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

Exploring Antenna Effects and Metal Ion Sensing in a 2D Europium(III) Coordination Network with a Rigid Diyne-Based Ligand

Catiúcia R. M. O. Matos,[1] Carolina B. P. Ligiero,[1] Mikaelly O. B. de Sousa,[1] Henrique C. S. Junior,[1] Gláucio B. Ferreira,[1] Jackson A. L. C. Resende,[2] and Célia M. Ronconi[1]

[1]Departamento de Química Inorgânica, Campus do Valonguinho, Universidade Federal Fluminense, 24020-141, Niterói, RJ, Brazil.
[2]Instituto de Ciências Exatas e da Terra, Campus Universitário do Araguaia, Universidade Federal do Mato Grosso, 78600-000, Barra do Garças, MT, Brazil.
E-mail:cmronconi@id.uff.br

Thematic Area: Rare Earths

Keywords: Europium(III), coordination network, sensor

Coordination Networks (CNs) featuring emissive components, such as lanthanide(III)-based 2D CNs, show great promise as fluorescence-sensing systems.[1] Through an indirect mechanism, the sensitizer ligand coordinated to the Ln(III) center harvests excitation energy and transfers it to the metallic center within the structure.[2] In this study, a novel 2D Eu^{3+} coordination network (**EuCN**) was synthesized by a solvothermal reaction at 120 °C for 48 h using $Eu(NO_3)_3{\cdot}6H_2O$ and the rigid **H_2L1** proligand, which contains an elongated and rigid spacer bearing two triple bonds.[3,4] The unreported crystal structure of **EuCN** was determined by single-crystal X-ray diffraction. Spectroscopic measurements of **EuCN** in DMSO (0.3 $mgmL^{-1}$) showed that upon excitation at 350 nm, the emission spectra displayed the typical emission pattern of Eu^{3+}, characterized by five narrow emission bands at 579, 591, 616, 653 and 698 nm, attributed to the $^5D_0 \rightarrow {}^7F_J$ (J = 0-4) transitions. Notably, the ligand's emission was absent, suppressed by the antenna effect. Theoretical calculations using time-dependent density functional theory (TD-DFT) methods (at the ωB97X-D3/Def2-TZVP level) supported this phenomenon, predicting efficient ligand-to-metal charge transfer transitions that sensitize the Eu^{3+} luminescence in this binuclear system. Investigation into the sensing properties of **EuCN** towards various metal ions revealed distinct responses: its fluorescence was completely quenched in the presence of Cu^{2+} and Fe^{3+} ions due to the inner filter effect. Conversely, the addition of Hg^{2+} ions resulted in an increase in emission, attributed to the chelation-enhanced fluorescence (CHEF) process. Therefore, the development of **EuCN**-based sensors represents a promising field for environmental monitoring, particularly in the detection of trace amounts of hazardous metal ions in water sources.

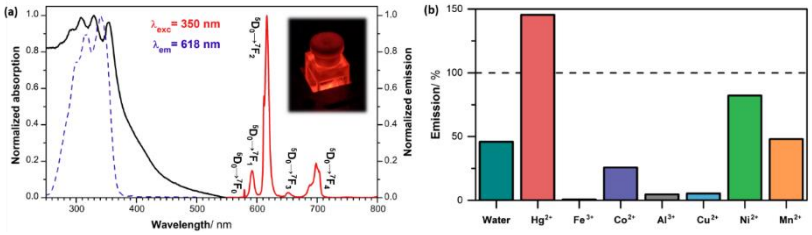

Figure 1. (a) Absorption (full line), excitation (dotted blue line) and emission (red line) spectra of **EuCN** in DMSO; (b) Emission (%) of **EuCN** in the presence of metal ions.

Acknowledgments: CAPES, CNPq, FAPERJ

References

[1] Li, B. *et al.*, Advanced Materials, **28**, 8819 (2016).
[2] Wu, L. *et al.*, JACS Au, **2**, 853 (2022).
[3] Martins, V. *et. al.*, CrystEngComm, **19**, 3103 (2017).
[4] Matos, C. R. M. O. *et al.*, Dalton Transactions,**50**, 15003 (2021).