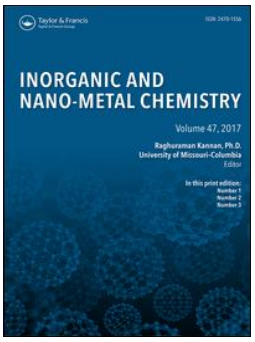

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Synthesis and spectral Studies of Some Rare Earth Metal Complexes of a Heterocyclic Mesogenic Schiff-base

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Abstract:

A heterocyclic liquid crystalline Schiff's base, *N*-(4'-(4''-hexyl-1*H*-1'',2'',3''-triazol))-4-dodecyloxysalicylaldimine (HL) and a series of lanthanide(III) complexes of the type $[Ln(LH)_3(NO_3)_3]$ (Ln^{III} = La, Pr, Nd, Sm, Eu, Tb and Dy) have been synthesized and characterized by elemental analyses, mass spectrometry, FT-IR, NMR, and UV/Vis spectral techniques. All the complexes involve binding of HL (through phenolate oxygen in zwitter-ionic form) and bidentate chelation of nitrato groups. The ligand exhibits smectic-A (SmA) mesophase over a wide temperature range as evidenced by DSC and polarizing optical microscopic studies. Fluorescence studies show emission of HL and of the Tb^{III} complex.

Key words: Mesogenic Schiff's base, zwitterionic coordination, Ln^{III} complexes

Introduction

Numerous liquid crystalline materials designed and synthesized with rings other than six-membered rings have received relatively less attention owing to their non-linearity and less mesogenic stability. It was found that some of the non-linear heterocyclic liquid crystals, such as pyrazole, thiophene, furan and isoxazole derivatives with a terminally positioned heterocyclic ring, form smectic/nematic phase over wide low-temperature range. In addition, hetero atom plays a key role in increasing molecular dipole moment and dielectric anisotropy, thereby producing molecular level polar organizations [1].

Compounds containing five-membered [1,2,3]-triazole ring have attracted attention in the fields of materials chemistry [2], organic chemistry [3] and drug discovery [4] based upon their advantageous properties [5, 6]. Schiff-base ligands with N, O donor sets have often been used since such ligands may assemble coordination architectures directed by the lanthanide(III) ions [7-12] while the lanthanide ions can promote Schiff-base condensation while providing access to complexes of otherwise inaccessible ligands [13]. The technological applications of lanthanide complexes (including lanthanide metallomesogens) are largely governed by their interaction with light. All these aspects were dealt with in detail in a critical review [14] tailored for a broad audience of chemists, biochemists and materials scientists. However, the design of lanthanide metallomesogens [15] is rather difficult because their high coordination numbers seem to be incompatible with the structural anisotropy that is necessary to exhibit liquid crystalline behavior.

In continuation of our earlier work on metallomesogens [16-22] we now report here synthesis and spectral studies of a [1,2,3]-triazole-containing mesogenic Schiff-base (having terminal alkyl chain next to triazole ring) and of some Ln(III) complexes.

EXPERIMENTAL

Starting materials

All the required reagents of analytical grade, obtained from commercial sources, were used without further purification; 1-bromododecane, PMDETA and 2,4-dihydroxybenzaldehyde are from Sigma–Aldrich, USA; all the $Ln(NO_3)_3.xH_2O$ salts are from Alfa Aesar and 4-nitro aniline, 1-octyne, $NaNO_2$, NaN_3, CuBr, KI and $KHCO_3$ are from Merck. Organic solvents obtained from commercial vendors were dried when required using standard methods [23].

***Synthesis*:** All the experimental details are given in Scheme 1.

***Synthesis of 1-azido-4*-nitrobenzene, 1:**

4-Nitro aniline (6.90g, 50 mmol) was suspended in hydrochloric acid (17%, 100 mL) at room temperature followed by stirring with ethanol until a clear solution was obtained. $NaNO_2$ (5.18g, 75 mmol) was added to the solution at ~ 0 °C, stirred for 15-30 min, followed by slow addition of NaN_3 (4.88g, 75 mmol); the resultant solution was magnetically stirred for ~2h at room temperature and the product was extracted thrice into ethereal portions, each portion washed with saturated $NaHCO_3$ solution and then with brine; the ether was removed after drying over $MgSO_4$ under reduced pressure and the desired nitro-azide was isolated. ^1H NMR (300.40 MHz; $CDCl_3$; Me_4Si at 25 °C, J (Hz), ppm) δ = 8.25 (d, J = 8.7, 2H, Ar-H), 7.15 (d, J = 8.7, 2H, Ar-H); $^{13}C\{^1H\}$ NMR (75.45 MHz; $CDCl_3$; Me_4Si at 25 °C, ppm) δ = 119.4, 125.7, 144.7, 146.9; IR (KBr): cm^{-1} = 2126 (ν_{azide}), 1505(ν_{-NO}).

Synthesis of 4-hexyl-1-(4′-nitrophenyl)-1H-1,2,3-Triazole),* 2, *by 'click' chemistry:

Compound **2** was synthesized by adapting the reported method [24]; a light pink colored solid was obtained. Yield - 70%, mp = 156 °C. ^1H NMR (300.40 MHz; $CDCl_3$; Me_4Si at 25 °C, J (Hz), ppm) δ = 0.89 (t, J = 5.1, 3H,-CH_3), 1.34–1.75 (m, 8H,(-CH_2)$_4$), 2.84 (t, J = 6.1, 2H, triazole-CH_2), 7.82 (s, 1H, triazole ring-H), 7.97 (d, J = 8.7, 2H, Ar-H), 8.42 (d, J = 9.0, 2H, Ar-H); $^{13}C\{^1H\}$ NMR (75.45 MHz; $CDCl_3$; Me_4Si at 25 °C, ppm) δ =14.0, 22.5, 25.5, 28.8, 29.1, 31.5, 118.4, 120.1, 125.4, 141.3, 146.9, 150.2; IR (KBr, cm^{-1}): 1598: $\nu_{\text{triazole ring}}$,1522: ν_{as} (-NO_2).

***Synthesis of 4-(4′-hexyl-1H-1′, 2′, 3′-triazol-1-yl)aniline* 3:**

Compound **3** was obtained using the method described earlier [25]; the solid product was re-crystallized from ethanol; Yield 65%; mp 96 ºC. ^1H NMR (300.40 MHz; $CDCl_3$; Me_4Si at 25 °C, J (Hz), ppm) δ = 0.89 (t, J = 5.4, 3H,-CH_3), 1.34–1.71 (m, 8H,(-CH_2)$_4$), 2.77 (t, J = 7.5, 2H, triazole-CH_2), 3.81 (s, 2H, -NH_2), 7.47 (d, J = 8.7, 2H, Ar-H), 6.76 (d, J = 8.4, 2H, Ar-H), 7.57 (s, 1H, triazole ring-H); $^{13}C\{^1H\}$ NMR (75.45 MHz; $CDCl_3$; Me_4Si at 25 °C, ppm) δ = 14.0, 22.5, 25.6, 28.9, 29.4, 31.5, 115.2, 118.9, 122.1, 128.9, 146.7, 148.74.

***Synthesis of Schiff base (HL),* 4:**

A mixture of compound **3** (2.40g, 10 mmol) and 4-dodecyloxysalicylaldehyde (3.06g, 10 mmol) was refluxed in absolute ethanol (15 mL) in presence of a catalytic amount of glacial acetic acid for ~ 4h. The mesogen, **4**, obtained as a precipitate from the hot reaction mixture, was recrystallized from a mixture of ethanol and chloroform and dried under vacuum; yield 70%. mp 210 ºC, ^{1}H NMR (300.40 MHz; $CDCl_3$; Me_4Si at 25 °C, *J* (Hz), ppm) (Fig.S1) δ = 0.88 (t, *J* = 4.8, 6H,$(-CH_3)_2$), 1.27-1.77 (m, 28H,$-(CH_2)_{14}-$), 2.80 (t, *J* = 7.5, 2H, triazole $-CH_2$), 4.01 (t, *J* = 6.3, 2H, $-OCH_2$), 6.41 (s, 1H, Ar-H), 6.51 (d, *J* = 7.2, 2H, Ar-H), 7.33 (d, *J* = 7.8, 1H, Ar-H), 7.40 (d, *J* = 8.1, 1H, Ar-H), 7.71 (1H, triazole ring-H), 7.78 (d, *J* = 8.1, 2H, Ar-H), 8.56 (s, 1H, -N=CH), 13.40 (s, 1H, phenolic-OH). ^{13}C{^{1}H} NMR (75.45 MHz; $CDCl_3$; Me_4Si at 25°C, ppm) (Fig.S2) δ = 68.38 ($-OCH_2$), 104.21 ($-C_3$), 108.11 ($-C_5$), 113.04 ($-C_1$), 118.69 (triazole ring-$\underline{C}_{4''}$), 122.20 ($-C_{2'}$), 128.03 ($-C_{4'}$), 132.10 (triazole ring-$\underline{C}_{5''}$), 133.20 ($-C_6$), 136.46 ($-C_{3'}$), 149.33 ($-C_{1'}$), 162.14 ($-C_4$), 165.83 (C-OH); 168.37 (-N=CH); IR (KBr, cm^{-1}): 1230, ν_{C-O}; 1622, $\nu_{C=N}$, 3423, $\nu(OH)_{phenolic}$; formation of HL was further confirmed by ESI mass spectrum (Fig. S3) on the basis of [M+H] base peak (m/e value of 534).

***Synthesis of La^{III} complex, [La(LH)$_3$(NO$_3$)$_3$],* 5:**

Anhydrous solutions of HL (0.47g, 0.9 mmol in 30 mL dichloromethane) and of $La(NO_3)_3.6H_2O$ (0.12 g, 0.3 mmol in 20 mL methanol) were refluxed together for ~ 10h and the reaction mixture left overnight. The micro-crystalline solid complex obtained was filtered off under suction, washed repeatedly with methanol and dried over fused $CaCl_2$ in a desiccator to get as a light yellow colored solid; Yield: 60%; mp 225 °C (decompose). ^{1}H NMR (300.40 MHz; CDCl$_3$; Me$_4$Si at 25 °C, *J* (Hz), ppm) (Fig.S4) δ = 0.89 (t, *J* = 5.1, 3H, -CH$_3$), 1.77–1.27 (m, 28H, -(CH$_2$)$_{14}$-), 2.82 (t, *J* = 9.0, 2H, Triazole-CH$_2$), 4.03 (t, *J* = 5.4, 2H, -OCH$_2$), 6.48 (s, 1H, Ar-H), 6.5 (d, *J* = 8.4, 2H, Ar-H), 7.34 (d, *J* = 8.4, 1H, Ar-H), 7.44 (d, *J* = 6.3, 1H, Ar-H), 7.83 (d, *J* = 7.8, 2H, Ar-H), 7.77 (s, 1H, triazole ring-H), 8.61 (s, 1H, HC=N-), 13.45 (br, s, 1H, –N$^+$H); ^{13}C{^{1}H} NMR (75.45 MHz; CDCl$_3$; Me$_4$Si at 25 °C, ppm) (Fig.S5) δ = 67.99 (-OCH$_2$), 101.26 (-C$_3$), 107.43 (-C$_5$), 112.49 (-C$_1$), 118.53 (triazole ring-$\underline{C}_{4''}$), 120.97 (-C$_{2'}$), 121.86 (-C$_{4'}$), 132.01(triazole ring-C$_{5''}$), 133.61 (-C$_6$), 136.66 (-C$_{3'}$), 148.14 (-C$_{1'}$), 162.01 (-C$_4$), 163.67 (-C-OH); 181.60 (-$\underline{C}$H=N$^+$H); IR (KBr, cm^{-1}): 1214, $\nu_{\mathrm{C-O}}$; 1635, $\nu_{\mathrm{C=N}}$; 3153, $\nu_{\mathrm{N^+H}}$. The other Ln$^{\mathrm{III}}$ complexes (Ln$^{\mathrm{III}}$ = Pr, Nd, Sm, Eu, Tb and Dy) were synthesized in an analogous way by using the appropriate hydrated Ln$^{\mathrm{III}}$ nitrate.

Physical measurements

The metal contents of the complexes were determined by complexometric titrations against EDTA-disodium salt solution using xylenol orange as indicator. C, H and N were micro-analyzed on an Exeter (Model CE-440) CHN Analyzer. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a JEOL AL-300 MHz multinuclear FTNMR spectrometer. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer over 4000-400 cm^{-1} range. Mass spectrum was recorded on a WATERS Q-TOF Premier mass spectrometer. UV-Vis spectra were recorded on Shimadzu Pharmaspec-UV 1700 spectrometer. Molar conductance of the complexes was determined in 0.001*M* DMF solutions at room temperature on a CON-510 bench conductivity meter, using a 2-ring stainless steel ultem body conductivity electrode (cell constant, K = 1.0). Room temperature magnetic susceptibility measurements were carried out on a Cahn-Faraday balance. Mesophases were identified by the textures observed on a polarized hot-stage (heating and cooling rates, 2 °C/min) binocular microscope (LOMO, USA) equipped with digital camera (Nikon Coolpix 4500). Differential scanning calorimetry studies were made on METTLER DSC-25 unit (with heating and cooling cycle rate of 10 °C/min).

Results and discussion

Synthesis and structural studies

The data on elemental analyses, important physical properties and general behavior of the Ln^{III} complexes are given in table 1. The molar conductivity measurements in $10^{-3}M$ DMF solutions (14.80 − 16.50 Ω^{-1} cm^2 mol^{-1}) are consistent with non-ionic (coordinated) nature of the nitrate groups [26] and non-electrolytic behaviour of the complexes. The μ_{eff} values of all the present Ln^{III} complexes have been found to be in good agreement with the reported van Vleck values [27].

The important infrared spectral data of HL and its Ln^{III} complexes are presented in table 2. The broad peak, centered at 3423 cm^{-1}, characteristic of $\nu(O–H)_{phenolic}$ [28], disappears in the spectra of the complexes due to shifting of the phenolic proton to the azomethine nitrogen atom resulting in the formation of zwitter ion. The weak/medium intensity band (of HL) at 1230 cm^{-1} is assignable to $\nu(C–O)_{phenolic}$. The strong intensity band occurring at 1622 cm^{-1}, assignable [29] to azomethine moiety, undergoes a hypsochromic shift in all the complexes on account of zwitter-ion formation. Thus, the complexation of HL to the Ln^{III} ion results in migration of the phenolic protons onto the three uncoordinated imino nitrogens, which then get intramolecularly hydrogen-bonded to the metal-bound phenolate oxygens to give rise to zwitter-ionic structure, $N^{+}–H\cdot\cdot O^{-}$ [30]. The observed shift to higher wave numbers upon complexation implies presence of $-C=N^{+}$ group [31]. Further, all the present complexes are characterized by a strong band at 1634-1636 cm^{-1} due to $\nu_{C=N}$ and a weak broad band at about 3153–3157 cm^{-1} due to H-bonded $N^{+}–H\cdot\cdot\cdot O^{-}$ vibration of the protonated imine [32]. Thus, the ligand may be considered to coordinate to the metal ion via the negatively charged phenolate oxygen. The Ln^{III} complexes also exhibit three additional bands around 1478–1482, 1287–1290 and 835-836 cm^{-1} which can be assigned to the vibrational modes of the coordinated nitrate groups (C_{2v} symmetry) [33, 34].

A comparison of the NMR spectral data [^{1}H and $^{13}C\{^{1}H\}$ NMR] of the ligand with that of the La^{III} complex shows absence of the phenolic–OH signal in the latter. We found that the signal corresponding to the imine hydrogen, –CH=N-, got broadened in the La^{III} complex (δ, 8.61) when compared with that of the ligand (δ, 8.56); further, a new signal, characteristic of $–N^{+}H$ resonance, appeared in the spectrum of the La^{III} complex at 13.45 δ while the parent ligand does not show any such signal. These observations are in accordance with those made by *Binnemans et al.* [35] who reported similar results. Thus, the IR and NMR spectral data provide sufficient evidence to show that the present Schiff-base (HL) exists in the metal complex in a zwitter-ionic form, (as shown in Scheme 2) and provides monodentate coordination through phenolate oxygen. The observed shift of the $–N=\underline{C}H-$ signal (δ, 168.37 in the case of HL and 181.60 in the La^{III} complex) provides experimental evidence for coordination of the ligand with the metal ion. Similar shifts were observed in the case of the carbon atoms directly attached to the bonding atoms (phenolate carbons) while those for the other carbons were of lesser magnitude.

Spectrophotometric and spectrofluorimetric studies

The qualitative electronic spectral bands (Fig.1a) of the ligand (at 246 & 294 nm) in chloroform solution are assignable due to π-π* intra-ligand transitions of the aromatic rings while the single peak of the selected Ln^{III} complexes (in a mixed solvent of $CHCl_3$ + DMSO; 3:1 v/v) around 350 nm is due to π-π* transition of the imine (-C=N) chromophore. The considerable red shifts in the λ_{max} values of the Ln^{III} complexes (Ln = Pr^{III}, Nd^{III}, Sm^{III} and Dy^{III}), compared to those of the corresponding aqua ions, implies Nephelauxetic effect [36], which is regarded as a measure of covalency of the bonding between the metal ions and the ligands [37]. Various bonding parameters (Table S1), *viz.*, Nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), Sinha's parameter (%δ) and covalency angular overlap parameter (η), calculated by the procedures as reported in literature [38], suggest weak covalent nature of the metal‑ligand bonds.

Fluorescence emission spectra (Fig.1b, 1c) recorded in $CHCl_3$/DMSO solutions (3:1 v/v ratio; 10^{-6} mol L^{-1}; λ_{ex}, 350 nm) show an emission band at 405 nm in the case of HL due to intra ligand transition; the four typical metal-centered emission bands of the Tb^{III} complex at 490, 575, 619 and 682 nm imply emission due to $^5D_4\rightarrow{}^7F_6$, $^5D_4\rightarrow{}^7F_5$, $^5D_4\rightarrow{}^7F_3$ and $^5D_4\rightarrow{}^7F_0$ transitions respectively.

Optical and Thermal Studies

The liquid crystalline studies were made on DSC (recorded in the second heating and second cooling cycle with heating rate of 10 °C/min; Fig.2; thermal data in table 3) and polarizing optical microscope (heating and cooling rates of 2 °C/min); the texture of HL (Fig.3) at 175 °C implies *SmA* mesophase while the Ln^{III} complexes were found to be non-mesogenic.

Conclusion

The mesogenic (SmA) Schiff-base, *N*-(4'-(4"-hexyl-1*H*-1",2",3"-triazol))-4-dodecyloxysalicylaldimine (HL), coordinates to Ln^{III} ions (Ln = La, Pr, Nd, Sm, Eu, Tb and Dy) forming non-mesogenic complexes of the formula, $[Ln(LH)_3(NO_3)_3]$. HL bonds through exclusively phenolate oxygen while the nitrato groups act as bidentate chelating ligands. Luminescence of the ligand arises due to intra-ligand transition and that of the Tb^{III} complex originates in metal-centered emission.

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References

1. V. S. Bezborodov, C. J. Lee, K.H. Uh, 6th *International conference on ferroelectric liquid crystals; conference summaries.* Brest, France, 152 (1997).
2. (a) M. Parent, O. Mongin, K. Kamada, C. Katan, M.B. Desce, *Chem. Comm.*, 2029 (2005); (b) B. C. Englert, S. Bakbak, U.H.F. Bunz, *Macromolecules*, **38**, 5868 (2005).
3. (a) K. Kacprzak, *Syn. lett.* 943 (2005); (b) Z. Li, T. S. Seo, J. Ju, *Tetrahedron Lett*., **45**, 3143 (2004); (c) P. L. Suarez, Z. Gándara, G. Gómez, Y. Fall, *Tetrahedron Lett.*, **45**, 4619 (2004); (d) K. D. Bodine, D. Y. Jin, M. S. Gin, *J. Am. Chem. Soc.,* **126**, 1638 (2004); (e) J. C. Loren, K. B. Sharpless, *Synthesis,* 1514 (2005); (f) Y. M. Wu, J. Deng, Y. Li, Q. Y. Chen, *Synthesis*, 1314 (2005).
4. (a) F. Lenda, F. Guenoun, B. Tazi, N. B. Larbi, J. Martinezd, F. Lamatyd, *Tetrahedron Lett.*, **45**, 8905 (2004); (b) R. Manetsch, A. Krasinński, Z. Radić, J. Raushel, P. Taylor, K. B. Sharpless, H. C. Kolb, *J. Am. Chem. Soc.*, **126**, 12809 (2004); (c) H. C. Kolb, K. B. Sharpless, *Drug Discov. Today,* **8**, 1128 (2003).
5. A.C. Tomé, In: *Science of Synthesis:* R. C. Storr, T. L. Gilchrist *Thieme Stuttgart,* **13**, 415 (2004).
6. V. P. Krivopalov, O. P. Shkurko, *Russ. Chem. Rev.,* **74**, 339 (2005).
7. P. A. Vigato, S. Tamburin, *Coord. Chem. Rev*., **248**, 717 (2004).
8. C. Benelli, D. Gatteschi, *Chem. Rev*., **102**, 2369 (2002).
9. A. Dossing, *Eur. J. Inorg. Chem*., **8**, 1425 (2005).
10. J. C. G. Bünzli, C. Piguet, *Chem. Rev*., **102**, 1897 (2005).

11. D. Parker, R. S. Dickins, H. Puschmann, C. Crossland, J. A. K. Howard, *Chem. Rev.*, **102**, 1977 (2002).

12. W. Radecka-Paryzek, V. Patroniak, J. Lisowski, *Coord. Chem. Rev.*, **249**, 2156 (2005)

13. M. Tsiouria, N. Hadjiliadis, T. Arslan, B. M. Kariuki, J. C. Plakatouras, *Inorg. Chem. Commun*., **9**, 429 (2006).

14. J. C. G. Bünzli, C. Piguet, *Chem. Soc. Rev*., **34**, 1048 (2005).

15. K. Binnemans, K. Lodewyckx, *Angew. Chem*., **113**, 248 (2001).

16. A. K. Singh, S. Kumari, T. R. Rao, *Mater. Sci. Eng.*, C **31**, 1144 (2011).

17. A. K. Singh, S. Kumari, K. R. Kumar, B. Sridhar, T. R. Rao, *Polyhedron,* **27**, 1937 (2008).

18. A. K. Singh, S. Kumari, T. N. G. Row, J. Prakas, K. R. Kumar, B. Sridhar, T. R. Rao, *Polyhedron,* **27**, 3710 (2008).

19. S. Kumari, A. K. Singh, T. R. Rao, *Mater. Sci. Eng. C,* **29**, 2454 (2009).

20. S. Kumari, A. K. Singh, K. R. Kumar, B. Sridhar, T. R. Rao, *Inorg. Chim. Acta*, **362**, 4205 (2009).

21. P. R. Shakya, A. K. Singh, T. R. Rao, *Mater. Sci. Eng. C,* **32**, 1906 (2012).

22. M. Karunakar, R. Yerrasani, R. Dubey, A. K. Singh, T. R. Rao, *Journal of Molecular Liquids,* **222**, 377 (2016).

23. A. Weisberger, F. S. Praskver, *Organic Solvents, International publishers Inc.,* New York, pp. 1263 (1956).

24. X. Huan, D. Wang, R. Dong, C. Tu, B. Zhu, D. Yan, X. Zhu, *Macromolecules*, **45**, 5941 (2012).

25. T. Narasimhaswamy, K. S. V. Srinivasan, *Liq. Cryst.*, **31**, 1457 (2004).

26. W. J. Geary, *Coord. Chem. Rev.*, **7**, 81(1971).

27. I. H. V. Vleck, *Theory of electronic and magnetic susceptibilities, Oxford University Press*, Oxford, pp. 239 (1932).

28. R. M. Silverstein and F. X. Webster, *Spectroscopic identification of organic compounds, sixth ed., John Wiley & Sons*, New York, pp. 82-83, 87–88, 90–91, (2002).

29. N. B. Colthup, L. H. Daly, S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3rd ed., Academic Press, New York (1990).

30. H. A. R. Pramanik, G. Das, C. R. Bhattacharjee, P. C. Paul, P. Mondal, S. K. Prasad, D. S. Shankar Rao, *Chemistry–A European Journal*, **19**, 13151 (2013).

31. K. Binnemans, R. V. Deun, C. G. Walrand, W. Haase, D. W. Bruce, L. Malykhina, Y. G. Galyametdinov, *Mater. Sci. Eng. C*, **18**, 247 (2001).

32. P. Bag, U. Flörke, K. Nag, *Dalton Trans.*, 3236 (2006).

33. B. Keshavan, P. G. Chandrashekara, N. M. M. Gowda, *J. Mol. Struct.*, **553**, 193 (2000).

34. J. Nawrocka, V. Patroniak, *J. Alloys Compd.*, **380**, 159 (2004).

35. K. Binnemans, Y. G. Galyametdinov, R. V. Deun, D. W. Bruce, S. R. Collison, A. P. Polishchuk, I. Bikechantaev, W. Hasse, A. V. Prosvirin, L. Tinchurina, I. Litvinov, A. Gubajdullin, A. Rakhamatullin, K. Uytterhoeven, L. V. Meervelt, *J. Am. Chem.Soc.*, **122**, 4335 (2000).

36. R. Reisfeld, C. K. Jørgensen, *Lasers and excited states of rare earths, Springer-Verlag*, Berlin Heidelberg New-York (1977).

37. P. R. Shakya, A. K. Singh, T. R. Rao, *Spectrochimica Acta Part A*, **79**, 1654 (2011).

38. R. Yerrasani, M. Karunakar, R. Dubey, A. K. Singh, R. Nandi, R. K. Singh, T. R. Rao, *Journal of Molecular Liquids*, **216**, 510 (2016).

Table 1. General and analytical data of HL and of Ln^{III} metal complexes

HL / Complex Formula weight. (Emp. Formula)	Colour, Yield	m.p. (°C)	μ_{eff} (van Vleck) value, B.M.	Found (Calc) %			
				C	H	N	M
HL 532.76,$C_{33}H_{48}N_4O_2$	Yellow 70%	210		74.42 (74.40)	9.09 (9.08)	10.54 (10.52)	-
[La(LH)$_3$(NO$_3$)$_3$],1923.2, La$C_{99}H_{144}N_{15}O_{15}$	Light yellow 60%	225^d	Diamag.	61.88 (61.83)	7.56 (7.55)	10.95 (10.92)	7.25 (7.22)
[Pr(LH)$_3$(NO$_3$)$_3$],1925.20, Pr$C_{99}H_{144}N_{15}O_{15}$	Light yellow 65%	235^d	3.45 (3.40-3.60)	61.85 (61.76)	7.58 (7.54)	10.96 (10.91)	7.45 (7.32)
[Nd(LH)$_3$(NO$_3$)$_3$],1928.5, Nd$C_{99}H_{144}N_{15}O_{15}$	Light yellow 72%	220^d	3.44 (3.50-3.60)	6169 (61.66)	7.59 (7.53)	10.94. (10.89)	7.51 (7.48)
[Sm(LH)$_3$(NO$_3$)$_3$],1934.6, Sm$C_{99}H_{144}N_{15}O_{15}$	Light yellow 69%	260^d	1.26 (1.50-1.60)	61.48 (61.46)	7.56 (7.50)	10.81 (10.86)	7.80 (7.77)
[Eu(LH)$_3$(NO$_3$)$_3$],1936.2, Eu$C_{99}H_{144}N_{15}O_{15}$	Light yellow 75%	240^d	3.58 (3.40-3.60)	61.54 (61.41)	7.55 (7.50)	10.89 (10.85)	7.89 (7.85)
[Tb(LH)$_3$(NO$_3$)$_3$, 1943.22, Tb$C_{99}H_{144}N_{15}O_{15}$	Light yellow 65%	262^d	9.60 (9.10-9.60)	61.25 (61.19)	7.51 (7.47)	10.85 (10.81)	8.25 (8.18)
[Dy(LH)$_3$(NO$_3$)$_3$],1936.2, Dy$C_{99}H_{144}N_{15}O_{15}$	Light yellow 65 %	245^d	10.45 (10.40-10.50)	61.15 (61.08)	7.49 (7.46)	10.85 (10.79)	8.41 (8.35)

d = decomposition

Table 2. IR spectral data (cm^{-1}) of HL and of Ln^{III} metal complexes[a]

HL / Complex	ν(O-H) *phenolic*	ν (N^+H)	$ν_{as}$ (CH_3)	$\boldsymbol{ν_s}$ (CH_2)	ν (C=N)	$ν_{C\text{-}O}$ *(phenolic)*
HL	3423	-	2924	2854	1622	1230
$[La(LH)_3(NO_3)_3]$	-	3153	2926	2856	1635	1214
$[Pr(LH)_3(NO_3)_3]$	-	3155	2927	2856	1634	1215
$[Nd(LH)_3(NO_3)_3]$	-	3155	2925	2854	1636	1215
$[Sm(LH)_3(NO_3)_3]$	-	3153	2926	2856	1635	1215
$[Eu(LH)_3(NO_3)_3]$	-	3155	2925	2855	1634	1216
$[Tb(LH)_3(NO_3)_3]$	-	3155	2925	2855	1635	1216
$[Dy(LH)_3(NO_3)_3]$	-	3157	2924	2855	1635	1215

[a]Spectra recorded as KBr pellets; as: asymmetric; s: symmetric

Table 3. Thermodynamic data (transition temp. and enthalpy changes)

Compound	**Transition**[a]	**T**[b]**/ °C**	***δH***[b]**/ kJ mol^{-1}**
HL	Cr— Cr^1	42.8	3.8
	Cr^1—SmA	100.9	29.1
	SmA—I	205.5	2.9
	I—SmA	203.1	4.8
	SmA—Cr	82.6	19.9

[a] Cr: crystal, SmA; smectic-A, I: isotropic liquid.

[b] Data as obtained from the DSC cycle

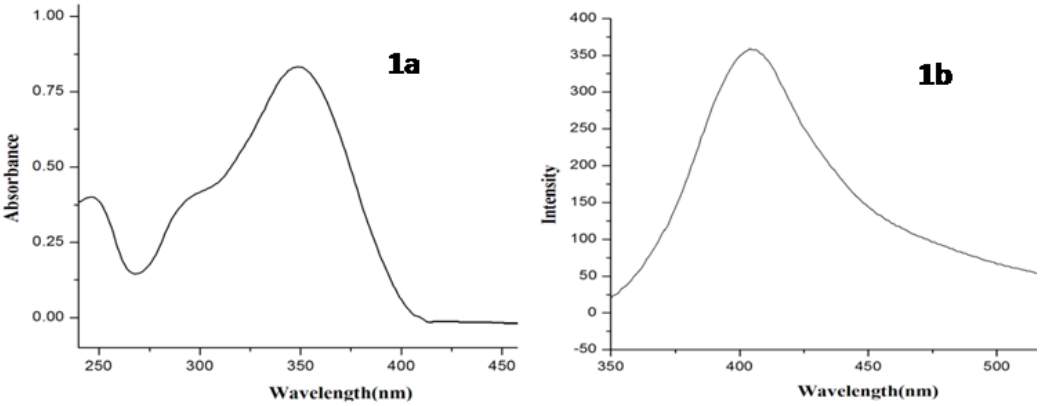


Fig. 1a & 1b. UV-Vis and Fluorescence spectra of HL in $CHCl_3$

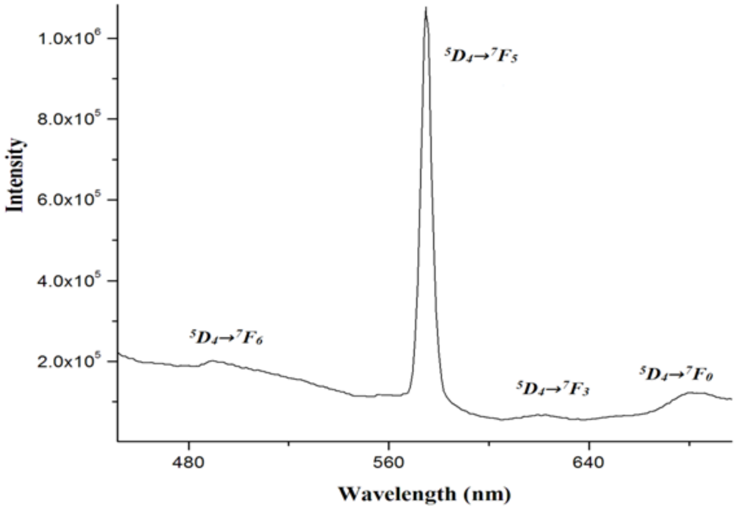


Fig. 1c. Photoluminescence spectrum of Tb^{III} complex

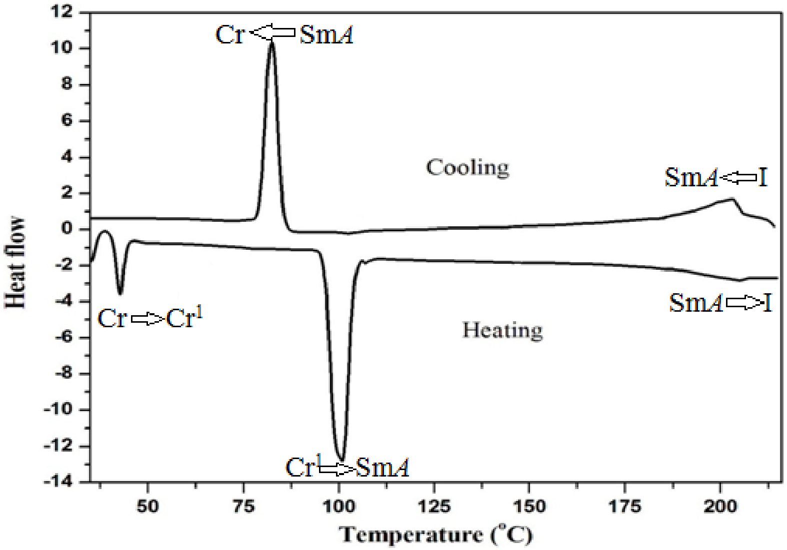
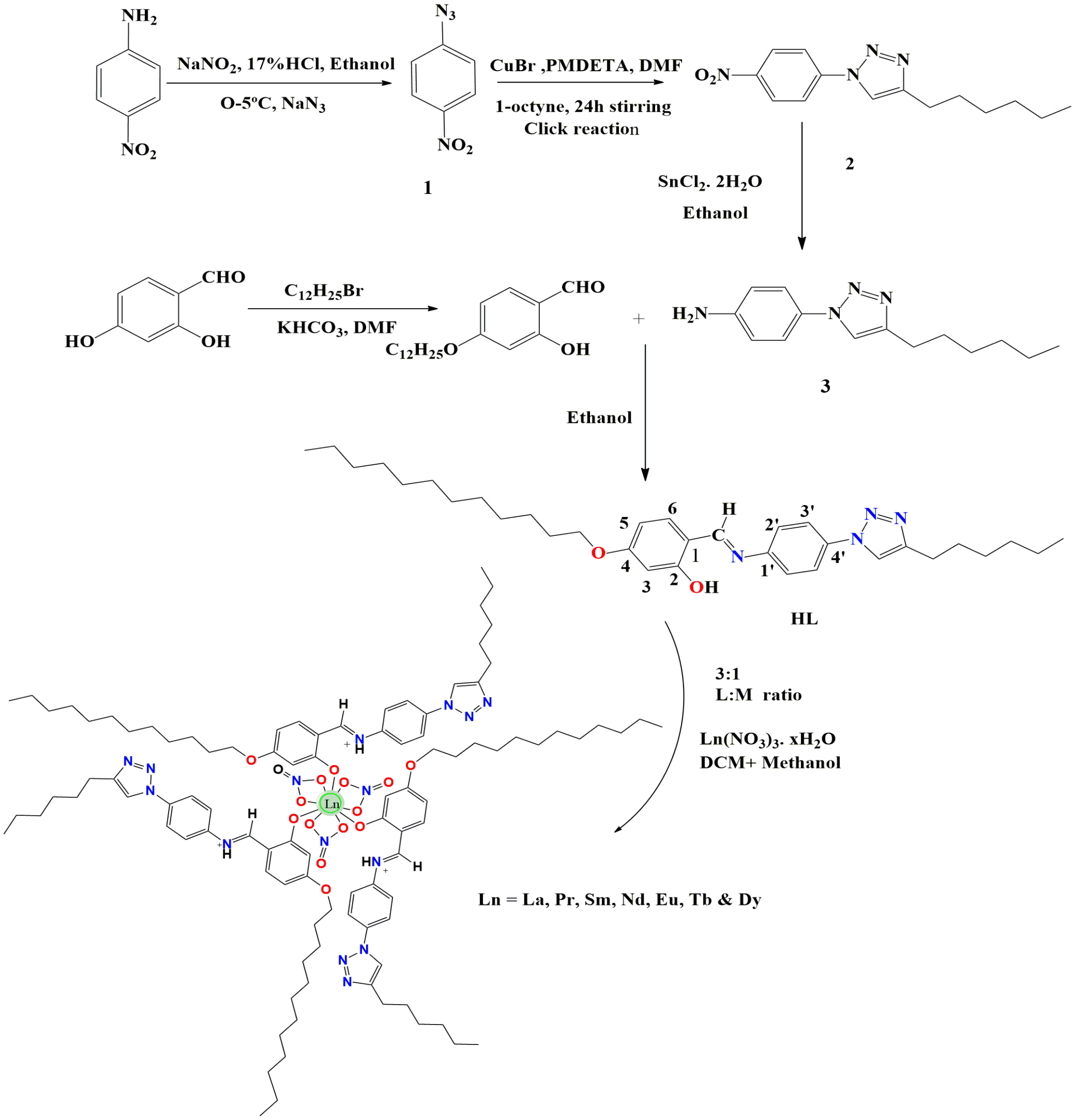
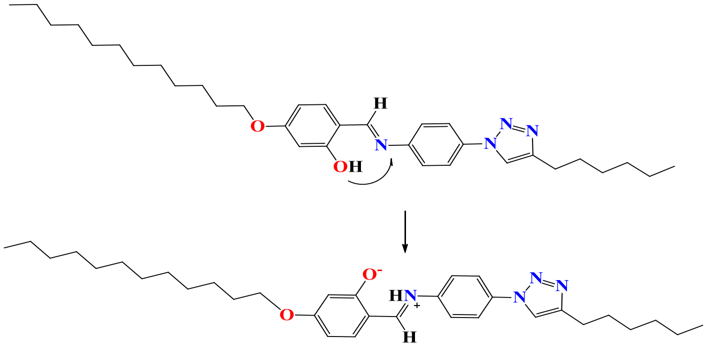


Fig. 2. DSC Thermogram of HL

Fig. 3. Optical Texture of ligand (HL) at 175 ºC



Scheme 1. Synthetic steps for 1, 2, 3, HL and LnIII complexes



Scheme 2. Depiction of migration of phenolic protons to imine nitrogens of the ligand,HL, during the formation of zwitter ion.