Área: INO

Influence of different terminal ligands and the molar ratio of $Tb^{3+}$and Eu^{3+}ions on the luminescent thermometric properties of 1D polymers

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Highlights

This work aims to evaluate the luminescent properties of coordination polymers involving the lanthanides europium and terbium with a 1:1 molar ratio, in addition to the variation of the bridge ligands that allows the non-radiative energy transfer from one lanthanide to another. This work presents a study of the influence of molar ratio of lanthanide ions, different beta-diketones and bridging ligands on the luminescent properties of coordination polymers.

Resumo/Abstract

Systems involving Eu(III) and Tb(III) ions have been investigated as luminescent ratiometric temperature probes in luminescent 1D coordination polymers due to Tb(III) → Eu(III) non-radiative energy transfer (ET). To better understand how these lanthanide ions correlate within a system, this study evaluated how the molar ratio between the ions, different terminal ligands, and bridging ligands influence the energy transfer between species and the luminescent properties of the coordination polymer. For this purpose, eight distinct polymers were synthesized: $[Tb_{0.75}(tfa)_3(L)Eu_{0.25}(tfa)_3]_n$, $[Tb_{0.75}(hfa)_3(L)Eu_{0.25}(hfa)_3]_n$, $[Tb_{0.25}(tfa)_3(L)Eu_{0.75}(tfa)_3]_n$ and $[Tb_{0.25}(hfa)_3(L)Eu_{0.75}(hfa)_3]_n$ (tfa^- = trifluoroacetylacetonate, hfa^- = hexafluoroacetylacetonate, L = Oxide of (diphenylphosphoryl)Rphosphine, R = ethyl - dppeo - or butyl - dppbo). To analyze the formation of the desired chemical bonds for the coordination polymer, FT-IR characterization was performed to evaluate the vibrational bands attributed to C-O, C=O, C-F, and P=O. The band observed around 1164 cm^{-1} is evidence of the formation of the P=O bond present in the bridging ligand dppeo and dppbo, the C-O bond band is present around 1450 cm^{-1}, the C=O bond band around 1620 cm^{-1}, and the C-F bond band around 1280 cm^{-1}. The spectra shows particular profiles due to the structural difference of the bridging ligand and the terminal ligand, which have different numbers of fluorine atoms between tfa^- and hfa^-, as well as the number of carbon atoms present in each bridging ligand. To confirm the structure of the coordination polymers, single-crystal X-ray diffraction analysis was performed, also allowing the determination of their molecular structures. In these structures, the 1D coordination polymer is based on Ln(III) lanthanide ion sites linked by the phosphine oxide bridging ligand. The coordination sphere, with a coordination number of 8, is completed by three bidentate β-diketone bridging ligands (tfa^- or hfa^-). The products containing hfa^- and the bridging ligands dppeo or dppbo form nearly linear chains. On the other hand, the dppbo bridging ligand combined with the terminal tfa^- ligand induces a 1D chain organized in a zigzag pattern. Thus, the terminal and bridging ligands influence the distances between the Ln(III) ions, which will impact the luminescent properties. To understand the percentage of carbon and hydrogen in these coordination polymers, an elemental analysis was performed to obtain the experimental composition for both carbon and hydrogen and compare it with the expected composition. While the bridging ligand μ-dppeo leads to a more linear polymer structure conformation, the bridging ligand μ-dppbo results in a more compact zigzag-shaped conformation. Consequently, the emission intensities are temperature-dependent due to ion–ion non-radiative energy transfer (ET), enabling the development of luminescent temperature probes with a maximum relative thermal sensitivity up to 5.20%·K^{-1} at 309.81 K for $[Tb_{0.75}(hfa)_3(\mu\text{-}dppbo)Eu_{0.25}(hfa)_3]_n$) coordination polymer.

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