Preparation and study of the spectroscopic properties of Ln^{3+} complexes with benzophenone ligand.

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Keywords: *Coordination compounds, benzophenone, photoluminescence, europium, antenna effect.*

Abstract

In the $[Ln(bzf)_3(H_2O)_2]$ complexes, prepared by a simple chemical route, the ligand acts transferring energy to the $^5D_0$ emission level of the Eu^{3+} and the luminescence properties may be useful in application of optical devices.

Introduction

Luminescent coordination compounds have been employed as light emitting devices and luminescent markers[1]. These applications are possible due to lanthanides ions (Ln^{3+}) singular properties, like that high colour purity, strong emission lines, and high values of quantum yield. When appropriate organic ligand is selected, the design of efficient lanthanide complexes has become an important research goal, the benzophenone (2-Hydroxy-4-methoxyphenyl, bzf) choice is interesting because of high UV absorption and bidentade coordination mode. In this context, the aim of this work is to report the preparation and study of the spectroscopic properties of europium or gadolinium complexes with benzophenone (bzf) ligand.

Results and Discussion

To obtain $[Ln(bzf)_3(H_2O)_2]$ complexes, $EuCl_3$ (pH 4.5-5.0) aqueous solution was added dropwise to a methanolic bzf ligand solution (deprotonated by NaOH 0.1 mol.L^{-1} addition), under stirring at 45 °C during 1h. The yellow solid formed was filtered out, washed with methanol and dried in vacuum. Complexometric titration data are consistent with the stoichiometric general formula proposed (%Eu^{3+}: calc.17.5 - exp.17.2 and %Gd^{3+}: calc.18.0 - exp.17.6). Carbon and Hydrogen quantities have been investigated. Figure 1a displays FT-IR spectra of ligand and complexes, mainly indicating frequencies changes associated with ν_s and ν_{as}(C=O). A 28 cm^{-1} displacement of ν_s(C=O) band to the $[Ln(bzf)_3(H_2O)_2]$ complexes spectra suggests a strong interaction between oxygen atoms and lanthanide ion, demonstrating an evidence that bzf ligand coordinates to the Ln^{3+} ions.

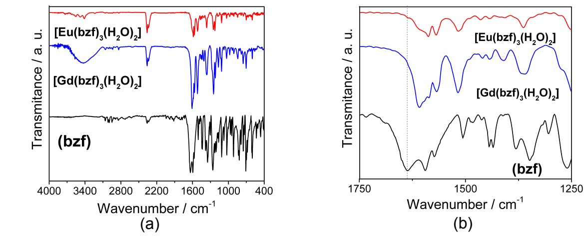

Figure 1. Infrared spectra of (a) (bzf) ligand and $[Ln(bzf)_3(H_2O)_2]$ complexes; (b) In detail, region between 1250 - 1750 cm^{-1}.

Excitation spectra exhibit an intense and large band assigned to the ligand absorption (355-500 nm) confirming a bzf – Eu^{3+} energy transfer mechanism, suggesting that ligand acts as an antenna. The emission spectra displayed at Figure 2a present narrow lines arising from 4f-4f intra-configurational transitions $^5D_0 \rightarrow {}^7F_J$ (J=0-4), dominated by the hypersensitive lines due to the transition $^5D_0 \rightarrow {}^7F_2$, indicating that Eu^{3+} occupies low symmetry sites. The only $^5D_0 \rightarrow {}^7F_0$ transition shows the presence of at least one site without symmetry center. The excited state lifetime (τ) was determined by decay emission curve (Figure 2b), τ = 0.17 ms. The triplet energy state, T~1.7x10^4 cm^{-1}, was determined by $[Gd(bzf)_3(H_2O)_2]$ emission spectra. The proximity of energy to the Eu^{3+} $^5D_0$ emissor level (1.75x10^4 cm^{-1}) favours the energy transfer from T to the emitter ion.

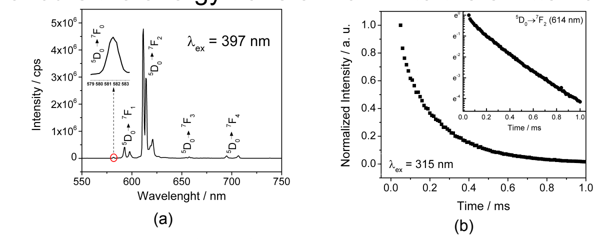

Figure 2. (a) $[Eu(bzf)_3(H_2O)_2]$ emission spectra registered at 77 K monitoring ($^7F_0 \rightarrow {}^5L_6$) at λ_{ex} = 397 nm. (b) Emission decay curve monitoring the $^5D_0 \rightarrow {}^7F_2$ transition at λ_{ex} = 315 nm.

Conclusions

The chemical route has been successfully processed and the ligand acts as antenna in the absorption and energy transfer process in complexes, this mechanism allows that Eu^{3+} displays intense emission under UV excitation.

Acknowledgements

UTFPR, FAPESP and CNPq

[1] COTTON, S. The lanthanides: principles and energetics. In:_____. **Lanthanide and Actinide Chemistry**. 2nd ed. Hoboken: Wiley, 2006.