XXI Brazilian Meeting on Inorganic Chemistry
X Brazilian Meeting on Rare Earths
III Workshop on Theoretical Bioinorganic Chemistry
Belo Horizonte, September 12 - 15th 2024

Ir^{III}-Ln^{III} Heterobimetallic complexes: The solvent role in the sensitization process of the Eu^{III} ion

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Thematic Area: Rare-Earths

Keywords: heterobimetallic complex, energy transfer, europium

In luminescent devices, the combination of red, green, and blue luminophores (RGB system) allows the perception of a gamut of colors, including the white light sensation[1]. A strategy to improve emission properties, such as color purity and emission quantum yield (Φ), is the synthesis of bimetallic *d*-*f* complexes to join the high Φ of the *d*-metal complexes with the high color purity of the lanthanide^{III} ions, in which three situations may happen, mostly influenced by the gap between the donor state from the *d*-metal complexes and the *f*-acceptor state from the Ln^{III} ion: (i) emission only from *d*-complex; (ii) emission from both *d* and *f*; (iii) emission only from *f* [2]. Herein, we show that the energy transfer between Donor (D) and Acceptor (A) state is strongly influenced by solvent properties, since the D state in a Ir^{III} complex has a predominantly ^{3}MLCT character, strongly influenced by solvatochromic effect. Thus, two Ir^{III}-Ln^{III} bimetallic complexes (Ln^{III} = Gd^{III} or Eu^{III}) were synthesized. Ir^{III}-Gd^{III} - Yield: 77.8%. Elemental analysis; found(calcd.) C: 40.79%(40.17%), H: 2.71%(2.66%), N: 5.67%(5.41%) to $C_{104}H_{82}Cl_3Gd_2F_{12}Ir_3N_{12}O_{24}$ – $[\{Ir(dfppy)_2(\mu\text{-}bpdc)\}_3Gd_2]Cl_3\cdot10H_2O\cdot2CH_3OH$. Fluorescence: excitation λ_{max} (in aerated DCM solution, 4.62×10^{-6} mol L^{-1}) 451 nm, emission 560 nm. Quantum yield (Φ_{fl}) 40.5%, τ = 8.9 µs. And the Ir^{III}-Eu^{III} - Yield: 86.5%. Elemental analysis; found(calcd.) C: 39.45%(39.39%), H: 2.87%(2.86%), N: 5.90%(5.30%) to $C_{104}H_{90}Cl_3Eu_2F_{12}Ir_3N_{12}O_{28}$ – $[\{Ir(dfppy)_2(\mu\text{-}bpdc)\}_3Eu_2]Cl_3\cdot14H_2O\cdot2CH_3OH$. Fluorescence: excitation λ_{max} (in aerated DCM solution, 4.62×10^{-6} mol L^{-1}) 451 nm, emission Ir^{III} component 560 nm, Eu^{III} component 616 nm. Quantum yield (Φfl) 31.7%, τ_{Ir} = 12.4 µs, and τ_{Eu} = 0.82 ms. From photophysics measurements it was possible to verify some favorable aspects which help the energy transfer process and enhance the luminescent properties in solution of Ir^{III}-Eu^{III} bimetallic complexes: (i) Highly polar solvents (DMSO and acetonitrile) play an important role in Eu^{III} sensitization, demonstrating that even when the ^{3}MLCT donor state is low in energy, energy transfer is a favorable process; (ii) The energy of the ^{3}MLCT donor state is the most important parameter when performing luminescence measurements in nonpolar (chloroform) or low-polarity (dichloromethane and ethyl acetate) solvents, similar to the solid state; (iii) Non-coordinating solvents (chloroform and ethyl acetate) moderately increase the values of the emission quantum yields compared with coordinating solvents with OH oscillators, such as methanol and water. However, coordinating solvents free of OH oscillators (DMSO and acetonitrile) highly increase the emission quantum yields, especially the intrinsic quantum yield of the Eu^{III} ion. (iv) Solvents with OH oscillators are strong quenchers of Eu^{III} luminescence.

Acknowledgments: FAPESP (19/26103-7), CAPES, and CNPq (308868/2022-6).

References

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