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Investigations into Luminescent Properties of Sm(III), Eu(III), Tb(III) and Dy(III) Complexes of Some Schiff-base Ligands

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ABSTRACT

Luminescent properties of Sm(III), Eu(III), Tb(III) and Dy(III) complexes of three Schiff-base ligands *viz.*, H_2L^1, H_2L^2 and H_2L^3 [where H_2L^1 = *N,N'*-di-(4-decyloxysalicylidene)-1',4'-diaminobutane; H_2L^2 = *N,N'*-di-(4-decyloxysalicylidene)-2',6'-diaminopyridine; and H_2L^3 = *N,N'*-di-(4-decyloxysalicylidene)-1',3'-diaminobenzene] synthesized in our earlier work were investigated. The homo dinuclear lanthanide complexes were of the type, $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$. Luminescence analysis revealed that among the lanthanide complexes, only Sm(III) complex of H_2L^1 was found to have displayed characteristic metal-centered emission (solution state) whereas Sm(III), Eu(III) and Tb(III) complexes of H_2L^2 and Eu(III) and Tb(III) complexes of H_2L^3 exhibited ligand-centered emissions.

Key word: Ln(III) complexes, Luminescence, Schiff-base ligands, metal/ligand centered emissions

INTRODUCTION

Synthesis of luminescent lanthanide complexes has been of considerable interest because of their potential applications, such as fluorescent labeling reagents, imaging agents, and emitter materials in organic light-emitting diodes (OLEDs) (Diaz-Garcia *et al.* 2002; Frias *et al.* 2003; Bunzli & Piguet, 2005). Generally, complexes of Eu^{3+}, Sm^{3+}, Tb^{3+}, and Dy^{3+} are considered to have the brightest emission, but the luminescence efficiency of these complexes largely depends on the choice of organic ligands (Crosby *et al.* 1962). Since the forbidden *f-f* transitions make direct photoexcitation of lanthanide ions unfavored, the organic ligands function like an antenna by absorbing light and transferring this energy to the excited states of the central lanthanide ion. The excited lanthanide ion then undergoes radiative transitions to lower energy states resulting in characteristic multiple narrowband emissions. The commonly accepted mechanism of energy transfer from the organic ligand to the lanthanide ion is that of Crosby and Whan (Bunzli & Eliseeva, 2009) and generally occurs in three steps: (i) light harvesting by the host or ligands, (ii) energy transfer onto the metal ion, and (iii) metal-centered emission. A simplified scheme of these energy transfers is given in Fig. 1. The overall process is quite complex and involves several mechanisms and energy levels. Since the intensity of the emission (brightness) and choice of lanthanide (i.e., color of emission) both depend on the sensitizer, new sensitizing chromophores are highly sought after (Pope *et al.* 2004). Several nitrogen- and oxygen-donor ligands have been utilized in the sensitization of lanthanide luminescence (Cui *et al.* 2007; Zhou *et al.* 2008).

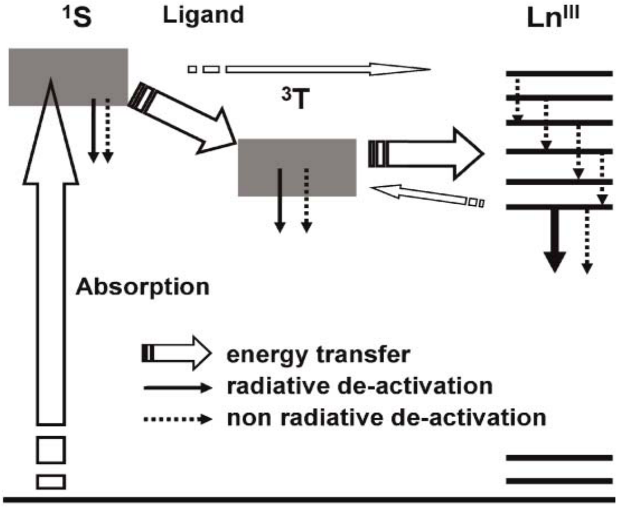


Fig. 1. Simplified diagram showing the main energy flow paths during sensitization of lanthanide luminescence via its surroundings (ligands) (Source: Bunzli & Eliseeva, 2009).

More recently, we performed a systematic study on lanthanide complexes consisting of the mesogenic Schiff-base ligands and we found an overall stoichiometry $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$ for all the complexes (Shakya *et al.* 2012a, 2012b, 2014). In continuation of our earlier work, a study on room temperature luminescent properties of the complexes of some Ln(III) ions (Ln = Sm, Eu, Tb and Dy) is reported in this paper. The effect of varying the neutral bi-dentate ligands on the luminescence behaviour of these complexes is investigated.

MATERIALS AND METHODS

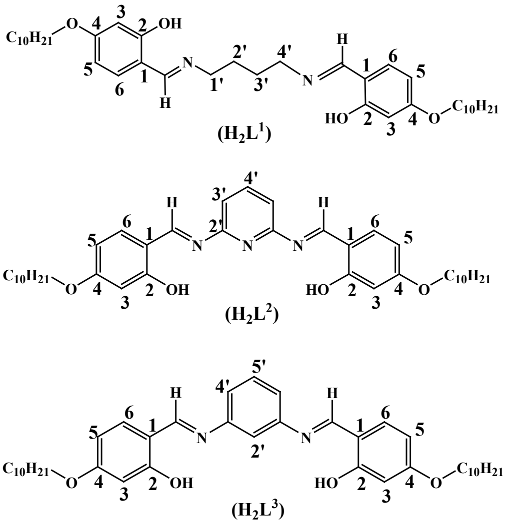
General Information

All operations were performed in an open atmosphere. The Schiff-base ligands (Fig. 2) *viz.*, *N,N'*-di-(4-decyloxysalicylidene)-1',4'-diaminobutane (H_2L^1), *N,N'*-di-(4-decyloxysalicylidene)-2',6'-diaminopyridine (H_2L^2) and *N,N'*-di-(4-decyloxysalicylidene)-1',3'-diaminobenzene (H_2L^3) were prepared by condensation of 4-decyloxysalicylaldehyde with different spacers such as 1,4-diaminobutane, 2,6-diaminopyridine and 1,3-diaminobenzene in absolute ethanol in presence of acetic acid as reported in our earlier work (Shakya *et al.* 2012a, 2012b & 2014). $Ln(NO_3)_3.6H_2O$ (Ln = Sm, Eu, Tb and Dy) were prepared by reactions of lanthanide oxide and nitric acid. All other chemicals were used as purchased. Infrared spectra were recorded on a JASCO FT/IR (model-5300) spectrophotometer in the 4000-400 cm^{-1} region using KBr pellets. Elemental (C, H, and N) analyses were performed on an Exeter Analyzer, Model CE-440 CHN. The metal contents of the complexes were determined by complexometric titrations against EDTA using xylenol orange as an indicator. Magnetic susceptibility measurements were made at room temperature on a Cahn-Faraday balance using $Hg[Co(NCS)_4]$ as the calibrant. Luminescence measurements were made in solution state (mixed solvent of $CHCl_3$/DMSO; 3:1, v/v) on a Perkin Elmer LS-45 luminescence spectrometer with a 10 nm slit width on both excitation and emission.

Synthesis of Ln(III) complexes

All complexes (Fig. 2) were synthesized by direct addition of the hydrated lanthanide nitrate $Ln(NO)_3.xH_2O$ (Ln = Sm, Eu, Tb and Dy) in THF solution to a stirred THF solution of the Schiff-base ligands *viz.*, H_2L^1, H_2L^2 and H_2L^3 as reported in our earlier work (Shakya *et al.* 2012a, 2012b & 2014). For instance, a solution of $Sm(NO_3)_3.6H_2O$ (0.89 g, 2.0 mmol in 20 mL) in THF was added dropwise to a stirred THF solution of the ligand, H_2L^1 (1.83 g, 3.0 mmol in 30 mL). After addition, the solution was left under magnetic stirring for ~3 h at room temperature when a light yellow solid product separated out which was filtered, washed repeatedly with cold methanol and dried over fused $CaCl_2$. Yield: 70% (1.75g). Elemental analysis calculated for $Sm_2C_{114}H_{180}N_{12}O_{30}$ (*Mw* =2499.43): C, 54.78%; H, 7.26%; and N, 6.72%; found: C, 54.74%; H, 7.28%; and N, 6.74%.

All the other complexes of Eu(III), Tb(III) and Dy(III) ions were obtained via the same synthetic method as described above.



$$3\ H_2L^n + 2\ Ln(NO_3)_3.\ xH_2O \xrightarrow[\text{Stir \& reflux, ~3 h.}]{\text{THF}} [Ln_2(L^nH_2)_3(NO_3)_4](NO_3)_2 + xH_2O$$

Where,
n = 1, 2 or 3
Ln = Sm, Eu, Tb and Dy

Fig. 2. Schiff-base ligands and Ln(III) complexes discussed in this paper.

RESULTS AND DISCUSSION

Nature of the Sm(III), Eu(III), Tb(III) and Dy(III) complexes

The Schiff-base ligands *viz.*, H_2L^1, H_2L^2 and H_2L^3 were obtained by condensing 4-decyloxysalicyldehyde with different spacers such as 1,4-diaminobutane, 2,6-diaminopyridine and 1,3-diaminobenzene (Fig. 2). Reaction of excess $Ln(NO)_3.xH_2O$ with the Schiff-base ligands in absolute ethanol then led to the formation of the complexes with the general formula, $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$ indicating 2:3 metal to ligand stoichiometry. The nitrate groups were found to be present both within as well as outside the coordination sphere; the number of the ionic species was implied by the molar conductance data showing 2:1 electrolytic behavior. Besides, it has been shown earlier by IR and NMR studies that in each case of the nitrate complexes, coordination occurs through the phenol oxygen only, the ligand being present in a zwitter-ionic form. The four nitrate counter-ions coordinate in a bidentate fashion, bringing the coordination number of the lanthanide ion to seven and the polyhedron being possibly distorted mono-capped octahedron.

Luminescent properties of the complexes

Luminescent emission spectra (with the excitation and emission slit widths of 10.0 nm) of the Sm(III), Eu(III), Tb(III) and Dy(III) complexes of the Schiff-base ligands, *viz.,* H_2L^1, H_2L^2, and H_2L^3 in a mixed solvent of $CHCl_3$/

DMSO (3:1, v/v; 1.0 x 10^{-4} mol L^{-1}) were recorded at medium PMT voltage. Under identical experimental conditions, the luminescent characteristics of all the above complexes under discussion are listed in Table 1 while the corresponding spectra of the same are shown in Figs. 3-5.

Table 1. Luminescence data of the complexes

S. No.	Complexes	Slit width (nm)	λ_{ex} (nm)	λ_{em} (nm)	^{a}FI	Assignment
1.	$[Sm_2(L^1H_2)_3(NO_3)_4](NO_3)_2$	10	386	468, 560 598 , 644	28, 10 12, 7	$\pi - \pi^*$, $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$, $^4G_{5/2} \rightarrow {}^6H_{9/2}$
2.	$[Eu_2(L^1H_2)_3(NO_3)_4](NO_3)_2$	10	380	441	< 2	-
3.	$[Tb_2(L^1H_2)_3(NO_3)_4](NO_3)_2$	10	380	438	< 2	-
4.	$[Dy_2(L^1H_2)_3(NO_3)_4](NO_3)_2$	10	369	426	~2.5	-
5.	$[Sm_2(L^2H_2)_3(NO_3)_4](NO_3)_2$	10	380	436	<14	$\pi - \pi^*$
6.	$[Eu_2(L^2H_2)_3(NO_3)_4](NO_3)_2$	10	383	487	8	$\pi - \pi^*$
7.	$[Tb_2(L^2H_2)_3(NO_3)_4](NO_3)_2$	10	382	457	128	$\pi - \pi^*$
8.	$[Dy_2(L^2H_2)_3(NO_3)_4](NO_3)_2$	10	384	495	< 1	-
9.	$[Sm_2(L^3H_2)_3(NO_3)_4](NO_3)_2$	10	348	-	-	-
10.	$[Eu_2(L^3H_2)_3(NO_3)_4](NO_3)_2$	10	348	460	103	$\pi - \pi^*$
11.	$[Tb_2(L^3H_2)_3(NO_3)_4](NO_3)_2$	10	347	515	4	$\pi - \pi^*$
12.	$[Dy_2(L^3H_2)_3(NO_3)_4](NO_3)_2$	10	348	419	< 1	-

^{a} Fluorescence intensity

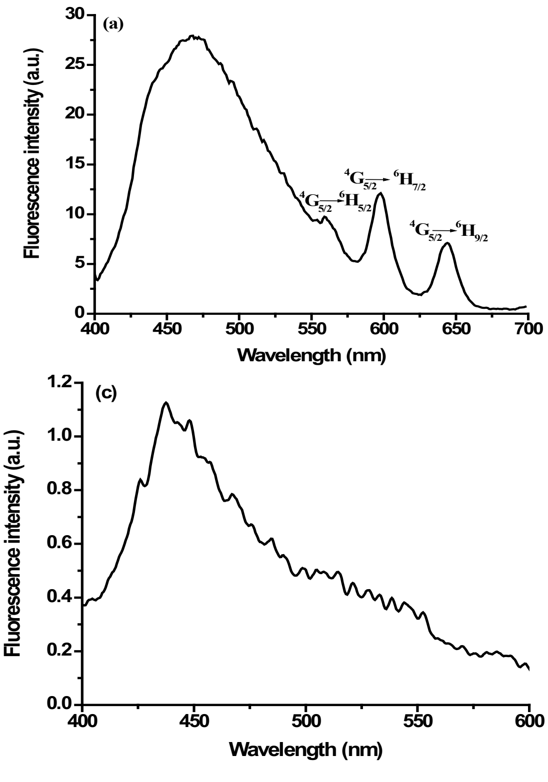


Fig. 3. Luminescent emission spectra of (a) Sm^{III}, (b) Eu^{III}, (c) Tb^{III} and (d) Dy^{III} complexes of H_2L^1.

Among the complexes of H_2L^1 studied, none of the complexes except Sm(III) under present discussion exhibits spectral bands characteristic of metal-centered emission [Fig. 3(a-d)]. The excitation of the Sm(III) complex at 386 nm leads to emission of Sm^{3+} with four typical emission bands [Fig. 3 (a)] at 468, 560, 598 and 644 nm due to π - π^* transitions of the ligand and $^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2) transitions (An *et al.* 2004, Yan *et al.* 2007). The ligand retains its emission at a shorter wavelength. Some absorbed energy was transferred to the central Sm(III) ions, emitting characteristic fluorescence of the Sm^{3+} ion. Among the emission bands, the band around 598 nm is attributed to the hypersensitive $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition in accordance with those already reported for some samarium coordination polymers (An *et al.* 2004; Song & Yan, 2005). The fluorescence of the Sm(III) complex indicates that the energy level of the triplet state of the ligand, H_2L^1 corresponded to the lowest excited state ($^4G_{5/2}$) level of Sm^{3+} ion. Apparently, one of the metal centered bands (560 nm) is found to be partially overlapped with the broad band of ligand emission. The Eu(III), Tb(III) and Dy(III) complexes exhibit very weak emissions and hence may be considered to be non-fluorescent in behaviour.

All the complexes of H_2L^2 are devoid of any spectral bands characteristic of metal-centered emission [Fig. 4(a-d)]. However, a broad emission band at 436 nm (excitation energy, λ_{ex} of 380 nm) observed in the Sm(III) complex [Fig. 4(a)] may be attributed to ligand-centered emission (Shi *et al.* 2009). Similarly, the Eu(III) complex also exhibits a non metal-centered broad emission [Fig. 4(b)] at 487 nm when excited at 383 nm, probably because of ligand emission (Zhang *et al.* 2009). Besides, an emission band with a relative fluorescence intensity of 124a.u. appearing at 457 nm (excitation energy, λ_{ex} of 382 nm) in the spectrum of Tb(III) complex [Fig. 4(c)] may be attributed to the ligand-centered emission (Yang & Wong, 2001). The Dy(III) complex is found to be non-fluorescent.

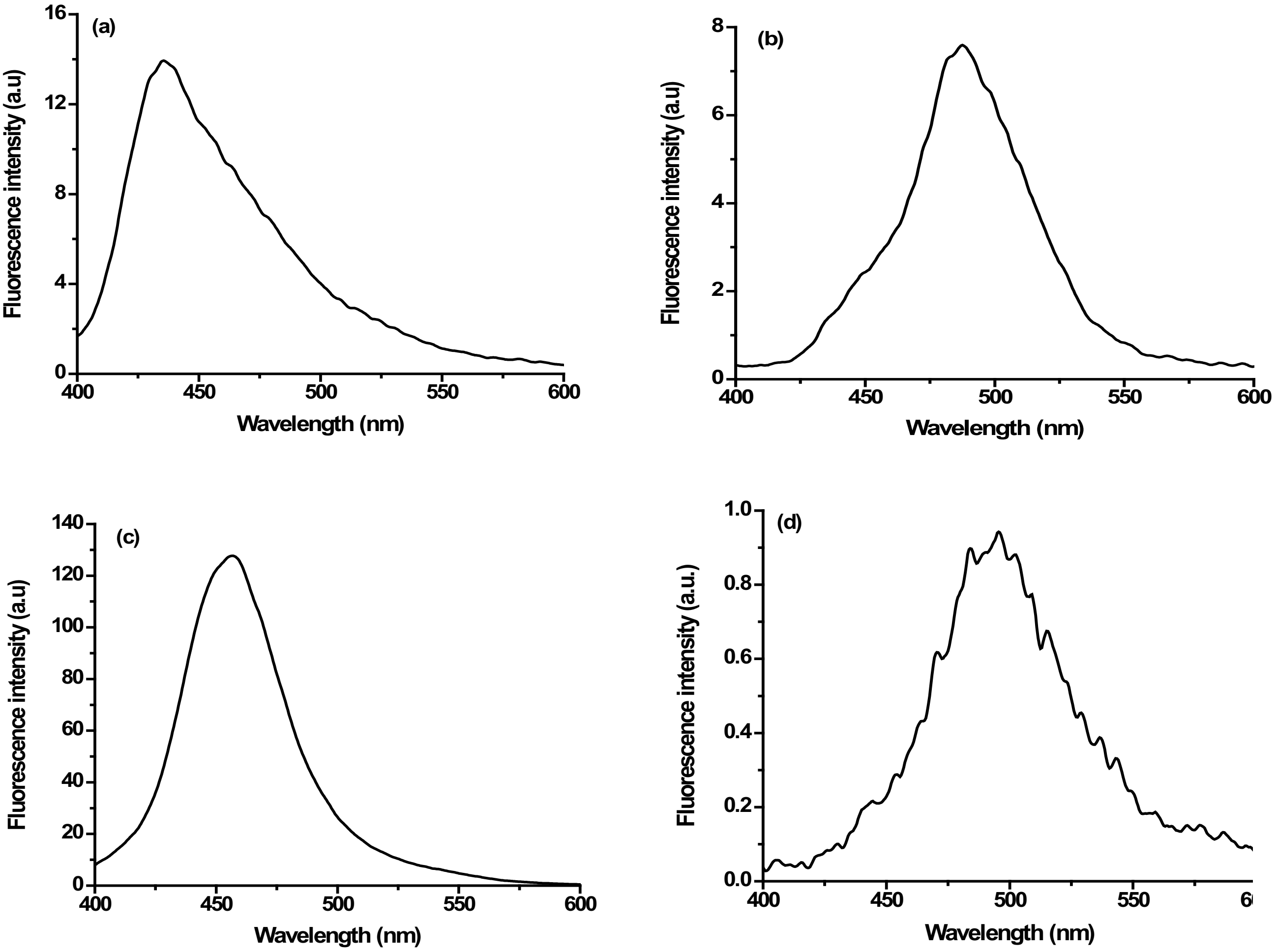


Fig. 4. Luminescent emission spectra of (a) Sm^{III}, (b) Eu^{III}, (c) Tb^{III} and (d) Dy^{III} complexes of H_2L^2.

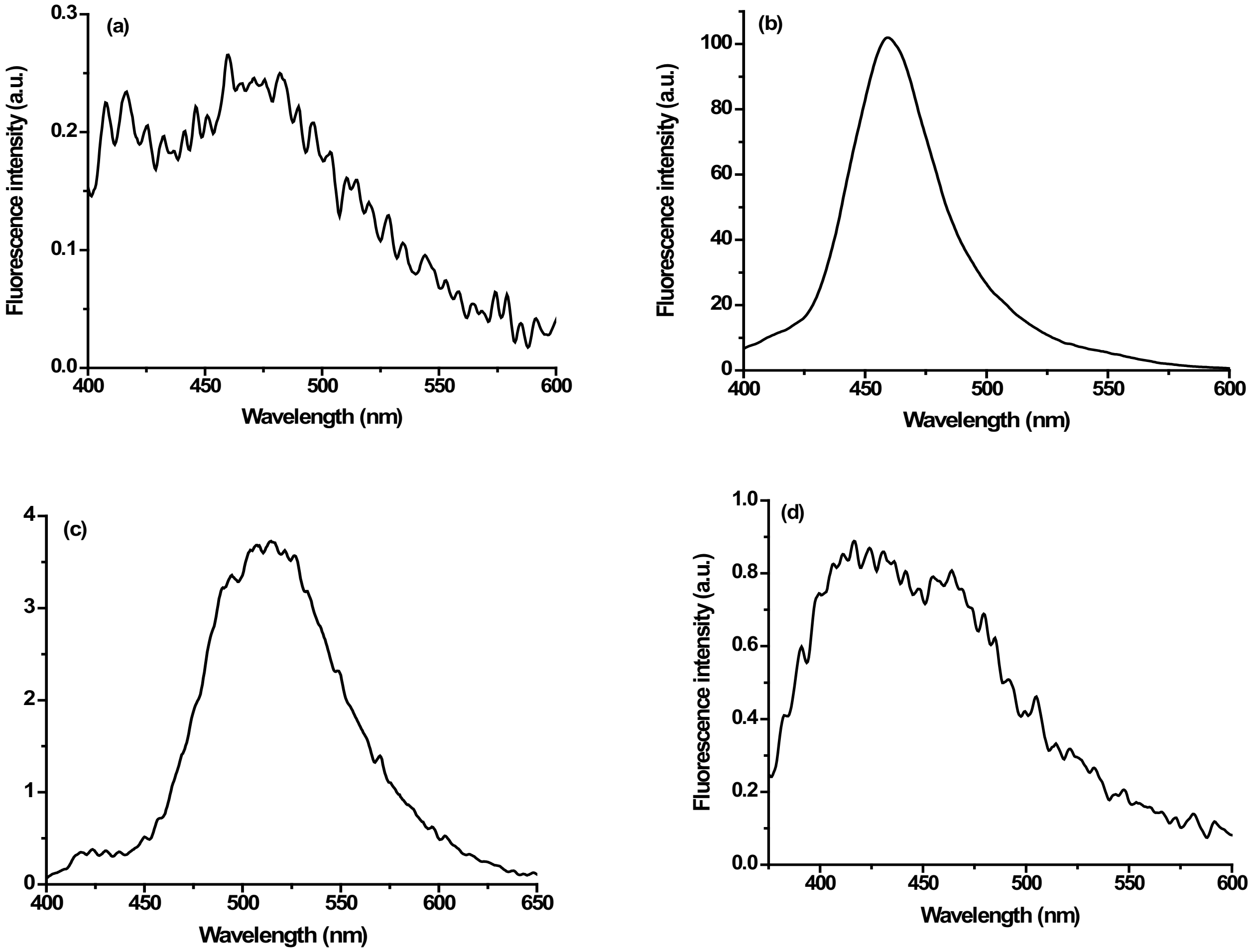


Fig. 5. Luminescent emission spectra of (a) Sm^{III}, (b) Eu^{III}, (c) Tb^{III} and (d) Dy^{III} complexes of H_2L^3.

Among the metal complexes of H_2L^3, the Eu(III) and Tb(III) complexes show broad emission bands respectively at 460 nm (excitation energy, λ_{ex} of 348 nm) and 515 nm (excitation energy, λ_{ex} of 347 nm) [Fig. 5(b&.c)]. However, both the emissions are non-metal centered and hence may be attributed to emissions from their respective ligands (Zhang *et al.* 2009, Yang & Wong, 2001). The Sm(III) and Dy(III) complexes [Fig. 5(a&.d)] may be considered to be non-fluorescent.

CONCLUSION

Due to the inherently weak luminescence of lanthanides, sensitization of their luminescence by organic ligands has been widely investigated. In this paper, the room temperature luminescence behaviour of Sm(III), Eu(III), Tb(III) and Dy(III) complexes of the Schiff-base ligands H_2L^1, H_2L^2 and H_2L^3 is reported. Among the metal complexes under investigation, the characteristic metal-centered luminescence (solution state) has been observed on complexation of H_2L^1 with Sm(III) ion only whereas Sm(III), Eu(III) and Tb(III) complexes of H_2L^2 and Eu(III) and Tb(III) complexes of H_2L^3 show ligand-centered emissions. Thus, it may be inferred that the ligand, H_2L^1 is likely to be a suitable organic chelator to absorb energy and transfer the same to Sm(III) ion. The suitability of the energy gap between the lowest excited ligand-localized triplet state and the metal-centered emissive states is a critical factor for the sensitization of lanthanide luminescence. Moreover, the molecular structure of the ligand should also be considered in designing highly emissive lanthanide complexes

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