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Frédéric Hapiot[a]
[a] Laboratoire de Physico-Chimie des Interfaces et Applications, Université d'Artois, Faculté Jean Perrin, 62307 Lens Cedex, France

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Improvement of the dopant compatibility in a chiral LC mixture by structural modification of lanthanide complexes

FRÉDÉRIC HAPIOT

Laboratoire de Physico-Chimie des Interfaces et Applications, Université d'Artois, Faculté Jean Perrin, rue Jean Souvraz, S.P. 18, 62307 Lens Cedex, France; E-mail: hapiot@univ-artois.fr

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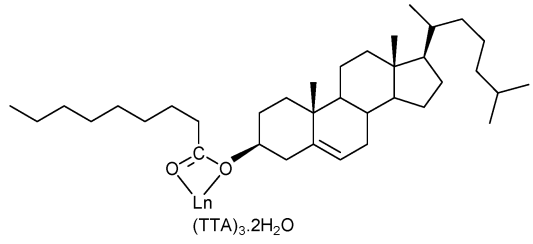
The syntheses of Eu^{3+}- and Nd^{3+}-cholesterol derivative complexes are described. All complexes have been characterized by ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR, IR spectroscopies and elemental analysis. They have been incorporated in various amounts into chiral LC mixtures. The influence of the complex's shape, the alkyl chain length and the dopant concentration on the phase transition temperatures of these rare earth-doped liquid crystals was investigated. Lanthanide dopants with calamitic cholesteryl ester ligands were mixed in the chiral LC at a level of 6 mol% without altering the liquid crystal texture.

1. Introduction

Due to the existence of a macroscopic helicoidal structure, cholesteric liquid crystals (CLCs) exhibit many remarkable properties such as selective light reflection. They have been the subject of considerable attention due to their application potential in optical devices such as laser end mirrors [1], polarizers [2], filters [3] and displays [4]. In most of these applications the CLCs are used as passive constituents. When mixed with dopants, in most cases organic dyes, they can also behave as active elements. The optical properties of the resulting photoluminescent materials make them useful in amplifiers, active polarizers or filters for display technologies [5]. In particular, low molar mass cholesterol derivatives have shown interesting properties for rewritable full colour image applications [6]. Moreover, when a fluorescent dye whose emission matches the reflection band is incorporated into a CLC, the distributed feedback properties of the dye–CLC mixture can result in laser emission [7] which makes these materials potential optical fibre sensors [8]. This particular kind of active optical media can also be realized using a rare earth complex–CLC mixture [9]. One of the main advantages of fluorescent rare earth complexes is their high stability, which contrasts that of commonly used organic fluorophores [10]. Thus, dispersed as a dopant in a host medium, these rare earth ions support the high energy rate of a laser with no damage, in contrast to what is observed for a dye. For example, luminescent materials with liquid crystalline properties at room temperature were recently obtained by doping nematic liquid crystal host matrices with a europium^{3+}-diketonate complex [11]. In this case, a very well resolved crystal field fine structure was observed in the europium^{3+} emission spectra.

We have been interested for some time in elaborating new short and compact CLC lasers using rare earth complexes as a dopant. The performance of these lasers is mainly linked to the rare earth doping level. Increasing the lanthanide concentration is then a key factor in enhancing the efficiency of the fluorescence process. Our previous work has shown that the lanthanide–cholesteryl ester complex is useful in terms of luminescence properties in a liquid crystal mixture [12]. In addition, these complexes could be mixed with cholesteryl nonanoate and tetradecanoate and other nematic liquid crystals up to 2.5 mol% without destroying the liquid crystal texture. Although the dopant was successfully stabilized by the cholesteryl moiety, a spectroscopic study revealed that the bent structure of the complex obtained locally distorted the chiral LC texture (scheme 1) [13].



Scheme 1. Bent structure of nonanoate cholesteryl ester-lanthanide complexes. (Ln=Eu^{3+}, Nd^{3+}, Sm^{3+}; TTA= thenoyltrifluoroacetonate).

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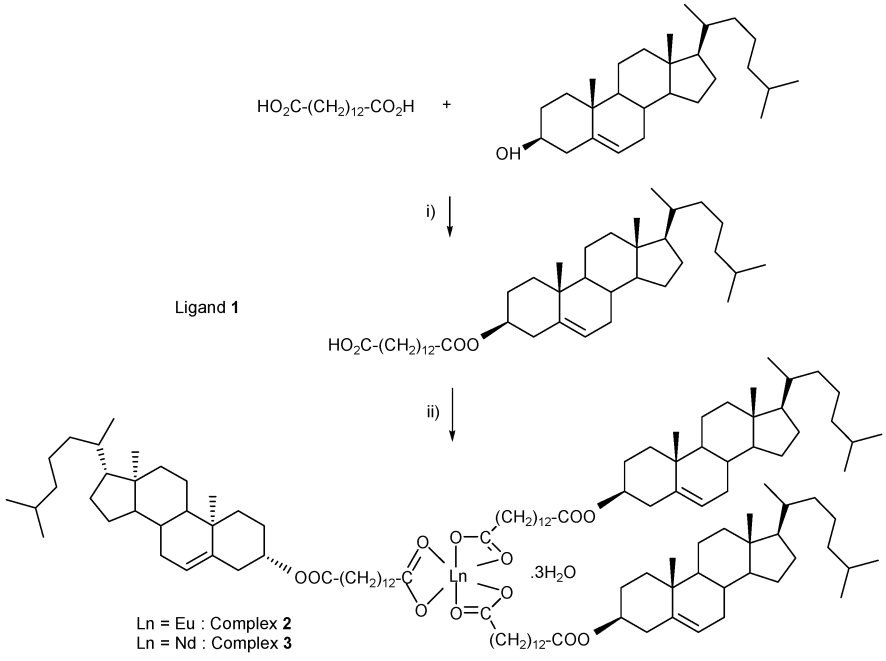
Therefore the shape of this dopant was not optimal since a lengthening of the pitch of the chiral LC was observed when the dopant content was greater than 2.5 mol% [14]. The optical properties of the material were then modified. For example, the selective light reflection band was shifted to higher wavelenghts (near IR), which was not of interest for our applications. To bring this band back into the visible region, two solutions were envisaged. Firstly, the concentration of the nematic was reduced, but crystallization occurred at room temperature preventing any optical application. Therefore, the percentage of nematic was kept constant in this study. Secondly, for the pitch to be unchanged, we considered moving the fluorescent ion away from the cholesteryl fragment. This led us to suggest that a modification of the fluorescent complex structure may allow the quantity of dopant in the liquid crystal host to be increased without interfering with the constituents responsible for the chiral LC texture. The elaboration of numerous organometallic lanthanide-based compounds have been widely described [15], some of them being metallomesogens [16], but to our knowledge, none of them included a cholesteryl group. In this paper, we describe the synthesis and characterization of Eu^{3+}- and Nd^{3+}-cholesterol derivative complexes and preliminary results on their behaviour when mixed with chiral LC mixtures.

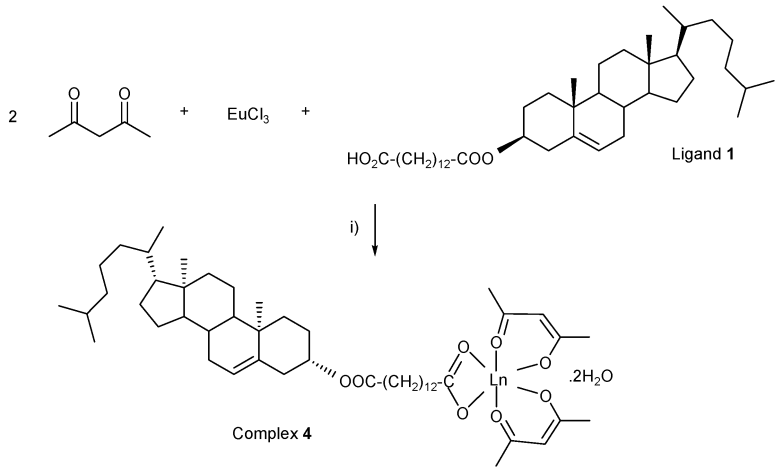
2. Synthesis

The alkanoic acid monocholesteryl ester **1** was prepared by the esterification of cholesterol with an excess (10 equiv.) of 1,12-dodecanedicarboxylic acid in the presence of dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) in a mixture of CH_2Cl_2 and THF (scheme 2). Excess of diacid was removed by precipitation in toluene. The resulting product was purified by column chromatography followed by crystallization. In such conditions, no cholesteryl diester was observed. Indeed, the ^1H NMR integration of three characteristic signals of **1** at 2.2 ppm (6H, HOOC–C<u>H</u>$_2$–, –C<u>H</u>$_2$–COOcholesteryl, $H_{4\alpha}$ and $H_{4\beta}$), 4.6 ppm (1H, $H_{3\alpha}$) and 5.4 ppm (1H, H_6) showed unambiguously the formation of the monoester-acid derivative. An 8/1/1 integration ratio would have been obtained in the case of a diester. Furthermore, a resonance at 179.97 ppm in the $^{13}C\{^1H\}$ NMR spectrum confirmed the presence of an acid group in this ligand.

Secondly, similar procedures for the reaction of **1** with anhydrous $EuCl_3$ or $NdCl_3$ to give complexes **2** and **3** (scheme 2). The reaction of **1** (1 equiv.), acetylacetone (2 equiv.) and anhydrous $EuCl_3$ (1 equiv.) in a 10% NH_3 solution gave complex **4** (scheme 3). After removal of insoluble materials in chloroform, the complex was recrystallized from acetone and a light orange powder was obtained.



Scheme 2. Synthesis of complexes **2** and **3**. Reagents and conditions: (i) DCC (1.1 equiv./diacid), DMAP (0.1 equiv./diacid), stirred in CH_2Cl_2 (250 ml)+THF (70 ml) at rt, 24 h; (ii) $LnCl_3$ (0.33 equiv.), stirred in a 10% NH_3 solution (8 ml) at rt, 48 h.



Scheme 3. Synthesis of complex **4**. Reagents and conditions: ligand 2 (1 equiv.), acetylacetone (2 equiv.), $EuCl_3$ (1 equiv.), stirred in a 10% NH_3 solution (8 ml) at rt, 48 h.

All these complexes were characterized by ^1H, $^{13}C\{^1H\}$ NMR, IR spectroscopy and CHN microanalysis. ^1H and $^{13}C\{^1H\}$NMR spectroscopy confirmed the coordination of the ligands to the metal (see § 7). Two main changes were observed in the spectra: (i) broadening of the signals characteristic of the coordination to the paramagnetic lanthanide [17] and (ii) disappearance of the resonance of the carbon of the carboxylate around 180 ppm as described by others [18]. No significant change was observed in the other chemical shifts.

3. Thermal behaviour

The mesomorphic properties of the cholesteryl ester **1** and complexes **2**, **3** and **4** were investigated using polarizing optical microscopy. Compound **1** melted at 100.5°C to form a cholesteric LC phase, clearing at 111.7°C. Due to intermolecular hydrogen bonding, carboxylic acids are well known to form dimeric structures, and presumably compound **1** exists in dimeric form. Hysteresis in the transition temperatures was measured on cooling so that the cholesteric phase appeared from 102.9 to 88.1°C in the cooling cycle. The narrow range of temperature observed for the cholesteric LC phase on heating or cooling is consistent with previous observations made on similar cholesteryl mesogens containing an even number of carbons in shorter alkyl chains [19]. Complexes **2** and **3** exhibited no mesomorphic properties. Complex **2** melted at 195.5°C on heating and crystallized at 194.3°C on cooling. The melting and crystallizing temperatures of **3** were a little lower than those measured for **2** (192.9°C on heating and 192.2°C on cooling). The small temperature differences observed between complexes **2** and **3** were not surprising because of the small difference in size of the europium and neodymium atoms. This agreed with earlier studies on europium- and neodymium-containing metallomesogens whose transition temperatures were also very close [20].

Similarly, complex **4** exhibited no mesophism. The melting temperature of this complex was measured at 142.7°C on heating and recrystallized at 141.6°C on cooling. When compared with complex **2**, the lower melting temperature of complex **4** may be attributed to the higher degree of freedom of the lanthanide moiety which was only connected to one rigid cholesteryl fragment.

4. Realization of a doped cholesteric liquid crystal mixture

To prevent any crystallization at room temperature and to obtain an aggregate free doped cholesteric phase with a selective reflection band located in the visible region, a mixture of liquid crystals, namely cholesteryl nonanoate (24.6 mol%) and cholesteryl tetradecanoate (7.2 mol%), with Licristal® ZLI 1083 (ternary mixture of *n*-alkylphenylcyclohexanes, Merck) as a nematic medium (68.2 mol%) and lanthanide-cholesteryl derivative complexes was prepared. These percentages were empirically determined for the selective reflection band to be around 616 nm which corresponds to the average emission wavelength of the $^5D_0 \rightarrow {}^7F_2$ transition of the Eu^{3+} ion in our complexes [12].

A preliminary study of the phase exhibited by this mixture revealed a cholesteric texture from room temperature (20°C) to 51.1°C. From 51.1 to 57.5°C, the mixture exhibited a blue phase and at higher temperatures became isotropic. The phase transition temperature between the crystal and the cholesteric phase could not be determined under our experimental

conditions since the mixture exhibited a cholesteric phase at 20°C. In the following experiments, the nematic percentage remained constant. On the other hand, the cholesteryl ester percentages were decreased insofar as the dopant contained cholesteryl moieties. Thus, knowing that complexes **2** and **3** contained three cholesteryl moieties, the cholesteryl nonanoate and tetradecanoate percentages were diminished by 1.5 mol% for each mol % of dopant added in the CLC. In the same manner, knowing that complex **4** contained one cholesteric moiety, the cholesteryl ester percentages were diminished by 0.5 mol% for each mol% of dopant added in the chiral LC. The percentages of complex incorporated were 2, 4, 6 and 8 mol% and the phase transition temperatures of the mixtures obtained were observed using a microscope.

5. Results and discussion

The influence of the structural flexibility of the dopant on its solubility in the chiral LC was first evaluated. Specifially, the cholesteryl nonanoate-europium complex (**Eu-ester**) (scheme 1) was compared with complexes **2** and **3** (scheme 2). The former contains a europium atom in the neighbourhood of the cholesteryl fragment while in latter an alkyl spacer is placed between the cholesteric moiety and the lanthanide atom. These complexes were dissolved in various amounts in the chiral LC and the influence on the phase transition temperatures measured. The results are gathered in table 1.

The **Eu-ester**-containing mixture exhibited a Cr–N* transition phase (23.1°C) as soon as the percentage of dopant became too high (4%). Moreover, no more blue phase was observed and the isotropic phase appeared at a lower temperature, 35.6°C. When complex **2** was mixed with cholesteryl nonanoate, cholesteryl tetradecanoate and Licristal®, the cholesteric phase was observed whatever the percentage of the dopant (from 2 to 6%) at 20°C. The temperature of the N*→BP transition fell from 51.1 to 47.5°C when varying the percentage of complex **2** from 2 to 4% and to 41.9°C at 6% of complex **2**. At 8% of dopant, the clearing point became too low (27.4°C) for the mixture to be used in optical applications. In light of these results, it appears that separating the lanthanide ion from the cholesteryl group is a major parameter which influences the chiral LC texture. In fact, with the flexible complex **2**, the cholesteric phase was unaffected at 20°C and the temperature range in which the mixture was liquid crystal remained wide, even at high percentages of dopant (up to 6 mol%). Interestingly, although complex **2** was not mesogenic, its mesogen-like structure increased its compatibility with the chiral LC mixture. These results are in good agreement with those obtained with the **Eu-ester** complex since they clearly show that closer proximity of the cholesteryl group to the lanthanide ion was detrimental to the cholesteric phase. Varying the dopant percentage using the neodymium complex **3** revealed that the phase transition temperatures were independent of the nature of the lanthanide ion (table 1). Indeed, the phase transition temperatures were very close to those obtained with 6 mol% of complex **2** (for example, the N*–BP phase appeared at 41.9°C for **2** vs. 42.0°C for **3**).

Table 1. Phase transition temperatures of chiral LC mixtures containing cholesteryl nonanoate, cholesteryl tetradecanoate, Licristal® (68.2 mol%) and lanthanide-cholesteryl derivative complexes for various percentages of dopant. (Cr=crystal; N*=cholesteric phase; BP=blue phase; I=isotropic phase).

Complex	Dopant/ mol%	Transition temp./°C
Eu-ester	2	N*·50.3·BP·57.6·I
Eu-ester	4	K·23.1·N*·35.6·I
2	2	N*·51.1·BP·55.2·I
2	4	N*·47.5·BP·50.3·I
2	6	N*·41.9·BP·46.7·I
2	8	N*-I·27.4
3	6	N*·42.0·BP·46.9·I
4	6	N*·38.8· I

The major drawback of complexes **2** and **3** was their poor fluorescent character due to the presence of three cholesteryl ligands [21]. Thus, to preserve the fluorescent properties of the system, the synthesis of a complex bearing both a cholesteryl ligand with an alkyl spacer and a europium atom coordinated by two thenoyltrifluoroacetonate (tris-[4,4,4-trifluoro-1-(2-thienyl)butane-1,3-diono]) ligands was undertaken. Knowing that a long alkyl chain spacer was helpful in preventing interactions between the lanthanide and the rigid moieties of the LCs, ligand **1** was chosen because of the greater distance between the cholesteryl fragment and the chelating acid. Unfortunately, when trying to substitute one thenoyltrifluoroacetonate group of the fluorescent complex Eu(thenoyltrifluoroacetonate)$_3$.$3H_2O$ with one equivalent of **1**, a total substitution of the thenoyltrifluoroacetonates occured because of these ligands were too acidic. Thus, complex **2** was again obtained.

To approach the desired structure, the thenoyltrifluoroacetonate ligands were replaced by the more basic acetylacetonate (acac) ligands. giving complex **4**, which contains an alkyl chain comparable in length to that in **2** between the lanthanide and the cholesteryl moiety (scheme 3). When 6 mol% of **4** was incorporated in the CLC mixture, the cholesteric phase remained at

20°C due to the mesogen-like structure of **4** (table 1). Moreover, when comparing the phase transition temperatures obtained with **2** and **4**, only a N*–I transition could be observed for **4** at 38.8°C. Thus, the disappearance of the cholesteric phase occurred at a lower temperature for **4** than for **2** (N*–BP, 41.9°C). This small difference was attributed to some steric hindrance of the acac ligands which might disturb the helicoidal arrangement in the liquid crystal phase.

6. Conclusion

The syntheses of lanthanide-cholesteryl derivative complexes have been realized and the compounds fully characterized. We evaluated the quantity of these complexes which could be incorporated as a dopant into a cholesteric-nematic mixture. When compared with a previous study involving lanthanide–cholesteryl nonanoate and tetradecanoate complexes [13], these results showed that the complexes have a greater compatibility with the liquid crystal medium. Actually, the incorporation of 6 mol% of europium and neodymium complexes containing long alkyl chain cholesteryl ligands does not induce significant changes in the phase transition temperatures, and in addition does not modify the optical properties of the host liquid crystal. The results obtained for complexes only differing in their lanthanide atom were indicative of the small influence of the metal on the behaviour of the doped chiral LC mixture in terms of transition temperatures.

This study clearly demonstrates the structural requirements for the successful design of a lanthanide-cholesteryl ester dopant: (i) the presence of a strong liquid crystal promoter, the cholesteryl ester in this case, is of prime importance to counteract the unfavourable effects of the lanthanide ion; (ii) the use of flexible alkyl chains which leads to an increase of the dopant compatibility in the chiral LC phase.

Lanthanide complexes with strong fluorescent properties, and having on appropriate calamitic shape for enhanced incorporation into chiral LC mixtures, are currently under investigation.

7. Experimental

Organic reagents were obtained from Acros Organics and Sigma-Aldrich. Anhydrous rare earth chlorides and cholesteryl esters were purchased from Strem Chemicals. All chemicals were used as received, without further purification. Europium(thenoyltrifluoroacetonate)$_3$.xH$_2$O was synthesized according to literature procedures [22]. ^{1}H and ^{13}C NMR spectra were measured with a Bruker Avance DPX 300 spectrometer using an internal capillary with TMS as an external reference at a temperature of 298 K in $CDCl_3$. IR spectra were recorded on a Brucker Vector 22 spectrophotometer in the 4000–300 cm^{-1} wave range. Elemental analysis was performed on a ThermoQuest EA 110 CHNS instrument. Clearing points were observed using an Olympus model BH2 polarizing microscope equipped with a Mettler model FP90 hot stage.

7.1. *13-(Cholest-5-en-3β-yloxycarbonyl)tridecanoic acid (1)*

A mixture of cholesterol (0.75 g, 1.9 mmol), 1,12-dodecanedicarboxylic acid (2 g, 7.7 mmol), *N*,*N*-dicyclohexylcarbodiimide (DCC, 0.98 g, 8 mmol) and DMAP 4-dimethylaminopyridine (DMAP, 0.98 g, 0.8 mmol) was stirred in 250 ml THF at room temperature for a period of 24 h. The precipitated *N*,*N*-dicyclohexylurea was filtered off and washed with THF. Evaporation of the filtrate gave a viscous oil which was dissolved in 100 ml toluene. Excess of 1,12-dodecanedicarboxylic acid precipitated and was removed by filtration. The crude product obtained after removal of the solvent under reduced pressure was purified by column chromatography (SiO_2, hexane/CH_2Cl_2 gradient) to yield 0.9 g (74%) of a white solid which was recrystallized twice in a methanol/CH_2Cl_2 mixture. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5,41 (d, 1H, H_6), 4,63 (m, 1H, $H_{3\alpha}$), 2,33 (m, 6H, HOOC–C$\underline{H}_2$–, –CH_2COOChol., $H_{4\alpha}$, $H_{4\beta}$), 1.31 (20H, –$(CH_2)_6$–), 2.02–0.70 (41H, cholesteryl). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): 179,99 (HOO$\underline{C}$–), 173,72 (–O$\underline{C}$O–), 140.11 (C_5), 122.98 (C_6), 74.13 (C_3), 57.11–12.24 (cholesteryl). IR: 2923, 2851, 2845, 1736, 1701, 1487, 1433, 1405, 1387, 1329, 1294, 1224, 1180, 1003 cm^{-1}. Anal: calc. for $C_{41}H_{70}O_4$ C 78.55 H 11.24; found C 78.81, H 11.22%.

7.2. *Tris[13-(cholest-5-en-3β-yloxycarbonyl)tridecanoic acid]europium(III) trihydrate (2)*

Anhydrous $EuCl_3$ (51.7 mg, 0.2 mmol) was dissolved in a 10% NH_3 solution (8 ml). Compound **1** (376 mg, 0.6 mmol) was added and the mixture stirred at room temperature. Upon addition, a solid appeared as a suspension in solution; after two days of vigorous stirring, the precipitated compound was filtered off and washed with water. It was then dissolved and stirred in $CHCl_3$ for an hour and insoluble particules were removed by filtration. The filtrate was evaporated and the solid obtained was recristallized from toluene. The resulting light orange powder was dried *in vacuo*; yield 16%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.36 (br, 1H, H_6), 4.61 (br, 1H, $H_{3\alpha}$), 2.26 (br, 6H, OOC–CH_2–,

–CH_2COOChol., $H_{4\alpha}$, $H_{4\beta}$), 1.28 (20H, –$(CH_2)_6$–), 2.02–0.70 (41H, cholesteryl). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): 173.42 (–O<u>C</u>O–), 137.98(C_5), 124.95 (C_6), 73.71 (C_3), 56.75–12.01 (–$(CH_2)_6$–+cholesteryl). IR: 2919, 2848, 1714, 1600, 1544, 1457, 1450, 1446, 1412, 1390, 1362, 1300, 1249, 1184, 1141, 1011, 790, 720 cm^{-1}. Anal: calc. for $C_{123}H_{207}O_{12}Eu.3H_2O$, C 70.89, H 10.00; found, C 71.08, H 10.11%.

7.3. *Tris[13-(cholest-5-en-3β-yloxycarbonyl)tridecanoic acid]neodymium(III) trihydrate (3)*

Complex **3** was prepared in the same way as complex **2** from anhydrous $NdCl_3$ (50.1 mg, 0.2 mmol)) and compound **1** (376 mg, 0.6 mmol). A pale blue powder, yield 18% was obtained. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.38 (br, 1H, H_6), 4.62 (br, 1H, $H_{3\alpha}$), 2.28 (br, 6H, OOC–CH_2–, –CH_2COOChol., $H_{4\alpha}$, $H_{4\beta}$), 1.29 (20H, –$(CH_2)_6$–), 2.02–0.70 (41H, cholesteryl). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): 173.86 (–O<u>C</u>O–), 140.06 (C_5), 122.95 (C_6), 73.85 (C_3), 56.80–12.21 (–$(CH_2)_6$–+cholesteryl). IR: 2920, 2847, 1716, 1605, 1543, 1458, 1452, 1445, 1410, 1388, 1361, 1305, 1252, 1186, 1140, 1013, 787, 722 cm^{-1}. Anal: calc. for $C_{123}H_{207}O_{12}Nd.3H_2O$, C 71.16, H 10.03; found C 70.94, H 9.88%.

7.4. *(acetylacetonate)$_2$-[13-(cholest-5-en-3β-yloxycarbonyl)tridecanoic acid]europium(III) dihydrate (4)*

Complex **6** was prepared in the same way as complex **2** from anhydrous $EuCl_3$ (51.7 mg, 0.2 mmol), compound **2** (125 mg, 0.2 mmol) and acetylacetonate (40 mg, 0.4 mmol). Recrystallization from acetone gave a pale pink powder; yield 12%. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.4 (br, 1H, H_6), 4.8 (br, 1H, $H_{3\alpha}$), 4.96 (s, 2H, CO–CH=C–O), 2.07 (s, 12H, CO–CH_3), 2.5–0.5 (br, OOC–CH_2–, –CH_2COOChol., –$(CH_2)_6$–, cholesteryl). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): 191.05 (CH_3<u>C</u>O–), 173.69 (br, CH_2<u>C</u>OOChol), 140.23 (br, C_5), 123.00 (br, C_6), 74.10 (br, C_3), 57.08 (CO–<u>C</u>H=C–O), 28.42 (<u>C</u>H_3CO), 50.41–12.26 (–$(CH_2)_6$–+cholesteryl). IR: 2965, 2847, 1630, 1592, 1541, 1514, 1452, 1448, 1412, 1390, 1357, 1309, 1250, 1190, 1145, 1015, 786, 723 cm^{-1}. Anal: calc. for $C_{51}H_{83}O_8Eu.2H_2O$, C 60.52, H 8.65; found, C 60.54, H 8.71%.

7.5. *General procedure for the preparation and analysis of a lanthanide-doped CLC*

In a 50 ml round bottom flask, cholesteryl nonanoate, cholesteryl tetradecanoate (both in varying amount according to the nature of the complex), nematic Licristal® ZLI 1083 (20 mg, 0.079 mmol) and the lanthanide complex were dissolved in $CHCl_3$ (5 ml). The mixture was stirred for 15 min and the solvent removed by rotary evaporation. One drop of the resulting chiral LC mixture was then placed between two glass plates and analysed on a hot stage with a microscope.

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