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Optically active, mesogenic lanthanide complexes: design, synthesis and characterisation

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The synthesis, molecular structural characterisation and mesomorphic behaviour of lanthanidomesogens with the formula $[\mathbf{LnL(LH)_2}][\mathbf{X}]_2$ are reported. These mesogens were derived from ligands (**LH-*n***) formed by covalently linking the pro-mesogenic cholesterol segment with the *N*-(*n*-decyl)salicylaldimine core through either an even-parity (4-oxybutanoyloxy/6-oxyhexanoyloxy/8-oxyoctanoyloxy) or an odd-parity (5-oxypentano-yloxy) spacer. These ligands were designed based on the recently conceived concept of decoupling the anisometric segment from the metal-coordinating site by a flexible spacer to account for the stabilisation of nematic and/or smectic phases at lower temperatures. The even parity spacer ligands are polymesomorphic whereas the odd parity analogue exhibits only the chiral nematic phase. In contrast, the complexes display solely the smectic A phase indicating that the variation in the nature of lanthanide has no influence on the general phase behaviour of the complexes. The clearing temperatures of both the ligands and the complexes display an odd-even effect; the even members show relatively higher transition temperatures.

Keywords: cholesterol; salicylaldimine; chiral ligands; lanthanidomesogens; polymesomorphism; smectic A phase

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1. Introduction

The molecular design and synthesis of liquid crystals associated with particular magnetic, electronic or luminescence properties desirable for technological applications is a challenging task for chemists. This assignment seems to be fulfilled, in part, by realising metal-containing liquid crystals, metallomesogens (*1, 2*), which combine the unique properties of anisotropic fluids (e.g. orientational response to external fields) with the specific properties of metals (such as magnetic and electronic properties). For a long time, the study of metallomesogens tended to concentrate on metal ions with fairly low coordination numbers that readily formed anisotropic complexes. However, work gradually moved to higher coordination numbers (*3*) and eventually, through the work of Galyametdinov and co-workers (*4*) calamitic lanthanide-containing systems were demonstrated (*5*). Such materials not only possess a large magnetic anisotropy but also display interesting photophysical properties. Indubitably, lanthanides, offer unparalleled advantages in wide-ranging applications and, therefore, development of novel lanthanide-based mesogens is much needed both for basic research and applications.

More recently, Cardinaels *et al.* (*6*) showed how nematic liquid crystal phases could be induced in lanthanide complexes by using ligands that were functionalised with known liquid crystal groups (cyanobiphenyls), which were somewhat decoupled from the main ligand. Such an approach had proved valuable in the preparation of mesomorphic dendritic structures containing rather isotropic cores such as silsesquioxanes (*7*) and even fullerene[60] (*8*) and has been used more recently with simpler metal complexes. (*9*) Thus, the preparation of lanthanide complexes with a range of liquid crystal phases is now possible.

On the other hand, it has been well demonstrated that metallomesogens possessing molecular chirality can self-organise to form chiral phases such as the helical structures of the chiral nematic (N*) or chiral smectic C (SmC*) phases (*1, 2, 10–12*). These features have potential in several applications. In this respect, chiral lanthanide mesogens may exhibit such mesophases with improved magnetic and optical properties. Specifically, such materials may be promising in generating luminescent fast-switching ferroelectric mesophases and producing circularly polarised emission (*13, 14*). Thus, the concept of decoupling an anisometric rigid core from the lanthanide coordination site and the induction of molecular chirality are presently attractive research goals in this area of research.

In fact, the synthesis of chiral lanthanide complexes derived from cholesterol with the above mentioned concept has been previously reported; the complexes were non-mesomorphic but shown to be compatible dopants in chiral liquid crystal mixtures (*10*). In the light of these attractive aspects it occurred to us to interlink covalently a chiral, pro-mesogenic cholesterol core and the lanthanide coordination sphere by means of a flexible spacer.

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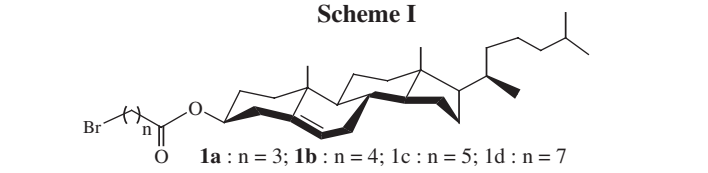
Accordingly, we designed and synthesised four ligands (hereafter referred to as **LH-*n***), wherein the cholesterol segment is separated from the chelating site, an *N*-decylsalicylaldimine core, by a flexible spacer of varying length and parity; the target metal complexes, namely lanthanum (**I-*n*** and **IV-5**), gadolinium (**II-*n***) and ytterbium (**III-*n***) were prepared by reacting the ligands with the corresponding metal salts. In the above abbreviations the symbol '***n***' represents the number of methylene units in the oxyalkanoyloxy spacer and while assigning the (odd/even) parity of the spacer, the total number of carbon atoms (***m*** = ***n***+1) are taken into account.

2. Results and discussion

2.1 Synthesis and characterisation

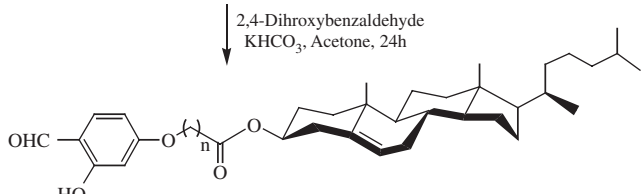
The synthetic route employed to prepare the free ligands (**LH-*n***) and the target complexes (**I-*n*/IV-5, II-*n*** and **III-*n***) is outlined in Scheme I. The key intermediates, cholesteryl ω-(3-hydroxy-4-formylphenoxy)alkanoates (**2a–d**) were synthesised by the selective mono-*O*-alkylation of 2,4-dihydroxybenzaldehyde with cholesteryl ω-bromoalkanoates (**1a–d**) in the presence of a mild base in acetone (*15*). In turn, the cholesteryl alkanoates **1a–d** were obtained by esterification of alkanoyl chlorides with cholesterol using pyridine as the base (*16, 17*). Ligands **LH-3**, **LH-4**, **LH-5** and **LH-7** were obtained in good yield by condensing aldehydes **2a–d** with decylamine. In the final step, three molar equivalents of ligands were reacted with either lanthanum(III) nitrate/trifluoromethanesulphonate or gadolinium(III) nitrate or ytterbium(III) nitrate to obtain complexes **I-*n*/ IV-5**, **II-*n*** and **III-*n***, respectively. All the complexes and free ligands were characterised by elemental analysis and standard spectroscopic techniques. As shown in Table 1, elemental (C, H and N) analytical data were found to be in excellent agreement with the proposed structure of ligands. However, for some complexes the composition data were found to deviate slightly from the expected values. This can be attributed to the general observation that while purifying complexes of the lanthanides by a recrystallisation technique in refluxing solvent, especially those possessing ester linkages in ligands, often leads to the generation of minute amounts of impurities. In fact, in this context, it may be mentioned here that the complexes **I-3**, **III-7**, **IV-3**, **IV-4** and **IV-7** were also

Scheme I



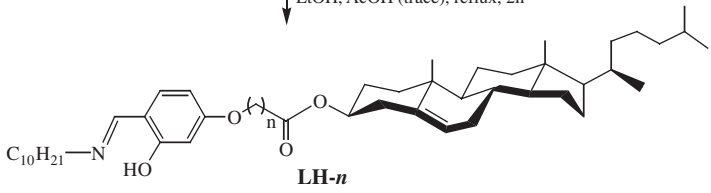
1a : n = 3; **1b** : n = 4; 1c : n = 5; 1d : n = 7

2,4-Dihroxybenzaldehyde
$KHCO_3$, Acetone, 24h



2a : n = 3; **2b** : n = 4; **2**c : n = 5; **2**d : n = 7

1-Decylamine
EtOH, AcOH (trace), reflux, 2h



LH-*n*

LH-3: n = 3; **LH-4**: n =4; **LH-5**: n = 5; **LH-7**: n = 7

Lanthanide
Reagents

[LnL(LH)$_2$][X]$_2$ (**I-*n*/IV-*n***, **II-*n*** and **III-*n***)

Where X = NO_3 or CF_3SO_3 ; Ln = La, Gd, and Yb
LH = Ligand ; L = Ligand without phenolic proton

I-4 : Ln = La, LH = LH-4, X = NO_3 **II-3** : Ln = Gd, LH = LH-3, X = NO_3 **III-3** : Ln = Yb, LH = LH-3, X = NO_3
I-5 : Ln = La, LH = LH-5, X = NO_3 **II-4** : Ln = Gd, LH = LH-4, X = NO_3 **III-4** : Ln = Yb, LH = LH-4, X = NO_3
I-7 : Ln = La, LH = LH-7, X = NO_3 **II-5** : Ln = Gd, LH = LH-5, X = NO_3 **III-5** : Ln = Yb, LH = LH-5, X = NO_3
II-7 : Ln = Gd, LH = LH-7, X = NO_3

IV-5: Ln = La, LH = LH-5, X = CF_3SO_3

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Table 1. Micro-analytical data of the optically active ligands and lanthanidomesogen.

Compounds	Molecular formula	Calculated (found) (%) N	C	H
LH-3	$C_{48}H_{77}NO_4$	1.91 (1.91)	78.75 (78.98)	10.6 (10.60)
LH-4	$C_{49}H_{79}NO_4$	1.88 (1.79)	78.87 (78.47)	10.67 (10.66)
LH-5	$C_{50}H_{81}NO_4$	1.84 (1.85)	79.0 (78.72)	10.74 (10.66)
LH-7	$C_{52}H_{85}NO_4$	1.78 (1.68)	79.24 (79.45)	11.56 (11.71)
I-4	$C_{147}H_{236}LaN_5O_{18}$	2.80 (3.01)	70.61 (69.91)	9.51 (9.4)
I-5	$C_{150}H_{242}LaN_5O_{18}$	2.75 (2.94)	70.86 (70.33)	9.59 (9.54)
I-7	$C_{156}H_{254}LaN_5O_{18}$	2.67 (2.77)	71.33 (71.33)	9.75 (9.78)
II-3	$C_{144}H_{230}GdN_5O_{18}$	2.83 (3.21)	69.83 (68.12)	9.36 (9.17)
II-4	$C_{147}H_{236}GdN_5O_{18}$	2.78 (3.21)	70.1 (68.72)	9.44 (9.38)
II-5	$C_{150}H_{242}GdN_5O_{18}$	2.73 (3.06)	70.35 (68.81)	9.53 (9.47)
II-7	$C_{156}H_{254}GdN_5O_{18}$	2.65 (3.04)	70.84 (69.38)	9.68 (9.73)
III-3	$C_{144}H_{230}N_5O_{18}Yb$	2.81 (3.22)	69.39 (67.49)	9.3 (9.3)
III-4	$C_{147}H_{236}N_5O_{18}Yb$	2.76 (3.15)	69.66 (68.14)	9.39 (9.38)
III-5	$C_{150}H_{242}N_5O_{18}Yb$	2.72 (3.11)	69.92 (68.62)	9.47 (9.55)
IV-5	$C_{152}H_{244}F_6LaN_3O_{19}S_2$ (with a molecule of water)	1.54 (1.47)	66.76 (67.39)	8.99 (8.41)

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prepared but their experimental C, H and N analytical data were found to be far from the expected data and therefore, they are not included here. Nonetheless, the transition temperatures obtained were consistent after two crystallisations and melting and clearing points were not unduly broad.

The infrared spectra of the ligands showed two prominent, sharp bands in the region 1724–1731 and 1629–1632 cm^{-1}, assignable to the C=O group of ester and C=N group of azomethine linkages, respectively. In the spectra of the complexes, these bands shifted to higher frequencies, namely 1733–1735 and 1652–1655 cm^{-1}, respectively, as expected. In view of the formula $[\mathbf{LnL(LH)_2}][\mathbf{X}]_2$ established by elemental analysis, it is reasonable to expect the presence of two different types of ligands in the complex. Conversely, the ^1H nuclear magnetic resonance (NMR) spectra in $CDCl_3$ recorded for the diamagnetic lanthanum complexes **I-4**, **I-5** and **I-7** were sharp and well resolved, which would not support such an assignment; such behaviour has been observed previously (*18*). As a representative case, a portion of the ^1H NMR spectrum showing well resolved signals of aromatic (H_A, H_B and H_C) and imine (H_D) protons of the complex **I-5**, $[\mathbf{LaL(LH\text{-}5)_2}][\mathbf{NO_3}]_2$, is illustrated in the top panel of Figure 1. Further, a considerable upfield shift in the peak positions of aromatic protons H_A and H_B as well as imine proton H_D in the ^1H NMR spectrum of complex **I-5** is apparent when compared with that of analogous protons of free ligand **LH-5** (see bottom panel of Figure 1). This clearly suggests the shielding of protons and thus, the binding of ligands to the metal ion. Most importantly, the broadening of the signal of imine proton H_D in the ^1H NMR spectrum of the complex suggests the existence of constituent ligands in the zwitterionic form that originates as a result of the transfer of phenolic proton to the imine nitrogen (*18*). This suggests that the ligands bind to the metal ion through a phenate oxygen. The ^{13}C NMR spectra of the complex **I-5** and the free ligand **LH-5** are respectively shown in the top and bottom panels of Figure 2. As can be seen, downfield from the $CDCl_3$ peaks (a 1:1:1 triplet at δ = 77), the ligand **LH-5** shows the expected ten signals at about δ = 173, 167.6, 163.4, 163.2, 139.7, 132.5, 122.6, 112, 106.7 and 102 (see bottom panel of Figure 2); the spectrum of the complex **I-5** possesses nine signals at about δ 173, 167.6, 162.7, 139.7, 134.7, 122.6, 109.1, 108.5 and 104.2 (see top panel of Figure 2). Thus, the merging of two signals and change in the peak positions of several signals in the spectrum of the latter with respect to the former suggests coordination of the ligands with metal ion.

2.2 Mesomorphic behaviour

The thermal properties of the free ligands were ascertained with the aid of polarising optical microscopy (POM) and differential scanning calorimetry (DSC). However, the phase sequences and transition temperatures of the complexes were established using microscopy alone as none of the complexes showed thermal events in the DSC thermograms. This effect has been observed before (*19*) and in many cases, small experimental variations have allowed transitions to be observed, but not in this case; currently, we have no obvious or ready explanation for this phenomenon. Nonetheless, the phase transition temperatures were highly reproducible by microscopy, suggesting that the complexes under study are thermally stable. The details of these investigations on both free ligands and complexes are summarised in Table 2 and discussed below.

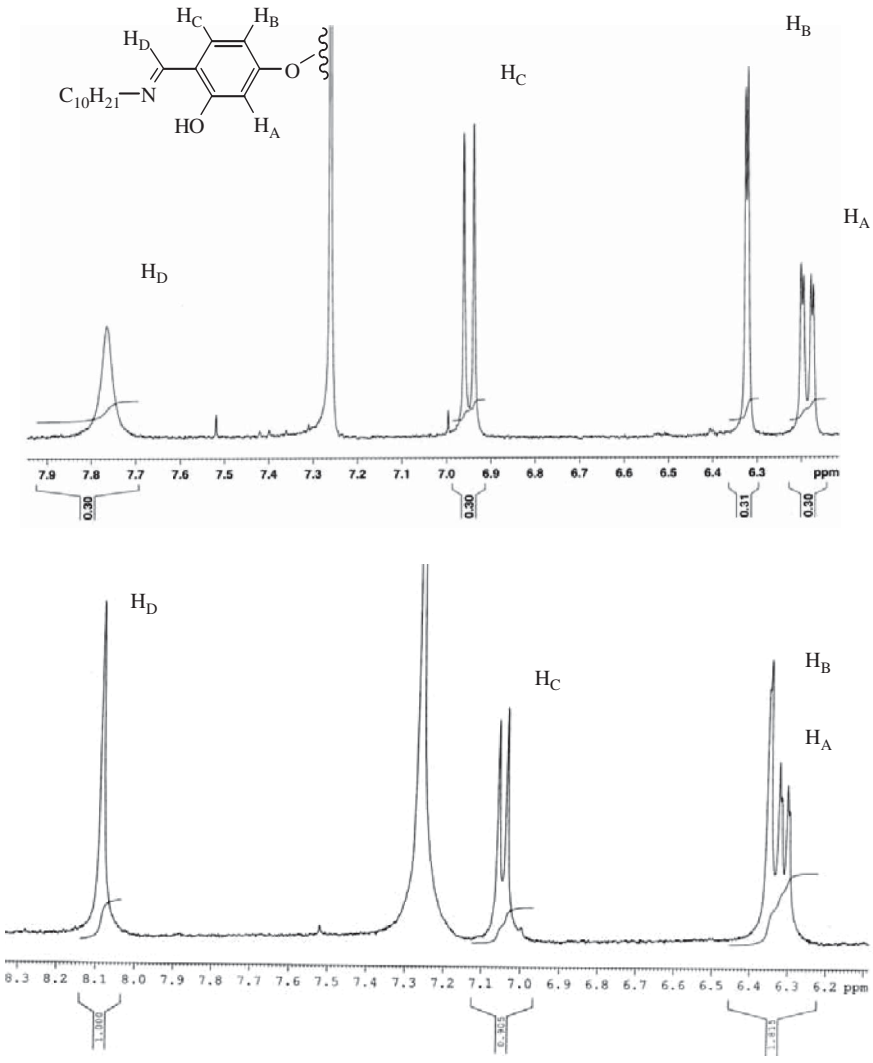

Figure 1. A portion of the ^{1}H nuclear magnetic resonance spectrum of lanthanidomesogen **I-5** (top) and free ligand **LH-5** (bottom) in $CDCl_3$ showing well resolved aromatic (H_A, H_B and H_C) and imine (H_D) protons. Note that the upfiled shift of aromatic protons H_A and H_B as well as imine proton H_D in the ^{1}H nuclear magnetic resonance spectrum of the lanthanidomesogen **I-5** implies chelation of the ligands with metal species.

It is apparent from Table 2 that the ligands **LH-3**, **LH-5** and **LH-7**, consisting of an even-parity spacer, exhibit enantiotropic mesomorphism. In particular, compounds **LH-3** and **LH-5** display an enantiotropic smectic A (SmA*), a twist grain boundary (TGB) and a chiral nematic (N*) phase in addition to a monotropic SmC* phase. Compound **LH-7** with a slightly longer even-parity (8-oxyoctanoyloxy) spacer stabilises enantiotropic N* phase and monotropic TGB, SmA* and SmC* phases. Notably, the technologically important SmC* phase supercools to well below room temperature and transforms to another phase whose characteristic could not be ascertained owing to its occurrence at low temperature (below 15°C) and hence, we hereafter refer to it as M. On the other hand, the ligand **LH-4** having the 5-oxypentanoyloxy (odd-parity) spacer shows a monotropic N* phase with lower transition temperatures. The loss of polymesomorphism in this ligand and reduction in the transition temperature can be interpreted in terms of loss of anisotropy owing to the odd number of carbon atoms leading to a bent molecular conformation. Thus, as observed commonly (*15, 20*), the transition temperatures, especially the clearing points of the ligands, depend critically on the parity of the spacer, in which the odd-member exhibits the lower value. It must be mentioned here that the phase transitions of all these ligands are highly reproducible for any number of heating and cooling cycles. The DSC thermograms of the first and subsequent heating and cooling scans corroborated the microscopic observations and further supported the repeatability of the phase transitions of the ligands.

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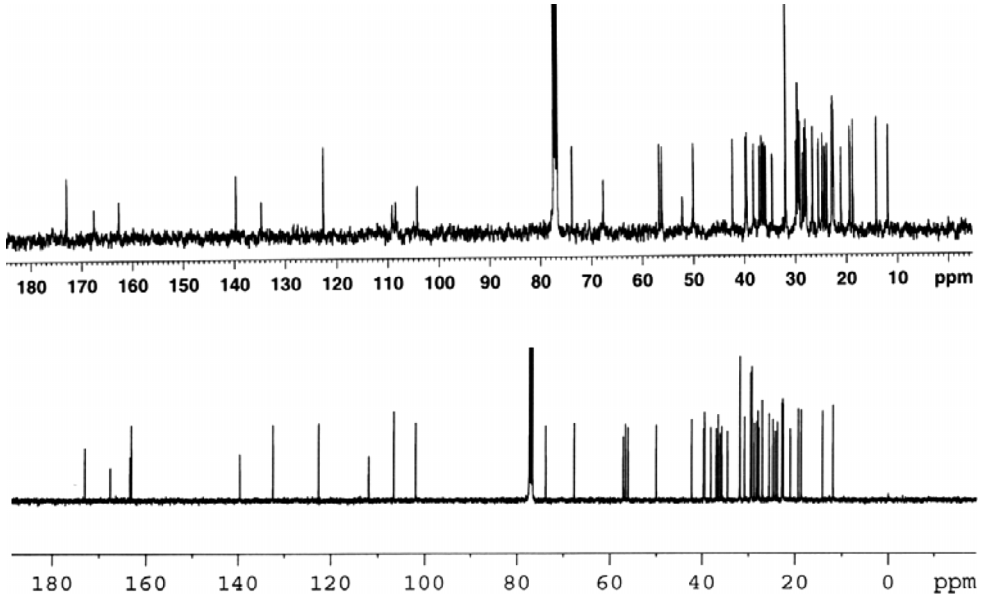

Figure 2. The ^{13}C nuclear magnetic resonance spectrum of lanthanidomesogen **I-5** (top) and ligand **LH-5** (bottom) in $CDCl_3$.

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Table 2. Phase transition temperatures (°C)[a,b] of chiral ligands and corresponding lanthanidomesogens.

Ligands and complexes	Phase sequence	
	Heating	Cooling
LH-3	Cr 99.1 [46.9] SmA* 111.9 TGB 113.3 [1.6][c] N* 119 [3.1] I	I 118.4 [2.9] N* 112.8 TGB 111.3 [1.4][c] SmA* (91.1[d]) SmC* 58.4 [10] Cr
LH-4	Cr 90 [39.1] I	I (76.9) [7.7] N* 64.1 [18.5] Cr
LH-5	Cr 97.5 [53.6] SmA* 103.3 TGB 104.9 [2][c] N* 109.8 [3.9] I	I 109.3 [3.9] N* 104.6 TGB 102.9 [1.8][c] SmA* (81.1[d]) SmC*[e]
LH-7	Cr 92.2 [55.9] N* 101 [3.9] I	I 100.6 [3.6] N* 91.4[d] TGB (90[d]) SmA* (72.9[d]) SmC* (14.6) [10.2] M
I-4	Cr 100 SmA* 183 I	I 180 SmA*[f]
I-5	Cr 136 SmA* 213 I	I 208 SmA*[f]
I-7	Cr 116 SmA* 193 I	I 189 SmA*[f]
II-3	Cr 141 SmA* 220 I	I 216 SmA*[f]
II-4	Cr 134 SmA* 182 I	I 180 SmA*[f]
II-5	Cr 141 SmA* 213 I	I 211 SmA*[f]
II-7	Cr 141 SmA 201 I	I 199 SmA*[f]
III-3	Cr 137 SmA* 209 I	I 207 SmA*[f]
III-4	Cr 133 SmA* 177 I	I 174 SmA*[f]
III-5	Cr 135 SmA* 201 I	I 197 SmA*[f]
IV-5	Cr 102 SmA* 156 I	I 153 SmA* [f]

Temperatures in parenthesis () indicate monotropic transitions. Cr = crystal; SmC* = chiral smectic C phase; SmA* = chiral smectic A phase; TGB = twist grain boundary phase with either SmA or SmC blocks (SmC = smectic C phase); N* = chiral nematic phase; M = unknown phase; I = isotropic phase.

[a]Phase transition temperatures of the ligands were determined by both polarising optical microscope (POM) and differential scanning calorimetry (DSC) studies: peak temperatures in the DSC thermograms obtained during the first heating and cooling cycles (scanning rate = 5°C minute^{-1}) coupled with optically measured temperatures are given. [b]Transition temperatures of the complexes were determined with the aid of a POM study (at a rate of 5°C minute^{-1}) as the expected well-resolved thermograms of both heating and cooling cycles could not be obtained. [c]Although N*–TGB/TGB–N* and TGB–SmA*/SmA*–TGB phase transitions were observed in POM, they were not resolved in DSC traces; hence the enthalpy value represents the combined enthalpy for N*–TGB/TGB–N* and TGB–SmA*/SmA*–TGB transitions. [d]Phase transition was observed under POM; too weak to be detected by DSC. [e]No crystallisation was observed until the limitation of the DSC (-60°C) instrument. [f]The SmA* phase structure freezes into a glassy state below 90°C while cooling from the isotropic phase; indeed until this temperature, the SmA phase can be easily sheared.

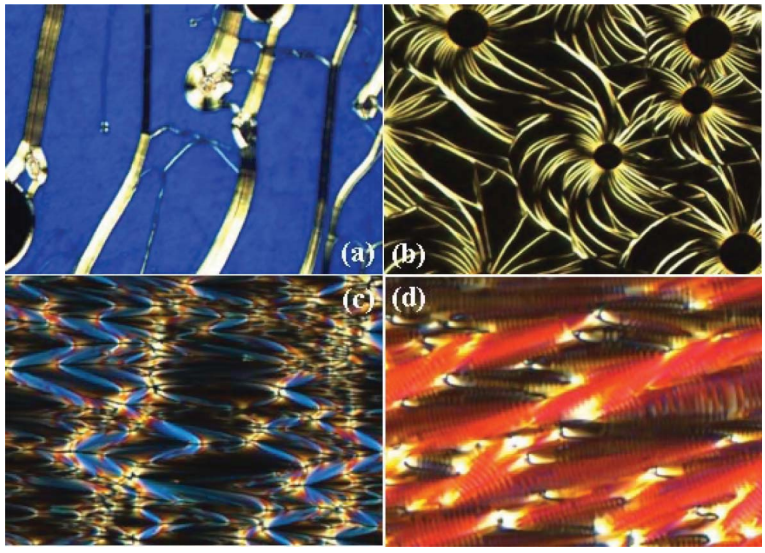

Figure 3. Photomicrographs of the textures of different mesophases observed for the ligand **LH-5**: (a) planar oily streak texture of the N* phase (108°C); (b) filamentary texture of the homeotropically aligned twist grain boundary phase (104°C); (c) focal-conic texture of the homogeneously aligned SmA* phase (98°C); (d) an equidistant line pattern superimposed on the focal-conics of SmC* phase (30°C).

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All the mesophases, namely the SmC*, SmA*, TGB and N* phases, were identified based on the observation of their characteristic textural patterns. For example, for the ligand **LH-5** microscopy revealed a focal-conic texture for the N* mesophase on cooling from the isotropic phase held between untreated glass slides; indeed, the focal-conic texture changes into an oily streak texture (see Figure 3(a)) on shearing gently. On further cooling, the N* phase passes through a transient TGB phase to the SmA* phase. The TGB phase showed a filament texture (Figure 3(b)) in regions where there was homeotropic alignment of the molecules, as expected. The presence of the TGB phase signifies that the ligands are strongly chiral and thus, the pitch of their N* phase is shorter; this can be attributed to the presence of cholesterol moiety (*22*) in ligands. It may be mentioned here that chirality is a stereochemical (symmetry) property, and thus it is qualitative. Nonetheless, quantitative measures of chirality are well known in the field (*21*). For example, in the case of the chiral nematic phase, the structure which is always chiral, is termed strongly or weakly chiral by considering whether the pitch is shorter or longer, respectively. The SmA* phase was recognised based on the observation of a focal-conic texture (see Figure 3(c)) in slides treated for planar orientation and a dark field of view in slides treated for homeotropic alignment. Subjecting the SmC* phase to planar boundary conditions revealed dechiralisation lines on top of the focal-conic fan texture (see Figure 3(d)); with the surfaces treated for homeotropic alignment, it exhibited a cloudy texture. On cooling further, the SmC* phase froze into a glassy state; this is supported by the fact that the phase lost fluidity at about 60°C. The DSC thermograms recorded for the two heating and cooling cycles at a rate of 5°C min^{-1} corroborate the optical observation (see Figure 4).

Contrary to the rich phase behaviour shown by the free ligands, the complexes displayed one enantiotropic mesophase only. The mesophase assignment was based on two inherent properties, i.e. birefringence and fluidity. The samples, placed between a pair of ordinary glass slides and cooled from the isotropic phase, exhibited a mesophase with bâtonets (see Figure 5(a)) that coalesced to form a focal-conic pattern as shown in Figure 5(b). This textural pattern

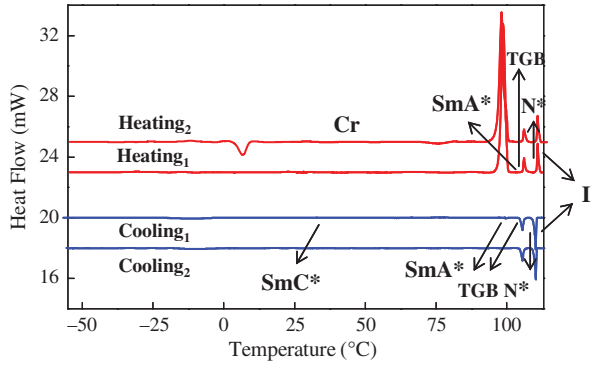

Figure 4. Differential scanning calorimetry traces obtained during the first and second heating/cooling cycles at a rate of 5°C $minute^{-1}$ for **LH-5**. Note that the SmC* phase supercools well below the room temperature.

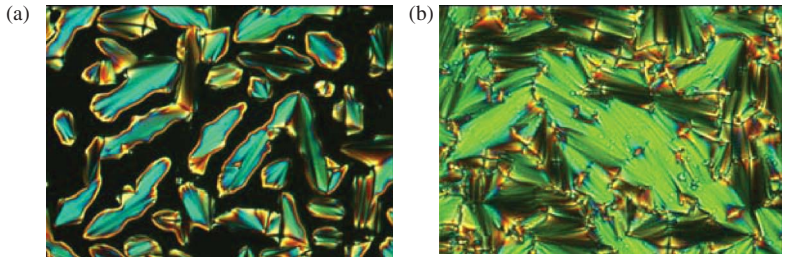

Figure 5. Microphotographs of the textures observed for the SmA* phase of complex **I-7**: (a) bâtonets appearing just below the isotropic phase (at 188.5°C); (b) a focal-conic texture of the fully grown phase (at 187°C).

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persisted until room temperature while losing fluidity at about 90°C, implying that the SmA* glass was formed. If the fluid SmA* phase was sheared, the focal-conic texture transformed into an oily streak texture characterised by bands of bright lines embedded in the pseudo isotropic background; thus, the use of ordinary slides made it possible to visualise the optical textural patterns arising due to both planar and homeotropic alignment of the molecules. As expected, the focal-conic texture was observed exclusively when slides treated for planar alignment were used. In general, the phase transitions, especially the clearing temperatures, were reproducible indicating that the complexes were thermally stable. Thus, all the lanthanide complexes synthesised display the SmA phase exclusively. This behaviour is not surprising given the two general observations: (i) all the one-ring *N*-alkyl chain substituted *N*-salicylaldimine-based lanthanide complexes reported hitherto, without any exception, are known to exhibit the SmA phase solely (*5*); (ii) when cholesterol is used to induce chirality into the molecular architecture of mesogens such as monomers, dimers and polymers, the stabilisation of smectic phase/s is not uncommon (*22*).

Apparently, the transition temperatures depend mainly on the length and parity of the spacer largely, and the nature of the counter ion to some extent. For example, the complexes with odd-parity (5-oxypentanoyloxy) spacer (**I-4**, **II-4** and **III-4**) exhibit lower transition temperatures when compared with the even members. Thus, the prominent odd-even effect observed for the free ligands is reflected in the thermal behaviour of the complexes also; Figure 6 illustrates such an effect observed for the gadolinium(III) complexes, in which the even-members **II-3**, **II-5** and **II-7** exhibit the higher transition temperatures with the indication that the effect tends to attenuate on increasing the number of carbon atoms in the spacer (***m*** = ***n***+1). In fact this behaviour is in agreement with a recent observation that the copper complexes exhibit an odd-even effect for the nematic-isotropic transition

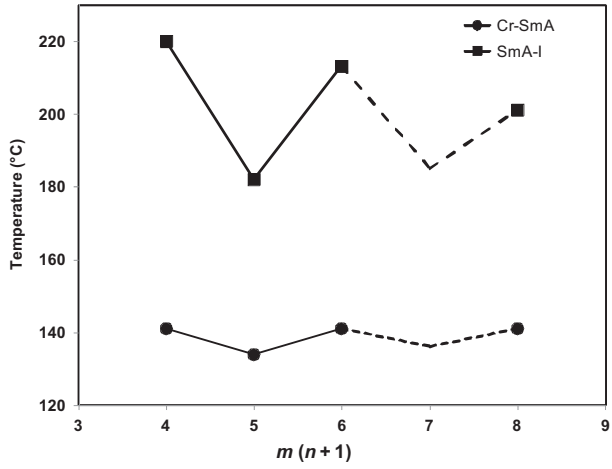

Figure 6. The dependence of the transition temperatures on the number of carbon atoms (***m*** = ***n*** + 1) in the oxyalkanoyloxy spacers for gadolinium(III) (**II-*n***) series) complexes in the heating cycle. The dashed lines joining points are suggestive of the general trend; it may be noted that experimental data do not cover for ***m*** = 7.

temperatures (*20*). Furthermore, the lanthanum complex with a triflate counter anion (**IV-5**) shows a lower transition temperature when compared with nitrate complexes, which is in accordance with the results of an earlier report (*23*).

3. Summary

The synthesis and mesomorphism of lanthanum(III), gadolinium(III) and ytterbium(III) complexes with nitrate or triflate counter anion are described. These complexes, primarily conceived to explore the possibility of stabilising chiral phases, were derived from the ligands wherein the metal coordination sphere was decoupled from the mesogenic core by means of a flexible spacer. Precisely, optically active ligands comprising an *N*-decylsalicylaldimine unit as a complexing

function, and a cholesterol segment as a pro-mesogenic core, linked through an oxyalknoyloxy spacer of varying length and parity were prepared and treated with lanthanide salts to obtain the mesogenic complexes. The free ligands exhibited a rich phase behaviour while, contrary to expectation, all the complexes, irrespective of the variations in length and parity of the spacer as well as metal ions, exhibited smectic mesomorphism. Interestingly, the complexes, like the ligands, exhibited an odd-even effect as the parity of the spacer was varied, a feature not reported hitherto for the lanthanidomesogens.

4. Experimental

4.1 General information

2,4-Dihydroxybenzaldehyde, cholesterol, 4-bromobutyric acid, 5-bromovaleric acid, 6-bromohexanoic acid, 8-bromooctanoic acid, lanthanum(III) nitrate hydrate [$La(NO_3)_3{\cdot}H_2O$], lanthanum(III) trifluoromethanesulphonate hydrate [$La(CF_3SO_3)_3{\cdot}8H_2O$], gadolinium(III) nitrate [$Gd(NO_3)_3{\cdot}6H_2O$] and ytterbium(III) nitrate [$Yb(NO_3)_3{\cdot}5H_2O$] were purchased from Sigma-Aldrich chemical company and used as received. Solvents used in chemical reactions were purchased locally and purified/dried according to literature methods. The ligands and complexes were purified by recrystallisation choosing an appropriate mixture of solvents. The intermediates were suitably purified by column chromatographic and/or recrystallisation techniques. Column chromatography was carried out using either silica gel (100–200) or neutral aluminium oxide as stationary phases. Aluminium sheets pre-coated with silica gel (Merck, Kieselgel60, F_{254}) were used for thin layer chromatography. Infrared spectra of all the compounds were measured on a Perkin-Elmer Spectrum 1000 FTIR spectrometer. The spectral positions (absorption maxima) are given in wave numbers (cm^{-1}). ^1H NMR spectra were recorded using a Bruker AMX-400 spectrometer; the chemical shifts are reported in ppm relative to $SiMe_4$ (TMS) as an internal standard and coupling constants are presented in Hz. ^{13}C NMR spectra were also recorded using the same instrument. Elemental analyses (C, H and N) were performed at the University of Newcastle upon Tyne, UK. Mass spectra were determined on a JOEL JMS-600H spectrometer in FAB^+ mode using 3-nitrobenzyl alcohol as a liquid matrix. The phase transitions and corresponding temperatures of both ligands and complexes were determined by a POM (Leitz DMRXP or Leica DMLP) equipped with a programmable hot stage (Metler FP90 or FP82HT). The optical textural observations of the mesophases were performed using untreated glass slides; for confirmation, surface-coated slides treated for either planar alignment or homeotropic alignment were used. A DSC (Perkin Elmer DSC-7), calibrated using pure indium as a standard, was used to record thermograms of heating and cooling cycles at a rate of $5^\circ C\ min^{-1}$. The phase transition temperatures and associated enthalpies, especially those of the ligands, were deduced from these DSC traces.

4.2 General procedure for the synthesis of ligands: cholesteryl ω-(3-hydroxy-4-(n-decyliminomethyl) phenoxy)alkanoates (LH-3, LH-4, LH-5 and LH-7)

To a vigorously stirring solution of *n*-decylamine (0.51 mmol, 1.5 equivalent) in absolute ethanol (25 ml) was added cholesteryl ω-(3-hydroxy-4-formylphenoxy) alkanoate (**2a**, **2b**, **2c** or **2d**) (0.34 mmol, 1 equivalent) and a drop of acetic acid. The reaction mixture was heated to reflux for 1 hour. A yellow solid separated from the reaction mixture upon cooling was filtered and washed repeatedly with hot ethanol. It was purified by repeated recrystallisation from a mixture of CH_2Cl_2:EtOH (1:9). They were characterised by standard spectroscopic methods and elemental analyses; as a representative case, the complete characterisation data for one of the ligands is given below.

Cholesteryl 6-(3-hydroxy-4-(decyliminomethyl)-phenoxy)hexanoate (**LH-5**): a yellow solid; yield: 77%; infrared (KBr Pellet): ν_{max} (cm^{-1}) 3428, 2920, 2851, 1724, 1630, 1579, 1518, 1232 and 1172; ^1H NMR (400 MHz, $CDCl_3$): δ 14.20 (s, 1H, OH), 8.08 (s, 1H, N=CH), 7.05 (d, J = 8.6 Hz, 1H, Ar), 6.35 (d, J = 2.2 Hz, 1H, Ar), 6.32 (dd, J_1 = 8.6 Hz, J_2 = 2.4 Hz, 1H, Ar), 5.37 (brd, J = 3.6 Hz, 1H, 1 × olefinic), 4.62 (m, 1H, 1 × CHOCO), 3.97 (t, J = 6.4 Hz, 2H, 1 × OCH_2), 3.52 (t, J = 6.7 Hz, 2H, 1 × NCH_2), 2.32–2.02 (m, 4H, 2 × allylic methylene), 1.99–0.86 (m, 57H, 21 × CH_2, 6 × CH, 3 × CH_3), 1.01 (s, 3H, 1 × CH_3), 0.96 (d, J = 6.9 Hz, 3H, 1 × CH_3) and 0.67 (s, 3H, 1 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): 173.05, 167.63, 163.42, 163.15, 139.72, 132.51, 122.65, 111.95, 106.7, 102, 73.84, 67.68, 57.2, 56.72, 56.16, 50.06, 42.35, 39.77, 39.56, 38.19, 37.03, 36.63, 36.22, 35.84, 34.61, 31.92, 31.9, 30.89, 29.61, 29.58, 29.36, 29.35, 28.81, 28.27, 28.06, 27.85, 27.1, 25.63, 24.82, 24.33, 23.87, 22.87, 22.72, 22.61, 21.07, 19.36, 18.76, 14.16 and 11.90; MS (FAB+): m/z calculated for $C_{50}H_{81}NO_4$: 760.6, found: 760.6. For micro-analytical data see Table 1.

4.3 General procedure for the preparation of lanthanide complexes

A flask equipped with a magnetic stir bar and nitrogen inlet was charged with ligand (LH-3, LH-4, LH-5 or LH-7) (0.34 mmol, 2.71 equivalent) and dry

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tetrahydrofuran (5 ml). Then a solution of lanthanum(III) nitrate/lanthanum(III) trifluoromethanesulphonate salt (0.13 mmol, 1 equivalent) in dry acetonitrile/tetrahydrofuran (2 ml) was added drop-wise and the reaction mixture was stirred at room temperature for 3 hour. The solvents were removed *in vacuo* from the reaction mixture to obtain a solid mass. It was dissolved in chloroform and filtered through filter paper twice. To the filtrate, absolute ethanol was added drop-wise until a pale yellow complex appeared; this was redissolved by heating (this step involving the heating exercise may be avoided, perhaps reduces the generation of impurities) and left the clear solution to attain room temperature. A pale yellow compound separated in the form of a gel was collected by filtration and then dried thoroughly under vacuum. The complexes were characterised by spectroscopic methods (wherever applicable) and elemental analyses; as a representative case, the characterisation data for one of the complexes is given below.

I-5: infrared (KBR Pellet): ν_{max} in cm^{-1} 2933, 1733, 1613, 1528, 1230 and 1176; ultraviolet-Vis: λ_{max} = 318.66 nm, $\varepsilon = 4.64 \times 10^3$ dm^3 mol^{-1} cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 12.65 (s, 3H, 3 × OH), 7.88 (s, 3H, 3 × N=CH), 6.99 (d, J = 8 Hz, 3H, 3 × Ar-H), 6.32 (d, J = 2.2 Hz, 3H, 3 × Ar-H), 6.20 (dd, J_1 = 8.7 Hz, J_2 = 2.1 Hz, 3H, 3 × Ar-H), 5.37 (brd, J = 3.7 Hz, 3H, 3 × olefenic), 4.63 (m, 3H, 3 × CHOCO), 3.7 (t, J = 4 Hz, 6H, 3 × OCH_2), 3.5 (t, J = 7.1 Hz, 6H, 3 × NCH_2), 2.31–2.0 (m, 12H, 6 × allylic methylene), 1.99–0.85 (m, 153H, 3 × CH_3, 63 × CH_2, 18 × CH), 1.01 (s, 9H, 3 × CH3), 0.94 (d, J = 6.9 Hz, 9H, 3 × CH_3), 0.89 (d, J = 1.9 Hz, 9H, 3 × CH_3), 0.87 (d, J = 1.6 Hz, 9H, 3 × CH_3) and 0.67 (s, 9H, 3 × CH_3);^{13}C NMR (100 MHz, $CDCl_3$): 173, 167.59, 162.74, 139.69, 134.70, 122.58, 109.14, 108.48, 104.19, 73.8, 67.66, 56.7, 56.16, 52.2, 50.04, 42.31, 39.74, 39.51, 38.17, 37.01, 36.59, 36.18, 35.78, 34.51, 31.88, 29.79, 29.55, 29.30, 29.11, 28.57, 28.21, 27.99, 27.82, 26.6, 25.45, 24.7, 24.27, 23.84, 22.79, 22.67, 22.54, 21.03, 19.31, 18.71, 14.09 and 11.84.

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