

CHAPTER 6
SALICYLALDIMINE BASED ZWITTERIONIC
O-COORDINATED SCHIFF BASE COMPLEXES OF
LANTHANIDES(III), (Ln = La, Pr, Sm, Gd, Tb, Dy and Tb)

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6.1 Introduction:

Lanthanide complexes have continued to garner the interest of chemists, spectroscopists, physicists and recently biologists owing to their unique applications as contrast agents for magnetic resonance imaging,¹ luminescent probes,² magnetic materials,³ biologically active,⁴ organic catalyst⁵ and NLO active materials.⁶ The valence $4f^n$ shell in lanthanides is screened from external perturbation by filled outer $5s^2$ and $5p^6$ shells causing (i) metal–ligand bonds to possess mainly ionic interactions, (ii) atomic, optical and magnetic properties unaffected in coordination complexes and (iii) negligible ligand-field stabilization energies. This lead to a variable and large coordination numbers in lanthanide complexes rendering their chemistry quite different from those of the main group elements and transition metals.⁷ Among organo-lanthanide complexes, Schiff base-lanthanide complexes are currently under intense scrutiny due to their relatively easier synthesis and multidentate encapsulating nature of the ligand which results in very high binding constants with f-block metals.⁸ Discovery of metal-containing liquid crystals have spurred the pursuit of transition metal based compounds.⁹⁻¹¹ Associated with higher coordination numbers, the lanthanide mesogens combine the typical properties of lanthanides, such as high magnetic anisotropy and the bright photoluminescence of high colorimetric purity, with those of liquid crystals.¹² In 1991, Galyametdinov *et al.*¹³ synthesized the first calamitic lanthanide-containing liquid crystal following the discovery of the first columnar liquid crystalline lanthanide complex by Piechocki *et al.*¹⁴ in 1985. Nitrate often coordinate in a bidentate fashion allowing the lanthanide ion to easily attain a high coordination number. The best investigated lanthanide-containing liquid crystals are those with salicylaldimine Schiff base ligands.¹⁵⁻²⁰ The Schiff base ligands often bind lanthanide ion in zwitterionic form in these complexes. The formation of a

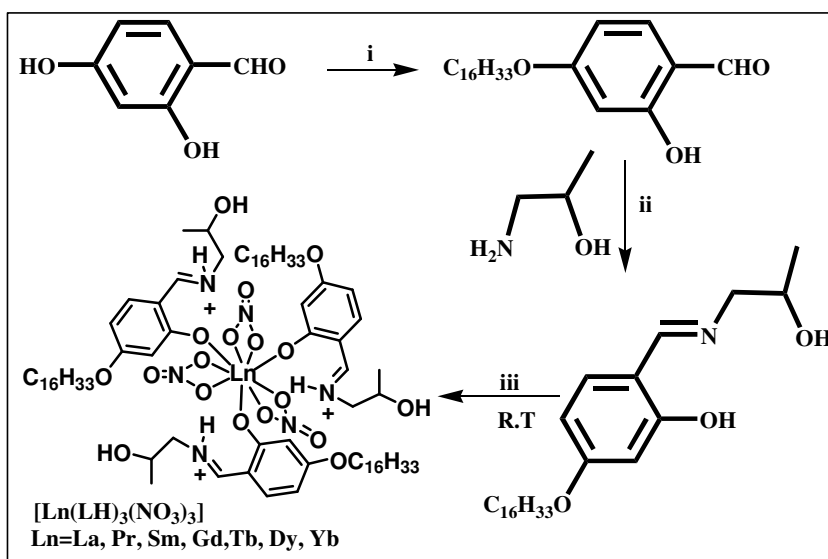
zwitterion can be rationalized by the tendency of the lanthanide ions to coordinate to negatively charged ligands with a preference for O-donor ligands. By transfer of the phenolic proton to the imine nitrogen, the phenolic oxygen becomes negatively charged and can coordinate to the lanthanide ion.²¹

In this chapter, we report synthesis of lanthanide complexes with Schiff base derived from amino alcohol and long chain alkoxy aldehyde of general formulae $[\text{Ln}(\text{LH})_3(\text{NO}_3)_3]$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}$ and Tb) exhibiting SmA mesomorphism. The ligands are blue light emitters while the complexes show intense emission in the visible range.

6.2 Experimental:

6.2.1 Synthesis of lanthanide Schiff base complexes:

The synthesis of ligand (E)-5-(hexadecyloxy)-2-((2-hydroxypropan-2-ylimino) methyl) phenol was achieved by proceeding through two major steps, viz., alkylation of 2,4-dihydroxybenzaldehyde with 1-bromohexadecane, followed by Schiff base formation with prepared long alkoxy chain aldehyde and amino-2-propanol. The mononuclear lanthanide complexes $[\text{Ln}(\text{LH})_3(\text{NO}_3)_3]$ ($\text{Ln}^{\text{III}} = \text{La}, \text{Pr}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}$ and Yb) complexes were accessed from the ligand, LH and the appropriate metal nitrate. The experimental details are given in **Scheme 1**.



Scheme 1: i. $\text{C}_{16}\text{H}_{33}\text{Br}$, KHCO_3 , KI , dry acetone, Δ , 40h, and ii. glacial AcOH , absolute EtOH Δ , 4h iii. $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, acetonitrile, stir, 4h.

Synthesis of hexadecyloxysalicylaldehyde:

2, 4-Dihydroxybenzaldehyde (10 mmol, 1.38g), KHCO_3 (10 mmol, 1g), KI (catalytic amount) and 1-bromohexadecane (10mL, 2.8g) were mixed in 250 mL of dry acetone. The mixture was heated under reflux for 24h, and then filtered, while hot, to remove any insoluble solids. Dilute HCl was added to neutralize the warm solution, which was then extracted with chloroform (100mL). The combined chloroform extract was concentrated to give a purple solid. The solid was purified by column chromatography using a mixture of chloroform and hexane (v/v, 1/1) as eluent. Evaporation of the solvents afforded a white solid product.

Synthesis of ligand (E)-5-(hexadecyloxy)-2-((2-hydroxypropan-2-ylimino), (LH):

An ethanolic solution of 2-hydroxy-(4-hexadecyloxy)-salicylaldehyde (0.39g, 1mmol) was added to an ethanol solution of amino-2-propanol (0.07g, 1mmol). The solution mixture was refluxed with a few drops of acetic acid as catalyst for 4h to yield the yellow Schiff base (E)-5-(hexadecyloxy)-2-((2-hydroxypropan-2-ylimino) methyl) phenol. The compound was collected by filtration and recrystallised from absolute ethanol to obtain a pure compound.

Yield: 0.322g (75%) yellow colored solid; m.p. 88°C. *Anal.* Calc. for $\text{C}_{26}\text{H}_{45}\text{NO}_3$ (419.3): C, 74.42; H, 10.81; N 3.34. Found: C, 74.41; H, 10.83; N, 3.33%. ^1H NMR (400 MHz, CDCl_3): δ 0.89 (t, J=6.4Hz, $-\text{CH}_3$, 3H), 1.28 (s, $-\text{CH}_3$) 1.27-1.83 (m, $-\text{CH}_2$ of methylene proton in side chain), 3.62 (t, J=4.1Hz, $-\text{CH}_2\text{N}=\text{C}$, 2H), 4.08 (m, 1H $-\text{CH}_2\text{OH}$), 3.93 (t, J=8.1Hz, $-\text{OCH}_2$, 2H), 7.08 (d, J= 8.6Hz, $-\text{C}_6\text{H}_4$, 1H), 8.51 (s, $-\text{N}=\text{CH}$, 1H), 13.7 (s, 1H, OH); FAB Mass (m/e, fragment): m/z: calc. 419.3; found: 420.3 $[\text{M}+\text{H}^+]$; IR (ν_{max} , cm^{-1} , KBr): 3432(ν_{OH}), 2917($\nu_{\text{as(C-H)}}$, CH_3), 2916($\nu_{\text{as(C-H)}}$, CH_2), 2845($\nu_{\text{s(C-H)}}$, CH_3), 2851($\nu_{\text{as(C-H)}}$, CH_2), 1622($\nu_{\text{C=N}}$), 1283($\nu_{\text{C-O}}$).

Syntheses of the lanthanide(III) complexes $[\text{Ln}(\text{LH})_3(\text{NO}_3)_3]$:

A solution of $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, [Ln= La (1mmol, 0.43g), Pr (1mmol, 0.43g), Sm (1mmol, 0.44g) Gd (1mmol, 0.45g), Dy (1mmol, 0.43g), Tb (1mmol, 0.45g), Yb (1mmol, 0.45g)] in a minimum volume of acetonitrile was added dropwise to an dichloromethane solution of the ligand, LH (3mmol, 1.13g) at room temperature. The reaction mixture was left to stir for 4h. A cream colored solid formed was filtered and washed with dichloromethane/acetonitrile mixture and dried *in vacuo*.

[La(LH)₃(NO₃)₃]:

Yield: 1.2g, (78%) a cream colored solid; m.p. 62°C Anal. Calc. for LaC₇₈H₁₃₅N₆O₁₈ (1581.1): C, 60 ; H, 8.5; N, 5.7. Found: C, 60.3; H, 8.7; N, 5.5%. ¹H NMR (400 MHz, CDCl₃): δ 0.89(t, J=6.9Hz, 9H, 3CH₃), 1.25-1.58 (m, -3CH₂ of methylene proton in side chain), 6.64 (d, J= 8.8Hz, -3C₆H₄, 3H), 7.85 (s, 3H, 3CH=N), 12.31 (br, s, -3N⁺H); 4.0 (m, 1H, -3CH₂OH), FAB Mass (m/e, fragment): m/z: calc. 1581.1; found: 1582.1[M+H⁺]; IR (ν_{max}, cm⁻¹, KBr): 3476 (ν_{OH}, -CH₂OH), 1222(ν_{C-O}, ether), 1646(ν_{C=N}), 1471(ν₄(NO₃)), 1230(ν₁(NO₃)), 1137(ν₂(NO₃)), 845(ν₆(NO₃)).

[Pr(LH)₃(NO₃)₃]:

Yield: 1.18g, (76%) a cream colored solid; m.p. 65°C Anal. Calc. for PrC₇₈H₁₃₅N₆O₁₈ (1583.1): C, 60; H, 8.4; N, 5.5. Found: C, 59.9; H, 8.6; N, 5.6%. FAB Mass (m/e, fragment): m/z: calc. 1583.1; found: 1584.1[M+H⁺]; IR (ν_{max}, cm⁻¹, KBr): 3314 (ν_{OH}, -CH₂OH), 1240(ν_{C-O}, ether), 1655(ν_{C=N}), 1474(ν₄(NO₃)), 1239(ν₁(NO₃)), 1135(ν₂(NO₃)), 850(ν₆(NO₃)).

[Sm(LH)₃(NO₃)₃]:

Yield: 1.17g, (75%) a cream colored solid; m.p. 67°C Anal. Calc. for SmC₇₈H₁₃₅N₆O₁₈ (1593.7): C, 59.8; H, 8.6; N, 5.5. Found: C, 59.9; H, 8.4; N, 5.4%. FAB Mass (m/e, fragment): m/z: calc. 1593.7; found: 1594[M+H⁺]; IR (ν_{max}, cm⁻¹, KBr): 3312 (ν_{OH}, -CH₂OH), 1238(ν_{C-O}, ether), 1657(ν_{C=N}), 1472(ν₄(NO₃)), 1237(ν₁(NO₃)), 1130(ν₂(NO₃)), 851(ν₆(NO₃)).

[Gd(LH)₃(NO₃)₃]:

Yield: 1.14g, (70%) a cream colored solid; m.p. 68⁰C Anal. Calc. for GdC₇₈H₁₃₅N₆O₁₈ (1600): C, 60.1; H, 8.4; N, 5.7. Found: C, 60; H, 8.2; N, 5.4%. FAB Mass (m/e, fragment): m/z: calc. 1600; found: 1601[M+H⁺]; IR (ν_{max}, cm⁻¹, KBr): 3316 (ν_{OH}, -CH₂OH), 1234(ν_{C-O}, ether), 1652(ν_{C=N}), 1470(ν₄(NO₃)), 1280(ν₁(NO₃)), 1130(ν₂(NO₃)), 850(ν₆(NO₃)).

[Tb(LH)₃(NO₃)₃]:

Yield: 1.14g, (70%) a cream colored solid; m.p. 70°C Anal. Calc. for TbC₇₈H₁₃₅N₆O₁₈ (1601.2): C, 60.2; H, 8.4; N, 5.7. Found: C, 60; H, 8.2; N, 5.4%. FAB Mass (m/e, fragment): m/z: calc. 1601.2; found: 1602[M+H⁺]; IR (ν_{max}, cm⁻¹, KBr): 3316 (ν_{OH}, -CH₂OH), 1234(ν_{C-O}, ether), 1652(ν_{C=N}), 1470(ν₄(NO₃)), 1281(ν₁(NO₃)), 1132(ν₂(NO₃)), 856(ν₆(NO₃)).

[Dy(LH)₃(NO₃)₃]:

Yield: 1.14g, (70%) a cream colored solid; m.p. 72°C Anal. Calc. for DyC₇₈H₁₃₅N₆O₁₈ (1605.2): C, 60.2; H, 8.4; N, 5.7. Found: C, 60.1; H, 8.2; N, 5.4%. FAB Mass (m/e, fragment): m/z: calc. 1605.2; found: 1606[M+H⁺]; IR (ν_{max}, cm⁻¹, KBr): 3316 (ν_{OH}, -CH₂OH), 1234(ν_{C-O}, ether), 1652(ν_{C=N}), 1470(ν₄(NO₃)), 1281(ν₁(NO₃)), 1132(ν₂(NO₃)), 856(ν₆(NO₃)).

[Yb(LH)₃(NO₃)₃]:

Yield: 1.14g, (70%) a cream colored solid; m.p. 74°C Anal. Calc. for YbC₇₈H₁₃₅N₆O₁₈ (1616.2): C, 60.1; H, 8.5; N, 5.7. Found: C, 60; H, 8.2; N, 5.4%. FAB Mass (m/e, fragment): m/z: calc. 1616.2; found: 1617[M+H⁺]; IR (ν_{max}, cm⁻¹, KBr): 3316 (ν_{OH}, -CH₂OH), 1234(ν_{C-O}, ether), 1652(ν_{C=N}), 1470(ν₄(NO₃)), 1281(ν₁(NO₃)), 1132(ν₂(NO₃)), 856(ν₆(NO₃)).

6.3 Results and discussion:

Synthesis and structural assessment:

The Schiff-base ligands were synthesized by condensation of 4-alkoxy-substituted aldehyde with amino-2-propanol with slight modification of literature procedure.¹⁸ The synthetic strategy for the ligand, [LH = (E)-5-(hexadecyloxy)-2-((2-hydroxypropan-2-ylidene) methyl) phenol], and mononuclear lanthanide complexes, [Ln(LH)₃(NO₃)₃] (Ln = La, Pr, Sm, Gd, Dy, Tb, Yb) is presented in **Scheme 1**. The compounds were all characterized by elemental analyses, FAB mass spectrometry, FT-IR, UV-Vis and ¹H NMR studies. Complexes were accessed from a reaction of the appropriate ligand with lanthanide nitrate in dichloromethane and acetonitrile mixture in Ln:LH as 1:3 ratio at ambient temperature and isolated as cream colored solids in good yield. In the IR-spectra of the complexes the C=N stretching frequency at ~1620cm⁻¹ is observed to be shifted to higher wave numbers ~1645cm⁻¹ in the complexes. The shift of ν_{C=N} values to higher wave numbers in the complexes compared to the corresponding values in the ligands indicate that the nitrogen atom is not involved in complex formation and that a C-N⁺ group is present.²² A broad band at ca.3300cm⁻¹ in the complexes is due to ν_{N-H} vibration in hydrogen-bonded (-C=N⁺-H) protonated imine.²³ The broadness of the band suggest that the hydrogen atom on -C=NH⁺ is engaged in intramolecular H-bonding with the phenolic oxygen

and thus, the ligands coordinate to the metal ion via the negatively charged phenolic oxygen only; no binding occurs between the lanthanide ion and the imine nitrogen. The additional four bands observed in the IR spectra of the complexes at ca. 1471, 1230, 1137, and 845 cm^{-1} can be assigned to ν_4 , ν_1 , ν_2 , and ν_6 vibrational mode of the coordinated nitrate group respectively. The difference (ca. 241 cm^{-1}) between the ν_4 and ν_1 peak positions is typical of bidentate nitrate groups (monodentate nitrate groups display a much smaller splitting).²¹ The FAB-mass spectra of the ligand and their Ln(III) complexes are concordant with their formula weights. The ^1H NMR spectrum of the diamagnetic lanthanum(III) complex showed a slightly broadened imine (CH=N) proton signal at 7.7 δ compared to 8.2 δ in the uncoordinated ligand. The phenolic-proton appears at 13.6 δ in the ligand (**Fig.1**). In fact, the absence of signal due to phenolic-OH proton and the appearance of a new signal at 12.3 δ characteristic of $-\text{N}^+\text{H}$ resonance in the La-complex (**Fig.2**) explicitly suggest the occurrence of the Schiff base ligand in zwitterionic form with the phenolic-H shifted to imine-N. The ethanolic proton which appeared as a multiplet at 4.1 δ in the ligand remained almost unaffected in the complex. The ^1H NMR spectral features corroborates the FT-IR observations providing additional evidence for the 'zwitterionic' Schiff base ligand. Thus with three chelated nitrato groups and an equal number of unidentate O-coordinated Schiff base ligands, the lanthanide(III) attains a nine coordinate structure. Amino-ethanol based salicylaldimine complexes of lanthanides prepared at a relatively higher temperature ($>40^\circ\text{C}$) are known to afford $[\text{Ln}(\text{LH})_2\text{LX}_2]$ while those accessed at ambient temperature or below 40°C have been found to possess $[\text{Ln}(\text{LH})_3\text{X}_3]$ stoichiometry. It is believed that at higher temperature, the dissociation of the phenolic proton is facilitated. Considering that the complexes in the present case have been synthesised at ambient temperature ($<40^\circ\text{C}$) the interpretation of stoichiometry and coordination mode appeared consistent with earlier reports¹⁶ on analogous lanthanide-complexes involving monobasic, zwitterionic Schiff base ligands.

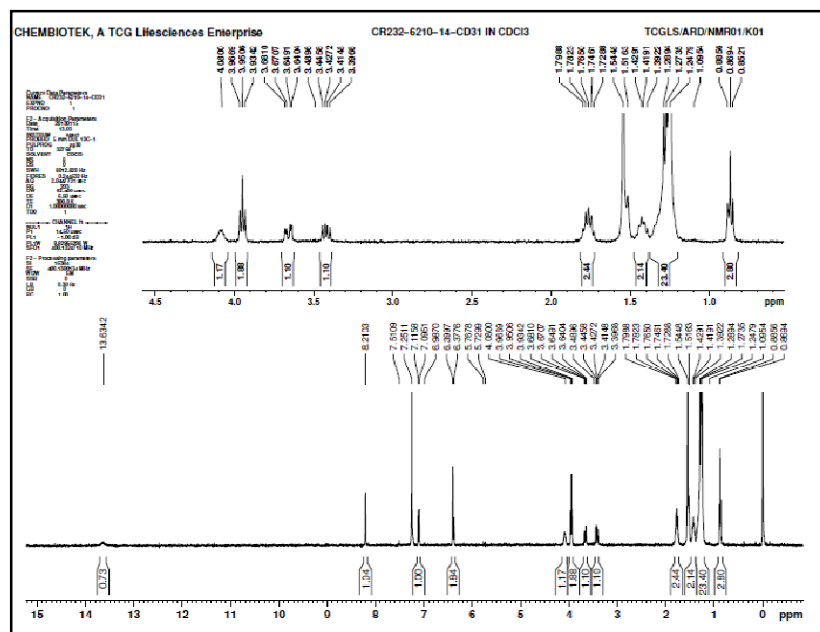


Fig. 1: ^1H NMR spectrum of LH

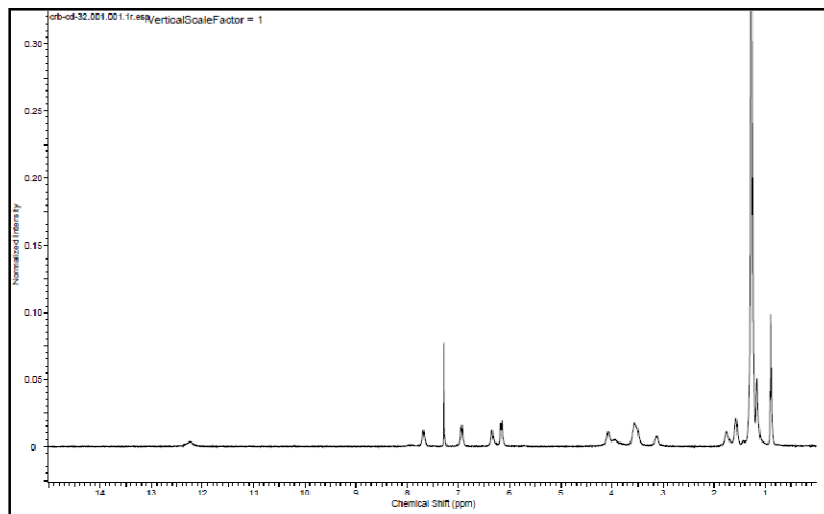


Fig. 2: ^1H NMR spectrum of $[\text{La}(\text{LH})_3(\text{NO}_3)_3]$

Photophysical properties:

The electronic absorption spectra of the free ligands in dichloromethane show strong absorption bands ($\sim 232\text{-}307\text{nm}$) in UV-Vis region attributable to the $\pi\text{-}\pi^*$ transition.^{24,25} The spectra of complexes generally show the characteristic bands of the free ligands with some changes both in frequencies and intensity, **Fig.3**. In complexes, the absorption band at $\sim 283\text{nm}$ appeared as shoulder and an additional band at

~370nm is attributed to the n- π^* transition. These alterations (Table 1) in energy of absorptions and intensity of the bands confirmed the coordination of the ligand to the metal ion.

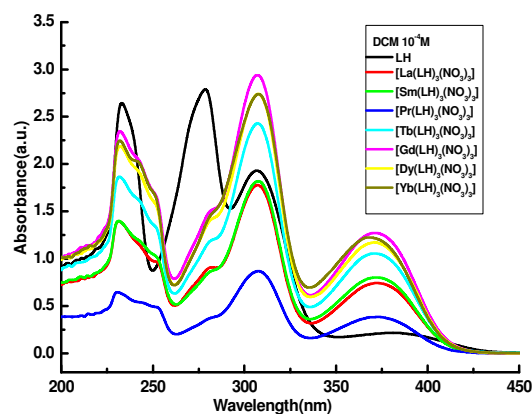


Fig.3: UV-visible spectra of ligand and lanthanide complexes.

Table 1: UV-visible data of ligand and lanthanide complexes.

Compounds	λ_{nm} (ϵ , $l\text{mol}^{-1}\text{cm}^{-1}$)	
	π - π^* transition	n- π^* transition
LH	230(26561) 275(27974) 300(19493)	-
[La(LH) ₃ (NO ₃) ₃]	230(13839) 280sh(9100) 305(17893)	370(7499)
[Sm(LH) ₃ (NO ₃) ₃]	230(14151) 281.9sh(8913) 305(18287)	370(8206)
[Pr(LH) ₃ (NO ₃) ₃]	230.2(6480) 280sh(3654) 305(8809)	370(4069)
[Tb(LH) ₃ (NO ₃) ₃]	232.2(18682) 280sh(11823) 307(24336)	370(10409)
[Gd(LH) ₃ (NO ₃) ₃]	235(23629) 280sh(15170) 307(29596)	370(12842)
[Dy(LH) ₃ (NO ₃) ₃]	232.2(22320) 283.4sh(14546) 307(27163)	370(11823)
[Yb(LH) ₃ (NO ₃) ₃]	230(22632) 280sh(14962) 308(27371)	360(12239)

The photoluminescence properties of the compounds in dichloromethane solution were investigated at room temperature. The emission spectra of ligands and complexes were recorded upon the excitation at 370nm. The ligand presents photoluminescence band at 438nm. Generally, Schiff base systems exhibit fluorescence due to intraligand $\pi-\pi^*$ transitions.²⁶ Upon complexation, the emission maxima are red shifted with enhanced luminescent intensity. Schiff base can efficiently absorb excitation energy and transfer to lanthanide leading to a metal-centred, sensitized luminescence. The radiative energy transfer from chromophore (L) to metal centre occur either from a singlet excited state (S_1) or a intersystem crossed triplet excited state (T_1).²⁷ The emission band for lanthanum complex appears at 459nm. The SmL_3 complex shows strong orange emission with four emission bands (**Fig.4**) at 450nm, 563nm, 598 nm and 645nm, due to $\pi-\pi^*$, ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$, ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ and ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ transitions respectively.^{28,29} Excitation at 370nm for Pr, Gd, Dy and Yb complexes causes intense blue light emission at 435, 455, 458 and 457 nm, respectively. The terbium complex shows three characteristic emissions centred at 488, 546 and 586 nm resulting from the deactivation of the 5D_4 excited state to the corresponding ground state 7F_J ($J = 6, 5, 4, 3, 2, 1$) of the Tb^{3+} ion (**Fig.4**). The strongest emission is centred at 546nm, which is ascribed to the hypersensitive transition of ${}^5D_4 \rightarrow {}^7F_5$.

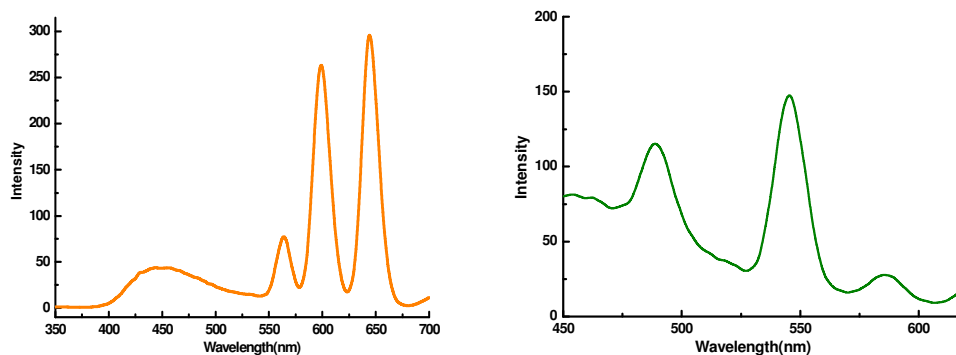


Fig. 4: Photoluminescence spectra of the representative compounds

Mesomorphic properties:

The mesomorphic behaviour was studied by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The azomethine ligand do not show liquid crystalline properties but melt directly to an isotropic liquid at $\sim 84.7^\circ\text{C}$. The

probable reason for the lack of mesogenicity may be due to greater conformational flexibility of the ligand. However, on complexation with lanthanides there occurs an enhanced rigidity and smectic mesomorphism is induced. The lanthanide complexes pass through a mesophase before clearing to the isotropic liquid and are enantiotropic except for La and Gd complexes which exhibit monotropic transition. This mesophase is identified by polarizing optical microscopy as a smectic A. Batonnets growing from the isotropic liquid upon cooling coalesce to a broken fan-like texture with the coexisting homeotropic regions (**Fig.5**). In SmA mesophase, the complexes form layers, and the long molecular axis of the complexes is perpendicular to the layer planes.³⁰ The thermal behaviour of the complexes was confirmed by DSC on subsequent heating-cooling runs (Table 2). The complexes, as evident from the DSC data, exhibited a fairly wide mesophase stability range $\sim 100^\circ\text{C}$ (**Fig.6**). The relatively high enthalpy value points to a highly ordered smectic phase. Temperature dependent powder X-ray diffraction analysis of the lanthanide complexes could not be carried out successfully due to early crystallization of the compounds.



Fig.5: Broken fan-like texture of SmA phase of $[\text{Dy}(\text{LH})_3(\text{NO}_3)_3]$ complex

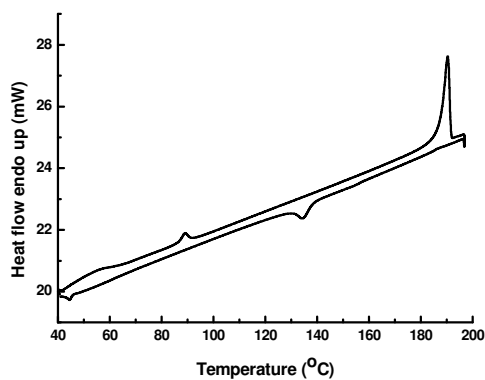


Fig.6: DSC thermogram of $[\text{Dy}(\text{LH})_3(\text{NO}_3)_3]$ complex

Table 2: Phase transition temperatures (T°C), associated enthalpies (ΔH , kJmol⁻¹) of lanthanide complexes.

Compounds	Heating	Cooling
[La(LH) ₃ (NO ₃) ₃]	Cr72.2(9.4)Cr ₁ 85.8(4.4) SmA187.8 (65.1)I	-
[Pr(LH) ₃ (NO ₃) ₃]	Cr78.7(10.9)Cr ₁ 92.0(2.0) SmA190.1 (77.9)I	I124.5(5.8) SmA44.9(0.6)Cr
[Sm(LH) ₃ (NO ₃) ₃]	Cr70.9(18.2)Cr ₁ 93.5(3.8) SmA192.2 (84.0)I	I135.6(14.6) SmA45.2(1.9)Cr
[Gd(LH) ₃ (NO ₃) ₃]	Cr61.1(15.3)Cr ₁ 92.8(5.4) SmA193.6 (64.2)I	-
[Tb(LH) ₃ (NO ₃) ₃]	Cr72.4(5.2)Cr ₁ 90.0(5.5) SmA192.4(193.2)I	I138.2(18.1) SmA44.7(3.0)Cr
[Dy(LH) ₃ (NO ₃) ₃]	Cr56.3(2.5)Cr ₁ 88.9(4.4) SmA190.3(67.1)I	I134.6(11.0) SmA44.5(3.7)Cr
[Yb(LH) ₃ (NO ₃) ₃]	Cr52.2(2.4)Cr ₁ 86.5(4.0) SmA180.9(89.5)I	I120.4(7.9) SmA42.5(3.5)Cr

6.4 Conclusion:

Salicylaldimine based zwitterionic O-coordinated Schiff base complexes of lanthanides(III) have been successfully synthesized. The lanthanide complexes, [Ln(LH)₃(NO₃)₃] (Ln = La, Pr, Sm, Gd, Tb, Dy and Tb) are both liquid crystalline and photoluminescent with the Schiff base occurring as zwitterions binding through phenolic-oxygen with nitrate coordinating as bidentate ligand completing a nine coordination around the lanthanide ion. The ligand is non-mesomorphic whereas the complexes exhibited high ordered smectic phase. The ligands are blue light emitters with broad emission maxima at ~438nm while the lanthanide complexes show intense emission in the visible range (~450-645nm).

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