Área: INO

Synthesis, characterization and photoluminescent properties of mono-, bis- and tris-dicetonate lanthanide complexes

Ashley A.S.S. Jesus (PG),[1*] Adrihellen L. Gouveia (IC),[2] Paulo R.S. Santos (PQ),[1] Joaldo G. Arruda (PQ),[3] Israel F. Costa (PQ),[1] João H. Araujo Neto (PQ),[1] Maria C.F.C. Felinto (PQ),[4] Hermi F. Brito (PQ),[1] Ercules E.S. Teotônio (PQ).[2]

ashleypb12@gmail.com

[1]Departamento de Química Fundamental, Instituto de Química, USP; [2]Departamento de Química, UFPB; [3]Instituto de Química de São Carlos, USP; [4]Instituto de Pesquisas Energéticas e Nucleares.

Palavras Chave: *Lantanídeos, Luminescência, Terpiridina, Transferência de carga*

Highlights

- This work investigates the photoluminescent properties of mono-, bis- and tris-diketonate complexes of Ln^{3+} ions, using β-diketonate and 2,2':6',2''-terpyridine ligands.

Resumo/Abstract

Compounds based on trivalent lanthanide ions (Ln^{3+}) have applications in several areas, such as lighting (LEDs, OLEDs, fluorescent lamps), lasers, biological markers, safety signage, among others. Among the Ln^{3+} complexes, tris-diketonates with formula $[Ln(\beta\text{-dic})_3L]$ are undoubtedly the most widely studied class, where L represents an auxiliary ligand. However, other classes of lanthanide ion diketonate compounds have attracted the interest of researchers due to their spectroscopic properties that are significantly different from those observed in tris-diketonates with the same β-diketonate ligand. These compounds are characterized by the general formulas $[Ln(\beta\text{-dic})_2X(L)_2]$ and $[Ln(\beta\text{-dic})X_2(L)_2]$, and are referred to in this work as bis- and mono-diketonates, where X is a small ionic ligand, such as nitrate (NO_3^-). The intramolecular energy transfer rates from the triplet excited state (T) of the ligands to the excited states of the Ln^{3+} ion vary according to the class of the compound, be it tris-, bis- or mono-diketonate. Furthermore, ligand-to-metal charge transfer (LMCT) processes may become more pronounced in the quenching of luminescence, as observed experimentally in mono- and bis-diketonate compounds. Although there are advances in the investigation of the nature of the LMCT states, the main structural factors that influence these quenching processes are still not fully understood in the literature. Therefore, the aim of this work is to investigate the intramolecular (ligand-metal) energy transfer rates, the position of the LMCT states and their variations as a function of structural factors. In this context, this study reports the synthesis, characterization and analysis of the photoluminescent properties of mono-, bis- and tris-diketonate complexes of trivalent lanthanide ions (Ln^{3+}: Eu^{3+} and Gd^{3+}). The β-diketonate ligands used are acetylacetonate (acac), dipivaloylmethanate (dpm) and benzoylacetonate (bzac), resulting in the following general formulas: $[Ln(\beta\text{-dic})(NO_3)_2(terpy)]$, $[Ln(\beta\text{-dic})_2(NO_3)(terpy)]$ and $[Ln(\beta\text{-dic})_3(terpy)]$, with 2,2':6',2''-terpyridine (terpy) acting as an auxiliary ligand. It is worth mentioning that this study focuses particularly on a class of compounds that exhibit low-energy ligand-metal charge transfer (LMCT) states. The structural characterization of the new mono-diketonate compounds was performed by single crystal X-ray diffraction, while the other compounds were characterized by powder X-ray diffraction and infrared absorption spectroscopy. The photoluminescence study was conducted using diffuse reflectance and static and time-resolved luminescence spectroscopy techniques. The results evidenced the presence of low-energy LMCT states in the mono- and bis-diketonate compounds. In the europium compounds, the emission spectra showed narrow bands resulting from the intraconfigurational-4f transitions. In addition, the Judd-Ofelt intensity parameters were calculated for these compounds. Finally, the ligand- Ln^{3+} energy transfer mechanisms of the compounds were elucidated using the JOYSpectra platform.

[1] P. R. S. Santos et al., Journal of Luminescence, **226**, 117455 (2020).

[2] Y. C. Miranda et al., Eur. J. Inorg. Chem, **18**, 3019-3027 (2015).

Agradecimentos/Acknowledgments

This work was supported by CNPq, CAPES, FAPESP, FINEP, USP and UFPB.