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Theoretical and spectroscopic study of two europium(III) complexes containing the zwitterionic form of 4-picolinic acid or 3-thiophenecarboxylate as antenna ligands

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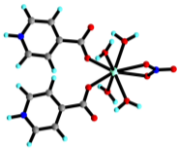
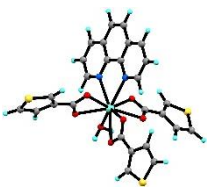
Lanthanide(III) complexes are widely studied due to their possible optical applications.[1] Although the emission of lanthanide ions is usually of low intensity, it can be intensified when coordinated to antenna ligands, which transfer energy to the lanthanide excited levels.[2] In this work, the spectroscopic properties on the UV-visible region of two europium(III) complexes with different antenna ligands were studied through semiempirical methods, in order to compare the ligands' ability to sensitize the lanthanide ion. Compound **1**, Eu(4pic), presents the zwitterionic form of 4-picolinic acid as antenna ligand,[3] while compound **2**, Eu(3tca), contains 3-thiophenecarboxylate. Based on the coordinates of the crystal structures and the experimental emission spectra, the singlet and triplet states of the ligands were calculated with the semiempirical method INDO/S, on ORCA 5.0.3 software, considering the lanthanide ion a point charge of +3*e*. Those calculations were also performed considering the ethanol solvent effects with COSMO method; the coordinates were obtained from a geometry optimization in solution with the RM1 model implemented in the MOPAC 2019 software. **Table 1** presents the experimental and theoretical Judd-Ofelt parameters, calculated on LUMPAC 1.4.1 software as well as the radiative and non-radiative decay rates. Afterwards, the energy transfer rates, and quantum efficiency will be calculated and compared to experimental values, to allow an increasing understanding of the energy transfer process occurring in these coordination compounds.

Table 1. Experimental and theoretical Judd-Ofelt parameters for compounds Eu(4pic) and Eu(3tca). Green: Eu; Red: O; Blue: N; Gray: C; Yellow: S; Light-blue: H.

Compound	Vacuum / Solid state				Solution			
	Ω_2 / 10^{-20} cm^{-2}		Ω_4 / 10^{-20} cm^{-2}		Ω_2 / 10^{-20} cm^{-2}		Ω_4 / 10^{-20} cm^{-2}	
	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.
 **1**	5.1	5.1	6.9	6.8	7.3	6.4	4.8	6.0
 **2**	10.0	10.0	5.9	5.9	11.7	11.7	7.1	7.1

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References

[1] J. Monteiro, N. Fetto, M. Tucker, F. Sigoli, A. Bettencourt-Dias. J. Lumin. **245**, 118768 (2022).
[2] A. Singh. Coord. Chem. Rev. **455**, 214365 (2022).
[3] E. Areas, B. Rodrigues, A. Nascimento, H. Silva Junior, G. Ferreira, F. Miranda, F. Garcia, S. Safeer, S. Soriano, G. Guedes. J. Braz. Chem. Soc. **35**, e-20230160 (2024).