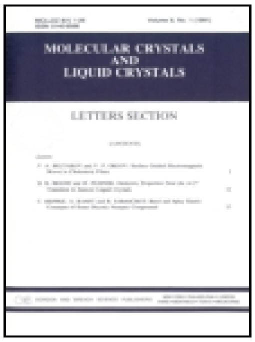
MOLECULAR CRYSTALS AND LIQUID CRYSTALS

LETTERS SECTION

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Tomoyuki Itaya, Ayaha Hachisuga, Kazuchika Ohta, Daniela Pucci, Elisabeta I. Szerb, Massimo La Deda & Mauro Ghedini (2014) Liquid Crystalline and Luminescent Behavior of Lanthanide Complexes Composed of Terbium or Europium and Dendritic Amphiphile, Molecular Crystals and Liquid Crystals, 605:1, 70-81, DOI: 10.1080/15421406.2014.889536

To link to this article: http://dx.doi.org/10.1080/15421406.2014.889536

Mol. Cryst. Liq. Cryst., Vol. 605: pp. 70–81, 2014
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.889536

Liquid Crystalline and Luminescent Behavior of Lanthanide Complexes Composed of Terbium or Europium and Dendritic Amphiphile

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Luminescent lanthanide (Tb^{3+}, Eu^{3+}) complexes were prepared by reaction of Tb^{3+} or Eu^{3+} with dendritic amphiphile (3,4,5-tris(dodecyloxy)benzoate), then their liquid crystalline and luminescent behavior were studied. The complexes exhibited thermotropic liquid crystalline mesophases with columnar hexagonal structure. The complexes emitted the characteristic luminescence of the core metals. Additionally, in the Eu^{3+} complex, the ratio of the intensity of 614 nm to the intensity of 585 nm (I_{614}/I_{585}) remarkably decreased around the transition temperature from crystal to mesophase, suggesting that the coordination environment of Eu^{3+} gets more symmetrical due to the phase transition.

Keywords Columnar mesophase; lanthanide complex; liquid crystal; luminescence

1. Introduction

The introduction of a metal ion into a mesomorphic system (metallomesogen) can significantly modify its properties and anticipate development of materials with unusual optical and magnetic properties [1–3]. Metal-containing salts of long-chain fatty acids are commonly known as metal soaps and some metal soaps act as metallomesogens. In metal soaps, lanthanide soaps are of particular interest due to their optical and magnetic properties [4–6]. The lanthanide soaps comprised of lanthanide ions and long-chain fatty acids have been prepared and studied by Binnemans and coworkers, where the thermotropic behavior of lanthanide soaps and the effects of chain length and lanthanide ion size on their mesophases

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were reported [7]. The self-assembly of soap molecules into liquid-crystalline mesophases is influenced by the shape of the molecule. However, there are few studies on the effect of shape of the metal soaps [8]. In this work, we prepared lanthanide complexes consisting of Tb^{3+} or Eu^{3+} core and surrounding dendritic amphiphile (3, 4, 5-tris(dodecyloxy)benzoate), that are different from normal metal soaps.

K. Ohta et al. have reported that sodium diphenylacetate exhibits a hexagonal columnar mesophase and each of the columns may have a metal wire in the center, which is formed by one-dimensional aggregates of sodium metal [9]. This would be expected to form a lanthanide metal wire in a columnar mesophase of a terbium-amphiphile complex. Moreover, the formation of the metal wire can modify the metal's properties. In fact, the lanthanide complexes we prepared in this study exhibited columnar mesophases, suggesting the formation of one-dimensional aggregates of lanthanide metal. Herein, we report the liquid crystalline behavior of the Tb^{3+} or Eu^{3+} complexes consisting of metal core and surrounding dendritic amphiphile (3,4,5- tris(dodecyloxy)benzoate). In addition, we report the luminescence behavior of the complexes in crystal and mesophases and discuss the influence of the formation of columnar mesophases on the fluorescence behavior.

2. Experimental

2.1. Materials

3,4,5-tris(dodecyloxy)benzoic acid was synthesized as described in the literature [10]. Terbium nitrate and europium nitrate were purchased from Aldrich and used without further purification.

The Tb^{3+} complex was prepared by the reaction between the sodium salt of 3,4,5-tris(dodecyloxy)benzoic acid and the terbium nitrate as follows. An ethanol solution of terbium nitrate (0.0130 g (2.86×10^{-5} mol)) was added dropwise to an ethanol solution (15 mL) of the sodium salt of 3,4,5-tris(dodecyloxy)benzoic acid (0.105 g (1.51×10^{-4} mol)) obtained by neutralization with NaOH. The terbium complex immediately precipitated. After the mixture was stirred at 70°C for 1 h, the precipitate was filtered off and washed with water and ethanol, and then dried in a vacuum. The Eu^{3+} complex also was prepared in the same way.

Elemental analysis (%) found (calc.): Tb^{3+} complex = $C_{129}H_{231}O_{15}Tb$: C, 70.79 (71.04); H, 10.95 (10.67), N, 0.30 (0.00). Eu^{3+} complex = $C_{129}H_{231}O_{15}Eu$: C, 70.97 (71.26); H, 10.98 (10.71), N, 0.13 (0.00).

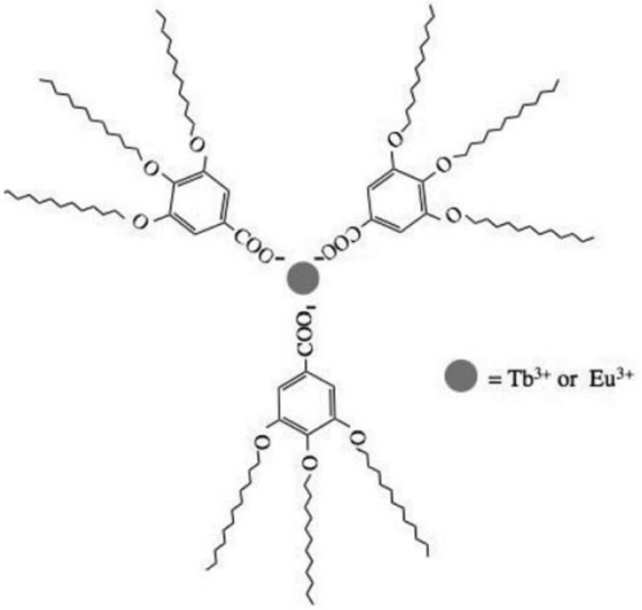
2.2. Measurements

The complexes were identified by using FT-IR (Perkin-Elmer FT-IR spectrometer) and elemental analysis (Perkin-Elmer elemental analyzer 2400). Thermogravimetry measurements were performed with a PyrisTGA6 Perkin-Elmer thermogravimetric analyzer. The phase transition behavior of the complexes was observed with a Leica DMLP polarizing optical microscope equipped with a Leica DFC280 camera and a CalCTec (Italy) heating stage, and measured with a Perkin-Elmer Pyris1 Differential Scanning Calorimeter with a heating and cooling rate of 10°C/min. For the mesophase identification, we employed a small angle X-ray diffractometer (Bruker Mac SAXS System) equipped with a temperature-variable sample holder adapted Mettler FP82HT hot stage [11]. Absorption spectra were recorded with a UV-Vis Perkin-Elmer Lambda 900 spectrophotometer. Steady-state emission spectra were recorded on a Horiba Jobin Yvon Fluorolog 3 spectrofluorometer, equipped with a Hamamatsu R-928 photomultiplier tube. Emission quantum yields of the complexes were determined using the optically dilute method with $Ru(bpy)_3Cl_2$ (bpy = 2,2'-bipyridine) in H_2O as a standard ($\varphi = 0.028$ in aerated solution) [12,13]. Temperature-dependent fluorescence spectra of the complexes were recorded by using a Horiba Fluorolog FL3-21-NIR-OS spectrofluorometer equipped with a handmade hot plate [14] with a temperature controller.

3. Results and Discussion

3.1. Synthesis and Characterization

The reaction of lanthanide ions (Tb^{3+} or Eu^{3+}) with sodium 3,4,5-tris(dodecyloxy)benzoate in ethanol gave white solid. The carbonyl absorption peak at 1685 cm^{-1} in the FT-IR spectra of the 3,4,5-tris(dodecyloxy)benzoic acid was not observed at 1685 cm^{-1} in the spectra of the lanthanide complexes. This can be interpreted as supporting evidence for the coordination of carboxylato anions to the lanthanide ions. From elemental analysis, the stoichiometry of the complexes was shown to be metal : 3,4,5-tris(dodecyloxy)benzoate anion = 1:3. In addition, the coordination of solvent molecules (water or ethanol) to the metal ions was examined by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements, but the molecules were not detected. These results show that the lanthanide complexes are formed as shown in Scheme 1. This kind of 1:3 complexes without coordinated solvent molecules is also reported in the cases of the Tb^{3+} or Eu^{3+} - *p*-methylbenzoic acid and – *p-tert*-butylbenzoic acid complexes [15].



Scheme 1. The Tb^{3+} and Eu^{3+} complexes.

Table 1. Phase transition temperatures and enthalpy changes of the Tb^{3+} and Eu^{3+} complexes

complex	$\text{Phase} \xrightarrow{T(^{\circ}C)\ \Delta H(kJ/mol)} \text{Phase}$
Tb^{3+} complex	$Cr \overset{41.7\ [45.0]}{\rightleftarrows} Col_{h1} \overset{207\ [58.5]}{\rightleftarrows} Col_{h2} \overset{279\ [22.6]}{\rightleftarrows} I \xrightarrow{ca.\ 300} \text{Decomp.}$
Eu^{3+} complex	$Cr \overset{43.7\ [55.2]}{\rightleftarrows} Col_{h1} \overset{241\ [75.8]}{\rightleftarrows} M_x \xrightarrow{ca.\ 300} \text{Decomp.}$

Phase nomenclature: Cr = crystal, Col_h = hexagonal columnar mesophase, M_x = unidentified mesophase and I = isotropic liquid.

3.2. Phase Transition Behavior and Mesophase Structure

The phase transition sequences and the mesophase structures of the complexes were observed by DSC measurements, polarizing optical microscopic (POM) observations, and temperature-dependent X-ray diffraction measurements. The phase transition sequences are summarized in Table 1. When the virgin sample of the Tb^{3+} complex was heated from room temperature, it melted into a Col_h mesophase at 42°C. On further heating, a transition from the Col_h phase (Col_{h1}) to another Col_h phase (Col_{h2}) was observed 207°C. The Col_{h2} phase cleared into an isotropic liquid at 279°C. The mesophases were confirmed by POM. Figure 1 shows the texture at 240°C, indicative of liquid crystalline texture. As both mesophases have the same Col_h structure, the texture for Col_{h1} is almost the same as that for Col_{h2}. In the case of the Eu^{3+} complex, however, the virgin sample melted into a Col_h mesophase at 44°C. On further heating a transition from the Col_h phase (Col_{h1}) to another mesophase was observed at 241°C. The identification of the mesophase was impossible

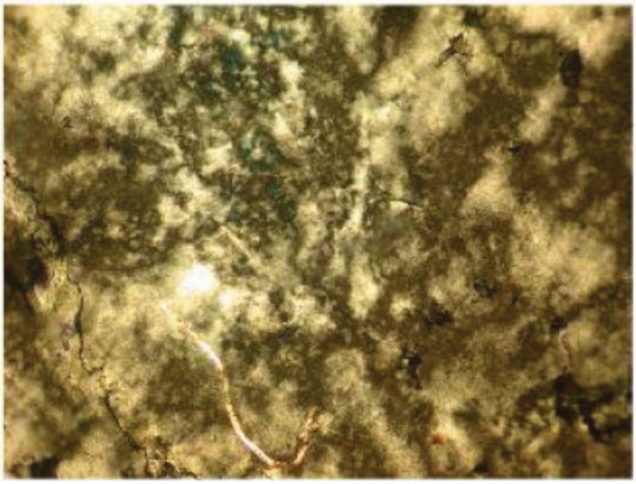


Figure 1. Photomicrograph of the Tb^{3+} complex at 240°C.

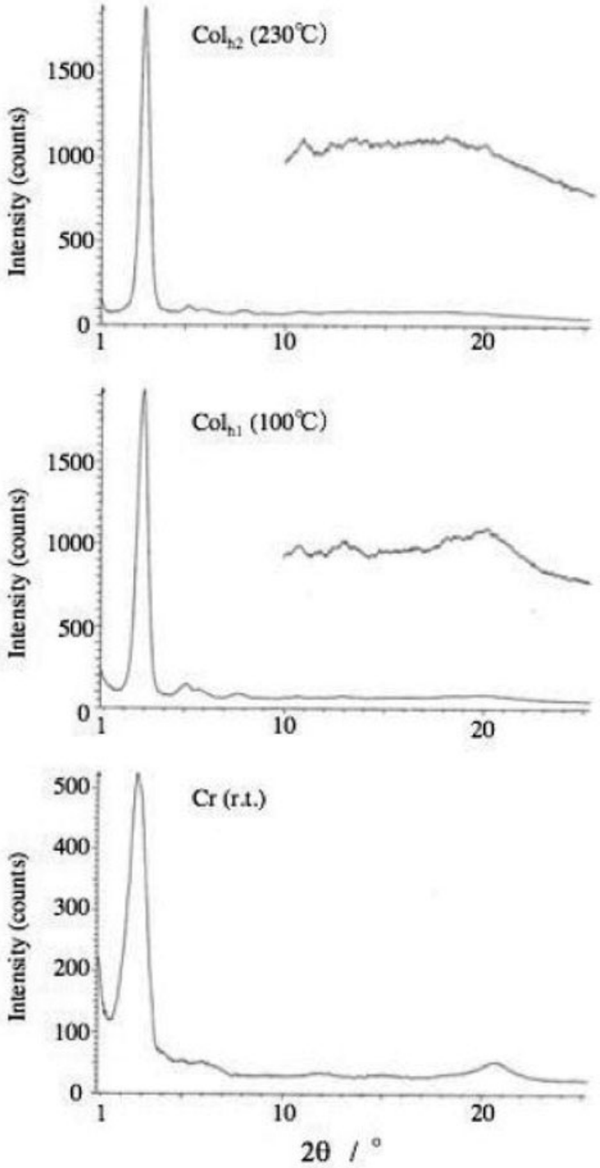


Figure 2. X-ray diffraction patterns of the Tb^{3+} complex at room temperature, 100°C and 230°C. The upper patterns in the graphs, Col_{h1} (100°C) and Col_{h2} (230°C), are the enlarged image of the change in the intensity of the corresponding parts of the lower patterns.

because of the thermal decomposition, as mentioned later. The sample decomposed at ca. 300°C without clearing into an isotropic liquid. These suggest that the core lanthanide ion in the complex has an effect on the thermal behavior of the complexes.

For the mesophase identification, temperature-dependent X-ray diffraction analysis was carried out. Figure 2 shows the X-ray diffraction patterns for the Tb^{3+} complex and Figure 3 shows the X-ray diffraction patterns for the Eu^{3+} complex. These corresponding

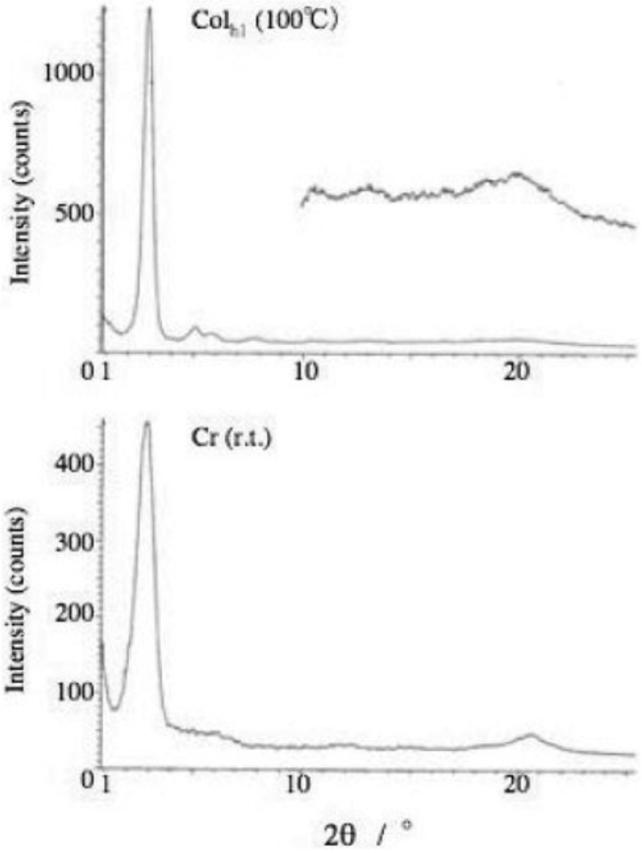


Figure 3. X-ray diffraction patterns of the Eu^{3+} complex at room temperature and 100°C. The upper pattern in the graph, Col_{h1} (100°C), is the enlarged image of the change in the intensity of the corresponding part of the lower pattern.

X-ray data are listed in Table 2. It was impossible to observe the X-ray diffraction patterns of the Eu^{3+} complex above 250°C because of the thermal decomposition. The decomposition in the air started even at temperatures lower than the DSC decomposition temperatures (ca. 300°C) under a nitrogen atmosphere. The color of the sample, measured above 250°C, changed from white to brown.

The diffraction patterns at 100°C, 230°C for the Tb^{3+} complex and at 100°C for the Eu^{3+} complex, gave some peaks with spacing in the ratio of 1: $1/\sqrt{3}$: 1/2 : etc., indicating that the mesophases could be assigned to hexagonal columnar mesophases. These complexes seem to have a propeller-like structure, which is based on the ability of the lanthanide ion to form 1:3 complexes by coordination of carboxylato ligands. Therefore, the propeller-like complexes may pile up a hexagonal columnar phase and the lanthanide ions seem to be arranged linearly in the center of the column.

In the diffraction patterns at room temperature for the Tb^{3+} complex and the Eu^{3+} complex, the peak originated from alkyl chain crystallites was observed at $2\theta = 21°$. The peak completely disappeared in the pattern at 230°C for the Tb^{3+} complex. But, the peak seems to remain a little at $2\theta =$ ca. 20° in the patterns at 100°C for the Tb^{3+} complex and the

Table 2. X-ray data of the Tb^{3+} and Eu^{3+} complexes

Compound	Mesophase lattice constants (Å)	Spacing (Å) Observed	Spacing (Å) Calculated	Miller indices (h k l)
Tb^{3+} complex	Col_{h1} at 100°C	30.7	30.7	(1 0 0)
	a = 35.4	17.4	17.7	(1 1 0)
		15.5	15.3	(2 0 0)
		11.5	11.6	(2 1 0)
		8.30	8.51	(3 1 0)
		6.84	6.70	(4 1 0)
		4.42	–	#
	Col_{h2} at 230°C	30.0	30.0	(1 0 0)
	a = 34.6	17.3	17.3	(1 1 0)
		15.0	15.0	(2 0 0)
		11.1	11.3	(2 1 0)
		8.17	8.32	(3 1 0)
Eu^{3+} complex	Col_{h1} at 100°C	31.0	31.0	(1 0 0)
	a = 35.8	17.5	17.9	(1 1 0)
		15.3	15.5	(2 0 0)
		11.4	11.7	(2 1 0)
		8.42	8.61	(3 1 0)
		6.82	6.77	(4 1 0)
		4.48	–	#

#: alkoxy chains.

Eu^{3+} complex. In addition to this result, the enthalpy change of 59 kJ/mol at 207°C of the Tb^{3+} complex seems to be too big for the enthalpy change of the transition (from Col_{h1} to Col_{h2}), as can be seen from Table 1. The enthalpy change of 104 kJ/mol between 42°C and 207°C of the Tb^{3+} complex seems to correspond to the complete melting of alkyl chains for the Tb^{3+} complex that has nine dodecyloxy chains. In addition, the enthalpy change from crystal to liquid crystal is 98.7 kJ/mol for a discotic compound 2, 3, 9, 10, 16, 17, 23, 24-octakis(4-dodecyloxyphenoxy) phthalocyaninto copper(II) that has eight dodecyloxy chains [16]. Judging from these facts, the transition behavior of the complexes is supposed as follows. In the case of the Tb^{3+} complex, the flexible long chains melt at first at 42°C and the rigid core and the alkyl chains close by the core do not melt but still aggregate each other. This premelting of peripheral long chains initiates the soft part to induce the Col_{h1} phase [7,11]. After that the alkyl chains close to the core melt at 207°C and the core does not melt but the Col_{h2} phase is kept. The above stepwise melting of the alkyl chains seems to give rise to the difference between the thermal behavior of the Tb^{3+} complex and that of the Eu^{3+} complex. The stepwise melting of alkyl chains is also observed for fatty acids [17]. Both the Tb^{3+} complex and the Eu^{3+} complex melt to exhibit Col_h mesophase at about 40–45°C. The melting of the distant alkyl chains from the core is not influenced by the core metal. However, the melting of the alkyl chains close to the core is influenced by the core metal. Therefore, the Tb^{3+} complex and the Eu^{3+} complex exhibit the transition from Col_{h1} to Col_{h2} (M_x) at 207°C and 241°C, respectively, although the reason remains unclear.

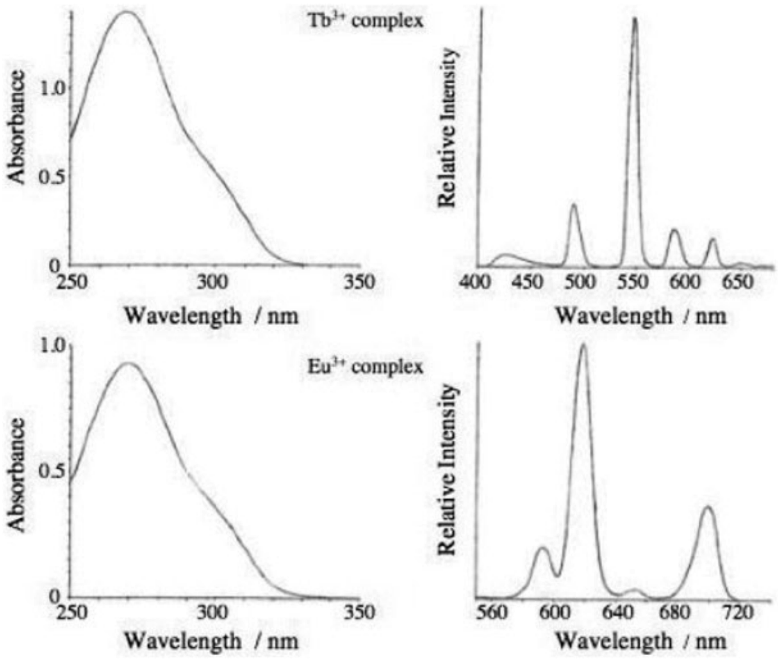


Figure 4. Absorption and emission spectra of the Tb^{3+} and Eu^{3+} complexes in chloroform solution. [Tb^{3+} complex] = 6.0×10^{-5} M, [Eu^{3+} complex] = 4.6×10^{-5} M, λ_{ex} = 300 nm.

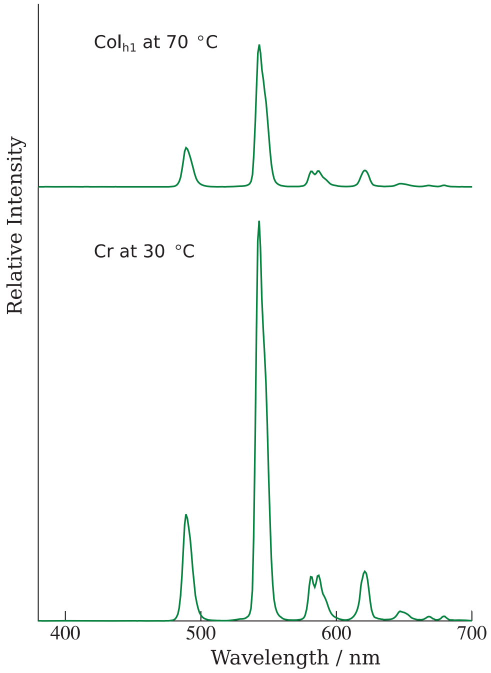


Figure 5. Emission spectra of the Tb^{3+} complex in the solid (at room temperature) and liquid crystal state (at 70°C).

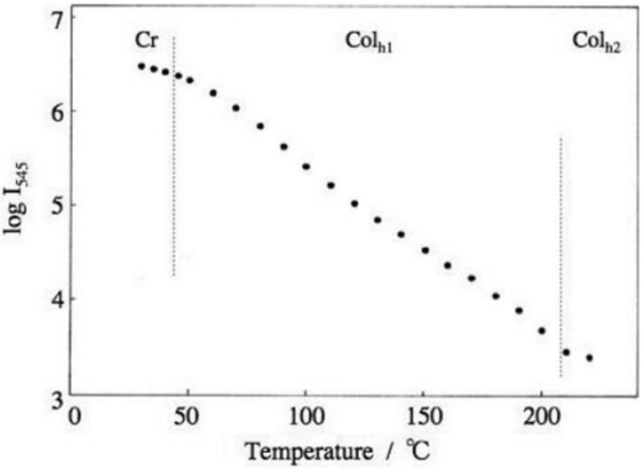


Figure 6. Dependence of log I_{545} on temperature.

3.3. Fluorescence Behavior

A metal center can add unique fluorescence properties to the liquid crystal [18–20]. The lanthanide complexes are also luminescent [21]. Figure 4 shows the absorption and emission spectra of the Tb^{3+} and Eu^{3+} complexes in chloroform. The absorption spectra of the Tb^{3+} and Eu^{3+} complexes are almost the same, suggesting that the spectra originated from

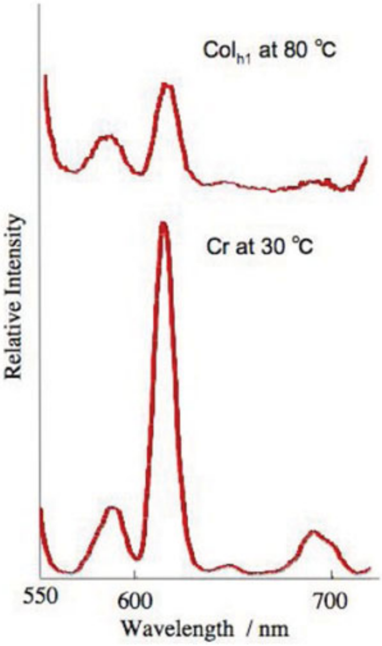


Figure 7. Emission spectra of the Eu^{3+} complex in the solid (at room temperature) and liquid crystal state (at 80°C).

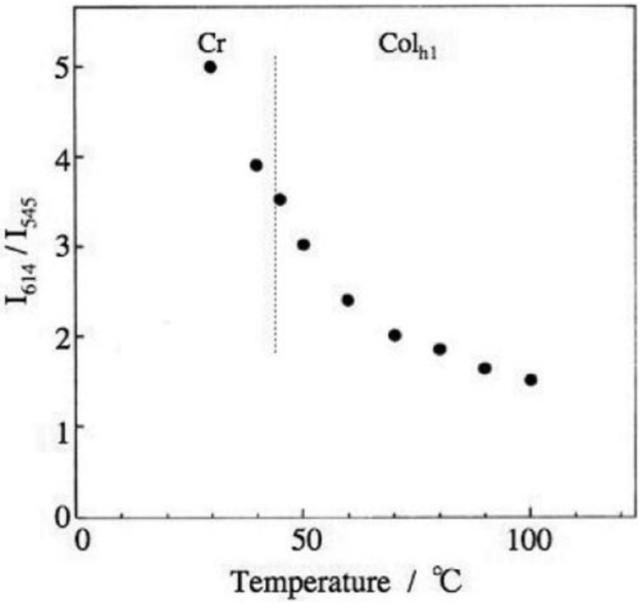


Figure 8. Dependence of the intensity ratio (I_{614}/I_{585}) on temperature.

ligands (3,4,5-tris(dodecyloxy)benzoate moieties). The emission spectra of the Tb^{3+} and Eu^{3+} complexes excited at 300 nm exhibit the characteristic luminescence of Tb^{3+} and Eu^{3+}, respectively. These results indicate that the luminescence of these complexes is due to the energy transfer from the ligands to the core metal ion. The emission quantum yields of the Tb^{3+} and Eu^{3+} complexes in chloroform are 9×10^{-3} and 4×10^{-4}, respectively. These values are not high. This might be due to the inefficient energy transfer from ligands (3,4,5–tris(dodecyloxy)benzoate moieties) to the lanthanide ions.

Figure 5 shows the emission spectra of the Tb^{3+} complex in the solid (at room temperature) and liquid crystal state (at 70°C). At 70°C, the emission intensity of the complex decreased due to the strong tendency of the excited states to deactivate via nonradioactive transitions [22,23], maintaining the overall shape of the fluorescence spectra. In Fig. 6 the logarithm of the intensities at 545 nm (log I_{545}) versus temperature are plotted. The intensity at 545 nm is due to the $^5D_4 \rightarrow {}^7F_5$ transition that is the most intense in the $^5D_4$ emission and quite sensitive to the metal ion environment. As can be seen in Fig. 6, the dependence of log I_{545} on temperature changed around the transition temperature from the crystal to the liquid crystalline state (Col_{h1}), i.e., the slope clearly became acute by the phase transition, suggesting that the coordination environment of Tb^{3+} seems to change due to the phase transition, although the details remains unclear.

We have carried out a similar study on the Eu^{3+} complex. The emission of Eu^{3+} complex is sensitive to the microenvironment of the ion, especially to the coordination environment. Figure 7 shows the emission spectra of the Eu^{3+} complex in the solid (at room temperature) and liquid crystal state (at 80°C). The fluorescence intensity of the Eu^{3+} complex also decreases as the temperature rises. In Fig. 7, we observed that the ratio of the intensity of 614 nm to the intensity of 585 nm changed drastically. The most important probe transitions for Eu^{3+} complexes are $^5D_0 \rightarrow {}^7F_1$ (585 nm) and $^7F_2$ (614 nm). Their emission splitting pattern is known to be related with the symmetry of the coordination environment of Eu^{3+} [24]. The intensity ratio (I_{614}/I_{585}) is large when the coordination environment of Eu^{3+} is unsymmetrical. As can be seen in Fig. 8, the I_{614}/I_{585} value decreases rapidly at the transition temperature (44°C) from crystal to liquid crystalline phase (Col_{h1}), while the slope becomes less acute around 60°C. This indicates that the coordination environment of Eu^{3+} gets more symmetrical due to the formation of columnar hexagonal mesophase. This structural change seems to be easy to pile up the propeller-like complexes.

4. Conclusion

The luminescent liquid crystalline lanthanide complexes composed of Tb^{3+} or Eu^{3+} and dendritic amphiphile were synthesized and their mesomorphism and luminescent behavior were investigated. The complexes, which have a propeller-like central core with nine long surrounding alkyl chains, exhibit columnar hexagonal mesophases. In the center of the column, the lanthanide ions seem to be arranged linearly. The fluorescence behavior was influenced by the transition from crystal to columnar mesophase, suggesting that the formation of columnar mesophase affects the coordination environment of the lanthanide ions. To study the effect of cored lanthanide ion on the liquid crystalline behavior and the effect of the liquid crystalline formation on the magnetic and spectroscopic properties of cored lanthanide ions in the complexes, other lanthanide complexes are currently being investigated.

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