

The influence of different amphiphilic counter-ions in Eu^{3+} *Tetrakis* β -diketonate complexes on optical properties

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Eu^{3+} complexes have been extensively studied to develop molecular light conversion devices, which may be employed in a variety of applications such as OLEDs, fluoroimmunoassays, among others¹. This work reports on the synthesis and spectroscopic characterization of *tetrakis* complexes containing the β -diketonate ligands: dibenzoilmetanate (**dbm**) and 1,1,1-trifluoro-2,4-pentanedione (**tfaa**), with different caudate counter-ions, in order to explore the amphiphilic character for later use in thin films production. The successful synthesis of $[\text{C}_{26}\text{H}_{56}\text{N}][\text{Eu}(\text{dbm})_4]$, $[\text{C}_{19}\text{H}_{42}\text{N}][\text{Eu}(\text{dbm})_4]$, $[\text{C}_{17}\text{H}_{38}\text{N}][\text{Eu}(\text{dbm})_4]$, $[\text{C}_{26}\text{H}_{56}\text{N}][\text{Eu}(\text{tfaa})_4]$, $[\text{C}_{19}\text{H}_{42}\text{N}][\text{Eu}(\text{tfaa})_4]$ and $[\text{C}_{17}\text{H}_{38}\text{N}][\text{Eu}(\text{tfaa})_4]$ complexes were based on a established methodology in literature². The same route was employed to prepare Gd^{3+} analogues complexes to study the counter-ion influence in the ligand triplet state energy (**L-TSE**). FTIR data confirmed the caudate counter-ions are present in the product due to the detection of $\nu(\text{CH}_2)$ stretching at 2927 and 2853 cm^{-1} , and also the split and shifted $\nu(\text{C}=\text{O})_s$ and $\nu(\text{C}=\text{O})_{ass}$ stretching assigned to the enolate ion, suggesting a strong interaction between oxygen atoms of the carbonyl groups and Eu^{3+} . UV-Vis spectra profiles showed a small red shift for both carbonyl groups $\pi-\pi^*$ ($\text{C}=\text{C}_{\text{ring}}$ and tautomerism) and $n-\pi^*$ transitions when comparing **dbm** free ligand and the complexes. **Tfaa** complexes also exhibited a slight shift, however only the $\pi-\pi^*$ was detected, suggesting the coordination with Eu^{3+} . Excitation spectra of the complexes using both ligands, Fig. 1, exhibit the wide bands related to the ligands and the ligand to metal charge transfer (CT) band. The emission spectra display the $\text{Eu}^{3+} {}^5\text{D}_0 \rightarrow {}^7\text{F}_{0-4}$ transitions and the absence of wide bands arising from ligand phosphorescence, indicating the efficient intramolecular energy transfer between **L-TSE** and Eu^{3+} emitter level. Analyzing **TSE** estimated values from Gd^{3+} complexes emission spectra, Fig. 2, the counter-ions do influence the **TSE** of both ligands. Regarding the size of the carbon chain, the trend is the smaller the chain the higher the **TSE**; this effect is more pronounced for **dbm**, most probably due to steric effects.

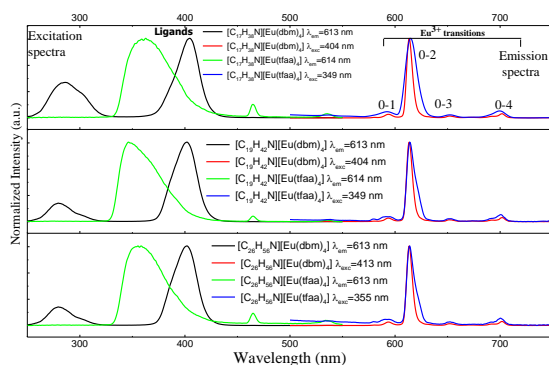


Fig. 1- Complexes photoluminescence spectra at RT.

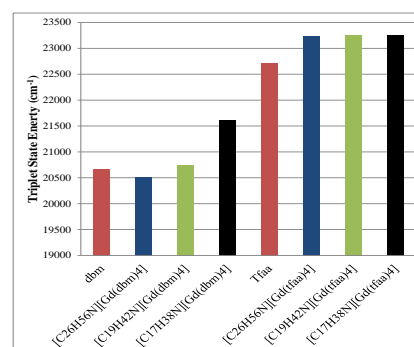


Fig. 2- TSE evaluated from Gd^{3+} complexes emission spectra.

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Authors are grateful to FAPESP, CAPES and CNPq for financial support and “Núcleo de Inovação Tecnológica em Borracha Natural”, FCT-UNESP, headed by Prof. Dr. Aldo Eloizo Job for laboratory facilities.