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# A theoretical-experimental study of the luminescence quenching effects of europium *trans*-cinnamates with heterobiaryl ligands

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In this work, a theoretical-experimental study of europium and gadolinium complexes with trans-cinnamic acid (tcin) was carried out. The water molecules (H) present in the primary coordination sphere were replaced by the heterobiaryl ligands 2,2'-bipyridine (bpy - B) and 1,10-phenanthroline (phen - P). Experimental luminescence spectroscopy data showed that substituting water molecules (EuH) with heterobiaryl ligands caused luminescence suppression, an unusual behavior reported in the literature. The EuH complex exhibited luminescence intensity approximately six times higher than the EuB and EuP complexes. Thus, the possible causes of this phenomenon were evaluated. The complexes were characterized in the solid phase due to their insolubility in polar and nonpolar solvents. The diffractogram of the europium complex (EuH) corresponded to the trigonal $R3c$ system, being a non-centrosymmetric, dimeric, and neutral species with trigonal prismatic geometry,[1] as well as EuB, which also provided the trigonal $R3c$ system. However, similar complexes with hydrocinnamic acid containing bpy and phen ligands, with space groups P1 and $P2_1/m$, respectively, are reported in the literature.[2,3] In infrared spectroscopy, a sharp and broad OH absorption band was found for the EuH and GdH complexes. Bands shifted from the tcin carbonyl to lower wavenumbers around 1631 cm$^{-1}$ were also observed, suggesting that coordination occurs through the carboxylate ion. When complexed with bpy or phen, bands shifted to lower wavenumbers around 1540–1590 cm$^{-1}$ are observed, corresponding to the C=N stretch. TG curves show the presence of coordination water for the EuH and GdH complexes. For the complexes containing bpy and phen, no mass losses related to the coordination or water hydration are observed, suggesting the substitution of water molecules by heterocyclic ligands. In photoluminescent stability studies, no variation in intensity was observed for the EuH complex after 12 min, indicating structural stability over time. Computational modeling was performed based on the crystallographic structure of similar species from the literature.[2,3] The DFT method used were the B3LYP, M062X, PBE1PBE, and ωB97XD functionals, with MWB52 bases for europium and 6-31G*, 6-31+G, and 6-31+G* for the other atoms. An MWB52 pseudopotential was assigned to europium. The approach evaluated a more appropriate theoretical model for binuclear systems. Thus, the trans-cinnamic systems will be modeled through the reference structures, and then the excited states will be studied using the LC-wPBE functional.

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