5D_0 \rightarrow {}^7F_0$ transition (579 nm). The solid line represents the data best fit ($\chi^2_{red}=3.1\times10^{-4}$) using a single exponential function. The inset shows the fit residual plot.

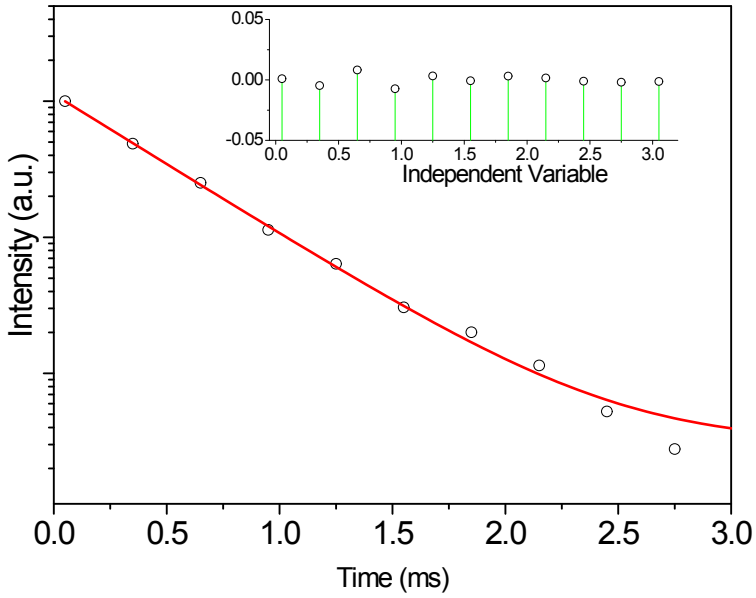

Figure S11. Emission decay curve (300 K) of $Pb_{0.50}Eu_{0.50}$-BDC excited at 315 nm and monitored at the $^5D_0 \rightarrow {}^7F_0$ transition (579 nm). The solid line represents the data best fit ($\chi^2_{red}=2.1\times10^{-5}$) using a single exponential function. The inset shows the fit residual plot.

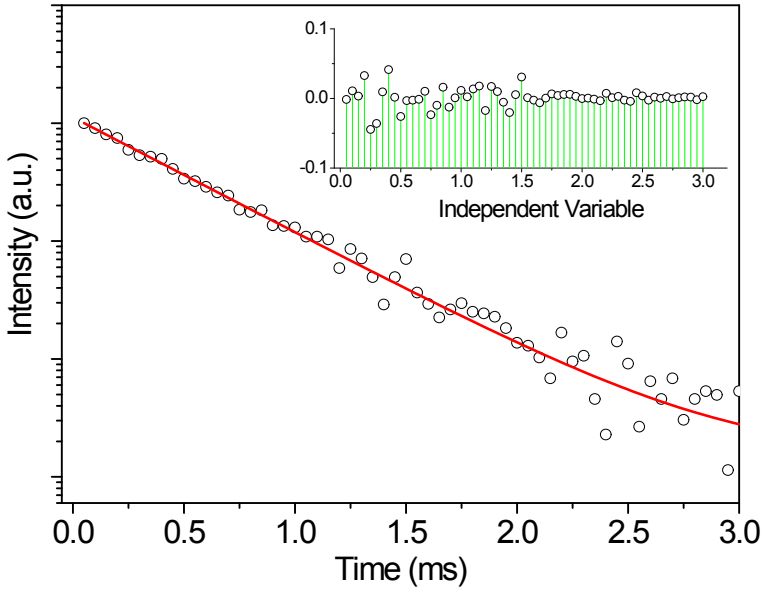

Figure S12. Emission decay curve (300 K) of $Eu_2(BDC)_3(H_2O)_4$ excited at 315 nm and monitored at the $^5D_0 \rightarrow {}^7F_0$ transition (579 nm). The solid line represents the data best fit ($\chi^2_{red}=1.9\times10^{-4}$) using a single exponential function. The inset shows the fit residual plot.