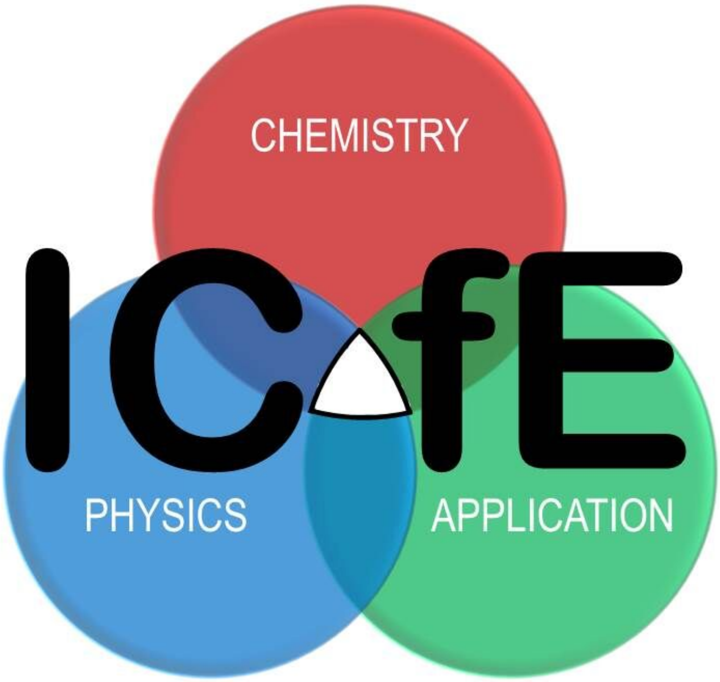

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## Programme and Book of Abstracts

# HIGHLY LUMINESCENTE $Eu^{3+}$- (2-ACYL-1,3-INDANDIONATO) COMPEXES

P.R. Santos [a] H.F. Brito,[b] M.C.F.C. Felinto,[c] W.M. Faustino, [a] J.A. Vale,[a] J.B.M. Resende Filho.,[a] J.G.P. Espínola,[a] E.E.S. Teotonio[1]*[a]
[a] Departamento de Química-Universidade Federal da Paraíba-Paraíba-João Pessoa - Brazil
[b] Instituto de Química – Universidade de São Paulo – São Paulo – São Paulo – Brazil
[c] Instituto de Pesquisas energéticas e Nucleares-IPEN, 05508-900, São Paulo - SP, Brazil.

The study of the photoluminescence properties of the lanthanide-(β-diketonate) complexes plays an important role in development of new kind of compounds for practical applications in photonics, optical probe in clinical analyses and OLEDs. Although the great interest in this kind of compounds, there are only a few works reporting on $Eu^{3+}$-complexes with 2-acyl-1,3-indandionates ligands [1]. In this work, we report the synthesis, characterization and studies on photophysical properties of the novel $[Ln(aind)_3(L)_2)]$ and $[Ln(bind)_3(L)_2]$ complexes in the solid state, where aind: 2-acetyl-1,3-indandione, bind: 2-benzoyl-1,3-indandione, Ln: $Eu^{3+}$ or $Gd^{3+}$, and L is an ancillary neutral phosphine oxide ligand such as triphenylphosphine oxide (tppo), triphenylarsene oxide (tpAso), trihexylphosphine oxide (thpo), hexamethylphosphoraminde(hmpa) and tributhylphosphine oxide(tbpo). These complexes were synthesized by direct reaction between acetone solutions of hydrated complexes $Eu(2\text{-acyl-1,3-indandionate})_3(H_2O)_2$ and neutral ligands. All of these systems were characterized by elemental analysis, infrared spectroscopy and thermogravimetric analyses. The photoluminescence properties of the $Eu^{3+}$-compounds have been discussed in terms of experimental intensity parameters ($\Omega_2$ and $\Omega_4$), radiative ($A_{rad}$), non-radiative ($A_{nrad}$) spontaneous emission coefficients and emission quantum efficiency (η). The highly luminescence Eu-2-acyl-1,3-indandionate compounds obtained reflect the operative intramolecular ligand-to-metal energy transfer.

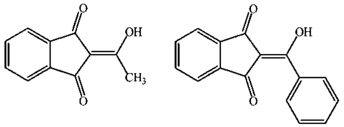

Figure 1. Structural formulas of the 2-acetyl-1,3-indandione (aind) and (b) 2-benzoyl-1,3-indandione (bind) ligands

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# STRUCTURE, POSITRON FORMATION AND THE ROLE OF THE LMCT STATE ON THE LUMINESCENT PROPERTIES OF ANUSUAL DIKETONATE LANTHANIDE COMPLEXES

P.R. Silva [a] D. K.S. Pereira,[a] F. Fulgêncio,[b] D. Windmöller,[b] W.F. Magalhães, [b] H.F. Brito,[c] W.M. Faustino, [a] M.C.F.C. Felinto,[d] J.R. Sabino,[e] E.E.S. Teotonio[1]*[a]
[a] Departamento de Química-Universidade Federal da Paraíba-Paraíba-João Pessoa - Brazil
[b] Departamento de Química-Universidade Federal de Minas Gerais – Minas Gerais - Brazil
[c] Instituto de Química – Universidade de São Paulo – São Paulo – São Paulo – Brazil
[d] Instituto de Pesquisas energéticas e Nucleares-IPEN, 05508-900, São Paulo - SP, Brazil.
[e] Departamento de Física – Universidade Federal de Goiás-Goiânia – Goias -Brazil

The unusual kind of mono- and bis-diketonate coordination compounds of trivalent lanthanide ions ($Ln^{3+}$) with phosphine oxide (tppo and hmpa) ligands are of great interest because of their uncommon spectroscopic properties, as compared with tris- and tetrakis-diketonate complexes. In particular, the luminescence properties of these complexes have been investigate on the bases of the augment of the excited triplet states centred on the diketonate ligand coordinated to the $Ln^{3+}$ ion. However, the very low emission quantum efficiency for some Eu-complexes suggests that a very strong luminescence quenching channel is operative in these systems. In this vein, the present work report on the structural and spectroscopic properties of unusual dibenzoylmethanate (dbm) complexes presenting the formulas $[Ln(dbm)_2(NO_3)L_2]$, $[Ln(dbm)(NO_3)_2(hmpa)_2]$ and $[Ln(dbm)_2(NO_3)(hmpa)_2]$, where Ln: $Eu^{3+}$, $Gd^{3+}$ and $Tb^{3+}$; L: hmpa (hexamethylphosphoramide) or tppo (triphenylphosphine oxide), taking into account the role of the ligand-to-metal charge transfer (LMCT) state on their luminescence intensities. Furthermore, Positron Annihilation Lifetime Spectroscopy (PALS) measurements were performed and the positronium (bound state between a positron and an electron) formation intensities ($I_3$) have been correlated with electronic spectroscopy and structural data. The results have been compared with those ones for tris-dbm complexes containing these same phosphine oxide neutral ligands. Single crystal XRD data showed that tris-dbm complexes crystallize in the triclinic $P_{\bar{1}}$ while bis- and mono-dbm complexes crystallize in the monoclinic Cc space groups. The diffuse reflectance and photoluminescence spectra suggest the presence of ligant-to-metal charge transfer states (LMCT) of low energy in the $Eu^{3+}$ complexes, which decrease the energy in the following trend: $[Eu(dbm)_3L] > [Eu(dbm)_2(NO_3)L_2] > [Eu(dbm)(NO_3)_2(hmpa)_2] \sim [Eu(dbm)_3(H_2O)]$. PALS data showed that $Tb^{3+}$ and $Gd^{3+}$ complexes form positronium, while in $Eu^{3+}$ complexes positronium formation depend on the position of the LMCT state.

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