Área: INO

Complex of luminescent europium containing bis(diphenylphosphine)oxide ligands

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Highlights

Novel kind of Eu^{3+}-β-diketonate complexes with phosphine oxide ligands have been successfully synthesized. The ligand-to-metal energy transfer processes in these complexes have been investigated.

Abstract

Trivalent lanthanide coordination compounds are characterized by their long luminescence lifetime of emitting level, narrow emission band and high color purity, which makes them fascinate for application in LCMDs, OLEDs, immunoassay, bioimaging probes, luminescent sensors and in telecommunications systems etc. Among this class of compounds, those ones in which β-diketonate ligands act as luminescence sensitizers have found a prominent position. However, most of these systems are obtained in the form of simple molecular entities. Recently, interest in new polynuclear systems containing diketonate ligands has been growing significantly. Therefore, this work reports on the synthesis, characterization, and photophysical properties of the lanthanide compounds of general formula $[Ln_2(\beta\text{-dik})_6(dppeO_2)]$, where β-dik = tta, bzac, dbm, $[Ln(\beta\text{-dik})_3(dppeO_2)]$ where β-dik = btf and $[Ln(\beta\text{-dik})_3(dppeO_2)_2]n$ where β-dik = fod, $dppeO_2$ = 1,2-Bis(diphenylphosphino)ethane oxide, Ln = Eu^{3+} and Gd^{3+}. These complexes were prepared by direct reaction among ethanolic solutions of the $[Ln(\beta\text{-dik})_3(H_2O)]$ complexes and $dppeO_2$ ligands in the molar ratios $[Ln(\beta\text{-dik})_3(H_2O)]$: $dppeO_2$ of 2:1. The FT-IR spectra of complexes show red-shifted of 20–41 cm^{-1} for the band assigned to the ν(C=O) vibrational mode (Fig 1a), suggesting that β–diketonate ligands are coordinated to the Ln^{3+} ion in chelating mode. Diffuse reflectance spectra of the Eu^{3+}-complexes show strong absorption bands in the range of 200–450 nm ascribed to the $S_0 \rightarrow S_n$ (ππ* or mixed nπ*) transitions from the diketonate ligands. The high relative intensities between excitation bands from ligand and 4f-4f transitions in the complexes with tta, btf and bzac indicates an efficient ligand-to-metal energy transfer process. On the other hand, for complexes with fod, dbm and bzac (Fig 1b) a lower intensity of the ligand bands is observed, suggesting that a luminescence suppression channel is operative. The emission spectra present the bands assigned to the $^5D_0 \rightarrow {}^7F_J$ (J = 0–4) transitions of the europium ion (Fig 1c). The Ω_2 and Ω_4 intensity parameters, lifetime (τ) and luminescence intrinsic quantum yield ϕ_{Eu}^{Eu} were calculated from the emission spectral data and luminescence decay curves of the compounds in solid state (Table 1). According with these data, the polymeric or dimeric investigated systems exhibit high luminescence intensities in the red region, which make them potential candidates for application as emitting layer in molecular light-converting devices.

Table 1. Experimental intensity parameters (Ω_λ), lifetime (τ), radiative (A_{rad}) and non-radiative (A_{nrad}) coefficients, and intrinsic quantum yield ϕ_{Eu}^{Eu} of complexes 77 K.

	τ (ms)	Ω_2 ($10^{-20}cm^2$)	Ω_4 ($10^{-20}cm^2$)	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	Φ_{Eu}^{Eu} (%)
$[Eu(btf)_3(dppeO_2)]$	0.7938	23.41	7.14	897	669	1566	46.8
$[Eu_2(tta)_6(dppeO_2)]$	0.6909	21.88	6.34	839	857	1697	40.7
$[Eu_2(bzac)_6(dppeO_2)]$	0.6445	17.95	6.08	727	961	1688	38.0
$[Eu(fod)_3(dppeO_2)_2]$	0.5209	17.28	8.49	773	1330	2103	30.7
$[Eu_2(dbm)_6(dppeO_2)]$	0.4863	23.51	8.75	940	1406	2.346	28.6

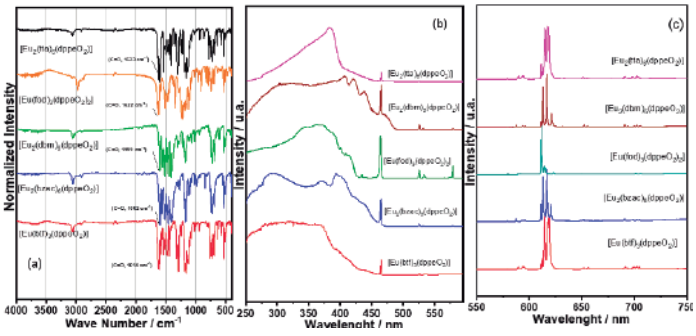

Figure 1. (a) Absorption spectra in the infrared region of the complexes. (b) Complex excitation spectra 77 K and (C) Complex emission spectra 77 K

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[1] Lima, D. A. (2019), *Disertação de Mestrado.* Universidade Estadual de Campinas.
[2] Kitagawa, Y. *et al.* (2021) *Chemistry - A European Journal*, 27(1), pp. 264–269.
[3] Teotonio, E. E. S. et al. (2009) *Optical Materials*, 32, pp. 345-349.