Recent Advances in Transition Metal Sensitizers for Lanthanide NIR Emission

Brian Bellott Literature Seminar October 11, 2005

Materials that emit in the near infrared (NIR) are useful in biological applications because tissue is relatively transparent to NIR radiation but relatively opaque in the ultraviolet or visible range. NIR devices could be used to perform deep tissue studies in real time, thus avoiding the delays associated with ex situ analyses.[1]

Lanthanides have unusually sharp NIR absorption and emission spectra due to the small radial extension of the f-orbitals relative to the filled 5s and 5p orbitals.[2] The narrow spectroscopic features enable lanthanides to be used in a variety of applications, such as lasers, flat panel displays, contrast agents, and numerous biological applications.[3-11]

Due to the Laporte forbidden nature of the f-f transitions, the lanthanides have very small molar absorptivities. As a result, direct photogeneration of the lanthanide emissive states is very inefficient. The use of sensitizers can compensate for the symmetry-forbidden nature of the f-f transitions. Sensitizers act by absorbing light energy to generate a sensitizer-localized excited state; subsequent energy transfer from the sensitizer to the lanthanide generates the emissive lanthanide excited state. The use of sensitizers results in higher quantum yields for the lanthanide emission: effective sensitizers have larger molar absorptivities than the lanthanide elements and serve as antenna chromophores. The antenna effect is demonstrated in Figure 1.[11]

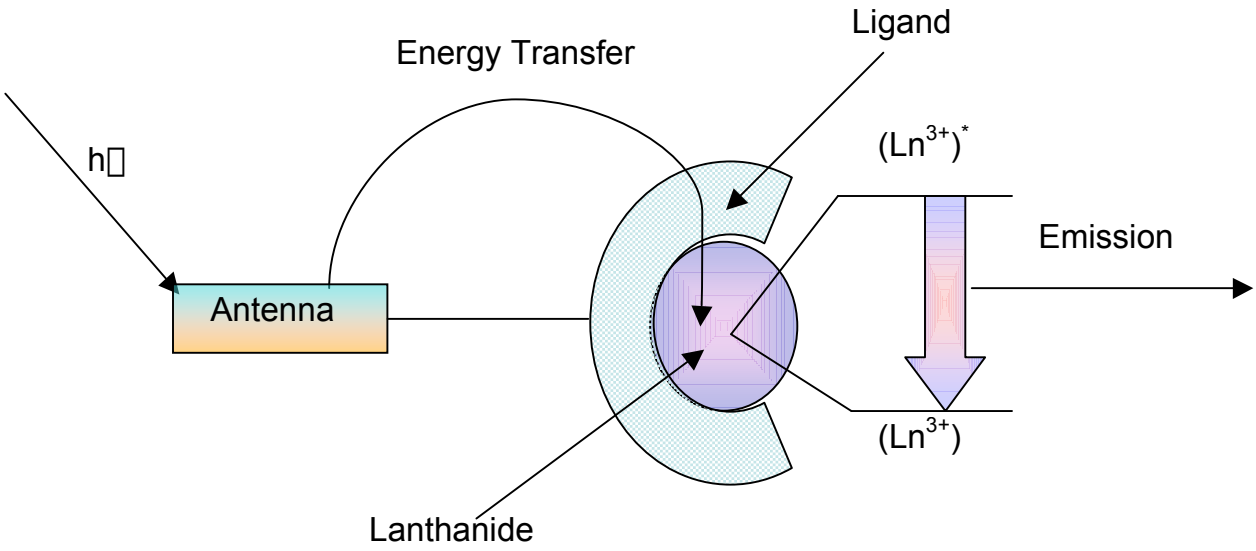

Figure 1: The antenna effect (Adapted from ref 11).

Organic based sensitizers have been studied since the early 1990s.[12] Recently, researchers have been interested in synthesizing lanthanide compounds connected to transition metal sensitizers.[13] Transition metals have many properties that make them good sensitizers. Transition metal complexes often have high molar extinction coefficients and their absorption

properties can be tuned: with proper choice of metal and ligand, the absorption maximum can be selected anywhere in the ultraviolet, visible, and near infrared windows.

In 2000, the research groups of van Veggel[13] and Parker[14] synthesized the first two NIR emitters in which a lanthanide compound bears a transition metal sensitizer. Van Veggel's complexes contained either ruthenium(III) tris(bipyridine) or ferrocene sensitizers covalently attached to erbium(III), neodymium(III), and ytterbium(III) complexes, whereas Parker's complexes contained a palladium porphyrin sensitizer covalently attached to neodymium(III) and ytterbium(III) complexes. Van Veggel and co-workers demonstrated that the absorption spectrum of the transition metal was directly related to the emission spectrum of the lanthanide. Compounds from Parker research group were based on a porphyrin sensitizer that has a triplet energy of 580-830 nm, that is well matched with the excited states of the lanthanides studied: Yb^{3+} (980 nm) and Nd^{3+} (880 nm). Parker also demonstrated that addition of $[(CG)_6]_2$ oligonucleotide or calf thymus DNA in an aerated solution increased the emission intensity of the lanthanides by a factor of 2. The increase occurs because DNA binds to the assembly, preventing the quenching of the porphyrin excited state by dioxygen. Additional evidence that the DNA interacts with the porphyrin is provided by the red shift (9 nm) of the Soret band in the UV/Vis spectrum when DNA is present.

Since 2000, several different transition metal-lanthanide complexes have been synthesized. Examples include a Cr(III)-Ln(III) complex with a luminescence lifetime in the millisecond range,[15] a $Pt(II)_2$-Ln complex that exhibits increased luminescence upon binding of DNA,[16] and an emissive molecular square constructed from $Ru(bpy)_2$ and $Nd(TTA)_3$ (TTA=2-thenoyltrifluoroacetonate) building blocks.[17] Transition metal sensitized lanthanide complexes are versatile as shown by their long lifetimes (ms range) and ability to emit light in both the UV/Vis and NIR.

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