

New β -diketonate lanthanide complexes: synthesis and intramolecular energy transfer

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Lanthanide complexes with β -diketonate ligands have garnered significant attention due to their high potential for use in optical sensors, fluoroimmunoassays, and optical devices, owing to their luminescent properties. However, non-radiative processes such as ligand-to-metal charge transfer (LMCT) and multiphonon relaxation may reduce their intrinsic quantum yield [1]. To investigate these luminescence quenching processes, this work presents the synthesis, characterization, and analysis of the structural and spectroscopic properties of lanthanide complexes with the general formula $[\text{Ln}(\text{dpm})(\text{NO}_3)_2(\text{tchpo})_2]$, where Ln : Eu, Gd, and Tb, dpm: dipivaloylmethanato, and tchpo: tricyclohexylphosphine oxide [2]. X-ray diffraction data show that these compounds are isostructural and crystallize in the monoclinic system with the space group $P2_1/n$. The chemical environment of the Ln^{3+} ions can be described as a distorted triangular dodecahedral geometry, belonging to the D_{2d} point group. The diffuse reflectance spectrum of the Eu-complex displays intraligand ($S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$) transitions as well as $\text{dpm} \rightarrow \text{Eu}^{3+}$ charge-transfer transitions. Photophysical data suggest efficient luminescence quenching via the LMCT state in the Eu-complex. In contrast, the analogous Tb-complex exhibits high luminescence intensity due to an intramolecular energy transfer process from the ligand to Tb^{3+} ion. Theoretical studies based on Time-Dependent Density Functional Theory (TD-DFT) and simulations using the JOYSpectra platform further support the experimental findings.

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References

- [1] P. R. S. Santos et al., J. Lumin, vol. 226, 2020
- [2] J. G. Arruda et al, Polyhedron, vol. 267, 2025