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Title: Photoluminescence, Optical Absorption and ^{1}H NMR Studies of Fluorinated and Non-Fluorinated 2, 4–Pentanedione Complexes of Trivalent Lanthanides. The mechanism of Energy Transfer in Europium(III) Complexes.

Abstract

The trivalent lanthanide complexes are highly sought after for a variety of applications ranging from material sciences to biological applications **(Chapter 1**). The Ph.D. thesis work deals with the design and synthesis of fluorinated and non-fluorinated 2, 4-pentanedione complexes of trivalent lanthanides.'which are thermally stable and highly volatile and potentially excellent candidates for the applications in optoelectronic devices.The^{1}H NMR of the diamagnetic and paramagnetic complexes were studied. The optical absorption of the complexes of praseodymium, neodymium, holmium and erbium is discussed. The photoluminescence of Sm(III), Eu(III), Tb(III) and Dy(III) complexes are investigated and discussed. The Ph.D. thesis work has been divided into following chapters.

In first the strategy **(Chapter 2)**, acetylacetone (acac) and pyrazine (pyz) were chosen as ligands to form complexes with Ln(III) ions. The synthesis, characterization and NMR study of the mononuclear complexes of the type [Ln(acac)$_3$(pyz)$_2$] (Ln = La, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm and Yb) were the focus of this chapter. The complexes are thermally stable. The NMR spectra of the complexes exhibit four resonances in the intensity ratio of 18:3:4:4; of the four resonances two are due to acetylacetone (methyl and methine) and two are due to pyrazine moieties [H (1) and H(2)]. This indicates that β-diketone to pyz ratio is 21 : 8 in the eight coordinate complexes. This substantiates the presence of two pyz units in the eight coordinate complexes, besides three units of acac. The observed paramagnetic shift in the NMR spectra of the paramagnetic complexes is dipolar in nature. The huge upfield and downfield shifts are induced by the heavy paramagnetic lanthanides.

In second the strategy **(Chapter 3)**, we have used fluorinated β-diketones of trifluoroacetylacetone and hexafluoroacetylacetone, as primary ligands and heterocyclic amines- 4,4′-bipyridyl (4, 4′-bpy); 2-(1H-Imidazol-2-yl) pyridine (impy) and 2,3-bis(2-pyridyl)-pyrazine (bpp), as ancillary ligands. Air and moisture stable seven-coordinate dinuclear complexes of the type [(tfaa)$_3$Ln(μ-4,4′-bpy)Ln(tfaa)$_3$], eight-coordinate complexes of the type [Ln(hfaa)$_3$(bpp)] and ten-coordinate complexes of the type [Ln(hfaa)$_3$(impy)$_2$] were synthesized and thoroughly characterized. The complexes are thermally stable. The NMR spectra show heavier lanthanide complexes exhibit large upfield and downfield shifts. The chemical shifts noted for [(tfaa)$_3$Tb(μ-4,4′-bpy)Tb(tfaa)$_3$] is huge covering the chemical shift range of about 291.59 ppm (from – 159.62 to +131.97 ppm). The shift of the methine resonance in opposite direction to H(2) reveals (a) that the paramagnetic shift in these complexes is dominated by dipolar interaction and (b) the importance of geometric factor ($3\cos^2\theta-1$) in changing the sign of the chemical shift.

In the third strategy **(Chapter 4)**, the 4f-4f absorption studies of [Ln(acac)$_3$(pyz)$_2$] (**1**); [(tfaa)$_3$Ln(μ-4,4′-bpy)Ln(tfaa)$_3$] (**2**); and [Ln(hfaa)$_3$(bpp)] (**3**) (Ln = Pr, Nd, Ho and Er), in chloroform were studied and discussed. The effect of changing the environment (ligands) around the Ln(III) ions on the oscillator strength and the band shape of the hypersensitive as well as non-hypersensitive transitions of the complexes were discussed. The neodymium complexes display distinctively different band shapes for $^{4}G_{5/2}$, $^{2}G_{7/2} \leftarrow {}^{4}I_{9/2}$ transition in eight-coordinate complexes of (**1**) and (**2**), and seven-coordinate complex (**3**). This feature is useful for determining the geometry of Nd(III) complexes. The oscillator strength of the hypersensitive transitions of the Nd(III) complex (**3**) is two-fold higher than the mononuclear analogues indicating the presence of two Ln(III) centers in the complex and the band shape

of Nd(III) complex is similar to characteristic seven-coordinate β-diketonate complexes. Among the complexes studied, the oscillator strength of the hypersensitive transitions of the tfaa and hfaa complexes of Nd(III), Ho(III) and Er(III) are much higher than the acac complexes. It reflects that higher polarizability is observed in fluorine containing ligands.

In the fourth strategy **(Chapter 5)**, the photoluminescence and colour investigations of the following samarium and europium complexes is described and discussed: $[Sm(acac)_3(pyz)_2]$ (**1**); $[Sm(hfaa)_3(impy)_2]$ (**2**); $[Sm(hfaa)_3(bpp)]$ (**3**); $[(tfaa)_3Sm(\mu\text{-}4,4'\text{-}bpy)Sm(tfaa)_3]$ (**4**); $[Eu(acac)_3(pyz)_2]$ (**5**);$[Eu(hfaa)_3(impy)_2]$ (**6**); $[Eu(hfaa)_3(bpp)]$ (**7**); $[(tfaa)_3Eu(\mu\text{-}4, 4'\text{-}bpy)Eu(tfaa)_3]$ (**8**).The complexes are highly quantum efficient. The emission intensity observed for the polymer based hybrid films is much higher than their bare analogues; these complexes exhibit phase controlled colour tuning property exploring their possible use as 'colour indicators.' In addition to variation in the excitation wavelength these complexes also show fine tuning of the emission colour upon changing a concentration in polymer substrates. These results are new. The emission colour variations are very simple and can be easily performed. The photostability of PMMA and PVA hybrid films of the complex (**1**), (**2**), (**5**) and (**6**) reveals that these complexes are quite stable and do not undergo photodegradation. Thus, encapsulation of the luminescent lanthanide complexes increases photostability. The simple synthesis method and excellent photophysical properties under normal conditions are promising for use of such materials in technological device applications and their simplified use as 'colour indicators.'

In the fifth strategy **(Chapter 6)**, In this chapter, the luminescence of terbium and dysprosium complexes: $[Tb(acac)_3(pyz)_2]$ (**1**); $[(tfaa)_3Tb(\mu\text{-}4,4'\text{-}bpy)Tb(tfaa)_3]$ (**2**); $[Tb(hfaa)_3(impy)_2]$ (**3**); $[Tb(hfaa)_3(bpp)]$ (**4**); $[Dy(acac)_3(pyz)_2]$ (**5**); $[(tfaa)_3Dy(\mu\text{-}4,4'\text{-}bpy)Dy(tfaa)_3]$ (**6**); $[Dy(hfaa)_3(impy)_2]$ (**7**); $[Dy(hfaa)_3(bpp)]$ (**8**) were studied. The complexes are quantum efficient. Among the β-diketones (acetylacetone, trifluoroacetylacetone and hexafluoroacetylacetone) used, acetylacetone is found to be more efficient for the sensitization of terbium than dysprosium. The complex (**1**) was doped in PMMA and its emission intensity was highest as compared to the bare analogue. The intensity ratio of $^5D_4 \rightarrow {}^7F_5$ and $^5D_4 \rightarrow {}^7F_6$ transitions for the terbium complex and their thin film are similar in magnitude (Tb(III) complex ~3.0 (solid); hybrid film 3.01). It reflects that the local symmetry around the Tb(III) in the complex is retained in the thin hybrid films irrespective of the chemical conditions imposed. The white light was obtained from complex (**5**) only while complexes (**6**), (**7**) and (**8**) could emit in the blue region. The excellent photoluminescence together with tunable emission colours under normal conditions is promising features for use of these materials in designing and developing optoelectronic devices. These complexes can also be used as 'white light or colour indicator diodes.'

In the sixth strategy (**Chapter 7**), this chapter deals with the energy transfer mechanism of $[Eu(acac)_3(pyz)_2]$ (**5**) and $[Eu(hfaa)_3(impy)_2]$ (**6**) in order to unravel supramolecular chemistry behind their structure stabilization. The geometry of the complexes (**5**) and (**6**) were fully optimized using Sparkle/PM3 and Sparkle/RM1 models, respectively. The resulting parameters were utilized for determining the photophysical parameters: Judd–Ofelt intensity parameters, radiative parameters and to understand the mechanism of intra-molecular energy transfer rates in Eu(III) complexes. A good agreement was found between the theoretical and experimental Judd-Ofelt intensity parameters of $[Eu(acac)_3(pyz)_2]$ and $[Eu(hfaa)_3(impy)_2]$. The intramolecular energy transfer rates (W_{ET} and W_{BT}), in the case of acac complex, demonstrate that the major energy transfer channels are triplet → $^5D_1$ contributes 74% and triplet → $^5D_0$ allows only 21%, while a very small contribution, less than 4%, comes from singlet → $^5D_4$ path to the total overall energy transfer. In Hfaa complex, the major energy transfer channels are triplet state → $^5D_1$ (contributes 55.33%) and triplet state → $^5D_0$ (contributes 44.65%). The exchange mechanism dominates during the energy transfer from the triplet state → $^5D_1$ level. The energy transfer follows the path $S_0 \rightarrow S_1 \rightarrow T_1 \rightarrow {}^5D_1 \rightarrow {}^5D_0 \rightarrow {}^7F_{0,4}$. The branching ratio calculated is highest for $^5D_0 \rightarrow {}^7F_2$ in both the cases. The stimulated emission cross (SEC) was found to be highest for $^5D_0 \rightarrow {}^7F_2$ transition in 7.5% w/w PMMA hybrid film. In conclusion, we can say that Sparkle model employed is proficient in determining the ground state geometries of the Eu(III) complexes.