Development of Metallacrowns into Lanthanide Based Luminescent Agents

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Abstract

The field of optical biological imaging is growing explosively in recent years due to technological advances related to detection techniques and image treatment. Luminescent probes allow for the visualization and/or quantification of biological objects or events with a high detection sensitivity and resolution at the cellular level. Lanthanide(III)-based complexes are a class of luminescent compounds that possess fascinating and unique optical properties due to the electronic structure of the lanthanide(III) cations (Ln^{3+}) they incorporate. More specifically, Ln^{3+} exhibit f-f emission bands from the visible to the near-infrared (NIR) range and a number of complementary properties with respect to the fluorescent probes: sharp emission wavelengths that are highly insensitive to the microenvironment, large energy differences between the absorption and emission bands and high resistance toward photobleaching (allowing long term or repetitive quantitative experiments). Metallacrowns are the inorganic analogues of organic crown ethers and have been shown to be excellent vehicles for the encapsulation of lanthanides. We have reported previously the design, synthesis, characterization and luminescence properties of Ln^{3+} "encapsulated sandwich" metallacrown complexes (MC) based on Zn^{2+} ions and bivalent aromatic hydroximate ligands (L^{2-})[1,2] that sensitize NIR emitting Ln^{3+}= Nd, Er, Yb and $Ln^{3+}Ga^{3+}$ 12-MC-4 structures[3] that sensitive the full range of lanthanide emission across the visible and NIR regions. In both classes of complexes, we observed some species with the highest quantum yield values (in comparison to NIR emitting Ln^{3+}-based complexes containing C-H bonds) and longest luminescence lifetimes in the solid state and in methanol solutions due to an efficient Ln^{3+} sensitization and a strong protection against non-radiative deactivation pathways (resulting from overtones of high energy C-H, N-H, and O-H vibrations located in solvent molecules and ligands close to the Ln^{3+} ion). We will discuss how the pyrazinehydroxamic acid (H_2pyzHA) analogue that forms Ln^{3+}[12-$MC_{Zn(II),pyzHA}$-4]$_2$[24-$MC_{Zn(II),pyzHA}$-8] (Ln^{3+}[Zn(II)MC_{pyzHA}], Ln^{3+}= Yb, Nd) may be used as a highly photostable probe and labels preferentially necrotic cells[4] and may be used in one step dual fixation and staining of human cells. A Ga_8Ln_2 class of molecules will also be presented[5,6].

References

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