

Lanthanide isothiocyanate complexes: Structures and the role of the LMCT state in intramolecular energy transfer

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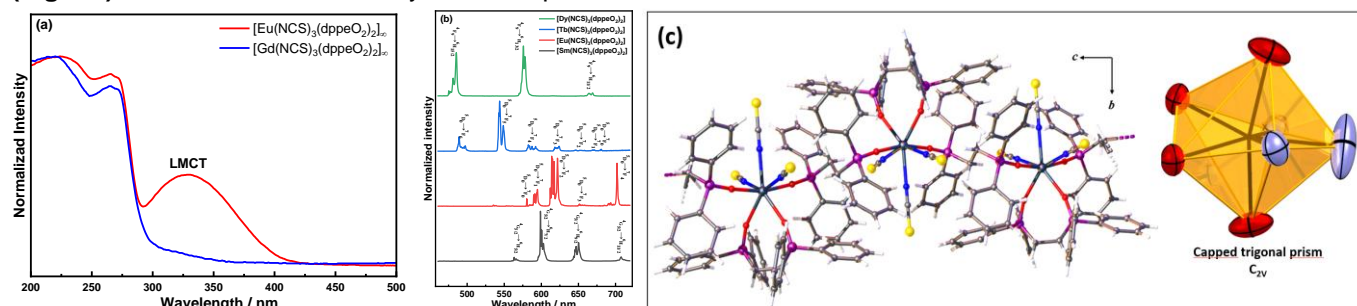
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Highlights

New polymeric complexes of Ln-isothiocyanates with dppeo2 ligands were successfully synthesized. The role of LMCT states in the luminescent properties was investigated.

Resumo/Abstract

Luminescent compounds based on Ln³⁺ ions are widely investigated due to their unique photophysical properties, which give these species applications in optical materials, sensors, biological markers, luminescent thermometers and catalysis. On the other hand, a large class of materials and compounds in the form of single entities have been obtained, and recently, new polymeric complexes containing diketonate ligands have been synthesized. With the focus on an in-depth investigation of energy transfer processes, and based on this, new compounds containing Ln-isothiocyanates were prepared to investigate the presence of low-energy ligand to metal charge transfer states.^[1] In this scenario, the present work reports the synthesis, characterization and spectroscopic properties of the compounds with formula [Ln(NSC)₃(dppeO₂)₂]_n, NSC: isothiocyanates and dppeO₂: 1,2-bis(diphenylphosphino)ethane oxide, Ln: Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺ and Dy³⁺. These complexes were prepared using the methodology adapted from the literature.^[2] The FT-IR spectra of the complexes show a red shift of the band attributed to the ν(C=O) vibrational mode, suggesting that NSC is coordinated to the Ln³⁺ ion. The structures of the Sm³⁺, Eu³⁺ and Dy³⁺ complexes had their were elucidated by X-ray diffraction technique, it was observed those that are isomorphous and crystallize in a monoclinic crystalline group, space group I2/a. Furthermore, the formation of a polymer is evidenced, in which the lanthanide ion is found in a chemical environment belonging to the C_{2v} point group (**Fig. 1c**). The diffuse reflectance spectra of the Eu³⁺ and Gd³⁺ complexes (**Fig. 1a**) exhibit strong absorption bands in the 200-450 nm range attributed to the S₀→S₁ transition centered on the dppeO₂ ligand. For the [Eu(NSC)₃(dppeO₂)₂]_n complex, a shoulder was observed in the longer wavelength region indicating the presence of the low-energy LMCT state. For the Eu³⁺ complex, the band corresponding to the excitation of the ligand exhibits very low intensity (**Fig. 1b**), which corroborates the presence of an efficient energy suppression channel via LMCT. On the other hand, the high relative intensities between the ligand excitation band and the 4f-4f transitions in the Tb³⁺, Sm³⁺ and Dy³⁺ complexes indicate an efficient ligand-Ln³⁺ energy transfer process. Overall, the emission spectra exhibit characteristic narrow bands attributed to the intraconfigurational Ln³⁺ ion transitions. The absence of a broad band in these spectra suggests an efficient intramolecular energy transfer (**Fig. 1b**) for the Tb³⁺, Sm³⁺ and Dy³⁺ ion complexes.



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