



Structure impact in antenna effect of novel upper rim substituted tetra-1,3-diketone calix[4]arenes on Tb(III) green and Yb(III) NIR-luminescence



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ABSTRACT

Two novel calix[4]arene macrocyclic ligands functionalized with four 1,3-diketone groups at the upper and hydroxyl (**3**) or propoxy-groups (**6**) at the lower rims were synthesized and characterized using NMR, IR spectroscopy, mass spectrometry, and elemental analysis. UV–vis spectrophotometry and ESI mass spectrometry studies indicate 1:1 complex formation of ligands **3** and **6** with Ln(III) (Ln=Tb, Yb) in alkaline DMF solutions resulted from coordination of Ln(III) with 1,3-diketone groups. Luminescence study of Ln(III) complexes with **3** and **6** reveals significant difference in antenna effects of their deprotonated forms on both Tb(III)- and Yb(III)-centered luminescence. Comparison of ligand-centered emission for ligands **3** and **6** points to the latter as more efficient antenna for Tb(III) and Yb(III). Different conformational behavior of ligands **3** and **6** in alkaline media is assumed as a reason for the experimentally observed difference in sensitization pathways in Ln(III) complexes with **3** and **6**.

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1. Introduction

Luminescent Ln(III) complexes attract great research attention due to their wide application as fiber amplifiers operating at telecommunication wavelength,¹ OLEDs^{2–4} as well as UV light converters transforming high energy UV irradiation to visible or NIR-emission,⁵ immune-fluorescent analysis and therapy,⁶ and information security.⁷ Usually, the small absorption of Ln(III) ions due to Laport forbiddance of 4f–4f transitions results in poor emission from the excited 4f levels under direct excitation unless powerful lasers are used. One of the most popular ways to overcome this limitation is complexation of Ln(III) ions with organic ligands that sensitize emission of the metal ion by the well-known antenna effect.⁸ However, NIR emitting lanthanide complexes with organic ligands often show low emission efficiencies compared to inorganic and cluster systems. Radiationless decay through high-frequency

oscillators (O–H, N–H, and C–H) resulting from organic ligands or the solvent molecules is the reason for quenching NIR luminescence.⁹

Many recent efforts have been made to synthesize the appropriate antenna-ligands for the Er(III) and Yb(III) NIR-luminescence according to the general requirements of the organic antenna—an energetically well-matched triplet state of the ligand or d-block chromophore to the first Ln(III) excited state, a rigid structure, and the number of O–H, N–H, C–H oscillators minimized via chelating or fluorination processes (for C–H bonds).¹⁰

1,3-Diketones have been reported as very promising antenna-ligands for Ln(III)-centered emission,^{11,12} where the rigidity of the complex structure is a reason for lesser radiationless decay.^{13–16} For example, the luminescence of the Ln(III) bis(1,3-diketone) dinuclear complex was found to be 11 times more intense than the luminescence of mononuclear analogues.¹³ Anchoring 1,3-diketone fragments to a cyclic calix[4]resorcinarene backbone was recently documented as a route for efficiently sensitizing Tb(III)-centered luminescence due to the rigidity of the complex structures or/and

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