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Synthesis and Characterization of Coordination Polymers 2D with High Thermal Stability

M. A. M. Lucena(1)*, A. J. G. Melo(1), I. T. Weber(1), S. A. Júnior(1), M. O. Rodrigez(1).

(1) DQF, Universidade Federal de Pernambuco, e-mail: marcella_mlucena@hotmail.com
* Corresponding author.

Abstract - Coordination polymers [Ln (DPA) (HDPA)] (Ln = Tb, Eu, and Dy DPA = 2,6-pyridinedicarboxylate), prepared by hydrothermal synthesis have been characterized by Fluorescence Spectroscopy in the UV-Vis area, X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The results showed that the polymers have characteristics of transitions Tb^{3+} and Eu^{3+}, responsible for the intense green and red luminescence. Yellow luminescence, originated by Dy, is also observed, but is less intense. The profile showed by diffratograms is of crystalline material with narrow and well defined peaks and the micrographs show the laminar structure (2D) of the polymer. Besides, the material has behaved thermally stable when subjected to high temperature.

Phosphors are materials able to convert certain types of energy in electromagnetic radiation, usually in the visible region. These materials are composed by a luminescent center, that can be a lanthanide ion, and an inert matrix that absorbs and transfers energy to the emitter center (antenna effect). [1]

Materials that employ lanthanide ions (Ln) as emitter centers have promising applications in several areas, ranging from Light Conversion Molecular Devices (LCMD) [2] to luminescent markers and to the most advanced types of clinical diagnoses[2]. Lanthanide ions (Ln) have important characteristics as long luminescence lifetime and very narrow "line-like" emission bands [1,3].It is of first importance to design the material (matrix + emitter center) according to the desired applications. Therefore, the nature of the matrix material used has a direct influence in the efficiency of transfer of energy to the Ln ion [1,3] and thermal and chemical stability of this matrix may limit some applications.

The 2,6-dipicolinic acid (H_2DPA) has been widely used as ligand to lanthanide complexes due to its ability to function as a bridge between metal centers and to adopt different coordination [3].

In this work, the coordination polymers were prepared from the mixture of 0.35 mmol of ligand H_2DPA, 0.70 mmol of Ln $(NO_3)_3 6H_2O$ (Ln = Tb^{3+} ,Eu^{3+} and Dy) and 4.0 mL of deionized water. This mixture was sealed in a stainless steel reactor with capacity for 8.0 mL and was submitted to different temperatures. All synthesis taken 72 hours, and then they were cooled to room temperature with an rate of 1°C/min. The resulting crystals were washed with deionized water and acetone. The obtained materials were characterized by Fluorescence Spectroscopy in the UV-Vis, X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

The emission spectra of synthesized coordination polymers show the characteristics emission bands of Eu^{3+} and Tb^{3+}, as one can see in Figures 1.a and 1.b, respectively. The micrographs (Figure 2) show that both polymers have 2D rectangular shaped structure, with clusters of approximately 50µm.

After characterization, the coordination polymers were submitted to high temperature for a short period of time, remaining luminescent. This showed these materials have high thermal stability, increasing even more the number of their possible applications.

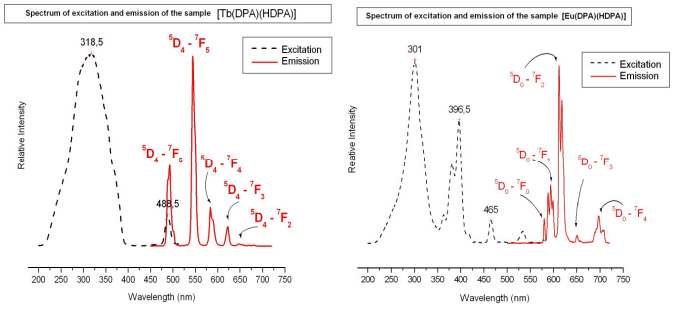

Figure 1 - Spectrum of excitation and emission of the samples a) [Tb (DPA) (HDPA)]. b) [Eu (DPA) (HDPA)].

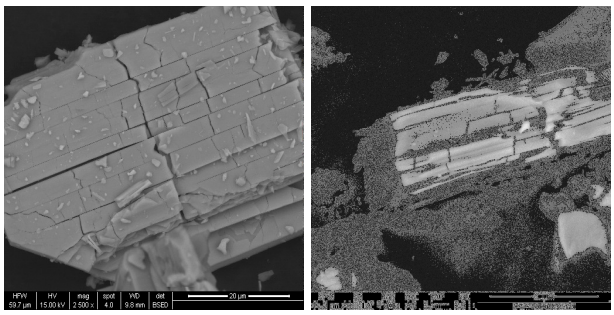

Figure 2 - micrographs of samples a) [Tb (DPA) (HDPA)] b) [Eu (DPA) (HDPA)].

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