XXI Brazilian Meeting on Inorganic Chemistry
X Brazilian Meeting on Rare Earths
III Workshop on Theoretical Bioinorganic Chemistry

Belo Horizonte, September 12 - 15th 2024

Critical Investigation of Structural Parameters to Optimize the Molecular Upconversion of Lanthanide(III)-based 1D Coordination Polymers

Stefano A. de Andrade [1], Airton G. Bispo-Jr[1], Deborah A. Simoni[1], João H. A. Neto[2], Javier A. Ellena[3], Italo O. Mazali[1], Fernando A. Sigoli[1]

[1] Institute of Chemistry, State University of Campinas, Campinas, São Paulo, Brazil.
[2] Institute of Chemistry, University of São Paulo, São Paulo, São Paulo, Brazil.
[3] Institute of Physics, University of São Paulo, São Carlos, São Paulo, Brazil.
E-mail:s236637@dac.unicamp.br; fsigoli@unicamp.br

Thematic Area: Rare-Earths

Keywords: Upconversion, Coordination Polymers, Luminescence

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 particularly popular for converting near-IR radiation in visible light, involving 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 is still lower when compared to Ln^{III}-doped inorganic matrices. To tackle 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 foundations on the correlation between structural parameters that control the molecular upconversion of polynuclear Ln^{III} complexes.

Acknowledgments: INCT/INOMAT (CNPq 465452/2014-0 and FAPESP 50906-9/2014), FAPESP (2021/06326-1, 2021/09755-0, and 2020/02614-0).

References

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