

Green and blue emissions by a terbium(III) complex, [Tb(bbpen)(NO₃)], in solution and thin films

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Lanthanide complexes have been extensively studied for the development of electroluminescent devices such as organic light emitting diodes (OLEDs)¹. Terbium(III) complexes, in particular, are of great interest in green-emitting devices, because of their high quantum efficiency, extremely sharp emission bands and the possibility to modify the ligand structure without necessarily affecting the typical emission lines of the metal ion². In this work we describe the optical behaviour of the recently reported [Tb(bbpen)(NO₃)] compound (**A**), a mononuclear complex with a terbium(III) ion coordinated to the six donor atoms of an N₄O₂-ligand (bbpen²⁻)³ and to a bidentate nitrate group, in a slightly distorted dodecahedral geometry⁴. Its optical behaviour was analysed in the solid state, in acetonitrile solution and processed as a thin film, both in pure form and incorporated in a polymeric matrix. The incorporation was carried out by mixing 50 µL of a colourless MeCN solution of PEO:LiClO₄ [11 mg/mL; PEO = poly(ethylene oxide)] with 200 µL of a 9 mg/mL MeCN solution of **A**. The clear, colourless mixture thus obtained (**A:PEO**) was drop casted onto a clean glass substrate. The emission spectra recorded for **A** (after excitation at 290 nm) in the solid state or in acetonitrile solution presents typical emission bands for the ⁵D₄ → ⁷F_J decay of the Tb^{III} ion around 550 nm (green emission), whereas the spectrum of **A** processed as a thin film shows, besides the ⁵D₄ → ⁷F_J emissions, also the ⁵D₃ → ⁷F_J bands around 420 nm (blue emission); the two sets present similar intensities. In the spectrum recorded for **A:PEO**, on the other hand, the ⁵D₃ → ⁷F_J band set is present with greater intensity with respect to the ⁵D₄ → ⁷F_J emission bands. The blue emission coming from the thin films, as well as its increased intensity observed for **A:PEO**, can be initially explained as an effect of the lower complex concentration in the films. In solid state or in solution, the ⁵D₃ luminescence is usually quenched due to an energy-transfer process involving neighbouring terbium(III) ions, which is minimized in the films. The probability of this process is strongly dependent on the distance between metal ions⁵, and for the thin film, as the distance between neighbouring Tb^{III} ions increases, the probability of quenching decreases and therefore the bands for the ⁵D₃ → ⁷F_J transitions arise. This phenomenon is even more noticeable when the complex is isolated in the polymeric matrix. Further investigation is under way in order to better understand other factors, besides concentration, that affect the observation of the blue emission.

¹Eliseeva, S. V.; Bünzli, J.-C. G. *New J. Chem.* **2010**, 35, 1165. ²Xin, H. *et al. J. Am. Chem. Soc.* **2003**, 125, 7166. ³Neves, A. *et al. Inorg. Chem.* **1992**, 31, 4749. ⁴Gregório, T. *et al. Acta Crystallogr., Section E: Crystallogr. Commun.* **2015**, 71, 65. ⁵Armellini, C. *et al. J. Non-Cryst. Solids* **1999**, 245, 115.

CNPq, CAPES, Fundação Araucária, UFPR and UTFPR.