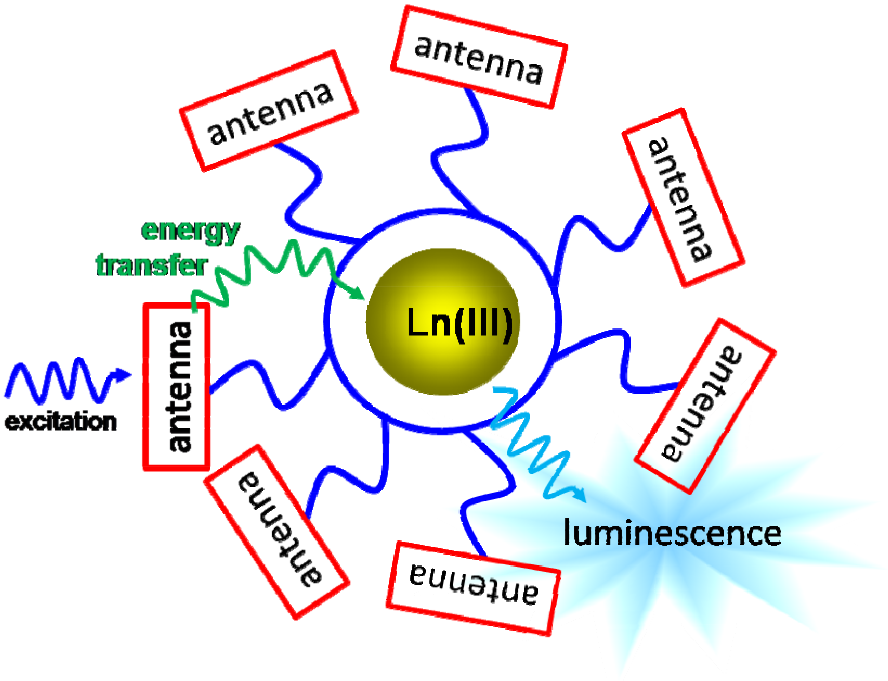
Lanthanide Dendrimer-Polymer Hybrids (Ln-Dendri-Pols)

Coordinator: Prof. Paola Ceroni, Fellow: Dr. Evan Guy Moore

Ln(III) metal ions (Ln = Eu, Tb) exhibit unique luminescent properties, which include long luminescence lifetimes, very sharp emission bands, and resistance to photo-bleaching. However, direct excitation of lanthanide ions is inefficient because of the forbidden nature of their electronic transitions. Therefore, coordinating organic or inorganic chromophores are usually exploited to sensitize their luminescence (antenna effect). The resulting complexes have become increasingly useful in biological assays, specifically due to their luminescent properties. However, the overall quantum yields (ratio between the number of emitted photons and the number of absorbed photons) of commercially available compounds are far from ideal, and are typically less than 5-10%. Furthermore, the overall utility of detecting a given Ln(III) complex also depends on its relative 'brightness', defined as the product of the quantum yield and the molar absorptivity of the complex, as measured by its molar extinction coefficient at a given excitation wavelength.

The Ln-Dendri-Pols project (see logo attached) was aimed at synthesising a series of novel molecules in which a core Ln(III) complex was appended to multiple absorbing chromophores (usually called antenna units), inserted in a polymeric and/or dendritic structure, in order to improve their overall performance. A pictorial representation is shown in the figure below and on the project website http://www.ciam.unibo.it/ln-dendri-pols.



Dendrimers are organic molecules comprising a central 'core' surrounded by regular outstretched 'branches' similar to those of a tree. As a result of this form, they can offer particular advantages for the sensitization of luminescent lanthanide cations when the metal centre is placed at the core. Multiple generation dendritic structures provide an ideal method to protect the metal from solvent interactions. In addition, the incorporation of multiple light harvesting antennae as chromophores in the dendrimer can function to increase the maximum number of photons harvested. ‘Star-shaped’ polymers are less ordered compared to dendrimers, but they offer the advantage of a less demanding synthetic methodology. In particular, in this project controlled/living radical polymerisation such as the Reversible Addition Fragmentation chain Transfer (RAFT) technique was used as an effective way of obtaining well defined polymers with specific architectures.

A series of Ln(III) complexes with Ln = Eu, Tb, Nd, and Yb were synthesised and their photophysical properties have been evaluated. It was determined that the dianion of pyrazine-2,6-dicarboxylic acid is a good ligand for Ln(III) and a particularly efficient sensitiser for Eu(III) based emission (total emission quantum yield ~ 62% in CH_3CN).

Having identified several highly emissive core Ln(III) complexes, synthetic modifications of several of the organic ligands were undertaken in order to introduce functional groups suitable for living radical polymerisation using the RAFT process. A series of polymers with ancillary poly-(2-naphthalene) (‘nap’) chromophores, chosen as an additional light harvester, were successfully prepared and fully characterised. The photophysical properties of the hybrid Ln(III) polymer systems prepared demonstrate significantly improved absorbance properties due to the covalently attached ancillary chromophores and a high efficiency of sensitisation of lanthanide emission. However, after a limiting number of chromophores are appended (which is chromophore/Ln(III) core complex dependent), the improvement in complex ‘brightness’ declines as a result of diminished energy transfer efficiency from distant ancillary chromophores toward the Ln(III) complex core.

Our results have demonstrated the incorporation of additional secondary chromophores to increase the overall absorbance of Ln(III) based complexes is a viable approach for improving their photophysical performance, in terms of their overall brightness. This project led to an improved fundamental understanding of the photophysical processes involved in sensitised lanthanide luminescence.

The socio-economic impacts of the project derive from the potential applications of the investigated compounds as luminescent labels of biologically relevant molecules and in high throughput screening assays in drug development, where luminescence signals are used to detect interactions between pharmaceuticals and other important biomolecules.