

# Synthesis, Characterization and Photoluminescence Study of aquatri(2-phenylbutyrate)Lanthanate(III) Complexes

Ivan G.N. Silva<sup>1</sup>, Lucas C.V. Rodrigues<sup>1</sup>, Pedro R.P. Cech<sup>1</sup>, Maria C.F.C. Felinto<sup>2</sup>,  
Hermi F. Brito<sup>1</sup>, Jiang Kai<sup>1</sup>

<sup>1</sup>Instituto de Química, Universidade de São Paulo, São Paulo-SP, Brazil

<sup>2</sup>Instituto de Pesquisas Energéticas e Nucleares, São Paulo-SP, Brazil

\*kaijiang@iq.usp.br

## Summary

Novel aquatri(2-phenylbutyrate)Lanthanate(III) complexes [Ln(PBT)<sub>3</sub>(H<sub>2</sub>O)] (Ln<sup>3+</sup>: Eu<sup>3+</sup>, Gd<sup>3+</sup> and Tb<sup>3+</sup>) were synthesized and characterized by elemental analysis, X-ray diffraction, infrared absorption spectroscopy and thermal analysis. Their photoluminescence properties were investigated based on the excitation and emission spectra, as well as the photoluminescent decay curves.

## Keyword

Photoluminescence, Energy Transfer, Lanthanides, Carboxylate Complex

## Introduction

Trivalent lanthanide ions (Ln<sup>3+</sup>) have been widely employed as visible light emitters in various applications, e.g. light-emitting devices, lasers, optical markers and displays [1]. The majority of these materials are characterized by their highly monochromatic emission color of the corresponding ions, such as Eu<sup>3+</sup> (red), Tb<sup>3+</sup> (green) and Tm<sup>3+</sup> (blue). However, the Ln<sup>3+</sup> ions present small absorptivity coefficients ( $\ll 1 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), resulting in low luminescence intensity. In Ln<sup>3+</sup> coordination compounds, some organic ligands can act as sensitizer, absorbing and transferring energy efficiently to the emitting level of Ln<sup>3+</sup> ions, consequently increasing their overall luminescence quantum yield [2]. In this work, it is reported the synthesis, characterization and photoluminescence study of Eu<sup>3+</sup>, Gd<sup>3+</sup> and Tb<sup>3+</sup> complexes with 2-phenylbutyrate (PBT) ligand.

## Results and Discussion

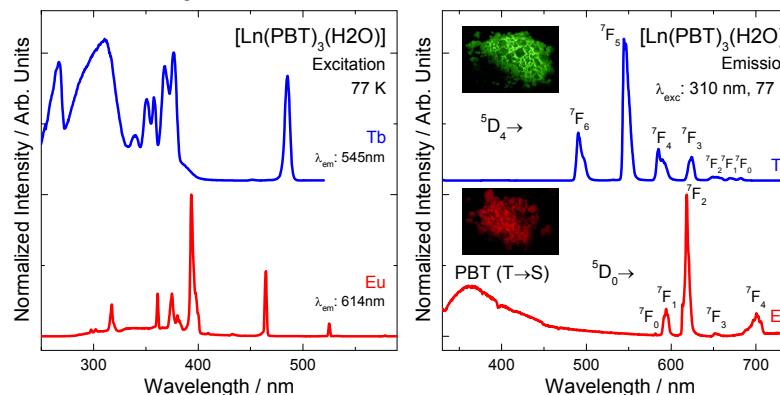
Aqueous solution of LnCl<sub>3</sub>·6H<sub>2</sub>O was slowly mixed with the deprotonated aqueous solution of ligand in boiling point, by 1:3 molar ratio. The general formula of the complexes [Ln(PBT)<sub>3</sub>(H<sub>2</sub>O)] was confirmed by elemental analysis.

Infrared spectra of these complexes exhibit a broad band in the spectral range from 3200 to 3600 cm<sup>-1</sup> indicating that these complexes are hydrated. The coordination between the ligand and the Ln<sup>3+</sup> ion was investigated by comparing the infrared spectra of the complexes with that of the sodium PBT salt, indicating bridge coordination mode [3]. High signal-noise ratio was observed in the X-ray diffraction patterns, indicating high crystallinity of the complexes.

Phosphorescence emission spectrum of [Gd(PBT)<sub>3</sub>(H<sub>2</sub>O)] complexes shows that the triplet state of the PBT ligand is located approximately at 23500 cm<sup>-1</sup>. This broad-band emission

originated from the PBT ligands can be also observed in the spectral range from 350 to 500 nm in the emission spectrum of [Eu(PBT)<sub>3</sub>(H<sub>2</sub>O)], indicating high degree of non-radiative energy transfer pathway from PBT to Eu<sup>3+</sup> ion. The <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> hypersensitive transition with (2J+1) Stark components indicates that the Eu<sup>3+</sup> ion is situated in non-centrosymmetric chemical environment with low symmetry and the dynamic coupling mechanism being predominant.

The [Tb(PBT)<sub>3</sub>(H<sub>2</sub>O)] complex exhibits high intensity of green luminescence due to the <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>J</sub> (J: 0–6) transition of Tb<sup>3+</sup> complex. The broad emission band assigned to the ligand in the spectral range between 350 and 550 nm was not observed, suggesting an efficient energy transfer from PBT ligand to Tb<sup>3+</sup> ion.



**Figure 1:** Excitation (left) and emission (right) spectra of the [Ln(PBT)<sub>3</sub>(H<sub>2</sub>O)] complexes where Ln<sup>3+</sup>: Tb<sup>3+</sup> (top) and Eu<sup>3+</sup> (down). The inset figures are the photographs of the respective complexes under UV irradiation.

## Conclusions

The [Eu(PBT)<sub>3</sub>(H<sub>2</sub>O)] complex exhibits intense red emission under UV irradiation and can be used as optical markers. The triplet state of the PBT is in the resonance with the <sup>3</sup>D<sub>4</sub> emitting level of the Tb<sup>3+</sup> ion. Therefore, the PBT ligand acts as efficient sensitizer in the radiative energy transfer process for the [Tb(PBT)<sub>3</sub>(H<sub>2</sub>O)] complex, enabling its possible application as molecular light conversion device.

## References

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