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Tailoring Optimal Structural Parameters in 1D Coordination Polymers: Lanthanide(III) Ions and the Occurrence of Upconversion.

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Palavras Chave: *Terras-raras, espectroscopia, upconversion, coordenação, luminescência, cristalografia.*

Highlights

Lanthanide coordination polymers; Shorter bridging ligands help boost upconversion. Fluorine in ligands have a major role in the polymerization. Coordination polymers can show upconversion emission.

Resumo/Abstract

The upconversion of trivalent lanthanide ions (Ln^{III}) has been extensively studied over the past decades owing to its potential use in energy conversion or in biological imaging.[1] The Yb^{III}/Er^{III} pair is well known for converting near-IR radiation into visible light, in a process where Yb^{III} absorbs low-energy photons, transfers energy to Er^{III} that in its turn emits visible light.[1] Recently, the possibility of achieving molecular upconversion in complexes of Ln^{III} ions with organic ligands has garnered significant attention due to their ease of synthesis and processing.[1] However, the efficiency of molecular upconversion by complexes still frails when compared to Ln^{III}-doped inorganic matrices. To face the exciting challenge of improving the molecular upconversion of Ln^{III} ions, 1D coordination polymers were used to provide further guidance on structural parameters to optimize the molecular upconversion of the Yb^{III}/Er^{III} pair. For that, two different ligand bridges were chosen - dppeo = 2-(diphenylphosphoryl)ethyl(diphenyl)phosphine oxide or dppbo = 1,4-bis(diphenylphosphinyl)butane - to tune the Ln – Ln distances (Ln = Er^{III} and Yb^{III}) and chain packing. Moreover, three different terminal ligands, acac = 2,4-pentanedione, tfa = 1,1,1-trifluoro-2,4-pentadione, or hfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, were employed to understand the role played by steric and electronic effects on the structure and upconversion. Both tfa^- and hfa^- terminal ligands combined with dppeo or dppbo bridges induce the formation of 1D coordination polymers with formula $[Ln(\mu\text{-}L)(X)_3]_n$ (μ-L = dppeo or dppbo, X = hfa^- or tfa^-), evidenced by single-crystal X-ray analysis. On the other hand, $acac^-$ combined with dppeo promoted the formation of a dinuclear structure with formula $[Ln_2(\mu\text{-dppeo})(acac)_6(H_2O)_2]$. The LnO_8 coordination polyhedra are described by a distorted D_{4d} point group in all structures, except for $[Ln(\mu\text{-dppeo})(hfa)_3]_n$, whose LnO_8 polyhedron is described by a distorted D_{2d} point group. Moreover, intramolecular F-F and F-H interactions have great influence on the formation and linearity of the polymer chain. Alongside, upconversion was detected exclusively for the structures containing the dppeo bridging ligand, whose Ln-Ln distances were measured to be up to 20% shorter than the dpbbo equivalents. This observation suggests that shorter Ln – Ln distances favor brighter molecular upconversion in the series of structures. Altogether, this study provides a bedrock on structural parameters that rule the molecular upconversion of polynuclear Ln^{III} complexes.[2]

References:

[1] Loïc J. Charbonnière et al, Chem. Sci., **15**, 3048 (2024).

[2] S. A. Andrade, A. G. Bispo-Jr, D. S. Alencar, J. H. A. Neto, J. A. Ellena, I. O. Mazali, F. A. Sigoli, *J. Mater. Chem. C*, **2024**, Accepted Manuscript.

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