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Synthesis, characterization and photophysical studies of rare earth metal complexes with a mesogenic Schiff-base



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ABSTRACT

A mesogenic (SmC) Schiff-base ligand, *N*,*N'*-di-(4'-octyloxybenzoate)salicylidene-1,12-diaminododecane (H₂L), has been synthesized and its phase transition behaviour and thermal stability were investigated by differential scanning calorimetry, thermogravimetric analysis, polarizing optical microscopy and temperature-dependent Raman study. Ln(III) complexes (Ln = La, Pr, Nd, Sm, Eu, Tb and Dy) of the H₂L were synthesized and the bonding behaviour/emission property was studied by electronic, IR and NMR and fluorescence spectral data.

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1. Introduction

Metallomesogens (metal containing liquid crystals) have attracted broad interest because of their unique combination of the characteristic properties of liquid crystals and metal complexes [1–3]. The lanthanide containing mesogens (lanthanidomesogens) are the best known class of luminescent metallomesogens [4–6]. An advantage of luminescence by trivalent lanthanide ions is that the luminescence spectra consist of narrow emission lines of intense colour [7–9]. The design of lanthanide-containing liquid crystals is marred with complication because of their high coordination numbers that often seem to be incompatible with the structural anisotropy required to exhibit liquidcrystalline behaviour [10–11]. Nitrate is often chosen to be the counterion because it can coordinate in a bi-dentate fashion, allowing the lanthanide ion to easily obtain a high coordination number. Such materials not only possess a large magnetic anisotropy but also display interesting photophysical properties.

In continuation of the earlier work [12–16] carried out in our laboratory on systematic structural and spectroscopic studies of 4*f* metal complexes of a series of mesogenic organic Schiff-bases, we now report here the synthesis and spectral studies of a mesogenic Schiff-base, N,N'-di-(4'-octyloxybenzoate)salicylidene-1,12-diaminododecane (H₂L), and its non-mesogenic rare earth complexes.

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2. Experimental section

2.1. Materials

All the required reagents of analytical grade (AR) were obtained from commercial sources and used without further purification; 1-bromooctane, 2,4-dihydroxybenzaldehyde, 4-hydroxybenzoic acid and 1,12-diaminododecane are from Sigma-Aldrich, USA; all the $Ln(NO_3)_3 \cdot xH_2O$ salts are from Alfa Aesar and KHCO₃ is from Merck. The organic solvents obtained from commercial vendors were dried using standard methods [17] when required.

2.2. Synthesis and analysis

N,*N*'-di-(4'-octyloxybenzoate)salicylidene-1,12-diaminododecane (H₂L), **3** (Scheme 1), was synthesized from the precursor materials **1** and **2** as reported [18–19]. The Ln^{III} complexes [Ln₂(LH₂)₃(NO₃)₄](NO₃)₂ (Ln = La, Pr, Nd, Sm, Eu, Tb and Dy), were prepared by refluxing together appropriate metal nitrate Ln(NO₃)₃·xH₂O in methanol and the ligand (H₂L) in dichloromethane for ~6 h. The solid complex, yielded by evaporating the solution, was further purified by washing repeatedly with methanol.

2.2.1. Synthesis of N, N'-di-(4'-octyloxybenzoate)salicylidene-1,12-diaminododecane,(H_2L), ${\bf 3}$

The ligand (H_2L) was synthesized by refluxing together solutions of 4-octyloxy (4'-formyl-3'-hydroxyphenyl)benzoate (7.4 g, 20 mmol) and 1,12-diaminododecane (2.0 g, 10 mmol) in ethanol for ~3 h in the



Scheme 1. Reagents and Conditions i) 1-bromooctane, KOH, ethanol, ~12 h reflux ii) 2,4-dihydroxybenzaldehyde, DCC, DMAP, ~24 h stirring at room temp., iii)1 or 2 drops acetic acid, ethanol, ~3 h reflux iv) Ln(NO3)3·xH2O, Methanol/DCM, ~6 h reflux.

presence of few drops glacial acetic acid; the yellow precipitate thus obtained was washed thrice with hot ethanol and dried at room temperature: yield: 70%, as yellow-colour solid; mesogenic (SmC); Anal. calcd for C₅₆H₇₆N₂O₈ (905.21) (%): C, 74.30; H; 8.46; N, 3.09. Found: C, 74.34; H, 8.44; N, 3.08. ¹H NMR (300.40 MHz; CDCl₃; Me₄Si at 25 °C, *J* (Hz), ppm) δ 0.89 (t, *J* = 6.6, 3H, -CH₃), 1.28–1.83 (m, 32H, (-CH₂)₁₆), 3.57(t, *J* = 6.9, 2H, -NCH₂), 4.03 (t, *J* = 6.3, 2H, -OCH₂), 6.72 (d, *J* = 8.4, 1H, Ar-H), 6.78 (s, 1H, Ar-H), 6.96 (d, *J* = 8.7, 2H, Ar-H), 7.25 (d, *J* = 6.0, 1H, Ar-H), 8.12 (d, *J* = 8.7, 2H, Ar-H), 8.30 (s, 1H,CH=N-), 14.09 (s, br, ph-OH); ¹³C{¹H} NMR (75.45 MHz; CDCl₃; Me₄Si at 25 °C, ppm) δ : 164.40 (-COO), 163.71(-C₄), 163.65 (-NCH), 163.56 (-C₂), 154.15 (-C₄), 132.26 (-C₆), 131.90 (-C₂), 121.30 (-C₁), 116.47 (-C₁), 114.25 (-C₅),112.06 (-C_{3'}), 110.60 (-C₃), 68.28 (-OCH₂) and 58.89 (-NCH₂); MS (MALDI-TOF): m/z 905.78 (M + 1), calcd 905.21; IR (cm⁻¹, KBr): 3441 (ν-OH),1728 (ν_{C=0}) 1631 (ν_{C=N}), 1142(ν_{Cph-O}).

2.2.2. Synthesis of La^{III} complex, $[La_2(LH_2)_3(NO_3)_4](NO_3)_2$

A solution of $La(NO_3)_3 \cdot 6H_2O(0.87 \text{ g}, 2 \text{ mmol})$ in a minimum volume of methanol was added dropwise to a dichloromethane solution of the

ligand, H₂L (2.71 g, 3 mmol) at room temperature. The reaction mixture was refluxed for ~6 h and the pale yellow colour solid that formed was filtered off and washed thrice with methanol and dried over fused CaCl₂ in a desiccator. Yield: 60%, as a pale yellow-colour solid; m.p. 210 °C (decompose); Anal. calcd for La₂C₁₆₈H₂₂₈N₁₂O₄₂ (3365) (%): C, 59.96; H, 6.83; N, 4.99 and La, 8.25. Found: C, 59.88; H, 6.79; N, 4.89 and La, 8.29. ¹H NMR (300.40 MHz; CDCl₃; Me₄Si at 25 °C, *J* (Hz), ppm) δ 0.92(t, *J* = 6.6, 3H, -CH₃), 1.78-1.17 (m, 22H, -(CH₂)₁₁), 3.49 (t, *J* = 6.9, 2H, -NCH₂), 3.96 (t, *J* = 6.3, 2H, -OCH₂), 6.28-7.25 (m, 7H, Ar-H), 7.93 (s,1H,CH=N), 12.62 (s, br, 1H, -N⁺H); ¹³C{¹H} NMR (75.45 MHz; CDCl₃; Me₄Si at 25 °C, ppm) δ = 176.68 (-NCH), 165.05 (-COO), 164.25 (-C₄'), 163.52 (-C₂), 158.27 (-C₄), 136.95 (-C₆), 132.38 (-C₂'), 121.07 (-C₁'), 114.69 (-C₁), 114.17(-C₅), 112.71 (-C₃'), 110.89 (-C₃), 68.30(-OCH₂) and 55.39 (-NCH₂); IR (cm⁻¹, KBr); 3189 (ν_{N+H}), 1724 ($\nu_{C=O}$), 1651 ($\nu_{C=N}$), 1116 (ν_{ph-O}).

All the other complexes $(Ln^{III} = Pr, Nd, Sm, Eu, Tb and Dy)$ were synthesized in an analogous way by using the appropriate hydrated salt of Ln^{III} nitrate; the physical properties and the analytical data of all the complexes are given in Table 1.

Table 1

Analytical data and general data of lanthanide complexes of H₂L.

H ₂ L/complex formula wt. (emp. formula)	Colour yield	m.p.(°C)	Found (calcd)%			
			С	Н	Ν	М
H ₂ L 905.21(C ₅₆ H ₇₆ N ₂ O ₈)	Yellow 76%	130	74.34 (74.30)	8.44 (8.46)	3.08 (3.09)	-
[La ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂ 3365(La ₂ C ₁₆₈ H ₂₂₈ N ₁₂ O ₄₂)	Light yellow, 65%	210 ^d	59.98 (59.96)	6.79 (6.83)	4.95 (4.99)	8.29 (8.25)
[Pr ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂ 3369(Pr ₂ C ₁₆₈ H ₂₂₈ N ₁₂ O ₄₂)	Light yellow, 60%	230 ^d	59.79 (59.88)	6.78 (6.82)	4.97 (4.99)	8.41 (8.36)
$[Nd_{2}(LH_{2})_{3}(NO_{3})_{4}](NO_{3})_{2}$ 3376(Nd_{2}C_{168}H_{228}N_{12}O_{42})	Light yellow, 65%	210 ^d	59.79 (59.77)	6.77 (6.81)	4.96 (4.98)	8.51 (8.54)
$[Sm_2(LH_2)_3(NO_3)_4](NO_3)_2 3388(Sm_2C_{168}H_{228}N_{12}O_{42})$	Light yellow, 60%	220 ^d	59.47 (59.55)	6.71 (6.78)	4.98 (4.96)	8.92 (8.88)
[Eu ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂ 3391(Eu ₂ C ₁₆₈ H ₂₂₈ N ₁₂ O ₄₂)	Light yellow, 60%	200 ^d	59.41 (59.49)	6.72 (6.78)	4.95 (4.96)	8.99 (8.96)
$[Tb_2(LH_2)_3(NO_3)_4](NO_3)_2$ 3405(Tb_2C_{168}H_{228}N_{12}O_{42})	Light yellow, 60%	210 ^d	59.30 (59.25)	6.78 (6.75)	4.89 (4.94)	9.45 (9.33)
$ [Dy_2(LH_2)_3(NO_3)_4](NO_3)_2 \\ 3412(Dy_2C_{168}H_{228}N_{12}O_{42}) $	Light yellow, 65%	210 ^d	59.20 (59.13)	6.81 (6.73)	4.97 (4.93)	9.55 (9.52)

d: decomposes.

2.3. Physical measurements

The ¹H and ¹³C NMR spectra were recorded on a JEOL AL-300 MHz FT-NMR multinuclear spectrometer; C, H, N contents were micro analysed on Vario EL III Carlo Erba 1108 analyser. Infrared spectra were recorded on JASCO FTIR (model-5300) spectrophotometer in 4000–400 cm⁻¹ region. Mass spectrum was recorded on AB Sciex TOF/TOF 5800 MALDI mass spectrometer. UV-VIS spectra were recorded on Shimadzu spectrophotometer, model, Pharmaspec UV-1700. Emission spectra were recorded on JY HORIBA Fluorescence spectrophotometer. The mesophases were identified by using polarized hotstage microscope (LOMO, USA) equipped with digital camera (Nikon Coolpix 4500). Differential Scanning Calorimetry studies were made on METTLER DSC-25 unit. Molar conductance of the complexes was determined in 0.001 M solutions at room temperature on a CON 510 bench conductivity metre (cell constant, K = 1.0). Thermogravimetric analysis (TGA) (RT to 1000 °C) was performed on Perkin-Elmer-STA 6000 under high purity nitrogen; The Raman spectrum of the ligand was recorded on Raman spectrometer (Renishaw, UK) equipped with 785 nm lasers; laser-induced heating in the sample was nullified by using 0.5% of the diode laser (λ , 785 nm with maximum power of 300 mW) and the incident laser beam was focussed on the sample by a $50 \times \log$ distance objective attached to a Leica DM 2500 M microscope; the Raman scattered light was collected in back-scattering geometry by the same objective (a grating of 1200 grooves/mm was used as the dispersion element); variable temperature spectra (± 0.1 K) were recorded by using THM 600 hot stage and a dedicated computer with Wire 4.0 software.

3. Results and discussion

The structures of the ligand and the corresponding metal complexes were studied by IR & NMR spectral techniques and elemental analysis. The analytical data (Table 1) of the complexes corresponds to 2:3 metal to ligand stoichiometry with the general formula $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$. The IR and NMR spectral data imply bidentate coordination through non-deprotonated zwitterionic form of the ligand in the Ln^{III} complexes. Further, molar conductance data (160–165 Ω^{-1} cm²/mol) measured in 10⁻³ *M* DMF solutions corresponds to 2:1 electrolytic behaviour [20] indicating the presence of two of the six nitrate groups outside the coordination sphere.

3.1. IR spectral studies

The infrared spectral data assignments regarding bonding through specific functional groups have been made by a careful comparison of specific vibrational bands of H₂L with the corresponding bands of the Ln^{III} complexes (Table 2). The broad band at 3441 cm⁻¹ in the IR spectrum of the ligand, characteristic of phenolic–OH [21], may be understood to involve considerable amount of intra molecular hydrogen bonding with –C==N group. This band disappears in the spectra of the complexes due to shifting of the phenolic proton to the azomethine nitrogen resulting in the formation of zwitter ion. The v_{CN} band of the

Table 2	
IR spectral data of the	lanthanide complexes of H ₂ L.

ligand at 1631 cm^{-1} undergoes a hypsochromic shift to 1651 cm^{-1} in all the complexes on account of zwitterionic formation; further, the appearance of a weak, broad band at 3189 cm^{-1} reflects the zwitterionic ($-C=N^+H$) nature of the ligand [22]. The vibrational modes of the coordinating nitrate groups (C_2v) appear at characteristic frequencies around 1483–1467, 1290–1280 and 853–840 cm⁻¹ in the Ln^{III} complexes [23]; the magnitude of splitting, 194–181 cm⁻¹, at higher energies may be indicative of a bi-dentate ligation of the coordinated nitrate groups [23,24]. The additional band observed at 1384 cm⁻¹ may be attributed to the non-coordinated nitrate groups of the complexes.

3.2. ¹H and ¹³C NMR spectral studies

The ¹H and ¹³C{¹H} NMR spectral data show that the phenolic–OH signal at 14.09 δ of the ligand disappears in the La^{III} complex; during coordination the phenolic protons of the ligand are shifted to the imine nitrogens, which then get intra-molecularly hydrogen bonded to the metal-bound phenolate oxygens giving rise to the zwitterionic structure ($=N^+-H-O_-$) and the macrocycle under this condition is designated as LH₂ [25]. We found that the signal at 8.30δ of the imine hydrogen (-CH=N) shifted to 7.93δ in the La^{III} complex with the simultaneous formation of a new signal at 12.62 δ , characteristic of $-N^+H$ resonance, in the latter; these observations are in good agreement with systems reported previously [10,13,26]. The ¹³C NMR spectra show a significant shift of the -N=CH- signal of the ligand (163.65 δ) to 176.69 δ in the La^{III} complex. Shifts of similar magnitude were observed in the case phenolate carbons (owing to direct attachment to the bonding atom) while those observed for the other carbons were of lesser magnitude. Thus, the NMR spectral data imply bonding through two phenolate oxygens of the ligand in the zwitterionic form to the La^{III} metal ion.

3.3. Photophysical properties

The electronic spectra (Fig.1) of the ligand and the complexes were recorded in chloroform and 3:1(ν/ν ratio) mixed solution of chloroform and DMSO. Of the two intra-ligand bands, the one centred at 310 nm may be due to $\pi-\pi^*$ transition localized on the aromatic ring while the other at 405 nm is due to $n-\pi^*$ transition of the imine chromophore. The spectra of the Pr^{III}, Sm^{III}, Nd^{III} and Dy^{III} complexes show considerable red shift in the λ_{max} values in comparison with those of their corresponding aqua ions [27]; these red shifts are presumably due to the Nephelauxetic effect [28] and thus imply the extent of covalency of the metal–ligand bond. Various bonding parameters (Table 3), viz., Nephelauxetic ratio (β), bonding parameter (η), calculated by the procedures as reported in literature [29] suggest weak covalent nature of the metal–ligand bonds.

A photoluminescence spectrum of the ligand in CHCl₃ solution, when excited with monochromatic radiation of 390 nm, shows (Fig.1) a λ_{max} at 435 nm due to intra-ligand transition. The Sm^{III} complex,

	-									
H ₂ L/Complex	ν (O–H) Phenolic	$\nu(N^+H)$	ν(C==0)	ν (C=N)	ν (C–O) phenolic	$\nu(NO_3)$				
						ionic	v_5	ν_1	ν_2	$v_5 - v_1$
H ₂ L	3441b	-	1728	1631	1142	-	-	-	-	-
$[La_2(LH_2)_3(NO_3)_4](NO_3)_2$	-	3189w	1724	1651	1116	1384	1469	1280	846	189
$[Pr_2(LH_2)_3(NO_3)_4](NO_3)_2$	-	3189w	1728	1650	1118	1383	1467	1283	846	184
$[Nd_2(LH_2)_3(NO_3)_4](NO_3)_2$	-	3193w	1726	1658	1116	1383	1479	1287	845	192
$[Sm_2(LH_2)_3(NO_3)_4](NO_3)_2$	-	3193w	1731	1651	1117	1384	1479	1290	853	189
[Eu ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂		3193w	1725	1650	1118	1383	1483	1289	841	194
[Tb ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂	-	3179w	1724	1651	1118	1384	1469	1280	846	189
$[Dy_2(LH_2)_3(NO_3)_4](NO_3)_2$		3196w	1737	1656	1115	1384	1493	1312	846	181

b: broad, w: weak.



Fig. 1. UV–Vis spectrum of ligand, H₂L (dotted line) and Photoluminescence spectrum of ligand, H₂L (continuous line) $\lambda_{exc.} = 390$ nm in CHCl₃ (1 × 10⁻⁵ *M* solution).

when excited with 410 nm radiation, shows three major luminescence bands (Fig.2) at 563, 599 and 645 nm which may be assigned from the lowest emitting state of ${}^{4}G_{5/2}$ to the ${}^{6}H_{J}$ (J = 5/2, 7/2 and 9/2) states [28, 30,31]. The bright luminescence observed for the Sm^{III} complex is reflective of a good match between the ligand-centred triplet state and the three Sm^{III} emissive states; intense emission, however, is only observed from the ${}^{4}G_{5/2}$ level. It was reported that the close proximity of these three excited states to each other causes electrons from the higher states to rapidly relax to the ${}^{4}G_{5/2}$ level, from which radiative transitions occur [32].

3.4. Thermal property and liquid-crystallinity behaviour

The phase transitions of the ligand and its complexes were studied by using polarizing optical microscopy (POM), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The POM studies imply smectic–C phase (Fig. 4.) of the ligand (H₂L). The corresponding transition temperatures (Fig. 3.) and enthalpy changes (Table 4) from DSC and its TGA measurements proved good thermal stability up to 250 °C (Fig. 5). All the Ln^{III} complexes under present study are found to be non-mesogenic.



Fig. 2. Photoluminescence spectrum of Sm^{III} complex at $\lambda_{exc.}$ 410 nm.

3.5. Temperature dependent Raman spectral studies

In order to understand changes in intermolecular interactions and molecular rearrangement upon phase transition, temperature-dependent Raman spectra (RT – 133 °C) of the ligand (H₂L) were recorded in 1000–2000 cm⁻¹ region in both heating and cooling cycles. At the phase transition, Cr \rightarrow SmC, prominent Raman signatures were observed that are consistent with DSC and POM studies. A systematic study of peak position and line width variation of some Raman marker bands with temperature may give information of structural transformation and also change in interaction environment during phase transitions. In next sections, we focused on temperature dependence of Raman bands in two regions, 1500–1850 cm⁻¹ and 1120–1380 cm⁻¹ in cooling cycle.

3.5.1. The region 1500–1850 cm^{-1}

The Raman spectra ($1500-1800 \text{ cm}^{-1}$ region) are presented as a function of temperature in Fig. 6. At room temperature the bands at 1580 and 1606 cm⁻¹ are due to C=C stretching modes of the rings. At Cr \rightarrow SmC transition the 1580 cm⁻¹ band undergoes a hypsochromic shift while the 1606 cm⁻¹ band remains unshifted. In SmC phase, the molecules are loosely packed with one dimensional positional order

Table 3

Electronic spectral data of various metal complexes of the ligand (H₂L).

Pr ^{III}			Nd ^{III}			Sm ^{III}			Dy ^{III}			
Transitions	$\lambda_{max}(cm^{-})$	-1)	Transitions	$\lambda_{max}(cm)$	-1)	Transitions	$\lambda_{max}(cm^{-1})$		Transitions $\lambda_{max}(c)$		m^{-1})	
	aq. ion	complex		aq. ion	complex		aq. ion	complex		aq. ion	complex	
${}^{1}G_{4} \leftarrow {}^{3}H_{4}$ ${}^{1}D_{2}^{*} \leftarrow$ ${}^{3}P_{0} \leftarrow$	9900 16,850 20,800	9784 16,863 -	$\begin{array}{c} {}^{4}F_{3/2} \leftarrow {}^{4}I_{9/2} \\ {}^{4}F_{5/2} \leftarrow \\ {}^{4}F_{7/2} \leftarrow \\ {}^{4}S_{3/2} \\ {}^{4}F_{9/2} \leftarrow \\ {}^{2}H_{11/2} \leftarrow \\ {}^{2}G_{7/2}^{*} \leftarrow \\ {}^{4}G_{7/2} \leftarrow \\ {}^{4}G_{9/2} \leftarrow \end{array}$	11,450 12,500 13,500 14,800 15,900 17,400 19,100 19,500	11,507 12,531 13,440 - - 17,182 19,083 -	$\label{eq:F92} \begin{array}{l} {}^{6}F_{9/2} \leftarrow {}^{6}H_{5/2} \\ {}^{6}F_{11/2} \leftarrow \\ {}^{4}G_{5/2} \leftarrow \\ {}^{6}P_{7/2} \leftarrow \\ {}^{4}D_{7/2} \leftarrow \end{array}$	9200 10,500 17,900 26,750 29,100	9216 9950 - - 28,735	$\label{eq:1.1} \begin{array}{c} {}^{6}H_{7/2}{}^{6}F_{9/2} \leftarrow {}^{6}H_{15/2} \\ {}^{6}H_{5/2} \leftarrow \\ {}^{6}F_{7/2} \leftarrow \\ {}^{6}F_{5/2} \leftarrow \\ {}^{6}F_{3/2} \leftarrow \end{array}$	9100 10,200 11,000 12,400 13,200	- 9784 11,098 12,406 -	
Spectroscopic	bonding parc	imeters										
β	0.99	6		0.997			0.981		().990		
$b^{1/2}$	0.04	4		0.038			0.097		(0.070		
%δ	0.40	1		0.200			1.020			010		
η	0.00	2		0.300			1.936			.010		
				0.002			0.01		(0.006		

*Hypersensitive transition.



Fig. 3. DSC thermogram of ligand (H₂L).

 Table 4

 DSC data for H₂L and its complexes.

Compound	Transition	T/°C	$\Delta H/kJ mol^{-1}$	$\Delta S/J \text{ mol}^{-1} \text{ K}^{-1}$
H ₂ L	Cr–SmC	122.33	57.11	144.41
	SmC–I	129.86	6.01	14.92
	I–SmC	128.57	8.05	20.04
	SmC–Cr	70.95	30.93	89.89

and orientational order compared to crystal phase, that is characterized by larger interaction and close molecular packing due to three dimensional positional orders as well as orientational order. This implies temperature-induced intramolecular changes leading to a small charge density shift from one region to the other. The band at 1632 cm^{-1} is due to C=N stretching vibration of linking group. At room temperature the C=N bond is involved in intramolecular hydrogen bonding with O-H of phenyl ring; at $Cr \rightarrow SmC$ transition this band undergoes hypsochromic shift with simultaneous increase in intensity and line width. This may be due to the weakening of intramolecular hydrogen bonding between C=N and phenolic O-H groups (as in SmC phase) as the molecules are loosely packed compared to crystal phase. Due to this ortho oxygens have greater possibility to form lateral interaction with other molecules to form SmC phase. The ν (C=O)_{ester} band appears at 1732 cm⁻¹ at room temperature; it is well documented that this type of C=O bonds are likely to form inter-molecular hydrogen bonds in LCs [33,34]. At $Cr \rightarrow SmC$ transition this band shifts to 1737 cm⁻¹ (with broadening)



Fig. 4. Optical Texture of ligand (H_2L) at 112 °C.



Fig. 5. TGA thermogram of ligand (H₂L).



Fig. 6. Raman spectra of ligand (H_2L) in the region 1500–1850 $\rm cm^{-1}$ at variable temperatures in cooling cycle.

while at SmC \rightarrow Iso transition it shifts to 1740 cm⁻¹; these hypsochromic shifts may be on account of the change in the microenvironment around C=O bonds. It is most plausible to assume that the H⁻ bonds associated with C=O group weaken at SmC phase compared to crystal phase, but in isotropic phase most of the hydrogen bonds associated with C=O bond are broken. The hydrogen bonds associated with C=O group (which are weaker compared to crystal) are understood to mainly contribute to lamellar SmC phase. It is also interesting to see that all the bands associated with C=C stretching of rings, C=N



Fig. 7. Raman spectra of ligand (H_2L) in the region 1120–1380 cm⁻¹ at variable temperatures in cooling cycle.

bond and C==O bond are broadened at Cr \rightarrow SmC transition. The broadening of these bands is due to the changes in intermolecular interactions at Cr \rightarrow SmC transition and temperature-induced reorientational freedom of the bonds in SmC phase.

3.5.2. The region $1120-1380 \text{ cm}^{-1}$

The temperature-dependent Raman spectra in the region 1120-1380 cm⁻¹ (Fig. 7) contain prominent bands at 1145, 1168, 1198, 1215, 1256 and 1320 cm⁻¹ at room temperature. The band at 1145 cm⁻¹, due to ν (C–O)_{phenloic} vibration, undergoes hypsochromic shift with simultaneous increase in line width at phase transition; this is due the effect of weakening of intra-molecular hydrogen bonding between C==N and O-H groups; this, in turn, causes a hypsochromic shift in v_{C-O} resulting in more re-orientational motion that contributes to increment in linewidth. The band at 1168 cm⁻¹, due to δ (C–H) mode of the rings at room temperature, was considered to be very sensitive at phase transitions for many liquid crystalline systems [34,35]. In the present case this band shows only broadening without any shift at phase transition. The bands at 1198, 1215 and 1256 cm $^{-1}$ are due to ν (C–O), ν (C–C) (attached to imine and phenyl ring) and ν (C–C) (attached to ester and phenyl ring) modes of linking groups. At $Cr \rightarrow SmC$ transition the band at ~1215 cm⁻¹ shifts to higher frequency while the band at 1256 cm^{-1} shifts to lower frequency. It is remarkable to note that the ν (C–C) band shifts to lower frequency while the other Raman bands show a higher frequency shift. This lower shift of ν (C–C) band implies that the molecule is rotating around C-C bond and as a result charge cloud shifts from C-C bond in both sides that increases the strength of the other Raman bands. The alkyl chains and alkyl spacer will get stabilized themselves in the lowest energy conformation by reorienting the peripheral rings around C-C bond. The band at 1320 cm^{-1} , due to the twisting motion of the alkoxy chain, is also shifted to higher frequency during phase transition. These changes in Raman spectral features of this region very clearly confirm the $Cr \rightarrow SmC$ transition between 65 and 75 °C as observed in DSC and POM measurements.

4. Conclusion

The mesogenic (SmC) Schiff-base, *N*,*N*'-di-(4'-octyloxybenzoate) salicylidene-1,12-diaminododecane (H₂L), coordinates to Ln^{III} as a neutral bi-dentate species through two phenolate oxygens in zwitterionic manner to yield non-mesogenic seven coordinate complexes of the general formula, $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$ where Ln = La, Pr, Nd, Sm, Eu, Tb and Dy. Temperature-dependent Raman study gave clear signature of Cr \rightarrow SmC transition in both the heating and cooling cycles. The transition temperatures are also consistent with those observed in DSC. The fluorescence studies indicate that the Schiff-base ligand (H₂L) and exclusively its Sm^{III} complex show photo-luminescence.

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