

# Synthesis and Spectroscopic Characterization of a new Anionic Complex series: $[\text{Ln}(\text{bpda})_3]^{3-}$ , $\text{Ln} = \text{Eu}^{3+}$ , $\text{Tb}^{3+}$ e $\text{Gd}^{3+}$

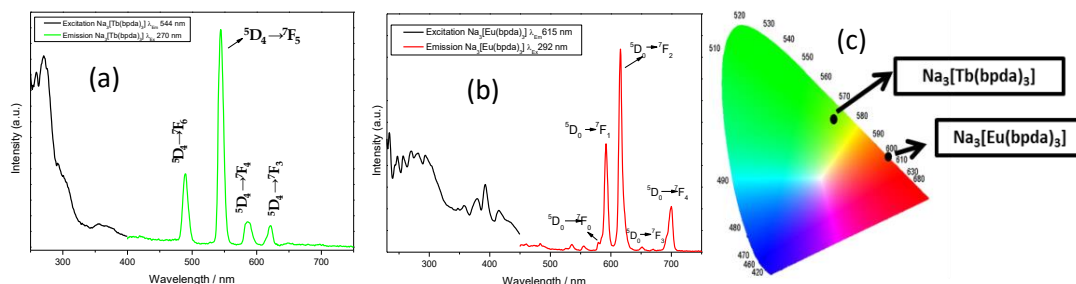
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Lanthanide (Ln) ions are excellent light emitter<sup>1</sup>, nonetheless, they have very low molar absorption coefficient since their f-f transitions are forbidden by Laporte selection rule. An energy transfer mechanism, known as Antenna Effect<sup>2</sup>, is normally used to sensitize Ln ions in order to overcome this problem. This is obtained by coordinating Ln ions with an organic molecule that has high molar absorption coefficient and can effectively transfer its energy to the Ln ions. Carboxylic acids form a class of interesting ligands that fulfill this requirement, and also exhibit high thermal stability, what is desirable if the complex is going to be applied as emitter layer in OLEDs. The objective of the present work is to synthesize and characterize anionic Ln complexes of  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Gd}^{3+}$  with the ligand 2,2'-bipyridine-3,3'-dicarboxylic acid ( $\text{H}_2\text{bpda}$ ). The synthesis was performed in ethanol, by adding the corresponding Ln chloride solution and the ligand in a ratio 1:3.1, then it was slowly added a solution of NaOH in ethanol; at pH~7 a precipitate was formed, which was filtered out the solution, washed in ethanol and dried in desiccator. Through the analysis of the FTIR spectra we infer that the complex was formed by coordination of the carboxylic group to the respective Ln ion, since the C=O stretching band at  $1717\text{ cm}^{-1}$ , and the O-H deformation band at  $904\text{ cm}^{-1}$ , observed for the free ligand, just vanish for the complexes. By comparing FTIR spectra of the  $\text{Na}_2\text{bpda}$  with the complexes, we conclude that the ligand form a bidentate chelate<sup>3</sup>. By conductivity we confirmed a charge -3, indicating the general formulae  $\text{Na}_3[\text{Ln}(\text{bpda})_3]$  for the complexes. Thermal analysis for the complexes of terbium and europium indicated high thermal stability, up to  $278.5\text{ }^\circ\text{C}$ , and  $339\text{ }^\circ\text{C}$ , respectively. The triplet energy of the ligand was estimated at  $24,942\text{ cm}^{-1}$ , by photoluminescence spectroscopy (PLS) of the gadolinium complex, what is enough to sensitize both terbium and europium, as can be observed in Fig.1 (a) and (b) for the emission spectra of terbium and europium complexes, respectively. In Fig.1 (c), is shown the CIE color diagram<sup>4</sup> with the location of the color emitted by the two complexes. For the terbium complex the dominant wavelength is  $536\text{ nm}$  with  $80.6\%$  of color purity, and for the europium complex the dominant wavelength is  $604\text{ nm}$  with  $100\%$  of color purity.

Figure 1: Excitation and emission spectra for the terbium complex (a), and the europium complex (b). In (c) is shown the CIE color diagram indicating the corresponding color of both complexes.



<sup>1</sup>Bünzli, J.-C, et. Al., Chemical Society Reviews, v. 34, n. 12, p. 1048–77, 2005. <sup>2</sup>D’Aléo, A. et al. Coordination Chemistry Reviews. 2012, 256, 1604-1620. <sup>3</sup>SOCRATES, George., Infrared and Raman Characteristic Group Frequencies, 3ª edição, 2001. <sup>4</sup>Spectra Lux Software v.1.0, Ponto Quântico Nanodispositivos / RENAMI, 2003, P.A. Santa-Cruz, F.S. Teles