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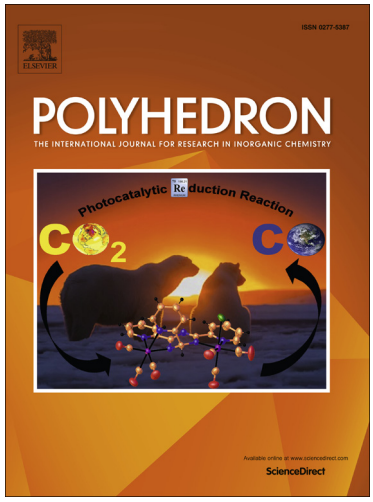

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Tuning the Structural and Lanthanide Luminescence Properties of Macrocyclic Tetraiminodiphenolate Europium(III) Complexes

Alexandra K. Duncan,[a] Chelsea N. McBride,[a] Tavya G. R. Benjamin,[b] Melanie P. Madsen,[b] Kyle T. Bowers,[b] Ana de Bettencourt-Dias,[c] Eric J. Werner[b]*

[a]Department of Chemistry and Physics, Armstrong State University, 11935 Abercorn Street, Savannah, Georgia 31419, United States
[b]Department of Chemistry, Biochemistry and Physics, The University of Tampa, Tampa, Florida 33606, United States
[c]Department of Chemistry, University of Nevada, Reno, Nevada 89557, United States

***Corresponding author:** E. J. Werner (ewerner@ut.edu); Ph: +1-813-257-6340; Fax: +1-813-258-7496

Abstract

The synthesis, structural characterization, and luminescence properties of two novel macrocyclic tetraiminodiphenolate europium(III) complexes are reported. The macrocyclic ligands studied bind the lanthanide through four or five donor atoms, leaving space for additional nitrate ions or, in solution, solvent molecules within the inner coordination sphere of the Eu^{3+} ion. Structural aspects of the complexes, [Eu-TIDP-Pr-tBu$(NO_3)_3$] (**3**) and [Eu-TIDP-PrOH-tBu$(NO_3)_3$] (**4**), are probed in solution via absorption and fluorescence measurements, and in the solid state by IR spectroscopy and X-ray crystallography. Complex **3** crystallizes in the monoclinic P21/n space group with four molecules in the unit cell and cell dimensions a = 9.6309(3) Å, b = 21.4708(7) Å, c = 21.4442(7) Å, β = 94.565 ° and V = 4420.2(2) $Å^3$. Complex **4** crystallizes in the triclinic P-1 space group, also with four molecules per unit cell and cell dimensions a = 13.3847(2) Å, b = 16.1381(2) Å, c = 20.5803(3) Å, α = 82.674(1) °, β = 72.787(1) °, γ = 71.871(1) ° and V = 4032.45(10) $Å^3$. As confirmed by the crystal structure, an extra hydroxyl oxygen atom within the propanol linked derivative binds the metal center, leading to a significant decrease in solvent mediated quenching of the Eu^{3+} luminescence of complex **4**. Finally, preliminary anion binding studies were conducted and suggest potential application of such complexes in the area of anion sensing via changes in emission intensity when select anions such as phosphate replace metal-bound water molecules in solution.

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