

A new look at the ligand-lanthanide energy transfer pathways

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Single Lanthanide (Ln^{3+}) compounds are of great interest due to their special luminescence properties and their various applications for technological purposes. Ln^{3+} luminescence is associated with transitions within the $4f$ subshell. Due to the small value of the molar absorption coefficient, Ln^{3+} emission requires sensitization. One way involves the so-called antenna effect, i.e. the use of organic ligands with strong absorption, which transfer excitation energy to the excited levels of Ln^{3+} via intramolecular non-radiative energy transfer (IET). We provide insights into the different pathways and mechanisms of IET for two series of Ln^{3+} coordination compounds with N-phosphorylated sulfonyl- and carboxamides, which were designed as UV to Vis converters. We will show that the pathways and mechanisms of IET are also affected by slight changes in the crystal structure of the chelates in the second coordination sphere, such as counter ions or solvent molecules. We will analyze the influence of the ligand-to-Ln charge transfer state (LMCT), which, by depopulating the ligand singlet state (S_1), dramatically reduces the sensitization efficiency of the Eu^{3+} emission while changing the dominant mechanism of IET. The key role of the 7F_5 state of Tb^{3+} in IET will be proved, as well as the dominance of IET through the S_1 state for Tb^{3+} coordination compounds with 2,2'-bipyridine and 1,10-phenanthroline as the co-ligand. We will also demonstrate how proper ligand design, combined with stiffening of the crystal structure of the coordination compound by introducing alkali metal cations into the first coordination sphere, affects IET efficiency and the intensity of sensitized emission. The above examples provide new insights into the sensitization processes of Tb^{3+} and Eu^{3+} coordination compounds:

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