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### **Thesis Title**

## **Photoluminescence and Optical Absorption Studies of Trivalent Lanthanide Complexes Based on $\beta$ -diketone and Hetero-Cyclic Amines**

The research work is based on the synthesis, characterization, photophysical and optical absorption studies of trivalent lanthanide complexes. The thesis comprises of seven chapters. Chapter-1 is the introductory chapter, explains various aspects of the work, which covers a detailed history of the synthesis of trivalent lanthanide complexes. In particular a detailed literature review on lanthanide complexes based on  $\beta$ -diketones and heterocyclic amines is presented. The emphasis of the literature survey is to give broader overview of the 4f-4f absorption and photoluminescence properties of these complexes. Finally, the chapter is concluded by defining the objectives of the research work. Chapter-2 deals with the synthesis and characterization of dinuclear complexes of  $\text{La}^{3+}$ ,  $\text{Lu}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ , based on 6,6,7,7,8,8,8,-heptafluoro-2,2-dimethyl-3,5-octadione (Hfod) and bis-chelating 2,3-bis(2-pyridyl) pyrazine (bpp). The photoluminescence of  $\text{Pr}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ , complexes is studied in different solvents, solid state and of polymer based thin hybrid films. Chapter-3 discusses the Single crystal and Sparkle/PM7 structures and photophysical parameters of dinuclear,  $[\text{Ln}(\text{fod})_3(\mu\text{-bpp})\text{Ln}(\text{fod})_3]$  complexes of Pr, Sm, Eu and Tb. Chapter-4 reports the stoichiometrically controlled synthesis of seven- and eight-coordinate complexes of type  $[\text{Ln}(\text{fod})_3(\text{im})]$  and  $[\text{Ln}(\text{fod})_3(\text{im})_2]$  ( $\text{Ln} = \text{La}, \text{Sm}, \text{Eu}$  and  $\text{Tb}$ , fod is the anion of 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (Hfod) and im is imidazole). The steady state and time resolved spectra of the complexes are investigated in solutions, solid state and of doped PMMA thin hybrid films to study the effect of coordination geometry on the luminescence properties of a lanthanide ion. A prominent distinction of the luminescent properties is observed between the two types of the complexes. It has been shown that the site symmetry could have profound effects on the luminescence properties (emission intensity, radiative

lifetime, quantum yield and stark splitting of the emission transitions) of a lanthanide complex. Chapter-5 of the thesis includes the synthesis of two sets of seven-coordinate lanthanide complexes of type  $[\text{Ln}(\text{fod})_3(\text{pz})]$  and  $[\text{Ln}(\text{acac})_3(\text{pz})]$  ( $\text{Ln} = \text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ ). These complexes are thoroughly characterized by elemental and thermal analysis, infrared and  $^1\text{H}$  NMR spectroscopy. A comparative photoluminescence study of the two sets of complexes,  $[\text{Ln}(\text{fod})_3(\text{pz})]$  and  $[\text{Ln}(\text{acac})_3(\text{pz})]$  is carried out in solutions, solid and PMMA doped thin films. The primary ligands, fod and acac are important in shaping the luminescence properties. Chapter-6 includes the synthesis of four heteroleptic neodymium complexes,  $[\text{Nd}(\text{fod})_3(\text{phen})]$  (**Nd-1**),  $[\text{Nd}(\text{fod})_3(\text{bpy})]$  (**Nd-2**),  $[\text{Nd}(\text{fod})_3(\text{im})_2]$  (**Nd-3**) and  $[\text{Nd}(\text{fod})_3(\mu\text{-bpp})\text{Nd}(\text{fod})_3]$  (**Nd-4**) (fod is the anion of 6,6,7,7,8,8,8- heptafluoro-2,2-dimethyl-3,5-octanedione (Hfod), phen is 1,10-phenanthroline, bpy is 2,2'-bipyridine, im is imidazole and bpp is 2,3-bis(2-pyridyl) pyrazine). These complexes were thoroughly characterized by elemental analysis, TGA, DTA,  $^1\text{H}$  NMR and infra-red spectroscopy. It has been shown that the ancillary ligands are efficient in enhancing luminescence in the complexes and the C-H vibrational quenching of the excited state of  $\text{Nd}^{3+}$  can effectively be reduced by using fluorinated ligands in the coordination sphere. Chapter-7 presents the synthesis of six ytterbium complexes using fluorinated  $\beta$ -diketone (fod) as main chromophore along with the different heterocyclic amines as ancillary ligands. These complexes are thoroughly characterized by various experimental techniques. Upon the excitation in the ultraviolet region of the spectrum, the ytterbium ion of the complexes emits in near IR region with the maxima at 980 nm. The solid-state emission shows more prominent stark splitting of the emission peak than in the solutions. The role of lowest triplet state of the ligand on the emission properties of the ytterbium ion reveals that there is no direct correlation of the energy gap between the triplet state of the ancillary ligand and the emitting level of the ytterbium ion in determining the efficiency of the emission and the lifetime of the excited state of the complexes.