# Lanthanide complexes as potential luminescent markers and temperature probes.

**Jorge H. S. K. Monteiro[1,2] (PQ), Ana de Bettencourt-Dias[2] (PQ), Fernando A. Sigoli[1, *] (PQ)**

*[1]LMF, Institute of Chemistry, UNICAMP, [2]Department of Chemistry, University of Nevada, Reno, EUA.*
**fsigoli@iqm.unicamp.br*

Keywords: Lanthanides, Luminescence, Temperature probes.

## Abstract

Lanthanide(III) complexes with the ligand dipicCbz show interesting emission and temperature probing in DMSO:water solution.

## Introduction

Lanthanide(III) based materials have drawn a lot of attention in the last years as efficient luminescent markers in biological systems and also as *in situ* temperature probes. For applications in biological systems is desirable: (i) solubility or dispersibility in aqueous system, (ii) lifetimes in the microseconds range and (iii) high brightness. Due to the experimental setup of the most confocal microscopes, excitation band as close as possible from the visible is a highly desirable property for luminescent markers. The possibility to combine, in the same compound, the luminescent marker and the temperature sensing properties gives a new dimension to this application.

Thus, there is a critical need for the development of new luminescent markers that can also act as *in situ* temperature probes. Therefore, the goals of this work are: (i) synthesis of the ligand dipicCbz (dipicCbz = 4-(*9H*-carbazol-9-yl)pyridine-2,6-dicarboxylic acid) and the lanthanide(III) complexes; (ii) study of the photoluminescent properties and (iii) application of the Tb(III) complex as temperature probe.

## Results and Discussion

The ligand dipicCbz was synthesized in a synthetic route composed by 3 steps. The ligand was characterized by $^1$H-NMR and mass spectrometry techniques. The $K_3[Ln(dipicCbz)_3]$ complexes (Ln = $Eu^{3+}$, $Gd^{3+}$ or $Tb^{3+}$) were synthesized by mixing the ligand dipicCbz, the lanthanide, in a 3:1 (L:Ln) molar proportion, and $K_2CO_3$ for 24 h at 120 ºC using DMF:$H_2O$ (1:1 v/v) as the solvent. The complexes obtained were characterized using high-resolution mass spectrometry. The energy of the triplet state, determined at 77 K using the Gd(III) complex, is equal to 24471 cm$^{-1}$. The presence of TICT state (*Twisted Intramolecular Charge Transfer*) was confirmed by the shift of the ligand emission band upon lowering the temperature of the system. All the complexes showed emission lifetimes close to 1 ms and quantum yields of 1.8% for Eu(III) and 3.7% for Tb(III) complexes in a TRIS/HCl (pH ~7.4) buffered water:DMSO (25:1 (v/v)) solution. The excitation spectra of the Eu(III) and Tb(III) complexes show a bathochromic shift, when compared with the $Cs_3[Eu(dpa)_3]$ (dpa = dipicolinic acid), due to the presence of the carbazole unit. The emission intensity of the $^5D_4 \rightarrow {}^7F_5$ transition of the Tb(III) complex is temperature-dependent in the range 5 – 70 ºC. The thermal sensitivity at 35 ºC is 1.4x10$^{-2}$ ºC$^{-1}$. A graph of ln(Intensity) as a function of 1/T showed two different slopes, indicating different deactivation mechanisms. At low temperatures, the quenching mechanism happens through CT states deactivation while, at high temperatures, it is through triplet level deactivation. The Tb(III) complex showed full reversibility after 3 cycles of heating to 70 ºC and cooling to 5 ºC.

## Conclusions

The solubility of the compounds in water:DMSO, the bathochromic shift of the excitation spectra and the temperature-dependent emission intensity make these compounds interesting for use as luminescent markers in biological systems and also as temperature probes.

## Acknowledgments

FAPESP, CAPES, CNPq, NSF, LMEOA.

---

[1] Curtis, M. D.; Shiu, K.; Butler, W. M. e Huffmann, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3335.