Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 07 Oct 2011

To cite this article: Elisabeta I. Szerb, Alessandra Crispini, Massimo La Deda, Daniela Pucci, Paola F. Liguori & Claudio Pettinari (2011): Europium(III) and Terbium(III) Luminescent Lanthanidomesogens, Molecular Crystals and Liquid Crystals, 549:1, 86-99

To link to this article: http://dx.doi.org/10.1080/15421406.2011.581149

Mol. Cryst. Liq. Cryst., Vol. 549: pp. 86–99, 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.581149

Europium(III) and Terbium(III) Luminescent Lanthanidomesogens

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Liquid-crystalline columnar phenanthroline-based ligand, for the first time substituted in 4,7-positions, is synthesized and used to induce low temperature mesomorphism in his corresponding lanthanide complexes. Stable liquid crystalline Eu(III) and Tb(III) complexes with low transition temperatures and low viscosity mesophases are obtained and their thermal and photophysical properties investigated as a function of their different solid, soft and liquid crystalline organisations. The eight-coordination around the metal lanthanide centre is further fulfilled by six oxygen atoms of three bidentate 1-phenyl-3-methyl-4-benzoylpyrazol-5-one proligands.

Keywords Coordination chemistry; lanthanidomesogens; phenanthroline mesogenic ligand; acylpyrazolone proligands; luminescence.

Introduction

Currently lanthanide luminescent complexes are essential for a landscape of applications ranging from telecommunications to life sciences, due to their ability to emit with high quantum yields and narrow bandwidth lines, spanning the visible and NIR spectral regions [1–9]. Therefore the design of lanthanide compounds with increased thermal and photophysical stabilities is a living matter, different strategies being used to circumvent the limited applicability arising from the presence of solvent molecules in the coordination sphere of these systems.

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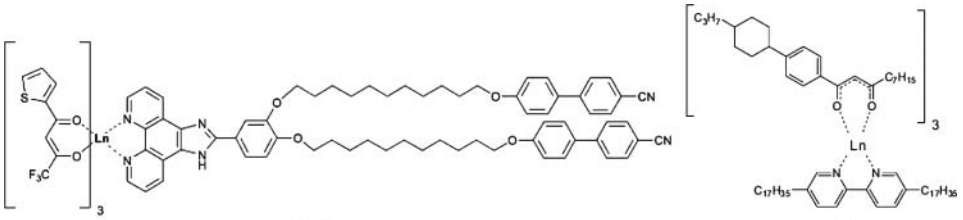
The best strategy seems to be the synthesis of highly coordinated heteroleptic complexes where the lanthanide ions are coordinated in the same time to a neutral chelating nitrogen ligand and to three β-diketonate units [10], protecting the metal centre from vibrational coupling and thus increasing their light absorption cross section by the "antenna effect". In particular 1,10-phenanthrolines have been proposed as the most versatile and appealing partners for lanthanide centers, whereas Eu(III) and Tb(III) derivatives were found to be the strongest emitters, red and green respectively [11]. Recently, increasing interest has been shown in the use of the acylpyrazolones, a class of asymmetrical heterocyclic ligands analogues of β-diketones, since their presence as ancillary ligands in rare earth metal complexes is beneficial for both luminescence and stability properties, offering new possibilities in their application [12].

Furthermore, the possibility of conjugating the unique electronic, magnetic and optical properties of lanthanide complexes with the advantages of anisotropic soft materials such as liquid crystals, opens new perspectives in the application of lanthanide complexes as molecular components for more efficient probes or devices. Thus, a lot of work in the field of thermotropic lanthanide containing metallomesogens, namely lanthanidomesogens, has been performed in the last years, and different mesomorphic organisations from lamellar to cubic and columnar ones were obtained [13–15]. From the beginning it was a challenge to obtain lanthanide complexes with low temperature and low viscosity mesophases in order to perform luminescence studies in the liquid crystalline phase [16], the polarized luminescence from oriented materials being a strategic goal in different fields [17, 18].

Some recent crucial contributions in this direction have been reported by Binnemanns [19] on nematogenic complexes based on imidazo 1,10 phenanthroline ligands and thenoyltrifluoroacetonate as coligands (A in Chart 1) whose luminescence has been measured in a solution of liquid crystal host, followed by compounds of 5,5'-substituted 2,2'-bipiridines and tris-diketonates (B in Chart 1) [20] for which polarized emission has been observed for aligned samples of the supercooled nematic phase.

As part of our research in exploring the potential of forming luminescent and liquid crystalline complexes of lanthanide complexes with aromatic N-donor and suitable β-diketonate ligands [21] herein we report the synthesis of a new 1,10-phenanthroline functionalized in 4,7-positions with groups containing several long peripheral alkyl chains (***phen-16***), used to induce liquid-crystalline properties in their Eu(III) and Tb(III) complexes containing as ancillary O,O ligands the 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (**HQ**). Furthermore, a similar ligand but lacking of alkyl chains (***phen***) was synthesized and used to obtain model Eu(III) and Tb(III) complexes.



(A) **(B)**

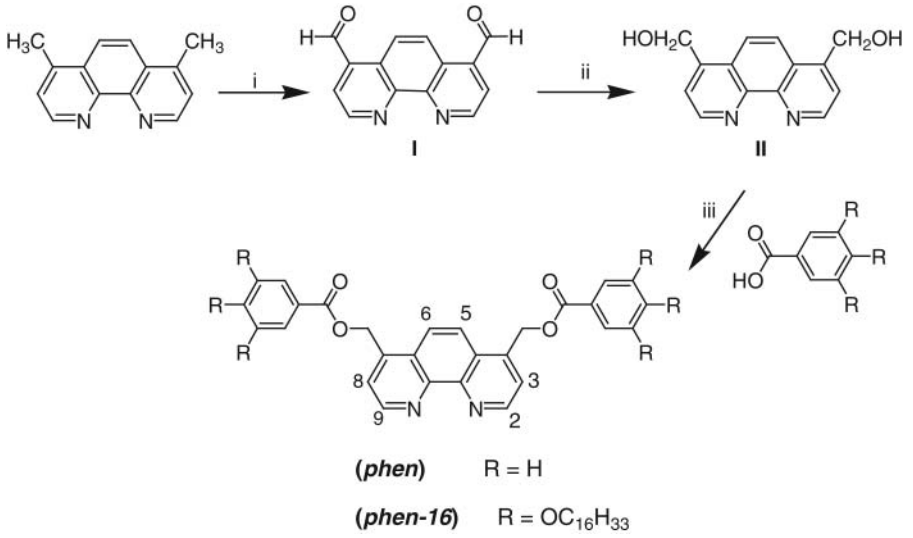
Chart 1.

Results and Discussion

Synthesis and Characterization

The proligand 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (**HQ**) was synthesized as previously reported [22].

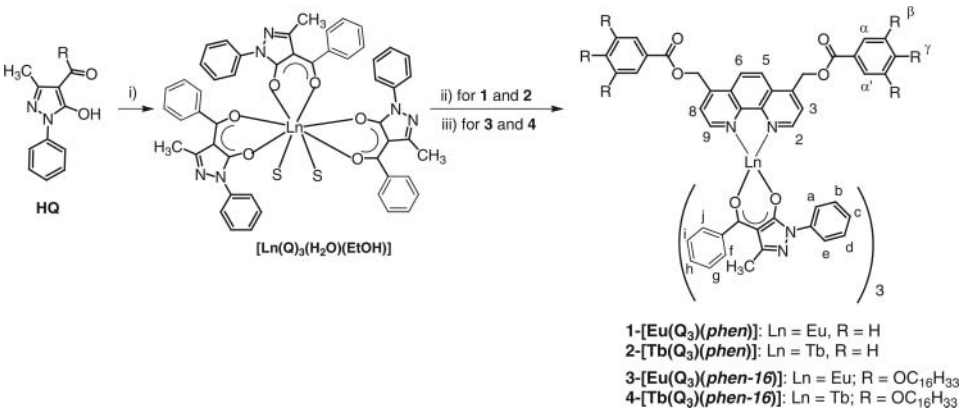
The phenanthroline-based ligands (***phen)*** and **(*phen-16*),** were prepared through a three step synthesis as shown in Scheme 1. In particular, precursor **II** was obtained by a synthetic methodology reported for similar derivatives [23], starting from the commercially available 4,7-dimethyl-1,10-phenantroline which was first oxidized to dicarboxaldehyde (**I**) with selenium dioxide, and successively reduced with sodium borohydride. In the final step, the hydroxymethyl compound **II** reacts with the appropriate benzoic acid by a DCC-PPY esterification, to give (***phen)*** and **(*phen-16*)** ligands, which were separated in satisfactory yields as white solids [24].



Scheme 1. Synthesis of ligands (***phen***) and (***phen-16***): i) SeO_2, dioxane, ΔT, ii) NH_4BF_4, EtOH, ΔT; iii) DCC, Ppy, CH_2Cl_2, r.t.

The synthesis of the lanthanide model complexes **[Ln(Q)$_3$(*phen*)], 1–2** and the highest homologues **[Ln(Q)$_3$(*phen-16*)], 3–4** (Ln = Eu(III) and Tb(III)), requires a previous preparation of tris-pyrazolonate eight-coordinated lanthanide precursors **[Ln(Q)$_3$(H$_2$O)(EtOH)]** using a method described for similar complexes (Scheme 2) [25]. In particular, the appropriate lanthanide nitrate is reacted with the ligand **HQ** in presence of KOH to give the lanthanide precursor **[Ln(Q)$_3$(H$_2$O)(EtOH)]**, that was subsequently reacted with the ligand (***phen***) in refluxing ethanol for 3 hours, to obtain the model complexes **[Ln(Q)$_3$(*phen*)], 1** and respectively **2,** in high yields (Experimental Section). Because of the insolubility of (***phen-16***) ligand in ethanol, the synthesis of complexes **[Ln(Q)$_3$(*phen-16*)], 3** and **4,** was conducted in toluene, increasing the reaction time to 7–8 days.

The structural characterization and purity of the new derivatives reported herein, respectively the phenanthroline-based ligands (***phen***) and (***phen-16***), the lanthanide precursors **[Ln(Q)$_3$(H$_2$O)(EtOH)],** and the final heteroleptic complexes **1–4,** were investigated



Scheme 2. Synthesis of complexes **1–4**: i) $Ln(NO_3)_3 \cdot 5H_2O$, KOH, EtOH, 2h, r.t.; ii) **(*phen*)**, EtOH, ΔT, 3h; iii) ***(phen-16)***, Toluene, r.t., 9 days.

by combined elemental analysis, IR and UV spectroscopies. Moreover, the diamagnetic Eu(III) compounds **1** and **3** were characterized by ^{1}H NMR spectroscopy.

The IR spectra of the heteroleptic complexes **1–4** show the C=O bands of both the N,N (1720–1730 cm^{-1}) and O,O ligands (1645–1630 cm^{-1}), shifted with respect to their corresponding precursors (Experimental Section).

The absorption spectra of the Eu(III) and Tb(III) complexes in dichloromethane solution are very similar, being the change of the metal irrelevant on the spectral shape, therefore, as an example, in Figure 1 is reported only the electronic spectra of the Eu(III) complex **3** and its precursors **HQ**, **(*phen-16*)** and **[Eu(Q)$_3$(H$_2$O)(EtOH)]**. In particular, the starting complex **[Eu(Q)$_3$(H$_2$O)(EtOH)]** shows two bands at 250 and 297 nm, clearly reminiscent of the two analogues bands of the parent ligand **HQ**, which are attributed to π-π^* transitions on the aromatic rings. In the spectrum of complex **[Eu(Q)$_3$(*phen-16*)], 3,** an intense band at 275 nm and a shoulder at about 305 nm are detected; these features, which are due to transitions localized on the phenanthroline ligand, superimpose the bands originated from the **Q** excitations.

The coordination mode of the diamagnetic Eu(III) derivatives in solution was examined through proton ^{1}H NMR measurements. In the ^{1}H NMR spectrum of the precursor **[Eu(Q)$_3$(H$_2$O)(EtOH)]** very broad signals are found due to the presence of solvent molecules (water and/or ethanol) [26]. Therefore the spectral patterns of the Eu(III) complexes **1** and **3** were compared with those of the parent ligands, **HQ** and **(*phen*)** or ***(phen-16)***. The ^{1}H NMR spectra of either **1** or **3** contain signals related to both ligands (**Q** and (***phen***), or **Q** and (***phen-16***) respectively), shifted with respect to the uncomplexed ligands, confirming once again their successful coordination to the Eu(III) metal centers. Indeed, upon coordination**,** the signals of the phenanthroline protons ($H_{2,3,6,8,9}$) are shifted about 1.0–2.0 ppm downfield with respect to the uncomplexed ligand. Also the protons related to the pyrazolonate ligand **Q** suffer a sizeable shift with respect to the neutral **HQ**, downfield of about 0.2–0.7 ppm for H_a, H_e and $H_{f\text{-}j}$ or upfield of aproximatively 0.7 ppm for $H_{b\text{-}d}$.

Furthermore, for all complexes **1–4,** the absence of any co-crystallized solvent molecules in their structures was verified by TGA analysis, whose traces showed no weight loss until decomposition, which occurs at ca. 300°C for **[Ln(Q)$_3$(*phen*)]** complexes **1** and **2** and at about 200°C for **[Ln(Q)$_3$(*phen-16*)]** complexes **3** and **4.**

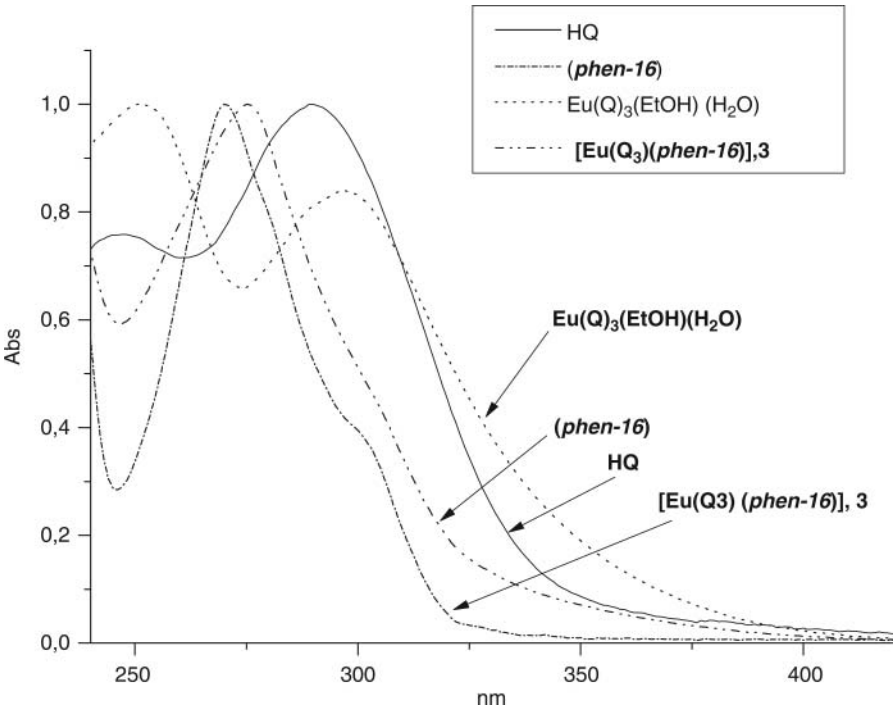


Figure 1. Absorption spectra of ligand **HQ** (solid line), ligand ***(phen-16)*** (dash dot dot) precursor **[Ln(Q)$_3$(H$_2$O)(EtOH)]** (dot) and complex **3 -[Eu(Q$_3$)(*phen-16*)]** (short dash dot).

These results and a comparison with related structures previously reported on similar neutral lanthanide complexes [21], suggest an eight-coordination around the metal centre fulfilled by six oxygen atoms of the three bidentate **Q** ligands and two nitrogen atoms of the bidentate (***phen***) or (***phen-16***) ligand respectively, as presented in Scheme 2.

Mesomorphism

The thermal behaviour of the ligand ***(phen-16)***, decorated with 6 long peripheral alkyl chains, as well as that of the corresponding lanthanide complexes **3** and **4** was investigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and small-angle X-ray diffraction on powder samples (PXRD). An overview of the transition temperatures and the corresponding detectable enthalpies is given in Table 1.

The substituents on the 4 and 7 positions of the 1,10-phenanthroline skeleton confers the anisotropy necessary for inducing liquid crystalline properties on the ligand (***phen-16***) and on the corresponding complexes **[Ln(Q)$_3$(*phen-16*)], 3** and **4**.

The ligand (***phen-16***) exhibits an enantiotropic liquid crystalline phase from 46°C to 100°C, with a non-typical schlieren texture observed by POM (Figure 2a). The identification of the mesophase, with reference to both its nature and symmetry, was made by PXRD. The X-ray pattern of the ligand (***phen-16***) (Figure 2b) consists at small angle in four reflections in the ratio $1 : \sqrt{3} : \sqrt{4} : \sqrt{9}$ characteristic of a 2D lattice of a hexagonal columnar phase, corresponding to the indexation $(hk) = (10)$, (11), (20) and (30), with a cell parameter $a =$ 50.1 Å. The fluid-like nature of the phase is confirmed by the diffuse and broad-scattering

Table 1. Optical and thermal data.

Compound	Transition[a]	T/°C[b]	$\Delta H/kJ \cdot mol^{-1}$
(*phen-16*)	C – Col_h	46.3	13.7
	Col_h – I	100.4	40.8
	I – Col_h	79.7	42.2
	Col_h – C	54.8	14.3
[Eu(Q_3)(*phen-16*)],3	S_{lam} – *Lam*	45.7	107.6
	Lam – I	75.0[c]	—
	I – S_{lam}	70.0	—
	Lam – S_{lam}	26.0	9.5
	S_{lam} – *Lam*	33.5	26.1
	Lam – I	75.0	—
	I – *Lam*	70.0	—
	Lam – S_{lam}	26.2	9.8
[Tb(Q_3)(*phen-16*)],4	S_{lam} – *Lam*	45.6	89.0
	Lam – I	80.0[c]	—
	I – *Lam*	75.0	—
	Lam – S_{lam}	24.4	16.8
	S_{lam} – *Lam*	31.8	16.1
	Lam – I	80.0	—
	I – *Lam*	75.0	—
	Lam – S_{lam}	24.9	26.9

[a] C: crystal; Col_h: columnar hexagonal mesophase, S_{lam}: 'soft' lamellar crystal phase; *Lam*: lamellar liquid crystalline phase I: isotropic liquid.

[b] Temperature data as onset peaks obtained on second heating and cooling cycle;

[c] POM observations.

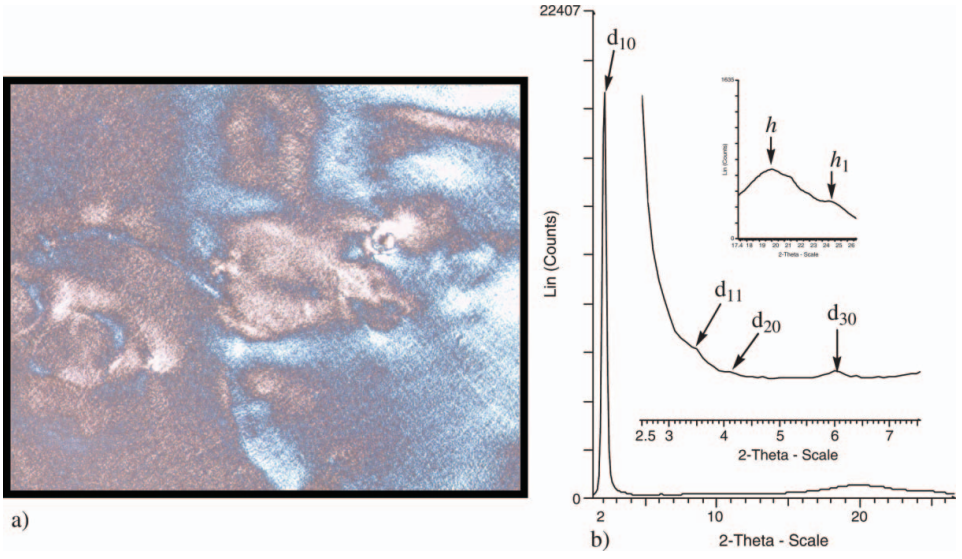


Figure 2. a) POM micrograph of the texture developed by ligand **(*phen-16*)** on cooling at 70°C; b) PXRD pattern of Col_h phase of ligand **(*phen-16*)** on cooling at 70°C.

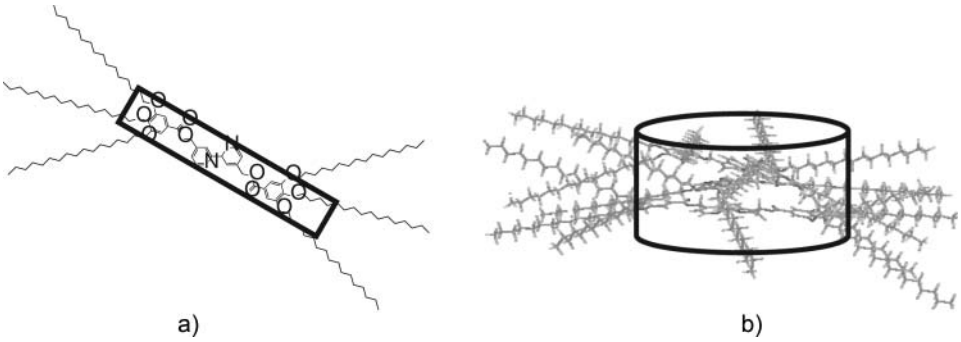


Figure 3. Shape of the a) bipyridine-based analogues ligand previously reported; b) ligand ***(phen-16)*** and the arrangement for the latter in the columnar slice.

halo *h* centred at 4.4 Å at wide angles of the X-ray pattern. This columnar mesophase is well organised by relatively strong π-π interactions, as indicated by the existence in the wide angle region of the PXRD pattern of a broad reflection centred at 3.6 Å and the high transition Col_h – I enthalpy detected by DSC measurements.

The analogues 2,2'-bipyridine-based ligand previously reported [24], bearing the same *tri*-hexadecyloxy-benzoyloxymethyl groups in 4,4'-position, is a solid crystalline that melts directly into isotropic liquid at 90°C, and has excellent promesogenic properties for a series of bulky metal centres like Zinc(II) [24], Ruthenium(II) [27] or Iridium(III) [28]. Despite of the rod-like shape of the uncomplexed bipyridines that have the nitrogen atoms in *cis*-configuration (therefore a transoid molecular shape) (Figure 3a), more compatible with liquid crystalline formation than the shape of the polycatenar phenanthroline (***phen-16***), the planarity and rigidity of the aromatic system of the latter assures the proper interactions that favours the π-π stacking of the aromatic cores forming discs that furthermore assemble into columns. Indeed, when compared with 2,2'-bipyridines, the 1,10-phenantrolines have increased rigidity, extended planar aromatic cores and the two nitrogen atoms held in juxtaposition [29].

The number of the molecules forming a columnar stratum given by *h*, may be estimated taking into account the relationship between the columnar cross-section S_{col} and the molecular volume V_{mol} calculated at 70°C, method commonly used in LCs. [30] From this analysis we obtain that 3 molecules of ligand (***phen-16***) form the columnar cross-section with a mean stacking distance of 4.4 Å (Figure 3b).

Both complexes have similar thermal behaviour, the type and size of the lanthanide ions having no noticeable effect on the transition temperatures, or the organizations in the different soft or liquid-crystalline phases. At room temperature both complexes are waxy soft solids, whose lamellar nature was evidenced by PXRD analysis. Indeed, the powder patterns of the pristine solids recorded at room temperature consist at small angle in three reflections with reciprocal spacings in the ratio 1 : 2 : 3 indexed as (001), (002) and (003) with d_{001} of 36.4 Å for complex **[Eu(Q)$_3$(*phen-16*)], 3** (Figure 4b—bottom) and 36.3 Å respectively for complex **[Tb(Q)$_3$(*phen-16*)], 4** having a certain degree of intralayer order as revealed in the wide angle of the spectra by the relatively intense and broad reflection centred for both complexes at 4.1 Å. This reflection superimposed to the diffuse halo corresponding to the molten chains order, centred at 4.3 Å, whose intensity is low, indicates that these phases can be classified as 'soft' crystalline phases (S_{lam} in Table 1).

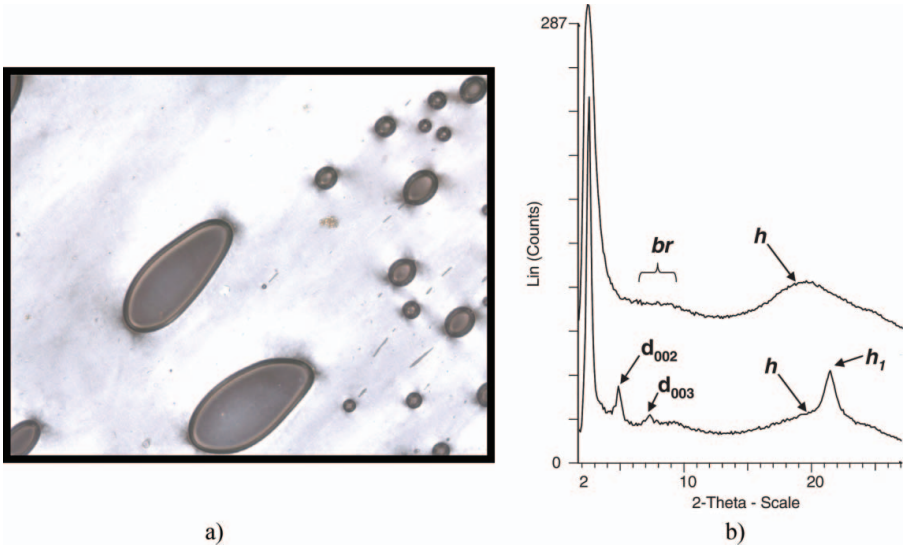


Figure 4. a) POM micrograph of the texture developed by complex **[Eu(Q$_3$)(*phen-16*)], 3** after mechanical stress at 60°C; b) PXRD pattern of S$_{lam}$ phase of complex **[Eu(Q$_3$)(*phen-16*)], 3** at room temperature (bottom) and *Lam* mesophase at 60°C on first heating (top).

The transition to the true liquid crystalline phase (*Lam*) at 45°C, is accompanied by high transition enthalpies, for both complexes (Table 1). This mesophase has no recognizable textures. On heating, the samples orient nearly perpendicular to the glass surface giving rise to homeotropic textures whose order is disrupted by mechanical stress. A certain birefringence can be induced by pressing on the glass cover slips of the microscope preparations, as showed in Figure 4a. The textures obtained on POM are mantained until room temperature.

The PXRD analysis reveals that the wide-angle pattern contains only the wide halo corresponding to the molten alkyl chains with the total loss of the intralayer correlation. In the small angle, a variation of d_{001} to 33.5 Å for complex **3** (Figure 4b—top) and 35.5 Å respectively for complex **4** is observed, accompanied by a broadening of the reflections, whereas the second and third harmonics are hided under a broad halo. Nevertheless, the existence of these broad halos implies that the molecules are organised into lamellar liquid crystalline phases, with no intralayer order.

Complexes **3** and **4** melt into the isotropic liquid at 75°C and 80°C respectively. The values for the enthalpy and the corresponding entropy changes of the lamellar mesophase – isotropic state transitions are very small and these transitions are not detected by DSC, confirming once again the low order of the lamellar mesophase.

Photophysical Behaviour

All the complexes **1–4** show appreciable luminescence at room temperature in their pristine solid and soft states (Figure 5 and 6). As well known, the emission spectra of lanthanide complexes can be assigned simply on the basis of the spectroscopic terms of the free Tb(III) or Eu(III) ions, due to the lack of significant crystal field effects in their complexes, and thus the shape and peak position are characteristic of the ion, regardless of the ligands. However,

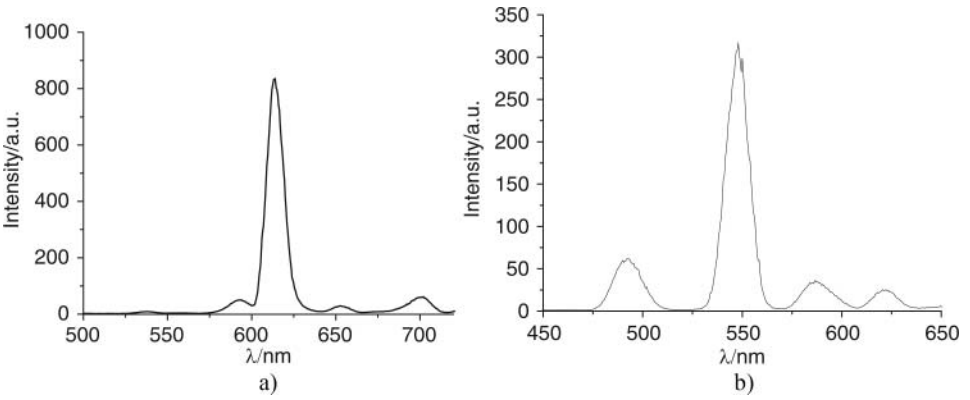


Figure 5. Emission spectra of pristine solid of a) complex **[Eu(Q$_3$)(*phen-16*)],3** and b) complex **[Tb(Q$_3$)(*phen-16*)], 4**.

a direct excitation of the lanthanide ions is very difficult, due to the low intensities and narrowness of their f-f absorption bands; a viable excitation mechanism is provided by the indirect excitation of the lanthanide ions through energy transfer from an excited state of a ligand, which act as an antenna system, to the emissive central ion. Thus, the spectra of both Eu(III) complexes (**1** and **3**) are superimposable and display characteristic sharp peaks

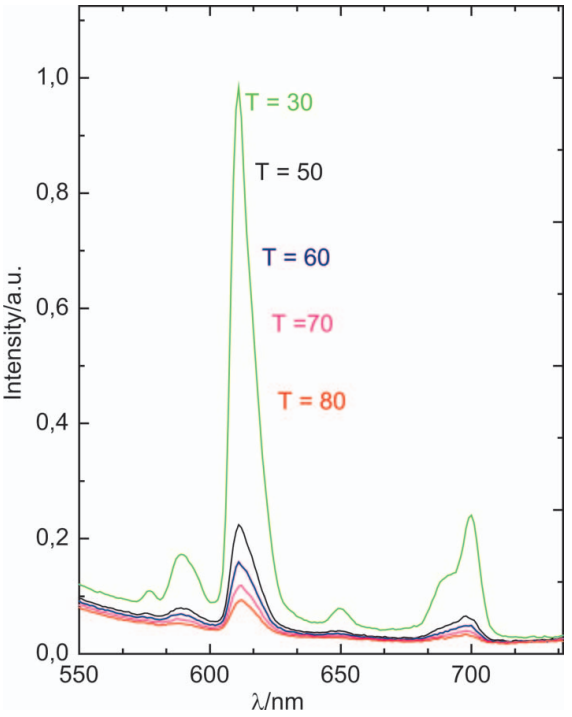


Figure 6. Emission spectra of complex **[Eu(Q$_3$)(*phen-16*)],3** on first cooling at variable temperatures.

in the 593–700 nm region associated with the $^5D_0 \rightarrow {}^7F_J$ ($J = 0 \div 4$) transitions of the Eu^{3+} ion [30]. Interestingly, at 537 nm is detected a low-intensity band due to the electric dipole $^5D_1 \rightarrow {}^7F_1$ transition sensitive to the coordination environment (Figure 5a). Also the emission spectra of Terbium(III) complexes **2** and **4** are superimposable with each other in their initial pristine condensed states, and show a series of a well defined peaks in the 492–622 nm range, attributed to the $^5D_4 \rightarrow {}^7F_J$ ($J = 6 \div 3$) transitions of the lanthanide ion (Figure 5b).

Moreover, both mesomorphic complexes **[Eu(Q)$_3$(*phen-16*)], 3** and **[Tb(Q)$_3$(*phen-16*)], 4** show luminescence in their mesomorphic state and their photophysical behaviour were investigated at different temperatures. The pristine samples were heated until the isotropic transition, then cooled slowly to room temperature and their emission spectra collected during the cooling phase, at different temperatures. For both complexes, the emission intensity increases by decreasing temperature, and, at 30°C, the spectral features are well defined; this behaviour is probably due to the competitive non-radiative deactivations, which are favoured by increased temperature. For Terbium(III) complex **[Tb(Q)$_3$(*phen-16*)], 4**, the spectra features remain essentially unchanged with respect to the pristine sample. For the Eu(III) complex **[Eu(Q)$_3$(*phen-16*)], 3**, two changes may be observed: the $^5D_1 \rightarrow {}^7F_1$ transition, positioned at 537 in the solid sample spectrum (Figure 5), is red-shifted at 577 nm in the mesophase spectrum (Figure 6), and this behaviour is attributed to the band sensitivity on passing from the solid to the mesophase. Furthermore, the liquid-crystalline spectrum of complex **[Eu(Q)$_3$(*phen-16*)],3** shows a peak at 691 nm; this features is assigned to a satellite of the $^5D_1 \rightarrow {}^7F_4$ transition (which, in turn, is centred at 700 nm), due to an electron/phonon coupling that occurs because, with respect to the pristine sample, in the mesophase the ions or ligands are not fixed in the crystal lattice but oscillate around an equilibrium position. This interaction between the phonon density of states and the electronic sublevels splits the electronic sublevels by a few cm^{-1} [31].

Conclusions

The new phenantroline-based ligand (***phen-16***), for the first time functionalised in 4,7-position with promesogenic groups, has intrinsic liquid crystalline properties. The planarity and rigidity of the aromatic system of the phenantroline ligand (***phen-16***), when compared with analogues bipyridine-based ligands, assures the proper interactions that favours the π-π stacking of the aromatic cores into columnar mesomorphic structures, with 3 phenanthroline molecules forming a columnar slice.

Furthermore, (***phen-16***) resulted to be a versatile ligand for the synthesis of low temperature mesomorphic lanthanide complexes. The high capacity of metal binding of the phenanthroline ligands (***phen***) and (***phen-16***), yielded stable Eu(III) and Terbium(III) eight coordinated complexes (**1–4**). The coordination around the metal centre is furthermore fulfilled by three O,O-proligands, yielding stable neutral lanthanide derivatives. The photophysical properties of the complexes were investigated in their different mesomorphic states at variable temperatures. All complexes show appreciable luminescence in their condensed states, having the characteristic spectral features of the corresponding lanthanide metal centre.

Experimental

Materials and methods: All commercially available starting materials were used as received without further purification. The proligand **HQ** and the corresponding lanthanide

precursors **[Ln(Q)$_3$(H$_2$O)(EtOH)]** derivatives were synthesized according to the procedure previously described [25].

The ^{1}H NMR spectra were recorded on a Bruker Avance AC-300 spectrometer in [D$_6$]DMSO, $CDCl_3$ or CD_3OD solution, using tetramethylsilane (TMS) as internal standard. Elemental analyses (CHN) were performed with a Perkin Elmer 2400 microanalyzer by the Microanalytical Laboratory at the University of Calabria. Infrared spectra (KBr) in the range 4000–400 cm^{-1} were recorded on a Spectrum One FT-IR Perkin Elmer spectrometer.

Mesomorphism: The textures of the mesophases were examined with a Leica DMLP polarising microscope equipped with a Leica DFC280 camera and a CalCTec (Italy) heating stage. The thermal stability was measured on a Perkin-Elmer Thermogravimetric Analyser Pyris 6 TGA, respectively the transition temperatures and enthalpies were measured on a Perkin-Elmer Pyris1 Differential Scanning Calorimeter with a heating and cooling rate of 10 °C/min. The apparatus was calibrated with indium. Three heating/cooling cycles were performed on each sample. The powder X-Ray diffraction patterns were obtained using a Bruker AXS General Area Detector Diffraction System (D8 Discover with GADDS) with Cu-Kα radiation ($\lambda = 1.54056$ Å). The highly sensitive area detector was placed at a distance of 20 cm from the sample and at an angle ($2\theta_D$) of 14°. A CalCTec (Italy) heating stage was used to heat the samples at a rate of 5 °C/min to the appropriate temperature. Measurements were performed by placing the samples in Lindemann capillary tubes with an inner diameter of 0.5 mm.

Photophysical Measurements. Spectrofluorimetric grade solvents were used for the photophysical investigations in solution, at room temperature. A Perkin Elmer Lambda 900 spectrophotometer was employed to obtain the solution absorption spectra. The examined compounds are fairly stable in solution, as demonstrated by the constancy of their absorption spectra over a week. Steady-state emission spectra were recorded on a HORIBA Jobin-Yvon Fluorolog-3 FL3–211 spectrometer equipped with a 450 W xenon arc lamp, double-grating excitation and single-grating emission monochromators (2.1 nm/mm dispersion; 1200 grooves/mm), and a Hamamatsu R928 photomultiplier tube. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. Powder samples have been prepared by placing the powder between two quartz plates, in such a position that the luminescence has been measured in reflection mode, in front-face arrangement to reduce the scattered light. The emission quantum yields of the solid samples were obtained by means of a 102 mm diameter integrating sphere coated with Spectralon® and mounted in the optical path of the spectrofluorimeter. The experimental uncertainty on the emission quantum yields is 5%.

To reach the mesophase, the two quartz plates were heated in the sample compartment of the spectrofluorimeter by means a customized hot stage realized by CaLCTec s.r.l. (Rende, Italy).

Synthesis

4,7-dicarboxaldehyde-1,10-phenanthroline (I): To solution of selenium dioxide (2.92 g, 26.52 mmol) in dioxan containing 4% water (40 ml), was added dropwise a solution of 4,7-dimethyl-1,10-phenanthroline (2 g, 8.84 mmol) in dioxan (140 ml). The mixture was heated under reflux for 5 h, and then filtered through celite while still hot. The filtrate was evaporated to dryness and the residue was recrystallized from chloroform/hexane to give the aldehyde **I** (1,253 g, 60%) as a yellow powder. M.p. > 300°C; Anal. Calcd. for $C_{14}H_8N_2O_2$ (236.23 gmol^{-1}): C, 71.10; H, 3.40; N, 11.80; Found: C, 71.60; H, 3.50; N,

11.90); ν_{max}/cm^{-1}: 1700–1684 (C=O), 1385 (CHO); δ_H (300 MHz, DMSO-d_6) 10.71 (2H, s, CHO), 9.48 (2H, d, $J_{(H,H)} = 4.78$ Hz, $H_{2,9}$), 9.14 (2H, s, $H_{5,6}$), 8.30 (2H, d, $J_{(H,H)} = 4.43$ Hz, $H_{5,8}$).

4,7-Bis(hydroxymethyl)-1,10-phenanthroline (II): A solution of **I** (2.00 g, 8.47 mmol) and $NaBH_4$ (4.80 g, 126.9 mmol) in ethanol (200 ml) was heated under reflux for 5 h. The mixture was then concentrated and diethyl ether was added to the solution. The precipitate formed was filtrated out and dried to give the pure hydroxymethyl compound **II** as a yellow powder (1,322 g, 65%). M.p. > 300°C. Anal. Calc. for $C_{14}H_{12}N_2O_2$ (240.2 $gmol^{-1}$): C, 70.00; H, 5.03; N, 11.66; Found: C, 70.10; H, 5.20; N, 12.10; ν_{max}(KBr)/cm^{-1}: 3290–3234 (OH), 2898–2878 (C—H), 1618–1423 (C = C); δ_H (300 MHz, DMSO-d_6) 9.07 (2H, d, $J_{(H,H)} = 4.43$ Hz, $H_{2,9}$), 8.10 (2H, s, $H_{5,6}$), 7.82 (2H, d, $J_{(H,H)} = 4.43$ Hz, $H_{3,8}$), 5.72 (2H, s, OH), 5.13 (4H, s, CH_2OH).

4,7-Bis(benzoyloxymethyl)-1,10-phemanthroline (*phen*): 4,7-Bis(hydroxymethyl)-1,10-phenanthroline (**II**) (0.150 g, 0.62 mmol), benzoic acid (0.167 g, 1.36 mmol) and 4-pyrrolidinopyridine (PPY) (0.203 g, 1.36 mmol) were suspended in dry dichloromethane (20 mL). The reaction mixture was cooled down to 0°C and *N*,*N*-dicyclohexylcarbodiimide DCC (0.228 g, 1.36 mmol) dissolved in 5 mL dichloromethane was added slowly. The reaction was left under stirring at room temperature for 72 h. The colorless precipitate formed was separated by filtration, and recrystallized from chloroform/methanol to give ligand (***phen***) (0.551g, 74%) as a colorless solid. Anal. Calc. For $C_{28}H_{20}N_2O_4$ (448.14 $gmol^{-1}$): C, 74.99; H, 4.50; N, 6.20; Found: C, 74.86; H, 4.35; N, 6.30); ν_{max}(KBr)/cm^{-1}: 2946 (C—H), 1729 (C=O); δ_H (300 MHz, $CDCl_3$): 9.25 (2H, d, $J_{(H,H)} = 4.77$ Hz, $H_{2,9}$), 8.13 (6H, t, $J_{(H,H)} = 7.52$ Hz, $H_{5,6}$ and $H_{\alpha,\alpha'}$), 7.81 (2H, d, $J_{(H,H)} = 4{,}40$ Hz, $H_{3,8}$), 7.60 (2H, t, $J_{(H,H)} = 7.53$ Hz, $H_{\gamma,\gamma'}$),7.47 (4H, t, $J_{(H,H)} = 7.52$ Hz, $H_{\beta,\beta'}$), 5.93 (4H, s, CH_2).

4,7-Bis[3,4,5-(trihexadecyloxy)benzoyloxymethyl]-1,10-phenanthroline (*phen-16*): 4,7-Bis(hydroxymethyl)-1,10-phenanthroline (**II**) (0.129 g, 0.54 mmol), 3,4,5-trihexadecyloxy benzoic acid (1.0 g, 1.186 mmol) and 4- pyrrolidinopyridine (PPY) (0.176 g, 1.186 mmol) were suspended in dry dichloromethane (20 mL) under N_2 atmosphere. The reaction mixture was cooled down to 0°C and *N*,*N*-dicyclohexylcarbodiimide DCC (0.245 g, 1.186 mmol) dissolved in 5 mL dichloromethane was added slowly. The reaction was left under stirring at room temperature for 72 h. The solution was filtrated through Celite, concentrate and precipitate with methanol, to give the ligand (***phen-16***) as a colorless solid (0,611 g, 60%). Thermal behaviour in Table 1. Anal. Calc. For $C_{124}H_{212}N_2O_{10}$ (1891.17 g mol^{-1}): C, 78.75; H, 11.30; N, 1.50; Found: C, 78.90; H, 11.50; N, 1.60; ν_{max}(KBr)/cm^{-1}: 2919–2851 (C—H), 1720 (C=O); δ_H (300 MHz, $CDCl_3$): 9.24 (2H, d, $J_{(H,H)} = 4.38$ Hz, $H_{2,9}$), 8.12 (2H, s, $H_{5,6}$), 7.76 (2H, d, $J_{(H,H)} = 4.38$ Hz, $H_{3,8}$), 7.33 (4H, s, Hα,α'), 5.92 (4H, s, CH_2), 4.02 (12H, m, $OCH_2(CH_2)_{14}CH_3$), 1.77 (12H, m, $CH_2(CH_2)_{13}CH_3$), 1.36 (156H, m, $(CH_2)_{13}CH_3$), 0.87 (18H, t, $J_{(H,H)} = 6.58$, CH_3).

General synthesis of lanthanide precursors, [Ln(Q)$_3$(H$_2$O)(EtOH)]: To a colorless solution of proligand HQ (1.76 mmol) in 15 mL of ethanol was added a solution of the appropriate lanthanide salt $Ln(NO_3)_3 \cdot 5H_2O$ (0.59 mmol) in 5 mL ethanol and KOH (1.76 mmol). The resulting mixture was stirred at room temperature for 2 hours. The yellow precipitate formed was filtered out and washed with water. The pure products were obtained after recrystallisation from chloroform/petroleum ether as yellowish solids.

[Eu(Q)$_3$(H$_2$O)(EtOH)]: Yield: 70%. M. p. 228°C. Anal. Calc. For $EuC_{53}H_{47}N_6O_8$ (1048.27) g mol^{-1}): C, 60.74; H, 4.52; N, 8.02; Found: C, 60.30; H, 4.32; N, 8.10. ν_{max}(KBr)/cm^{-1}: 3200–2800 (O-H), 2948–2865 (C—H), 1623 (C=O).

[Tb(Q)$_3$(H$_2$O)(EtOH)]: Yield: 68%. M. p. 240°C. Anal. Calc. For $TbC_{53}H_{47}N_6O_8$ (1054.91 g mol^{-1}): C, 60.34; H, 4.49; N, 7.97; Found: C, 60.53; H, 4.23; N, 7.71; ν_{max}(KBr)/cm^{-1}: 3200–2800 (O-H), 2948–2865 (C—H), 1624 (C=O).

Synthesis of Lanthanide Complexes 1–4:

Complex 1, [Eu(Q)$_3$(*phen*)]: A solution of the ligand **(*phen*)** (0.064 g, 0.143 mmol) in hot EtOH (20 ml) was added to a stirred solution containing a stoichiometric quantity of **[Eu(Q)$_3$(H$_2$O)(EtOH)]** (0.150 g, 0.143 mmol) in EtOH (10 ml). A yellow precipitate is formed. The reaction mixture was heated under reflux for 3 h and then cooled to room temperature. The yellow precipitate was separated by filtration, washed with hot ethanol and dried under vacuum. Yield 0.174 g (85%). M.p. 226 °C; Anal. Calc. For $EuC_{79}H_{59}N_8O_{10}$ (1432.34 g mol^{-1}): C, 66.25; H, 4.15; N, 7.82; Found: C, 66.10; H, 4.30; N, 7.56); ν_{max}(KBr)/cm^{-1}: 1724 (C=O (***phen***)), 1633 (C=O **Q**); δ_H (300 MHz, $CDCl_3$): 11.1 (2H, s, $H_{2,9}$); 9.21 (2H, s, $H_{5,6}$); 8.52 (8H, t, $J_{(H,H)} = 7.7$ Hz, $H_{a,e}$ and $H_{3,8}$); 8.19 (4H, s, $H_{\alpha,\alpha'}$); 7.76 (21H, m, $H_{f,g,h,i,j,}$ and $H_{\beta,\beta',\gamma,\gamma'}$); 6.71 (9H, s, $H_{b,c,d}$); 4.74 (4H, S, CH_2); 0.44 (9H, S, CH_3 Q^{Ph}); λ_{max}(CH_2Cl_2)/nm 254 (ε/mol^{-1} dm^3 cm^{-1} 74467.89); 275 (103018.5); 298.80 (60377.73).

Complex 2, [Tb(Q)$_3$(*phen*)]: A solution of the ligand **(*phen*)** (0.064 g, 0.143 mmol) in hot EtOH (20 ml) was added to a stirred solution containing a stoichiometric quantity of **[Tb(Q)$_3$(H$_2$O)(EtOH)]** (0.150 g, 0.143 mmol) in EtOH (10 ml). A yellow precipitate is formed. The reaction mixture was heated under reflux for 3 h and then cooled to room temperature. The yellow precipitate was separated by filtration, washed with hot ethanol and dried under vacuum. Yield 0.163 g (80%). M.p. 260 °C; Anal. Calc. For $TbC_{79}H_{59}N_8O_{10}$ (1439.30 g mol^{-1}): C, 65.93; H, 4.13; N, 7.79; Found: C, 65.78; H, 4.03; N, 7.81; ν_{max}(KBr)/cm^{-1}: 1724 (C=O (***phen***)), 1634 (C=O **Q**).

Complex 3, [Eu(Q)$_3$(*phen-16*)]: A solution of the ligand **(*phen-16*)** (0.100 g, 0.053 mmol) in toluene (10 ml) was added to a solution containing a stoichiometric quantity of **[Eu(Q)$_3$(H$_2$O)(EtOH)]** (0.055 g, 0.053 mmol) in Toluene (5 ml). The solution was stirred at room temperature for 9 days. The solvent was then removed by evaporation, and the residue was dissolved in hexane and filtered through celite. Complex **3** was obtained after recrystallization from chloroform/acetone as yellow solid. Yield 0.100 g (66%). Thermal behaviour in Table 1. Anal. Calc. For $EuC_{175}H_{251}O_{16}N_8$ (2874.91 g mol^{-1}): C,73.11; H, 8.80; N, 3.90; Found: C, 73.30; H, 9.05; N, 3.68; ν_{max}(KBr)/cm^{-1}: 1724 (C=O **L^{16}**), 1632 (C=O **Q**); δ_H (300 MHz, $CDCl_3$): 11.3 (2H, s, $H_{2,9}$); 9.32 (2H, s, $H_{5,6}$); 8.38 (2H, s, $H_{3,8}$); 8.16 (6H, s, $H_{a,e}$); 7.79 (19H, m, $H_{f,g,h,i,j,}$ and $H_{\alpha,\alpha'}$); 6.69 (9H, s, $H_{b,c,d}$); 4.79 (4H, S, CH_2); 4.08 (12H, m, $OCH_2(CH_2)_{14}CH_3$); 1.82 (12H, s, $CH_2(CH_2)_{13}CH_3$), 1.37 (156H, m, $(CH_2)_{13}CH_3$); 0.86 (18H, s, CH_3 (***phen-16***)); 0.43 (9H,s, CH_3 Q).

Complex 4, [Tb(Q)$_3$(*phen-16*)]: A solution of the ligand **(*phen-16*)** (0.100 g, 0.053 mmol) in toluene (10 ml) was added to a solution containing a stoichiometric quantity of **[Tb(Q)$_3$(H$_2$O)(EtOH)]** (0.056 g, 0.053 mmol) in Toluene (5 ml). The solution was stirred at room temperature for 10 days. The solvent was then evaporated, the residue dissolved in hexane and filtered through Celite. After recrystallization from chloroform/acetone, complex **4** was obtained as a yellow solid. Yield 0.090 g (59%);. Thermal behaviour in Table 1. Anal. Calc. For $TbC_{175}H_{251}O_{16}N_8$ (2881.88 g mol^{-1}): C, 72.93; H, 8.78; N, 3.89; Found: C, 73.10; H, 9.00; N, 3.52; ν_{max}(KBr)/cm^{-1}: 1725 (C=O (***phen-16***)), 1634 (C=O **Q**).

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