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Novel wide-range columnar and lamellar photoluminescent liquid crystalline lanthanides complexes with mesogenic 4-pyridone derivatives

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Abstract: A series of novel liquid crystals with various lanthanide ions (Eu(III), Sm(III) and Tb(III)) was designed and prepared starting from corresponding lanthanide nitrates and N-alkylated 4-pyridones derivatives with mesogenic 3,4,5-tris(alkyloxy)benzyl moieties (alkyl = hexyl, octyl, decyl, dodecyl, tetradecyl or hexadecyl). These new lanthanidomesogens were investigated for their mesogenic properties by a combination of differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and temperature dependent powder X-ray diffraction (XRD). Additionally, their thermal stability was assessed by thermogravimetric analysis (TG). All these complexes display an enantiotropic liquid crystalline behavior with either a lamellar (SmA), in the case of shorter chains analogues (6 and 8 carbon atoms) or a hexagonal columnar (Col_h) phase, for complexes with higher number of carbon atoms (12, 14 and 16), assigned on the basis of their characteristic texture and XRD studies. For complexes with an intermediate number of carbon atoms in the side chains (10), both a lamellar phase at lower temperatures and a Colh phase at higher temperatures were evidenced. In solid state, all these complexes show characteristic emissions assigned to the corresponding lanthanide ion. In addition, the luminescence decay curves showed single exponential decays with the characteristic times in the ms range (0.75-0.90 ms for Eu(III), 0.045-0.060 ms for Sm(III) and 0.75-1.05 ms for Tb(III), respectively).

Introduction

In the last decades, introduction of d- or f-block metals in organic liquid crystalline matrices to give metallomesogens was widely studied for their interesting electronic, magnetic and optical properties.[1-3] Liquid crystals are very attractive materials with various interesting applications (manufacturing of LCDs, molecular sensors and detectors, optical switches, etc.) [4-8] In search for highly emissive metallomesogens, the lanthanide-containing liquid crystals (lanthanidomesogens) play a central

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role and they are regarded as a promising class of light-emitting liquid crystals with excellent emission properties such as the narrow emission lines of high purity colors, the choice of tuning the emission color by changing the lanthanide ion or the possibility to create luminescent materials with polarized emission in the liquid crystal (LC) state.[9-22] Due to their wide-ranging applications, from telecommunications to life sciences, development of novel lanthanide-based mesogens is much needed both for fundamental research and applications.[23-26] Among the f-block metals, the Eu(III) and Tb(III) complexes were found to be the strongest emitters, red and green respectively, while the Sm(III) compounds were less studied due to their weaker luminescence intensity in comparison to Eu(III) or Tb(III) compounds.[27, 28]

The design of advanced material based on lanthanide ion with higher coordination number (usually 8 or 9) in a highly anisotropic molecule presenting both mesomorphism and emission properties, represents a challenge for the current research. Furthermore, the fact that the trivalent lanthanide ions absorb weakly the radiation due to their forbidden $f \rightarrow f$ transitions poses additional challenges to the development of novel lantanidomesogens with interesting photophysical properties. Indeed, the low emission of the lanthanide ions can be improved by using an organic ligand with a large absorption coefficient that play the antenna role, by absorbing light and transfer excitation energy to the emitting levels of the lanthanide ion.[29,30] Thus, the choice of suitable ligands capable of having the antenna properties while forming thermodynamically stable complexes with lanthanide ions becomes essential in the design of novel luminescent lanthanidomesogens. Preparation of metallomesogens with highly coordination number might be possible either through the separation of mesogenic units and coordination units via long flexible alkyl spacers or by increasing the number of long flexible alkyl chain attached to the coordinating unit.[31, 32] The two mechanisms mentioned above have led to the research and development of several classes of lanthanidomegens starting from ligands such as: Schiff bases, macrocyclic ligands (phtalocyanine, porphyrine, etc.), alkanoates, β-diketonate, bis (benzimidazolyl) pyridine, etc.[1] A new class of thermotropic lanthanidomesogens bearing mesogenic ligands derived from 4-pyridone was reported recently.[31] Mesogenic compounds based on the 4-pyridone core have been known since long time ago; [33, 34] but, as far as we are concerned, these compounds have not been utilized in the coordination of metals to give metallomesogens despite the fact that they show excellent coordination abilities, in particular to lanthanides.[35-37] Importantly, the 2- or 4-pyridone derived compounds have been previously employed as O-coordinated ligands in the study of lanthanide complexes with interesting magnetic and optical properties.[38-45] The group of mesogenic monodentate ligands

developed by us possesses cyanobiphenyl groups attached to the 4-pyridone coordinating unit via a flexible long alkyl spacer. The new Eu(III) complexes show lamellar phases (SmA) and a very high thermal stability while preserving the emission properties in the LC phase at high temperature up to clearing point. Their mesogenic properties depend on the spacer length; while the transition temperatures were influenced by the number of mesogenic group employed and the spacer length.[31]

In this paper, we would like to show that, by employing relatively easy to design and synthesize non-chelating O-donor monodentate ligands, it is possible to tune the liquid crystalline properties of the lanthanidomesogens, ranging from lamellar, as proven earlier, to long range lamellar and hexagonal columnar phases in the present study, and, in the meantime, preserving the emission properties of the lanthanide ions. The present work reports on the synthesis of some new ligands, N-3,4,5tris(alkyloxy)benzyl-4-pyridone, and their new thermotropic lanthanidomesogens containing the Eu(III). Sm (III) and Tb(III) ions. In this case, the organic ligand has three long flexible alkyl chains with variable number of carbon atoms (6 to 16) attached to the coordinating unit, represented by the 4-pyridone unit. Moreover, these new complexes have mesomorphic properties either a lamellar or hexagonal and exhibit columnar mesophase, depending on the alkyl chain length, over a large temperature range, in some cases more than 200°C, as shown differential scanning calorimetry (DSC). A detailed bv characterization of their thermal and self-organization properties were investigated by powder X-ray diffraction (XRD) and polarizing optical microscopy (POM) observations.

Results and Discussion

Synthesis and characterization of ligands and complexes

The novel monodentate ligands having three alkoxy chains with variable number of carbon atoms were prepared through the reaction of 4-hydroxypyridine with 3,4,5-tris(alkyloxy)benzyl bromide derivatives in THF, in the presence of NaOH and tetrabutylammonium bromide (TBABr) as phase transfer catalyst to give the 4-pyridone derivatives **PyO-***n*, as the main product in relatively high yield 65-70% (Scheme 1). [46, 47] All the new N-alkylated-4-pyridone derivatives were fully characterized by ¹H- and ¹³C-NMR and IR spectroscopies as well as by elemental analyses.

In the next step, the nitrate lanthanide (III) complexes were obtained by reacting the 4-pyridone ligands with the corresponding $M(NO_3)_3 xH_2O$ salt (Ln = Eu, Tb, Sm, x = 5 or 6) in hot ethanol (Scheme 1). By mixing the two hot solutions, white precipitates were obtained within minutes. The solids were isolated by filtration and then recrystallized from a mixture of dichloromethane/ethanol 1/1 v/v at -20°C. The TG and elemental analyses indicated that there is no crystallization or coordination water or solvent molecules. Based on the crystal structure of the related Eu(III) complex with *N*-benzyl-4-pyridone ligand, the structure of these complexes can be described in the following way: three molecules of 4-pyridone ligand are coordinated to lanthanide ion by means of the oxygen atom, and three

bidentate nitrate ions complete the coordination geometry with coordination number CN=9.[31]



Scheme 1. General reaction pathway for synthesis of *N*-alkyl-4-pyridones ligands and their lanthanide complexes: i) $C_nH_{2n+1}Br,K_2CO_3/MEK$, reflux for 3 days, ii) LiAlH₄/THF, iii) PBr₃/CH₂Cl₂, iv) 4-hydroxypyridine, THF/H₂O, NaOH 2N, TBABr, reflux 24h, 75°C, v) M(NO₃)₃xH₂O (x=5 or 6), EtOH, stirring 2h at room temperature.

Thermal stability of the ligands and complexes

The results of the thermogravimetric analyses show that the lanthanide complexes have a high thermal stability, their decompositon started at temperatures around 300°C. For exemplification, Figure 1 gives the TG curves for 4-pyridone ligand PyO-10 and its lanthanide complexes Eu-10, Sm-10 and Tb-10. The ligand PyO-10 is highly stable in the 25 - 350°C range. At temperatures higher than 350°C, the thermogram indicates a small mass loss, followed by the total decomposition at a temperature higher than 370°C. In comparison, the thermogravimetric analysis of the corresponding Ln(III) complexes show that these materials are stable in the 0-300°C region, while their decomposition started at temperatures higher than 300°C. On the other hand, these TG curves do not contain steps or other indication of mass loss in this region, therefore the complexes do not contain small molecules (water or solvent). All the lanthanide complexes undergo complete decomposition up to 450°C.

Liquid crystalline properties

The liquid crystalline properties were investigated by a combination of hot stage polarizing optical microscopy (POM) and differential scanning calorimetry (DSC), followed by powder X-rays diffraction (XRD) in the mesophase range to confirm the nature of the LC phases. The transition temperatures for ligands and their corresponding lanthanide (III) complexes are presented in Table 1. Only selected ligands and their lanthanide

(III) complexes were studied by variable-temperature powder Xray diffraction with the aim of elucidating the nature of the liquid crystalline phase and getting insights regarding the effects of delicate structural modifications onto the packing of molecules within the LC phase and the mesophase temperature range.



Figure 1. TG curves for ligand PyO-10 and its lanthanide complexes Eu-10, Sm-10 and Tb-10.

It was found that both ligands and their corresponding lanthanide(III) complexes show mesogenic properties. For example, the 4-pyridone ligands, PyO-n display monotropic hexagonal columnar LC phases with isotropic to mesophase transitions in the 40 - 65°C temperature range. The heating run of DSC curves recorded for these organic compounds show only one transition assigned to a crystal-to-isotropic state transition. On cooling from the isotropic state, two transitions were observed, an isotropic to hexagonal columnar mesophase transition followed by a crystallization step (Figure 2a). The only exception seen was compound PyO-6, which, upon cooling, the occurrence of a hexagonal columnar texture around 48°C was not detected by DSC but was rather seen by POM observations. On the other hand, compound PyO-8 show a slightly different behavior; thus, on cooling the material from the isotropic liquid, no crystallization was detected, and the compound remains in the glassy state at ordinary temperature. The clearing temperatures recorded for the 4-pyridone derivatives depend on the number of carbon atoms of the terminal alkyl groups; a general trend of increasing the clearing temperature was seen on increasing the number of carbon atoms with the exception of PyO-8 that clears at 65°C. The assignment of the hexagonal columnar phases was done based both on the polarized microscopy optical textures and XRD analysis. Typical textures of a hexagonal columnar phase were developed from the isotropic state (Figure 3a and Figure S5). Due to the monotropic character of the LC phase, the XRD measurements were difficult to perform for each product. Still an XRD diffractogram of the compound PyO-10 was possible to be recorded at 40°C (Figure S14a), right below the transition temperature from the isotropic to columnar phase. Two diffraction Bragg peaks were observed in the low-angle region, in the 1:2 ratio, giving an interplanar distance of 28.85Å (d₁₀₀) and a corresponding lattice parameter a=33.3Å. By calculating the number of molecules per column unit, N = V_{cell}/V_{mol}, where V_{cell}=S_{col}xh (assuming that h~4.5Å, S_{col}= $\sqrt{3a^2/2}$ and V_{mol}=M_w/(N_A· ρ); M_w is the molecular weight, ρ is the density and it was approximated to 1 g cm⁻³ and N_A is the Avogadro' number), [1, 48] then it is fair to assume that the discs are composed of three molecules of 4-pyridone ligands having in total nine alkyl chains at the periphery. The aggregation of three molecules of 4-pyridone derivative produces a rough disklike arrangement of the three benzylic groups compatible with a hexagonal columnar organization.

The melting temperatures of the complexes, measured during the first heating run, do not depend much on the size of the lanthanide(III) ion, their variation being more influenced by the size of the side chains, ranging between *ca.* 53° C for compounds with twelve carbon atoms **Eu-12**, **Sm-12** and **Tb-12**, and 110° C for compounds with six carbon atoms **Eu-6**, **Sm-6** and **Tb-6** (Figure 4).

The clearing temperatures of the three series of lanthanide complexes (Table 1, measured during the first heating run) again do not depend significantly on the size of the lanthanide ion (Figure 4). The lowest clearing temperature was recorded for **Eu-10** and **Tb-10** ($189^{\circ}C$), while the highest clearing temperature was measured for **Sm-12** ($238^{\circ}C$).

Further, the new lanthanidomesogens described in this study show similar mesomorphic behaviors, no matter the lanthanide ion employed. Interestingly, mesogenic compounds were obtained for shorter chain length (6 or 8 carbon atoms), with large temperature ranges for all three lanthanide ions employed. The mesophase displayed by these materials is stable over a large temperature range, with clearing temperatures higher than 190°C for all compounds with the exception of **Tb-10**. When the comparison is made with the non-coordinated ligands, it is easily seen that these transition temperatures are higher by more than 120°C. Additionally, besides the high stability of the LC phase induced by these complexes has an enantiotropic character.



Figure 2. DSC first heating–cooling cycle for PyO-14 (a) and second heating-cooling cycles for Eu-6 (b), Tb-10 (c) and Sm-14 (d).

Depending on the type of phases exhibited at room temperature, these compounds could be divided into two groups: the compounds with 4-pyridone derivatives with shorter terminal alkyl groups (6, 8, 10 and 12 carbon atoms) show a glass transition below 50°C after a previous heating run to isotropic state (Figure 2b), while the compounds with longer alkyl groups (14 and 16 carbon atoms) show a crystalline phase at room temperature (Figure 2d).

For the first group of compounds, with the exception of compounds with 4-pyridone ligands with ten carbon atoms, two transitions were observed on the DSC traces recorded on the second cooling steps: first transition correspond to an isotropic-to-mesophase transformation and the second one assigned to a glass transition. This behaviour was confirmed by POM when the previously isolated LC phases freeze on further cooling down to room temperature (Figures S10 and S11). For the second group of complexes, with longer terminal alkyl chains, n=14 and 16, the second transition was assigned to the crystallization process at lower temperatures.

All of the complexes display perfectly reproducible subsequent heating-cooling cycles with the same onset temperatures meaning that these complexes are stable during the heating on the thermal range investigated. Homeotropic extended regions were observed by POM for compounds with shorter alkyl chains (6, 8) at the temperatures below the clearing points; by shearing, poorly developed textures with low birefringence were seen for these compounds (Figure S9), so that the microscopy observations were not helpful enough for the phase identification and the assignment was mainly done based on the XRD measurements. The other complexes, having longer alkyl side chains, give well-defined textures when cooling from the isotropic state and several examples are presented in Figure 3. The XRD analysis revealed different features of the LC phase displayed by shorter chains complexes (n=6, 8 and 10) when compared to their longer chains analogues (n=12, 14, 16). In the XRD patterns of the lanthanide complexes with shorter alkyl chains, a series of three or four equidistant sharp diffraction peaks were observed in the low-angle region assigned to d₀₀₁, d_{002} , d_{003} and d_{004} reflections leading to a rather lamellar structure of the mesophase (Figure 4a). An additional peak around ~5Å found for Eu-8 suggests that there is a periodicity at this distance, and it could be assigned to an interaction between neighboring molecules arranged in a typical lamellar packing model.[49-51] Several lanthanidomesogens were found to adopt a lamello-columnar mesophase organization, having different type of ligands such as substituted imidazo[4,5-f]-1,10phenanthroline with cyanobiphenyl mesogenic groups [32] or 2,6-bis(1-ethyl-benzimidazol-2-yl)pyridine substituted with lipophilic gallic acid derivatives.[52] A particular thermal behavior was seen for compounds with ten carbon atoms in the side alkyl chains. These compounds can be regarded as bridging the behavior of shorter chains analogues with the one of the longer chains compounds. In fact, their thermal properties are the sum of those displayed by shorter chains complexes (n=6 and 8) with the properties displayed by the longer chains analogues (n=12,14,16).

Table 1. Transition temperatures^a (in $^{\circ}$ C) and enthalpies (kJ·mol⁻¹) for ligands and their lanthanide (III) complexes.

Compound	Heating/cooling scans
РуО-6	1 st : Cr 56 (17.3)lso 48 Col _h ^[c] 26 (14.2) Cr
РуО-8	1^{st} : Col _h 65 (0.7) Iso 65 (0.4) Col _h ^[b]
РуО- <i>10</i>	$1^{st.} Cr_1$ 58 (45.7) Iso 40 (0.9) Col_h 12 (5.2) Cr_2 $2^{nd.} Cr_2$ 25 (10.4) Cr_3 42 (1.2) Cr_1 58 (10.4) Iso 40 (1.2) Col_h 12 (7.8) Cr_2
РуО-12	$1^{st}: Cr_1$ 71 (74.4) Iso 56 (1.4) Col_h 13 (22.3) Cr_2 $2^{nd}: Cr_2$ 12 (13.3) Cr_3 29 (25.0) Cr_1 70 (80.3) Iso 56 (1.5) Col_h 13 (19.0) Cr_2
РуО- <i>14</i>	1 st : Cr ₁ 80 (79.7) Iso 58 (1.3) Col _h 30 (47.4) Cr ₂ 2^{nd} :Cr ₂ 37 (35.3) Cr ₁ 79 (98.5) Iso 58 (1.6) Col _h 30 (44.3) Cr ₂
РуО-16	$1^{st}\!$
Eu-6	1 st : Cr ₁ 52 (7.7) Cr ₂ 105 (34.1) SmA 236 (5.9) Iso 236 (4.7) SmA 40 g 2^{nd} : g 40 SmA 236 (5.4) Iso 236 (4.9) SmA 40 g
Eu-8	1 st : Cr 54 (18.2) SmA 193 (2.8) Iso 193 (1.9) SmA 50 g 2 nd : g 50 SmA 193 (1.9) Iso 193 (1.9) SmA 50 g
Eu-10	$1^{\rm st}:$ Cr 67 (6.2) SmA 115 (1.1) Col_h 189 (1.4) Iso 189 (1.5) Col_h 115^{\rm [c]} SmA 38 g $2^{\rm nd}:$ g 38 SmA 115 (0.7) Col_h 189 (1.0) Iso 189 (1.1) Col_h 114 (0.3) SmA 38 g
Eu-12	$1^{st}\!$
Eu- <i>14</i>	$1^{st}\!\!:\!Cr~67~(220)~Col_h~217~(4.0)$ lso 216 $(3.4)~Col_h~22~(66.7)~Cr~2^{nd}\!:\!Cr~20~(66.4)~Col_h~218~(3.8)$ lso 217 $(3.4)~Col_h~22~(66.8)~Cr$
Eu-16	
Sm-6	1 st : Cr ₁ 52 (6.0) Cr ₂ 107 (23.1) SmA 235 (3.0) Iso 235 (3.3) SmA 45 g 2^{nd} : g 45 SmA 235 (3.3) Iso 235 (3.9) SmA 45 g
Sm-8	1 st :Cr 54 (9.9) SmA 195 (2.0) Iso 194 (2.2) SmA 46 g 2 nd : g 46 SmA 195 (1.9) Iso 194 (2.1) SmA 46 g
Sm-10	
Sm-12	1 st : Cr 57 (65.0) Col _h 238 (4.1) Iso 237 (3.6) Col _h 50 g 2 nd : g 50 Col _h 238 (3.4) Iso 237 (3.4) Col _h 50 g
Sm-14	1^{st} : Cr ₁ 48 (21.4) Cr ₂ 90 (92.0) Col _h 220 (2.9) Iso 220 (0.9) Col _h 23 (67.7) Cr ₁ 2^{nd} : Cr 23 (61.0) Col _h 220 (2.3) Iso 220 (0.9) Col _h 23 (60.0) Cr

Sm- <i>16</i>	$1^{st}: Cr_1 \; 54 \; (5.0) \; Cr_2 \; 73 \; (156.0) \; Col_h \; 221 \; (1.4) \; Iso \; 220 \; (1.5) \\ Col_h \; 43 \; (108) \; Cr_1 \\ 2^{nd}: \; Cr \; 46 \; (112.0) \; Col_h \; \; 221 \; (1.0) \; Iso \; 220 \; (2.7) \; Col_h \; 43 \\ (108.0) \; Cr \\ \end{array}$
Tb-6	$1^{\rm st}:$ Cr_1 66 (4.7) Cr_2 110 (50.8) SmA 228 (4.2) Iso 227 (4.4) SmA 50 g $2^{\rm nd}:$ g 50 SmA 228 (4.6) Iso 227 (4.7) SmA 50 g
Tb-8	1 st : Cr 65 (4.2) SmA 191 ^[c] Iso 185 ^[c] SmA 60 g 2 nd : g 60 SmA191 ^[c] Iso 185 ^[c] SmA 60 g
Tb- <i>10</i>	$ \begin{array}{l} {}^{st}\!: Cr_1 \ 36 \ (8.4) \ Cr_2 \ 82 \ (4.0) \ SmA \ 125 \ (1.0) \ Col_h \ 189 \ (0.6) \ Iso \\ 189 \ (1.1) \ Col_h \ 125 \ (1.4) \ SmA \ 36 \ g \\ 2^{nd}\!: g \ 36 \ SmA \ 121 \ (1.0) \ Col_h \ 189 \ (1.2) \ Iso \ 188 \ (1.3) \ Col_h \ 123 \\ (1.3) \ SmA \ 36 \ g \\ \end{array} $
Tb-12	$1^{st}: Cr_1 54 \ (175) \ Cr_2 85 \ (8.8) \ Col_h \ 235^{[c]} \ Iso \ 231^{[c]} Col_h \ 50 \ g \ 2^{nd}: g \ 50 \ Col_h \ 235^{[c]} \ Iso \ 231^{[c]} \ Col_h \ 50 \ g$
Tb- <i>14</i>	$ \begin{array}{l} 1^{st}: \mbox{ Cr}_1 \ 51 \ (6.1) \ \mbox{ Cr}_2 \ 95 \ (134.0) \ \mbox{ Col}_h \ 207 \ (3.0) \ \mbox{ Iso} \ 206 \ (3.6) \\ \mbox{ Col}_h \ 23 \ (64.1) \ \mbox{ Cr}_1 \\ 2^{nd}: \ \mbox{ Cr} \ 21 \ (66.7) \ \mbox{ Col}_h \ 207 \ (3.3) \ \mbox{ Iso} \ 206 \ (3.0) \ \mbox{ Col}_h \ 23 \ (62.2) \ \mbox{ Cr} \\ \end{array} $
Tb-16	
	^[a] g, br, Cr, SmA, Col _h , Iso denotes glass transition, broad transition, crystalline state, lamellar smectic A and hexagonal columnar phases respectively; ^[b] glass transition or crystallization could not be detected by DSC or POM:

^[c]transition detected by POM.

Three transitions were detected in the DSC traces both during the heating and cooling runs: a transition from the isotropic state to a hexagonal columnar phase, a second transition from the hexagonal columnar phase to a lamellar phase followed by a third transition assigned to a glass transition near 50°C. All these transitions were detected by POM as well, and an example of textural changes for compound **Tb-10** is presented in Figure 6. The existence of two different LC phases for these compounds having an intermediate number of carbon atoms in the side alkyl chains was also confirmed by temperature dependent XRD analysis. For compound Tb-10, the XRD pattern recorded at 145°C shows a series of three sharp diffraction peaks in the $1/\sqrt{3}/2$ ratio indicating a hexagonal columnar phase (Figure S15a). On the other hand, the XRD pattern recorded at 95°C contains a series of four equidistant sharp peaks in the lowangle region, located at 2.84, 5.62, 8.42 and 11.14°, with spacing in the 1/2/3/4 ratio assigned to the (001), (002), (003) and (004) of a lamellar phase (Figure S15b). The hexagonal columnar (Col_h) mesophase of the compounds with longer alkyl chains (n=12,14,16) were confirmed by XRD studies. The XRD data of one compound for each lanthanide ion were selected as representative examples to be discussed here. These XRD results are summarized in Table 2 and in Tables S1-S4 (suplemmentary information). For complexes Eu-14 and Sm-16, the X-rays diffraction pattern, recorded on cooling the compounds from the isotropic state to liquid crystalline phase,

shows a strong fundamental reflection (100), followed by a series of less intense, but sharp small angle peaks in the $1/\sqrt{3/2}$ ratio, assigned to (110) and (200) reflections (Figure 5b and c), respectively, compatible to a 2D-hexagonal packing.





Figure 3. Pictures taken at the polarizing optical microscope showing the optical textures of PyO-12 at 55°C (a), Eu-14 at 210°C (b), Sm-14 at 215°C(c), Eu-10 at 164°C (d).



Figure 4. Plot of phase-transition temperatures recorded during the second cooling run for the lanthanide complexes.

These results are consistent with the POM studies, where typical optical textures of a hexagonal columnar (Col_h) phase were observed for all the lanthanide complexes with higher number of carbon atoms (n=12,14,16) (Figure 3).

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Lattice parameter

a/ $\hat{A}^{[b]}$

32.91

37.25

40.02

38.88

38.66



Figure 5. X-ray powder diffractograms, recorded on cooling from the isotropic state, for selected compounds: Eu-8 at 100°C (a); Eu-14 at 85°C (b) and Sm-16 at 125°C (c).

Additionally, the XRD patterns of the mesomorphic lanthanide complexes exhibit one broad signal with the maxima located around 4.5 - 4.6Å assigned as usually to the lateral short-range order of the molten alkyl chains. Interestingly, the XRD pattern of Sm-16 contains an additional broad peak around 8Å which presumably could be assigned to some additional correlations within the columns at this distance (Figure 5c).







Figure 6. Pictures taken at the polarizing optical microscope showing the change of optical textures of Tb-10 on cooling from the isotropic state.

Taking into account the distance and the breadth of this signal, together with the absence of any signal around 3.5-3.6Å which is

normally assigned to the stacking distance within the columns, one presumably consider the minimum thickness of a single disc of approximately $h \sim 8$ Å. Then, the associated volume of the unit cell can be calculated with the relation: $V_{cell} = S_{col} xh$ to give a value of 11039 Å³. Based on a density value of 1 grcm⁻³, the calculations will give N~2.17, meaning that two molecules of **Sm-16** must occupy a column slice of 8 Å thickness.

Some interesting properties of these complexes can be seen by further analysis of the X-ray data. A plot of the interplanar distance versus the number of carbon atoms in the terminal chain for Eu(III) and Sm(III) complexes is linear (Figure S13). Similar correlation for analogue Tb(III) complexes could not be made as only three complexes, Tb-8, Tb-10 and Tb-14 were selected for XRD analysis. For the first series of complexes, Eun, a highly linear relationship (R=0.999) was found, with a slope of 0.934Å/CH₂ and an intercept of 22.36Å. A close behavior was found for the second series of complexes, Sm-n, (R=0.997) with a slope of 0.733 Å/CH₂ and an intercept of 23.41Å. It seems that for extended chain length (n=12.14.16), due to packing constraints, the molecules tend to self-assemble in a hexagonal columnar fashion: while for shorter chains (six and eight carbon atoms) a lamellar packing is preferred. Their analogues with ten carbon atoms lie at the border between the two groups, as these complexes display both hexagonal columnar phase at higher temperatures and a lamellar phase at lower temperatures.

Photoluminescence properties

All eighteen Eu(III), Sm(III) and Tb(III) complexes show strong and characteristic emission spectra in the solid state with longlived (millisecond timescale) excited states. As displayed in Figure 7a, the Eu(III) complexes Eu-n exhibit the strong and characteristic emission spectrum of Eu(III) ions upon UV excitation. The spectra contain characteristic sharp bands of the Eu(III) ion in the 570-720 nm spectral range, which can be assigned to ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 1, 2, 3, 4) transitions. For all complexes, the spectrum is dominated by the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition at 616 nm, which gave a strong red luminescent output for these compounds (Figure 8). The luminescence spectra recorded for Sm(III) complexes Sm-n are represented in Figure 7b. These spectra show the typical emission of the Sm(III) ion, which displays four maxima assigned to the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$ at 564 nm, ${}^{4}\text{G}_{5/2} \rightarrow {}^{6}\text{H}_{7/2}$, at 599 nm, ${}^{4}\text{G}_{5/2} \rightarrow {}^{6}\text{H}_{9/2}$ at 644 nm, ${}^{4}\text{G}_{5/2} \rightarrow {}^{6}\text{H}_{11/2}$ at 707nm transitions, respectively. The ${}^4G_{5/2} \rightarrow \, {}^6H_{9/2}$ transition at 648 nm presents the highest relative emission intensity and this transition is responsible for the orange luminescence of the compounds (Figure 8b). Under UV light excitation, the Tb(III) complexes Tb-n give the characteristic Tb(III) ion emissions, in the 480 to 640 nm range, as shown in Figure 7c. These emission bands were assigned to transitions from the excited ${}^{5}D_{4}$ state to the different J-levels of the lower ${}^{7}F_{J}$ state: ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ at 491 nm, ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ at 544 nm, ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$ at 588 nm and ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$ at 621 nm, respectively. These spectra are dominated by the ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition, which gave a strong green luminescent output for the Tb(III) compounds (Figure 8c).





Figure 7. Emission spectra of lanthanide complexes: Eu-n (a); Sm-n (b) and Tb-n (c) in solid state at room temperature. Within the insets are represented the lanthanide-luminescence characteristic lifetime dependence on the number of carbon atoms in the terminal alkyl chains, n; luminescence decay curves have been recorded for the strongest luminescence and showed single exponential decays.



Figure 8. POM pictures of **Eu-16** in hexagonal columnar mesophase at 55° C, (a) and of **Eu-16** in columnar hexagonal mesophase under UV light at 55° C (b); pictures of **Eu-14**, **Sm-14** and **Tb-14** deposited on glass slides under UV light (254 nm) (c).

Moreover, the europium(III), samarium(III) and terbium(III) complexes have proven to be luminescent both in solid state at room temperature and in LC phases. To study the thermal stability of photoluminescence in the LC phase, the temperature dependence of fluorescence intensity was measured between room temperature and clearing temperature. One example of variable temperature luminescence spectra recorded during the

heating from 25° C up to 205° C is presented in Figure S16a for a Sm(III) complex, **Sm-12**. It is obvious that the luminescence intensity decreased monotonically along with molecular disorder due to the increase of the temperature. The reverse process takes place on cooling from the isotropic state, the increase of the emission intensity due to the molecular reordering in the mesophase and in the glassy state when the temperature decreases down to room temperature (Figure S16b).

The photoluminescence spectra of all lanthanide complexes show a clear influence of the number of carbon atoms (n) in the side alkyl chains attached to the bulky metal centre on the optical properties (Figure 7 a-c). It was observed an inhomogeneous broadening of the luminescence peaks that becomes more obvious as the number of carbon atoms (n) increases; the effect is more evident for the Eu(III) complexes (Figure 7a). The broadening effect was assigned to a certain distorsion of the lanthanide ion nine-fold coordination polyhedron but still close to its original C3 symmetry.[31] In addition, the luminescence decay curves showed single exponential decays with the characteristic times in the ms range (not shown) and a shortening with about 30% (insets of the Figure 7 a-c) associated with an increase of the nonradiative decay channels. Therefore, it is presumable that as the alkyl chains length increases they become less rigid and more flexible affecting both the coordination polyhedron of the lanthanide ion and the radiative decays rates.

Conclusions

These novel lanthanidomesogens with 4-pyridone ligands having mesogenic 3,4,5-tris(alkyloxy)benzyl moieties are able to form lamellar and columnar mesophases (SmA and Col_h) on a large temperarure ranges. It was found that the number of carbon atoms contained in the side alkyl chains influence the thermal behaviour of these liquid crystals. The DSC analysis and POM observations revealed that all these complexes display an enantiotropic liquid crystalline behavior with either a lamellar phase (SmA), in the case of shorter chains analogues (six and eigth carbon atoms) or a hexagonal columnar (Col_h) phase, for complexes with higher number of carbon atoms (twelve, fourteen and sixteen). The phase assignment was made on the basis of their characteristic texture and confirmed by temperature variable XRD studies. As a particular case, the complexes with an intermediate number of carbon atoms in the side chains (ten), display a lamellar phase at lower temperatures and a Col_b phase at higher temperatures. On the other hand, the clearing temperatures of the three series of lanthanide complexes do not depend significantly on the size of the lanthanide ion. The lowest clearing temperature was recorded for Eu-10 and Tb-10 complexes (189°C), while the highest clearing temperature was measured for Sm-12 (238°C). In solid state, all these complexes show characteristic emissions assigned to the corresponding lanthanide ion. Moreover, the emission properties are preserved also in the LC phase. In addition, the luminescence decay curves showed single exponential decays with the characteristic times in the ms range

(0.75-0.90 ms for Eu(III), 0.045-0.060 ms for Sm(III) and 0.75-1.05 ms for Tb(III), respectively). The photoluminescence spectra have showed a clear influence of the number of carbon atoms in the side alkyl chains attached to the bulky metal centre on the optical properties: both a broadening effect was seen on analyzing the shape of the emission peaks and a shortening of the lifetimes with about 30% on going from the shorter chains analogues with six carbon atoms, **Eu-6**, **Sm-6** and **Tb-6**, to the longest chains complexes with sixteen carbon atoms, **Eu-16**, **Sm-16** and **Tb-16**.

Experimental Section

All the chemicals were used as supplied. C, H, N analyses were carried out with a with an EuroEA 3300 instrument. IR spectra were recorded on a Bruker spectrophotometer using an ATR device. ¹H and ¹³C NMR spectra were recorded on an Avance 300 Bruker spectrometer operating at 300 MHz, using CDCl₃ as solvent. ¹H chemical shifts were referenced to the solvent peak position, δ 7.26 ppm. Variable temperature emission spectra in solid state were recorded with an OceanOptics QE65PRO spectrometer attached to the microscope and using a Nikon Intensilight excitation source. Photoluminescence (PL) spectra and PL lifetimes measurements have been recorded at room temperature using a Jobin Yvon Fluorolog spectrophotometer; the spectra were not corrected for the spectral sensitivity. Thermogravimetric analysis was performed on a TA Q50 TGA instrument using alumina crucibles and nitrogen as purging gas. The heating rate employed was 10°C min⁻¹ from room temperature (approximately 25°C) to 550°C.

Synthesis of ligands PyO-n

N-Alkyl-4-pyridone was produced through a slightly modified known procedure. [46, 47] The **PyO-***n* (n=6,8,10,12,14,16) ligands were obtained by adding to a solution of 4-hydroxypyridine and tetrabutylammonium bromide (phase transfer catalyst) in tetrahydrofuran a 2N aqueous solution of sodium hydroxide. Water was added and the mixture was stirred until the muddy solution became clear, then 3,4,5-trialkoxybenzyl bromide was added and heated under reflux for 24 hours (Scheme 1). After cooling, the solvent was evaporated and the product was extracted with dichloromethane and water (1/1). The organic layer was collected and the solvent was removed using a rotary evaporator. The crude product was treated with ethyl acetate and the precipitate was filtered and purified by column chromatography using dichloromethane and methanol (95/5) as eluents. White products were obtained with yields between 65-70%.

 $\label{eq:py0-6: Anal. Calcd. For $C_{30}H_{47}O_4N$: $C\%74.19, $H\%9.75, $N\%2.88$. Found: $C\%74.12, $H\%9.72, $N\%2.88. ^1H $NMR(CDCl_3, 300 $MHz)$: $7.38(d, 2H)$; $6.39(d, 2H)$; $6.32(d, 2H)$; $4.80(d, 2H)$; $3.81-3.85(m, 6H)$; $1.6-1.78(m, 6H)$, $1.2-1.43(m,18H)$; $0.76-0.84(m, 9H)$. $IR (ATR, $cm^-1)$: $2955, $2931, $2860, 1639, 1590, 1114, 856, 728$. }$

 $\label{eq:py0-8: Anal. Calcd. For $C_{36}H_{59}O_4N$: C\%75.88, $H\%10.44, $N\%2.46$. Found: C\%75.86, $H\%10.45, $N\%2.46$. ^1H NMR(CDCl_3, 300 MHz)$: 7.38(d, 2H); 6.42(d, 2H); 6.36(d, 2H); 4.82(d, 2H); 3.82-3.88(m, 6H); 1.65-1.82(m, 6H), 1.2-1.46(m, 30H); 0.9(m, 9H)$. IR (ATR, cm^{-1}):2955, 2926, 2855, 1639, 1589, 1114, 853, 723$. \\$

PyO-10: Anal. Calcd. For $C_{42}H_{71}O_4N$: C%77.13, H%10.94, N%2.14. Found: C%77.16, H%10.94, N%2.13. ¹H NMR(CDCl₃, 300 MHz): 7.4(d, 2H); 6.44(d, 2H); 6.31(d, 2H); 4.8(d, 2H); 3.85-3.95(m, 6H);1.68-1.8(m, 6H), 1.26-1.48(m,42H); 0.87(m, 9H). IR (ATR, cm⁻¹): 2956, 2922, 2852,1640, 1574, 1211, 847, 72.

PyO-12-structural characterization for this ligand was reported by us in a previous study. [46]

 $\label{eq:pyo-16: Anal. Calcd. For $C_{60}H_{107}O_4N$: C%79.50, H%11.90, N%1.55$. Found: C%79.49, H%11.92, N%1.55$. ^1H NMR(CDCl_3, 300 MHz): 7.4(d, 2H); 6.45(d, 2H); 6.36(d, 2H); 4.87(d, 2H); 3.84-4(m, 6H); 1.7-1.9(m, 6H), 1.2-1.54(m,78H); 0.85(m, 9H). IR (ATR, cm^{-1}): 2956, 2917, 2850, 1640, 1574, 1116, 846, 721. \\ \end{tabular}$

Synthesis of Eu(III) complexes, Eu-n

Eu(NO₃)₃x6H₂O (1 mmole) in ethanol (5 ml) was added to the solution of N-alkyl-4-pyridone (3 mmole) in ethanol (5ml) dropwise and with constant stirring. The solution became turbid with the addition of the europium nitrate. The reaction mixture was stirred at room temperature for two hours. The white precipitate formed was filtered off, taken up in dichloromethane and filtered over celite. Then the solvent was removed by rotary evaporator and the residual complex was recrystallized from dichloromethane and diethyl ether. The white precipitates of **Eu-n** were filtered, washed with diethyl ether and dried in vacuo. White products were obtained with yields about 50%.

Eu-6: Anal. Calcd. For $C_{90}H_{141}EuN_6O_{21}$: C%60.22, H%8.65, N%4.68. Found: C%59.41, H%8.22, N%4.52. IR (ATR, cm⁻¹): 2955, 2932, 2859, 1636, 1591,1442, 1248, 1112, 1033, 852, 786, 737, 468.

 $\begin{array}{l} \textbf{Eu-10:} \ \ Anal. \ \ Calcd. \ \ For \ \ C_{126}H_{213}EuN_6O_{21}: \ C\%65.80, \ \ H\%9.33, \ N\%3.65.\\ \ \ Found: \ \ C\%65.65, \ \ H\%9.42, \ \ N\%3.51. \ \ IR \ (ATR, \ \ cm^{-1}): \ \ 2955, \ 2924, \ 2854, \\ \ \ 1635, \ \ 1590, \ 1442, \ \ 1245, \ \ 1115, \ \ 1031, \ 857, \ 817, \ \ 737, \ 468. \end{array}$

Eu-12: Anal. Calcd. For $C_{144}H_{249}EuN_6O_{21}$: C%67.76, H% 9.83, N%3.29. Found: C%67.19,H% 9.87, N%3.22. IR (ATR, cm⁻¹): 2956, 2921, 2851, 1636, 1590, 1442, 1242, 1115, 1030, 856, 817, 721,467.

 $\begin{array}{l} \textbf{Eu-14:} \ \mbox{Anal. Calcd. For } C_{162}H_{285} \mbox{EuN}_6 O_{21}; \ \mbox{C}\%69.37, \ \mbox{H}\%10.24, \ \mbox{N}\%3.00. \\ \mbox{Found: } C\%69.26, \ \mbox{H}\%10.32, \ \mbox{N}\%2.76. \ \mbox{IR} \ \mbox{(ATR, cm}^{-1}): \ \mbox{2955, 2919, 2851, } \\ \mbox{1636, 1590, 1442, 1242, 1115, 1030, 861, 817, 721, 467. \\ \end{array}$

 $\begin{array}{l} \textbf{Eu-16:} \ \ Anal.\ \ Calcd.\ \ For\ \ C_{180}H_{321}EuN_6O_{21}:\ \ C\%70.71,\ \ H\%10.58,\ \ N\%2.75.\\ \ \ Found:\ \ C\%70.65,\ \ H\%10.72,\ \ N\%2.44.\ \ IR(ATR,\ \ cm^{-1}):\ \ 2956,\ 2918,\ 2850,\\ \ \ 1635,\ 1590,\ 1442,\ 1244,\ 1117,\ 1030,\ 857,\ 817,\ 721,\ 467.\\ \end{array}$

Synthesis of Sm(III) complexes, Sm-n

Over a solution of N-alkyl-4-pyridone (3 mmole) in ethanol (5 ml) was added dropwise to a solution of $Sm(NO_3)_3x6H_2O$ (1 mmole) in ethanol (5 ml). The reaction mixture was stirred at room temperature for two hours. The white precipitate formed was filtered off, taken up in dichloromethane and filtered over celite. The solvent was removed by rotary evaporator

and the residual solid was recrystallized from a mixture of dichloromethane and diethyl ether. The white precipitates of **Sm**-*n* complexes were filtered, washed with diethyl ether and dried in vacuo. White products were obtained with yields in the 45-50% range.

 $\begin{array}{l} \textbf{Sm-8:} \ \text{Anal. Calcd. For } C_{108}H_{177}SmN_6O_{21}:\ C\%63.40,\ H\%8.72,\ N\%4.11.\\ \text{Found: } C\%63.56,\ H\%8.64,\ N\%3.39. \ IR \ (ATR,\ cm^{-1}):\ 2956,\ 2926,\ 2855,\\ 1636,\ 1591,\ 1442,\ 1244,\ 1114,\ 1023,\ 857,\ 787,\ 723,\ 468. \end{array}$

 $\begin{array}{l} \textbf{Sm-10:} \mbox{ Anal. Calcd. For } C_{126}H_{213}SmN_6O_{21}:\ C\%65.84,\ H\%9.34,\ N\%3.66. \\ \mbox{ Found: } C\%65.16,\ H\%9.15,\ N\%3.54. \ IR \ (ATR,\ cm^{-1}):\ 2955,\ 2924,\ 2853, \\ 1635,\ 1590,\ 1442,\ 1246,\ 1115,\ 1031,\ 857,\ 787,\ 722,\ 468. \end{array}$

 $\begin{array}{l} \textbf{Sm-12:} \mbox{ Anal. Calcd. For } C_{144}H_{249}\mbox{SmN}_{6}O_{21}\mbox{:} C\%67.80, \mbox{ H}\%9.84, \mbox{ N}\% \mbox{ 3.29}. \\ \mbox{Found: } C\%67.28, \mbox{ H}\%9.69, \mbox{ N}\% \mbox{ 3.33}. \mbox{ IR } (\mbox{ATR, cm}^{-1})\mbox{:} \mbox{ 2956, 2922, 2852, } \\ \mbox{ 1635, 1590, 1441, 1245, 1116, 1030, 857, 787, 721, 468. } \end{array}$

 $\begin{array}{l} \textbf{Sm-14:} \mbox{ Anal. Calcd. For $C_{162}H_{285}SmN_6O_{21}$: $C\%69.41$, $H\%10.25$, $N\%3.00$. \\ \mbox{Found: $C\%69.36$, $H\%10.31$, $N\%2.83$. IR (ATR, cm^{-1})$: 2955, 2919, 2851, 1634, 1589, 1441, 1247, 1118, 1023, 856, 787, 721,468$. \\ \end{array}$

 $\begin{array}{l} \textbf{Sm-16:} \mbox{ Anal. Calcd. For $C_{180}H_{321}SmN_6O_{21}$: $C\%70.75$, $H\%10.59$, $N\%2.75$. \\ \mbox{Found: $C\%69.26$, $H\%10.31$, $N\%2.68$. IR (ATR, cm^{-1})$: 2956, 2918, 2850, 1635, 1589, 1441, 1243, 1117, 1023, 856, 787, 721, 467. \\ \end{array}$

Synthesis of Tb(III) complexes, Tb-n

Over a solution of N-alkyl-4-pyridone (3 mmole) in ethanol (5 ml) was added dropwise a solution of $Tb(NO_3)_3x5H_2O$ (1 mmole) in ethanol (5 ml). The reaction mixture was stirred at room temperature for two hours. The white precipitate formed was filtered off, taken up in dichloromethane and filtered over celite. The solvent was removed and the residual complex was recristalized from dichloromethane and diethyl ether. The white precipitates of **Tb-***n* complexes were filtered and then washed with diethyl ether and dried in vacuo. White products were obtained with yields around 45%.

Tb-6: Anal. Calcd. For $C_{90}H_{141}TbN_6O_{21}$: C%60.84, H%8.62, N%4.66. Found: C%59.92, H%8.14, N%4.53. IR (ATR, cm⁻¹):2956, 2919, 2851, 1634, 1588,1441,1248, 1118, 1023, 856, 787, 721, 468.

 $\begin{array}{l} \textbf{Tb-10:} \ \ Anal. \ \ Calcd. \ \ For \ \ C_{126}H_{213}TbN_6O_{21}: \ \ C\%65.60, \ \ H\%9.31, \ \ N\%3.64. \\ Found: \ \ C\%65.32, \ \ H\%9.29, \ \ N\%3.51. \ \ IR \ (ATR, \ \ cm^{-1}): \ \ 2956, \ 2923, \ 2852, \\ 1641, \ \ 1590, \ 1442, \ 1254, \ 1112, \ 1036, \ \ 847, \ 774, \ 718, \ 463. \end{array}$

 $\label{eq:thm:constraint} \begin{array}{l} \textbf{Tb-14:} \ \mbox{Anal. Calcd. For $C_{162}H_{285}$TbN_6O_{21}: $C\%69.20$, $H\%10.22$, $N\%2.99$. \\ \mbox{Found: $C\%69.10$, $H\%10.41$, $N\%2.70$. IR (ATR, cm^{-1}): 2955, 2930, 2859, 1635, 1591, 1441, 1249, 1113, 1022, 855, 786, 741, 469. \\ \end{array}$

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Tb-16: Anal. Calcd. For $C_{180}H_{321}$ TbN₆O₂₁: C%70.55, H%10.56, N%2.74. Found: C%70.47, H%10.62, N%2.48. IR (ATR, cm⁻¹): 2955, 2918, 2850, 1636, 1589, 1441, 1243, 1117, 1023, 857, 788, 721, 468.

Polarizing optical microscopy analysis (POM)

Mesophases of the 4-pyridone ligands and their lanthanide complexes were identified by observation of sample microscopic textures using a Nikon 50iPol polarized optical microscope equipped with a Linkam THMS600 hot stage and TMS94 control processor. These observations were made on untreated glass slides.

Differential scanning calorimetry (DSC)

Temperatures and enthalpies of transitions were investigated using differential scanning calorimetry (DSC) with a Diamond DSC Perkin Elmer instrument. The materials were studied at different scanning rates after being encapsulated in aluminium pans. Two or more heating/cooling cycles were performed on each sample with variable scanning rate (2, 5 and 10° C/min).

Powder X-ray diffraction

The powder X-ray diffraction measurements were made on a D8 Advance diffractometer (Bruker AXS GmbH, Germany), in parallel beam setting, with monochromatized Cu–K_{a1} radiation (λ =1.5406 Å), scintillation detector, and horizontal sample stage. The measurements were performed in symmetric (θ - θ) geometry in the 2 θ range from 1.5° to 10° or 30° in steps of 0.02°, with measuring times per step in the 5-40 s range. The temperature control of the samples during measurements was achieved by adapting a home-made heating stage to the sample stage of the diffractometer.The samples were heated at a rate of 10.0°C min⁻¹ to the appropriate temperature.

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