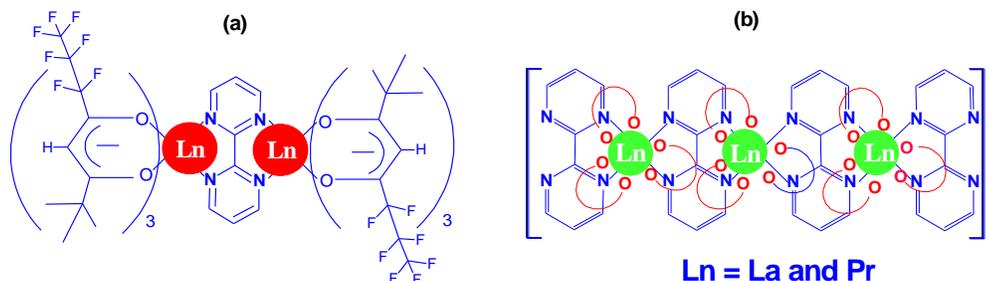


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 Title of the PhD thesis : *Photoluminescence, 4f-4f Absorption and Hypersensitivity in Mono- and Dinuclear Lanthanide Complexes*

## Abstract of the thesis

The luminescent lanthanide complexes are highly sought after for variety of applications ranging from display devices and sensors to various biological applications such as bio-probes. This PhD work deals with the design and synthesis of a variety of new luminescent dinuclear lanthanide complexes which are thermally stable and highly volatile and potentially excellent materials for the fabrication light emitting devices. The visible light photoluminescence, 4f-4f absorption and hypersensitivity of these complexes are studied along with know mononuclear analogues in different environments. Three different types of dinuclear lanthanide complexes are synthesized based on a bulky fluorinated  $\beta$ -diketone ligand, **6,6,6,7,7,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione** (Hfod) and two different bridging ligands, **2,2'-bipyrimidine** (bpm) and **pyrazine** (pyz).

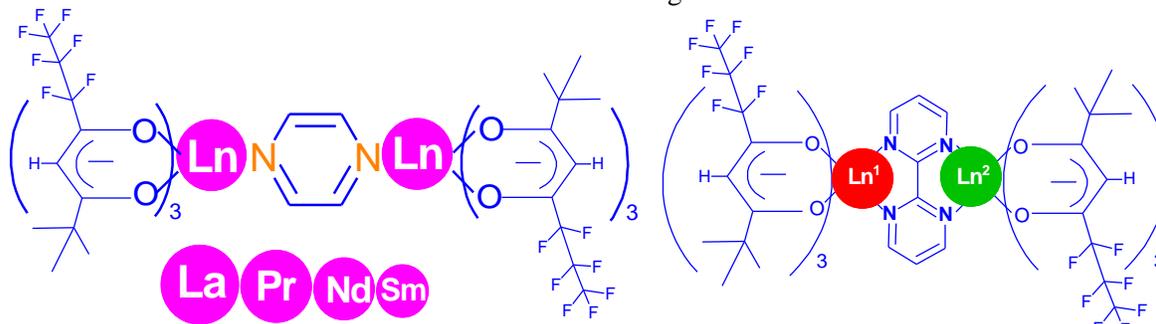
In the first strategy (Chapter 2), the bpm (a bis-diimine ligand) has been used as connecting ligand to synthesize an extended series new homodinuclear lanthanide complexes of the form  $[\text{Ln}_2(\text{fod})_6(\mu\text{-bpm})]$  ( $\text{Ln} = \text{Nd-Lu}$ ), Chart 1a. Amazingly, with larger lanthanides (La and Pr) coordination polymers of the type  $[\text{Ln}(\text{fod})_3(\text{bpm})]_n$  were isolated instead of expected dinuclear complexes (Chart 1b).



**Ln = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu**

**Chart 1** (a) Chemical structure of the new homodinuclear lanthanide complexes of the type  $[\text{Ln}_2(\text{fod})_6(\mu\text{-bpm})]$ ;  
 (b) Chemical structure of the lanthanide coordination polymers of the type  $[\text{Ln}(\text{fod})_3(\text{bpm})]_n$

These complexes are thermally more stable over their mononuclear analogues. The solution structures of the complexes are thoroughly investigated by NMR. The paramagnetic shifts are dipolar in origin. The 4f-4f absorption spectra of  $[\text{Nd}_2(\text{fod})_6(\mu\text{-bpm})]$  is investigated in a series of solvents. Due to the presence of two  $\text{Nd}^{\text{III}}$  centres, the oscillator strength of the f-f transitions of this complex is twofold higher than the corresponding mononuclear analogues. The remarkable sensitivity of the  ${}^4\text{G}_{5/2}, {}^2\text{G}_{7/2} \leftarrow {}^4\text{I}_{9/2}$  hypersensitive transition of  $\text{Nd}^{\text{III}}$  in different environments is investigated. The typical sensitized red, pink, green and yellow luminescence of  $\text{Pr}^{\text{III}}/\text{Eu}^{\text{III}}$ ,  $\text{Sm}^{\text{III}}$ ,  $\text{Tb}^{\text{III}}$  and  $\text{Dy}^{\text{III}}$  complexes, respectively, is observed upon excitation of the coordinated ligands in chloroform. The work emphasizes that the combination of fod and bpm is most effective for the sensitization of red  $\text{Eu}^{\text{III}}$  luminescence and least effective for the sensitization of green  $\text{Tb}^{\text{III}}$  luminescence.



**Chart 2** Chemical structure of the homodinuclear lanthanide complexes of the type  $[\text{Ln}_2(\text{fod})_6(\mu\text{-pyz})]$

**Chart 3** Chemical structure of the hetero dilanthanide complexes of the form  $[\text{Ln}^1\text{Ln}^2(\text{fod})_6(\mu\text{-bpm})]$

In another strategy (Chapter 3), pyz, a simplest non-chelating bridging ligand is employed to synthesize new homodinuclear complexes,  $[\text{Ln}_2(\text{fod})_6(\mu\text{-pyz})]$  (Ln = La, Pr, Nd and Sm), *first examples of the type* (Chart 2). The rest of the lanthanides, Eu-Lu give known mononuclear complexes. The solution structure of the complexes is investigated by NMR. The oscillator strength of the  ${}^4\text{G}_{5/2}, {}^2\text{G}_{7/2} \leftarrow {}^4\text{I}_{9/2}$  hypersensitive transition of neodymium complex is comparable to its homodinuclear analogue,  $[\text{Nd}_2(\text{fod})_6(\mu\text{-bpm})]$ . The band shape of this complex is consistent with the band shape of seven-coordinate complex. Typical sensitized pink luminescence of samarium is observed and thoroughly discussed.

In the third strategy (Chapter 4), bpm is employed to synthesize eight new hetero dilanthanide complexes, *also first examples of the type*. These complexes of general composition  $[\text{Ln}^1\text{Ln}^2(\text{fod})_6(\mu\text{-bpm})]$  (Chart 3) are synthesized by reacting  $\text{Ln}^1(\text{fod})_3$  and  $\text{Ln}^2(\text{fod})_3$  sequentially with bpm in 1:1:1 ratio in ethanol. The NMR of the hetero dilanthanide complexes displays more than one resonance for equivalent protons due to the presence of two different  $\text{Ln}^{\text{III}}$  ions. The 4f-4f absorption spectra display transitions of both the  $\text{Ln}^{\text{III}}$  ions in the complex. The oscillator strength of the hypersensitive transitions is comparable to their mononuclear analogues which confirm that two different  $\text{Ln}^{\text{III}}$  ions are present in 1:1 ratio. The luminescence spectrum of Eu-Tb complex displays intense red luminescence and it is remarkably found that a unique  $\text{Tb}^{\text{III}} \rightarrow \text{Eu}^{\text{III}}$  energy transfer takes place in this complex. The luminescence of Nd-Sm and Dy-Ho complexes are also investigated.

In chapter 5, the 4f-4f absorption properties of three mono- and dinuclear holmium complexes,  $[\text{Ho}_2(\text{fod})_6(\mu\text{-bpm})]$ ,  $[\text{Ho}(\text{fod})_3(\text{phen})]$  and  $[\text{Ho}(\text{fod})_3(\text{bpy})]$  and their **erbium analogues** are studied in a series of non-coordinating and coordinating solvents. The effect of environment on the oscillator strength and band shape of the  ${}^5\text{G}_6 \leftarrow {}^5\text{I}_8$  hypersensitive transition of  $\text{Ho}^{\text{III}}$  and  ${}^4\text{G}_{11/2} \leftarrow {}^4\text{I}_{11/2}$  and  ${}^2\text{H}_{11/2} \leftarrow {}^4\text{I}_{15/2}$  hypersensitive transitions of  $\text{Er}^{\text{III}}$  are thoroughly investigated and discussed. The study reveals that phen is a strong ancillary ligand and  $[\text{Ln}(\text{fod})_3(\text{phen})]$  (Ln =  $\text{Ho}^{\text{III}}$  and  $\text{Er}^{\text{III}}$ ) complexes remain stable in all solvents except DMSO. It is also pointed out that DMSO invades the inner coordination sphere of the complexes by replacing heterocyclic ligands to form similar species,  $[\text{Ln}(\text{fod})_3(\text{DMSO})_2]$ , for all the complexes.

In chapter 6, red luminescence of mono- and dinuclear europium complexes:  $[\text{Eu}_2(\text{fod})_6(\mu\text{-bpm})]$ ,  $[\text{Eu}(\text{fod})_3(\text{phen})]$  and  $[\text{Eu}(\text{fod})_3(\text{bpy})]$  and their green emitting **terbium analogues** are studied in a series of non-coordinating and coordinating solvents. The effects of environment on the intensity and band shape of the luminescence spectra are investigated. The study reveals that ancillary ligands play a great role as co-sensitizers. The rigid planar phen is found as best ligand to sensitize both  $\text{Eu}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$  luminescence.

In chapter 7, the 4f-4f absorption and luminescence of three  $\text{Pr}^{\text{III}}$  complexes:  $[\text{Pr}(\text{fod})_3(\text{bpy})]$ ,  $[\text{Pr}(\text{fod})_3(\text{phen})]$  and  $[\text{Pr}(\text{fod})_3(\text{bpm})]$ , in the visible region in a series of coordinating and non-coordinating solvents are investigated and remarkably correlated. Both f-f absorption and luminescence is found sensitive to the environment around  $\text{Pr}^{\text{III}}$ . The combined photophysical studies demonstrate that entry of the solvent molecule(s) to inner coordination sphere (complex-solvent interaction) is governed by the structure and basicity of the ancillary heterocyclic ligand attached to the  $\text{Pr}^{\text{III}}$  complex. The strong donor DMSO transforms the three complexes into a similar species,  $[\text{Ln}(\text{fod})_3(\text{DMSO})_2]$ , which results in similar electronic absorption and emission properties of the complexes in this solvent. The results of this chapter demonstrates that highly luminescent praseodymium chelates can be designed with ligands containing suitable energy levels and their emission properties can be further modulated through suitable ancillary ligands and donor solvents, thus opening perspectives for applications in Pr-based electroluminescent devices and luminescent probes.

Finally in chapter 8, bright pink luminescence of  $[\text{Sm}_2(\text{fod})_6(\mu\text{-bpm})]$  along with mononuclear analogues,  $\text{Sm}(\text{fod})_3$ ,  $[\text{Sm}(\text{fod})_3(\text{bpy})]$ ,  $[\text{Sm}(\text{fod})_3(\text{phen})]$  are investigated in a series of solvents. The study reveals that the addition of ancillary antenna unit to the coordinatively unsaturated  $\text{Sm}(\text{fod})_3$  chelate significantly enhances the luminescence intensity of  $\text{Sm}^{\text{III}}$  in a non-coordinating solvent while the intensity of the complexes show great sensitivity towards the type of the auxiliary antenna unit (co-sensitizer) attached to  $\text{Sm}^{\text{III}}$  chelate. The phen is the best co-sensitizer as compared to bpy and bpm. In potentially coordinating solvents, a remarkable sensitivity of the luminescence intensity and stark splitting is observed which is dependent both on the type of the ancillary antenna unit attached to the  $\text{Sm}^{\text{III}}$  ion and the type solvent environment. It is pointed out that pyridine competes for coordination and eventually replaces the weaker bpy and bpm ancillary antenna units from  $[\text{Sm}(\text{fod})_3(\text{bpy})]$  and  $[\text{Sm}_2(\text{fod})_6(\mu\text{-bpm})]$ , respectively, and transforms these complexes into similar species along with  $\text{Sm}(\text{fod})_3$  in this solvent while phen is a strong ligand and is not displaced by pyridine. In strong donor DMSO, all the ancillary units, phen, bpy and bpm are replaced from the complexes to give a similar species  $[\text{Sm}(\text{fod})_3(\text{DMSO})_2]$  in solution.

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