

Highly luminescent lanthanide complexes containing fluorinated β -diketonate and phenanthroline derivative. Elucidation of Energy Transfer Pathways

Plinio Cantero-Lopez, Alexander Carreno, Angelica Ramirez-Osorio, Lily Arrue, Alejandro Ortiz and Dayan Paez-Hernandez
Universidad Andres Bello, Chile

Statement of the Problem:

In recent decades, the synthesis of new lanthanide(III) complexes have become a hot area because of their potential use as materials for biological immunoassays, lasers, cathode ray tubes, lighting systems, electroluminescent devices, sensors, dosimeters, imaging agents, display applications, decoration purposes, light-emitting diodes (LEDs) and photodynamic therapy (PDT). The fascinating optical properties of Ln(III) is due to their unique spectroscopic properties attributed to the characteristic f-f transitions in their inner 4f shell. So, offering desirable spectroscopic properties that addresses various limitations of organic fluorophors.

Methodology & Theoretical Orientation: Lanthanide(III) complexes were prepared as follows: A solution of 1mmol of $\text{Ln}^{3+}(\text{Cl}_3)_6 \cdot 6\text{H}_2\text{O}$ ($\text{Ln}^{3+} = \text{Eu}^{3+}, \text{Tb}^{3+}, \text{Nd}^{3+}$) in ethanol was added dropwise to stirring ethanolic mixture of fluorinated β -diketonate (3 mmol) and phenanthroline derivative (3 mmol) containing 3 mmol of KOH. The mixture was heated to 75 °C for 30 minutes and stirred for 72 h giving a precipitate.

A multiconfigurational *ab initio* method along with scalar relativistic time-dependent DFT were employed to accurately elucidate the excited state energy transfer pathways and the corresponding electronic states involved in lanthanide complexes.

Findings: We have designed and synthesized a series of heteroleptic ternary coordinatively saturated Eu(III), Nd(III) and Tb(III) complexes $[\text{Eu}(\text{R-phen})(\text{Diceto-CF}_3)_3]$ and characterized by various physicochemical studies. The introduction the N,N-donor and β -diketonate ligands produce an increase of the luminescence. The triplet level of β -diketonate ligand is lower than the phenanthroline derivative. That's why, in this case, these kinds of ligands produce a better energy transfer to the resonant level of lanthanide ion.

Conclusion & Significance: A rigorous study from experimental and relativistic quantum chemical methods has been performed successfully to study the spectroscopic properties and sensitization pathways in highly luminescent lanthanide compounds

Recent Publications:

1. Pushkarev, A. P., Ilichev, V. A., Maleev, A. A., Fagin, A. A., Konev, A. N., Shestakov, A. F., ... & Bochkarev, M. N. (2014). Electroluminescent properties of lanthanide pentafluorophenolates. *Journal of Materials Chemistry C*, 2(8), 1532-1538.
2. Ahmed, Z., & Iftikhar, K. (2014). Efficient photoluminescent complexes of 400–1800 nm wavelength emitting lanthanides containing organic sensitizers for optoelectronic devices. *RSC Advances*, 4(109), 63696-63711.
3. Kitagawa, Y., Suzue, F., Nakanishi, T., Fushimi, K., & Hasegawa, Y. (2018). A highly luminescent Eu (iii) complex based on an electronically isolated aromatic ring system with ultralong lifetime. *Dalton Transactions*, 47(21), 7327-7332.
4. Jenks, T. C., Bailey, M. D., Corbin, B. A., Kuda-Wedagedara, A. N., Martin, P. D., Schlegel, H. B., ... & Allen, M. J. (2018). Photophysical characterization of a highly luminescent divalent-europium-containing azacryptate. *Chemical Communications*, 54(36), 4545-4548.

5. Beltrán Leiva, M. J., Fuenzalida-Valdivia, I., Cantero-López, P., Bulhoes Figueira, A., Alzate-Morales, J. H., Paéz-Hernández, D., & Arratia-Pérez, R.(2019). Classical and Quantum Mechanical Calculations of the Stacking Interaction of NdIII Complexes with Regular and Mismatched DNA Sequences. The Journal of Physical Chemistry B.DOI: 10.1021/acs.jpcc.9b00703

Biography:

Plinio Cantero Lopez is Ph.D. holder and he graduated in Molecular Physical Chemistry from University Andres Bello (Chile) with experience in the field of synthesis and computational study of lanthanides and transition metal coordination chemistry, by means of relativistic DFT and ab initio methods. I have work experience as assistant professor at the University of Cordoba, Colombia and University Andres Bello, Chile.

p.canterolopez@uandresbello.edu