

The effect of metal binding site changes on lanthanide emission efficiency

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Luminescent lanthanide(III) ions are attractive components of biological tools due to their long-lived, narrow, and fingerprint-like emissions that are readily identified even in complex milieux. As lanthanide emission arises from Laporte-forbidden transitions, efficient excitation usually requires a light-harvesting antenna that can transfer the excitation energy to the metal ion.¹ The parameters governing lanthanide sensitization have been extensively studied. There are useful guidelines available for the selection of good antennae that afford bright lanthanide-based emitters, even if the design and synthesis of a new luminescent complex from scratch is still a major undertaking.

We have recently become interested in understanding quenching pathways in carbostyryl- and coumarin-sensitized lanthanide emitters. The in-depth investigation of a small library revealed that photoinduced electron transfer to a potentially large group of lanthanide(III) ions is feasible from these widely used organic antennae. The lanthanides affected include the readily reducible Eu and Sm. However, under some circumstances, Dy, Nd and Tm have lanthanide(II) states that are at least theoretically accessible upon the reduction of the lanthanide(III) by the excited states of common organic antennae.² Crucially, photoinduced electron transfer is expected to be detrimental to lanthanide luminescence in these systems.³

We hypothesized that ligands that stabilize the +3 oxidation state of the lanthanide ion could meaningfully contribute to an improved lanthanide luminescence. We present the characterization of a series of complexes for testing this hypothesis. Metal-antenna distances and ligand denticities were kept constant in order to minimize changes in the energy transfer efficiencies, and in the numbers of quenching first- and second sphere solvent molecules within the series. The ligand donor atoms and the overall charges of the complexes were varied systematically to obtain Ln complexes with a range of redox potentials. Several sensitizing antennae were tested on every ligand framework.

References

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