



Full Length Article

Tuning the sensitization pathway $T_1 \rightarrow {}^5D_J$ in Eu-based MOF through modification of the antenna ligand. A theoretical approach via multiconfigurational quantum calculations

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ABSTRACT

The current study demonstrates the possibility of improving the efficiency of Eu^{3+} sensitization in an Eu-based MOF, labelled as **EuL-R**, by modifying the antenna ligand. The electronic structure of seven antenna ligand derivatives with the form **R-4-(pyrimidin-5-yl) benzoic acid (L-R)** ligand derivatives was thoroughly examined in this research. Also, the most likely energy transfer channels for the sensitization pathway of Eu^{3+} ions in the **EuL-R** systems (**R**: CH_3 , $-\text{OH}$, $-\text{SH}$ and $-\text{NH}_2$) was studied. The efficiency in the intersystem crossing (ISC) process from S_1 to T_1 in the antenna make plausible a subsequent energy transfer to the emissive state in the Eu^{3+} . This process was studied via multireference CASSCF/NEVPT2 calculations due to the multiconfigurational character of Eu^{3+} ions. Based on Latva and Reindhout's empirical rules, the 4-(2-(thiophen-2-yl)pyrimidin-5-yl)benzoic acid (**L6**) was chosen as efficient antenna for the sensitization process in this system. In conclusion, it was discovered that including the thiophenyl group at the **L** antenna (**L6**), increased the energy gaps $S_1 \rightarrow T_1$ and $T_1 \rightarrow {}^5D_J$ (Eu^{3+}) to an optimal range for the ISC and subsequent energy transfer. Finally, a deeply understanding of the sensitization and emission mechanisms was possible from the excited-state dynamics analysis of the **L6** antenna, via fluorescence, inter-system crossing (ISC), phosphorescence, and k_F , k_{ISC} , and k_P , rates calculations. This study therefore highlights the importance of a thorough theoretical procedure via a robust quantum mechanical tool to guide the development of novel luminescent lanthanide-based MOFs.

1. Introduction

Lanthanide-based metal-organic frameworks (Ln-MOFs) are outstanding materials of interest within the field of chemical sensors [1]. Ln-MOFs are an increasingly important material of interest in a wide range of fields, such as chemical [2], biomedical [3], environmental sciences [4], in between others [5,5]. Luminescent Ln-MOFs have been described as effective systems for detecting a variety of different

analytes *in situ*, including biomarkers [6], nitro aromatic compounds [7], volatile organic compounds [8], ions [9], pharmaceuticals, among others [10]. These materials are coordination polymers with open-framework structures featuring potential voids (pores) [11,12], which are made up of nodes (metal ions or cluster-metal ions) [13] connected together by organic ligands commonly known as linkers [14, 15]. The remarkable luminescent properties of Ln-MOFs, which are related to the electronic structure $[\text{Xe}]4f^n$ of Ln^{3+} ions, are driving their

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